

**TIME-RESOLVED SPECTROSCOPY ON THE
CARRIER DYNAMICS OF BiVO₄ PHOTOANODES FOR
SOLAR WATER OXIDATION**

by

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Koç University

Graduate School of Sciences and Engineering

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ABSTRACT

Solar water splitting is an attractive approach for utilizing sunlight energy in a sustainable way. This method is known as photoelectrochemical (PEC) conversion and aims to generate hydrogen as a potential carbon-free transportation fuel. PEC cells employ semiconductor materials to convert the solar energy into chemical bonds of hydrogen via splitting water molecules. BiVO_4 is a promising semiconductor material for the solar water splitting systems. Yet, as other potential semiconductors, its PEC conversion efficiency is inadequate for large scale production owing to low mobility and fast recombination dynamics of the charge carriers, and poor surface activity for attaining the water oxidation. Surface modification and bulk doping enhance the PEC conversion efficiency of BiVO_4 photoanodes, which are the potential strategies to fulfill practical applications. For instance, atomically thin co-catalyst accelerates the charge transfer from the semiconductor to water by leading a faster route for the water splitting reactions. Doping can enhance the carrier density and mobility thereby increase the charge carrier utilization. However, the challenge of the determination of the unstable carrier mobility and dynamics at surface in running cell conditions (*in situ* or *operando*) inhibits to take benefit from these methods competently. The purpose of this thesis is to improve the understanding of the charge carrier utilization of bare and modified BiVO_4 photoanodes and elucidate the obstacles in the chemical conversion by time-resolved and core-level spectroscopy investigations in the operational conditions.

Photogenerated carrier dynamics of BiVO_4 has been studied by ultrafast transient absorption spectroscopy (TAS) experiments and a numerical modelling to uncover the origins of the carrier relaxations. The numerical model, based on the rate equations, indicates the probability of both photogenerated electron and hole absorption dynamics below 500 nm, in contrast to the generally suggested photogenerated hole absorption mechanism. The experiments done in the ultrafast timescale highlight that the positive transient absorption peak at 470 nm reveals opposite behavior as compared to the broad-band feature represented at 550 nm in the presence of a hole scavenger, under anodic bias and at increasing excitation pump intensity. Merging TAS results under diverse conditions with the

numerical modeling unveils that both electron and hole absorption are likely in the spectral region above 500 nm while the excited electron absorption is the dominant transition at shorter wavelengths. Also, the major changes in transient absorption response occur in the ultrafast time scale and overall recombination dynamics reflects the ultrafast recombination mechanism.

TAS in the optical region exhibits the dynamics of the electron and hole carriers in the conduction and valence bands, and midgap states. The overlapped ultrafast carrier-carrier and carrier-phonon scatterings through both conduction and valence band complicates the attribution of the transient absorption signal to the carriers in the specified bands or in the bandgap. Still, the extensive analysis of ultrafast TAS of BiVO₄ in different spectral regions could present fingerprints to trace electron and hole carriers. Deconvoluting various optoelectronic interactions in the ultrafast scale provided us to realize the dominance of either electron or hole contribution on the transient absorption features of BiVO₄. Following analysis on different BiVO₄ photoanode surfaces specified by heat treatment and different film thicknesses revealed the structural signatures. Small polaron formation which reduces charge carrier transport, and the distortion of V-O structural units which significantly affects the carrier recombination were elucidated.

More explicit indication for surface recombination is acquired by recording photocurrent-voltage plots under chopped illumination, so called “Transient photocurrent (TPC)” spectroscopy. Further understanding of the recombination through the conversion at the interface was highlighted by utilizing TPC spectroscopy of BiVO₄ from microsecond (μ s) to ms. This was uncovered by elucidating the photocurrent improvement of nitrogen incorporated (doped) BiVO₄. Performing home built TPC experiments at the timescale of surface recombination and water oxidation, we confirm that nitrogen treatment facilitates hole transfer via generating additional oxygen vacancies and accelerating V₅₊/V₄₊ redox process while decreasing the surface recombination. Although the reduction of V₅₊ to V₄₊ via photogenerated electron trapping was also implied as recombination or trap centers, the role of the reduction at surface-interface was highlighted as a primary step of water oxidation.

Cobalt-based catalysts are both economic and efficient catalysts for BiVO₄ photoanodes. However, the questions of “how the bonds are breaking and new bonds are forming through the cobalt ions”, “which phase of the catalyst is the active phase”, “how the phase is changing during intermediate reactions and how they affect the carrier recombination and charge transfer” across the interface are unexplored. Further complication comes from the change of the reactions during the water splitting. The core level spectroscopy (CLS) is a correct tool to seek answers for such problems because reliable information of valence electron states can be identified via excitation of core electrons with a local and sensitive probe. We also utilized CLS to elucidate the differences between BiVO₄ photoanodes prepared by electrodeposition (ED) and spin-coating (SC). We imply that the presence of higher amount of oxygen vacancies in ED-BiVO₄ make it more efficient than SC-BiVO₄. CLS in vacuum and in the water ambient conditions of helped us to highlight the motives behind the improvement of Co(OH)₂-BiVO₄ photoanodes prepared by ED. The carrier dynamics of Co(OH)₂-BiVO₄ was elucidated and the change of electronic structure in water ambient was probed by *in situ* CLS. Hence, the change of the charge state and electronic structure of Co(OH)₂-BiVO₄ was discussed under water ambient.

Overall, this research mainly aims at improving the understanding of fundamental ultrafast carrier dynamics of BiVO₄, and the chemical and physical changes at the interface of water-BiVO₄ during water oxidation reactions. The results of this thesis might have a strong impact on our understanding of the nature of the charge recombination mechanisms and charge transfer between BiVO₄ and water. Thereby, it may present potential solutions for better utilizing from co-catalyst and doping materials for BiVO₄.

ÖZETÇE

Güneş enerjili su ayrımı, güneş ışığını sürdürülebilir bir şekilde kullanmak için çekici bir yaklaşımdır. Bu yöntem fotoelektrokimyasal (FEK) dönüşüm olarak bilinir ve potansiyel bir karbon içermeyen taşıma yakıtı olarak hidrojen üretmeyi amaçlar. FEK hücreleri, güneş enerjisini suyu moleküllerine ayrıştırma yoluyla hidrojenin kimyasal bağlarına dönüştürmek için yarı iletken malzemeler kullanır. BiVO_4 , güneş enerjili su ayırma sistemleri için umut verici bir yarı iletken malzemedir. Bununla birlikte, diğer potansiyel yarı iletkenler gibi, FEK dönüşüm verimliliği, düşük yük taşıyıcı mobilitesi ve yük taşıyıcılarının hızlı rekombinasyon dinamikleri, ve suyun oksijene dönüşümünü gerçekleştirme sırasındaki zayıf yüzey aktivitesi nedeniyle büyük ölçekli üretim için yetersizdir. Pratik uygulamaları yerine getirmek için potansiyel stratejiler olan, yüzey modifikasyonu ve hacim (bulk) katkılama (doping), BiVO_4 fotoanotlarının FEK dönüşüm verimliliğini artırır. Örneğin, atomik olarak ince ko-katalizör, su ayrıştırma reaksiyonları için daha hızlı bir yol başlatarak yarı iletken suya yük transferini hızlandırır. Katkılama, taşıyıcı yoğunluğunu ve hareketliliğini artırabilir, böylece yük taşıyıcı kullanımını artırabilir. Fakat, hücrenin çalıştığı koşullarda (*in situ* veya *operando*) yüzeydeki kararsız taşıyıcı hareketliliğinin ve dinamiklerinin belirlenmesinin zorluğu, bu yöntemlerden yetkin bir şekilde yararlanılmasını engeller. Bu tezin amacı, yük taşıyıcısının sade ve modifiye edilmiş BiVO_4 fotoanotlarının kullanımının anlaşılmasını geliştirmek ve çalışma koşullarında “zamana bağlı” ve “çekirdek düzeyinde” spektroskopi yöntemleri ile kimyasal dönüşümün önündeki engelleri açıklamaktır.

BiVO_4 'ün foto-üretilmiş taşıyıcı dinamiği, ultra hızlı geçici (transient) absorpsiyon spektroskopisi (TAS) deneyleri ve taşıyıcı durulmalarının kökenlerini ortaya çıkarmak için sayısal bir modelleme ile incelenmiştir. Hız denklemlerine dayanan sayısal model, genel olarak önerilen foto-üretilmiş deşik absorpsiyon mekanizmasının aksine, 500 nm'nin altındaki hem foto-üretilmiş elektron hem de deşik absorpsiyon dinamiklerinin olasılığını gösterir. Ultra hızlı zaman ölçeğinde yapılan deneyler, 470 nm'deki pozitif geçici absorpsiyon pikinin, bir deşik toplayıcı sıvı varlığında, anodik potansiyel altında ve artan pompa lazer demeti yoğunluğunda 550 nm'de temsil edilen geniş bant özelliğine kıyasla zıt bir

davranış sergilediğini vurgulamaktadır. Sayısal modelleme ile çeşitli koşullar altında yapılan deneyler ile birlikte, sonuçların hem elektron hem de deşik absorpsiyonunun 500 nm'nin üzerindeki spektral bölgede muhtemel olduğunu, uyarılmış elektron absorpsiyonunun daha kısa dalga boylarında baskın geçiş olduğunu ortaya koymaktadır. Ayrıca, geçici absorpsiyon karşılığındaki büyük değişiklikler, ultra hızlı zaman ölçeğinde meydana gelir ve genel rekombinasyon dinamiği, ultra hızlı rekombinasyon mekanizmasını yansıtır.

Optik bölgedeki TAS, iletim ve valans bantları ve bant aralığındaki durumlarındaki elektron ve deşik taşıyıcıların dinamiklerini gösterir. Hem iletim hem de valans bandı yoluyla üst üste binen ultra hızlı taşıyıcı-taşıyıcı ve taşıyıcı-fonon saçılımları, geçici absorpsiyon sinyalini belirtilen bantlardaki veya bant aralığındaki taşıyıcılara atfetmeyi karmaşılaştırır. Yine de farklı spektral bölgelerde BiVO₄'ün ultra hızlı TAS'sinin kapsamlı analizi, elektron ve deşik taşıyıcılarını izlemek için parmak izleri sunabilir. Ultra hızlı ölçekte çeşitli optoelektronik etkileşimlerin ters evrimi, elektron veya deşik katkısının BiVO₄'ün geçici absorpsiyon özellikleri üzerindeki baskınlığını anlamamızı sağladı. Isıl işlem ve farklı film kalınlıkları ile belirlenen farklı BiVO₄ foto-anot yüzeyleri üzerinde yapılan analizlerin ardından yapısal ip uçları ortaya çıkmıştır. Yük taşıyıcı naklini azaltan küçük polaron oluşumu ve taşıyıcı rekombinasyonu önemli ölçüde etkileyen V-O yapısal birimlerin bozulması tartışılmıştır.

Yüzey rekombinasyonu için daha açık belirti, “Geçici foto-akım (GFA)” spektroskopisi adı verilen kesilmiş aydınlatma altında foto-akım-voltaj grafiklerinin kaydedilmesiyle elde edilir. Arayüzeyde dönüşüm aracılığı ile rekombinasyonun daha iyi anlaşılması, mikro saniye (μ s) ile ms arasında BiVO₄'ün GFA spektroskopisi kullanılarak vurgulanmıştır. Bu, azot katkılı BiVO₄ sayesinde arttırılmış olan foto-akımın açıklanmasıyla ortaya çıkarılmıştır. Yüzey rekombinasyonu ve su oksidasyonlarının zaman ölçeğinde ev yapımı GFA deneyleri yaparak, azot işleminin ek oksijen boşluğu oluşturarak ve yüzey rekombinasyonunu azaltırken V_{5+}/V_{4+} redoks işlemini hızlandırarak deşik transferini kolaylaştırdığını doğrulamış olduk. V_{5+} 'nın V_{4+} ' ya foto-üretilmiş elektron yakalama yoluyla indirgenmesi de rekombinasyon veya tuzak merkezleri olarak ima edilmesine rağmen, yüzey arayüzündeki azalmanın rolü, su oksidasyonunun birincil adımı olarak vurgulanmıştır.

Kobalt esaslı katalizörler, BiVO_4 foto-anotları için hem ekonomik hem de verimli katalizörlerdir. Bununla birlikte, “bağların nasıl koptuğu ve kobalt iyonları yoluyla yeni bağların nasıl oluştuğu”, “katalizörün hangi fazının aktif faz olduğu”, “ara reaksiyonlar sırasında fazın nasıl değiştiği ve taşıyıcı rekombinasyonu ve yük transferini nasıl etkilediği” sorularına henüz cevap bulunmamıştır. Daha fazla komplikasyon, su bölünmesi sırasında reaksiyonların değişmesinden kaynaklanır. Çekirdek seviye spektroskopisi (ÇSS), bu tür problemlere cevap aramak için doğru bir araçtır çünkü değerlik elektronu durumlarının güvenilir bilgileri, çekirdek elektronların yerel ve hassas bir prob ile uyarılmasıyla tanımlanabilir. Ayrıca elektrodpozisyon (ED) ve spin kaplama (SK) ile hazırlanan BiVO_4 fotoanotları arasındaki farkları aydınlatmak için ÇSS'yi kullandık. ED- BiVO_4 'te daha yüksek miktarda oksijen boşluğunun bulunmasının SK- BiVO_4 'ten daha verimli hale getirdiğini ima ediyoruz. Vakumda ve su ortam koşullarında ÇSS, ED tarafından hazırlanan $\text{Co(OH)}_2\text{-BiVO}_4$ 'ün fotoanotlarının iyileştirilmesinin ardındaki güdülerimizi vurgulamamıza yardımcı oldu. $\text{Co(OH)}_2\text{-BiVO}_4$ 'ün taşıyıcı dinamikleri açıklandı ve su ortamındaki elektronik yapının değişimi, yerinde ÇSS ile araştırıldı. Bu nedenle, $\text{Co(OH)}_2\text{-BiVO}_4$ 'ün şarj durumunun ve elektronik yapısının değişimi su ortamı altında tartışılmıştır.

Genel olarak, bu araştırma temel olarak BiVO_4 'ün temel ultra hızlı yük taşıyıcı dinamiği, su-oksidasyon reaksiyonları sırasında su- BiVO_4 arayüzündeki kimyasal ve fiziksel değişiklikler anlayışını geliştirmeyi amaçlamaktadır. Bu tezin sonuçları, yük rekombinasyon mekanizmalarının doğası ve BiVO_4 ile su arasındaki yük transferini anlamamız üzerinde güçlü bir etkiye sahip olabilir. Böylece, BiVO_4 için ko-katalizör ve katkı maddelerinden daha iyi yararlanmak için potansiyel çözümler sunulabilir.

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To my mother...



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List of Abbreviations and Symbols

Å:	Angstrom
A:	Active geometric area (cm ²) – Absorption
$\alpha(\lambda)$:	Absorption-coefficient (cm ⁻¹)
AM 1.5:	Air mass 1.5
APPEs:	Ambient-pressure photoemission spectroscopy
BiVO ₄ :	Bismuth vanadate
ΔA :	The absorption difference between the ground and excited states
ΔJ :	The photocurrent density difference
CLS:	Core-level spectroscopy
CoO _x :	Cobalt-oxide
Co(OH) ₂ :	Cobalt di-hydroxide
CoPi:	Cobalt phosphate
CV:	Cyclic voltammetry
e:	Electron charge (1.6 x 10 ⁻¹⁹ C)
E:	Energy / energy level
E _b :	Binding energy
EC:	Electrochemical
ED:	Electrodeposition
E _F :	Fermi energy
E _{kin} :	Kinetic energy
Fe ₂ O ₃ :	Iron oxide
ϵ_0 :	Vacuum permittivity
ϵ_r :	Relative permittivity

η :	Efficiency
fs:	Femtosecond
FTO:	Fluorine-doped tin oxide
ϕ :	Work function
h :	Planck's constant
HEC:	Hydrogen evolution catalyst
HER:	Hydrogen evolution reaction
I :	Light intensity
ITO:	Indium tin-oxide
J :	Current density (mA cm^{-2})
J_{ph} :	Photocurrent density (mA cm^{-2})
J_{pulse} :	Pulse intensity
k_B :	Boltzmann constant
KPi:	Potassium phosphate
L_D :	Diffusion length (nm)
LED:	Light-emitting diode
LHE:	Light-harvesting efficiency
LSV:	Linear-sweep voltammetry
λ :	Wavelength
μ :	Carrier mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)
N_d :	Donor density (cm^{-3})
OEC:	Oxygen evolution catalyst
OER:	Oxygen evolution reaction
PEC:	Photoelectrochemical
PL:	Photoluminescence
ν :	Frequency (Hz)
RIXS:	Resonant inelastic x-ray scattering
SC:	Spin coating
SEM:	Scanning electron microscopy
σ :	Absorption cross-section
τ :	Time-constant

TA:	Transient absorption
TAS:	Transient absorption spectroscopy
TiO ₂ :	Titanium di-oxide
TMO:	Transition metal-oxide
TPC:	Transient photocurrent spectroscopy
tr:	Time-resolved
TT:	Thermal treatment
UV-Vis:	Ultraviolet-Visible spectral region
V _o :	Oxygen vacancies
V:	Vanadium
W _{sc} :	Depletion width
XAS:	X-ray absorption spectroscopy
XES:	X-ray emission spectroscopy
XPS:	X-ray photoelectron spectroscopy

1 Introduction

Current developments in the natural sciences have mostly been a matter of interdisciplinary approaches where the spectroscopy plays a critical role. Spectroscopy is the main tool of the studies in the field of light-matter interaction that gives fingerprints of the matter in various time scales and dimensions. I utilized the optical and core level spectroscopy to identify physical and chemical properties of bismuth vanadate (BiVO_4). BiVO_4 is a promising semiconductor material being used in renewable energy conversion-storage systems. The focus of this study is to enhance our understanding behind the limits of the utilization of BiVO_4 photoanodes by using the advanced spectroscopy techniques.

1.1 Solar-to-Hydrogen Conversion

Demand for more efficient conversion of sunlight energy continues due to the concerns associated with the use of fossil fuels. Among the estimated global power generation capacities by sustainable sources (solar, wind, hydroelectric, biomass, nuclear etc.), solar energy is the only source that has the potential to meet all our energy needs [1]. The solar cell market is among today's fastest growing markets that makes the solar energy as a significant part of the energy resources in the next decades. However, it is believed that at a certain point, grid-based storage capabilities will be surpassed, and large-scale energy storage solutions will be required [2]. One of the more appealing options is to store solar energy in the form of a chemical fuel. Compared to the batteries, chemical fuels combine the advantages of high energy storage densities and ease of transportation. Examples of chemical fuels involve hydrogen, gasoline, methane, methanol, diesel, etc. Except for hydrogen, all of these examples need a source of carbon and one major goal in solar energy conversion effort is to minimize the energy penalty involved in capturing the CO_2 [2].

Water is a convenient and plentiful source of hydrogen, and there is more than enough water accessible. Among many routes for the conversion of solar energy and water into hydrogen, photoelectrochemical (PEC) water splitting with

semiconductor electrodes comes into prominence owing to the certain advantages: First, hydrogen and oxygen are produced at separate electrodes. This avoids serious safety concerns and provides easy separation of these gases without paying any penalty for postseparation. Second, it can be implemented at room temperature, i.e., it is not required for wide-range solar concentrators that would restrict its application to huge central facilities in sunny lands. Last, a PEC water splitting cell can be fabricated completely from inorganic substances offering a chemical robustness and endurance that is difficult to attain for organic systems. Note that all these advantages are also valid for coupled photovoltaic–electrolysis systems in which the essential parts of such a system (PV + electrolysis) are commercially obtainable [3]. Its solar-to-hydrogen (STH) efficiency about 8% has been proven but the anticipated cost (\$5.1-10/kg) is well above the target (\$2–4/kg) set by the US Department of Energy for future hydrogen production routes. PEC water splitting may offer hydrogen production priced at \$3–5/kg that can compete with current energy sources [1], [4].

1.2 Photoelectrochemical Water Splitting

PEC cells simply merge the harnessing of solar energy and the electrolysis of water into a single device. The electrochemical response of TiO_2 and Ge was observed in Bell laboratory in 1960s but the PEC cells received wide attention with the paper [5] in early 1970s when energy crisis shook the world's economy. Basically, when a PEC semiconductor device is immersed in an aqueous electrolyte and illuminated by sunlight, the photon energy is converted to electrochemical energy, which can directly split water into hydrogen and oxygen: Hydrogen evolution reaction (HER) takes place in the cathode side, while oxygen evolution reaction (OER) occurs in the anode part [3], [6]. Among various configurations of PEC cells, the half-cell with photoanode as the working electrode and a promising metal counter electrode (i.e. Pt) is the most investigated one (Figure 1-1) to improve the understanding of OER because it is slower and more complex reaction than HER [3].

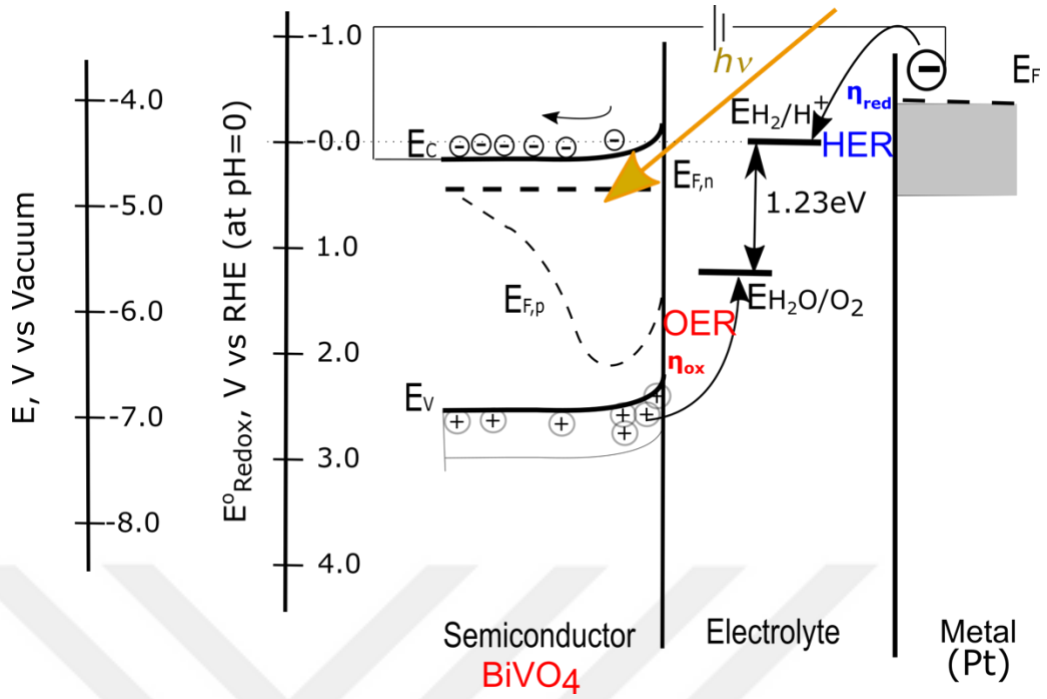
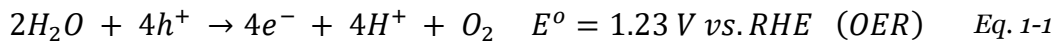


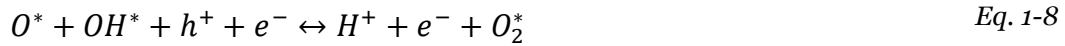
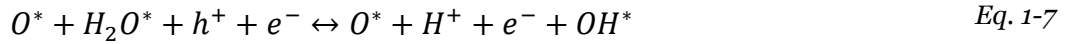
Figure 1-1 Schematic illustration of a photoelectrochemical half-cell with photoanode as the working electrode and Pt counter electrode.

The semiconductor converts incident photons to electron–hole pairs by exciting electrons to the conduction band (CB) from the valence band (VB) where they left hole carriers. Electron and hole carriers are spatially separated by band bending due to the presence of an electric field inside the semiconductor. The photogenerated electrons are extracted toward the counter electrode (CE) through the conducting substrate and external circuit. At metal-electrolyte interface the electrons drive the HER reducing water to hydrogen gas. The photogenerated holes are swept toward the semiconductor/electrolyte interface. At photoanode-electrolyte interface the holes drive the OER to form oxygen gas. OER and HER in acidic environment can be simply defined as [1]:



The requirements of the semiconductor characteristics for PEC conversion are explained via electrochemical levels [1], [3]. The VB edge of the semiconductor (E_v) must be energetically lower than oxidation level and the Fermi level (E_F) of the metal must be higher than reduction level of water from a thermodynamic

standpoint. Ideally, if the semiconductor possesses a bandgap >1.23 eV and having a CB edge and VB edge that straddles the electrochemical potentials E° (H_2/H^+) and E° (H_2O/O_2), can drive the HER and OER under irradiation of light (photon energy >1.23 eV). In this case, the cell could have 47% of solar-to-hydrogen (STH) efficiency (η_{sth}) as long as quantum efficiency (electron out per photons in) is unity. However, significant loss processes are inevitably involved in any energy conversion process. First, the chemical potential difference between the quasi fermi levels ($E_{F,n}$ and $E_{F,p}$) is necessarily lower than the bandgap (Figure 1-1). Second, kinetic overpotentials (η_{ox} and η_{red}) exist at both electrodes resulting from the subsequent complex reactions [3]. The complexity can be shown by the recent proposed reaction pathway of water splitting reactions on BiVO_4 photoanode (where * represents the adsorbed species)[7]:



Lastly, the various recombination channels minimize the utilization of photogenerated carriers to drive OER and HER [8]. Understanding the charge carrier dynamics in PEC systems is crucial to solve the kinetic challenge of fast recombination over the slow water oxidation [9].

1.3 The BiVO_4 Photoanodes

1.3.1 Semiconductor Photoanode Materials

STH efficiencies of higher than 10% have been proven with designs based on conventional high-efficiency photovoltaic materials (i.e., GaAs and GaInP) [10]. Yet, these materials corrode during contact with an aqueous electrolyte, a huge complexity is expected [6]. Considering the abundance, cost-effectiveness,

sunlight harvesting and the favorable band edges of the material, transition-metal-oxide (TMO) semiconductor photoanode materials are believed to be more applicable such as TiO_2 , Fe_2O_3 , WO_3 , BiVO_4 etc. that have been extensively reviewed [11]. The classic TMO semiconductors, such as TiO_2 ($E_g = 3.0\text{--}3.2$ eV) [12] and WO_3 ($E_g = 2.7$ eV) [13] attracted scientists for decades due to their extreme stability under PEC operation. However, the bandgaps of these binary oxides are very large to absorb an adequate portion of the solar spectrum. The origin of the differences in the VB in oxides is the d band occupancy of the metal [14]. TMOs based on vacant d bands with d_0 cations such as Ti^{4+} , W^{6+} , and V^{5+} have VB energy levels dictated strongly by the O 2p levels leading the VB low in energy and stable during OER. TMOs with d_n electronic configurations mostly have smaller bandgaps and decent chemical stability, such as Fe_2O_3 ($E_g = 2.1$ eV) and Co_3O_4 ($E_g = 1.3$ eV) [6]. However, poor carrier mobility and photogenerated charge separation of binary oxides owing to the low polaron conductivity [14], have triggered focus to turn recently to ternary oxides that can be synthesized by adding a cation. Mixing s_2 cations (i.e. Bi^{3+}) with d_0 cations (i.e. V^{5+} and Ti^{4+}) builds a coupling between the s and the O 2p that leads an upward dispersion of the VB, while the coupling of the d bands (from d_0 cation) with the p band (from the s_2 cation) maintains the CB edge low [15].

