QUANTUM DOT FUNCTIONALIZED TITANIA SYSTEMS FOR PHOTOCATALYTIC OXIDATIVE NO_x STORAGE

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By
Merve Balcı
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QUANTUM DOT FUNCTIONALIZED TITANIA SYSTEMS FOR PHOTOCATALYTIC OXIDATIVE NO_x STORAGE

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March 2018

We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Quantum Dot Functionalized Titania Systems for Photocatalytic Oxidative NO_x Storage

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March 2018

Increasing activities of industrial combustion systems, volcanic eruptions, agriculture activities and utilization of stationary and mobile fossil and biomass combustion systems are known to be the major causes of toxic nitrogen oxides (NO_x) pollution. These pollutants are not only highly hazardous for the ecosystem but also can trigger the formation of secondary pollutants such as acid rain and tropospheric ozone. Abatement of toxic NOx gases can be achieved by thermal catalytic processes or physical/chemical adsorption systems. However, environmentally friendly, cost-efficient and sustainable alternative photocatalytic systems can also be designed which can exploit readily abundant solar radiation.

One of the most well-known benchmarks for environmental photocatalysts is titanium dioxide with a wide band gap typically varying within 3.0-3.2 eV that can be activated via UV photons. This wide band gap prevents efficient absorption of visible light, which corresponds to around 5 times higher intensity compared to UV light. In order to increase the photocatalytic efficiency of the titanium dioxide, its visible-light exploitation capability should be enhanced. Although, this can be done by doping of TiO_2 with nonmetal main group elements, recently the research focus has shifted towards utilization of semiconductor quantum dots (QDs) for this purpose. Visible response of the QDs can be modified by tuning their particle size. Furthermore, QDs provide additional advantages such as the generation of hot electrons or multiple charge carriers with a single high-energy photon.

In the present work, CdTe QDs were employed as a direct band gap semiconductor (1.44 eV) compatible with the visible window of the solar spectrum to promote titania based photocatalysts. Due to its higher conduction band, CdTe can transfer its conduction band

electrons to the conduction band of TiO_2 and the hole that is created on the valence band of TiO_2 can be transferred to the valence band of CdTe; leading to efficient electron-hole separation. Thus, visible light exploitation capacity of TiO_2 can be enhanced along with its photocatalytic activity.

Current photocatalytic activity results on QD functionalized titania systems exhibited much higher NO_x storage in solid state and an enhancement of NO conversion values as compared to that of P25 titania benchmark photocatalyst. In addition, various reference materials were prepared and photocatalytically tested in order to shed light on the mechanism of this photocatalytic enhancement. These results provided insight regarding the functionality of the different structural components of the photocatalytic architecture in the photocatalytic NOx oxidative storage process.

The influence of each structural component in this catalytic architecture was studied. Control experiments were conducted with the dispersant water and the capping agent thioglycolic acid. The results revealed that NO conversion and selectivity can be enhanced by the adsorbed water on titania surface. By adding thioglycolic acid on titania, the NO conversion is suppressed but the selectivity of the system increased. Finally, by replacing titania with a photocatalytically inactive material alumina, it was shown that only in the presence of CdTe quantum dots, there can be NO oxidation/conversion.

In overall, utilizing CdTe quantum dots are advantageous for exploiting more of the solar irradiation; however, they suffer from low stability and short catalytic life time.

Keywords: Air purification, Photocatalytic NO_x abatement, Quantum dots, Titanium dioxide

ÖZET

Kuantum Noktalar ile İyileştirilmiş Titanya Sistemleri ile Fotokatalitik Yükseltgemeli NO_x Depolama

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Mart 2018

Endüstriyel yanma sistemlerindeki artış, volkanik patlamalar, tarım faaliyetleri, durağan ya da mobil fosil ve biyoyakıt tüketimi, oldukça toksik olan NO_x gazlarının oluşumunun temel nedenleri olarak bilinmektedir. Bu gazların ekosistem üzerinde doğrudan neden olduğu zararlarının yanı sıra, asit yağmurları ve troposferik ozon gibi ikincil hava kirliliği kaynaklarının oluşumuna da neden oldukları bilinmektedir. Bu gazların atmosferdeki yoğunluklarının azaltılması için termal katalitik sistemler ya da fiziksel/kimyasal adsorpsiyon sistemler halihazırda kullanılmaktadır. Bunların yanı sıra, çevreye dost, düşük maliyetli ve sürdürülebilir alternatif fotokatalitik sistemler tasarlanarak, halihazırda kolaylıkla ulaşılabilen güneş enerjisinden faydalanılabilir.

Bahsedilen fotokatalitik sistemlerde, en yaygın olarak kullanılan malzeme, titanya olup, 3.0-3.2 eV aralığında oldukça geniş bir enerji bant aralığına sahiptir. Bu geniş bant aralığı nedeniyle, titanya çoğunlukla UV ışıması altında aktifleştirilebilir. Güneş enerjisinin dağılımı göz önünde bulundurulduğunda, ultraviyole ışınları görünür ışığın sadece beşte birine karşılık gelmektedir. Titanyanın güneş enerjisinden daha fazla faydalanabilmesini sağlamak için, görünür dalga boylarını da soğurmasını sağlamak gerekmektedir. Titanyanın ametal elementlerle dopingi bu artışa yardımcı olsa da, son zamanlarda nano boyutlu yarı iletken malzemelerin (kuantum noktacıklar) kullanımı da oldukça önem kazanmıştır. Kuantum noktacıkların soğurduğu dalga boyları, parçacıkların boyutlarıyla oynanarak değiştirilebilmektedir. Ayrıca, kuantum noktacıklar soğurdukları fotonlar sayesinde elektron-boşluk ayrımı yaparak, fotokatalitik süreçte rol oynayabilirler.

Bu çalışmada, direkt-bant aralığına sahip CdTe kuantum noktacıkları kullanılmıştır. CdTe kuantum noktacıklarının iletim bandı titanyanınkinden yukarıda olduğu için, CdTe iletim bandında oluşturulan elektronlar, titanyanın iletim bandına rahatlıkla akabilir.

Böylelikle, oluşturulan elektron-boşluk çiftinin ayrımının daha uzun süreli ve efektif olması sağlanabilmektedir. Kullanılan kuantum noktacıklarının bant aralığı görünür ışıkla uyumlu olduğu için, titanyanın görünür ışık altındaki fotokatalitik aktivitesi de artırılabilir.

QD ile işlevselleştirilen titanya sistemleri, üzerinde yürütülen fotokatalitik aktivite çalışmaları, oldukça yüksek NO_x depolama özellikleri göstermiş olup, P25 referans titanya katalizörüne göre, NO gazının katalitik dönüşümünü de artırmıştır. Ayrıca, sunulan fotokatalizör sisteminin mekanizmasını aydınlatabilmek için farklı referans malzemeler de hazırlanmıştır. Ölçümlerde elde edilen bulgular, ilgi çekici fotokatalitik aktivite ve seçicilik sonuçları göstermiştir.

Katalitik mimarideki her yapı taşının etkisi incelenmiştir. Kuantum noktaların içinde bulunduğu suyun ve etrafını saran ligand merkapto asetik asidin etkileri incelendiğinde, titanya yüzeyine tutundurulan suyun hem fotokatalitik aktiviteyi hem de seçiciliği artırdığı görülmüştür. Merkapto asetik asit ise titanya aktivitesinde düşüşe neden olurken, seçiciliği artırmıştır. Son kontrol deneyinde, bu sistemde fotokatalitik aktivite göstermeyen alümina, titanya yerine kullanılmıştır. Bu deneyler sonucunda, CdTe kuantum noktalarının bulunmadığı hiçbir sistemde katalitik ya da katalitik olmayan bir aktivite gözlemlenememiştir.

Bu çalışma, CdTe kuantum noktalarının, titanyanın fotokatalitik aktivitesini ve seçiciliğini artırdığını göstermiştir. Fakat, oluşturulan sistemin katalitik ömrü kısadır.

Anahtar Kelimeler: Hava temizliği, Fotokatalitik NO_x bozunması, Kuantum noktacıklar, Titanya

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1. Introduction

1.1. AIR POLLUTION

Air pollution is one of the major problems brought by the age of modernization and is accounted for the increasing death rates globally. In 2012 World Health Organization (WHO) reported indoor and outdoor air pollution to be responsible for one eights of a total 7 million human mortality [1]. Also, air pollution related annual health cost of US is estimated to be £23 billion [2]. In Figure 1, the rates of estimated air pollution-originated fatal diseases were demonstrated.

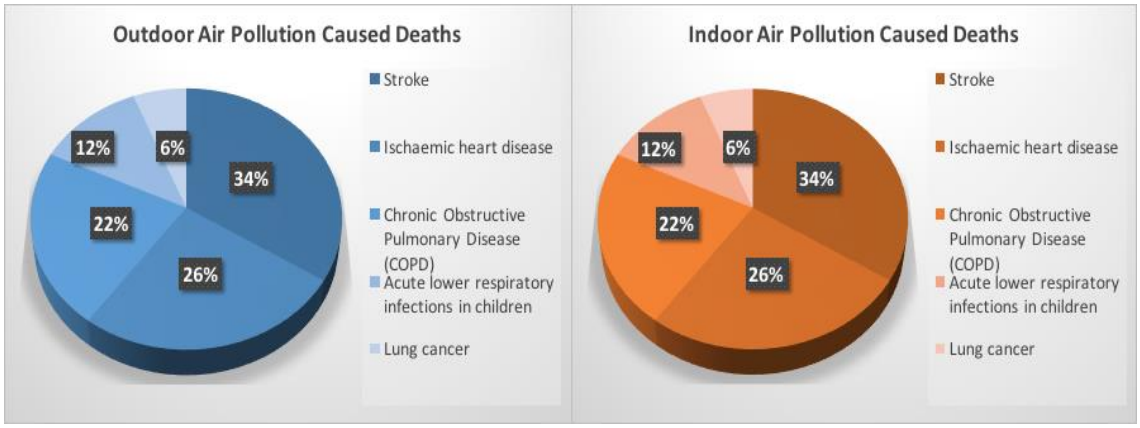


Figure 1. Estimated outdoor (left) and indoor (right) air pollution-caused deaths breakdown by disease adapted from Reference [1].

Air pollutants can be classified into two types based on their formations. Primary pollutants are released directly into the air whereas secondary pollutants are formed on consequent reactions of the primary pollutants with air. In Figure 2, primary and secondary pollutants are demonstrated together. Although natural causes such as agricultural activities, volcanic eruptions, forest fires, soil erosion may lead to air pollution; the main source of air pollution has anthropogenic origins such as vehicle exhaust gases, fuel combustions and so on [2].

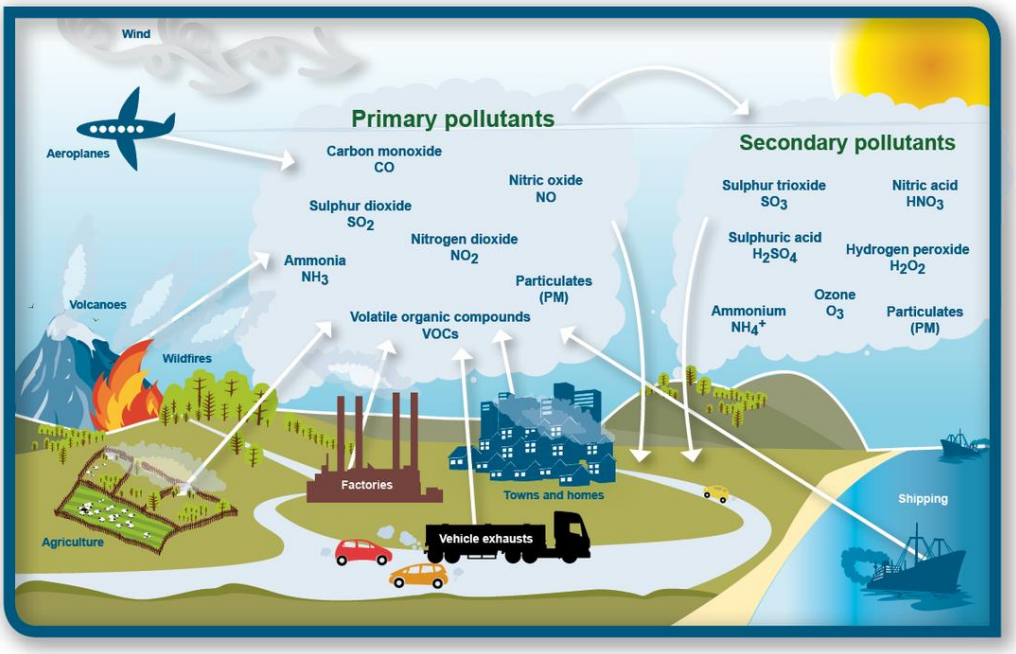


Figure 2. Primary and secondary air pollutants (Copyright notice © Scotland's Environment, 2018 [4]).

United States Environmental Protection Agency (EPA) has set ambient air quality standards for six common air pollutants (known as 'criteria air pollutants') which incorporate sulfur dioxide, carbon monoxide, lead, ground level ozone, particulate matter and nitrogen dioxide [3]. The standard levels for all criteria air pollutants are tabulated as Table 1. The major cause of the formation of criteria air pollutants is the fossil fuel combustions by power plants, vehicles and industry.

Sulfur dioxide has a distinct odor and its short term exposure can have a negative effect on the respiratory system for humans. It can also cause acid rains which is highly dangerous for the ecosystem [3]. As carbon monoxide has no color or smell, it is known as the 'silent killer' [5]. A carbon monoxide molecule has 210 times greater affinity to hemoglobin compared to an oxygen molecule, therefore hemoglobin begins to transfer carbon monoxide rather than oxygen in the blood stream [6]. Long exposures can be mortal. Lead can also decrease the capacity of the blood to carry oxygen. It is also accumulated in the bones and harms nervous system, kidneys and cardiovascular system [3]. Ozone is essential for the environment and all the living; however, its location is highly critical. As demonstrated in Figure 3, there is a naturally formed ozone layer in the stratosphere which plays a big role in preventing the harmful UV rays from reaching the surface of the earth. The layer is about 3-5 mm thick and it has about 0.2 to 0.4 ppm concentration of ozone [7]. Nevertheless, when the ozone is artificially formed (via the reactions of toxic pollutants in the air) in the troposphere, it is

called as the ground level ozone and is very harmful. It can have an adverse effect on the respiratory system and can reduce the intake of certain nutrients [3].

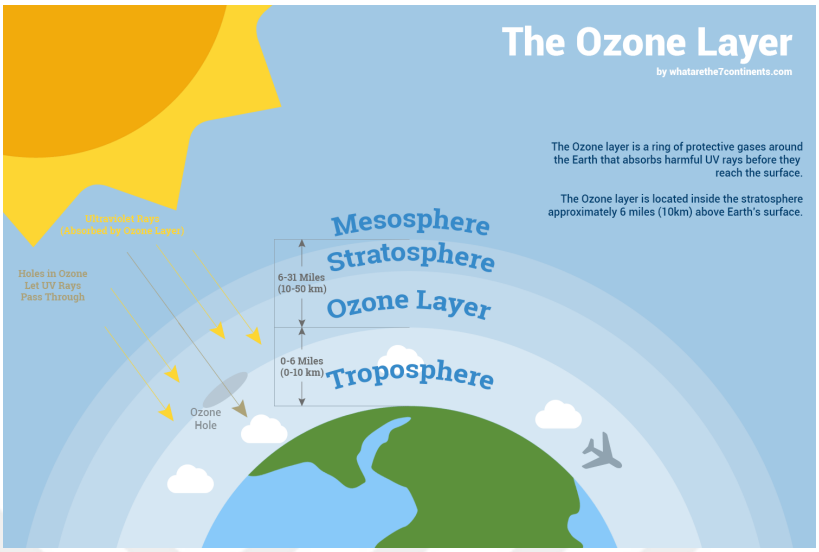


Figure 3. The ozone layer(Copyright notice © 7 Continents, 2018 [8]).

Particulate matter consists of different solid particles in liquid droplets in the air. PM_{10} particles are 10 µm diameter whereas $PM_{2.5}$ has 2.5 µm, and they both can be inhaled and transported to the lungs. Some can even reach the bloodstream causing adverse effects on the body [3].

Table 1. Current National Ambient Air Quality Standards for criteria air pollutants [3]

Pollutant		**Primary/ Secondary**	**Averaging Time**	**Level**
Carbon Monoxide (CO)		Primary	8 hours	9 ppm
			1 hour	35 ppm
Lead (Pb)		Primary& Secondary	Rolling 3 month average	0.15 µg/m^3
Nitrogen Dioxide (NO_2)		Primary	1 hour	100 ppb
		Secondary	1 year	53 ppb
Ozone (O_3)		Primary& Secondary	8 hours	0.070 ppm
Particulate Matter (PM)	**$PM_{2.5}$**	Primary	1 year	12.0 µg/m^3
		Secondary	1 year	15.0 µg/m^3
		Primary& Secondary	24 hours	35.0 µg/m^3
	PM_{10}	Primary& Secondary	24 hours	150 µg/m^3
Sulfur Dioxide (SO_2)		Primary	1 hour	75 ppb
		Secondary	3 hours	0.5 ppm

The effect of nitrogen dioxide is going to be mentioned in the following part, as this study will focus on nitrogen dioxide (NO_2) and nitric oxide (NO) based air pollution.

1.1.1. NITROGEN OXIDES (NO_x) POLLUTION

NO_x is a term for nitrogen oxides such as NO, N_2O and NO_2. During the combustion of nitrogen containing species, especially at higher temperatures, nitrogen gets oxidized in air and forms $NO_{(g)}$. With further oxidation of NO, NO_2 is formed [9]. Nitrogen oxides (NO_x) are toxic and also highly reactive. Hence they can cause the formation of secondary air pollutants via reacting with air. Formation of acid rain (nitric acid) can be an example of such possibilities. The reactions that take place are written in Equations (1-4) [10-12].

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \quad (1)$$

$$4NO + 3O_2 + 2H_2O \rightarrow 4HNO_3 \quad (2)$$

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3 \quad (3)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad (4)$$

Another secondary air pollutant which can be generated by NO_x species reacting in the atmosphere can be the ground level ozone. The reactions leading to the ground level ozone formation are given in Equations (5-8) [13].

$$VOC + OH\bullet \rightarrow HO_2\bullet + \text{other products} \quad (5)$$

$$HO_2\bullet + NO \rightarrow NO_2 + OH\bullet \quad (6)$$

$$NO_2 + hv \rightarrow NO + O\bullet \quad (7)$$

$$O\bullet + O_2 + M \rightarrow O_3 + M \quad (8)$$

Being highly toxic and reactive enough to trigger the formation of secondary pollutants, the abatement of these gases should be taken seriously.

1.1.2. NO_x REMOVAL TECHNIQUES

1.1.2.1.SELECTIVE CATALYTIC REDUCTION (SCR)

Selective Catalytic Reduction is one of the most common types of tailpipe NO_x removal techniques. This technique requires ammonia, carbon monoxide, hydrogen or hydrocarbons for the reduction of nitrogen oxides to nitrogen on the catalyst surface. Ammonia is first chemisorbed on the catalyst surface and then reduces the NO_x species. The SCR reactions using ammonia in the presence and absence of oxygen are as given in Equations (9-12) [14].

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (9)$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (10)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (11)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (12)$$

For thermal catalytic $DeNO_x$ applications, SCR technology requires a temperature range of 573 – 673 K depending on the utilized catalyst [15].

1.1.2.2.SELECTIVE NON CATALYTIC REDUCTION (SNCR)

Selective Non Catalytic Reduction (SNCR) technology resembles SCR techniques; however, it does not require a catalyst. Cutting off the cost of catalysts, SNCR seems to be a more attractive technique economically. Similar to SCR, the reactions are also carried out introducing active compounds such as ammonia and urea. Similar reactions (Eqns. 9-12) also take place for SNCR $DeNO_x$ techniques; however, this time the processes require much higher temperatures (1073 – 1273 K for ammonia). When urea is used as the active compound, the temperature range increases even further and the following reaction takes place [16].

$$H_2NCONH_2 + 2NO + \tfrac{1}{2} O_2 \rightarrow 2N_2 + CO_2 + H_2O \quad (13)$$

The high temperature dependence of these two techniques (SCR and SNCR) does not allow them to be environmentally friendly, sustainable and cost-efficient. Also further increase of the temperature (>1273 K) may cause ammonia to convert into NO_x as well [17].

Hence, there is a great demand for a sustainable, cost-efficient and more environmentally friendly $DeNO_x$ technique.

1.1.2.3.PHOTOCATALYTIC NO OXIDATION & STORAGE (PHONOS)

Photocatalytic oxidative NO_x storage is another $DeNO_x$ technique that is environmentally friendly and sustainable; and can exploit readily abundant solar radiation under ambient conditions.

Photocatalysis commences with the activation of a semiconductor via solar or artificial light sources. When the absorbed photon has sufficient energy to promote electrons from the valence band (VB) to conduction band (CB) of the semiconductor; electron-hole pairs are generated. As demonstrated in Figure 4, the generated electrons can reduce the oxygen in the air to form superoxide whereas the generated holes can lead the formation of hydroxyl radicals (blue dashed arrows) [19]. Consequent reactions of these generated radicals and ions can lead to oxidation of the air pollutants such as nitric oxide. Further reactions can be listed as in Equations (14-19) [18].

$$NO + HO^{\bullet}_{ads} \rightarrow HNO_2 \quad (14)$$

$$HNO_2 + HO^{\bullet}_{ads} \rightarrow NO_2 + H_2O \quad (15)$$

$$NO_2 + HO^{\bullet}_{ads} \rightarrow HNO_3 \quad (16)$$

$$NO + O_2^-{}_{ads} \rightarrow NO_3^- \quad (17)$$

$$2NO + O_2^- + 3e^- \rightarrow 2NO_2 \quad (18)$$

$$3NO_2 + 2OH^- \rightarrow 2NO_3^- + NO + H_2O \quad (19)$$

The photo-generated electrons and holes may also end up recombining (red dashed arrows) in the recombination centers (X) of semiconductors. This will result in a decrease in the photocatalytic activity of the semiconductor.

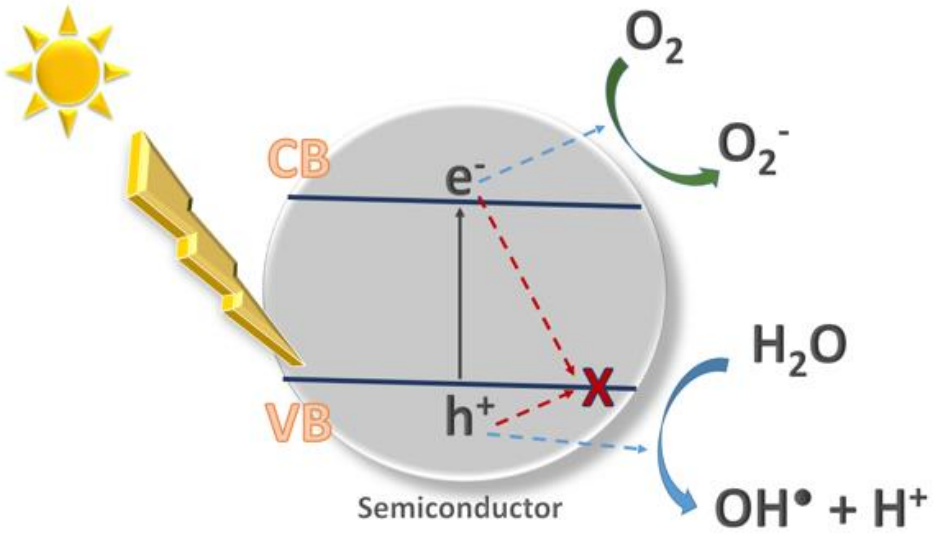


Figure 4. Main scheme of semiconductor photocatalysis.

Photocatalysis is a photoelectrochemical process and therefore requires an electrolyte support for the redox reaction promoted by the photo-generated electron-hole pairs. For $DeNO_x$ purposed photocatalysis, the electrolyte is the surface adsorbed water molecules [19]. Hence it is crucial to employ surface adsorbed water for the photocatalytic processes.

1.2. TITANIUM DIOXIDE

For the photocatalytic decomposition of pollutants, the most widely used semiconductor is titanium dioxide [20,21]. It is chemically and thermally stable, superhydrophilic, nontoxic, strong oxidizing and cost-efficient [20-23].

1.1.1. APPLICATIONS OF TITANIUM DIOXIDE

Titanium dioxide is the most widely used titanium product and it is processed using about 95% of overall titanium ore [24]. It does not efficiently absorb the incident light in the visible region of the solar spectrum and has a high refractive index (2.49-2.54 for anatase and 2.79-2.903 for rutile phases) [24]. According to Figure 5. the most commonly end-use of titanium dioxide in 2005 corresponds to coatings which include coatings of wood products, metal furniture, coil, appliances and so on [24]. The other uses may incorporate printing inks, pharmaceutical and cosmetic purposed pigments, textile pigments, food coloring,

photocatalytic water splitting, photocatalytic air and water purification and dye-sensitized solar cells [24,25].

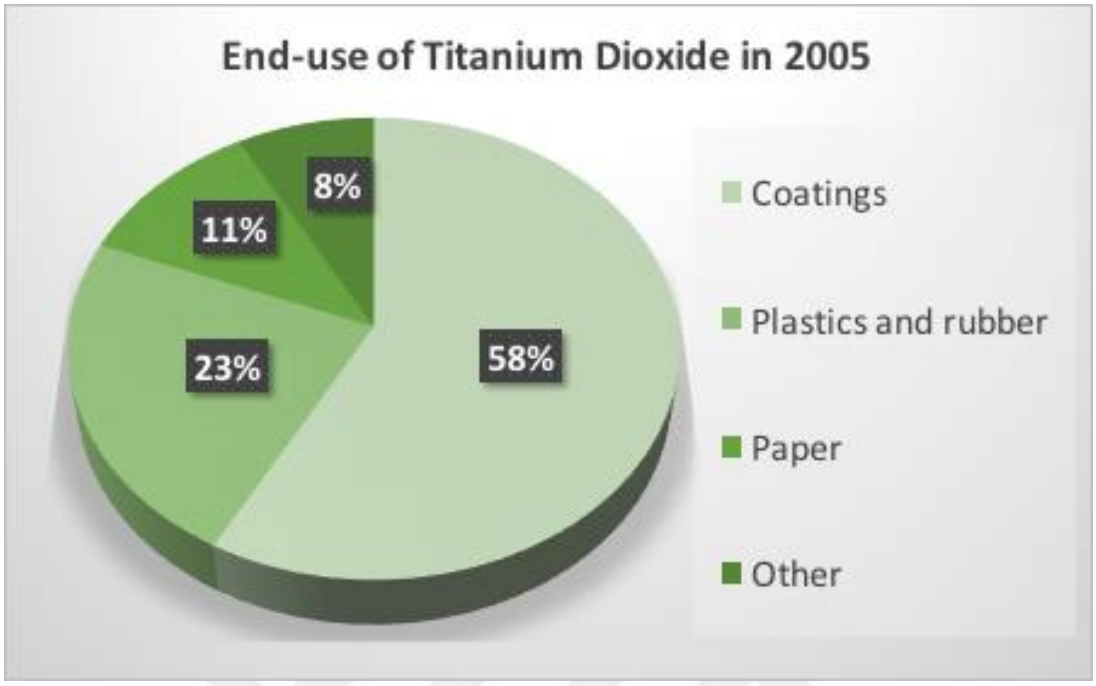


Figure 5. End-use of titanium dioxide in 2005, data adapted from Reference [24].

Titanium dioxide is also thermally stable, nontoxic and resistant to ultraviolet light degradation. Moreover, with the utilization of ultraviolet light, titanium dioxide can oxidize the organic materials that may cause fouling. When exposed to UV light, it becomes very hydrophilic and can be used for antifogging devices [26,27].

1.2.2. PHYSICAL PROPERTIES OF TITANIUM DIOXIDE

The photocatalytic activity of titanium dioxide has a great dependence on its physical properties such as its phase structure, specific surface area, and crystallite size [28].

In nature, titania is reported to exist in three different polymorphs which are rutile (tetragonal), anatase (tetragonal) and brookite (orthorombic) [29,30]. The bulk structures of these three polymorphs are as demonstrated in Figure 6.

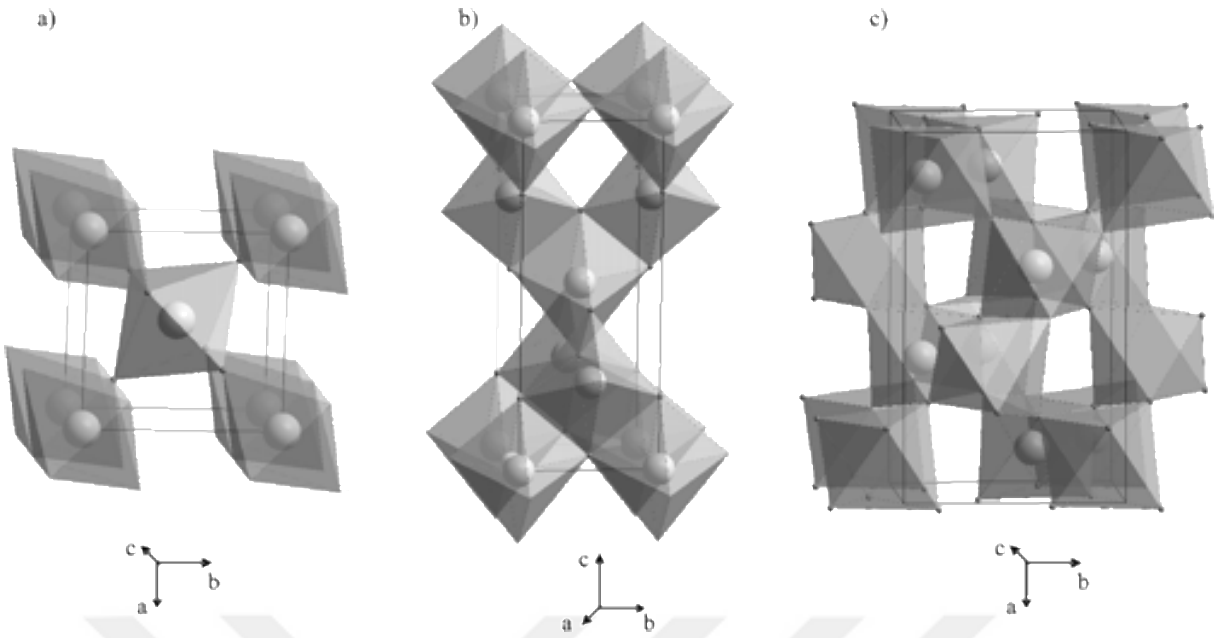


Figure 6. Bulk structures of a) rutile, b) anatase, c) brookite phases of titania. Reprinted from Ref. 23 Copyright 2018 with permission from Elsevier [23].

The anatase and brookite phases of titanium dioxide are metastable while the most stable form of titanium dioxide is the rutile phase in acidic medium. In a basic medium, anatase is more stable than rutile and brookite phases [31]. Anatase and brookite forms can be transformed into rutile when heated to higher temperatures. The product of a sol gel titanium dioxide synthesis in an acidic medium results mostly in the formation of anatase phase and brookite form can be observed as a side product. That is why it is a challenge to produce pure brookite titanium dioxide with the basic synthesis protocols and there is a numerous on-going research for its synthesis [30].

Gibbs thermodynamic principle states when a fluid is in contact with its medium, equilibrium can be achieved by minimizing the free energy of the surfaces in contact. For a crystal, the orientation of each element in such a surface is important for their contribution to the total free energy. For a constant volume, the minimum total surface energy determines the equilibrium shapes of crystals [32,33]. Wulff construction for crystal growth utilizes this theory as well [32]. The Wulff structures of anatase and rutile phases of titanium dioxide are given in Figures 7 and 8.

For the anatase phase of titanium dioxide, the {101} facet comprises the majority (94%) of the structure; however, the most reactive facet is the {001} facet (6%) [25,31, 34]. The {101} facet has the lowest surface energy of 0.44 J/m^2, whereas the {001} and {010} facets have higher surface energies which are 0.90 J/m^2 and 0.53 J/m^2 respectively [34]. Although these

numbers would suggest the dominancy of {010} facet to {001}, {010} facets do not appear in the predicted Wulff geometry in vacuum and can be observed as a 'belt around the center' if the surface is hydrogen poor (especially basic conditions) [25,31,35].

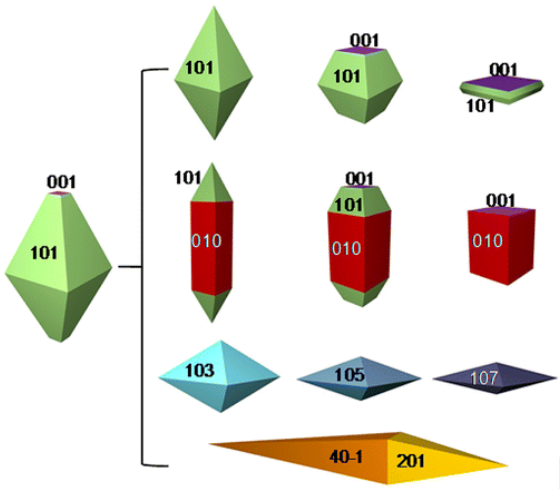


Figure 7. Equilibrium crystal shape of anatase TiO_2 through the Wulff construction and the evolved other shapes. Reprinted from Ref. 25 Copyright 2018 with permission from ACS [25].

For the rutile phase of titanium dioxide, with the lowest surface energy of 15.6 meV/au^2, {110} facets dominate the surface. With the highest surface energy of 28.9 meV/au^2, {001} facets exist but they are nearly invisible. {100} and {011} facets are also present in this polymorph with the surface energies of 19.6 and 24.4 meV/au^2 respectively [25].

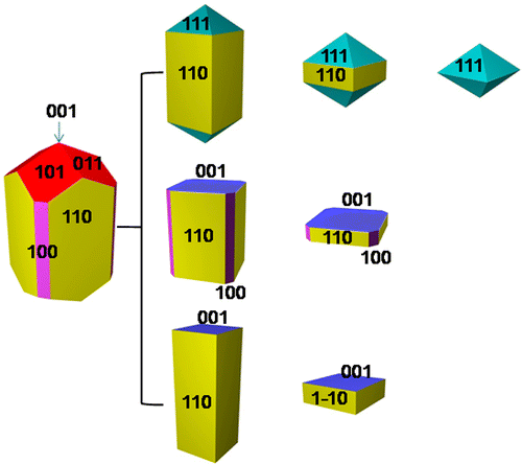


Figure 8. Equilibrium crystal shape of rutile TiO_2 through the Wulff construction and the evolved other shapes. Reprinted from Ref. 25 Copyright 2018 with permission from ACS [25].

Titanium dioxide has a band gap energy of 3.2 eV for anatase and 3.0 eV for rutile phases [39]. This wide band gap of titanium dioxide prevents efficient utility of the solar spectrum outside the ultraviolet region.

As indicated in Figure 9, on the surface of the earth, the visible region of the solar spectrum corresponds to about 45% of the solar energy whereas the ultraviolet region builds up only 5 % of it. Therefore, a great part of the solar spectrum cannot be utilized efficiently by titanium dioxide.

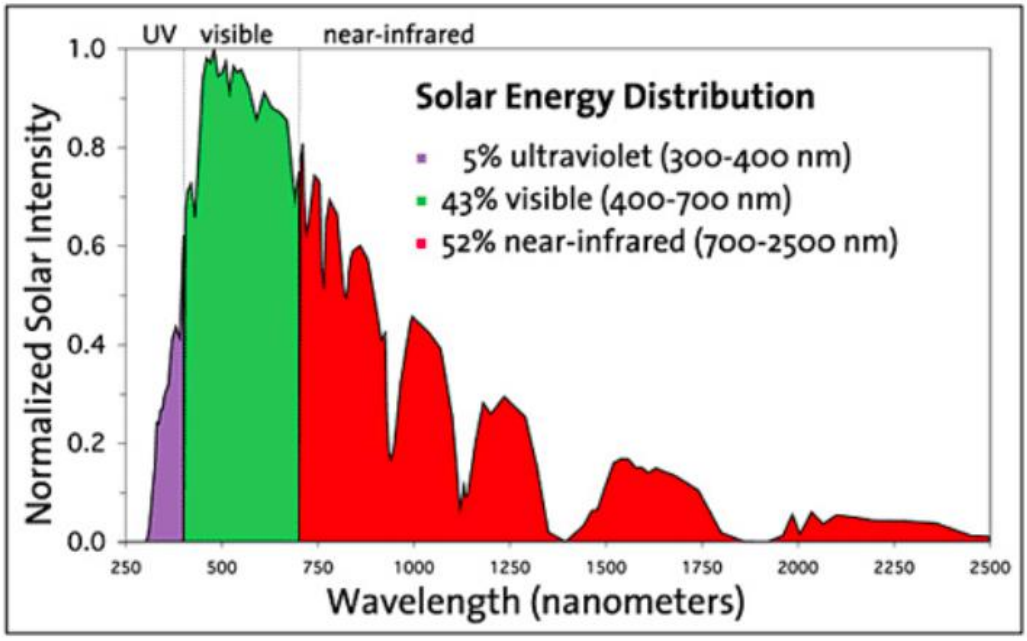


Figure 9. Solar energy distribution. (Copyright notice © Green Builder, 2018 [36])

1.2.3. PHOTOCATALYSIS WITH TITANIUM DIOXIDE

A general information of photocatalytic NO_x abatement was provided in previous parts. In this part, the utilization of titanium dioxide for photocatalytic NO_x abatement will be discussed with predicted mechanisms. The mechanism of photo-abatement of NO_x on titania surface can be issued under 3 main stages; adsorption of gas reactants to the surface of titanium dioxide, photogeneration of electron-hole pairs and oxidation of NO and water reduction [19].

In a photocatalytic NO_x abatement system, O_2 and H_2O are crucial elements. As photocatalysis is fundamentally a photoelectrochemical process, titanium dioxide is used as the semiconductor and the water in humidity is used as the electrolyte [19].

$$TiO_2 + H_2O_{(g)} \rightarrow H_2O_{(ads)} \quad (20)$$

$$TiO_2 + O_{2(g)} \rightarrow O_{2(ads)} \quad (21)$$

$$TiO_2 + NO_{(g)} \rightarrow NO_{(ads)} \quad (22)$$

When water vapor is adsorbed on the photocatalyst surface, the photo-generated holes can generate $OH^{\bullet}$ radicals; whereas the electrons can react with oxygen to generate superoxide anion O_2^- [19].

$$TiO_2 + hv \rightarrow e^-_{CB} + h^+_{VB} \quad (23)$$

$$TiO_2\ (e^-_{CB} + h^+_{VB}) \rightarrow TiO_2 \quad (24)$$

$$h^+ + H_2O_{(ads)} \rightarrow HO^{\bullet} + H^+ \quad (25)$$

$$e^- + O_{2(ads)} \rightarrow O_2^-{}_{(ads)} \quad (26)$$

The efficiency of the photocatalyst depends strongly on the electron-hole recombination (See Equation 24) rate of the semiconductor. If the semiconductor has a low recombination rate, the photo-generated electron-hole pairs can react easier in abovementioned processes. Using the generated $HO^{\bullet}$ radicals and O_2^- anions, NO can be oxidized.

$$NO_{(ads)} + HO^{\bullet} \rightarrow HNO_{2(ads)} \quad (27)$$

$$HNO_{2(ads)} + HO^{\bullet} \rightarrow NO_2 + H_2O \quad (28)$$

$$NO_{(ads)} + O_2^-{}_{(ads)} \rightarrow NO_3^- \quad (29)$$

$$NO_{2(ads)} + HO^{\bullet} \rightarrow NO_3^- + H^+ \quad (30)$$

For the oxidation steps of nitrogen oxides, the superoxide anions are proven to be less efficient when compared to hydroxyl radicals [37].