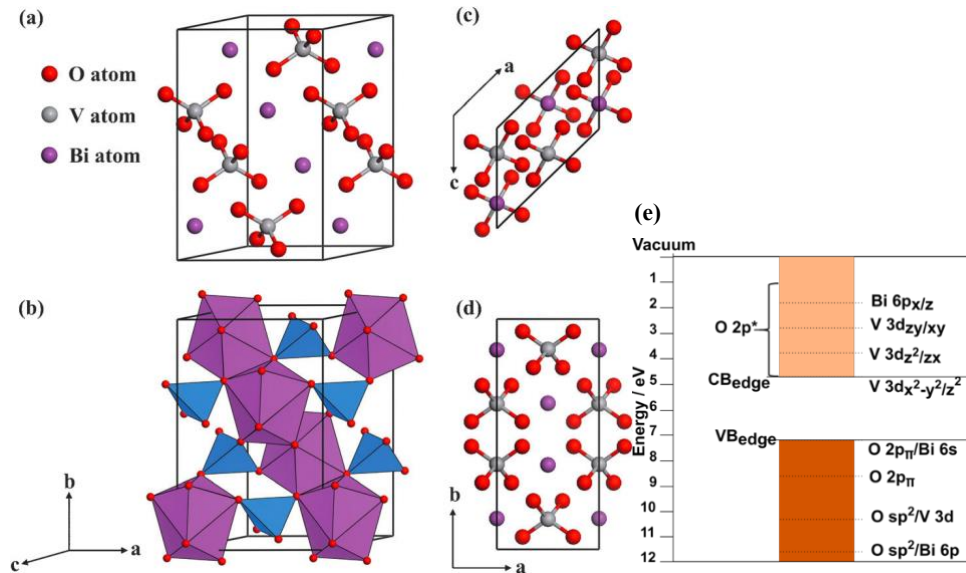


Figure 1-2 (a) Unit cell of monoclinic BiVO_4 , (b) VO_4 tetrahedrons (blue) and BiO_8 dodecahedrons (purple) respectively, (c) the top view and (d) side view of the structure [16]. The electronic band structure of monoclinic BiVO_4 .

Monoclinic n-type BiVO₄ has been demonstrated as the most successful ternary metal-oxide photoanode since the discovery of its photocatalytic water oxidation property in 1998 [17]. The unit cell of monoclinic BiVO₄ is composed of Bi₃₊ and V₅₊ coordinated with O₂₋ in VO₄ tetrahedrons where V atom is surrounded by four O atoms and BiO₈ dodecahedrons where each Bi atom is surrounded by eight O atoms (Figure 1-2a-d) [16]. The CB of BiVO₄ consists of triplet d-orbital splitting of the hybridized V 3d-O 2p orbitals while the VB edge is dominated by O2p states, with small contributions of Bi 6s (Figure 1-2e) [18] deriving a bandgap of 2.4 eV. Preliminary theoretical investigations predicted that BiVO₄ has direct bandgap [15] but its indirect bandgap character was later experimentally validated to be indirect [18]. The drastic progress has been developed upon the fabrication BiVO₄ film in 2003 [19] that is regarded as a “breakthrough” for metal oxide photocatalyst of PEC cells. However, BiVO₄ suffers from the obstacles such as low electron mobility due to hopping mechanism and slow reaction kinetics at the interface of semiconductor-electrolyte due to the surface recombination [20]. Still, theoretical maximum STH efficiency of BiVO₄ (around 10%) was reached in 2015 [21], further endeavors should aim at enhancing the fill factor to obtain such high current densities at lower applied potentials. This can be accomplished by further diminishing surface recombination which is still poorly understood [11], [22].

1.3.2 Charge Carrier Transport in BiVO₄

The charge carriers move by trapping and hopping (polaron formation) in the TMO semiconductors unlike conventional semiconductors. The charge carrier self-trapping through small polaron formation significantly decrease mobilities with reducing PEC conversion efficiency [20]. The hopping mechanism is simply illustrated in Figure 1-3 [23]: At first, the electron is trapped on M1 (blue ion), reducing it from M₁₄₊ to M₁₃₊ (a), the hop could happen when the electronic energies of the initial and final sites are equal (b). If the probability of a carrier hoping (c) is unity, the transfer ends and the electron resides in the final site at M₂ (red ion). The fate of transition from (b) to (c) depends on the carrier

interaction with either sites that is a measure of the orbital overlap, either directly between cations or via bridging oxygen atoms.

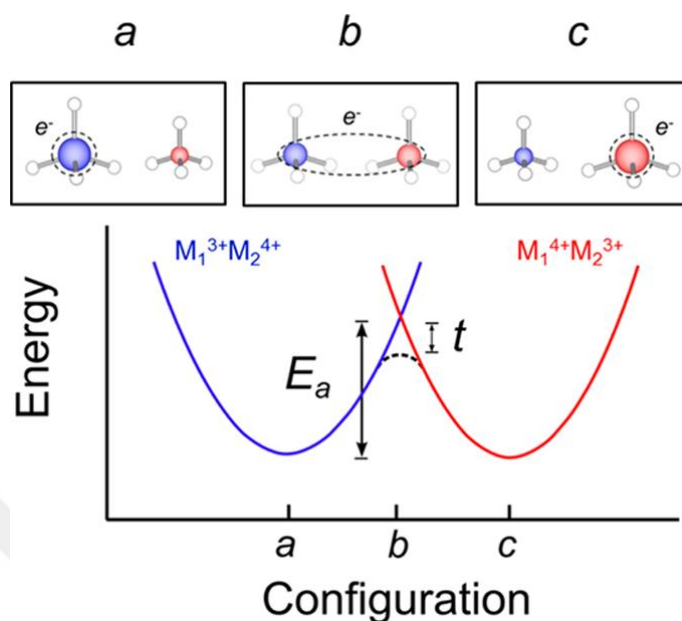


Figure 1-3 Simplified potential energy background and sketch for small polaron transport between two identical metal ions in MO_4 units [24]. Blue and red circles represent the initial and final sites, M_1 and M_2 , respectively, and white circles illustrate oxygen atoms. (a) The electron localizes on the initial site. (b) Positions are in concurrence, and the hopping is probable. (c) The electron transfer is fulfilled and localizes on the final site. E_a is the noninteracting activation energy, and t is the transfer integral at the concurrence outline. The dashed line denotes an adiabatic surface owing to exchanges between the two spots. Adapted with permission from J. Phys. Chem. Lett. 2016, 7, 3, 471-479. © (2016) American Chemical Society.

As an n-type semiconductor, a decent hole mobility of BiVO_4 is highly favorable because the hole transfer is pivotal for the water oxidation by photoanodes [25]. The hole diffusion length (L_D) of BiVO_4 was calculated as 70 nm which is much higher than Fe_2O_3 (2 - 4 nm) [26]. However, poor electron mobility ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is claimed [23] among the major restrictions of PEC conversion ability of BiVO_4 , while hole mobility was reported as $> \text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [27]. The difference of mobilities between holes and electrons is attributed to the nature of polaron formation [20]. It has been argued that a large polaron travels coherently with a modest mobility, whereas a small polaron moves incoherently via phonon-assisted hopping with a very small mobility [28]. Unlike small polarons, large polarons disperse over many structural units [23]. For BiVO_4 , small electron polaron state is found around CB minimum that consists of V 3d -

O 2p hybrid states [18], [20], [29] whereas large hole polarons are mostly associated with the BiO₈ structural units [23], [29], [30]. Despite solid indication for majority electron small polaron formation by the experiments [20], there are controversies on assigning the observed oscillations in the measurements either by THz conductivity [31] or transient absorption [32]–[34] to small polarons or large polarons. For instance, it is known that the mobility of the large polarons ($>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is much higher than the small polarons ($<<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [28] but the study implied that the polarons having the mobility of $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the frequency of 76 cm^{-1} (0.44 ps^{-1}) represents the hole polarons of BiVO₄ [31].

1.3.3 Basics of the Charge Carrier Recombination in BiVO₄

Any excited systems tend to relax into its ground system or thermodynamic equilibrium. In semiconductors, excitation of electrons from the VB to the CB typically recombine with the holes unless the carriers are immediately extracted by an adjacent conductive junction. The recombination occurs inside the semiconductor at various time scales due to the trap states in the bulk and the surface. In PEC cell, upon the illumination of the photoanode, the excited electrons migrate to the metal through conductive substrate, while holes transfer to electrolyte from the surface of the semiconductor photoanode. Since the polaronic structure of most TMOs results in trapping of the photogenerated carriers, to determine the relaxation of the carriers at either in the bulk or at the surface of the semiconductor is crucial for better understanding of the entire recombination dynamics. These regions and the proposed time scales [8], [35] are illustrated in Figure 1-4. OER is proposed to take place in the order of ms-s, therefore, the charge carriers in the bulk region could not drive water splitting owing to the fast recombination between femtosecond (fs) and nanosecond (ns) scale. The space-charge layer (SCL) region formed between the semiconductor and electrolyte after thermodynamic equilibrium is established by electron transfer from the semiconductor to the electrolyte. The band bending acts as a barrier for electron transfer to electrolyte while facilitate hole transport to the interface due to increased lifetime of the holes in the SCL [8]. Kinetic competition between surface recombination and charge transfer reaction determines how many surface charge carriers participate in the interfacial reactions. The

recombination dynamics of semiconductor is generally investigated by transient absorption spectroscopy (TAS) [36], transient photocurrent (TPC) spectroscopy [37] and time-domain frequency techniques [31].

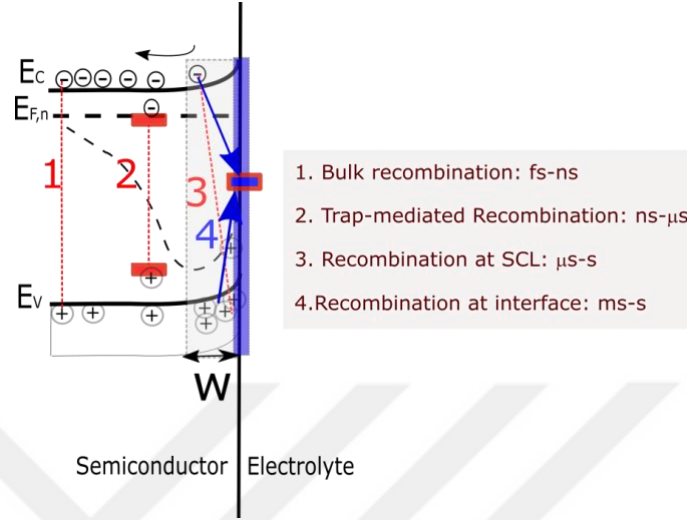


Figure 1-4 Schematic illustration of typical recombination channels in the semiconductor and interface.

Despite monoclinic BiVO_4 is a promising n-type semiconductor photoanode material for water oxidation due to its proper bandgap, abundance, environmental compatibility, and moderate stability under operational conditions [19], [20], it suffers from the major obstacles also faced by the other metal oxide photoanode materials (i.e. TiO_2 , WO_3 , Fe_2O_3) such as low mobility and fast recombination dynamics of the charge carriers. Moreover, poor surface activity for water oxidation generally limits those photoanodes being used in an efficient PEC device [38]. TAS has been employed to determine charge carrier dynamics of BiVO_4 from sub-ps to 200 μ s in 2013 [34], and from μ s to ms in 2014 [39], while the origin of the transient absorption (TA) spectrum has been discussed in 2018 [40]. Although these studies enhanced our understanding of carrier dynamics in BiVO_4 , the TAS is neither element- nor structure-sensitive tool. We recently elucidated the controversies results from the overlooking and the assumptions on the certain spectral regions of TA signal of BiVO_4 [33]. Since the hole carriers drive OER and the major obstacles are the recombination at surface and interface, the accurate attribution of the TA signal to the hole carriers is crucial. This is one of the major concerns of this thesis. TPC response to the pulse within a 1-10 s time scale has been typically attributed to the surface

accumulated hole dynamics due to complicated and multiple recombination channels on the surface and interface [41]–[44]. However, TPC at various applied potential [43] and with the correlation of other experiments can be extremely useful for having information on the charge carrier recombination, particularly the effect of the modification (i.e. co-catalyst or doping) on the carrier dynamics[37], [39], [41], [44], [45].

1.4 Ultrafast Spectroscopy of Charge Carrier dynamics in BiVO₄

1.4.1 Ultrafast Spectroscopy on Semiconductors

The most economic methods for the fabrication of semiconductor films are based on solution-processing methods. These semiconductor films have much more heterogeneous structures than single-crystalline semiconductor samples, having crystalline grain sizes on the order of 100 nm–100 μ m. They have also most likely nano-mesoporous morphologies with a large surface area. Therefore, the mechanisms and dynamics of carrier transport in solution processed semiconductors is more complicated and challenging to analyze than those in single-crystalline samples. There is a pressing need for meticulous understanding of the mechanism of photogenerated charge carriers in polycrystalline semiconductors to advance the design and performance of these semiconductors [9].

After decades of research in this field four overlapping regimes revealed upon photoexcitation [35]:

Coherent Regime (0~200 fs): The temporal regime during and immediately upon irradiation by ultrashort beam is the coherent regime in which the photoexcited states have maintained some certain phase relationship among themselves and with the electromagnetic radiation generating them.

Non-Thermal Regime ($\lesssim 2$ ps): Upon the dephasing of coherence, the distribution of the carriers is more likely to be non-thermal, i.e. the distribution function cannot be identified by a temperature.

Hot-carrier Regime ($\sim 1-100$ ps): Carrier-carrier scattering processes redistribute the energy within the carrier system leading to thermalization within a couple of picoseconds after photoexcitation, i.e. the distribution function can be identified by a temperature. In this regime, the temperature of the carriers (electrons, holes, excitons) is usually higher than the lattice temperature.

Isothermal Regime (≥ 100 ps): At the end of the hot-carrier regime, all the carriers, phonons and excitons can be characterized by the same temperature (are in equilibrium with each other) with the lattice. However, there is still extra electrons and holes compared to the thermodynamic equilibrium. These extra electron-hole pairs (or excitons) recombine and recover the semiconductor to the thermodynamic equilibrium.

The time range for these events rely strongly upon parameters such as band structure, the characteristics of excitation, the lattice temperature and so on. Although these four regimes provide a general frame, many of these physical processes can occur simultaneously. For instance, the events that break coherence can also contribute to thermalization of carrier distribution, and emission of phonons can occur while the electron and holes are thermalizing to a hot distribution. The non-thermal carrier distribution function emerged by the ultrashort pulse is affected by the dephasing of coherent polarization during the irradiation. Consequently, the accurate interpretation of carrier dynamics of a polycrystalline semiconductor is highly challenging. However, pump-probe spectroscopy, as a most common technique of the ultrafast spectroscopy, disclose many problems since the invention of ultrafast lasers [35].

1.4.2 Ultrafast Transient Absorption Spectroscopy of BiVO₄

Transient absorption spectroscopy (TAS) is a versatile tool that is commonly applied to investigate charge carrier recombination dynamics from sub-ps (ultrafast) to ms time scale [8]. TAS is a pump-probe technique in which a continuum probe beam monitors the variation in the absorbance of the materials perturbed by a strong pump beam at a frequency near or greater than the bandgap (Figure 1-5). The pump beam is blocked periodically (at 500 Hz in our system) to

monitor the absorbance difference (ΔA) between the pumped (excited) and unpumped conditions:

$$\Delta A(\lambda_{\text{probe}}, t) = A_{\text{pumped (excited state)}} - A_{\text{unpumped (ground state)}} \quad \text{Eq. 1-10}$$

In general, positive ΔA corresponds to excited state absorption (ESA), two-photon absorption, or product absorption in reactive systems, whereas, negative ΔA is caused by ground state bleaching (GSB) or stimulated emission [36]. The realizations of the charge carriers by TAS, whether ΔA at a certain wavelength is originated from electrons or holes is of significant importance, in particular for the hole carriers, since OER takes place via transport of the holes through the photoanode material. The transient absorption (TA) spectral features of BiVO_4 and Fe_2O_3 [46]–[48] have been interpreted in the light of pioneering investigations on TiO_2 dating back to 1980s [49]–[51]. The formation and utilization of electron and hole carriers upon illumination have been identified by the use of electron and hole scavengers [49]. TA spectral modifications in their presence [50]–[54] and under applied bias [55] have been used as evidence to substantiate the corresponding charge carrier population density changes. More specifically, the TA spectra of photoanode materials have been interpreted in terms of electron trapping, which was later assigned to photogenerated hole absorption (HA) [46], [54], GSB, and ESA of electrons.

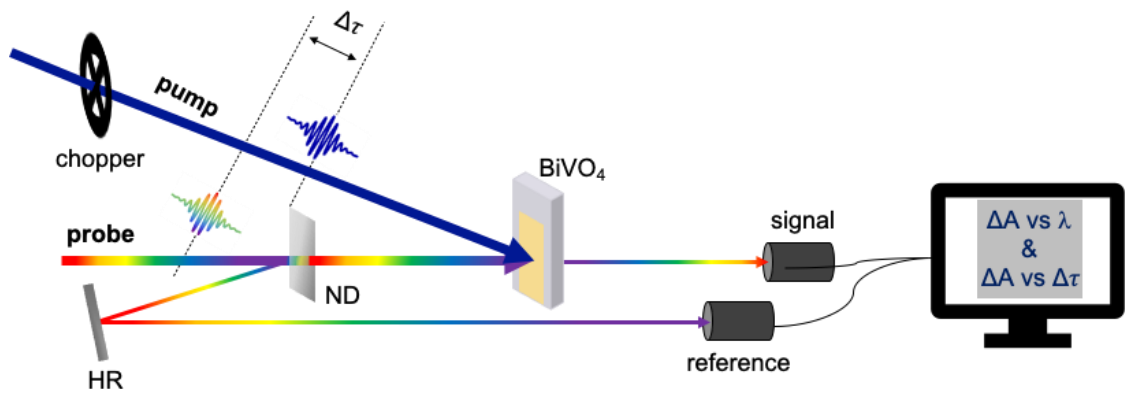


Figure 1-5 The scheme of pump-probe configuration

Earlier TA studies on BiVO_4 were performed to relate the transient peaks to the dynamics of the charge carriers [32], [34], [39], to investigate the effects of W

and Mo doping, and to identify the roles of the water oxidation catalysts in the surface charge recombination channels [56]–[58]. The hole scavenging effect of the ions (sulfite, hydroxide, and others) is attributed to the dynamics in the broad band region (>500 nm). TA spectral features in the 350–500 nm region have been attributed to hole dynamics and ΔA variations have been interpreted in combination with GSB picture [32], [34], [39]. Despite generalized attributions of positive ΔA above 350 nm to the HA channels, more recent investigations take the contribution of the carrier trappings into account. For example, electron-trapping process near CB edge has been found efficient in BiVO_4 , manifesting that the direct recombination of electrons with holes is suppressed [59]. The carrier-phonon interaction leads to the formation of a quasi-particle, “polaron”. Electron and hole trapping via polarons can severely decrease mobilities, reducing the PEC conversion efficiencies [20], however, the trapping can also prevent recombination and increase carrier lifetime [60]. The experimental evidence for small polaron formation has been well-documented [20], the non-monotonous decay in the 1–2 ps region in the TA spectra of BiVO_4 is attributed to polarons [32]. The interpretations that assume specific carrier-related transitions have been challenged, shifting and broadening of optical properties of BiVO_4 have been proposed to be the origin of the spectral variations, especially in short time delays [40]. Although these studies have tremendous contribution to the understanding of the carrier dynamics in BiVO_4 , there is still no consensus about the dynamical processes behind the spectral features.

In PEC investigations, TAS in ns–ms time scale is employed mostly to observe the changes in the carrier lifetime upon heterojunction making, doping, and internal and external modifications in the space-charge layer [61], [62]. Prolonged lifetime is associated with the enhanced PEC activities. However faster dynamical processes cannot be ignored, the merit of the ultrafast recombination under external bias conditions has been discussed for Fe_2O_3 , its impact on the PEC efficiency is remarked [60]. Although the entire recombination process is completed within μs –ms time scales, further in-depth investigations on the TA response are required for BiVO_4 in the presence of electrolyte and applied bias in the ultrafast time scale.

1.5 Modified Surface of BiVO₄ Photoanodes

1.5.1 The Impacts of Thermal Treatment and Film Thickness on TAS of BiVO₄

Ultrafast spectroscopy had an immense contribution to our understanding of chemical reactions since Nobel laureate Zewail showed the transition states of chemical reactions using femtosecond spectroscopy [63]. TAS studies significantly developed our understanding of the loss mechanisms associated with the carrier trapping, recombination, and relaxation of TiO₂ [53], [54], Fe₂O₃ [47], [48], [60], [64], BiVO₄ [34], [39], [40] etc. Still, the major obstacles to reach theoretical limits are related to charge carrier recombination channels [20]. Note that the erroneous attribution of the carriers to the TA signal will be frustrated when we analyze the “improved” photoanodes by TAS. The controversies in the interpretation of TAS results for Fe₂O₃ [114] and BiVO₄ [33] have been elucidated considering many possible electronic transitions based on their band structure. Despite various contributions (such as electronic, thermal, optical etc.) to the optical transient spectra of BiVO₄ have been recently disentangled, deconvolution of the main kinetic traces considering the electronic transitions in the structure has yet to be identified [40].

TAS in the x-ray and extreme-ultraviolet (XUV) spectral regions can give information about the localized carrier dynamics that can link the x-ray and molecular structure unambiguously [65]–[68]. These experiments can be performed via high-harmonic generation (HHG) sources, storage rings (synchrotron facilities) and x-ray free electron laser (XFEL) facilities [69]–[71]. The small-polaron formation of hematite within 3 ps has been recently highlighted by optical pump-XUV probe spectroscopy that produced by HHG [72]. They suggested that the small polaron formation restrains the hematite’s photoconversion efficiency. Optical pump and X-ray (absorption) probe investigation implied that 100 ps upon excitation, the electrons are trapped at the defect-rich surface shell of anatase TiO₂, while they are trapped in the bulk of amorphous TiO₂ [73]. By combination of picosecond x-ray absorption

spectroscopy (XAS) and x-ray emission spectroscopy (XES), the hole trapping at singly charged oxygen vacancies in ZnO was suggested to be occurred within 80 ps [74]. Still, less of such experiments for BiVO₄ [75] is available compared to other TMO semiconductors [65], [67], [76]. Although these experiments can present valuable structural information for TMOs, such experimental tools are not accessible as commercial optical time-resolved (tr) spectroscopy. As a result, the gap of the structural carrier dynamics in BiVO₄ complicates to utilize TAS of BiVO₄ effectively.

Collisions within a certain type of electronic structure (i.e. electrons in the valley sites) are mainly responsible for thermalizing a non-thermal distribution function, despite other scattering processes (i.e. carrier-phonon scattering) are arising concurrently and also affect thermalization to some extent. Although electron-electron scattering is usually the most effective process for thermalizing the electrons, the relative importance of numerous scattering processes depends strongly on the density, and each case is suggested to be scrutinized independently [35]. Despite these processes cannot be revealed independently by optical ultrafast TAS for BiVO₄, film thickness dependence on the TAS can be worthwhile which has not been studied yet. Thermal treatment can also give valuable hints about structural changes (crystallinity and crystal size). The impact of certain crystal facets has been implied on the recombination and transport of the carriers [77], [78], [79] [80]. The crystal-face dependence on the carrier dynamics was shown by tr-photoluminescence (PL) spectroscopy [81]. The enlarged particle size by thermal treatment was implied to increase the hole carrier lifetime [82]. The reduced local distortion in (VO₄)₃- units has been demonstrated after thermal treatment which was implied to increase the charge separation and decrease the charge recombination.

1.5.2 Nitrogen Incorporation into BiVO₄

Surface modification and bulk doping enhance the PEC conversion efficiency of BiVO₄ photoanodes, which have been suggested as a potential strategy to realize practical applications [27]. Heteroatom doping of BiVO₄ by replacing V

with W [83] and Mo [84] serve this purpose, since enhanced majority carriers result in higher performances. Additional oxygen vacancies (V_o) forming due to heteroatom doping also play a role in understanding the motives behind the enhanced activity and water oxidation steps [22], [85]. The V_o s formed via reduction of V from 5+ to 4+ in BiVO_4 under illumination are suggested to be a main loss channel for the photogenerated charge carriers [86]. However, V_o s could also take part in the PEC as active surface sites [22], [87], [88] and such a redox process has already been implied to be the first step of the water oxidation reaction for hematite photoanodes [89], [90]. Identifying the relationship between the V_o s and V_{5+}/V_{4+} redox exchange in the course of PEC water oxidation and surface recombination is an indispensable way to improve the charge transfer property and the stability of the BiVO_4 photoanodes, simultaneously [91], [92].

Nitrogen incorporation has been extensively applied to the transition metal oxides to modify their electronic structures [93]. For N- TiO_2 , it has been shown that a larger portion of the spectrum extending from the UV to the visible region could be harvested due to the localized states formed below the CB (V_o and Ti_{3+}) and above the VB (N 2p) [94]. Nitrogen in TiO_2 prevents charge carrier recombination by trapping photogenerated electrons [95]. Nitrogen incorporation lead to the formation of many additional V_o s [94], [96], thereby increasing the surface adsorption sites that enhances the photocatalytic activity further [97]. The studies of N- BiVO_4 , however, are scarce. The elevated PEC performance of N- BiVO_4 photoanode has been attributed to the decreased bandgap (higher light-harvesting), improved carrier mobility, and increased majority carrier density by generating V_o s [98]. It was also recently reported that the photoactivity was unaffected when molecular nitrogen resides in the lattice of BiVO_4 [99].

The V_o s in BiVO_4 are central due to their connection with water oxidation intermediates and intrinsic/extrinsic recombination centers; they pose a concentration-dependent influence on the majority carrier mobility and the polaron characteristics. Controversies exist, since several studies show positive effects of the V_o on BiVO_4 PEC activity, [7], [83], [98], [100], [101], [78], [102] whereas others claim detrimental impact [103]–[105]. While the energy level of

V_{os} affects the photogenerated electron conductivity due to their proximity to the CB edge states,[20] the relation between the energy levels of V_{os} and water oxidation intermediates is critical for understanding their role on the PEC activities [7], [22]. V_{os} in the bulk are suggested to be lying at either shallow states [105]–[108] or deep states [98], [109] within the bandgap. It has also been shown that modified activation of the surface species coordinated to the V_{os} on the surface of BiVO_4 promotes the interfacial charge transfer [83], [110]. A recent study has highlighted two distinct configurations of V_{os} in BiVO_4 and discussed their different functionalities in both bulk and the (001) surface: one forming a vacancy-trapped charge state with two electrons paired and localized at the vacancy site, the other quenching the vacancy by bridging V–O–V and concomitantly delocalizing one electron. It was concluded that both are nearly isoenergetic in the bulk while the (001) subsurface presents a large energetic sink for the creation of V–O–V units [78]. There are also controversies on the role of V_{os} on the transport properties of BiVO_4 . It has been reported that the majority carrier concentration increases due to the passivation of V_{os} upon annealing BiVO_4 in a hydrogen ambient, suggesting that H rather than V_o contributes to n-type conductivity [109]. However, increased majority carrier concentration after annealing BiVO_4 in nitrogen compared to hydrogen ambient was also reported.[98], [101]. The charge recombination on BiVO_4 surfaces can be investigated by analyzing TPC response to an excitation induced by chopped (or pulsed) light. Due to complicated and multiple recombination channels on the surface and interface, the decay of TPC response to the pulse within a 1-10 s time scale is typically attributed to surface recombination[41]–[44].