The photocatalytic reaction kinetics are described by Langmuir-Hinshelwood (L-H) model and considering a reaction of A + B → C + D, the following equations can be written [19].

$$r = k\theta_A\theta_B \quad (31)$$

$$\theta_A = \frac{K_A X_A}{1 + K_A X_A} \quad (32)$$

$$\theta_B = \frac{K_B X_B}{1 + K_B X_B} \quad (33)$$

K_A and K_B represent the adsorption equilibrium constants in the absence of a light source; X_A and X_B represent the partial pressure in the gas phase and k is the reaction rate constant. According to the Arrhenius and van't Hoff's laws k, K_A and K_B are dependent on temperature [19].

$$k = k_0 \exp(-\frac{E_a}{RT}) \quad (34)$$

$$K_i = K_{i_0} \exp(-\frac{\Delta H_i}{RT}) \quad (35)$$

In Arrhenius equation (34), E_a is the activation energy, T is the absolute temperature and R is the universal gas constant. Using L-H model, one can the the rate equation as follows [19].

$$-r_{NO} = \frac{k'_A C_{NO} C_{H2O} - k'_B C_{NO2}}{(1 + K'_{H2O} C_{H2O} + K'_{NO} C_{NO} - K'_{NO2} C_{NO2})^2} \quad (36)$$

In Equation (36), reaction rate of NO ($-r_{NO}$) is given where k'_A and k'_B are the reaction rate constants; K'_{H2O}, K'_{NO} and K'_{NO2} are the adsorption equilibrium constants of H_2O, NO and NO_2 respectively; C_{H2O}, C_{NO} and C_{NO2} are gas phase concentrations of H_2O, NO and NO_2 respectively [19].

The product of this process are HNO_3 and nitrates; however, HNO_2 and NO_2 can also be generated as side products. If the process yields NO_3^- and HNO_3 on the surface of the catalyst, it will begin to saturate the surface and cover the active sites. Therefore, a regeneration of the photocatalyst should be done by cleaning the surface with water which can dissolve the nitrates on the surface. For outdoor coating usages, this can be done by rain.

There are many factors affecting the efficiency of a photocatalyst. As mentioned earlier, one is the recombination rate of the semiconductor. A drawback of titanium dioxide is that it has a high recombination rate, hence it cannot efficiently employ the photo-generated electron-hole pairs in further steps [38]. When the photo-generated electron-hole pairs recombine,

they will release their extra energy as photons as long as they obey the transition rule of momentum conversation (See Equations 37-38) [39].

$$E_g = \hbar\omega_{photon} \tag{37}$$

$$\hbar k_e{}' - \hbar k_e = \pm\hbar q_{photon} \tag{38}$$

In above equations, $\hbar$ represents the reduced Planck constant, k_e' and k_e represent the electron wave factors at the valence and conduction band respectively, q_{photon} represent the wave vector of the assisted phonon and ω_{photon} represent the angular frequency of the emissive photon [39]. As rutile and brookite phases have direct band gaps, an electron emits a photon only for the recombination and $k_e' = k_e$. However, as the anatase phase is an indirect band gap semiconductor, $k_e' \neq k_e$. Hence, the excited electrons cannot directly recombine with the holes, which would increase the lifetime of the photo-generated excitons and decrease the recombination rate [39]. As a result, it can be claimed that anatase is a better photocatalyst compared to rutile.

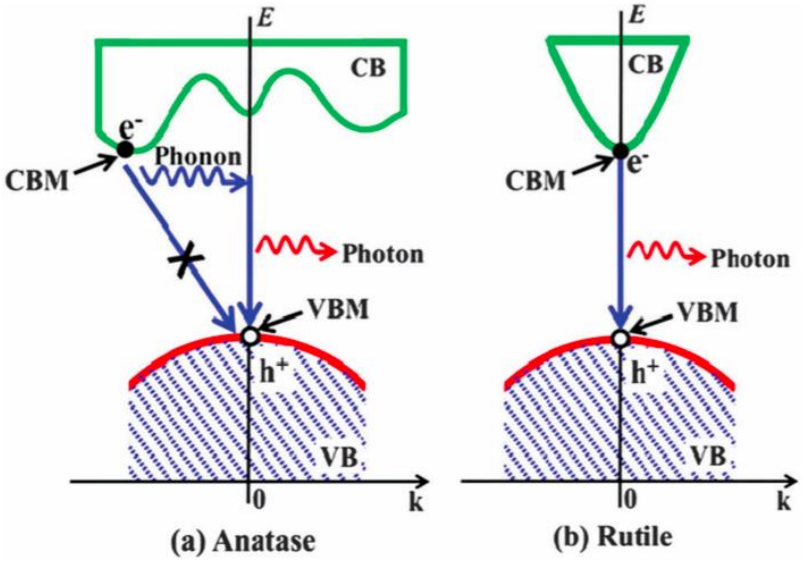


Figure 10. Recombination processes of photo-generated electrons and holes for a) indirect gap anatase and b) direct gap rutile. Reprinted from Ref. 39 Copyright 2018 with permission from Royal Society of Chemistry [39].

Second factor affecting the efficiency of the system is the inlet concentrations of gases. As demonstrated in Figure 11, as the inlet concentration of NO increases, saturation is achieved faster and photocatalytic degradation of NO decreases [40, 44].

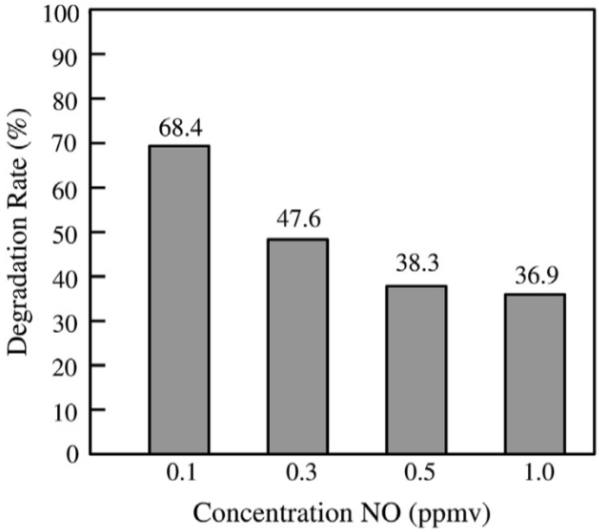


Figure 11. Effect of NO inlet concentration on photocatalytic NO_x abatement rate. Reprinted from Ref. 44 Copyright 2018 with permission from Elsevier [44].

The concentration of the water vapor (relative humidity) is also an important factor. Since water is crucial for photocatalysis, enhanced photocatalytic efficiency would be expected with increasing % relative humidity. In literature, it is experimentally shown that as the humidity rises, the % NO conversion increases. However, after 50% of relative humidity, system reaches a steady state as shown in Figure 12 [41].

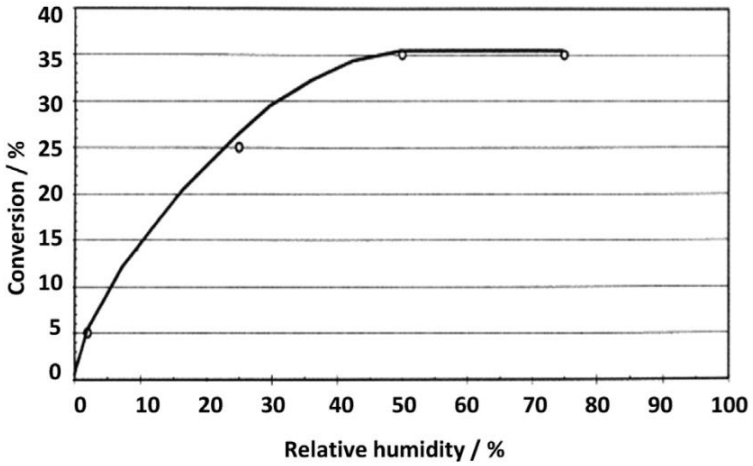


Figure 12. Effect of % relative humidity on %NO conversion (inlet NO concentration:40 ppm). Reprinted from Ref. 41 Copyright 2018 with permission from Elsevier [41].

Flow rate/residence time of the polluted air is also as important as the concentration of it. The higher the flow rate of the polluted air, the smaller the residence time will be, therefore it will have shorter contact with the photocatalyst.[10] In Figure 13, it can be observed that as the flow

rate increases, the %NO_x conversion decreases due to less contact of photocatalyst with polluted air [42].

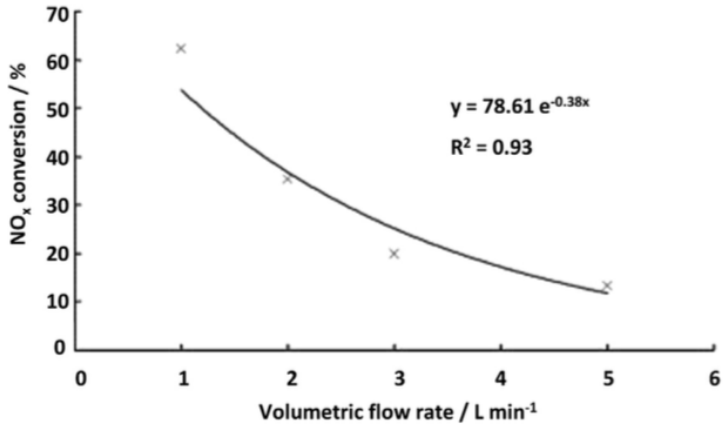


Figure 13. Effect of volumetric flow rate of polluted air on %NO_x conversion. Reprinted from Ref. 42 Copyright 2018 with permission from Elsevier [42].

Light intensity can also influence the photocatalytic activity of a photocatalyst. As indicated in Figure 14, Yu and Brouwers demonstrated the relation between light intensity and % NO_x conversion. By using two different inlet values (0.5 ppm and 1.0 ppm), they showed the effect of light intensity, varying from 1.0 to 13.0 W/m^2, on % NO_x conversion. It can be clearly observed that by increasing the light intensity, % NO_x conversion can be logarithmically increased [42].

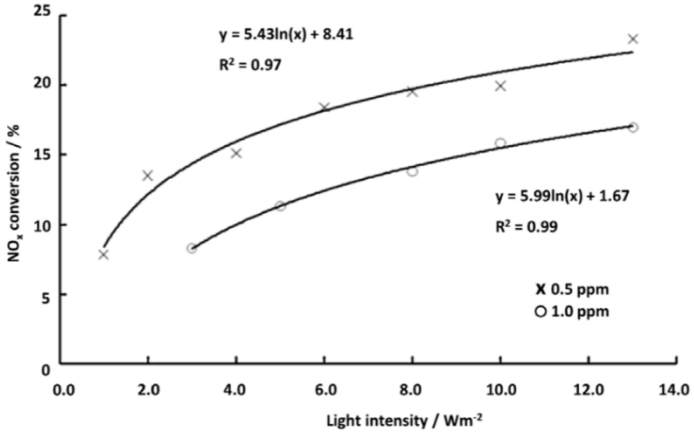


Figure 14. Effect of light intensity on % NO_x conversion. Reprinted from Ref. 42 Copyright 2018 with permission from Elsevier [42].

Amount of photocatalyst per irradiated area is also an important factor. Figure 15 demonstrates the effect of the mass of a catalyst on the pollutant conversion rate. By increasing the mass, one can increase the active sites of a photocatalyst that can utilize the

light for the degradation of the pollutants. However, keeping the irradiated catalyst surface constant, after the maximum thickness of the photocatalyst is reached, light cannot reach lower layers. Hence there is an optimal mass value (m_{opt}) [43,44].

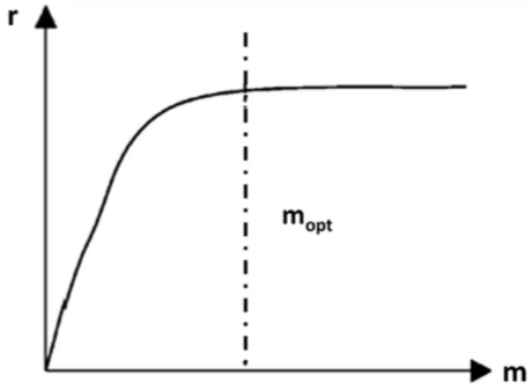


Figure 15. Effect of the mass of a catalyst on pollutant conversion rate. Reprinted from Ref. 45 Copyright 2018 with permission from Elsevier [45].

There have been many successful attempts to enhance the photocatalytic efficiency of titanium dioxide with nonmetal doping [40,46], metal doping [41], surface modifications with polymers [47] etc. In this study, an additional semiconductor with a more negative conduction band level than titanium dioxide was introduced to the catalyst composition so that the photo-generated electron from the quantum dot can be injected to the conduction band of titania whereas the photo-generated hole in the valence band of titania can be injected to the valence band of the quantum dot [38]. Also if the quantum dot has a photon absorption in the visible region of the solar spectrum, it would be possible to harvest more visible light which cannot be sufficiently achieved by titanium dioxide. Hence an enhancement of the photocatalytic efficiency is expected.

1.3. QUANTUM DOTS (QDs)

Quantum dots are semiconductor fragments that are only few nanometers in size. They keep their bulk bonding geometry; however, the optical and electronic properties can be altered by tuning their sizes [48].

QDs were first discovered by Alexei Ekimov in 1981 when he was working at the Vavilov State Optical Institute on semiconductor doped glasses. Working with CdS, CdSe, CuCl and CuBr; he noticed that there were nano-sized crystals in the glass matrix which can absorb light at much lower wavelengths than expected. He collaborated with the theoretician Alexander Efros from Ioffe Institute to demonstrate that the optical properties were

dominated by their size [49,50]. In 1985, Louis E. Brus from Bell Labs could successfully conduct the colloidal synthesis of CdS quantum dots. The synthesized colloids exhibited a blue-shift compared with bulk CdS, which is suggested by the quantum confinement effect as well [50]. However, the term of 'quantum dots' was first used in a published paper of Mark Reed in 1988 [51].

Since then, there has been a great number of research on the synthesis, characterization and applications of the QDs. They are most commonly used as light emitting devices (LED) and lasers [52]. They are recently applied to computers to enhance them in terms of speed and increased storage [53]. With the development of quantum bits (qubits), quantum computation field gained popularity. QDs are also widely utilized for bio-imaging and bio-labeling purposes [54]. Some of the major challenges for bio applications are the limited aqueous solubility of the quantum dots and immune response limitations. Both for in vivo and in vitro experiments, aqueous solubility is an important criterion. Since many quantum dots are prepared in organic dispersants and are not dispersable in water, there is a limitation [55]. Recently, the focus has shifted to the synthesis of aqueous soluble quantum dots. In this study, TGA-capped CdTe QDs are employed which are also an example of water soluble QDs.

In order for size to play a role in tuning the electronic and optical properties, the size of the semiconductor should be below the bulk semiconductor Bohr radius which can be defined by Equation (39), where ε represents the dielectric constant of the material, m* represents the mass of the particle whereas m is the rest mass of the electron and finally a_o is the Bohr radius of the hydrogen atom [56].

$$a_B = \varepsilon \frac{m}{m*} a_o \tag{39}$$

When the semiconductor crystal size gets so small, the quantum confinement effect causes an increase in the excitonic transition energy and a blue shift in the absorption and luminescence band gap energies [56].

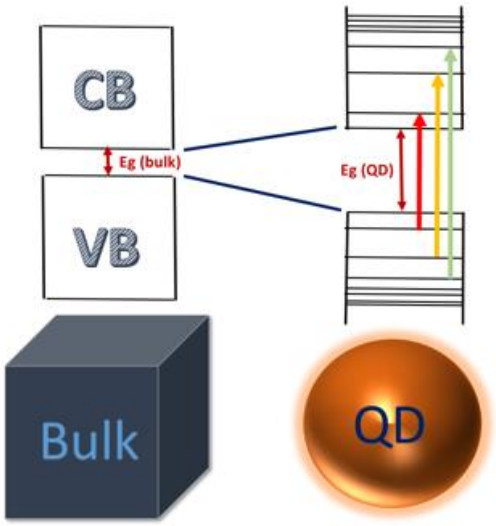


Figure 16. An illustration of the band gap difference for bulk and quantum dot.

Besides, as illustrated in Figure 16, quantum confinement creates discrete energy levels whereas for bulk materials, there are almost continuous valence and conduction bands [57]. Playing with only the size of these quantum dots, one can tune the electronic and optical properties (Figure 17).

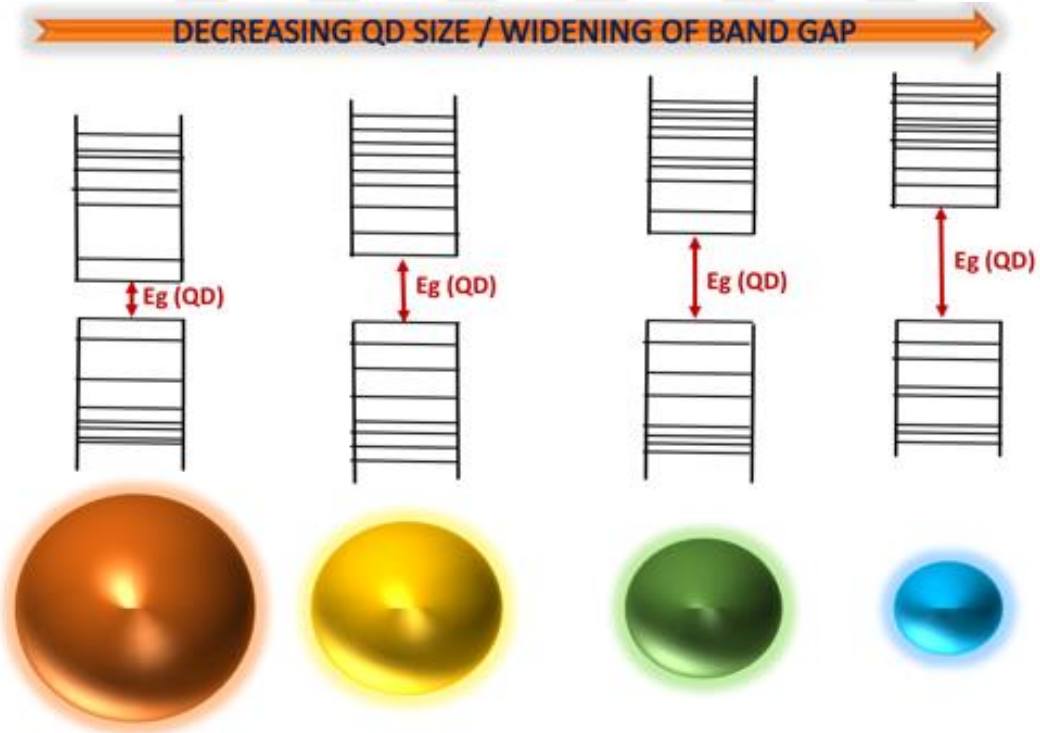


Figure 17. An illustration of the quantum dot size effect on the optical properties of the material (a red shift in emission wavelengths with increasing size).

In order to express the quantum confinement effect, time dependent Schrödinger Equation can be considered in the following form (40):

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{40}$$

where $\hbar$ is the reduced Planck constant, E is the Eigen energy value and Ψ is the wavefunction of the particle. 'Particle in a sphere' model, can be employed to model QD. In this model, while the interior of the sphere has a zero potential energy, outside the walls are assigned with an infinitely large potential energy. The potential energy is therefore given as in Equation (41).

$$V(x) = \begin{cases} 0, & 0 < x < r, \\ \infty, & otherwise,' \end{cases} \tag{41}$$

where x is the position within the sphere and r is the radius. It implies that the particle in the sphere has no force acting on it and it can freely move within that region. When it touches the wall, there is an infinite force on the particle to prevent it from escaping [58].
Hence, setting the potential to zero in Schrödinger equation, allowed electron and hole energy levels can be determined as in Equations (42-43).

$$E_{n_e l_e} = \frac{\hbar^2 \rho^2{}_{n_e l_e}}{2m_e R^2} \tag{42}$$

$$E_{n_h l_h} = \frac{\hbar^2 \rho^2{}_{n_h l_h}}{2m_h R^2} \tag{43}$$

In above equations, n_e, n_h, l_e, l_h represent the principal and orbital quantum numbers of the electrons and holes whilst $\rho_{n_h l_h}$ and $\rho_{n_e l_e}$ represent the sets of numbers specified by the roots of Bassel spherical functions which are ρ_{10}= 3.142, ρ_{11}= 4.493 and ρ_{12}= 5.763 for 1s, 1p and 1d quantum states [48]. The final equation for ΔE estimation can be written as follows.

$$\Delta E \approx E^e{}_{10} + E^h{}_{10} - E_g = \frac{\hbar^2\pi^2(m_e+m_h)}{2R^2 m_e m_h} - \frac{1.8e^2}{\varepsilon R} \tag{44}$$

where m_h and m_e are the effective masses of hole and electron, E_g corresponds to the band gap of a bulk semiconductor, R is the nanoparticle radius and ε represents the dielectric constant. The second term on the right hand side of the equation (44), incorporates the Coulomb interaction in the quantum dots [48].

1.4. SCOPE OF THE STUDY

In this study, aqueous suspension of thioglycolic acid capped CdTe quantum dots were employed in an attempt to enhance the photocatalytic activity of the titanium dioxide.

As titanium dioxide source, commercially available benchmark catalyst Degussa P25 (Evonik) was provided from Sigma Aldrich. Degussa P25 is a mixture of anatase and rutile phases of titanium dioxide with a tiny fraction of amorphous titania as well. In the literature, the composition of Degussa P25 is given as ~80% anatase, ~15% rutile and ~5% amorphous titania [59]. Due to the presence of two different titania polymorphs, Degussa P25 can create a synergetic effect between these crystalline phases [60]. It has been also claimed that photo-generated electrons of the rutile phase can migrate to the conduction band of the anatase phase, which would increase the lifetime of photo-generated excitons and decrease the recombination rate efficiently [61-63]. Nonetheless, most of the times, it was not possible to observe this synergetic effect when the separate phases were mixed together [64]. The reason could be the difficulty of getting the phases to contact. As demonstrated in Figure 18, Su et al. observed a distinct synergetic effect when the mixture has 40%-80% of the anatase phase and the optimum ratio of 60% anatase to 40% rutile mixture outperformed the pure anatase phase by ~50% [59].

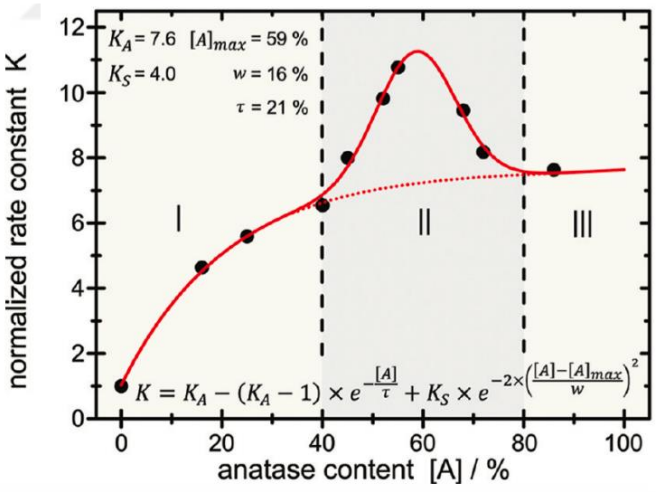


Figure 1. The effect of anatase content to rate constant K where a peak shaped offset (40%<[A]<80%) indicates the synergism between anatase and rutile phases. Reprinted from Ref. 59 Copyright 2018 with permission from American Chemical Society [59].

Hence, owing to the synergetic effect, Degussa P25 is preferred as the basis of our photocatalyst. However, due to the aforementioned drawbacks of titanium dioxide such as having a large band gap that makes it a UV active photocatalyst and high recombination rate; it needed to be enhanced. In this study, the enhancement was achieved by incorporating CdTe

QDs. The main purpose of the introduction of CdTe quantum dots to the titania system can be explained with Figure 19. By the addition of CdTe QDs, visible light can also be harvested by the QDs and due to the electron migration from the conduction band of CdTe to the conduction band of titania, charge separation can be achieved which would decrease the recombination rate.

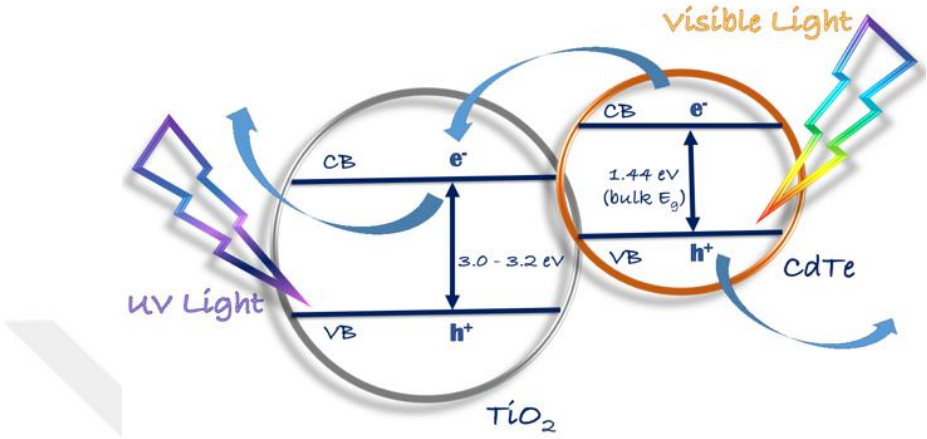


Figure 2. A possible scheme of electron and hole transport in CdTe/TiO_2 photocatalysis.

Thioglycolic acid-capped CdTe quantum dots (demonstrated in Figure 20) were preferred due to their narrow band gaps which can absorb both visible and UV light. Another important factor is that these quantum dots can be suspended in an aqueous medium rather than an organic dispersant. With the organic dispersants, especially with the highly volatile ones, it was not easy to sustain the stability of the suspension. As the dispersant can be evaporated, the quantum dots tend to agglomerate. Moreover, it is highly possible that these organic dispersants can alone functionalize the titania surface and affect the photocatalytic activity of the catalyst.

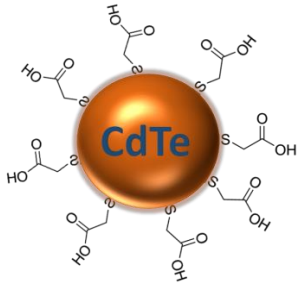


Figure 3. A representation of thioglycolic acid capped CdTe quantum dots.

2. EXPERIMENTAL

2.1. SAMPLE PREPARATION

Sample preparation of CdTe/TiO_2 composite materials commences with the colloidal synthesis of CdTe quantum dots and is followed by the incorporation of these quantum dots to the base photocatalyst titanium dioxide.

2.1.1. PREPARATION OF CdTe QUANTUM DOTS

The protocol for colloidal synthesis of water soluble TGA-capped CdTe quantum dots was adapted from Andrey Rogach's paper [65]. The chemicals used for this synthesis are listed on Table 2.

Table 2. The required chemicals for the colloidal synthesis of thioglycolic acid capped CdTe quantum dots.

Chemical Name	**Specification**
Cadmium perchlorate hexahydrate	Alfa Aesar
Aluminum Tellurite	CERAC Inc., pure 99.5%
Thioglycolic acid (TGA)	Fluka, purum 98%
Milli-Q Water	Milli-Q Academic
Sodium hydroxide	Riedel-de Haen
Sulfuric Acid	Fluka, 95-97%
Iso-propanol	TEKKIM
Silica gel	TEKKIM

First, 4.59 g of the Cd precursor cadmium perchlorate hexahydrate ($Cd(ClO_4)_2.6H_2O$) was dissolved in 250 ml Milli-Q water in a 1 L 3-neck flask. The reaction system was constantly stirred with a magnetic stirrer throughout the synthesis protocol. 250 ml Milli-Q water and 1 ml (1.33 g) of thioglycolic acid were injected simultaneously into the reaction flask. Thioglycolic acid (TGA) was used as the ligand for the functionalization of the quantum dots (capping agent). While the flask was stirred, 1 M sodium hydroxide (NaOH) solution was prepared aside. This NaOH solution was used to adjust the pH of the reaction system to 11.8-

12.0 on dropwise addition. Next, 0.8 g of the Te precursor aluminum telluride (Al_2Te_3) was placed into a 25 ml 3-neck flask as shown in Figure 21.

Since aluminum telluride is extremely sensitive to oxygen, argon gas was used to sweep off the oxygen from the reaction system. Since a harmful hydrogen telluride (H_2Te) gas was released from the system on the next steps, an absorption flask containing the 10% NaOH solution was connected to the system to capture this gas before escaping into the air. Then, 0.5 M sulfuric acid (H_2SO_4) was injected using a syringe into the 3-neck flask containing the aluminum tellurite dropwisely. Due to the chemical reaction in Equation (45), hydrogen telluride gas was released.

$$Al_2Te_3 + 3H_2SO_4 \rightarrow 3H_2Te + Al_2(SO_4)_3 \quad (45)$$

This gas was passed through the reaction flask with argon flow for half an hour where finally the color of the solution turned pinkish. Then, the 25 ml 3-neck flask was detached from the system and the reaction flask was heated while keeping the chiller on to condense the evaporated water. Quantum dot growth commenced with the boiling of the reaction suspension. By altering the time, the size of the quantum dots, hence the optical properties of the dots, were tuned. In the first minute, the emission spectrum of the dots appeared to be blue; for 5-10 minutes this shiftd to green and eventually to red. After deciding on the emission wavelength, therefore the time, the reaction was stopped by cooling the reaction medium. After the system was cooled down, the quantum dots were filtered and cleaned by centrifuging with Milli-Q water at 4500 rpm for 5 min. The quantum dots were stored in aqueous medium in dark. For this particular work, the molar concentration of the quantum dot suspension was increased 3 times. For 15 ml quantum dot aqueous suspension, 7.5 ml isopropanol was added to precipitate the dots. After centrifuging and drying, the precipitated dots were dissolved in 5 ml Milli-Q water and dispersed by sonication.

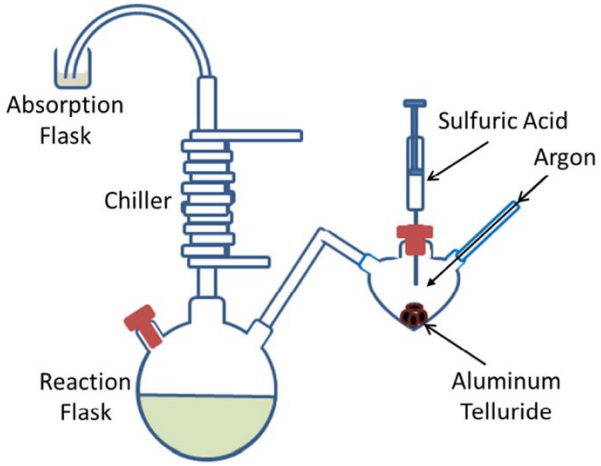


Figure 21. A scheme for the reaction system of thioglycolic acid-capped CdTe QDs [66].

2.1.2. PREPARATION OF CdTe/TiO_2 COMPOSITE MATERIALS

Commercially available titanium dioxide benchmark Degussa P25 (also known as Evonik) is chosen as the base material for being a 'gold standard' for titanium dioxide photocatalysis [67].

As mentioned in the previous part, thioglycolic acid capped CdTe quantum dots were suspended in de-ionized water. Hence, in order to rule out any possible influence of water on photocatalytic activity measurements, pure water samples were also dosed on P25 with the same loadings in control experiments.

Since the capping agent thioglycolic acid can play a part in the PHONOS (photocatalytic NO_x oxidation and storage) system, another control material was also prepared using aqueous solutions of thioglycolic acid (TGA) on TiO_2. The aqueous solution of TGA was prepared according to the initial concentration of TGA in the colloidal synthesis of the quantum dots. For this reason, 1 ml (1.33 g) of TGA was dispersed into 250 ml of de-ionized water. The solution was sonicated for 30 min.

As shown in Figure 22, for the preparation of CdTe/TiO_2 composite materials, different volumes of CdTe aqueous suspension were drop-casted on 250 mg of TiO_2 powder in a 6 cm diameter petri dish. After physically mixing for 2 min, the slurry was placed into oven and dried at 70 °C for 18 h (Figure 22.a). Same steps were followed for the blank material (Figure 22.b) and the $TGA_{(aq)}/TiO_2$ samples as well.

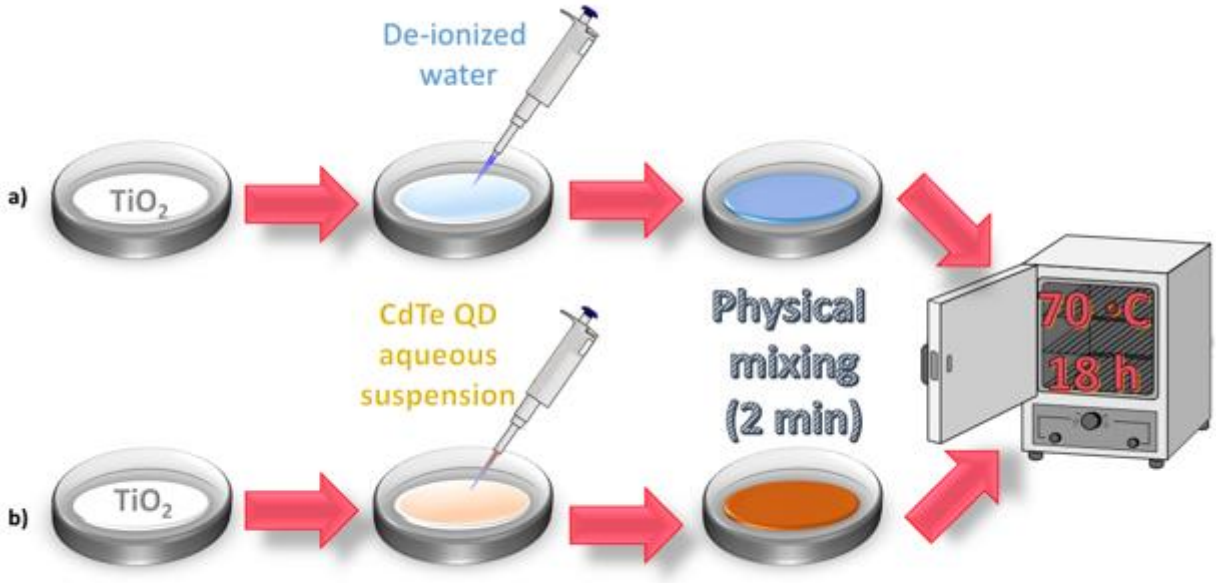


Figure 22. Stepwise preparation of a) H_2O/TiO_2 control material and b) $CdTe/TiO_2$ composite materials.

For the synthesis of the composite material $CdTe/TiO_2$, H_2O/TiO_2 blank (control) material and $TGA(aq)/TiO_2$ samples, different loadings were prepared. In Table 3, the abbreviated names of the samples were given with the required chemical amounts for their synthesis. Since the amount of powder TiO_2 was kept constant for each sample, the names of the samples were abbreviated with the volume of the additives (CdTe, H_2O and $TGA_{(aq)}$).

It was observed that addition of 0.5 ml of aqueous TGA solution on P25 led to poisoning of the active sites of TiO_2. Thus the preparation with further additive increase was not required for this particular sample.

Table 3. Required amounts of chemicals for the preparation of $CdTe/TiO_2$, H_2O/TiO_2 and $TGA(aq)/TiO_2$ materials.

Sample Name	TiO_2 powder (Degussa P25) amount (mg)	Aqueous CdTe suspension amount (ml)	De-ionized H_2O amount (ml)	Aqueous TGA solution (ml)
0.1 H_2O/TiO_2	250	0	0.1	0
0.5 H_2O/TiO_2	250	0	0.5	0
1.0 H_2O/TiO_2	250	0	1.0	0
2.0 H_2O/TiO_2	250	0	2.0	0
0.1 $CdTe/TiO_2$	250	0.1	0	0
0.5 $CdTe/TiO_2$	250	0.5	0	0
1.0 $CdTe/TiO_2$	250	1.0	0	0
2.0 $CdTe/TiO_2$	250	2.0	0	0
0.1 $TGA_{(aq)}/TiO_2$	250	0	0	0.1
0.5 $TGA_{(aq)}/TiO_2$	250	0	0	0.5

2.2. PHONOS (PHOTOCATALYTIC NO_X OXIDATION AND STORAGE) SYSTEM

2.2.1. EXPERIMENTAL SETUP OF THE PHONOS SYSTEM

For all photocatalysts, photocatalytic NO_x oxidation and storage performance measurements were conducted using the custom designed flow reactor system demonstrated in Figure 23. The flow of high purity gases (Linde 99.99 % pure N_2, 99.00% pure O_2 and NO diluted in 100 ppm N_2) were controlled with control valves (Swagelok, SS Belows-Sealed Valve, SS-4H) and mass flow controllers (abbreviated as MFC). The volumetric flow rates were set to be 0.750 SLM (standard liters per minute), 0.250 SLM and 0.010 SLM for N_2, O_2 and NO respectively. Before connecting with NO gas line, N_2 and O_2 gases were passed through a PermSelect silicone fiber membrane. On the periphery of the membrane, water is circulated using a pump chiller system. By tuning the temperature, the humidity of the gas mixture is adjusted. This artificially created polluted air of 1.010-liter volume carrying 1 ppm NO (g) was introduced to the reaction chamber. The changes in the gas concentrations (NO, NO_2, NO_x) inside the reaction chamber were monitored using a chemiluminescent NO_x analyzer, Horiba Apna-370. Figure 24 shows typical gas concentration changes as a function of time

during a typical PHONOS catalytic activity measurements. It demonstrates the decrease in NO inlet gas concentration and the production of NO_2 gas in the outlet.

The working principle of the chemiluminescent NO_x analyzer depends on the NO gas in the reactor. Inside the analyzer, there is an ozonizer unit which oxidizes the oxygen filtered from the atmospheric air into ozone (O_3) by using a UV light source inside the unit. This produced ozone gas is introduced to the reaction chamber where it reacts with the NO gas to form excited state NO_2* by Equation (46).

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (46)$$

NO_2* species luminesce broadband photons as they go back to lower energy states. This phenomenon can be shown in Equation (47) and it is called as chemiluminescence.

$$NO_2^* \rightarrow NO_2 + hv \quad (47)$$

In an alternating second line of the analyzer, NO_2 in the NO_x mixture is reduced to NO by a catalytic NO_x converter and then re-oxidized to excited NO_2 by ozone to measure the NO_2 concentration in the NO_x mixture. By adding the measured NO and NO_2 concentrations, the total NO_x concentration in the reactor is determined [68]. Note that the utilized NOx analyzer does not detect NO_x species other than NO and NO_2 (e.g. N_2O). However former studies indicate that formation of N_2O by the photocatalyst only occurs in the absence of H_2O in the gas inlet, while presence of water leads to negligible amounts of N_2O [80]. Thus, NO and NO_2 are the only predominantly existing NO_x species in the current photocatalytic studies.

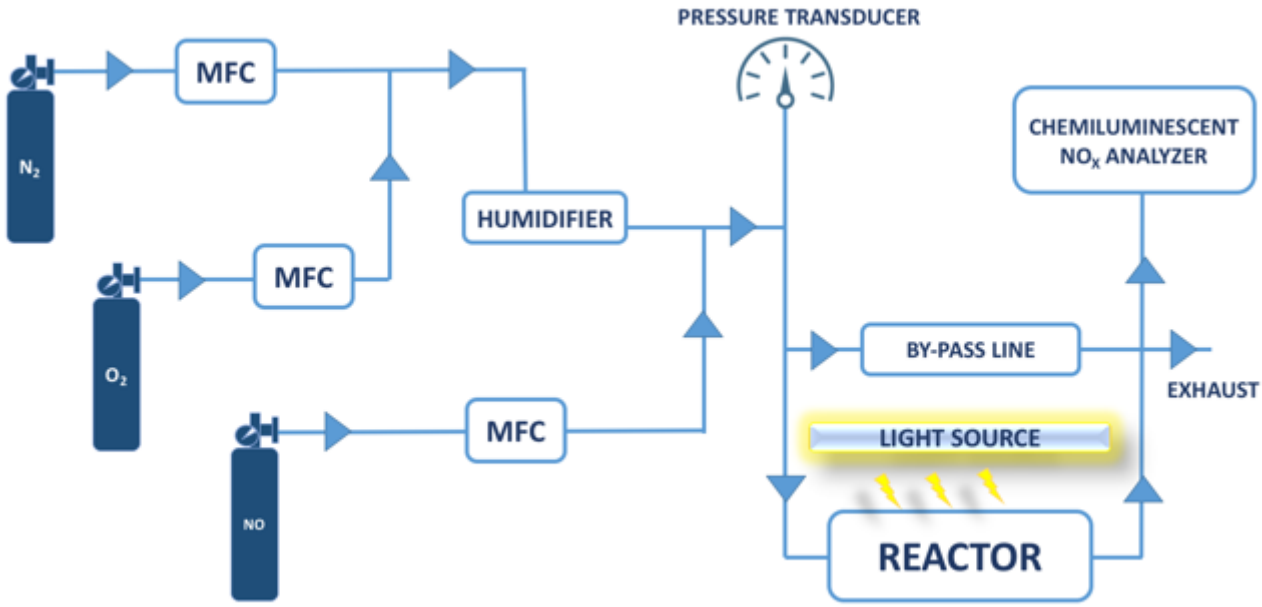


Figure 23. A block diagram of the currently used custom-made photocatalytic flow reactor system setup.