1.5.3 Co-catalyst Layer Deposition on BiVO_4 Photoanodes

A catalyst is a complex, accelerates the rate of a chemical reaction without being consumed through the reaction [111]. The catalyst stimulates the reaction by aiding the bond breaking of the reactants and the creation of new bonds to form the reaction product, typically by leading alternative route for the reaction. For use in a PEC cell, a good hydrogen evolution catalyst (HEC) and oxygen evolution catalyst (OEC) must fulfill two essential points [6]. First, the catalyst must be capable of yielding at a minimum overpotential, large quantities of

hydrogen or oxygen as quickly as the semiconductor can provide electrons or holes to the catalyst. Second, an applicable catalyst must conserve its productivity over commercial time scales. There is no single material that satisfies these requirements while having effective sunlight absorption capability[20].

BiVO_4 is a promising photocatalyst but its poor charge transfer ability and stability at the semiconductor-electrolyte interface requires a modification of its surface to produce a reasonable amount of OER [21]. These two problems can be unraveled concurrently by employing a cocatalyst. The cocatalyst is expected to decrease the activation energy of water oxidation through a superior pathway for holes, instead of the semiconductor itself. However, the role of the cocatalyst is highly complicated: It is expected from a cocatalyst to decrease the activation energy (EA) for OER in terms of classical catalysis but it can also suppress the recombination via passivating surface. On the other hand, a good OEC for electrochemical water oxidation does not always make good OEC for the photoanode. IrO_x and RuO_x are well-known OECs but their efficiency as cocatalysts on BiVO_4 is highly small compared to cobalt phosphate (CoPi) or FeOOH despite the electrochemical OEC activities CoPi and FeOOH are quite poorer [27], [112]. Co-Pi has been specially attracted owing to the abundance of cobalt and phosphate, applicable water oxidation characteristics and stability due to its “self-healing” mechanism [113]. The enhanced performance of Fe_2O_3 modified with CoPi has been ascribed to elevating the OER kinetics increasing band bending [114], suppressing surface recombination and assisting charge separation[115]. The reason behind the enhancement of the photocurrent of CoPi- BiVO_4 is also debatable: It was claimed that the CoPi overlayer (~1 nm) passivate surface recombination centers rather than enhancing the OER [116]. The suppression of back-electron recombination was reported upon modification of BiVO_4 surface with CoPi overlayer (100 nm), while they highlighted that there is no evidence of catalytic water oxidation via CoPi [57]. However, the increased catalytic activity of CoPi- BiVO_4 was observed by showing the lower onset potential and the optimum thickness of CoPi as 30 nm [117]. Still, even 30 nm cocatalyst layer might be high to discuss its catalytic effect in PEC conversion of BiVO_4 due to restriction of effective hole diffusion length.

Improved OER kinetics and faster charge transfer rate at the solid/electrolyte interface can be attained by other cobalt based catalyst, cobalt oxide (CoO_x) based catalysts. A thin layer of CoO_x deposited by atomic layer deposition (ALD) has been revealed to increase the stability and activity of BiVO_4 [118]. The improved performance, stability, and OER efficiency of CoO_x - BiVO_4 films was reported implying the optimum catalyst layer as a few nm [119]. CoO_x can be found in the form (or phase) of oxides, hydrated oxides, hydroxides, and oxyhydrides: It is likely that each CoO_x phase can act differently in the course of OER. For instance, the phase improving the interfacial charge transfer rate may not be as active for OER that was implied by Fourier-transform infrared (FTIR) spectroscopy under reaction conditions [120]. Despite the role of CoPi was discussed on carrier recombination and catalytic activity in detail, the investigation on the carrier dynamics of CoO_x - BiVO_4 is missing. Besides, the role of the local environment of Co, which defines the most active phase of these catalysts in water oxidation conditions has yet to be understood but can be resolved by core-level spectroscopy (CLS), specifically XAS [121]. While XAS presents structural and geometrical information through the unoccupied states of Co L-edge, TAS of CoO_x - BiVO_4 can be favorable to determine the catalyst role on the surface recombination dynamics.

When atoms condense into solids, the VB electron states and their arrangement in solids are fully disturbed depending on the atomic species. The study of VB electron states is the main object of solid-state physics that was mostly investigated with photons in the visible and infrared spectrum until the use of CLS has expanded in the 1970s due to development of the synchrotron radiation [122]. The core electrons of atoms are deeply bound inside the atoms and are nearly unaltered even when atoms condense into solids. CLS is a powerful tool to study VES, where a core electron is excited by incident x-rays and the VB electron states are monitored with the core electron (or hole) state as a probe. The core electrons can be excited by the photons with energies larger than the core level binding energies (up to about 30 keV) that belong mainly to the x-ray region. The synchrotron radiation that is produced in storage rings cover from a few eV (infrared) to hundreds of keV (hard x-ray) of electromagnetic spectrum with high brilliance. In laboratory conditions, however, the x-ray sources can emit

monochromatic x-rays such as the radiation of K α (Al) at 1486.6 eV K α (Mg) 1253.6 eV with much lower flux compared to the synchrotron radiation. The number of molecules bonded to the surface is $\sim 10^{15}$ atoms/cm² that means $\sim 10^3$ photons should involve to create one absorption event ($\sim 10^3$ photons correspond to $\sim 10^9$ photons/s that can be produced in the storage rings [123]. Still the contribution from the substrate is huge, that leads us to elucidate the structure by extreme-surface sensitive techniques among various CLS techniques. While X-ray photoemission spectroscopy (XPS) presents information of photo-emitted core electrons' binding energy through a few top atomic layers of the surface, electron-yield soft XAS is superior to elucidate the heterogeneous catalysts concerning the 3d transition metals, such as Fe, Co, Ni [123]. Further understanding of compositional and structural changes requires to deal with the surface in the operational conditions.

1.6 Research Objectives

The PEC conversion performance record of BiVO₄ photoanodes has been broken many times in the last decade. However, fundamental issues still exist which are required to be resolved for its commercial applications [21]. The hole transfer process to the electrolyte and electron conduction to the counter electrode through the bulk have not been clarified yet. Both are associated with the recombination mechanism, either in bulk or at the interface. The better understanding of the carrier dynamics will aid for benefitting from doping and co-catalyst more efficiently that will accelerate the utilization of BiVO₄ towards practical applications. The combination of the time-resolved and structure-sensitive spectroscopy can be game changer to find answers to such fundamental questions. In order to utilize the optical spectroscopy effectively, the assignment of the carriers to the spectroscopy signals is vital. Other critical point is to distinguish the trapping of charge carriers at interface as a recombination center or a reaction site which is directly related to the Vos of BiVO₄ [22]: the role of Vos has yet to be identified and it is a hot topic either for BiVO₄ [7], [22], [83], [98], [103] or other TMO semiconductors[74], [94], [95], [124].

The research objectives were:

- **The assignment of the main TA characteristics of BiVO₄ (Chapter 3)**

First studies of TAS of BiVO₄ focus on the spectrum at above 500 nm and assign the transient absorption signal to holes [34], [39]. Another case study implied the existence of recombination channels of BiVO₄ in ps and ns-μs scale [32] assigning the spectrum of 450-500 nm to hole carrier by inferring from the prior research [34], [39]. Many other studies utilized TAS to investigate the altered hole carrier lifetime upon modification of BiVO₄ photoanodes by taking the prior TAS studies as base studies when they interpret the TAS results [9], [125], [126]. The controversies originated by such assumptions have been elucidated for Fe₂O₃ [64] and CdTe [127]. Therefore, I preferred to fully analyze the TA signal in the spectral region 350-650 nm for BiVO₄.

The electronic band structure of BiVO₄ was demonstrated by various experimental measurements in 2014 [18]. In order to fully evaluate the TA characteristics of BiVO₄, I aimed to develop a numerical model based on the rate equations regarding all possible transitions upon pump excitation considering the band structure. The objective of the experimental part was to interrogate the outcomes of the numerical study and have rigid conclusion to see the dominance of electrons or holes on the certain TA characteristics of BiVO₄. I perturbed the electron and hole density during ultrafast TAS measurement by external anodic bias (*operando* TAS) and hole scavenger (*in situ* TAS), respectively. Since the results of these experiments contradicted with the assumptions of TAS of BiVO₄, I performed a third experiment to make sure the results by observing the change of the characteristics under increase of pump excitation intensity. Moreover, I repeated *operando* and *in situ* experiments in longer time scale (ns-ms) to see whether any major changes occur or not.

- **Investigation of the ultrafast response of TA characteristics of BiVO₄ to understand the effects of structural changes (Chapter 4)**

Ultrafast optical TAS can present information about the energy redistribution upon the excitation of the system, however it lacks structural and geometrical evidence. Yet, TAS contains some signatures of structural modifications in the ultrafast scales. These can be deduced from the spectral relationships of TA signal, while TAS experiments of perturbed structures can provide us to interrogate the outcomes. The aim of this chapter is to investigate the carrier dynamics predominantly at early stages (0-10 ps) when the cooling of the thermalized carriers is about to begin, thereby, to obtain fingerprints of structural variations and the mechanisms leads to the recombination and photocarrier trapping.

- **Understanding the motives behind the enhanced PEC activity upon nitrogen incorporation/doping into BiVO₄ (Chapter 5)**

The improved PEC activity of N-BiVO₄ has been attributed to the simultaneous improvement of light-absorption, carrier mobility and majority carrier density [98]. I aimed at to observe the motives behind the improvement by TPC experiments in the surface recombination and water oxidation scale. The results had strong indication that nitrogen leads a suppression of a recombination channel at the interface. Since the most critical processes take place at the semiconductor-electrolyte interface during OER, I wanted to focus on this intricate region performing complementary PEC measurements by populating the adsorbed species (i.e. OH-) at the interface. To isolate these findings from the effect of nitrogen in the bulk, modified TPC experiments have been performed to find diffusion length and depletion width of BiVO₄. In order to examine the impact of nitrogen incorporation further, I did also ultrafast TAS to observe the charge carrier dynamics in fs-ns scale and XPS experiments to have more surface sensitive information on elemental changes.

- **Understanding the effects of co-catalyst layer on BiVO₄ photoanodes (Chapter 6)**

A well-known electrocatalyst can have different impact on PEC process. The role of the co-catalyst (CoPi) is a hot debate whether it affects the oxidation reaction kinetics or only the passivation of surface recombination channels of BiVO₄ surface [116]. Despite it has been discussed elaborately [57], [116], [117], [128], the impact of CoO_x on the recombination mechanism of BiVO₄ has not been investigated yet. The combination of core-level and time-resolved spectroscopy can be valuable in our understanding of the mechanism underlying the improvement of the activity via the co-catalyst. In order to understand the effect of cobalt-oxide based OECs on BiVO₄ photoanodes, I performed TAS and CLS experiments. Different phases of the cobalt based catalysts were examined to find the active phase of CoO_x. The other goal is to further understand the change of the surface structure in H₂O ambient in order to simultaneously examine catalytic surfaces (Co) and adsorbates (i.e. OH⁻).

2 Experimental and Numerical Methods

2.1 Photoanode preparation

2.1.1 Spin-coating Method

BiVO_4 films were prepared on transparent conductive oxide coated on fluorine doped tin-oxide (FTO) glass by spin-coating method. A solution with Bi:V molar ratio of $\sim 1:1$ was prepared as follows: First, separate solutions were prepared by adding 1.5 g of bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Sigma-Aldrich, 99.99%) into 15 mL 2,4-pentanedione ($\text{CH}_3\text{COCH}_2\text{COCH}_3$, Sigma-Aldrich) and by adding 796 mg of vanadyl acetylacetonate ($\text{OV}(\text{C}_5\text{H}_7\text{O}_2)_2$, Sigma-Aldrich, 98%) into 100 mL of 2,4-pentanedione. Second, two solutions were mixed and stirred overnight. Before spin-coating, the top part of the FTO/glass was coated with Teflon tape to maintain conductive part available for electrical connections. The spin coating was achieved for 8 sec at 1000 rpm for two successive times. The films were then annealed at 450 °C in air for 10 min in a muffle furnace. This spin coating-heating cycle was repeated 10 times to have optimum thickness and the final annealing was done at 500 °C for 2 h in air. Prior to activity tests, the samples were soaked in a 1.0 M sodium hydroxide (NaOH) solution for 30 minutes while being gently stirred, and then rinsed with distilled water. This treatment is needed for removing the extra V_2O_5 from the films.

2.1.2 Electrodeposition Method

Nanoporous BiVO_4 photoanodes were prepared by electrodeposition (ED) of bismuth oxyiodide (BiOI) film followed by dripping of vanadium solution on it and heat treatment. A slightly different method was reported previously [129]. To prepare a BiOI electrodeposition solution, 0.75 g of sodium iodide (NaI) was dissolved in 12 mL of DI water and the pH of the solution was adjusted to 1.8 using nitric acid (HNO_3). Then, 240 mg of bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) was added to the NaI solution and stirred for 30 min. 120 mg of p-benzoquinone was dissolved in 5 mL dimethyl sulfoxide (DMSO) and stirred

for 15 minutes. The stirred solution was then added to the BiOI solution. The electrodeposition of BiOI film on FTO coated glass was performed under -0.1 V bias vs Ag/AgCl electrode for 2 min. After deposition, the films were washed with DI water and dried in air. 1 μ l of 0.4 M solution of vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) in ethanol was dropped on 0.5 cm^2 area of the films, followed by annealing at 450 $^{\circ}\text{C}$ for 2 h (ramping rate: 2 $^{\circ}\text{C}\cdot\text{min}^{-1}$). The samples were soaked in 1.0 M NaOH solution and stirred softly for 30 min to remove the extra vanadium oxide from the surface.

2.1.2.1 Nitrogen incorporation into BiVO_4 (N- BiVO_4)

N- BiVO_4 was prepared by further heat-treating or thermal treatment (TT) BiVO_4 in a tube furnace under N_2 flow at 350 $^{\circ}\text{C}$ for 2 h.

2.1.2.2 Co-catalyst layer deposition onto BiVO_4 (CoOxs- BiVO_4)

Nanoporous BiVO_4 photoanodes were prepared by the electrodeposition method. CoOx OEC layer was deposited on BiVO_4 electrodes by ALD using Cambridge Nanotechnology Savannah 200 system. Cobaltocene was used as the reactant precursor at a temperature of 85 $^{\circ}\text{C}$. The deposition was completed by setting the ALD reactor temperature to 150 $^{\circ}\text{C}$. H_2O and O_3 were used as oxidizing reagents during deposition. Each ALD cycle consisted of 3 sec pulse of cobaltocene, 10 sec purge in N_2 at 20 sccm and 1.5 sec pulse of H_2O vapor followed by 15 sec purge on N_2 again for the H_2O oxidized Co-based OEC ($\text{Co}(\text{OH})_2$). For deposition of CoOx- O_3 , 0.01 s O_3 pulses were used as an oxidant instead of H_2O vapor. The thickness of the overlayer OECs is about 1 nm that was quantified by XPS analysis.

The best activity was observed on $\text{Co}(\text{OH})_2$ deposited on BiVO_4 . TT is applied to $\text{Co}(\text{OH})_2$ - BiVO_4 as we recently demonstrate that this post-synthetic method enhances the activity of bare BiVO_4 [130]. HT was applied in a tube furnace under O_2 flow at 200 $^{\circ}\text{C}$ for 2 h.

2.2 Photoelectrochemical (PEC) Measurements

PEC measurements are typically performed in a quartz cell with three electrodes by potentiostat. For specifically water oxidation measurements, the three-electrode cell configuration contains a counter electrode (CE), Ag/AgCl (sat. KCl) reference electrode (RE) and photoanode as the working electrode (WE). The potentiostat is an electronic device that controls the voltage difference between the WE and RE that is achieved by introducing current into the cell through the CE. The potentiostat measures the current flow between the WE and CE by controlling cell. BiVO₄ is the photoanode in our photoelectrochemical measurements. The cell used in our measurements is shown in Figure 2-1.

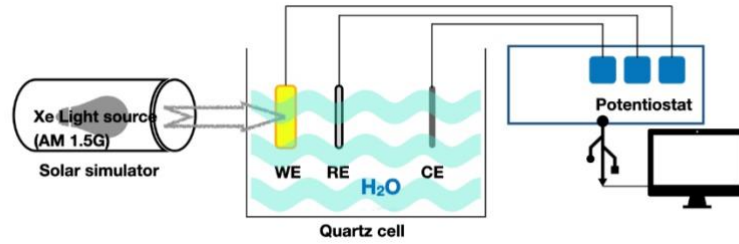


Figure 2-1 The configuration of the photoelectrochemical cell experiment consisting of the reference electrode (RE), working electrode (CE) and the working electrode (WE).

The PEC measurements were performed using an LCS-100 solar simulator with standard 1.0 SUN AM 1.5G irradiation from a 100 W Xenon light source coupled to a VSP-300 BioLogic potentiostat. The potentials were converted to V vs. RHE using the Nernst equation:

$$V_{RHE}(V) = V_{Ag/AgCl}(V) + 0.059 \times pH + V_{Ag/AgCl}^0(V) \quad Eq.2-1$$

where V_{RHE} is the applied potential versus RHE; $V_{Ag/AgCl}$ (V) is the applied potential versus Ag/AgCl reference electrode during measurements; $V_{Ag/AgCl}^0$ (V) is the standard potential of the reference electrode (0.197 V). All PEC measurements were carried out in pH=7.5 electrolytes made of 0.1 M potassium phosphate buffer in the presence and absence of 0.5 M sodium sulfite (Na₂SO₃) as a hole scavenger.

2.2.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is a widespread electrochemical technique employed to investigate the redox processes of molecular species. The potential of the WE is increased linearly in cyclical phases, and the current passing through the WE is measured. The number of repeating cycles can be increased as many times as required for the analysis. The CV plot presents the current versus potential. Scan rate is the rate of change of potential per time. Various information can be obtained from CV curves at different scan rates: the adsorbed species on the WE that play critical role on the interfacial charge transfer can be probed (see Chapter 5.2). Besides, the CV experiments in different solutions can give information about the charge injection into electrolyte and charge separation [130].

2.2.2 Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) is a voltammetry method that potential in a fixed range is swept between the working electrode and a reference electrode (Ag/AgCl), linearly and the current response at the working electrode is measured. Oxidation or reduction of the species is detected as a peak in current at the oxidation or reduction potential. Unknown species can be identified by LSV and the sensitivity of the current versus voltage can be increased by increasing the scan rate. The difference between LSV and CV is that after reaching the set potential in the CV experiment, the potential is ramped in the opposite direction and returns to the initial potential value. The number of repeating cycles can be increased as many times as required for the analysis.

2.3 Transient Absorption Spectroscopy

2.3.1 Experimental Methods

The experiments were performed using a commercial Ti:sapphire amplifier laser (Spectra-Physics, Spitfire Ace, 1 kHz repetition rate) that is seeded by femtosecond pulses mode-locked, Ti: sapphire laser system (Spectra-Physics Mai Tai SP). The energy required for amplifying the seed pulses is supplied by a Q-switched Nd:YLF pump laser (Spectra-Physics Empower 45). The pulse produced

by Spitfire Ace amplifier is based on “chirped pulse amplification (CPA)” that comprises an optical stretcher, regenerative amplifier and optical compressor. Spitfire Ace systems include two ancillary controllers, the Timing and Delay Generator (TDG), which provides the precise timing required to select pulses for amplification and eject all others from the amplifier, and the Temperature Control Unit (TCU), which maintains the Ti: sapphire amplifying crystal at its optimum temperature and humidity.

The Spitfire Ace amplifier output with a wavelength of 800 nm and pulse-width of <150 fs, is divided into two beams. One of the beams was converted to the desired wavelength of 320 nm by using a commercial optical parametric amplifier (Light Conversion, TOPAS). The other portion of the 800-nm beam was passed through crystals; the crystals generate a white light continuum from 350 nm to 1600 nm. Ultrafast TA measurements were then performed by using a commercial pump-probe spectrometer (Ultrafast Systems, HELIOS). In general, 320-nm pump fluence incident on the sample was set to 127 $\mu\text{J}/\text{cm}^2$ during the experiments.

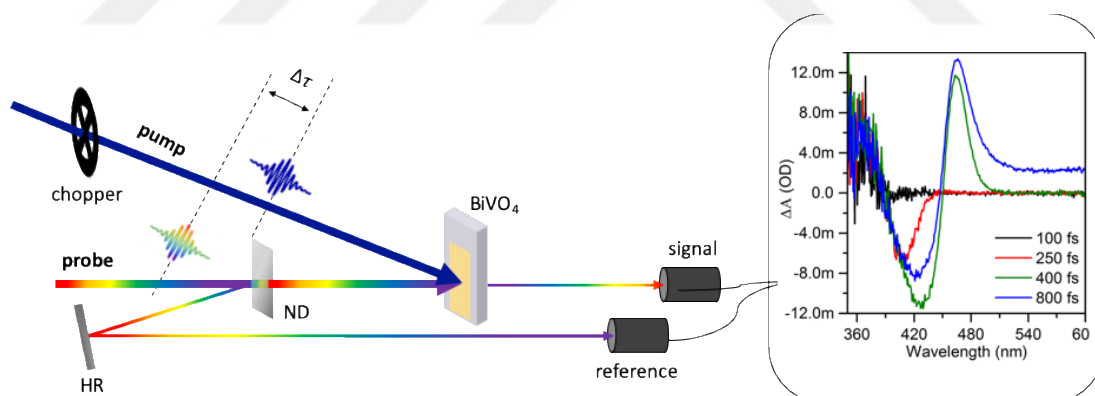


Figure 2-2 The pump-probe scheme and a typical time-evolution spectrum of BiVO_4 .

The probe light was split into signal and reference beams in the spectrometer, both of which were delivered through the fibers that were coupled to a multichannel spectrometer with a 1.5 nm spectral resolution between 350 and 850 nm (Figure 2-2). The pump-probe delay was controlled by means of a mechanical delay stage. Nanosecond transient absorption measurements were conducted by using the same ultrafast pump pulses along with another electronically delayed supercontinuum light source operating between 360 and

900 nm with a sub-nanosecond pulse duration (EOS, Ultrafast Systems). To record the nonlinear ΔA (pumped absorbance-unpumped absorbance) spectrum, the pump beam incident on the sample was periodically blocked with a 500-Hz chopper in femtosecond TA experiments.

In situ TAS experiments were conducted in three-electrode configuration using a BioLogic VSP 300 potentiostat. The potentials were converted to V vs. RHE (reversible hydrogen electrode) using the Nernst equation: $V_{\text{RHE}}(\text{V}) = V_{\text{Ag/AgCl}}(\text{V}) + 0.059 \times \text{pH} + V^{\circ}_{\text{Ag/AgCl}}(\text{V})$, where V_{RHE} is the applied potential versus RHE; $V_{\text{Ag/AgCl}}(\text{V})$ is the applied potential versus Ag/AgCl reference electrode during measurements. $V^{\circ}_{\text{Ag/AgCl}}(\text{V})$ is the standard potential of the reference electrode. Pt is used as a counter electrode. The measurements under bias were performed between 0.35-0.85 V vs RHE by increasing the bias voltage in increments of 0.1 V. The scavenger effect was further studied by comparing TA results obtained in the phosphate buffer solution (1.0 M KHPO₄, pH=6.35). 0.5 M sodium sulfite (Na₂SO₃) as a hole scavenger was added into the buffer solution (pH ~7.45).

2.3.2 Numerical Method

2.3.2.1 The Basics of the Rate Equations

The numerical method is based on the rate equations. Time rate of change of the population densities can be solved by the rate equations and they are dependent on the population density (N), absorption cross-section (σ), lifetime (τ) of the carriers in the excited states, the intensity (I) and the wavelength of the light (λ) [131], [132]. The spontaneous emission cross-section is negligible due to the scattering of photons in every direction; the stimulated emission cross-sections is negligible due to lack of resonant photons. For ideal two-level system (Figure 2-3), the rate equations can be written as:

$$\frac{\partial N_2}{\partial t} = \frac{I\sigma\lambda}{h \times c} N_1(t) - \frac{N_2(t)}{\tau} \quad \text{Eq. 2-2}$$

$$\frac{\partial N_1}{\partial t} = -\frac{I\sigma\lambda}{h \times c} N_1(t) + \frac{N_2(t)}{\tau} \quad \text{Eq. 2-3}$$

where h and c are Planck constant and speed of light, respectively. The initial conditions are $N_1(0) = N_1(t_{\text{final}}) = N_{\text{total}}$ and $N_2(0) = N_2(t_{\text{final}}) = 0$.

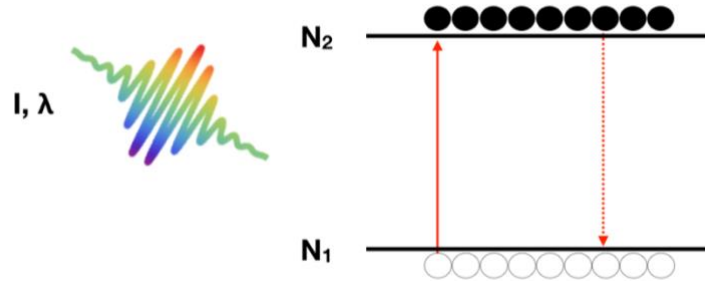


Figure 2-3 The ideal two-level system: Energy levels of populations in the ground state (N_1) and excited state (N_2) of an atomic system.

The real atomic or molecular system involves a great number of energy levels. For M levels $M-1$ rate equations with the time derivatives set equal to zero, plus the supplementary condition given by conservation of the total number of atoms. This gives a set of M coupled linear algebraic equations. Although $M \geq 3$ becomes highly complicated, that can be handled by computer-based programs [132]. In our study, we used a computing system, Wolfram Mathematica, to solve the linear equations.

Note that the pump beam is much stronger than probe beam in the pump-probe measurement: The function of the probe beam is only to monitor the time-varying absorption of the material by passing through the sample following the pump beam and in the absence of the pump beam. Therefore, only the σ of the pump beam is used in the rate equations because this analysis is based on the absorption difference arises by the pump beam. The role of the probe beam in the rate equations can be examined on the transitions among the energy levels of the electronic structure. The critical point in the analysis of rate equations is to determine these transitions introduced by the probe beam. Since the probe beam is super-continuum (350-650 nm) and there is a continuous absorption within this range for BiVO_4 , we concentrated on certain wavelengths that have strongest absorptions of BiVO_4 in TAS measurements: 370 nm, 430 nm and 470 nm. The photon energies of these wavelengths correspond to 3.35 eV, 2.88 eV and 2.64

eV. The primary goal of the rate equation analysis is to determine these transitions in the excited state of BiVO_4 . Next, to analyze the kinetics of these transitions to observe whether they fit to experimental results between 0-3 ns. Both the VB and CB of the electronic structure of BiVO_4 are continuous (Figure 1-2) that makes the problem highly complicated due to many allowed transitions at UV-Vis region of the spectrum. Moreover, BiVO_4 has either direct or indirect bandgap transitions [133]. Considering these issues, I could be able to propose a model (Figure 2-4) that successfully simulates the absorptions of 370 nm, 430nm and 470 nm from a few ps to 3 ns. The rate equations and the details of the variables are written below. The proposed model and the fitting results are elaborately discussed in Chapter 2.5.

2.3.2.2 The rate Equations Applied to TAS of BiVO_4

Measured transient absorption (TA) spectra of BiVO_4 showed three dominant nonlinear absorption peaks centered near the wavelengths of 370, 430, and 470 nm (Figure 3-1). To explain these features, the time evolution of populations at different energy levels was investigated by using a numerical model based on rate equations [131], [132].

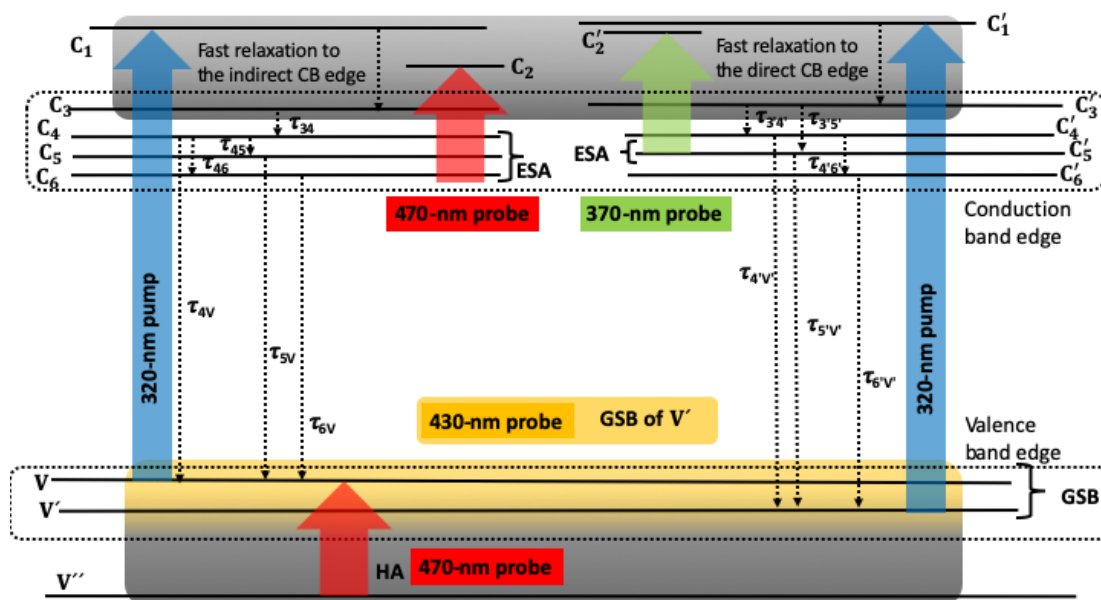


Figure 2-4 Detailed diagram of the transitions used in the numerical study.

In the rate equation model, it is assumed that the pump photons excite the electrons residing near the VB edge (designated as V and V' levels in Figure 2-4) to the upper levels C_1, C'_1 lying within the CB. Electrons then undergo relaxation via two possible channels to levels C_3 and C'_3 . The transition rate from C_1 (C'_1) to C_3 (C'_3) is assumed to be very fast leaving a negligible population in level C_1 (C'_1). Once in level C'_3 , electrons decay to levels C'_4 and C'_5 , whereas those in C'_4 further decay to the lower level C'_6 and ground state V' . Additionally, electrons in C'_5 and C'_6 decay to the ground state V' . Electrons ending up in level C'_5 undergo the ESA to upper level C'_2 corresponding to the probe absorption observed at 370 nm. Similarly, after the rapid decay from C_1 to the level C_3 , electrons decay to level C_4 . Electrons in C_4 further decay in successive steps to C_5, C_6 , and ground state V . In addition, electrons in C_5 and C_6 relax to the ground state V . The other nonlinear absorption band centered at 470 nm corresponds to the ESA of electrons from the levels C_4, C_5 , and C_6 to C_2 . Alternatively, the observed nonlinear absorbance at 470 nm can be analyzed by focusing on photogenerated holes near VB edge, whereby electrons in a deep VB level (V'') are promoted to the ground state V , referred to as photogenerated hole absorption (HA). We assumed that the ESA levels included in our model correspond to the V 3d states of BiVO_4 [18]. Furthermore, the intermediate states ($C_1 - C_6$ and $C'_1 - C'_6$) in the rate equation model represent possible trap states or other states exhibiting small polaronic behavior suggested in previous studies [20]. GSB observed at the center wavelength of 430 nm corresponds to the absorption of electrons from the state V' which is the edge of the CB. The full set of rate equations which summarizes these processes can be found in the equations from 2-4 to 2-13.

The full set of rate equations that was used in the simulations are:

$$\frac{\partial N_{C'_3}}{\partial t} = \frac{1}{h \times c} I_p \sigma_{320} \lambda_{320} N_{V'}(t) - \frac{N_{C'_3}(t)}{\tau_{3'4'}} - \frac{N_{C'_3}(t)}{\tau_{3'5'}} \quad \text{Eq. 2-4}$$

$$\frac{\partial N_{C_3}}{\partial t} = \frac{1}{h \times c} I_p \sigma_{320} \lambda_{320} N_V(t) - \frac{N_{C_3}(t)}{\tau_{34}} \quad \text{Eq. 2-5}$$

$$\frac{\partial N_{C_4'}}{\partial t} = \frac{N_{C_3'}(t)}{\tau_{3'4'}} - \frac{N_{C_4'}(t)}{\tau_{4'6'}} - \frac{N_{C_4'}(t)}{\tau_{4'V'}} \quad \text{Eq. 2-6}$$

$$\frac{\partial N_{C_4}}{\partial t} = \frac{N_{C_3}(t)}{\tau_{34}} - \frac{N_{C_4}(t)}{\tau_{45}} - \frac{N_{C_4}(t)}{\tau_{46}} - \frac{N_{C_4}(t)}{\tau_{4V}} \quad \text{Eq. 2-7}$$

$$\frac{\partial N_{C_5'}}{\partial t} = \frac{N_{C_3'}(t)}{\tau_{3'5'}} - \frac{N_{C_5'}(t)}{\tau_{5'V'}} \quad \text{Eq. 2-8}$$

$$\frac{\partial N_{C_5}}{\partial t} = \frac{N_{C_4}(t)}{\tau_{45}} - \frac{N_{C_5}(t)}{\tau_{5V}} \quad \text{Eq. 2-9}$$

$$\frac{\partial N_{C_6'}}{\partial t} = \frac{N_{C_4'}(t)}{\tau_{4'6'}} - \frac{N_{C_6'}(t)}{\tau_{6'V'}} \quad \text{Eq. 2-10}$$

$$\frac{\partial N_{C_6}}{\partial t} = \frac{N_{C_4}(t)}{\tau_{46}} - \frac{N_{C_6}(t)}{\tau_{6V}} \quad \text{Eq. 2-11}$$

$$\frac{\partial N_{V'}}{\partial t} = -\frac{1}{h \times c} I_p \sigma_{320} \lambda_{320} N_{V'}(t) + \frac{N_{C_4'}(t)}{\tau_{4'V'}} + \frac{N_{C_5'}(t)}{\tau_{5'V'}} + \frac{N_{C_6'}(t)}{\tau_{6'V'}} \quad \text{Eq. 2-12}$$

$$\frac{\partial N_V}{\partial t} = -\frac{1}{h \times c} I_p \sigma_{320} \lambda_{320} N_V(t) + \frac{N_{C_4}(t)}{\tau_{4V}} + \frac{N_{C_5}(t)}{\tau_{5V}} + \frac{N_{C_6}(t)}{\tau_{6V}} \quad \text{Eq. 2-13}$$

σ_λ : Absorption cross-section at the pump wavelength (λ).

τ_{ij} : Lifetime of the energy levels.

I_p : Pump intensity as a function of the pump power, spot size, time, and delay between pump and probe. Note that the probe induced population changes are neglected since probe intensity was much smaller than the pump intensity. Similarly, to ensure that the response of the sample was probed from the excited area, incident spot size of the pump was adjusted to be larger than that of the probe pulse. Furthermore, pump pulse profile was assumed to be Gaussian during the calculations.

$N_i, N_{i'}$: Populations of the energy levels which are schematically described as C_i in Figure 2-4.

h : Planck's constant and c : speed of light.

The initial conditions of the rate equations (initial population densities of the energy levels) were:

$$N_i(0) = N_{i'}(0) = N_i(t_{final}) = N_{i'}(t_{final}) = 0 \quad \text{Eq. 2-14}$$

$$N_V(0) = N_{V'}(0) = N_V(t_{final}) = N_{V'}(t_{final}) = 10^{24} m^{-3} \quad \text{Eq. 2-15}$$

where i and i' : 1,..6. During the calculation, the final time (t_{final}) was set to 10^{-6} s.

Input parameters of the simulation were:

Pulse duration: 150 fs.

Pulse repetition rate: 1 kHz.

Wavelengths of the probe pulses and pump pulse: 370, 430, 470, and 320 nm.

Spot size of the pump beam: 500 μm .

Pump power: 1 mW.

Thickness of the film: 300 nm.

Delay between the pump and probe beam: 144 fs.

The best fit between the measured and calculated time-resolved data was obtained by adjusting the cross sections (σ_λ) and lifetimes (τ_{ij}) that are given above.

At a given probe wavelength, the observed ΔA corresponds to the difference in the absorbance of the sample between pumped and unpumped cases and can be written as

$$\Delta A = A_{pumped} - A_{unpumped} \quad \text{Eq. 2-16}$$

In Eq. 2-16, the absorbance (A) of the sample can be determined from $A = -\ln(T)$ where T is the transmission of the sample. For the particular case considered here, the observed ΔA spectra for the central probe wavelengths of 370, 430, and 470 nm can then be simulated by using the following equations:

$$\Delta A(370, t) = \frac{\sigma_a(370)}{\ln(10)} [N_{c'_5}(t) - N_{c'_5}(0)]d \quad \text{Eq. 2-17}$$

$$\Delta A(430, t) = \frac{\sigma_a(430)}{\ln(10)} [N_{v'}(t) - N_{v'}(0)]d \quad \text{Eq. 2-18}$$

$$\begin{aligned} \Delta A(470, t)_{ESA} = & \frac{\sigma_a(470)}{\ln(10)} [N_{c_4}(t) + N_{c_5}(t) + N_{c_6}(t)) - (N_{c_4}(0) \\ & + N_{c_5}(0) + N_{c_6}(0))]d \end{aligned} \quad \text{Eq. 2-19}$$

Similarly, for the alternative mechanism of HA, the absorbance for the 470-nm band can be calculated from

$$\Delta A(470, t)_{HA} = -\frac{\sigma_a(470)}{\ln(10)} [N_v(t) - N_v(0)]d \quad \text{Eq. 2-20}$$

In Eqns. of 2-17 – 2-20, d is the film thickness (~ 300 nm BiVO₄, verified by SEM), $\sigma_a(\lambda)$ (cm⁻²) is the absorption cross-section of the sample at the selected probe wavelength, and $N_i(t)$ (cm⁻³) is the population density of the corresponding energy level i . The cross-sections as well as the lifetime of various levels were used as fitting parameters to obtain the best fit between measured and calculated time-resolved ΔA data.

Sellmeier Equation

Since the white light continuum pulse was used as a probe to monitor the decay dynamics of the BiVO₄ on a fused silica substrate, the transient decay kinetics at each probe wavelength were shifted in time due to their different group velocities (v_g) inside the 3.5-mm-long fused silica substrate. Hence, the delays for the short- and long-wavelength probe pulses were also considered in the simulations. For this purpose, the group velocities for the 370-, 430-, and 470-nm probe wavelengths were calculated by using the Sellmeier equation of fused silica[131], [134] given below

$$n_{fs}^2(\lambda) - 1 = \frac{0.6961663\lambda^2}{\lambda^2 - 0.0684043^2} + \frac{0.4079426\lambda^2}{\lambda^2 - 0.1162414^2} + \frac{0.8974794\lambda^2}{\lambda^2 - 9.896161^2} \quad \text{Eq. 2-21}$$

$$v_g(\lambda, n) = \frac{c}{(n_{fs}(\lambda) - (\lambda \times \frac{dn_{fs}(\lambda)}{d\lambda}))} \quad \text{Eq. 2-22}$$

where n_{fs} represents the refractive index of the fused silica. Since the thickness of the FTO (300 nm) was negligible compared to the thickness of the fused silica substrate (3.5 mm), the group velocity mismatch between the short- and long-wavelength probe pulses due to the FTO was neglected in the calculations.

Time delay of the probe pulses after passing through the fused silica substrate were further calculated by using:

$$t_{370 \text{ nm}} = \frac{d_{quartz}}{v_g(370, n(370))} \quad \text{Eq. 2-23}$$

$$t_{430 \text{ nm}} = \frac{d_{quartz}}{v_g(430, n(430))} \quad \text{Eq. 2-24}$$

$$t_{470 \text{ nm}} = \frac{d_{quartz}}{v_g(470, n(470))} \quad \text{Eq. 2-25}$$

2.4 Transient Photocurrent Spectroscopy

2.4.1 Conventional Transient Photocurrent Spectroscopy

A home-made light chopper was used for standard measurements under AM 1.5G illumination. In general, the frequency of light exposure intervals with 5 s⁻¹ was used. The photocurrent is measured at certain potentials in the chronoamperometry mode of the potentiostat. The measurements have been done in KPi buffer solution.

A white LED was used for faster pulsed experiments: the pulse width ranges from 1 ms to 500 ms, while the photocurrent was recorded at every 200 μs in the chronoamperometry mode of the potentiostat which is the minimum value for the photocurrent data acquisition. The measurements have been done in KPi buffer solution.

2.4.2 Modified Transient Photocurrent Spectroscopy

The measurements were performed by the addition of fast blue-LED light pulses onto AM 1.5G illumination in hole scavenger solution to calculate the depletion width (W_{sc}) and the hole diffusion length (L_D). The power of blue LED diode array was measured to be 15.2 mW by using a calibrated silicon diode detector, then converted to the intensity (J_{pulse}), 13.5 mA.cm⁻². A pulse width of 0.5 s was generated, and the additional photocurrent at steady state (ΔJ) is measured in a three-electrode cell configuration.

In the presence of a hole scavenger, it can be assumed that the charge carrier recombination at the surface is negligible, hence ΔJ upon by the blue-light absorption corresponds to the number of hole carriers reaching the surface for oxidation. The distance D , the sum of the L_D and W_{sc} , represents the total thickness in which photogenerated holes can react with the scavenger ions and can be calculated through the equations:

$$1 - LHE(\lambda) = 10^{-A(\lambda)} = 10^{-\frac{\alpha(\lambda)D}{2.303}} \quad \text{Eq. 2-26}$$

where $\alpha(\lambda)$ is the λ dependent absorption coefficient of the material. It is taken as 300 nm⁻¹ at 450 nm which is the center peak of the blue light emission [135], a negligible reflection was assumed to occur at the film surface. In pulsed LED experiments, $LHE(\lambda)$ can be defined in terms of ΔJ and J_{pulse} :

$$D = -\alpha^{-1} \log(1 - LHE(\lambda)) = -\alpha^{-1} \log\left(1 - \frac{\Delta J}{J_{pulse}}\right) \quad \text{Eq. 2-27}$$

ΔJ was measured at certain applied potential range (V , therefore D vs $\sqrt{V - V_{fb}}$ can be obtained by the following equation:

$$D = W_{sc} + L_D = \sqrt{\frac{2\varepsilon_r\varepsilon_0}{eN_D}} \sqrt{V - V_{fb}} + L_D \quad \text{Eq. 2-28}$$

where ε_r is the relative dielectric constant [136], ε_0 is the permittivity of vacuum (8.85×10^{-12} F.m⁻¹), e is the electronic charge (1.6×10^{-19} C), N_D is the donor

density, and V_{fb} is the flat band potential. The L_D and W_{sc} are extracted from the intercept and slope of the plot of D vs $\sqrt{V - V_{fb}}$ (see Chapter 5.2), respectively.

2.5 Core-Level Spectroscopy

Core level spectroscopies are utilized to gain element-specific information of the electronic structure around an absorption. Hence, they are proper instruments to investigate the chemical state, local geometric structure, nature of chemical bonding, and dynamics in electron transfer processes centered around one atomic site. The CLS experiments have been performed in the beamline 13-2 in Stanford Synchrotron Radiation Lightsource (SSRL). The spectrometer was used in the beamline was SES-100, VG-Scienta.

2.5.1 X-ray Photoemission Spectroscopy (XPS)

XPS, the most common technique among CLSs, is based on “photoelectric effect”: A core electron is excited by the incident x-ray to the high-energy continuum states (vacuum) and detected as a photoelectron (Figure 2-5) in ultra-high vacuum systems ($\sim 10^{-9}$ torr). According to the inelastic mean free-path (IMFP), the distance that photoemitted electrons (photoelectrons) can travel without losing energy, the photoelectrons having kinetic energy between 15 and 350 eV can be detected from top of ~ 1 nm. The kinetic energy commonly measured by deflection of electric field in hemispherical energy analyzer to only allow electrons of a given energy (Pass energy, PA) to arrive at the detector. The efficiency with which electrons are sampled by a spectrometer depends upon the lens functions. The kinetic energy (E_{kin}) of the photoelectrons is given by the formula:

$$E_{kin} = h\nu - E_b - \phi_s \quad \text{Eq.2-29}$$

where $h\nu$ is the photon energy of the x-ray, E_b is the binding energy of the electron and ϕ is the work function of the spectrometer (The fermi levels of the sample and the spectrometer is aligned). XPS is presented intensity vs E_b .

One of the most important features of XPS is its chemical sensitivity. Since BEs of core electrons are mostly distinctive for elements, the atomic compositions of a material or the chemical state of a certain element, electronic structure and band structure can be determined by XPS. Different kind of bonding change the binding energies that is observed as ‘chemical shifts’ in XPS. This provides us information on the modified chemical bonding of VES and the local coordination in a system [122]. Compared to the conventional XPS, synchrotron based XPS presents a greater surface and spectral sensitivity, due to the high photon flux and tunable X-rays of synchrotron radiation. Therefore, the surface modification of energy materials can be analyzed elaborately by XPS in synchrotron facilities. Such XPS studies performed for BiVO_4 and co-catalyzed BiVO_4 to observe the effect of the catalyst by analyzing the chemical shift of the characteristic peaks: Bi, V, O, Valence band (VB) [18].

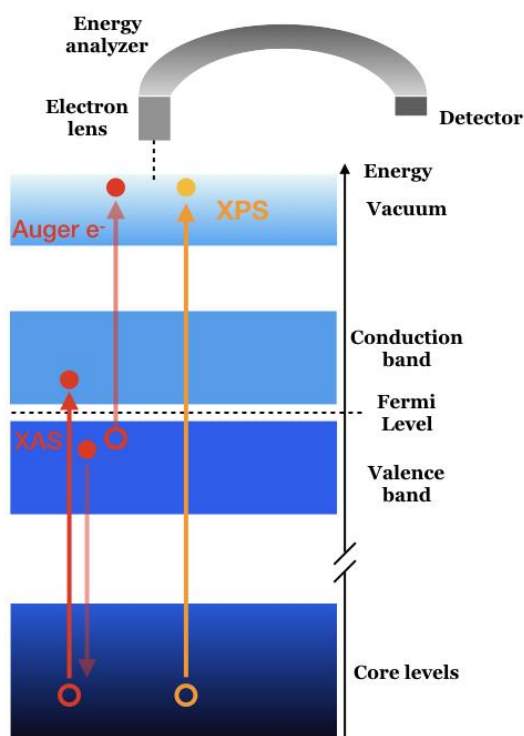


Figure 2-5 The illustration of the excitation of core level states with X-ray. Transitions depicted red and orange colors represent Auger electron-yield X-ray absorption spectroscopy (XAS) and X-ray photoemission spectroscopy (XPS), respectively.

2.5.2 X-ray Absorption Spectroscopy (XAS)

X-rays are divided into two categories, referred to as soft X-rays (<1000 eV) and hard X-rays (>1000 eV) that can be generated in synchrotron facilities. Heterogeneous catalysts involving the 3d transition metals (i.e. Fe, Co, and Ni) are investigated by the soft XAS because the photons in this energy range can probe the transitions from the L-edge (2p → 3d excitation). The L-edge is sensitive to the oxidation state and the structural symmetry of the heterogeneous catalysts. Besides, the transitions from the K-edge (1s → 2p excitation) of the 2p elements, such as C, N, and O, can be probed by the soft X-ray region. These elements are utilized in catalytic systems due to their abundancy, forming the most reacting species involving H₂O, CO, and NO. Hence, the local electronic geometric structure of the OEC can be monitored by soft XAS to understand the correlation between the catalytic activity and the active site of the catalyst.

The XAS measurement can be realized by electron-yield or fluorescence-yield detection. For soft XAS electron yield is the favored process of detection because the yield of Auger decay is significantly higher than the fluorescence decay in this regime. The electrons can be detected by total electron yield (TEY) or partial electron yield (PEY). While the information depth is up to several nm for TEY, it is 1-2 nm for the PEY that makes it highly surface-sensitive method. PEY can be recorded by the energy analyzer as in the XPS. The fluorescence yield is mostly preferred for studying the bulk of the materials.

The probability of the excitation of an electron from initial state (φ_i) to final state (φ_f) wavefunctions in XAS is based on the “Fermi’s Golden rule” where the probability of the transition is given by W:

$$W = \frac{2\pi}{\hbar} |\langle \varphi_f | T | \varphi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad \text{Eq.2-30}$$

The delta function represents the energy conservation that the transition occurs if the final energy state (E_f) equals the sum of the initial energy state (E_i) and the X-ray energy. The squared matrix gives the transition rate, transition operator (T) defines one-photon transitions (i.e. x-ray absorption) and involves the electric field term ($e i k r$) of the radiation and the momentum of the electron. Using the Taylor expansion, the exponential term is approximated as $1 + i k r +$ (higher

terms). According to the “electric dipole approximation”, the wavelength of the radiation is far longer than the atomic dimension, we can neglect second term and further terms of the expansion. In case we take 2nd term into account, the probability of the quadrupole transition would be smaller by $\sim 2 \times 10^{-3}$ compared to dipole transition (for x-ray energies < 10 keV, $k \cdot r < 10^{-2}$) [137]. Then the Fermi’s golden rule can be written as:

$$W \propto \sum_q |\langle \varphi_f | \hat{e}_q \cdot r | \varphi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad \text{Eq.2-31}$$

The single electron (excitation) approximation leads us to write the wavefunctions of initial and final states as the wavefunctions of a core (c_e) and a free electron (f_e), respectively.

$$|\langle \varphi_f | \hat{e}_q \cdot r | \varphi_i \rangle|^2 \approx |\langle f_e | \hat{e}_q \cdot r | c_e \rangle|^2 = M^2 \quad \text{Eq.2-32}$$

The squared matrix (M_2) is a number that slightly changes and can be assumed as a constant value in many cases. Eventually, x-ray absorption intensity is given by M_2 and the density of states (ρ) that is implied by the delta function:

$$I_{XAS} \sim M^2 \rho \quad \text{Eq.2-33}$$

For electric dipole approximation, according to the quantum selection rules, M is a non-zero value if $\Delta L = \pm 1$ (i.e. $s \rightarrow p$, $p \rightarrow d$, $p \rightarrow s$ etc.) and $\Delta S = 0$, where L is the orbital angular momentum and S is the spin angular momentum. Although the single particle approximation of X-ray absorption for all K edges is compatible with the calculation of the X-ray absorption cross-section, the agreement is poor for $L_{2,3}$ -edges. The reason, the deviation from the density-of-states, is the significant overlap between the core and valence wavefunctions [122].

2.5.3 Ambient-pressure photoemission spectroscopy (APPEs)

X-ray spectroscopy measurements require ultra-high vacuum conditions ($P < 1 \times 10^{-8}$ Torr) to reduce scattering of emitted photoelectrons by gases and to avoid discharges on the electrostatic elements and the detectors. However, many processes of interest in electrochemistry and catalysis occur at elevated pressure (> 760 Torr) and temperature. This constraint was partly prevented by the development of ambient-pressure XPS (APXPS) or photoemission spectroscopy

(APPES) that several chambers in synchrotron facilities provide XPS measurements at gas pressures of up to 100 Torr [138], [139]. APPES enabled XPS analysis under electrochemical reaction conditions of solid–gas interfaces in solid-state electrochemical cells [139]. The change of the oxidation state of the transition-metal OECs such as Mn, Co, and Ni was studied by utilizing *in situ* XAS [121] . Since the OER involves a complex set of reactions, XPS and XAS of transition metals in H₂O ambient has been critical to enhance the understanding of the reaction. Even, these *in situ* experiments have been performed in electrochemically driven conditions that is mostly called as operando experiments. In one study, the scientists show the change of oxidation state of the Ni–Fe Electrocatalyst [140]. In another study, the authors highlighted that among two geometrical sites (Co₂₊ in tetrahedral site and Co₃₊ in octahedral site) the Co₂₊ is the active species in spinel Co₃O₄ during OER [141].

3 Roles of Charge Carriers in the Excited States of BiVO₄

3.1 Introduction

Herein, we report a combination of numerical modeling and experimental investigations on the TAS features of BiVO₄ in the ultrafast time scale. We provide a general picture based on the ground state electronic structures of BiVO₄ and discuss the characteristic time evolution spectra at probe delays less than 800 fs. The goal of the numerical model is to relate the characteristic TA spectral features to the dynamics of BiVO₄ in the ultrafast time scale (0-3 ns). No significant spectral change is evident in the μ s-ms regime. The numerical model and dynamical processes considered are supported by the TA measurements performed in the presence of a hole scavenger, under anodic bias, and by varying the intensity of the pump beam.

3.2 Results

The characteristic TA spectrum of BiVO₄ presented in Figure 3-1a features two positive (370 and 470 nm) spectral peaks and one negative (430 nm) peak, together with a broad-band feature above 500 nm. Measured ΔA spectrum within the 350-600 nm wavelength interval is in agreement with previous reports [32], [40], [56]. However, these unique spectral features appear sequentially with temporal offsets up to a delay of 800 fs (Figure 3-1a and Figure 3-1b) and then remain unchanged until thermal equilibrium is completely re-established. It can be considered that this behavior originates either from the variation of time-evolution of carrier transitions or group delay dispersion (GDD). GDD gives the wavelength-dependent delay of pulses as they propagate through a dispersive medium. It originates from the wavelength dependence of the refractive index and can be calculated by using the Sellmeier equation [131]. To explore the GDD effect on the kinetics (ΔA vs. t in Figure 3-1c, Figure 3-1d), the group velocities associated with probe pulses centered at the three main peaks (370, 430, and 470

nm) were calculated by using the Sellmeier equation for fused silica (Chapter 2.3.2.2). The corresponding temporal delays between the onsets of these

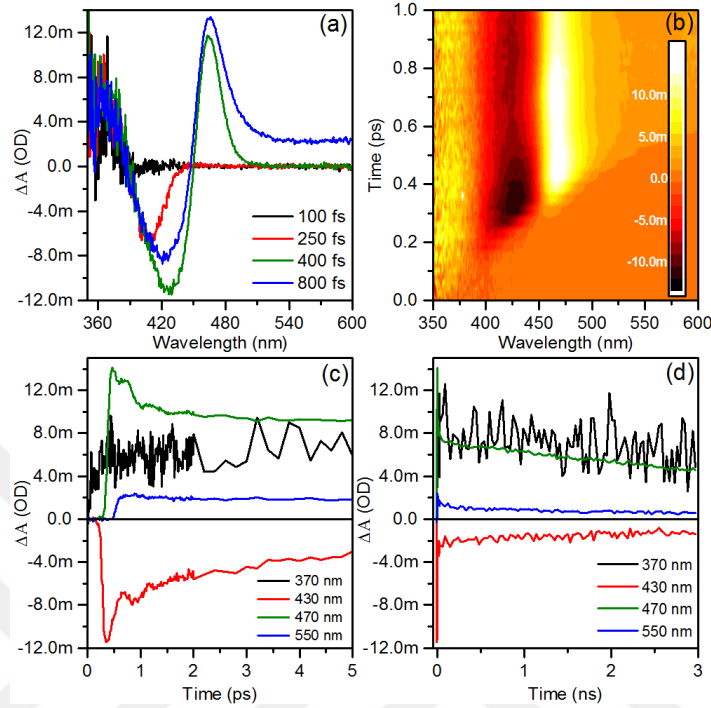


Figure 3-1 The time evolution of the TA spectra of BiVO₄ at certain time delays (a) and in 2D counter plots (b). The TA decay kinetic traces characteristic to BiVO₄ (370, 430, 470, and 550 nm) within 0-5 ps (c) and 0-3 ns (d).

kinetic traces were calculated by neglecting the thickness of the BiVO₄ layers and by assuming a thickness of 3.5 nm for the fused silica. The calculated time delays presented in the Table 3-1 agree well with the delays observed in the kinetic traces shown in Figure 3-1c and suggest that the temporal shifts of the onsets of the peaks indeed result from the GDD effect in fused silica rather than a variation of time evolution.