For the photocatalytic activity measurements, depending on the photocatalyst, two different light sources were used. For UVA light experiments, two 8W UVA lamps (F8W/T5/BL350, Sylvania/Germany) were used, whereas for visible light experiments, a 35 W metal halide lamp with ceramic burner (HCI-TC 35 W/942 NDL PB 400–700 nm range, Osram) was utilized. Since a small amount of UV light was emitted from the metal halide lamp, a commercial VIS-transparent UV-blocker/filtering film (LLumar window film UV CL SR PS (clear)) was placed on top of the reactor for visible light experiments. The incoming light flux was measured before and after each measurement with a photo-radiometer (HD2302.0, DeltaOhm/Italy) using a UVA probe (315-400 nm) and PAR probe (400-700 nm) for UVA and visible light measurements, respectively. The % relative humidity and temperature values in the reaction chamber were controlled before and after each measurement using a Hanna HI 9565 humidity analyzer. Typical values for % relative humidity and temperature were 50±3 % and 23±2 ºC, respectively. However, when using a visible lamp, the temperature values increased by up to 20 ºC, depending on its distance from the reactor. Therefore the influence of the thermal heating was also briefly studied (see Appendix).

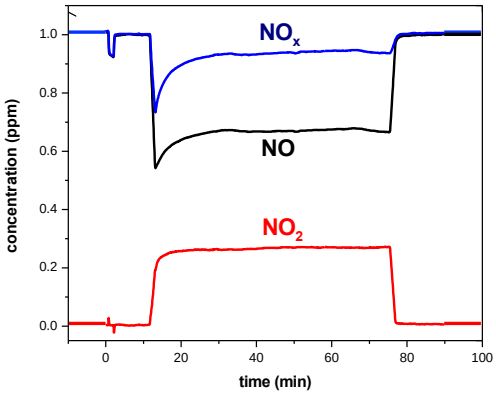


Figure 4. Operando diagram of photocatalytic NO_x oxidation and storage flow reactor for titanium dioxide.

For each measurement, 200 mg of the photocatalyst was pressed into a 0.5 mm deep 40x40 mm PMMA (polymethyl methacrylate) sample holder as demonstrated in Figure 25. PMMA was not only a lightweight and shatterproof material but also had high endurance for outdoor applications for being resistant to UV light and weathering [69].

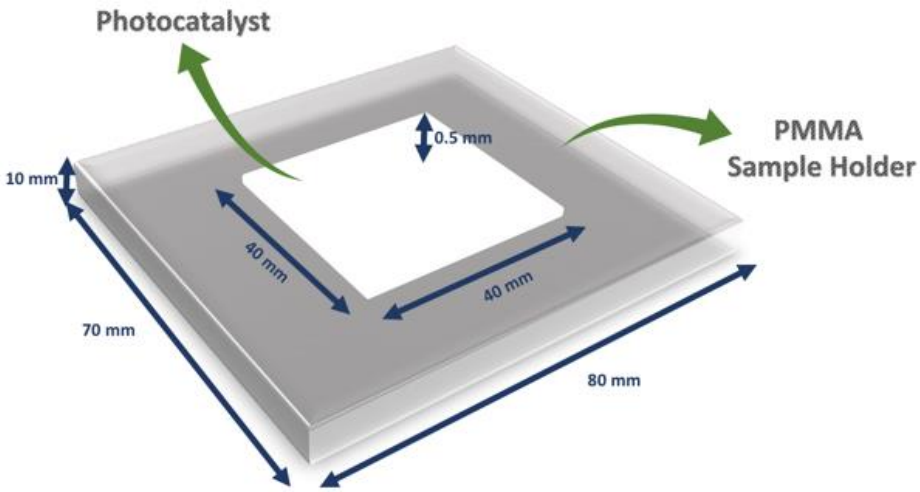


Figure 5. A sketch of PMMA sample holder manufactured for photocatalysis performance tests.

In order to observe the effect of aging on a photocatalyst, all samples were also measured after 18 h of UV or VIS light irradiation. For this measurement, samples were loaded on a PMMA grid and exposed to UV or VIS light irradiation for 18 h at room temperature in air. After 18 h of pre-irradiation, samples (aged catalysts) were directly placed into the reactor and photocatalytic activity measurements were started.

The photocatalytic activity of each sample was measured under light irradiation for 1 h and the recorded data was analyzed.

2.2.2. DATA ANALYSIS METHODS

There are several parameters that can indicate if the employment of a particular photocatalyst in a system is worth or not. The toxicity and cost of the photocatalyst material are important factors and the incorporation of CdTe quantum dots are neither cost efficient nor environmentally friendly. Nonetheless, this study can be regarded as a 'Proof of Principle' to demonstrate how it enhances the photocatalytic activity of a base catalyst.

In this study, three different methods are utilized to report the PHONOS data analysis and comparison: % photonic efficiencies, % NO conversion & % selectivity and $DeNO_x$ index.

2.2.2.1. % PHOTONIC EFFICIENCY

In this method, there are two parameters that can indicate the photocatalytic performance of a photocatalyst. First parameter is called 'NO_x Storage % Photonic Efficiency' and it represents the amount of NO_x species stored on the catalyst surface per photon. This value can be calculated using Equation (48) and 'NO_x Storage % Photonic Efficiency' is shown with the dark blue bars (Figure 26). Second parameter is called 'NO_2 Release % Photonic Efficiency' and it represents the amount of photocatalytically produced and released NO_2 gas per photon. This value can be obtained by using Equation (49) and it is depicted with the red bars (Figure 26).

$$NO_x\ Storage\ \%\ Photonic\ Efficiency\ (\xi) = \frac{n(NO_x\ stored\ on\ the\ catalyst\ surface)}{n(photon)}\ x\ 100 \quad (48)$$

$$NO_2\ Release\ \%\ Photonic\ Efficiency\ (\xi) = \frac{n(NO_2\ released\ to\ the\ atmosphere)}{n(photon)}\ x\ 100 \quad (49)$$

$$n(photon) = \frac{(I\ x\ \lambda\ x\ A\ x\ t)}{(N_A\ x\ h\ x\ c)} \quad (50)$$

In Equation (50), "*I"* represents the photon power density of the lamp; λ represents the emission wavelength of the lamp; "*A"* is the surface area of the photocatalyst exposed to light

irradiation; *"t"* represents the duration of the performance test; N_A is the Avogadro's number; *"h"* is the Plank constant and *"c"* is the speed of light.

In this method, the aim is to maximize the NO_x Storage % Photonic Efficiency (dark blue bars) and minimize the NO_2 Release % Photonic Efficiency (red bars). Hence the maximum amount of toxic NO_x species can be removed from the atmosphere and the least amount of toxic NO_2 gas is released.

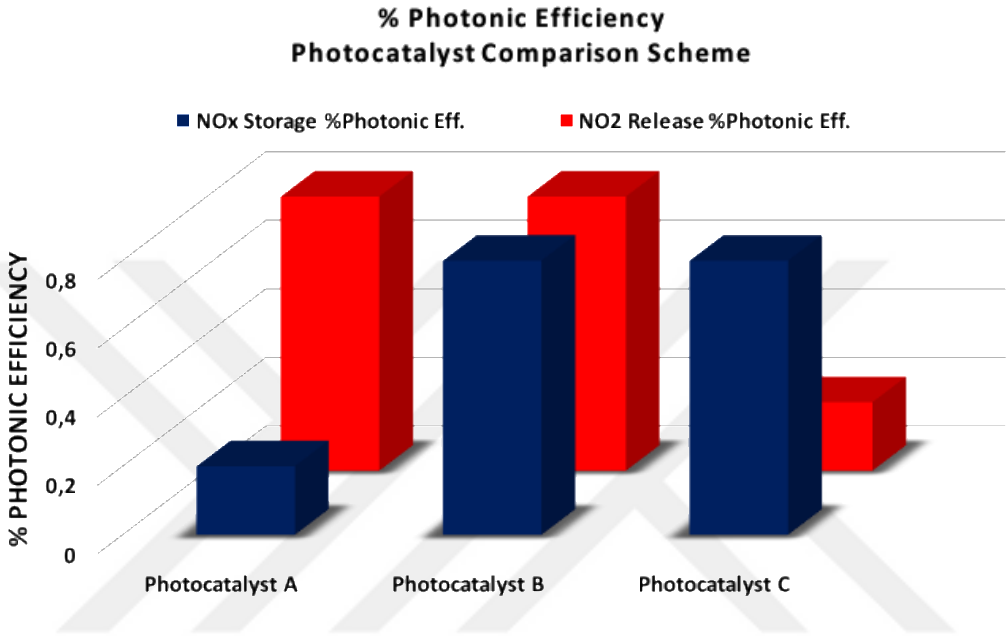


Figure 66. Comparison of three hypothetical photocatalysts in terms of % photonic efficiency method.

In Figure 26, three different hypothetical cases are compared in terms of % photonic efficiency results. In terms of NO_x Storage % Photonic Efficiency, Photocatalyst A fails to be the best photocatalyst due its poor storage capability. Furthermore, this catalyst also has high NO_2 gas formation, which is undesired. Photocatalyst B and Photocatalyst C have the same amount of stored NO_x species per photon; however, in terms of the NO_2 Release % Photonic Efficiency rates, it can be easily observed that Photocatalyst B produces about 4 times more NO_2 gas than Photocatalyst C. Thus, Photocatalyst pollutes the air more due its greater amount of NO_2 formation. Photocatalyst C can be chosen as the best photocatalyst with maximum NO_x storage and minimum NO_2 release.

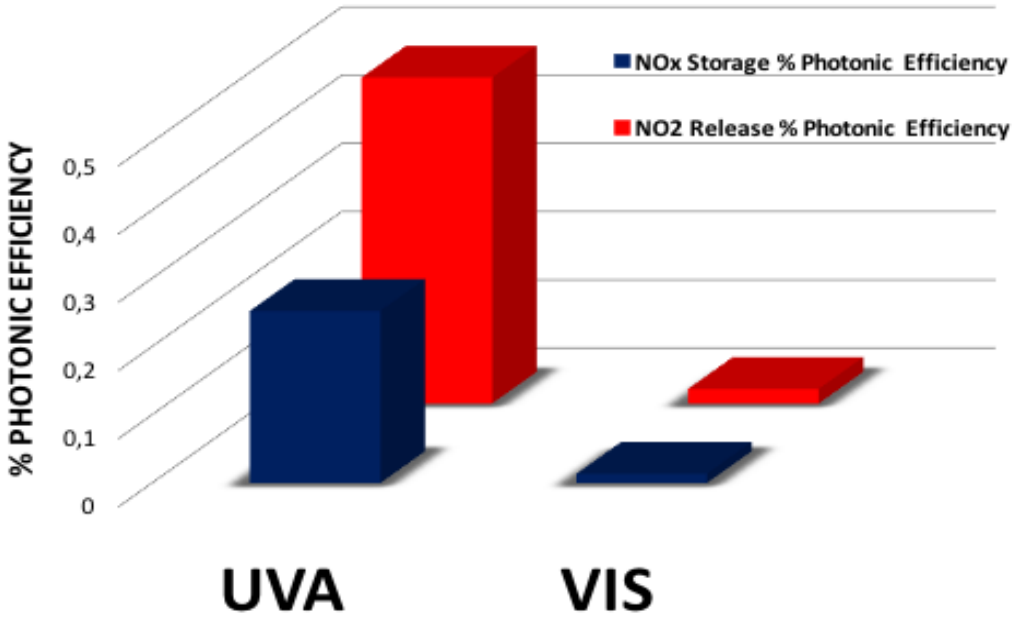


Figure 27. Comparison of % photonic efficiency results of titanium dioxide for two different light sources.

Since this technique normalizes the stored NO_x species and released NO_2 gas amounts by the incoming photon flux, it is difficult to compare two different light sources with relatively different incoming photon numbers. In Figure 27, % photonic efficiency values of titanium dioxide benchmark photocatalyst Degussa P25 are given for UV-A and visible light sources respectively. As mentioned in the introduction part, the incoming photon flux from a visible light source is almost 5 times greater when compared to a UV-A light source, therefore the denominator values in Equations (48) and (49) are quite different for these two different light sources. Thus, although photonic efficiencies for VIS light illumination are relatively small, they correspond to quite reasonable product conversion rates as will be discussed in the forthcoming section.

2.2.2.2. % NO CONVERSION & % SELECTIVITY

Another data analysis method is the % (Total) NO conversion and % NO_x storage selectivity. % NO Conversion indicates the total amount of photo-oxidized NO gas (where products can be both stored in solid state or released as gaseous NO_2) and it can be calculated from Equation (51). It is color coded with the purple bars (Figure 28) and it is related with the total photocatalytic oxidation activity of the photocatalyst. Second parameter is called % Selectivity (towards NO_x storage) and it corresponds to the percentage of the NO_x stored in

solid state as compared to the total NO conversion. % Selectivity values are shown with green bars (Figure 28) and can be calculated from Equation (52).

$$\%\ NO\ Conversion = \frac{\int([NO]_{in} - [NO]_{out})\ dt}{\int [NO]_{in} dt}\ x\ 100 \tag{51}$$

$$\%\ Selectivity\ (towards\ NO_x\ Storage) = \frac{\int([NO_x]_{in} - [NO_x]_{out})\ dt}{\int([NO]_{in} - [NO]_{out})\ dt}\ x\ 100 \tag{52}$$

In this method, the aim is to maximize both % NO Conversion (purple bars) and % Selectivity (green bars). Thus we intend to obtain a photocatalyst that has a highly NO oxidation ability and high NO_x storage in solid state. In Figure 28, three different hypothetical photocatalysts are compared with respect to their % NO Conversion and % Selectivity values. As can be seen in Figure 28, Photocatalyst A is an inactive but a selective photocatalyst; Photocatalyst B is active but not selective while, Photocatalyst C is both active and selective. Since the aim is to maximize both purple and green bars, Photocatalyst C can be chosen as the best performing photocatalyst.

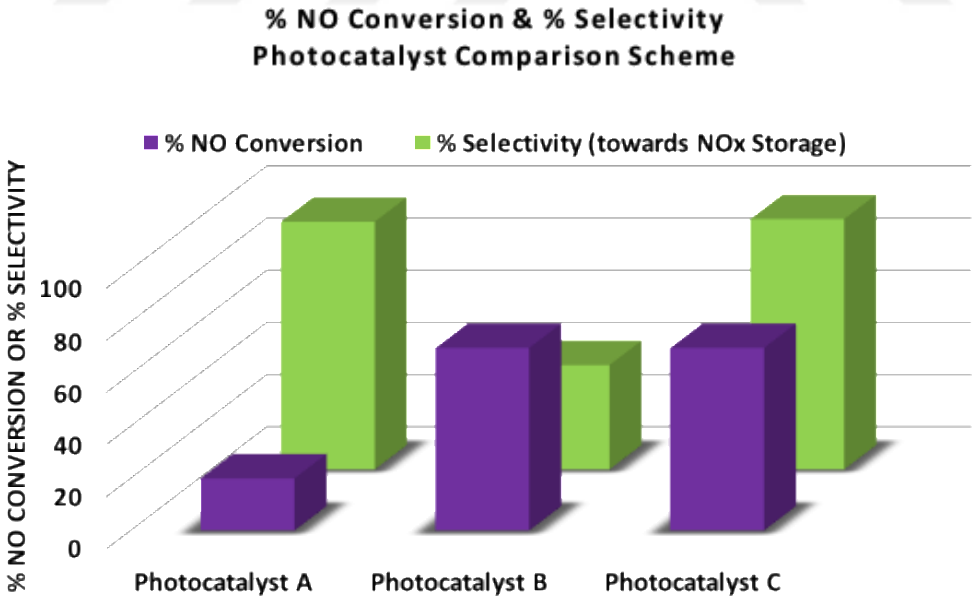


Figure 7. Comparison of three hypothetical photocatalysts in terms of % NO conversion and % selectivity method.

This analysis method does not include normalization by the incoming photon flux, hence comparison of the results with two different light sources is much more trivial than the % photonic efficiency method, as it shows actual amount of NO converted and actual amount of NO_2 generated. However it should be noted that this particular comparison method is only valid for a given set of light sources and all values are subject to change if properties of the light sources (emission spectrum, flux etc.) are changed. Figure 29 demonstrates the % NO Conversion and % Selectivity results of the Degussa P25 titanium dioxide benchmark photocatalyst under UV-A and VIS light sources, respectively. Unlike the drastic differences in the % photonic efficiency results for UV-A vs. VIS illumination, % NO conversion and % Selectivity results are rather comparable for VIS and UV-A measurements.

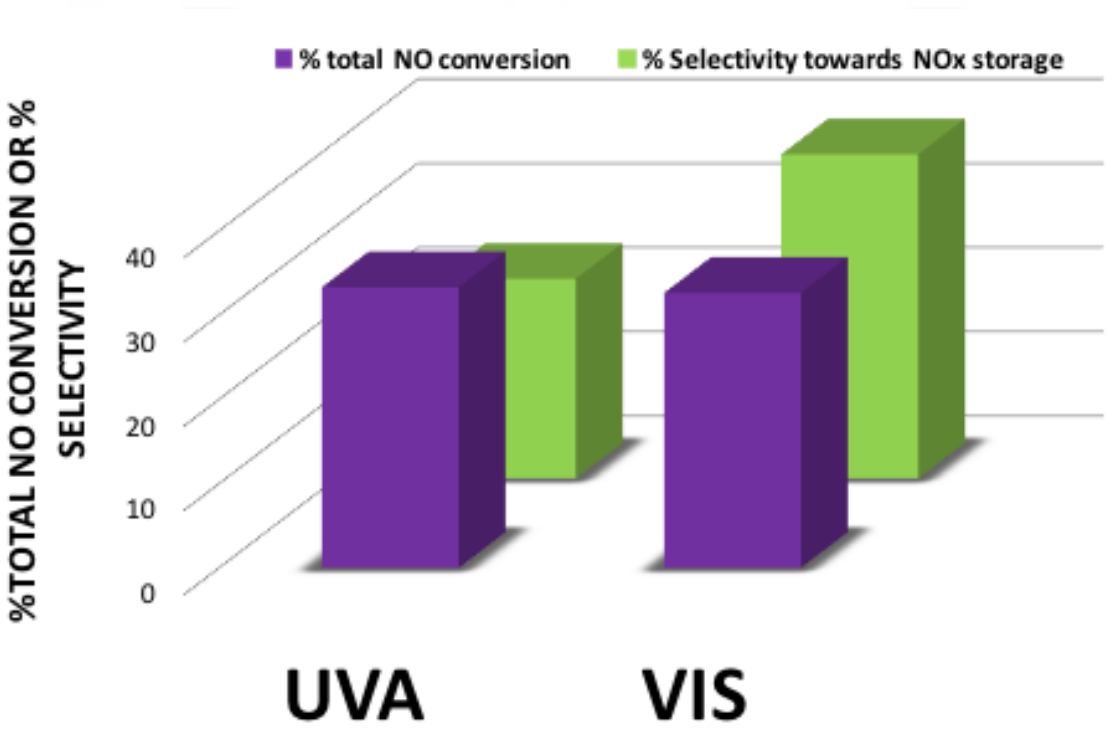


Figure 8. Comparison of % NO conversion and % selectivity results of titanium dioxide for two different light sources.