A non-monotonous decay behavior is also seen in the kinetic traces, most clearly for the peak at 470 nm (Figure 3-1c) in the first few ps, which is attributed to the polarons [20], [32], [34]. In a recent study, it has been suggested that coherent ionic displacement over a vibrational period induces dynamical changes of the band gap, which is revealed as damped oscillations observed in the ΔA kinetics (see Figure 3-1c) [40]. In contrast to the absorption at 470 nm, no such trap-state feature is evident at 550 nm. Another important observation is that the kinetics traces at 370 nm do not decay or show any notable change within 0-3 ns, whereas the kinetics traces at 430 and 470 nm demonstrate decay behavior as

negative and positive ΔA , respectively. The peak at 430 nm is commonly assigned to the GSB [32], [56]. After a sudden rise, it levels to lower negative ΔA values after 5 ps. Less dramatic decrease is obtained for the peak at 470 nm, which is commonly attributed to the photogenerated HA as discussed above. However, according to the band structure of monoclinic BiVO_4 and its TA response, the increase of absorption upon pump beam (positive ΔA) can also be attributed to the ESA.

Before the discussion of the numerical results, we note that it is considerably helpful to take the band structures of the materials into account in order to associate TA observations with the transitions in the occupied and unoccupied density of states (DOS) in VB and CB, respectively. The DOS presents us guiding information about the transition probability for the probe beam at the relevant energy range. For instance, in light of the calculated DOS, the TA spectra of Fe_2O_3 have been interpreted as exhibiting the ESA dominance over the HA in various spectral regions [64]. Despite its well-understood band structure and DOS projected on O 2p, V 3d and Bi 6 sp states, TA features of BiVO_4 have not been cross-examined to date. Electronic structures of BiVO_4 have been studied theoretically and experimentally, a reasonable agreement has been found between the calculated band structures of monoclinic BiVO_4 and DOS obtained by core level spectroscopy investigations [18].

We begin the discussion of the numerical model with the introduction of the possible transitions according to the band structure given in Figure 3-2. There has been a debate whether BiVO_4 has a direct or indirect band gap. Recent core level spectroscopy, UV-vis absorption spectroscopy, and ellipsometry investigations reveal that it has an indirect band gap with strong absorbance at 2.5 eV and direct transition near 2.7 eV [133]. By addressing this band structure model, the relaxation of photoexcited electrons is presented as fast decays into two separate levels (Figure 2-4). All possible transitions in the VB and CB are schematically displayed in I-IV in Figure 3-2, including the positive broad-band absorption, more detailed analysis used in the kinetic model is given the Chapter 2.3.2. The model was developed starting from a simpler kinetic analysis and perfected by including trap states for the charge carriers. The number of the trap

states included in the model is not arbitrary and the multi-level model was essential to account for the rather complicated temporal decay behavior with multiple decay constants.

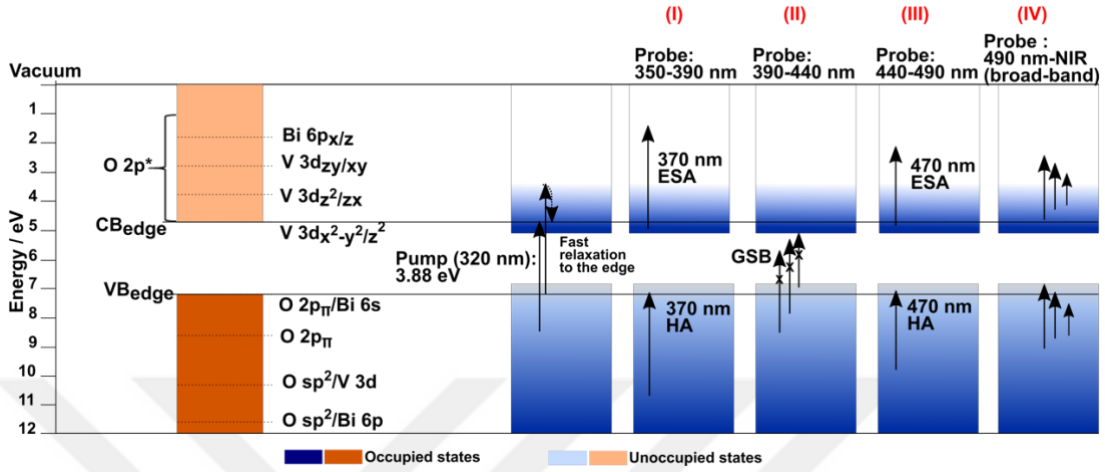


Figure 3-2 The band structure diagram is depicted from Cooper et al[18], and the possible specific transitions are shown accordingly after the excited carriers relax to the band edges. The darker regions illustrate occupied states, while the lighter ones indicate unoccupied or discharged states. The absorption peak around 370 nm is shown by having both ESA and HA possibilities (I). The negative peak exhibits the reduced absorption of the probe signal, GSB (II). The second positive peak can also be associated with either ESA or HA (III). The broad-band absorption is also shown by considering all possible transitions as free carriers (IV).

As stated before, for 370 nm, the behavior does not change notably within 0-3 ns, whereas the kinetics around 430 nm and 470 nm either manifest rapid changes in 0-5 ps or change relative to each other (Figure 3-1c). Therefore, having the kinetics being independent from GSB rules out the HA scenario for the peak at 370 nm, whilst nearly stationary behavior corresponds to the ESA within the CB. This stationary behavior is seen as one single decay from a trap level of direct band edge within 0-3 ns. Depopulation of the ground states is seen as negative absorption around 430 nm (GSB). The increase of ΔA at 470 nm could, in principle, be assigned to either the HA or the ESA. The HA might initially be considered as a more reasonable process since the decrease of the GSB peak is followed by the increase of the peak at 470 nm within 1 ps time frame. On the other hand, the ESA process for the electrons cannot be disregarded, there is enough DOS in the CB so that alternative mechanisms should be considered. Therefore, numerical analysis of the kinetic traces for 470 nm takes both the HA and the ESA processes into account.

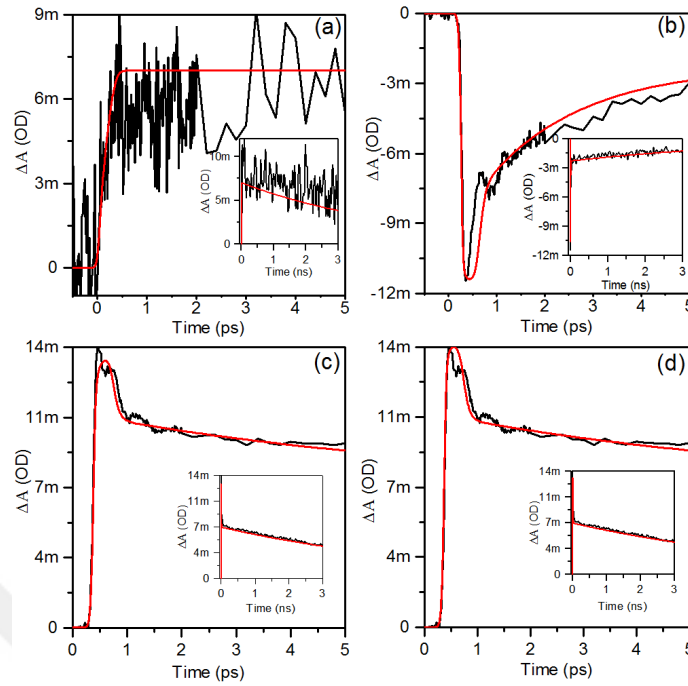


Figure 3-3 The numerical (red) and experimental (black) kinetics for the spectral features, 370 nm (ESA), 430 nm (GSB), 470 nm (ESA) and 470 nm (HA) within 0-5 ps scale seen as a, b, c, and d, respectively. The insets are the kinetics within 0-3 ns.

The ESA and the HA kinetics illustrated in Figure 3-3 can be understood more clearly by exploring the changes in the kinetic traces in various time frames. For the ESA, the rapid relaxation of photoexcited electrons to the trap states represents the rising part of the ΔA . The decay of these excited electrons to the ground states (or trap states near the VB) displays a decrease in the ΔA , which is seen as having a single decay constant for the peak at 370 nm, whereas three different decay constants describe the kinetics of the one at 470 nm, calculated by considering the contribution of multiple trap states. For the HA, the rising part of the kinetic trace is described by the excitation of electrons from the lower energy levels to the bleached state in the VB (from V'' to V). The probability of this excitation decreases in time due to the population of the bleached ground state that is seen as the decay of this ΔA (i.e. hole filling). The HA is described as the absorption at 470 nm from the lower energy levels to the bleached states whereas the ESA is described as the absorption at 470 nm from the levels near CB to the upper level (from C_{4-5-6} to C_2) that have V 3d character (Figure 3-2). The kinetics of the GSB is described by the decay of electrons from the levels where relaxations at 370 and 470 nm take place. In addition to these relaxations,

the other trap levels of direct band edge represent the quick decay of GSB peak compared to the kinetics of 470 nm. In consequence, this numerical model successfully explains the time evolution of the TA spectra by analyzing the kinetics of the main features, and by taking the GSB, the ESA, and the HA into account. The fitting results for the ΔA changes were in a very good agreement with the experimental data as can be seen in Figure 3-3. The numerical decay time constants were also compatible with the experimental ones (see Table 3-1). Simplifications in terms of the number of the trap states and decay channels would not give satisfactory results suggesting that recombination dynamics is very complex and multiple decay mechanisms must be taken into account to explain the time evolution of the TA features.

Table 3-1 Decay time-constants of three main peaks and absorption cross-section of the probe beam at different wavelengths.

$\Delta A(\lambda_{\text{probe}})$	τ_1 Exp.	τ_1 Num.	τ_2 Exp.	τ_2 Num.	τ_3 Exp.	τ_3 Num.	σ_{probe} (10^{-19}m^{-2})
370 nm	-	-	65 ps	1.8 ps	2.54 ns	6 ns	1.9
430 nm	94.7 fs	90 fs	2.55 ps	1.8 ps	2.96 ns	6 ns	0.58
470 nm	429 fs	100 fs	19.9 ps	7 ps	4.92 ns	6.5 ns	0.55

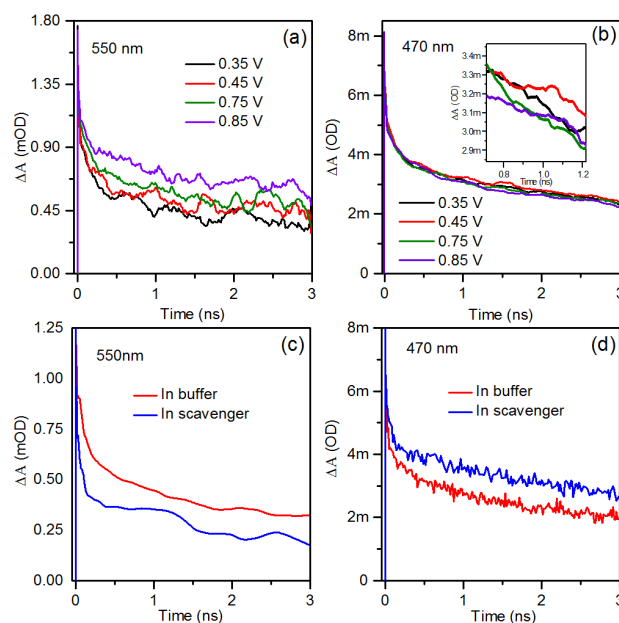


Figure 3-4 Transient absorption (TA) kinetics of BiVO_4 under applied bias (vs RHE) at 550 nm (a), 470 nm (b), and in different electrolytes at 550 nm (a), 470 nm (b), in fs-ns scale. All data are normalized to the peak maxima.

Further TAS experiments were performed to have a deeper understanding on the ultrafast carrier dynamics of BiVO_4 , particularly for ascribing the TA features to a specific carrier type. As stated before, the most common approach to attribute TA response to electrons or holes of a semiconductor photoanode is by the utilization of a scavenger and application of the external bias. Figure 3-4a and Figure 3-4b show the effect of the applied bias on the peaks at 550 and 470 nm. As anodic (positive) bias is applied, more electrons are extracted by the external circuit. If slower decays are observed, kinetic traces are mostly attributed to the photogenerated holes, which have been demonstrated within both ultrafast [60] (for Fe_2O_3) and μs -ms time scale for the TiO_2 [55], Fe_2O_3 [47], BiVO_4 [62]. The effect of the applied bias for the <500 nm region in the ultrafast time scale has not been demonstrated for the BiVO_4 yet. At 470 nm, faster decays are observed as the anodic bias is increased, manifesting that the origin of the decay of this peak is different than the one at 550 nm. The hole scavengers cause more hole utilization at the photoanode/electrolyte interface, hence the faster decay kinetics are attributed to promotions of the photogenerated holes [32], [34], [39], [47]–[53]. Figure 3-4a and Figure 3-4c clearly show that broad-band region can be attributed to the HA, whereas Figure 3-4b and Figure 3-4d suggest that the ESA

is more dominant than the HA at 470 nm. In consequence, Figure 3-4 presents two significant results for BiVO₄ carrier dynamics. First, both the scavenger and the applied bias affect the ultrafast recombination mechanism. Second, there is no strong evidence to consider whole positive TA region as HA.

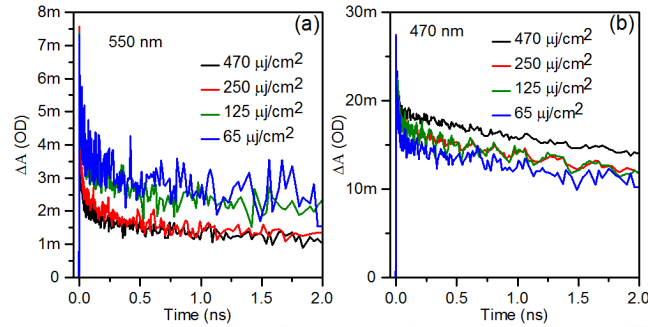


Figure 3-5 Normalized pump beam intensity dependence of TA kinetics of BiVO₄ at 550 nm (a), 470 nm (b) in fs-ns scale.

The pump intensity dependence of TA features was also explored to identify their relationship with the charge carriers. As seen in Figure 3-5a and Figure 3-5b, faster recombination rate was observed at 550 nm with increasing pump intensity whereas an opposite trend was apparent at 470 nm. The increased recombination rate at higher pump intensity is assumed to be due to a trap-filling effect for nanocrystalline TiO₂ films [53], [142]. It has been suggested that since the excited electrons are localized at deep trap states immediately, the effective mobility of other electrons increases. With decreasing pump intensity, by contrast, there are many unoccupied deep traps; therefore, slow recombination should be expected. In our study, faster recombination rate with increasing pump intensity is clearly seen for the kinetics at 550 nm. Rapid filling of the VB states at high pump intensity reduces HA probability, supporting that the broadband region in TA spectra represents the HA. At 470 nm, the increased population of the trapped electrons below CB and their longer lifetime opens a channel for ESA, leading to the kinetic behavior presented in Figure 3-5b.

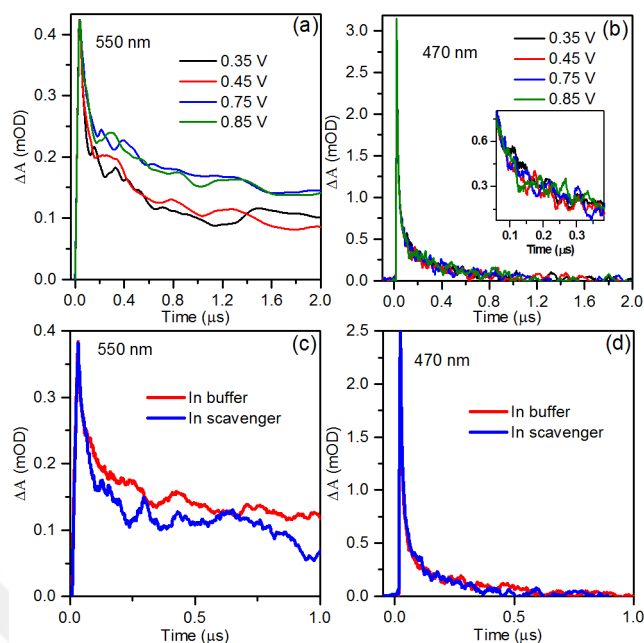


Figure 3-6 Transient absorption kinetics of BiVO_4 under applied bias (vs RHE) at 550 nm (a), 470 nm (b), and under different conditions at 550 nm (c), 470 nm (d), in ns-ms scale. All data are normalized to peak maxima.

3.3 Discussion

The results presented show that significant dynamical changes take place in ultrafast time scale. TA response in ns-ms region is the extension of unvarying decay behavior, as seen in Figure 3-6 and Figure 3-7. The trapping mechanism is explored by the localization of the carriers at trap energy levels just below CB within 0-5 ps. The kinetics at 370 nm is attributed to the ESA, negative ΔA is linked to GSB, whereas both the ESA and the HA are possible processes for the kinetics at 470 nm.

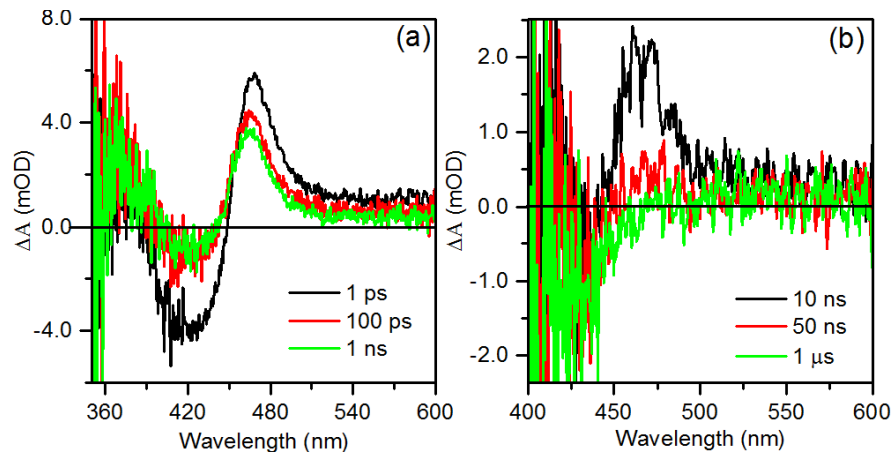


Figure 3-7 Time-evolutional spectra of BiVO₄ in air from 1 ps to 1 ns (a), and from 10 ns to 1 μ s (b).

The ambiguity of the TA response is in the positive ΔA assignment. Positive ΔA is mainly attributed to the HA for BiVO₄ by generalizing the broad-band signal behavior to entire positive ΔA [32], [39]. One important outcome of the kinetic model was the assignment of time-delays in TA spectra observed at different wavelengths to the GDD effect. Second, the kinetic model convincingly proves that ESA hypothesis for positive ΔA at 470 nm is valid, it is otherwise interpreted solely as HA based on the findings of the earlier investigations. The model, however, does not predict the extent of ESA dominance over HA, rather it just presents that both processes are plausible. Accurate assignment of the spectral features is critical because TAS is commonly utilized to identify the effects of the surface modification, doping and so on with the intention of increasing the carrier lifetime [56]. Herein, the ESA dominance over the HA process for the peak at 470 nm is demonstrated not only in ns-ms (Figure 3-6) time scale but also in fs-ns time scale under applied bias (Figure 3-4a and Figure 3-4b). Under such conditions, broad-band TA response (fs to ms) reveals the HA behavior that is in line with the previous investigations [32], [39]. In the presence of a hole scavenger, the observations (within fs to ms) are precisely in agreement with the results obtained under anodic bias conditions (Figure 3-4c, Figure 3-4d and Figure 3-6). In addition, the exactly opposite response is observed at 470 and 550 nm with the increase of the pump intensity, indicating that their origin is different. It is known that the carrier recombination mechanism is related to the

mobility of the carriers that could be better realized if they are interpreted in light of the polaronic effects [20], which are also seen in the kinetic traces of BiVO₄.

It is well established that the photocurrent of BiVO₄ is limited by majority electron carriers [18], [29]. It has been argued that a large polaron travels coherently with a modest mobility, whereas a small polaron moves incoherently via phonon-assisted hopping with a very small mobility [143]. Unlike small polarons, large polarons disperse over many structural units [23]. For BiVO₄, small electron polaron state is found around CB minimum that consists of V 3d - O 2p hybrid states [18], [20], [29], whereas large hole polarons are mostly associated with the BiO₈ structural units [23], [29], [30]. Therefore, we propose that the oscillatory behavior seen in the kinetic traces at 470 nm, ascribed to polaronic behavior [31], [32], arises from small polarons and is another sign of the ESA dominance. This suggests that the polaronic behavior can be differentiated in TA spectra of BiVO₄.

3.4 Conclusions

The charge carrier dynamics of BiVO₄ are comprehensively investigated by TAS in a broad timescale and the characteristic time evolutional spectral features of BiVO₄ have been studied by a kinetic modelling. The TA peak at 470 nm shows an opposite behavior compared to the broad-band region (at 550 nm) under applied positive bias, in the presence of a hole scavenger, and at increased pump intensities. Our rate equation analysis based on the band structure showed that either the HA or the ESA types of transitions can explain the observed dynamical behavior. However, when coupled with the experiments mentioned above, our results suggest that the ESA may be more dominant over the HA at 470 nm. We foresee that ultrafast spectroscopic studies on novel oxides described here will contribute to a more detailed understanding of the mechanisms involved in their operation as photoanodes in solar energy conversion.

4 Ultrafast Carrier Dynamics of Different BiVO₄ Surface Structures

4.1 Introduction

In this chapter, I concentrate on the TA characteristics of BiVO₄ in the ultrafast scale to show the relationship among the characteristic spectral regions that can give us valuable hints about the structural changes. Starting with an extensive analysis of unmodified 5 cycle spin coated BiVO₄, the effects of thickness and thermal treatment on the carrier dynamics are discussed. We modify the structure by such processes and focus on the trap state-related transitions, rather than perturbing specifically electron or hole concentration as we discussed in Chapter 3.2.

4.2 Results and Discussions

Typical TA spectral characteristics of 5 cycle spin coated BiVO₄ is shown in Figure 4-1. A positive ΔA spectrum at wavelengths between 500 and 900 nm has always been assigned to photogenerated holes, commonly defined as “hole absorption” or “trapped holes” (Figure 4-2), by *in situ* experiments such as use of chemical scavengers and applied anodic bias [32]–[34], [39], [56], [59], [144], [145]. The negative spectral TA signal around 430 nm has been attributed to GSB [32], [33], [144], [146]. Finally, the gaussian-like TA response around 470 nm has been attributed to the hole absorption [32], [146], while it has been recently implied that its dominant contribution come from the excited electron absorption [33]. The reason behind the complications in this spectral region of 450-500 nm is that this region corresponds to 2.5-2.75 eV, just above the GSB spectral region and below the broad-band region (>500 nm). Having indirect bandgap transition at 2.5 eV (496 nm) with a direct bandgap transition at around 2.7 eV (459 nm) [18] further complicates to assign these regions to the carriers. Moreover, considering the possible electronic transitions from both VB and CB by UV-Vis

light, and the existence of trap states within the bandgap, it can be plausible to rely on only broad-band region (>500 nm) to analyze hole carrier dynamics which are utilized for OER. However, elucidating the relationship between the main TA spectral regions can enhance our understanding of either the intricate carrier dynamics of BiVO_4 and the utilization of TAS in a broader sense.

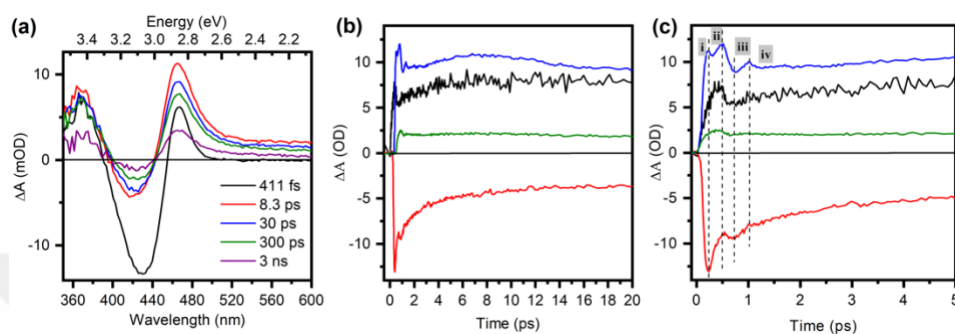


Figure 4-1 Time evolution of the TA spectra of BiVO_4 at different selected time delays (a). The normalized main TA kinetics at 370, 430, 470, and 550 nm within 0–20 ps without aligning the delay shift among the traces (b) and after the alignment of the shifts to guide the eye within 0–5 ps (c).

Three gaussian-like peaks and a broad-band spectral region are given at selected times (Figure 4-1a) where 411 fs represents the time of the GSB peaking, while 8.3 ps is the max. peak point for the peak at 470 nm. The intensity of the peak in the spectral region around 370 nm does not change significantly for ~ 300 ps, while the peaks in three regions decreases continuously after ~ 8 ps. The normalized kinetics of three peaks and representative broad band peak at 550 nm as the representative broad-band (>500 nm) region are given in Figure 4-1b. Exponential time decay constants are $\tau_1 = 3.23$ ns and $\tau_2 = 41.87$ ps for 550 nm, $\tau_1 = 3.01$ ns and $\tau_2 = 41.54$ ps for 470 nm, $\tau_1 = 3.35$ ns for 370 nm, while $\tau_1 = 218.7$ ps and $\tau_2 = 1.8$ ps for the negative kinetics of 430 nm. The values are compatible with the results of our numerical model (Table 3-1) in which we discussed the physical origins in detail (Chapter 3). The time delay shift among the kinetics (Figure 4-1b) come from the GDD, as we discussed in the Chapter 2.3.2, is neglected (Figure 4-1c) to observe the relationships among the TA characteristics of BiVO_4 . Figure 4-1c will be the main focus of the discussion in this section.