2.2.2.3. $DeNO_x$ INDEX

The ultimate data analysis method for the overall assessment of PHONOS performance is the $DeNO_x$ index, which can be calculated using Equation (56). $DeNO_x$ index is a single parameter combining the air pollution abatement efficacy of the catalyst through NO_x storage along with the unwanted air-polluting action of the catalyst via $NO_2(g)$ formation. Thus, by assessing this single parameter, one can decide whether the overall effect of the photocatalyst

is toxication or detoxication. Oxidation of NO to harmless NO_3^- species has several intermediate steps. Highly toxic NO_2 gas is produced as one of these intermediates [70]. The threshold limit for NO is set to be 25 ppm by OSHA, ACGIH and NIOSH whereas the limit for NO_2 is set to be 1-3 ppm [71]. Another problem of NO_2 is that it can undergo a photolysis in the presence of molecular oxygen as indicated in Equations (53-55) [72].

$$NO_2 + hv \rightarrow NO + O\ (^3P) \tag{53}$$

$$O\ (^3P) + O_2 \rightarrow O_3 \tag{54}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{55}$$

The produced ground level ozone is even more toxic with a threshold limit of 0.1 ppm [71]. Given all these outlying reasons, this index is constructed based on the estimation that in overall NO_2 gas is three times more toxic than NO gas [70, 73].

$$\mathrm{De}NO_x \text{ index} = \frac{\int([NO]_{in} - [NO]_{out})dt - 3\int([NO_2]_{out} - [NO_2]_{in})dt}{\int [NO]_{in} dt} \tag{56}$$

Thus, if the $DeNO_x$ index value for a photocatalyst is negative, then it can be argued that the photocatalyst increases the overall NO_x toxicity of the air; whereas if it is a positive value, the photocatalyst lowers the overall NO_x toxicity of the air.

In Figure 30, three different hypothetical photocatalysts are compared based on their $DeNO_x$ index values. With a negative $DeNO_x$ index value, Photocatalyst A increases the overall NO_x toxicity and should not be preferred in photocatalytic NO_x abatement processes. Photocatalyst B and Photocatalyst C have positive $DeNO_x$ index values, so they lower the overall NO_x toxicity. Due to its more positive $DeNO_x$ index value, Photocatalyst C can be chosen as the best photocatalyst for this method.

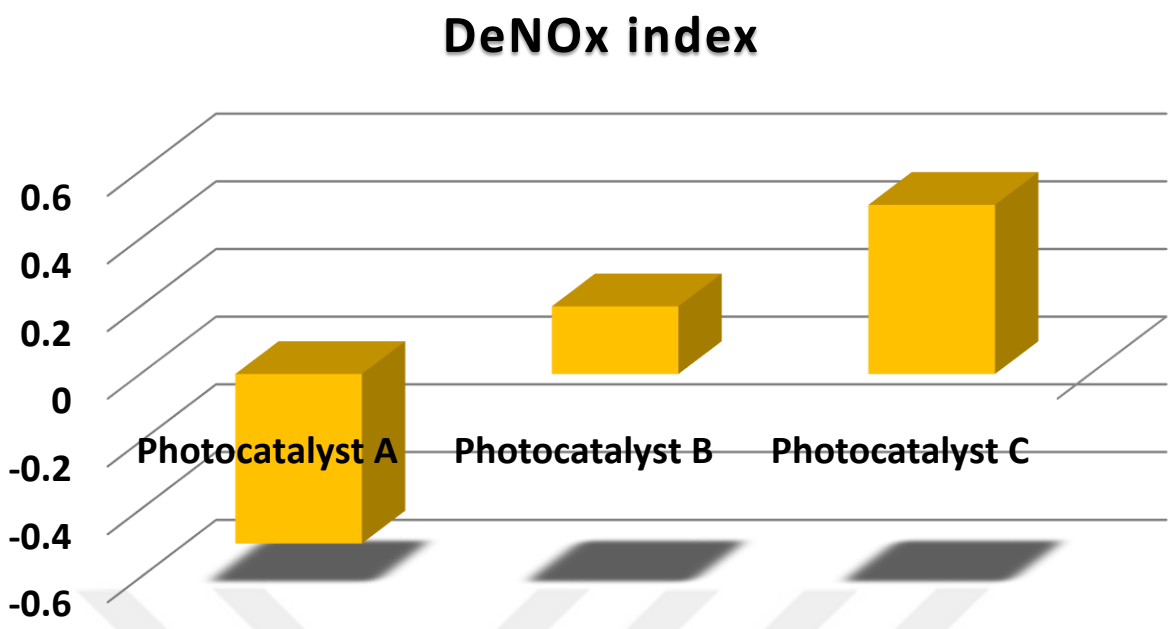


Figure 30. Comparison of three hypothetical photocatalysts in terms of their $DeNO_x$ index values.

2.3. CATALYST CHARACTERIZATION

TGA capped CdTe quantum dots and the prepared $CdTe/TiO_2$ composite materials were analyzed with different spectroscopic and optical techniques in order to understand the physical properties, optical and electronic structures of produced materials as well as a possible mechanism for the photocatalytic processes.

2.3.1. XRD MEASUREMENTS

XRD pattern of the quantum dots and the composite materials were obtained by using a Pananalytical Multi-Purpose X-Ray Diffractometer (XRD-MPD) equipped with a Cu Kα (1.5405 Å) X-Ray source operating at 45 kV/40 mA). This instrument was preferred because it can be operated with very small amounts of sample. For powder composite samples, the fine powder is placed on a silicon single crystal as shown in Figure 31 and then placed into the diffractometer. In order to scan the range of 10-90 degrees, the parameters were set as listed in Table 4.

Table 4. XRD-MPD Spectrometer parameters used for the measurements.

Parameter	Value
Range	80
2Theta	50
Offset	0
Step size	0.01
Time per step	30

Since it is difficult to prepare a powder form sample for the CdTe quantum dots, the XRD analysis sample is prepared by dropcasting the CdTe aqueous suspension on a silica piece. After the dispersant evaporation, the background spectrum for this particular sample was taken by using a silica piece. Ultimately, sample spectrum and background spectrum were normalized by the highest silica peak and the background spectrum is subtracted from the sample spectrum.

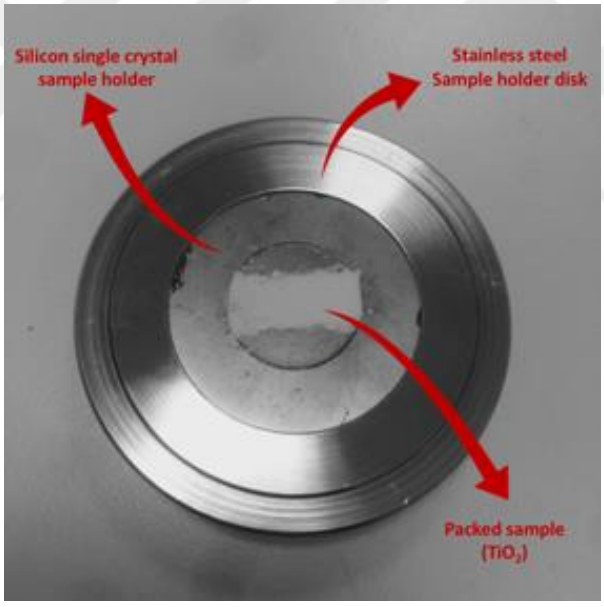


Figure 31. Powder sample loading for XRD-MPD measurements on a silicon single crystal.

2.3.2. TEM/EDX ANALYSIS

TEM images were obtained by using a FEI Technai G2 F30 Transmission Electron Microscope. Firstly, CdTe quantum dots were analyzed in the absence of the base catalyst titanium dioxide. 0.5 ml of CdTe aqueous suspension was dispersed in 4 ml of absolute ethanol and the mixture was sonicated for 15 minutes. About 2 µl of the mixture was drop-casted on a copper grid and placed into a vacuum tube at 60 °C for 18 hours so that the

solvent could completely evaporate. If the solvent was not successfully removed from the prepared sample, the organic carbon based substances could grow when exposed to X-Rays leading to the formation of an organic layer, poor contrast and low quality images. The same processes were carried out for CdTe/TiO_2 composite materials as well. About 2 mg of 5.0 CdTe/TiO_2 powder was dispersed into 4 ml of ethanol and the mixture was sonicated for 15 minutes. About 2 µl of the mixture was dropcasted on a copper grid and placed into a vacuum tube at 60 °C for 18 hours. For both samples, images of bright and dark fields were obtained.

2.3.3. UV/VIS & UV/VIS-DR MEASUREMENTS

A Cary 100 UV-Vis Spectrometer was used for UV-Vis absorption spectrum of TGA-capped CdTe QDs in aqueous medium. For the band gap energy calculations of the quantum dots, % Reflectance spectrum was obtained using a Cary 5000 UV-Vis-NIR Spectrometer equipped with a Varian Cary 2500 Internal Diffuse Reflectance Accessory (Figure 33). For samples in liquid form, their solvent was used for the baseline spectrum; whereas for powder samples, PTFE (polytetrafluoroethylene) was used as the baseline since the reflectance port was covered with PTFE reference disk. All liquid samples were measured inside a quartz cell.

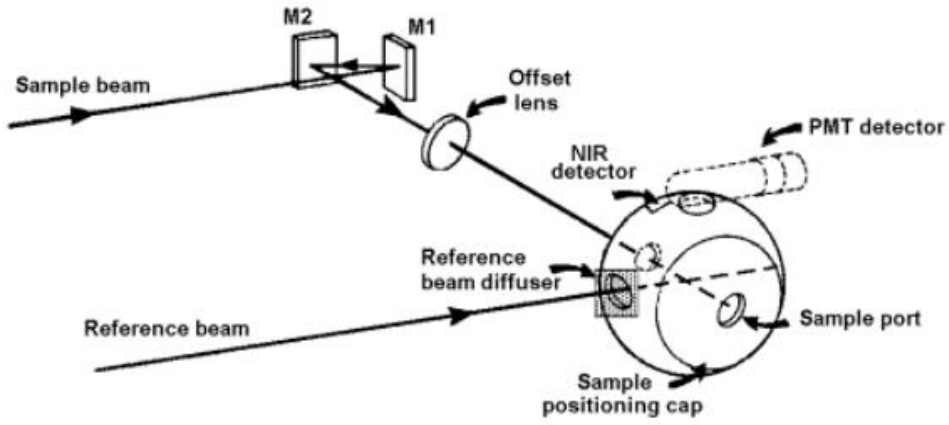


Figure 32. Optical design of internal diffuse reflectance accessory [75].

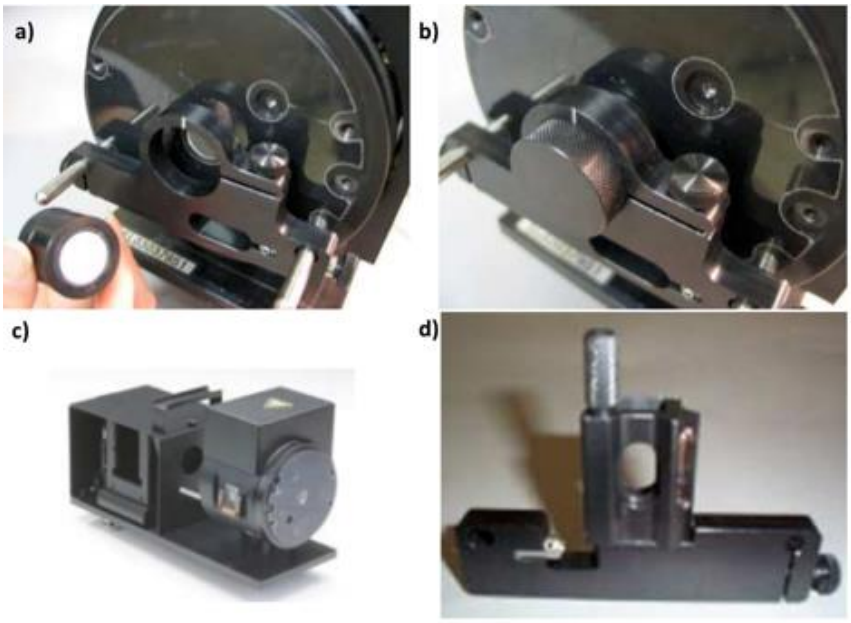


Figure 33. a) Powder sample cell b) powder cell inserted into sample holder c) Cary 2500 internal DR accessory d) liquid cell holder [75].

2.3.4. PL, PL-QY & TRF MEASUREMENTS

Photoluminescence spectra of CdTe quantum dots were obtained by using a Cary Eclipse Fluorescence Spectrophotometer. Also photoluminescence quantum yield measurements were performed according to the methodology described by de Mello et al. [76]. PL-QY measurement setup was equipped with an Ocean Maya 2000 Spectrometer using an integrating sphere, a Xenon lamp and a monochromator. For CdTe quantum dot measurements, the excitation wavelength was set to 400 nm.

Time resolved photoluminescence measurements were conducted using a Pico Quant FluoTime 200 Spectrometer. As the dispersion samples of QDs were excited with a picosecond pulsed laser at the wavelength of 375 nm, the fluorescence decay curves were recorded with TimeHarp time correlated single-photon counting (TCSPC) unit. For the instrument response function (IRF), FluoFit software was used to reconvolute mode fitting of the decay curves.

3. RESULTS & DISCUSSION

3.1. CATALYST CHARACTERIZATION

3.1.1. XRD ANALYSIS RESULTS

In order to analyze the crystal structure of the CdTe quantum dots and the CdTe/P25 composites, XRD measurements were carried out. XRD pattern corresponding to CdTe quantum dots is shown in Figure 34, where the peak positions at 23.7, 39.8º and 46.5º can be assigned to (111), (220) and (311) planes of CdTe respectively. As expected for nanoparticles, the peaks are broad and these peaks reconcile with the zinc blende structure of CdTe [78].

Figure 35 demonstrates the X-ray diffraction patterns of bare Degussa P25 and CdTe/P25 composites with increasing QD loadings. For Degussa P25, anatase and rutile polymorphs of titanium dioxide are observed and the corresponding peaks are labeled as shown. It can be interpreted from the intensities on the spectrum that Degussa P25 is an anatase rich mixture.

After introducing different ratios of CdTe quantum dots, there seems to be no change in the XRD patterns. Even for the 5.0 CdTe/TiO_2 sample which has the highest QD loading, no peaks for the cubic CdTe can be detected. Therefore, it indicates that for the proposed CdTe/TiO_2 photocatalyst, the required CdTe amount for the photocatalytic activity enhancement is very low. Considering the toxicity and cost of CdTe quantum dots, it would not be a reasonable choice to use greater amounts of QDs.

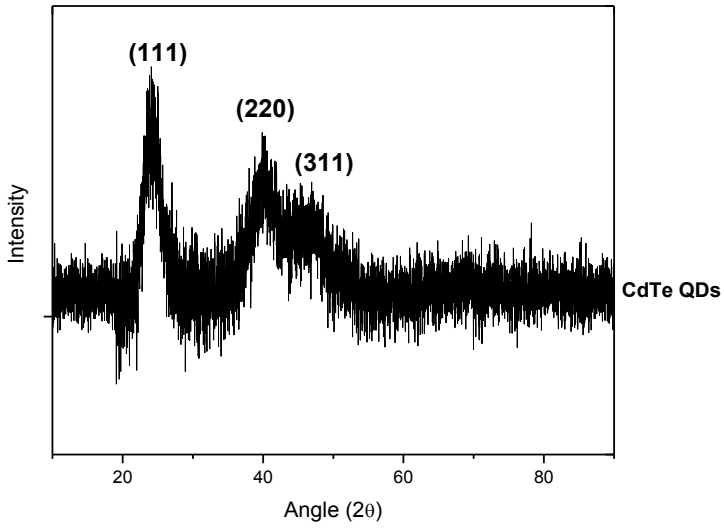


Figure 34. XRD pattern of TGA-capped CdTe quantum dots.

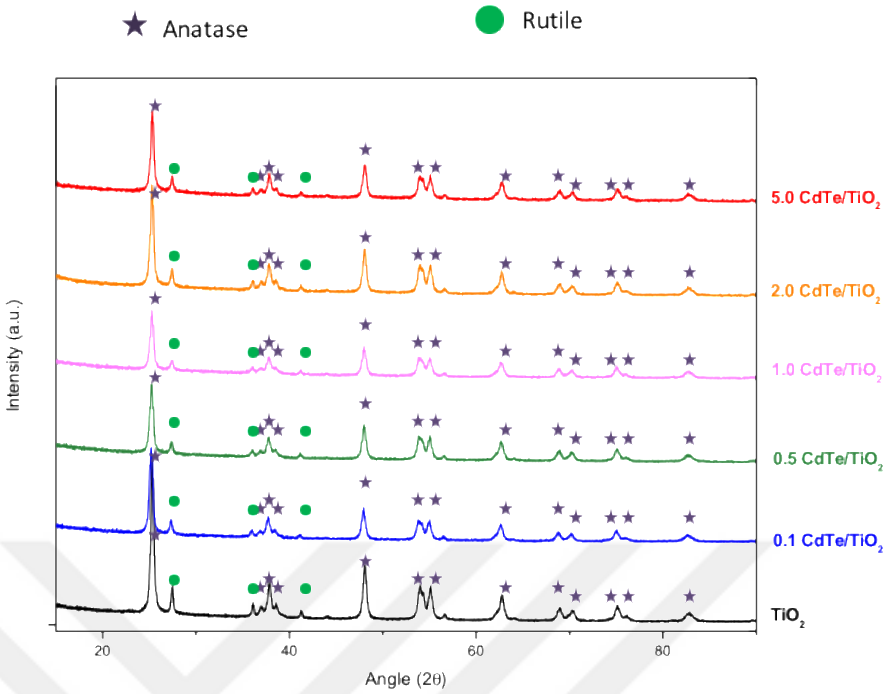


Figure 35. XRD patterns of TiO_2 (Degussa P25), 0.1 CdTe/TiO_2, 0.5 CdTe/TiO_2, 1.0 CdTe/TiO_2, 2.0 CdTe/TiO_2 and 5.0 CdTe/TiO_2.

3.1.2. TEM/EDX RESULTS

TEM images were obtained for bare CdTe QDs and CdTe/P25 composites. Figure 36 demonstrates a TEM image of bare CdTe quantum dots. In general, the size of the QDs were observed to be ~4 nm. In Figure 37, EDX results show the presence of cadmium and tellurium as well as sulfur due to the organic capping agent (thioglycolic acid).

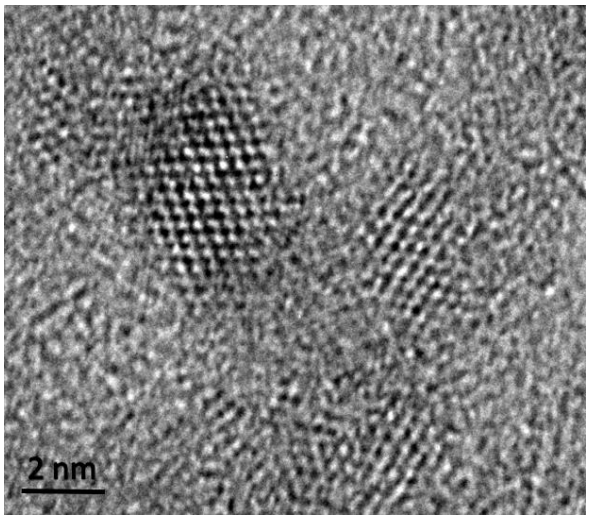


Figure 36. TEM image of CdTe quantum dots.

In terms of the quantification, it can be stated that these QDs are cadmium rich CdTe quantum dots and the atomic ratio of cadmium to tellurium is greater than 1.

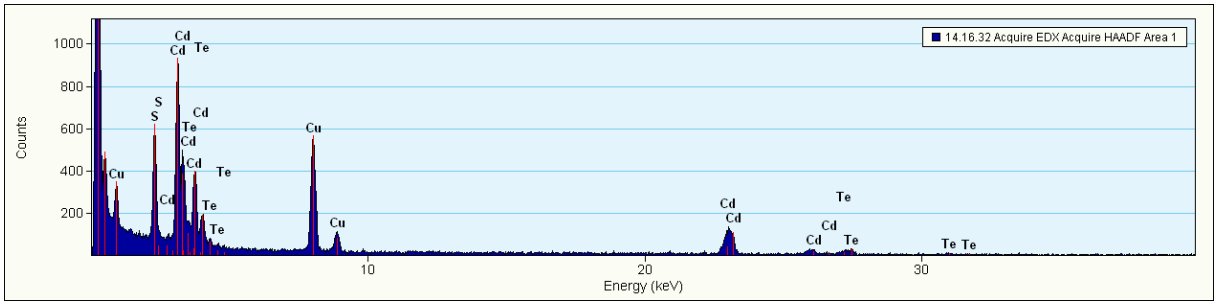


Figure 37. EDX analysis results of CdTe quantum dots.

Figure 38 provides the TEM images of CdTe/P25 composites where 3.5 – 4.0 nm sized CdTe quantum dots can be seen on titanium dioxide surfaces. Figure 109 demonstrates the composites in both bright and dark fields. As the mass difference between cadmium telluride and titanium dioxide is sufficiently big, a nice contrast can be observed and it is much easier to spot the quantum dots on titania. In bright field, titanium dioxide is light whereas the CdTe QDs are darker contrast. In dark field, QDs have a lighter contrast compared to titania.

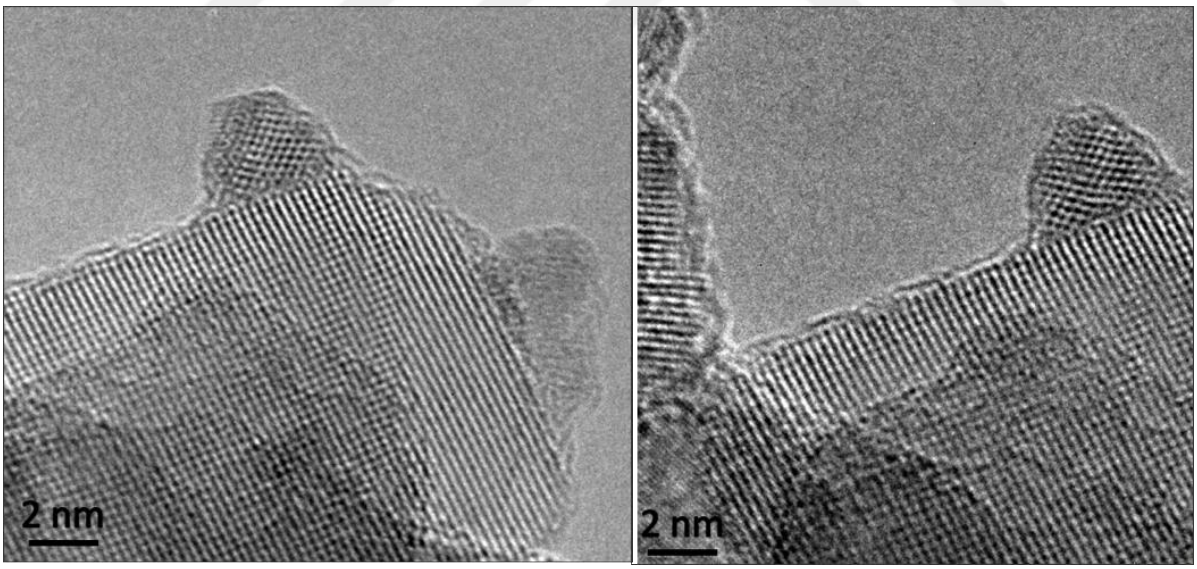


Figure 38. TEM images of 5.0 CdTe/P25 composite materials**.**

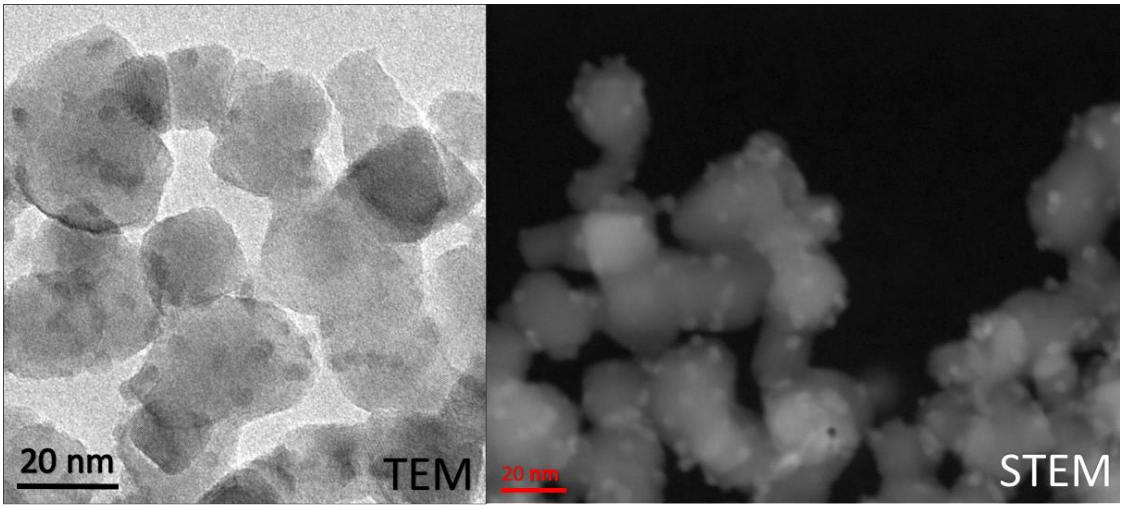


Figure 39. TEM images of 5.0 CdTe/P25 composite materials in bright (left) and dark (right) field.

The EDX analysis of 5.0 CdTe/P25 composites provides evidence of the presence of cadmium, tellurium, titanium and sulfur as well. It can be observed that the amount of CdTe is very low compared to titanium dioxide.

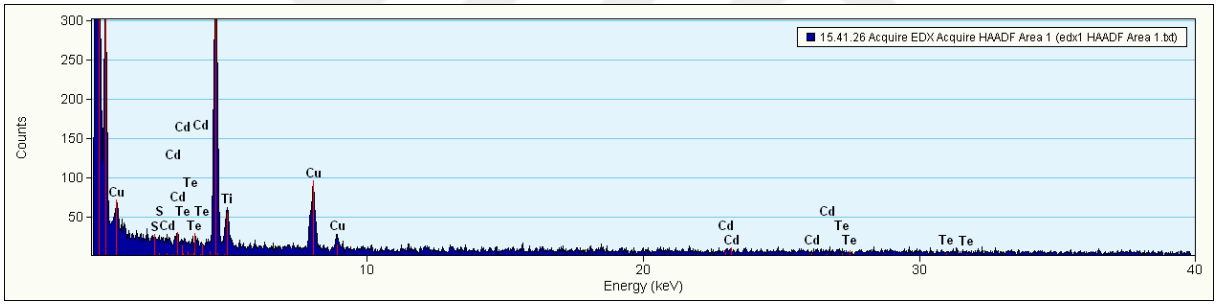


Figure 40. EDX analysis results of 5.0 CdTe/P25 composite materials.

3.1.3. UV/VIS & UV/VIS DR RESULTS

The absorbance spectrum of CdTe quantum dot suspension was obtained as shown in Figure 41 where the absorbance peak is located at 558 nm. For this measurement, 100 µl quantum dot suspension was diluted in 3 ml water.

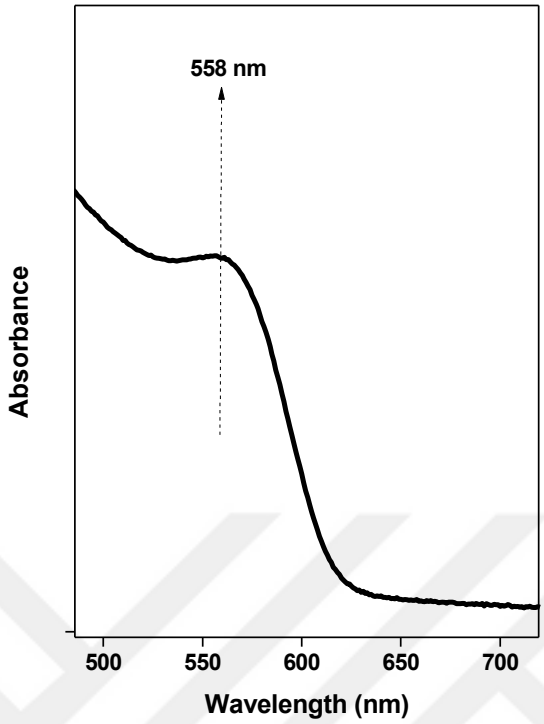


Figure 41. UV-Visible spectrum of CdTe quantum dots.

In order to calculate the band gap of the synthesized CdTe quantum dots, Tauc expression was utilized as in Equation (57).

$$(h\nu\alpha)^n = A(h\nu - E_g) \tag{57}$$

In this expression, E_g is the band gap, h represents Planck's constant, ν represents frequency of photon, α is the absorption coefficient and A is the proportional constant. For direct band gap materials, n equals to 2 whereas for indirect materials n is 0.5. As CdTe is a direct band gap semiconductor, n should be taken as 2.

Since diffuse reflectance data becomes proportional to absorption coefficient α when Equation (58) is used, the diffuse reflectance data was obtained and converted to Kubelka-Munk function, F(R) [74].

$$F(R) = \frac{(1-R)^2}{2R} \tag{58}$$

The resulting spectrum is demonstrated in Figure 42 and extrapolation of the linear portion of the plot provides the band gap energy information. According to these calculations, the band gap energy is found to be ~ 2.0 eV. Considering the 1.44 eV band gap energy of bulk CdTe [34], due to the quantum confinement effect, band gap widens as size decreases.

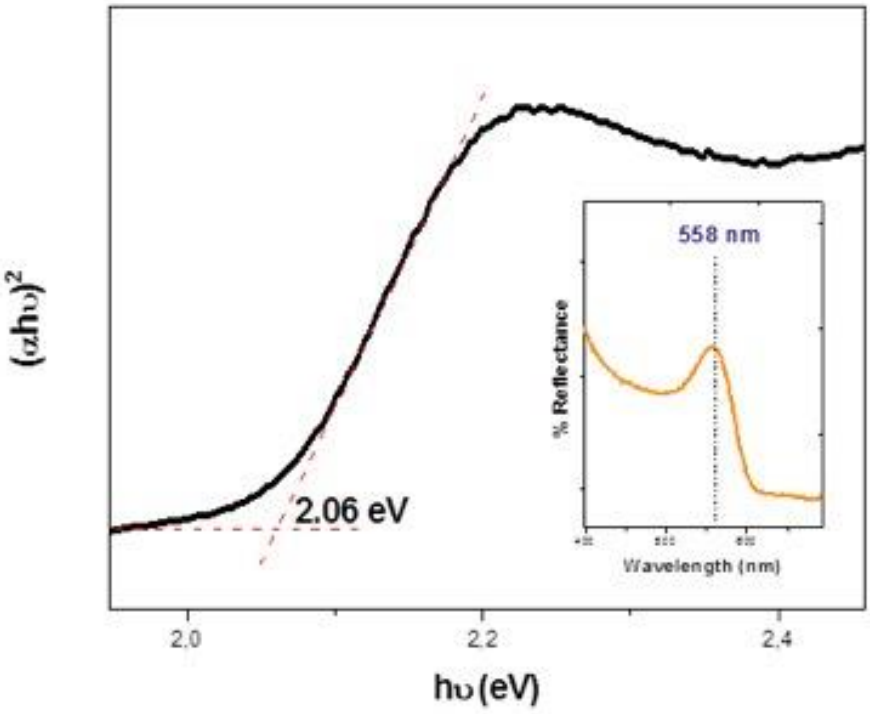


Figure 42. UV-Visible spectrum of CdTe QDs in terms of % Reflectance and band gap calculations.

The size of the CdTe quantum dots was calculated using Equation (59) where D is the diameter of particles and λ is the wavelength of the first excitonic absorption peak.

$$D = (9.8127\ x\ 10^{-7})\lambda^3 - (1.7147\ x\ 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84) \quad (59)$$

The diameter of the quantum dots can be found as ~3.3 nm by taking λ as 558 nm. Using the diameter in Equation (60), one can calculate the extinction coefficient of the quantum dots where ΔE is the transition energy corresponding to the first absorption peak.

$$\varepsilon = 3450\ \Delta E (D)^{2.4} \quad (60)$$

For a diameter of 3.3 nm, the extinction coefficient can be calculated as ~1.55x10^{5}cm^{-1}M^{-1}. Finally to calculate the concentration of the CdTe quantum dot suspension, Beer-Lambert law can be used as in Equation (61) where A is the absorbance at the first excitonic peak (0.269), ε is the extinction coefficient (~1.55x10^{5}cm^{-1}M^{-1}), c is the concentration and b is the path length (1 cm).

$$A = \varepsilon\, b\, c \tag{61}$$

Thus for a 100 µl quantum dot suspension diluted in 3 ml water, concentration can be found as ~1.74x10^{-6} mol/L and for the actual quantum dot suspension used in performance measurements it can be calculated as ~5.4 x10^{-5} mol/L.

In order to check if the quantum dots can still absorb light, UV-Visible spectrum of 5.0 CdTe/P25 sample is acquired as shown in Figure 43.

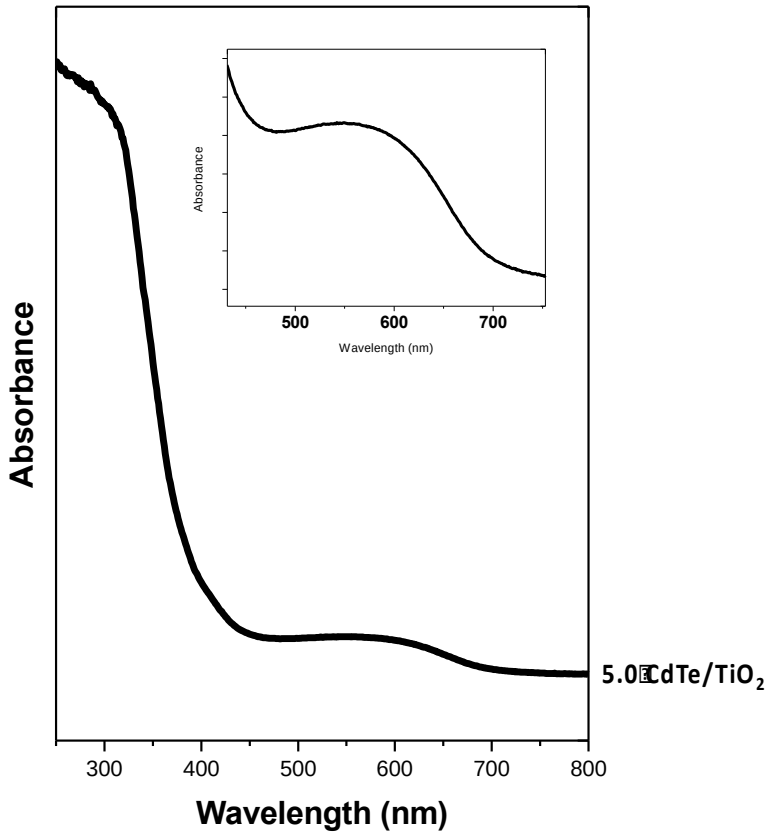


Figure 43. UV-Visible spectrum of 5.0 CdTe/P25 composite material (Inset demonstrates the absorbance peak of quantum dot.).

3.1.4. PL & TRF RESULTS

The emission wavelength and the full-width-half-maximum (FWHM) value of the emission profile of a quantum dot sample give an information about its size & size distribution. If the FWHM value is smaller (narrow FWHM), then the size distribution is also narrow. The photoluminescence measurement result of synthesized CdTe quantum dots is given in Figure 44, where the PL emission peak is centered at ~595 nm (2.08 eV) with a FWHM of ~40 nm. From the data, it can be said that these QDs have moderate particle size dispersion.

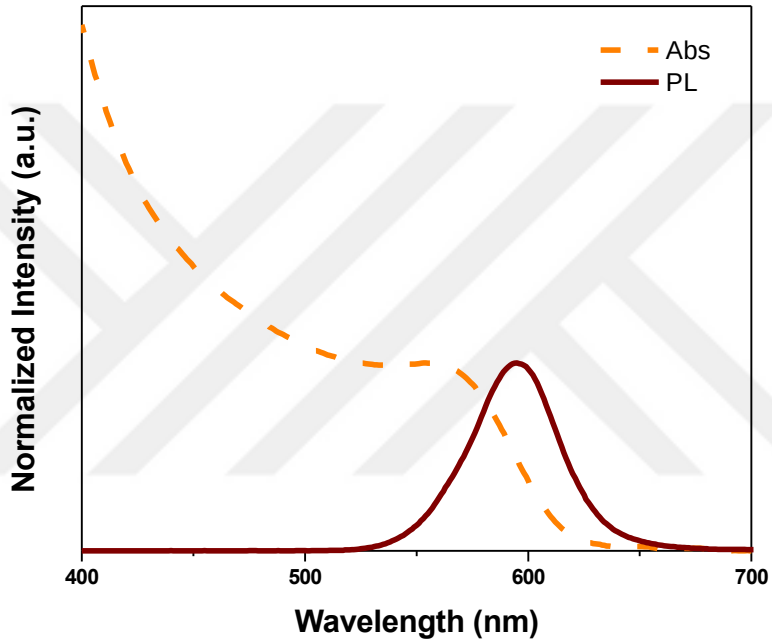


Figure 44. Photoluminescence results of CdTe quantum dots.

Fluorescence lifetime measurements were also conducted so as to determine variety of excited state dynamics of fluorescent or phosphorescent molecules. It examines the relaxation kinetics of the sample with the help of pulsed laser. This relaxation of the electron can occur in radiative and non-radiative transitions. Besides, some additional processes like Förster Resonance Energy Transfer (FRET), quenching, charge transfer can be examined. The time resolved fluorescence (TRF) measurement result of CdTe QDs is given in Figure 45.
Mostly, the decay curves are modeled as the sum of multi-exponential decays [77].

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + \cdots . + A_n e^{-t/\tau_n} \qquad (62)$$

In Equation (62), amplitude coefficients (A_x) and lifetime components ($e^{-t/\tau}$) of the data resulted in the following equation where the averaged lifetime of the QDs can be calculated as 20.612 ns.

$$I(t) = 567e^{-t/41.031} + 1165.5e^{-t/17.120} + 417.4e^{-t/2.612} \quad (63)$$

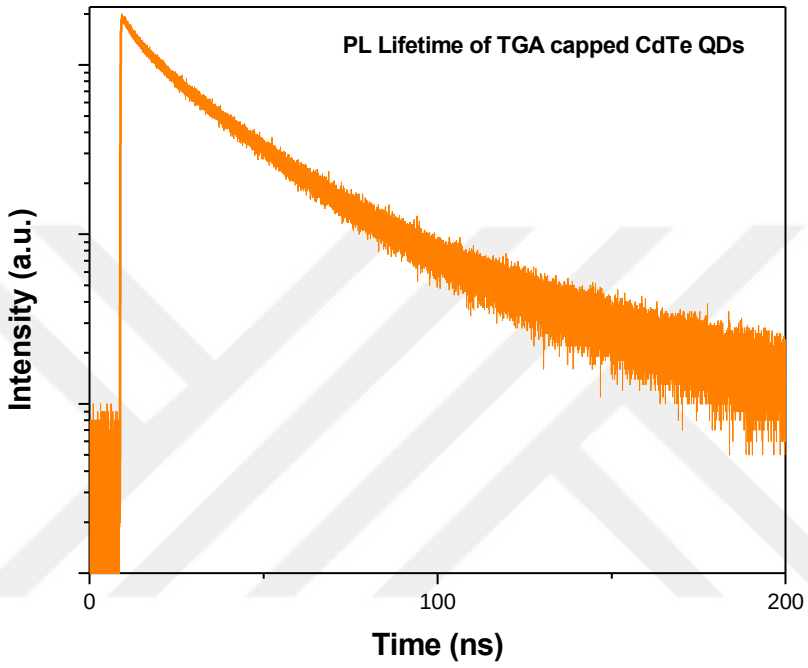


Figure 45. Time resolved fluorescence results of CdTe quantum dots.

3.2. PHOTOCATALYTIC PERFORMANCE TEST RESULTS

The photocatalytic performance tests were conducted as explained in the Experimental part. In this part, the results of these tests are going to be discussed in detail.

3.2.1. PHOTOCATALYTIC PERFORMANCE OF TITANIUM DIOXIDE (P25)

Titanium dioxide is the benchmark photocatalyst in this study. Hence in order to observe the influence of the additives on the photocatalytic performance, the photocatalytic activity of the benchmark titanium dioxide was measured. The photocatalytic activity measurements were conducted using both UV-A and VIS light sources on both fresh and aged catalyst. Aged catalyst was prepared by exposing the catalyst to UV or VIS light source in air for 18 h.