The coherent regime where the phase relationship between the excitation and with the electromagnetic field that generates the excitations (see Chapter 1.4.1),

can be deduced from Figure 4-1c. GSB peaking duration coincides with the pump pulse width as the sharp rising component has been associated with first TAS of BiVO₄ [34], and CdTe quantum dot (QD) [127]. The time between the initial and the maximum point of GSB is 210 fs (after eliminating GDD) which is compatible with the pump pulse width, shown as “i” in Figure 4-1c. Since the pump beam (320 nm = 3.88 eV) is able to deplete the VB of BiVO₄ down to 1.2 eV from the VB edge, the significant part of the probe beam will pass through the sample transparently without being absorbed that is normally absorbed in the ground (unpumped case) state. This is seen as negative absorption (GSB) which we see between 390 nm 450 nm for the first a few hundred fs which decreases afterwards due to likely the filling of depleted states. The spectral GSB region corresponds to 3.18 – 2.75 eV that imply the band gap is enlarged upon strong beam excitation [40]. Otherwise, we cannot explain why we do not see a negative peak beyond 2.75 eV. On the other hand, we do not see a decrease or GSB between 350 nm and 390 nm either (3.18 – 3.54 eV). The critical question is that “Why do not we observe positive absorption (ESA) where we observe negative absorption (GSB) considering the energy band diagram (Figure 4-2) ?” “What could be the reason of the increase and decrease of the probe beam absorption in terms of the transitions of electrons in the band structure of BiVO₄?” Or, “Should we consider the contributions to UV-Vis probe absorption from all possible transitions in the electronic band structure and deconvolute them?”.

The time marked as “i” in Figure 4-1d also coincides with the first maximum peak at 470 nm. The contribution to this peak might come from both ESA and HA and from the midgap states, however, the exact inverse response compared to the ΔA of 430 nm can imply that ESA is more dominant at 470 nm, at least within this time scale. Similar relationship between ESA and GSB has been observed in TAS of CdTe [127]. Upon the pump beam passing through the system, the photogenerated electrons and holes relax to the CB and VB edges, respectively but some portion likely to be moved to trap sites in the bulk and at the surface. First shallow and then deep trap states will be filled in the course of the relaxation (Figure 4-2). Hence, the second rising part (i-ii) can arise from the occupied midgap electron or hole trap states [34]. The decrease of GSB means that the depleted states begin to be filling. Considering the end of time “i” as the

annihilation of coherence, then the distribution of the free electron-hole pairs is expected to be in the non-thermal regime that is commonly observed in ≤ 2 ps (see Chapter 1.4.1). The non-thermal regime gives information about numerous processes such as carrier-carrier scattering, electron-phonon scattering etc. [35]. At around 500 fs (marked as “ii”) the decrease of GSB ceases and increases again until 710 fs (marked as “iii”), while the peak and valley points of ii and iii are exactly the opposite the peak at 470 nm. These imply that the transitions from the certain states that contributes to ΔA of 470 nm peak linked to the peak at 430 nm through the relaxation from trap states. This correlation is very likely to be originated by the electron-optical phonon scattering due to the timescale, because the hole-optical phonon scattering is likely to happen in the coherent regime (< 200 fs) [35]. Yet, the coherent phonon oscillations of BiVO_4 has been suggested to be originated from the surface hole trapping states observed in $500 \text{ nm} < \lambda < 700 \text{ nm}$, while the absorption at $\lambda > 700 \text{ nm}$ are mainly implied to be responsible for carriers in the bulk [34].

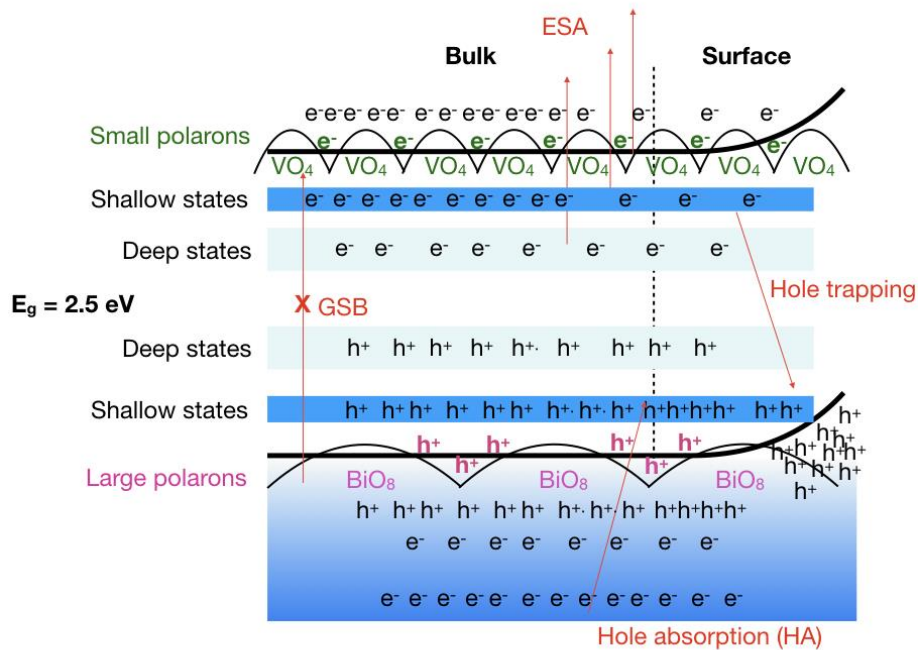


Figure 4-2 The band structure diagram of BiVO_4 upon the excitation that illustrates the possible specific transitions and trap states.

The time (720 fs) corresponds to **iv** (Figure 4-1) might be seen as the end of the non-thermal regime in which carrier-carrier scattering redistribute the energy that the distribution can be described by temperature: Hot-excitation or thermalized regime. Usually, the electrons and holes thermalize among themselves in hundreds of fs, while they reach a common temperature in a few of ps [35]. This can be seen in Figure 4-1c as well, the overall decay initiates after 10 ps: The thermalization of electron-hole pairs (not all processes in this regime) appear to be completed around 10 ps. As it was suggested that there is no thermal contribution to the spectrum of 460 nm within 3 ps, while its effect steadily increases and appeared upon 10 ps [40], same behavior of the kinetics at 470 nm was also observed elsewhere [32], [103].

The decrease of the kinetic trace at 550nm in the region of **ii-iii** might indicate the end of hole thermalization (Figure 4-1c): 550 nm corresponds to 2.25 eV that might be the absorption from shallow states, i.e. Bi 6s-O 2p states near VB edge. These hole carriers at shallow states near to VB are the potential hole carriers to drive OER [33], [34], [39]. We believe that the main contribution to ΔA of 550 nm mainly comes from the shallow hole trap states rather than photogenerated holes in the VB because neither decay behavior nor time constants are comparable.

The correlation between 430 nm and 470 nm is again observed between **iii** and **iv** (Figure 4-1c). However, we do not observe any correlation between 370 nm and 430 nm or 470 nm in the coherent and non-thermal regimes. The decay behavior and time constants in the longer time scale (hot-excitation regime) are similar to the peaks at both 470 nm and 550 nm which again does not help us to see its predominant contribution whether it comes from ESA or HA. Apart from these, the probe beam has less resolution at <400 nm makes it more difficult to analyze as other spectral regions. While we can suggest that the peak at 370 nm contributes both ESA and HA and also trap states due to its energy and allowed transitions in the band structure, deconvolution of it seems not likely.

As it is discussed in Chapter 1.3.2, the polaron formation plays critical role on both carrier transport and recombination. Figure 4-3 shows the oscillatory TA response of the peak at 470 nm clearly with frequency of 1.75 ps⁻¹ (the period of

572 fs), while the first a few oscillations of the peak at 430 nm fit with the 1.74 ps⁻¹ sinusoid. According to the observed correlations between 430 nm and 470 nm, it is expected to see similar oscillations in this timescale. For 550 nm, we could not observe such oscillations, but the oscillations observed in 500 nm < λ < 700 nm was attributed to coherent-phonon and hole trapping in the surface of BiVO₄ [34]. The rising component with the excitation and the following decay was suggested that the coherent phonon mode is strongly coupled with the electronic transitions accompanying with the trapped holes in the surface region. The slow carrier transport in metal-oxide semiconductors, unlike conventional semiconductors, favors the formation of slow moving, self-trapped charge carriers: small polarons. The small polaron state includes V 3d–O 2p hybrid states (VO₄ units) residing at the edge or at shallow states of CB in BiVO₄ [18], [20], [29]. However, there are controversies in the assignment of polaronic behavior of BiVO₄, whether the observed oscillations come from electrons (small polarons) or holes (as large polarons in BiO₈ units) [20]. Although, it is known that the mobility of the large polarons (>1 cm² V⁻¹ s⁻¹) is much higher than the small polarons (<<1 cm² V⁻¹ s⁻¹) [28], it has been suggested that the polarons having the mobility of 0.02 cm² V⁻¹ s⁻¹ and the frequency of 76 cm⁻¹ represents the hole polarons in BiVO₄ [31]. However, it was also suggested that weakly localized hole in monoclinic BiVO₄ undergoes faster diffusion ($\mu \approx 20$ V cm² V⁻¹ s⁻¹) were attributed to large polarons in a theoretical study [30]. Besides, many studies point to the small polaron formation considering the majority carrier limitation of BiVO₄ [18], [29], [147]. Most recently, localized hole and electron energy levels were suggested to be within the band gap, through binding energies of 0.11 (above VB) and 0.88 eV (below CB), respectively. They also implied that the electron localizes around the same vanadium atom reducing (V₅₊ to V₄₊) in 5 ps, whereas hole polaron localizes around various bismuth atoms distributing between one bismuth and eight oxygen atoms (no time indicated for hole polarons). According to a DFT study, the oscillations are due to electron–phonon coupling of the excited carriers to the LO mode with the frequency of 65 cm⁻¹ [40]. We suggested before [33] that the oscillatory behavior seen in the kinetic traces at 470 nm comes from small polarons, herein we evidence that (Figure 4-3a) the polaron

frequency 1.75 ps^{-1} (which corresponds to 59 cm^{-1}) agrees well with the small polaron frequency observed in the literature.

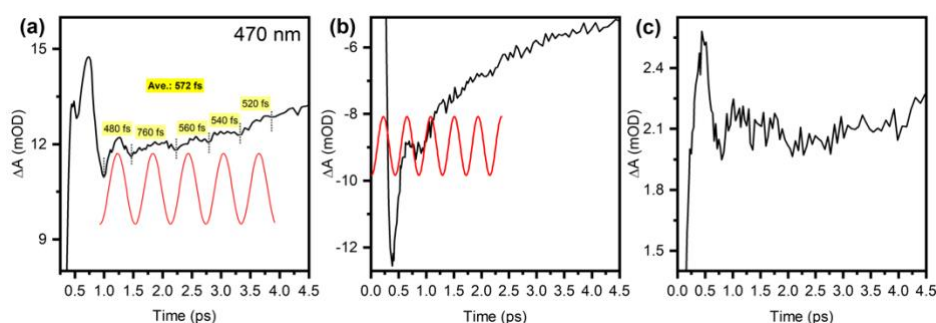


Figure 4-3 The closer inspection of the first 4.5 ps observations of the absorption peaks at 470 nm (a), 430 nm (b) and 550 nm (c).

The outcome of the TAS analysis of oscillations can be substantial for deducing structural information from ultrafast TAS. It was recently indicated that the polarons are formed from oxygen vacancies (V_o s) in the bulk might contribute to conductivity, whereas those at the surface possibly do not [148]. It was also stated that V_o formation leading to the localization of electrons in V_{4+} by reducing V_{5+} makes V_{4+} as primary loss pathway for photogenerated holes from the VB and V_{5+} as shallow traps for electrons from the CB [86]. However, this can increase the hole trapping and following by hole transfer to the adsorbed ion (i.e. OH^-) which is suggested to be the first step of the water oxidation for BiVO_4 [22]. As seen, the role of V_o is vital for BiVO_4 in terms of carrier transport, recombination, and interfacial charge transfer. This might be the hottest topic for the studies of BiVO_4 that will be elucidated in the Chapter 5 by showing the enhanced V_o s by nitrogen incorporation into BiVO_4 .

There are many ultrafast TAS studies of semiconductor photoanode materials in the literature [9], however, thickness dependent response of UTAS, at least for BiVO_4 is missing. The absorption can be expected to change linearly with the change of thickness (Chapter 2.3.2), because it is likely to have similar increase of occupied and unoccupied states. However, the TA signal upon defect density variations due to film thickness can be complementary for the outcomes of the ultrafast TA analysis of BiVO_4 . The effect of intragap states to TA signal of BiVO_4 was investigated, particularly the states close to CB [145], [149]. Since the decay

from electronic bands to trap states will be relatively faster than decay among the trap states, the effect of different film thicknesses can be observed at <100 ps.

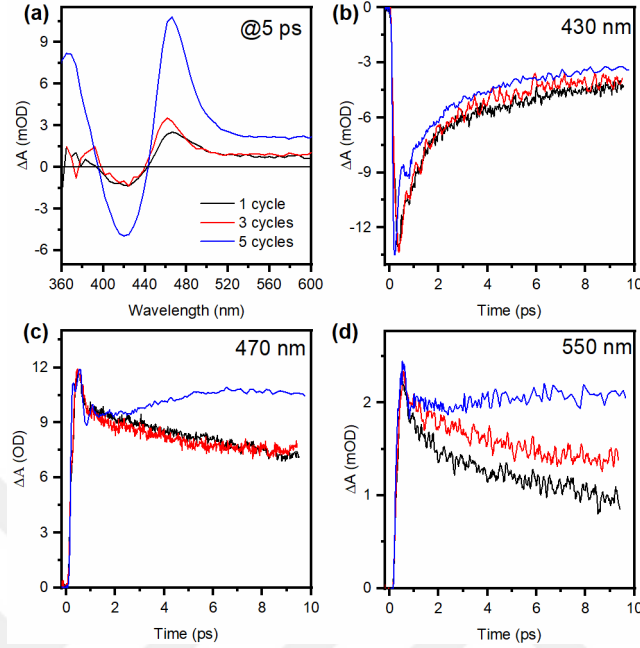


Figure 4-4 Time evolution of the TA spectra of 1 cycle (black), 3 cycles (red) and 5 cycles (blue) spin-coated BiVO₄ at 5 ps (a). The normalized main TA decay kinetic traces of 430 nm (b), 470 nm (c) and 550 nm (d) within 0–10 ps (Color codes of the figure (a) is valid for all). The excitation pulse is 85 $\mu\text{J}/\text{cm}^2$.

BiVO₄ films were prepared by the spin coating method with a different number of coating cycles to optimize the thickness. 1 cycle, 3 cycles and 5 cycles films are analyzed in ultrafast regime (0–10 ps) in which each cycle was measured as approximately 20 nm. The increase of thickness enhances the ΔA absorption as expected (Figure 4-4a), the slight shift in wavelength among the samples has no trend while the reason can be manifolded. The striking difference here is the variations in decay rates of the peaks at 430 nm and 470 nm: the intensity at 430 nm increases 3.7 times from 1 cycle to 5 cycles sample, while the intensity at 470 nm increases 4.3 times. This non-linear increase is also exhibited between 1 cycle and 3 cycles ones. The GSB is almost unchanged whereas the peak of 470 nm enhances 1.4 times between 1 cycle and 3 cycles ones. The irregular increase among these peaks for all three samples confirm the estimation above that the filling of trap states (defect states) is the source of the disproportional alteration. As discussed above, the transitions from the trap states close to CB edge are mainly contributed by the ΔA of 470 nm. The measurement of these kinetic traces

supports this assumption as seen in Figure 4-4b and Figure 4-4c. It was indicated above that the non-thermal regime ends up around 1 ps followed by the hot carrier regime until around 10 ps. The rise of the peak at 470 nm for 5 cycles sample is not observed for thinner ones indicates that the rising more likely come from the increased absorption from the enhanced trap states close to CB edge.

It was reported that the photogenerated hole is trapped into the intragap states close to the CB [149]; more specifically, the hole trapping (see Figure 4-2) was assigned to V_{4+} states observed at 550 nm [145]. We indicated in Chapter 3.2 that the main contribution of ΔA of 550 nm is originated from hole trap states in or close to the VB and we called HA (Figure 3-2). The increased intensity of the peak at 550 nm can be interpreted both HA [32] and hole trapping ([40]) as illustrated in Figure 4-2. Because *in situ* or *operando* TAS experiments tells us that the kinetic traces are more likely to be originated by electrons or holes, not the nature of the transition. Still, Figure 4-4d shows that the origin of the kinetics at 550 nm is different from than the kinetics at 470 nm (Figure 4-4c). On the other hand, the contribution of HA can be observed by comparing Figure 4-4b with Figure 4-4d in which the trends are similar. As a result, the peak at 550 nm has the influence of both the photogenerated holes in the bleached region within the vicinity of VB and CB. These findings support the notion of the “contribution” that leads us to deconvolute the main TA characteristics of BiVO_4 .

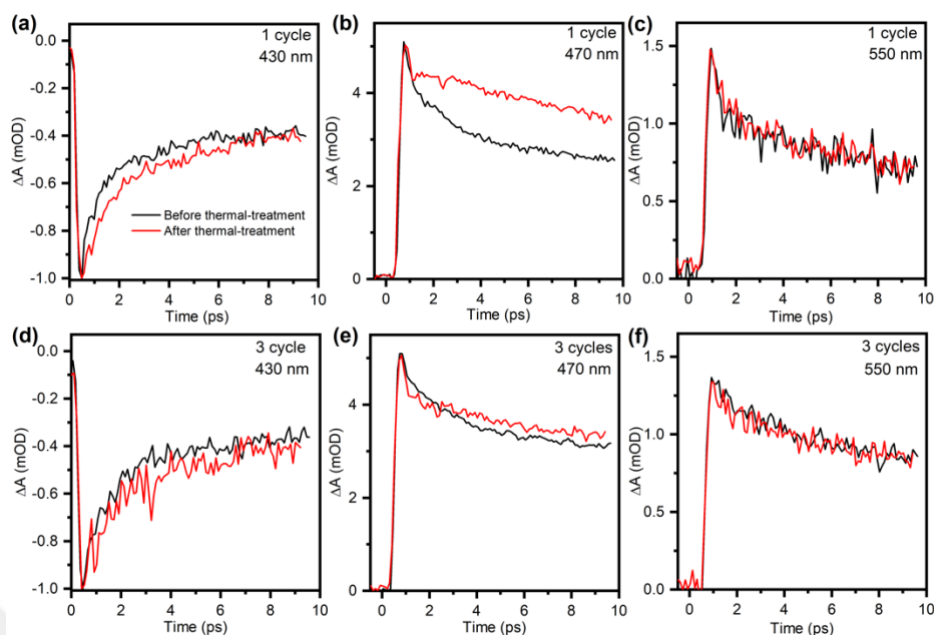


Figure 4-5 The TA kinetic spectra of 1 cycle (20 nm) BiVO_4 at 430 nm (a), 470 nm (b) and 550 nm (c) and 3 cycles (60 nm) BiVO_4 at 430 nm (d), 470 nm (e) and 550 nm (f).

Thermal treatment on BiVO_4 alters the crystallinity and crystal size which was shown by numerous studies. The unique role of certain crystal facets has been implied on the trapping and mobility of the carriers [77], [78], [79]. Specifically, the investigation of tr-photoluminescence (PL) spectroscopy of crystal-face dependent carrier dynamics suggested that the trapped hole carriers favorably reside on the lateral (110) facets of the BiVO_4 crystal [81]. Thermal treatment can also enlarge the particle size by expanding the grain boundaries such that the enlarged particle size was suggested to increase the hole carrier lifetime: For the hole reduced at the surface of a particle contacting with water, the lifetime should extend with enlarging particle size since the surface/bulk ratio declines with enlarging particle size [82]. thermal treatment also results in enhanced carrier transport by due to the enlarged grain size [80]. Despite the BiVO_4 photoanode was prepared by electrodeposition method, the reduced local distortion in $(\text{VO}_4)_3$ -units has been demonstrated upon thermal treatment [130] which result in enhancement of the charge separation and decreasing the charge recombination.

In the preparation of spin coated BiVO_4 , after each spin coating cycle sample was heated at 400°C for 10 minutes. At the end, the sample is heated for 2 hours

to increase crystallinity [87]. For ultrafast TAS investigation, the samples coated as 1 cycle and 3 cycles were analyzed before and after final annealing step to observe the crystallinity effect on the carrier dynamics (Figure 4-5). After final annealing, the slower decay of the kinetics at the peak of 430 nm (Figure 4-5a and Figure 4-5d) and the slow decay kinetics at the peak of 470 nm (Figure 4-5b and Figure 4-5e) are striking, while the kinetics at the peak of 550 nm nearly does not change (Figure 4-5c and Figure 4-5f). The slower decay of 430 nm and 470 nm after thermal treatment is obviously seen after 1 ps. This is almost end of non-thermal regime according to the discussions mentioned above. The correlation between the kinetics come from the trap states near the CB edge and the filling of ground states. Less distortion of V-O structural units [130] after thermal treatment might increase the lifetime of the electrons. This validate that the slower decay of the kinetic at 470 nm and the slower filling of ground states (430 nm) are correlated. As stated before, the poor wave function overlap between adjacent V atoms is expected to trigger a detrimental localization of CB electrons [18]. Therefore, the annealing can help to localize the photogenerated electrons that retard the recombination of these electrons giving slower decay for 470 nm. The change related to the V-O units can be the major alteration after the thermal treatment because the change of the hole carrier lifetime is negligible (Figure 4-5c and Figure 4-5f).

More experiments might need to be performed to have more rigid conclusion for the thermal treatment effect on the carrier lifetime, particularly *in situ* TAS experiments can be helpful. While this is beyond the scope of this chapter, we showed here that the annealing can play a critical role on the structural dynamics and this can be elucidated by TAS.

4.3 Conclusions

The essence of this chapter is to improve our understanding of optical ultrafast TAS of BiVO₄ by presenting valuable hints on the structural dynamics. Since TAS in the optical region neither structurally- nor elementally sensitive, deconvoluting various opto-electronic interactions in the ultrafast scale is a complicated task. This task has been elucidated by inspecting similar behavior of characteristic TA signals of BiVO₄ in the coherent regime, non-thermal regime

and in the thermalized regime. We interrogated these estimations by complementary experiments, seeking the role of film thickness and annealing on TAS of BiVO_4 considering their effect on elevated trap states and improved crystallinity.

I highlighted that the response of the main TA characteristics of BiVO_4 are interrelated due to the overlapped light-matter interactions in the ultrafast scale. The rational approach should be to resolve the carrier dynamics by establishing the “dominant contribution” of certain transitions to the TA signal in order to utilize TAS. Because the analyzed TA kinetic traces have inevitable contributions from the transitions in various energetic levels in the electronic structure of BiVO_4 . We concluded that the inspection of the contribution of TA signal can enhance our understanding the nature of the carrier recombination (i.e. dominant electronic transition) and the polaron formation. Besides, the role of the film thickness and annealing on TAS of BiVO_4 can give us significant information of the structural dynamics.

5 The Fast-track Water Oxidation Channel on BiVO₄ Opened by Nitrogen Treatment

5.1 Introduction

Additional oxygen vacancies (V_o) created by heteroatom doping of BiVO₄, like W [83], Mo [84] and N [98], can play a critical role in understanding the motives behind the improved activity and water oxidation steps [22], [85]. The V_o s generated via reduction of V from 5+ to 4+ in BiVO₄ under illumination are suggested to be a main loss channel for the photogenerated charge carriers [86]. However, V_o s could also take part in the PEC as active surface sites [22], [87], [88] and such a redox process has already been suggested to be the first step of the water oxidation reaction for hematite photoanodes [89], [90]. Identifying the relationship between the V_o s and V_{5+}/V_{4+} redox exchange in the course of PEC water oxidation and surface recombination is an indispensable way to improve the charge transfer property and the stability of the BiVO₄ photoanodes, simultaneously [91], [92].

5.2 Results and Discussion

The LSV tests performed in KPi (potassium phosphate) buffer solution under both illumination conditions are presented in Figure 5-1a. In general, higher J_{ph} is obtained under back illumination compared to front illumination, due to the low electron mobility for BiVO₄ [109]. We performed activity tests in buffer solution because the analysis of the effect of the surface modification on the charge transfer kinetics in the absence of the hole scavenger is more practical, compared to the measurements performed in their presence [27], [43]. The PEC activities under front illumination versus back should be distinguishable, particularly for the thick films. Differences in J_{ph} can be ascribed to the limited carrier mobility, as long as the film thickness is lower than the penetration depth

of light or inverse of the α^{-1} [1]. We observe that the J_{ph} under back illumination is 2 times higher than under front illumination for BiVO_4 , while almost no J_{ph} difference between two sides is witnessed for N-BiVO_4 at 1.23 V_{RHE} (Figure 5-1a). The significant increase of J_{ph} under front illumination in KPi buffer solution for N-BiVO_4 led us to concentrate on the changes at N-BiVO_4 /electrolyte interface by performing complementary experiments.

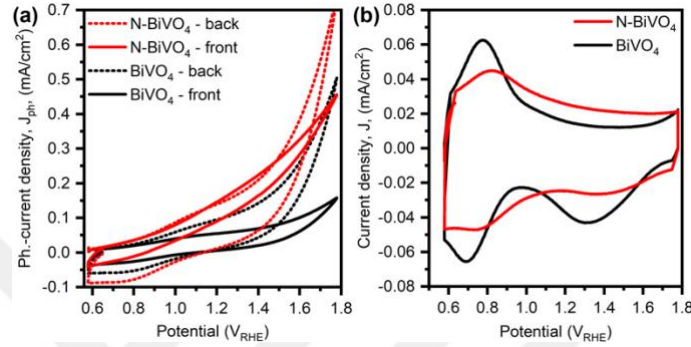
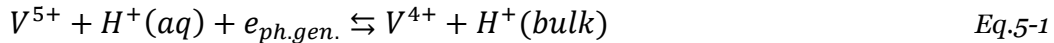


Figure 5-1 CV curves of BiVO_4 (black) and N-BiVO_4 (red) under front illumination (solid) and under back illumination (dashed) in 0.1 M KPi buffer solution ($\text{pH}=7.5$). The scan rate (v) was 100 mV/s (a). CV curves of BiVO_4 (black) and N-BiVO_4 (red) in dark recorded after anodic pretreatment, done by keeping the photoanode around 1.8 V_{RHE} for 2 minutes. v was 900 mV/s (b).

Figure 5-1b shows the CV curves obtained after an anodic pretreatment performed to build up additional surface reactive species and intermediates [22]. Anodic pretreatment promotes quenching the electrons at the surface, revealing a plenty amount of reaction sites available for catalytic turnover [89]. A reversible anodic and cathodic peaks between 0.6-0.8 V_{RHE} in the dark correspond to the reduction/reoxidation processes involving $\text{V}^{5+}/\text{V}^{4+}$ redox exchange. A similar process can be suggested involving trapping ($\rightarrow$)/detrapping ($\leftarrow$) in the presence of photogenerated electrons ($e_{\text{ph.gen.}}$) in BiVO_4 , as described by the equation [22], [88]:



Elevated CV scan rates (v) under dark and illumination conditions reveal the depletion of the redox species via trapping and detrapping of the photogenerated electrons (Figure 5-2). The redox peak current density increases linearly with v , which is characteristic to surface catalytic reaction with increased number of

active sites. We detect that the nitrogen treatment accelerates the reversible redox process on BiVO₄ (Figure 5-1b) that exhibits a motive behind the enhanced J_{ph} . The single cathodic peak seen at around 1.35 V_{RHE} implies that the surface activity of BiVO₄ is limited by both charge transfer through the trap states and by detrapping (irreversible reaction) involving VO₂⁺/VO₂⁺ reaction while the symmetric redox peak feature at 0.6-0.8 V_{RHE} suggests that the limitation arises only from the charge transfer [150]. We focus on the mechanisms of the trapping

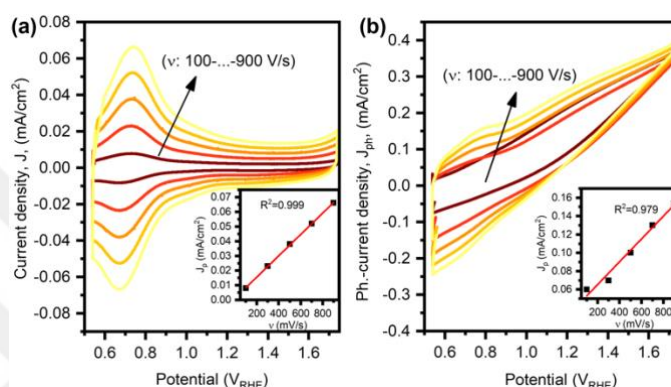


Figure 5-2 CVs of BiVO₄ without pretreatment (a) under dark and (b) under illumination. The corresponding relationship between peak current densities (J_p) and scan rates (v) is provided in the insets.

processes occurring at 0.4-1.2 V_{RHE} by utilizing TPC experiments and elucidate further the effect of the nitrogen treatment on the kinetics of the interfacial charge transfer and trapping processes at the time scale of water oxidation.

TPC response at the ms time scale can screen pivotal steps of the evolution of carrier trapping. In TPC investigations (see experimental details in the Chapter 2.4), as the light is switched on, photogenerated electrons move toward the back contact and holes toward the surface by creating space charge capacitance. This ‘instantaneous’ charging current is not correlated with the charge transfer across the interface [37], [151]. Charging can be evidenced by the cathodic (negative) J_{ph} response of the BiVO₄ in KPi buffer solution within a potential range (Figure 5-3a), while only anodic (positive) J_{ph} is observed in the sulfite hole scavenger solution (Figure 5-3b) at all potential values. J_{ph} of BiVO₄ does not exhibit a monotonous change with increased anodic potential (Figure 2a). The unexpected appearance of the cathodic peak within the potential range of 0.6 to 0.8 V_{RHE}

surprisingly coincides with the redox process of V_{5+}/V_{4+} (Figure 5-1b). In this potential range, the redox process perturbing the separation of the charge carriers is the reason for the anodic-to cathodic turning in J_{ph} , since simply fewer number of electrons moves to the back contact. Figure 5-3c shows that J_{ph} of N-BiVO₄ gets enhanced with increased potential, except for the potential range within 0.6-0.8 V_{RHE}. Nitrogen treatment accelerates the V_{5+}/V_{4+} surface redox, which is also an evident

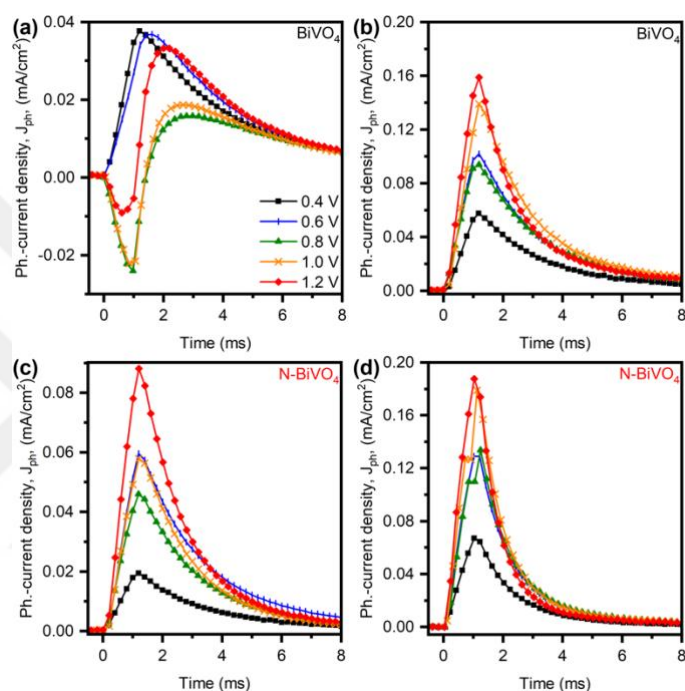
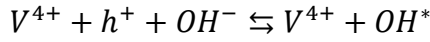


Figure 5-3 TPC measurements performed by 1 ms long LED pulses turning on at 0.0 ms and turning off at 1.0 ms for BiVO₄ in (a) KPi buffer and (b) in sulfite hole scavenger and for N-BiVO₄ (c) in KPi buffer (0.1 M, pH=7.5) and (d) in sulfite hole scavenger (0.5 M). The interval between data points corresponds to 200 μ s.

process in the presence of scavenger shown in Figure 5-3d. It can be stated that J_{ph} in N-BiVO₄ is higher, owing to the acceleration of the redox process induced by nitrogen treatment. Upon switching off the light (at 1.0 ms), the J_{ph} response of N-BiVO₄ suggests that detrapping of trapped electrons (Equation 5-1) or oxidation of surface species (Equation 5-2) continues but J_{ph} falls to zero (Figure 5-3c). Either detrapping of electrons or oxidation of the species is then the limiting step in BiVO₄ due to low V_o amount on its surface because V_{4+} formed via V_o could play a role in facilitating hole transfer to the surface species (i.e. OH⁻), converting them into surface hydroxyl groups (OH^{*}) according to [7], [22]:



Eq.5-2

Equation 5-2 shows that the first step of water oxidation involves the redox process that is slow in BiVO_4 , resulting in low J_{ph} but nitrogen treatment advances the water oxidation due to the critical number of reaction intermediates at the surface induced by V_o [91], [98], [101].

For both pristine and modified BiVO_4 , the dominant charge transfer channels in water oxidation have not been established well [116]. Photogenerated electrons

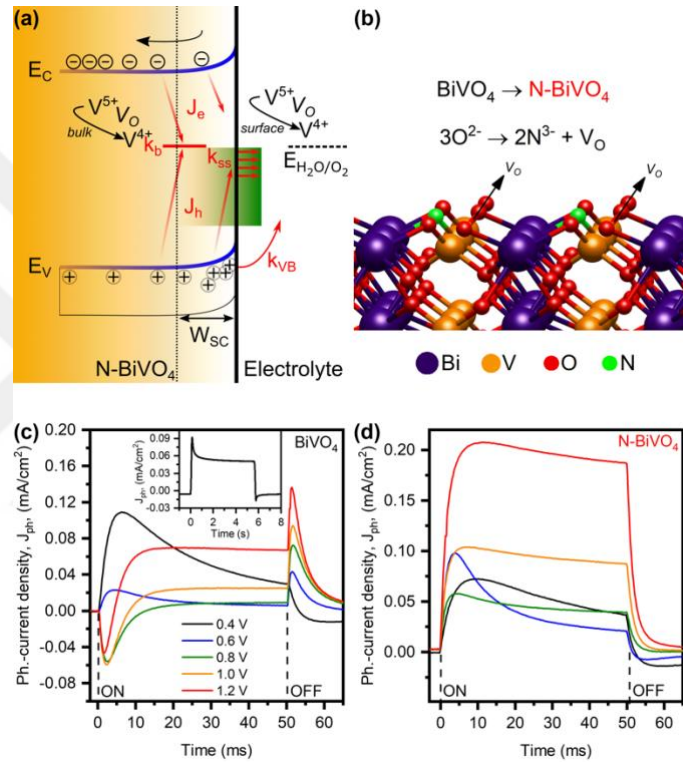


Figure 5-4 Energy band diagram and illustration of the charge transfer processes at the interface between BiVO_4 and electrolyte (a). A schematic model of the N-BiVO_4 surface (b). TPC measurements performed by 50 ms long LED pulses for BiVO_4 (c) and N-BiVO_4 (d) in KPi buffer solution (0.1 M, pH=7.5). The inset in (c) shows a representative TPC plot recorded under chopped AM 1.5 light. The illumination duration was 5500 ms.

and holes can be trapped in the bulk and at the surface, demonstrated as J_e and J_h in Figure 5-4a. In the bulk, electrons reduce V to 4+, majority of them migrate to the back contact, and a certain fraction recombines with photogenerated holes trapped in V_o in the bulk. This prevents the hole carriers from transferring to the interface (k_b). The photogenerated holes can transfer to the electrolyte through surface states (k_{ss}) and/or directly from the VB edge (k_{VB}). Both pathways are

plausible for nanoporous BiVO₄ [27] and can be identified by TPC investigations. The similar J_{ph} responses in the presence of the hole scavenger (Figure 5-3b and d) imply that the facile sulfite oxidation prevents identifying the role of nitrogen treatment. It is, however, apparent that J_{ph} does not monotonously increase in the range of 0.6-0.8 V_{RHE}. In KPi buffer solution, the trapping is maximized at 0.8 V_{RHE}, then it reduces due to the increase of band bending at higher voltages, however, a critical amount of trapping exists even at 1.2 V_{RHE} (Figure 5-3a). As shown in Figure 5-4, the charge transfer from BiVO₄ to the electrolyte is dominant through k_{ss} rather than k_{VB} since we expect obvious enhancement of hole transfer as band bending increases upon application of anodic potential. The V₅₊/V₄₊ reduction process at the interface, however, contributes to k_{ss} through Equation 5-2 since the V_o enhance the rate of adsorption of OH⁻ species.

Any improvement or deterioration induced by the modification of BiVO₄ are attributed to V_o as elucidated above. It is, however, crucial to identify the dominant charge transfer pathway governed by V_o upon nitrogen treatment. As pointed out in a theoretical study recently, V₅₊/V₄₊ reduction process in the charge transfer reaction and overall OER depend crucially on the surface termination of BiVO₄ [148]. The V_o in the bulk can facilitate electron mobility, while at interface their presence as the charge recombination centers perturbs the charge transfer to the electrolyte (Figure 5-4a). The concentration of V_o is augmented upon nitrogen treatment [91], [98]. Charge balance requirements reinforce the formation of additional V_o in BiVO₄ upon substitutional replacement of oxygen with nitrogen ions (Figure 5-4b). The transient response of N-BiVO₄ via pulses longer than 1 ms corroborates the efficacy of V_o thoroughly.

The TPC response to 50 ms light pulses involves unusual but valuable aspects of trapping and charge transfer mechanisms. Unlike the behavior under 1 ms light pulses, we could observe the saturation of the J_{ph} and the following transient decay by extending the illumination duration (Figure 5-4c-d) at various potentials. The most common TPC response (the inset in Figure 5-4c) has been usually discussed under longer pulses (a few seconds) generated by a chopped light. During illumination, the holes build up at the surface until an equilibrium is established via the charge recombination and interfacial charge transfer

processes [37], [151]. The steady J_{ph} following the transient response represents the Faradaic current that indicates the surface recombination is suppressed and the photogenerated holes transfer to the electrolyte [42]. When the light is switched off, the hole current drops immediately to zero, and the cathodic current appears if electrons continue to move towards the surface to recombine with the surface trapped holes [37], [151]. Apart from the classical TPC behavior, we are able to present the effects of anodic- and cathodic- charging and discharging of trapped carriers. As the anodic potential is above the redox peak at 0.6 V_{RHE}, the

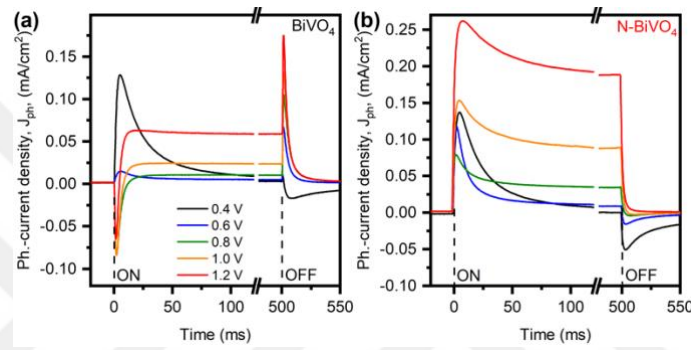


Figure 5-5 TPC measurements performed by 500 ms long LED pulses for BiVO_4 (a) and N-BiVO_4 (b) in KPi buffer solution.

light pulses result in the cathodic overshoot arising from the reduction of V_{5+} at the surface. Below 0.6 V_{RHE}, the anodic peak is only attributed to the accumulation of the holes at the surface. At the end of the light pulse, detrapping (≥ 0.6 V_{RHE}) and recombination of trapped electrons with accumulated holes in pristine BiVO_4 leads to an anodic overshoot (Figure 5-4c) [152], [153]. The behavior of J_{ph} under longer pulses further support the proposal of trapping-detrapping of the carriers on surface states and clarify the impact of nitrogen treatment on the PEC activity. The absence of anodic overshoot at the end of the pulse in Figure 5-4d confirms that nitrogen treatment facilitates the transfer of hole carriers towards the electrolyte while minimizing the trapping. As the light pulse elongates to 500 ms (Figure 5-5a and b) the trend in J_{ph} as a function of applied potential does not change but it becomes clear that the hole transfer predominantly occurs through the VB edge (k_{VB}) below 0.6 V_{RHE}. The impact of the nitrogen treatment is more evidently observed at >0.6 V_{RHE}, suggesting that the hole transfer becomes dominant through k_{ss} over k_{VB} .

It is expected that nitrogen treatment induces changes not only in the surface region but also in the bulk. Trapping-detrapping process does not necessarily take place on the surface and the participation of the V sites in the bulk cannot be ignored. The complementary optical time-resolved and X-ray spectroscopy experiments can provide further physical insight about the contribution of the nitrogen treatment to the overall activity. In this study, we employed UTAS, which is a pump-probe technique that has been applied to semiconductor photoelectrodes to monitor the time evolution of charge carriers by measuring

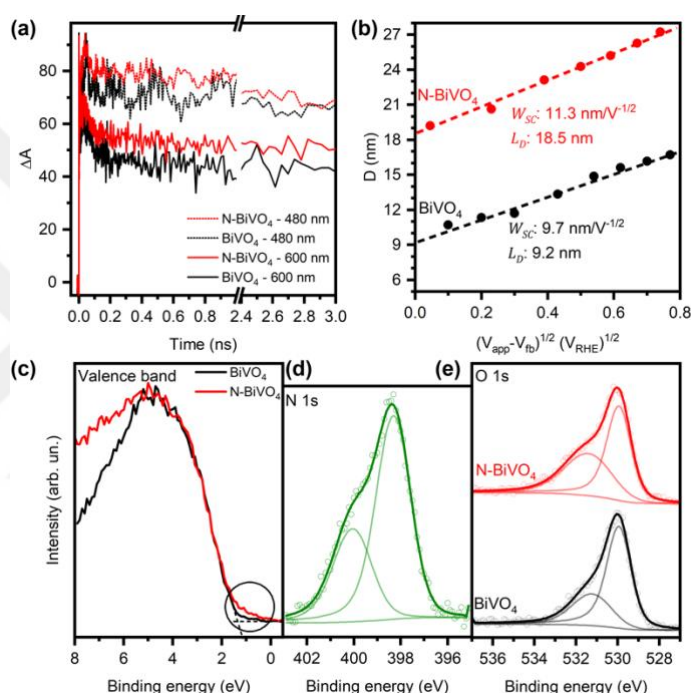


Figure 5-6 Transient absorption kinetics spectra probed at 480 and 600 nm (a). L_D and W_{sc} determined by light perturbation induced by blue LED light (b). VB XPS spectra recorded by setting the photon energy to 925 eV (c). N 1s (d) and O 1s (e) XPS spectra recorded by setting the photon energy to 700 eV. The spectra were deconvoluted using a Doniach-Sunjić function, a Shirley-type of background was used [154]. XPS measurements were performed using APPES system at SSRL [155].

the wavelength-dependent change in the nonlinear absorbance spectrum of materials in the presence of a strong pump beam. Transient absorption spectral features of metal-oxide semiconductors have been investigated for Fe₂O₃ [64] and BiVO₄ [33], to identify the characteristic features. In our recent study, we confirmed that the ΔA spectrum above 500 nm corresponds to the absorption of the photogenerated hole carriers and the positive peak appearing between 450-500 nm originates from the electron absorption at the excited state. The analysis

of the kinetics at 480 nm and 600 nm (Figure 5-7a) shows that the lifetime of photogenerated electrons increases from $\tau_1=15.5$ ps, $\tau_2=0.63$ ns to $\tau_1=26.7$ ps, $\tau_2=10.88$ ns, respectively, after nitrogen treatment. Similarly, the lifetime of holes increases from $\tau_1=50.3$ ps, $\tau_2=0.32$ ns to $\tau_1=45.7$ ps, $\tau_2=0.44$ ns, respectively, after nitrogen treatment (Figure 5-6a and Figure 5-7b). The associated decrease in the

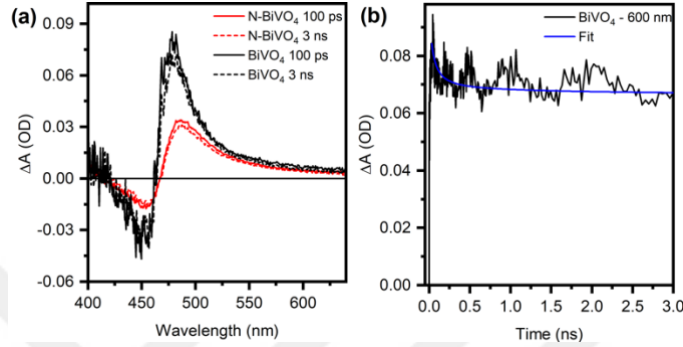


Figure 5-7 Time-evolution of the ΔA spectra of BiVO_4 and N-BiVO_4 probed at 100 ps (solid line) and 3 ns (dashed line) (a). TA kinetics spectrum of BiVO_4 probed at 600 nm and fitting with an exponential decay function (b).

rate of recombination could be linked to an increased number of V_O . However, bulk sensitivity of the TAS technique prevents us from identifying the depth of the BiVO_4 layer at which the nitrogen treatment has a strong influence. Since no major nitrogen induced changes were observed in UV-Vis and Raman spectra (see Figure 5-8c and d) we anticipate that the treatment has an effect only on the near surface region.

Table 5-1 Time constants obtained from the fittings of kinetic traces

TA signals	τ_1 (ps)	τ_2 (ps)
480 nm - BiVO_4	15.5 ± 0.6	630.2 ± 50.6
480 nm - N-BiVO_4	26.7 ± 0.6	10875.5 ± 2305.1
600 nm - BiVO_4	50.3 ± 1.9	316.2 ± 20.9
600 nm - N-BiVO_4	45.7 ± 1.0	438.6 ± 18.3

The TPC measurements emphasize the $\text{V}_{5+}/\text{V}_{4+}$ redox exchange at the interface. Nitrogen treatment could additionally increase the donor density (N_D) and thus, the width of the space charge layer (W_sc) can be modified. The distance (D) of the hole carriers reaching the surface could be determined [43] and sheds light on the extent of nitrogen treatment in the surface layer. In this approach, D

is the sum of the diffusion length (L_D) of hole carriers and W_{SC} ($D = L_D + W_{SC}$, see Chapter 2.4.2). It has previously been shown that the diffusion of the V ions toward Bi-rich BiVO_4 surface increases W_{SC} [130]. Investigations done in the presence of sulfite hole scavengers show that L_D almost doubles after nitrogen treatment while the increase in the W_{SC} is not too significant (Figure 5-6b). Overall, we could conclude that the increase in the PEC activity could be associated with the electronic structure changes in the near-surface region, with a depth < 20 nm, corresponding to the space charge layer.

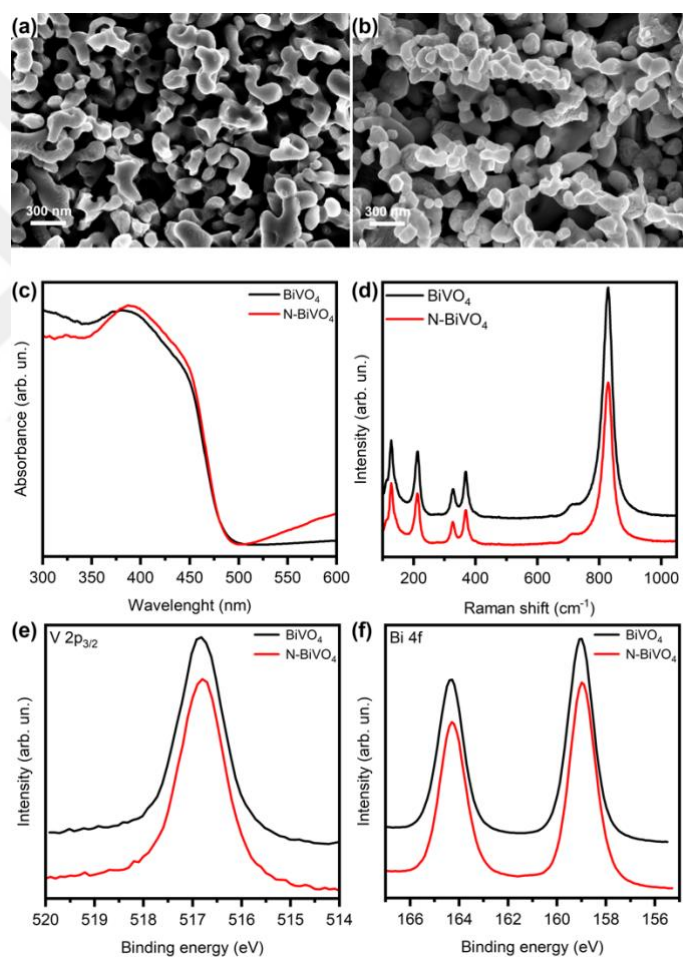


Figure 5-8 SEM images of (a) BiVO_4 and (b) N-BiVO_4 . (c) UV-Vis, (d) Raman, (e) $\text{V } 2p_{3/2}$ XPS, and (f) $\text{Bi } 4f$ XPS spectra of BiVO_4 (black) and N-BiVO_4 (red).

Originally, the purpose of the nitrogen treatment of oxide semiconductors is to increase their VB maximum and therefore, to narrow the bandgap. Such an

approach has extensively been applied to TiO_2 to make it harvest a larger portion of the solar spectrum [156]. While narrower bandgap could be expected in N- BiVO_4 , the formation of mid-gap states with the N and/or V_o character could be another viable possibility. VB of BiVO_4 shown in Figure 5-6c has primarily O 2p character that is observed as a broad peak centered at ~ 5 eV [133]. For BiVO_4 , VB maximum is found around 1.5 eV [157] while a new feature spanning between 1.5 and 0.4 eV is obtained after nitrogen treatment. It has been shown that new states above the VB maximum appear upon Mo and W doping in BiVO_4 and could be attributed to the shallow electron donor states due to V_o [158]. DFT calculations indicate that V_o [158] are not sufficient to change the bandgap of BiVO_4 [98], supported by our UV-Vis spectral measurements that do not indicate a significant bandgap narrowing (Figure 5-8c). The binding energy of Bi 4f_{7/2} found at 159.0 eV agrees well with the value of Bi₃₊ in bare BiVO_4 , while the binding energy of V 2p_{3/2} at 516.8 eV matches with V₅₊ (Figure 5-8e and f). There is no sign of V₄₊ or Bi₀ in XPS that can be associated with the surface reduction due to nitrogen treatment. High-resolution N 1s XPS presented in Figure 5-6d is composed of two peaks. The peak at 398.3 eV was assigned to the N₃₋ ions substitutionally replacing the O₂₋ ions in BiVO_4 . The origin of the smaller peak at 400 eV could either be assigned to NO_x species or N/N-H coordinated to the advantageous carbon on the surface [94]. NO_x and interstitial N species have been found in N- TiO_2 and could be present in N- BiVO_4 , too. However, we believe that substitutional N is playing the major role in the activity increase.

The V_o on the surfaces of the transition metal oxides can be stabilized by surface OH* groups. O 1s XPS spectra presented in Figure 5-6e demonstrate O₂₋ ions in BiVO_4 (529.9 eV) and OH* groups (531.3 eV) in the surface region. The analysis of the deconvoluted data indicates that the fraction of OH* groups increases from 30% to 44%, which can partly be correlated with an increased number of V_o after nitrogen treatment.

5.3 Conclusions

We have elucidated how the nitrogen treatment tailors the carrier trap mechanisms in BiVO_4 . This study has identified a new perspective of nitrogen treatment on BiVO_4 on the water oxidation reaction through a complementary set

of experiments to investigate the effect of surface modification. We evidence that the trap states in the space charge region and at the interface, substantiated through V_O and the redox process of V_{5+}/V_{4+} , differentiate water oxidation activity of BiVO_4 photoanodes. Employing TPC experiments at the timescale of surface recombination and water oxidation, we confirm that nitrogen treatment facilitates hole transfer via creating additional V_O and V_{5+}/V_{4+} redox channel while diminishing surface recombination. Nitrogen incorporation creates mid-gap states rather than moving the VB maximum closer to the Fermi level. Moreover, nitrogen treatment increases the diffusion length of the holes.



6 Transient Absorption Spectroscopy and Core-Level Spectroscopy of Cobalt Catalyzed BiVO₄ Photoanodes

6.1 Introduction

This chapter mainly concerns the elucidation of cobalt-based catalyst (Co(OH)₂) on BiVO₄. Still, it begins with the analysis of bare BiVO₄ prepared by different methods, spin coating (SC) and electrodeposition (ED). While the thickness of the films can be controlled by the number of spin-coating cycles having ideal film quality, uniformity, and reproducibility, ED-BiVO₄ has higher J_{ph} than SC-BiVO₄. Yet, the surface of thin ED-BiVO₄ films are not uniform, at least 800 nm deposition is required to have efficient films. Therefore, the fabrication method of BiVO₄ is expected to affect the efficacy of the co-catalyst as well.

Cobalt(II)hydroxide (Co(OH)₂) comprises of cobalt cations Co²⁺ and hydroxide anions OH⁻ and can be divided into two forms. β -Co(OH)₂ is a solid and insoluble in water, while α -Co(OH)₂, which includes other anions in its molecular structure, is highly unstable [159]. In this thesis, the investigation of different ambient on the Co-catalyzed ED-BiVO₄ was highlighted through *in situ* XAS of β -Co(OH)₂-BiVO₄. Finally, since further improvement of BiVO₄ photoanodes originated from the post-heat treatment of Co(OH)₂-BiVO₄, the carrier dynamics of modified BiVO₄ was investigated to reveal the effects of the untreated catalyst and heat-treated catalyst.

The surface of the practical photoanodes involves compositional and structural complexity compared to single-crystal surfaces. It is essential to clarify the structural aspects at the atomic/molecular scale to tailor new catalyst on photoanodes with targeted characteristics, such as the interaction of nanoparticles with the substrate, phase composition, the structure, and chemical state of the surface composition [160]. Dynamic structural and compositional

alterations further complicate the recognition of the heterogeneous nanocatalysts. In this regard, apart from electrochemical measurements, we utilize CLS to reveal the change of structural and chemical state upon co-catalyst deposition, while TAS help us to highlight the change of carrier lifetime.

6.2 Spin-coated vs Electrodeposited BiVO₄ Photoanodes

The preparation method significantly affects the morphology of the BiVO₄ films which is crucial in terms of the particle size that affect the charge transport properties and light absorption. The larger surface area advances catalytic activity of the photoanodes owing to the extended active contact with electrolyte at the interface. The morphology of ED- and SC-BiVO₄ photoanodes are investigated via scanning electron microscopy (SEM) images (Figure 6-1). The average particle sizes are ~95 nm and ~50 nm for ED and SC films, respectively.

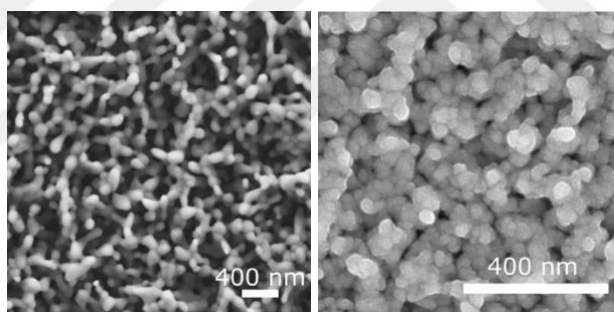


Figure 6-1 SEM images of (left) electrodeposited and (right) spin coated BiVO₄.

CV of the photoanode in dark presents its electrochemical current (EC) while under illumination presents its PEC current. The onset potential, the potential where the current sharply increases, denotes the potential in which a reaction starts taking place. Higher photocurrent and lower onset potential clearly shows that ED-BiVO₄ has better activity than SC-BiVO₄, either in dark (Figure 6-2a) or under illumination (Figure 6-2b).

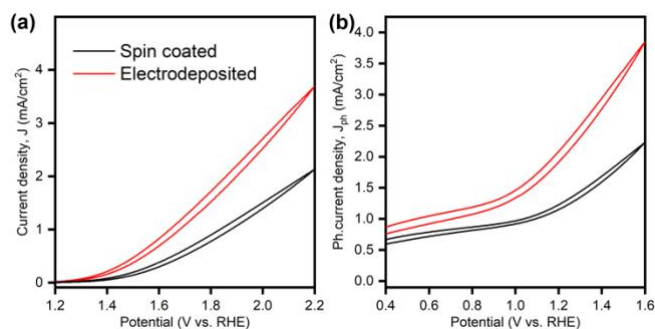


Figure 6-2 CV of electrodeposited and spin coated BiVO_4 in (a) dark and (b) under illumination measured in presence of $0.5\text{ M Na}_2\text{SO}_3$.

The valence electrons in VB and CB has shared by Bi-O and V-O units by hybridization (Figure 3-2). After photoexcitation, the electron localization and the change of DOS can be probed by core-electrons. O 1s at 529.7 eV is attributed to the bulk oxygen in metal oxides and the shoulder at 531.5 eV is assigned to the surface adsorbed oxygen species such as hydroxyl groups [161]. XPS peaks of V $2p_{3/2}$ and V $2p_{1/2}$ at 516.6 eV and 524.15 eV, respectively, denotes the existence of V_{5+} in BiVO_4 , while the small peak at 514.4 eV indicate the existence of V_{4+} [162]. O 1s XPS spectrum of ED- BiVO_4 shows a significant energy shoulder of high binding energy side compared to SC- BiVO_4 but energy shift between them does not exist (Figure 6-3a). This shoulder peak corresponds to hydroxyl groups (i.e. OH^-) [161] and it can be understood by the analysis of V $2p_{1/2}$. The low energy shoulder at low binding energy side of V $2p_{1/2}$ (at around 515.4 eV, see inset in the Figure 6-3a) indicates the existence of V_{4+} for ED- BiVO_4 [18] which signifies higher amount of V_o for ED- BiVO_4 than SC- BiVO_4 . Since XPS is a surface sensitive technique, we could say that the reason of having higher J_{ph} of ED- BiVO_4 can be originated from the higher amount of V_o in the surface region that attract more OH^- at interface facilitating a faster photogenerated hole utilization for OER, as stated in Chapter 5. As stated, this clarifies the large O 1s shoulder peak (531.5 eV) for ED- BiVO_4 because OH^- species are already exist on the surface in air as well. The low amount of V_o may be deduced from the ratio of O 1s to its high binding energy shoulder which is very high for SC- and low for ED- BiVO_4 . The shift to high binding energy of V_{5+} along with the rising of V_{4+} for ED- BiVO_4 further indicates the presence of more V_o . This finding, in fact, also evidence the relation between the reduction of V_{5+} to V_{4+} and V_o , showing the concurrently

arising of OH⁻ and V₄⁺ in the XPS spectra, which is discussed elaborately in Chapter 5.

Since XAS of V 2p can give more thorough information than XPS, V L-edge is presented by XAS spectra which are normalized to peak maxima to see the differences between the peak ratios. Spectra are dominated by two main peaks, L₃ and L₂, which denote the excitation to unoccupied CB V 3d states from the core levels of 2p_{3/2} and 2p_{1/2}, respectively. We focus on L₃-edge because the spectral features are not obvious in L₂-edge owing to the shorter lifetime broadening [163]. The L₃ splits into two main peaks at 516.4 eV and 518.5 eV, which are implied as the e_g and t_{2g} states respectively and the separation of ~2.1 eV is related to the ligand field splitting parameter [164]. Peaks at 515.4 and 517.4 eV are triplet states originated from atomic “multiplet effects”, the overlap of the core and final states, correlated with the transitions from 2p_{3/2} states to unoccupied 3d states of V₅₊. The strong ligand character are mixed through spin–orbit interactions and Coulomb repulsion in the L₃-edge [137]. The information of charge transfer between oxygen ligands and V 3d sites can be implicitly understood with RIXS measurement of V L₃-edge [122]. Still, the spectra present evidence of a distorted tetrahedral environment of V₅₊ of BiVO₄. The density of the 3d splitting energy levels are different for ED- and SC-BiVO₄ films (Figure 6-3b) which supports them having different nature of V-O hybridization and different amount of V_o.

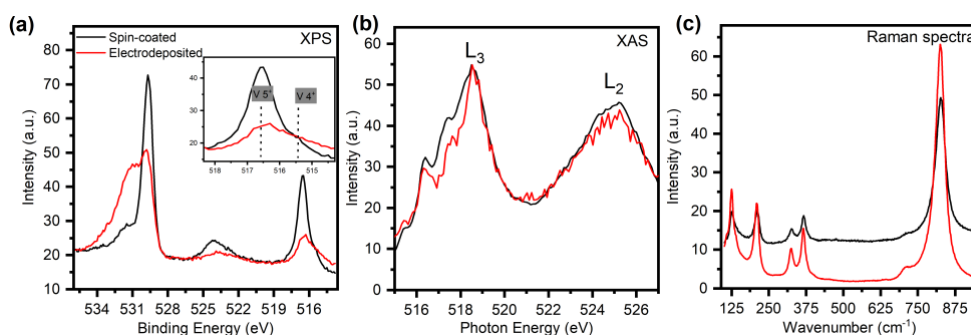


Figure 6-3 XPS peaks of Oxygen 1s and Vanadium 2p (a), XAS V L₂ and L₃ edges (b) and Raman spectra (c) of spin coated (black) and electrodeposited BiVO₄ (red).

The Raman spectra of ED- and SC-BiVO₄ have been compared to observe any possible change in the vibrational modes that can be associated with structural changes (Figure 6-3c). The sharpest peak at ~825 cm⁻¹ is attributed to the

symmetric stretching and the shoulder at $\sim 708\text{ cm}^{-1}$ is attributed to asymmetric stretching of VO_4 tetrahedrons. Peaks at $\sim 367\text{ cm}^{-1}$ and $\sim 326\text{ cm}^{-1}$ are the symmetric and asymmetric bending V-O units, respectively. The peaks at 210 cm^{-1} and 125 cm^{-1} are assigned to the rotation-translation modes of the lattice [165]. These peaks seen in the Raman spectra of ED- BiVO_4 exhibits redshift ($\sim 2\text{ cm}^{-1}$) compared with SC- BiVO_4 (except the peak at around 125 cm^{-1}), which signifies a slightly shorter V-O bond length for ED- BiVO_4 . This also signifies a partial disappearance of OH groups from the surface of SC- BiVO_4 . Besides, the peak ratio of the symmetric to asymmetric stretching modes, which is very sensitive to extended structures, are 18.5 and 18.0 for SC- and ED- BiVO_4 , respectively.

6.3 *In situ* XAS of $\text{Co}(\text{OH})_2\text{-BiVO}_4$

As other TMOs, dipole-allowed transitions related to L-edge is more probable than quadrupole transitions of K-edge for Co [122]. The L-edge are described by $2p_{63}d_n \rightarrow 2p_{53}d_{n+1}$ transitions and consists of spin-orbit splitting of $2p_{3/2}$ and $2p_{1/2}$ which are described as L_3 -edge and L_2 -edge, respectively. [164]. According to the extensive review of both experimental and theoretical results of XAS at the Co L-edge [166], the ultrathin overlayer on both ED- BiVO_4 and SC- BiVO_4 is $\text{Co}(\text{OH})_2$. We focus on XAS at the Co L_3 -edge, as approached for vanadium, rather than L_2 -edge because L_3 -edge provides more structural information about the

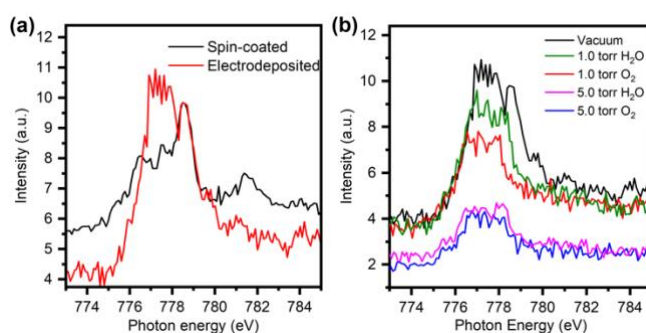


Figure 6-4 Co-L edge XAS of $\text{Co}(\text{OH})_2$ deposited on spin coated (black) and electrodeposited (red) BiVO_4 (a). Ambient pressure Co-L edge XAS of $\text{Co}(\text{OH})_2$ /electrodeposited BiVO_4 in various water and oxygen pressures (b).

valence states and hybridization of the metal-ligand orbitals. The main sharp peak of L_3 -edge of SC- BiVO_4 is seen at $\sim 778.5\text{ eV}$ with a separate peak at ~ 781.0

eV and multiplet peaks between ~ 775.5 eV and ~ 777.5 eV (Figure 6-4a). The values are compatible with the values indicated in the literature [166]. The main peak of L_3 -edges of ED- BiVO_4 and SC- BiVO_4 are normalized to peak maxima to guide the eye for better analysis. The multiplet peaks at higher energies are higher than the main peak of L_3 -edge and the shoulder peak at ~ 781.0 eV is very small for ED- BiVO_4 compared with the SC- BiVO_4 . While the multiplet peaks at higher energies exist, the ones at lower energies are negligible for ED- BiVO_4 . This might indicate that the different surface structures of $\text{Co}(\text{OH})_2$ on ED- and SC- BiVO_4 result in different population densities of the valence states of Co due to nature of the ligands. The peak at ~ 781.0 eV, gives further information on the differences of the two preparation methods which is seen as a shoulder of the main peak for ED- BiVO_4 but as a separate peak of SC- BiVO_4 . The separate peak in SC- BiVO_4 most likely arise from a cluster which might have Co_{3+} states rather than Co_{2+} that was observed in Co_3O_4 L-edge peak for the $3+$ state [167]. Yet, it might have ligands with OH^- ions with different structure. Lastly, the peak at ~ 784.0 eV has been explained by metal-to-ligand charge transfer (MLCT) effects to unoccupied ligand orbitals associated with π back-bonding to the Co metal [159]. This peak is only seen in ED- BiVO_4 , the absence of this “path” in SC- BiVO_4 might be another potential reason having less charge transfer ability compared ED- BiVO_4 . We performed *in situ* XAS experiments for ED- BiVO_4 for further understanding of the valence states of $\text{Co}(\text{OH})_2\text{-BiVO}_4$.

The peak at ~ 784.0 eV is disappeared under either O_2 or H_2O pressure (Figure 6-4b). This might indicate that MLCT transitions to unoccupied ligand orbitals becomes forbidden or saturated due to the H_2O and O_2 molecules [159]. The main peaks at ~ 778.5 eV and the shoulder peak at ~ 781.0 eV of Co L_3 -edge are almost completely lost under either 1.0 torr H_2O or 1.0 torr O_2 . As the pressure increases, the signal-to-noise ratio decreases but the ratio of the intensities of multiplet peaks to the main peak decreases. This might be related to recover of the bonding result from OH^- molecules introduced by H_2O . Besides, the shoulder peak surprisingly rises under 5.00 torr H_2O . This might support the idea that the peak seen as cluster in SC- BiVO_4 might result from the structures formed by Co-OH- ligands.

It is complicated to have rigid conclusions in the modified electronic structure of BiVO_4 and Co(OH)_2 owing to the multiplet effects [137], [168]. Even more structural sensitive techniques, such as RIXS, should be utilized to detach the differences in the ground state electronic structure [167]. Still, the complementary XAS of different edges for bare and co-catalyzed BiVO_4 indicates that SC- and ED- BiVO_4 results in different surface structure that affect both the PEC activity and the bonding of Co ions with the ligands. The less activity of SC- BiVO_4 might result from having less V_o compared to ED- BiVO_4 that can also affect the energy levels between the multiplets.

6.4 PEC Measurements of Co(OH)_2 - BiVO_4 photoanodes

We showed that mild post-heat treatment or thermal treatment of nanoporous BiVO_4 film in an oxidizing atmosphere at 200 °C increases the PEC performance notably and decreases the overpotential for water oxidation [130]. Increasing V:Bi ratio after heat treatment implies the migration of V ions towards the surface that releases the trapped electrons from the surface states and leads to photocurrent enhancement [169]. We implemented this strategy on the Co(OH)_2 - BiVO_4 photoanodes. LSV measurements of bare BiVO_4 , Co(OH)_2 - BiVO_4 and thermal-treated Co(OH)_2 - BiVO_4 (TT) in the sulfite hole scavenger, show that co-catalyst enhances J_{ph} , while TT promotes the improvement under either front or back illumination (Figure 6-5). The enhanced J_{ph} of BiVO_4 upon co-catalyst deposition is higher under front illumination (Figure 6-5a) than back illumination (Figure 6-5b), while the inverse situation is seen for the bare BiVO_4 photoanodes.

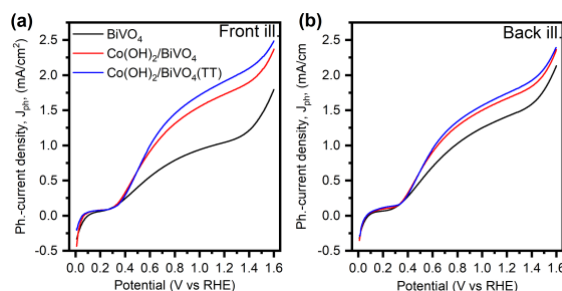


Figure 6-5 LSV measurements of bare BiVO_4 , $\text{Co(OH)}_2\text{-BiVO}_4$ and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) under front illumination (a) and back illumination (b) conditions.

The difference of J_{ph} of the bare BiVO_4 between front and back illumination has been discussed before [1]. The mobility of electrons is much lower than the holes of BiVO_4 due to nature of polarons of BiVO_4 , therefore, it is likely to observe higher J_{ph} under back illumination. However, the difference of front vs back illumination can be ascribed to the carrier mobility as long as the film thickness is lower than the penetration depth of light or inverse of the α^{-1} [1]. Thickness of BiVO_4 in our studies prepared by ED method is about $1.0 \mu\text{m}$, and the α^{-1} is 300 nm^{-1} at 450 nm . Then, higher J_{ph} under back illumination can be simply ascribed to higher number of excited electrons that can reach to the circuit under back illumination compared to the front illumination. As we compare J_{ph} of bare BiVO_4 and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) at 1.23 V vs RHE, the increase of 1.83 times is observed under front illumination, while 1.24 times increase is seen under back illumination. In this manner, the obvious difference of $\text{Co(OH)}_2\text{-BiVO}_4$ and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) under front illumination ought to be analyzed in detail. We suggest that Co can diffuse from the surface to bulk of BiVO_4 forming a p-type layer that results in a p-n junction and expected to have a higher charge separation upon thermal treatment. It was shown that forming p-n junction at the surface by depositing p-type catalysts as Co_3O_4 and NiO_x enhances the charge separation [170], [171]. Also, loading Co-doped BiVO_4 layers on Mo-doped BiVO_4 enhanced charge separation by generating p-n junction and kinetically accelerated the rate of the OER [172]. Co as a p-type dopant in n-type BiVO_4 can lower the Fermi level near the VB edge [173], [174]. Upward band bending takes place at the surface region enhancing the separation of charge carriers. Therefore, it can be concluded that in addition to the improved water oxidation kinetics by

Co(OH)₂ overlayer deposition onto BiVO₄, the charge separation efficiency was also improved significantly after thermal treatment by diffusion of Co ions into the bulk of BiVO₄.

6.5 TAS Measurements of Co(OH)₂-BiVO₄ Photoanodes

Cobalt-phosphate (CoPi) was deposited on BiVO₄ as an oxygen evolution catalyst (OEC) [41]. However, it was implied that its impact on the improvement is originated from the suppression of the surface recombination rather than facilitating the oxidation reaction [175]. The less active hole transfer kinetics for CoPi-BiVO₄ than for BiVO₄ was suggested. It was claimed that Co²⁺ oxidation to Co³⁺ showed that ~5% of activity arises from hole transfer through CoPi on BiVO₄, while suggesting that the time scale for CoPi to drive OER is three order times longer than that for direct hole transfer through BiVO₄ [41]. Although the thickness of these CoPi overlayers is 30-100 nm makes a doubtful expectation of CoPi as catalyst, this was further tested by comparing ~1 nm CoPi with well-known OER catalyst RuOx suggesting that the suppression of the recombination is the primary effect of CoPi on BiVO₄ [116]. The role of CoOx-BiVO₄ on the recombination mechanism, however, has not been investigated as CoPi. The study of CoFe Prussian blue (CoFe-PB) as OEC on BiVO₄ has been recently reported that CoFe-PB facilitates hole transfer and decrease the recombination due to covalent linkage of PB to BiVO₄ [62]. In this section, I present TAS investigations of Co(OH)₂-BiVO₄ in both microsecond (μs) and picosecond (ps) timescale.

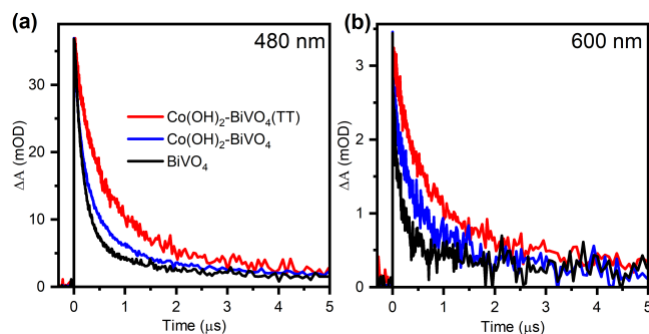


Figure 6-6 Transient absorption decay kinetic traces of bare BiVO_4 and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) probed at 475 nm(a) and 600 nm (b). Both are normalized to maximum. Pump intensity and wavelength are $530 \mu\text{J}/\text{cm}^2$ and 320 nm.

As seen in Figure 6-6, both carrier lifetime increases in the order $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) > $\text{Co(OH)}_2\text{-BiVO}_4$ > BiVO_4 as same order in J_{ph} , implies that Co(OH)_2 can suppress the recombination in the course of water oxidation that results in the improvement of the activity. In order to elucidate the origin of the retardation of the recombination of the carriers in $\text{Co(OH)}_2\text{-BiVO}_4$ (TT), whether it is related to the change in bulk on the surface of BiVO_4 , ultrafast TAS measurements have been performed. In the ultrafast time scale, there is almost no difference between the excited electron absorption of the bare BiVO_4 and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) photoanodes (Figure 6-7). The kinetic traces of 600 nm, correspond to the relaxation of photogenerated holes, has a slower decay for $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) than the bare BiVO_4 in the ultrafast scale. Under the light of discussion in Chapter 3, we suggest that co-catalyst layer of Co(OH)_2 (TT) can retard the photogenerated holes by two possible processes. First, the homojunction formation, owing to the diffusion of Co ions into the depletion width of BiVO_4 , results in enhanced band bending that retards the hole lifetime. Second, Co(OH)_2 (TT) might also lead to passivation of a certain recombination channel, that normally photogenerated hole is trapped at the midgap states.

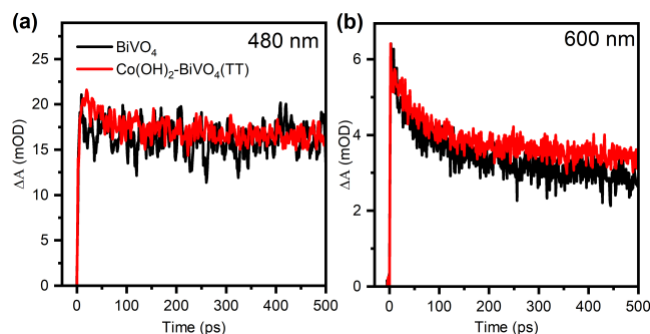


Figure 6-7 Ultrafast transient absorption decay kinetic traces of bare BiVO_4 and $\text{Co(OH)}_2\text{-BiVO}_4$ (TT) probed at 480 nm(a) and 600 nm (b). Both are normalized to maximum. Pump intensity and wavelength are $450 \mu\text{J}/\text{cm}^2$ and 320 nm, respectively.

6.6 Conclusions

We determine that ultrathin Co(OH)_2 cocatalysts significantly enhance the PEC oxidation activities of BiVO_4 photoanodes. Yet, SC- and ED- BiVO_4 results in different surface structure affect both the PEC activity and the bonding of Co ions with the ligands. The reason behind the less activity of SC- BiVO_4 is implied to having less V_o compared to ED- BiVO_4 that is also cause having different the energy levels between the multiplets. The change of the main peak of XAS Co L_{2-} edge and the adjacent peaks imply that the MLCT transitions to unoccupied ligand orbitals becomes forbidden or saturated under O_2 and H_2O ambient.

$\text{Co(OH)}_2\text{-BiVO}_4$ was further improved by TT and the results imply that diffusion of Co ions into the depletion region result in p-n junction due to p-type nature of cobalt in the n-type BiVO_4 . This has been supported by transient TAS results that suggest the activity improvement of modified BiVO_4 photoanodes by ultrathin Co(OH)_2 cocatalyst layer results from the increased lifetimes of electron and hole carriers. This enhancement is more likely originated by increased band bending owing to the formation of homojunction.

7 Summary and Outlook

BiVO_4 , used as a promising photoanode material in PEC cells, can be better utilized for water oxidation as the charge carriers are more effectively utilized. Photogenerated electrons are either trapped or transported into the cathode through the circuit, while photogenerated holes can either be trapped or directly migrated to the electrolyte to be utilized in OER. The OER is suggested to be completed at the end of 4-step electron transfer reactions and its sluggish kinetics limit the overall activity. Therefore, identification of the carrier dynamics in bulk, surface and interface is critical to understand the impediments and develop the photoanode to facilitate OER.

First of all, this research focuses on the accurate attribution of spectral TAS features of BiVO_4 to its charge carriers in optical domain, from tens of fs to ms timescale. This is a complicated task owing to many overlapped carrier-carrier and carrier-phonon interactions. The outcomes of the numerical model developed for having the best scenario of the electronic transitions in the ultrafast time scale were promising. Furthermore, perturbing either electron or hole population during TAS measurements, three complementary experiments clearly unveiled the ongoing controversies on TAS spectral assignment for the charge carriers of BiVO_4 . Specifically, these experimental findings under various conditions together with the numerical modeling show that both electron and hole absorption are probable in the spectral region above 500 nm, while electron absorption at the excited state is the principal process at shorter wavelengths. Additionally, it was revealed that the major changes in transient absorption response arise in the ultrafast time scale, and entire recombination dynamics reflects the ultrafast recombination mechanism.

Next, extensive analysis of ultrafast TAS of BiVO_4 has been realized to obtain further information about the signatures of structural dynamics. The photogenerated electron relaxation through V-O structural units, forming small polarons, decreases electron mobility thereby leading recombination with

photogenerated holes. The foremost outcome of this part is the notion of the “contribution” of the overlapped interactions to the TA spectrum which indicates the necessity of the deconvoluting the main TA characteristics. Besides, the frequency of small polaron oscillations was realized by TA kinetics at 470 nm which implies that the polaronic behavior can be recognized by TAS measurements of BiVO₄. The filling of trap states near CB edge was elucidated with respect to different film thicknesses of BiVO₄. Further critical outcomes are tested by TAS measurements of BiVO₄ photoanodes that are exposed to post-heat treatment. TAS of the heat-treated BiVO₄ films indicated how the crystallinity affects the charge carrier dynamics.

Since the reactions of PEC cells takes place at the interface of electrode-electrolyte, the carrier dynamics in bulk and interface must be distinguished well. Particularly, the interpretation of spectroscopy results can give misleading deductions if the carrier properties are inferred by only regarding bulk. However, the carrier population is different at surface-interface region compared with the bulk due to the band bending. As a hot topic for BiVO₄, the role of V_o has been recently discussed in this regard. The intrinsic V_o , which are suggested to be the reason of n-type feature of BiVO₄ and reduces vanadium from 5+ to 4+, are present in both bulk and interface naturally. The V_o also attract adsorbates (i.e. OH⁻ ions) from electrolyte into the interface region. Although, V_o is often considered as recombination center for photogenerated holes, we highlighted that the enhanced V_o at interface (by nitrogen treatment) significantly facilitates the reactions of holes with the OH⁻ ions. Consequently, the nitrogen incorporated BiVO₄ has been elucidated by emphasizing the critical role of V_o at interface in addition to the bulk. We suggested that the reduction process of V_{5+}/V_{4+} at interface leads the first step of the water oxidation reactions for BiVO₄ photoanodes that can be enhanced by increasing V_o at the interface. This has been realized by mainly home built TPC spectroscopy employed in the timescale of surface recombination and water oxidation, while CV, XPS and TAS measurements support the findings.

Atomically thin layer of co-catalyst, Co(OH)₂, was deposited on BiVO₄ to facilitate the kinetics of the OER. Yet, the role of co-catalyst is intricate in terms

of its effect on the surface and water oxidation reactions, particularly for cobalt-based catalyst deposited on TMO semiconductors. We present that the ultrathin Co(OH)_2 increases the PEC oxidation activities of BiVO_4 photoanodes. Still, SC- and ED- BiVO_4 result in different surface structure that changes both the PEC activity and the bonding of Co ions with the ligands. The reason behind the poor activity of SC- BiVO_4 was suggested to having less V_o compared to ED- BiVO_4 . Moreover, thermal treatment on $\text{Co(OH)}_2\text{-BiVO}_4$ further improved the PEC activity that was implied to p-n junction formation by diffusion of cobalt ions into the bulk upon thermal treatment. This is originated from the p-type nature of cobalt in the surface region of n-type BiVO_4 .



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Vita

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- Navid Solati, Sonia Mobassem, Abdullah Kahraman, Hirohito Ogasawara, Sarp Kaya “A comprehensive study on the characteristic spectroscopic features of nitrogen-doped graphene” *Applied Surface Science* 11/2019; 495, 30, 143518 <https://doi.org/10.1016/j.apsusc.2019.07.260>
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