Figure 46, demonstrates the % photonic efficiency results for titanium dioxide (P25) under UV-A light exposure. It can be easily observed that it can store some NO_x on the surface; however, it produces a great amount of NO_2(g). After irradiating with UV light for 18 h, NO_x storage slightly decreases while the NO_2(g) production is almost unchanged. This decrease can also be observed for the % selectivity values in Figure 47. The drop can be attributed to the surface saturation of titanium dioxide. Since the % selectivity of P25 towards NO_x storage is small, titanium dioxide has a negative DeNOx index (Figure 48), which makes it unfit for air cleaning purposes under UV-A illumination.

In the case of VIS light exposure, there is still a great amount of NO_2(g) production (Figure 49). Thus % selectivity is still low which results in a negative DeNOx index and makes titanium dioxide a ‘bad catalyst’ for air cleaning purposes under VIS light. Figure 50 indicates a drop in % selectivity results after the catalyst is exposed to visible light for 18 hours in air.

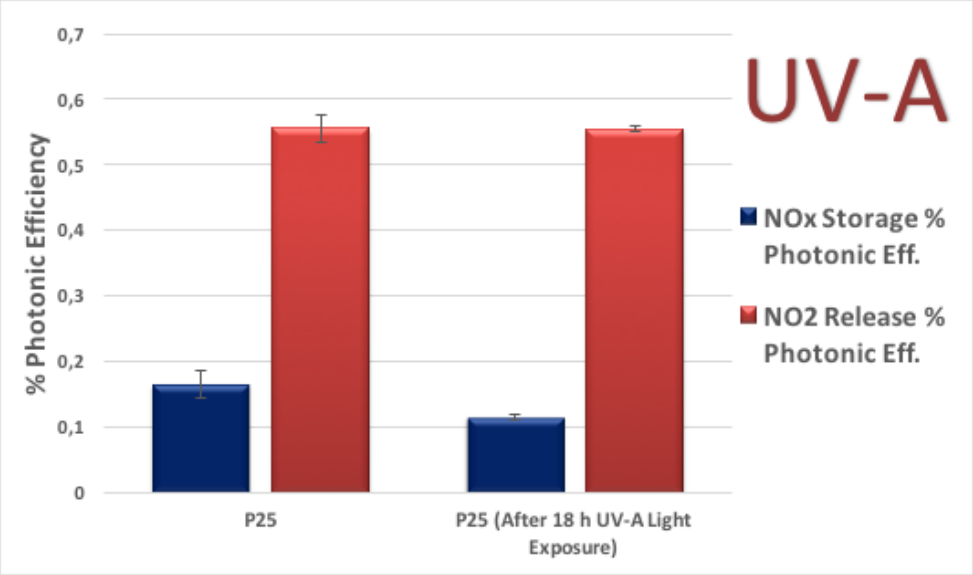


Figure 46. %Photonic efficiency results for titanium dioxide (P25) under UV-A light.

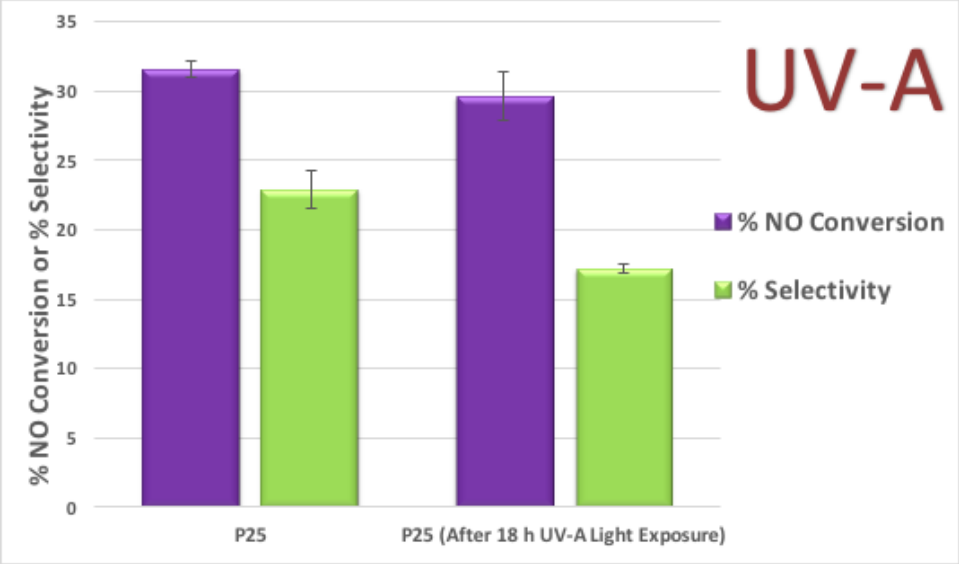


Figure 47. % NO Conversion & % Selectivity results for titanium dioxide (P25) under UV-A light.

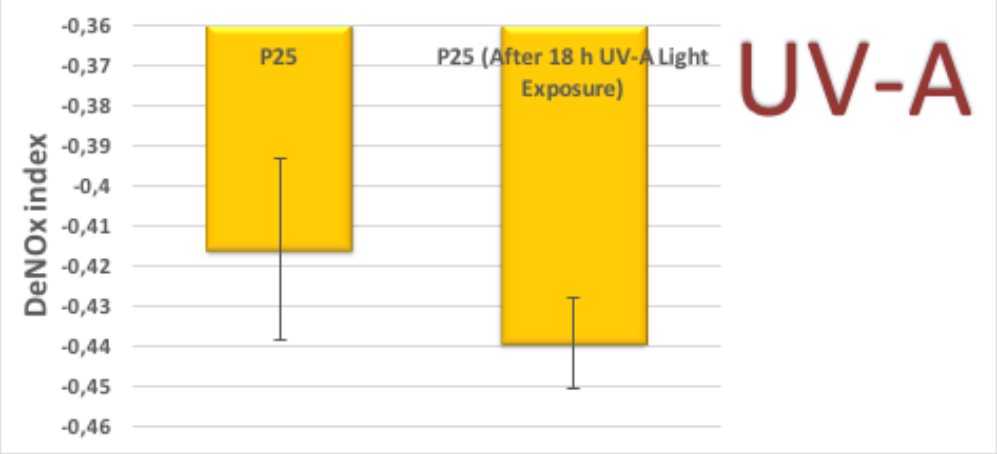


Figure 48. DeNOx index results for titanium dioxide (P25) under UV-A light.

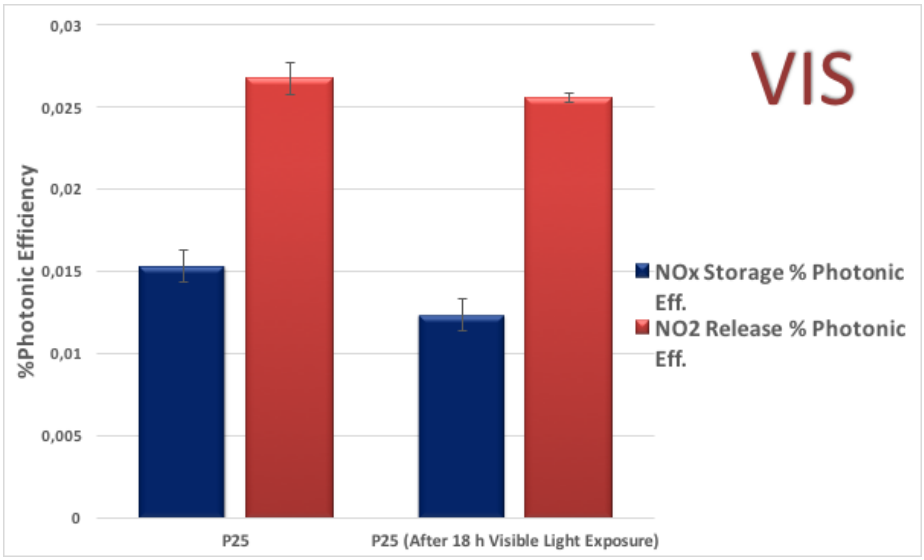


Figure 49. %Photonic efficiency results for titanium dioxide (P25) under visible light.

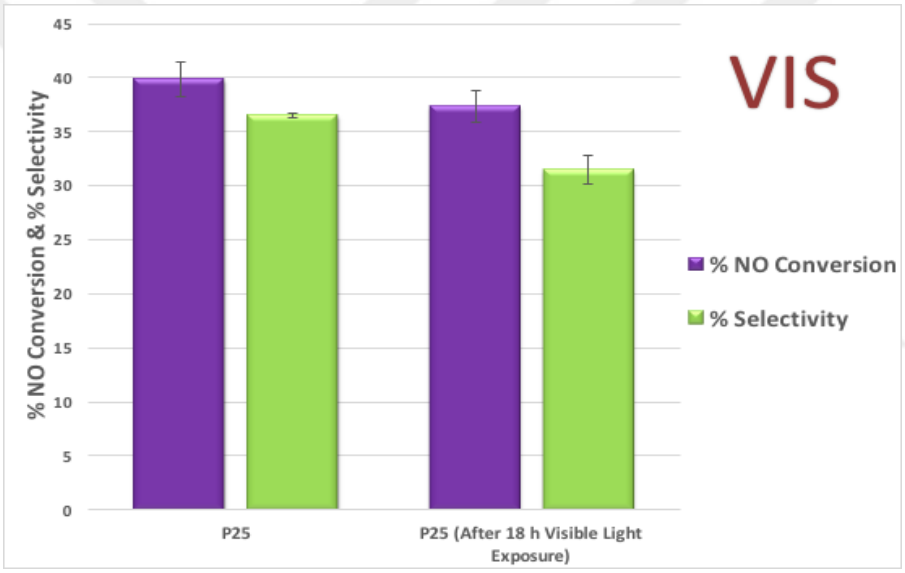


Figure 50. % NO Conversion & % Selectivity results for titanium dioxide (P25) under visible light.

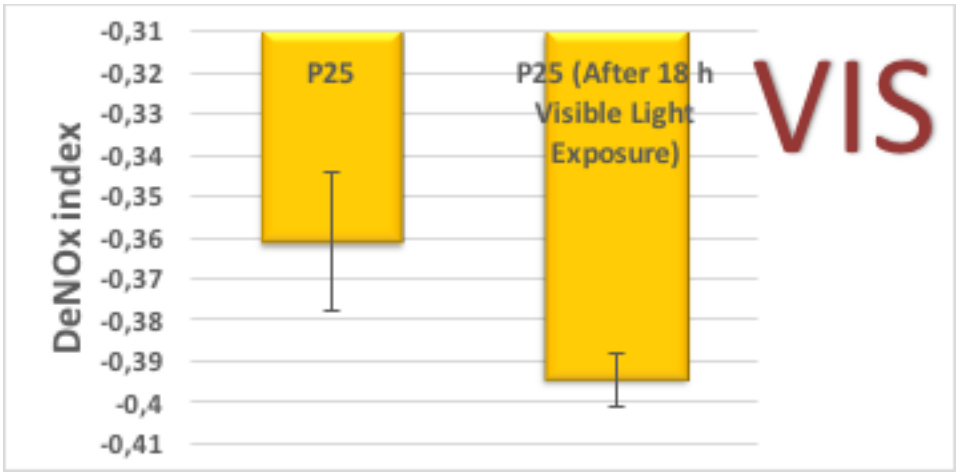


Figure 51. DeNOx index results for titanium dioxide (P25) under visible light.

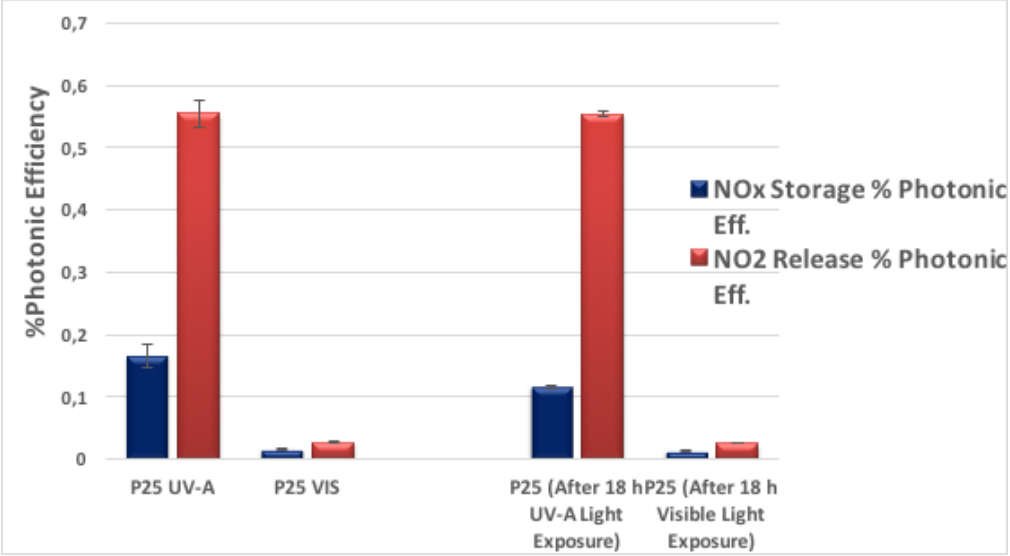


Figure 52. Comparison of %Photonic efficiency results for titanium dioxide (P25) under UV-A and visible light irradiation.

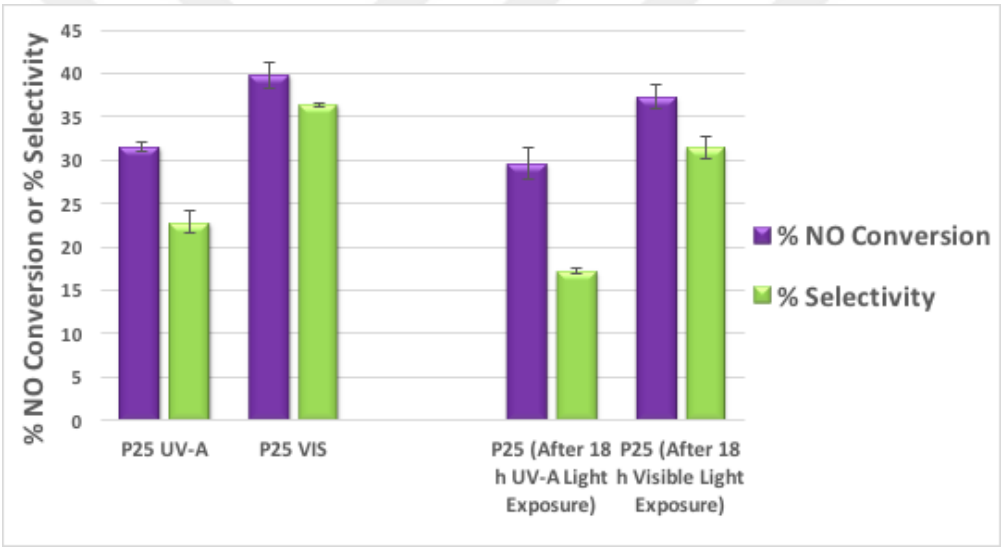


Figure 53. Comparison of % NO Conversion & % Selectivity results for titanium dioxide (P25) under UV-A and visible light irradiation.

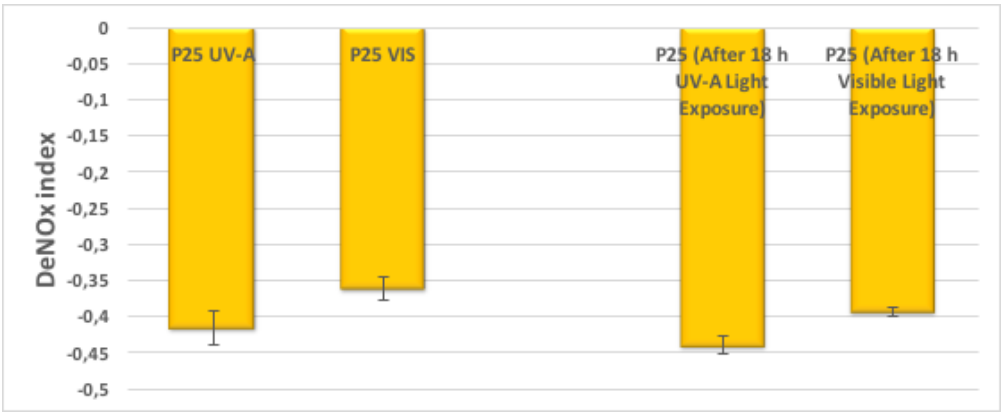


Figure 54. Comparison of DeNOx index results for titanium dioxide (P25) under UV-A and visible light irradiation.

When PHONOS performances under UV-A and VIS light sources are compared, it can be noticed that although titanium dioxide is regarded as a UV-active photocatalyst, in terms of %NO conversion & % selectivity, it seems to be more active under visible light irradiation (Figure 53). However, it should be taken into account that by replacing the UV-A light source with the currently chosen visible light source, the number of incoming photons are also increased by 15 times. The results of photocatalytic activity per photon are given in Figure 52. Since % photonic efficiency is an incoming photon normalized quantity, it is easier to observe what each photon does. This data also supports the statement that titanium dioxide is a UV active photocatalyst and that the high %NO conversion results under visible light can be attributed to the huge number of incoming photons. Nonetheless, under either of these light sources, titanium dioxide has a negative DeNOx index suggesting that its overall effect is toxication due to NO_2(g) production.

3.2.2. EFFECT OF CdTe QUANTUM DOTS ON THE PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE (P25)

Different volumes of aqueous CdTe quantum dot suspension were added onto P25 titanium dioxide in order to enhance its photocatalytic performance. In Figure 55, the % photonic efficiency results were demonstrated for different loadings of CdTe on titanium dioxide tested under UV-A light irradiation. It can be observed that by the addition of CdTe quantum dots, NO_x storage increased significantly. More surprisingly, the amount of NO_2(g) release decreased dramatically. For the NO_x storage % photonic efficiency results, there is a volcano plot with a maximum at 1.0 CdTe/P25 sample. Introducing CdTe quantum dots onto titania increased both % NO conversion and % selectivity results (Figure 56). For 1.0 CdTe/P25 sample, % selectivity value exceeded 90%. Thus, a positive DeNOx index was obtained. In Figure 57, it can be observed that adding CdTe quantum dots to titania, changes the negative DeNOx index of pure titania to positive values, rendering the CdTe/P25 system a preferable catalyst with a net detoxication effect.

In order to examine the photocatalytic performance of the aged catalyst, CdTe/P25 composite materials were exposed to UV-A light for 18 h in air before the measurement starts. The effect of aging is demonstrated in Figure 58-60.

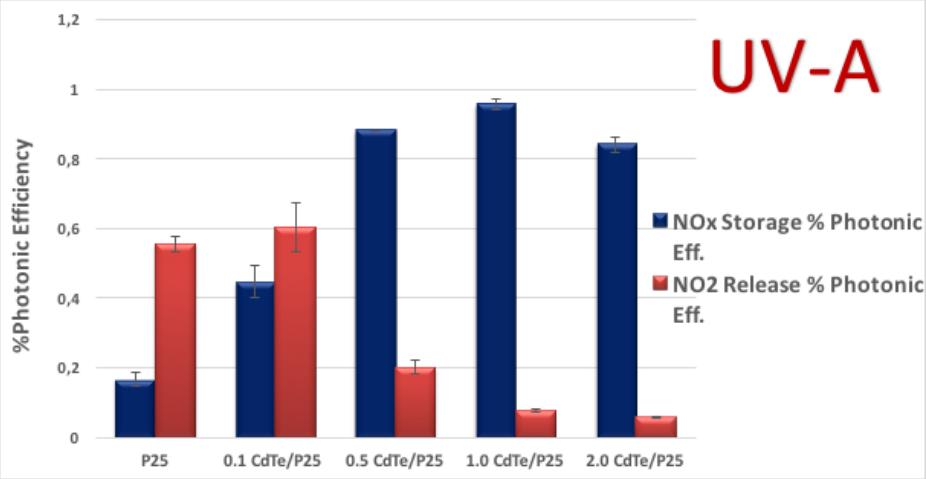


Figure 55. %Photonic efficiency results for CdTe/P25 composites under UV-A light.

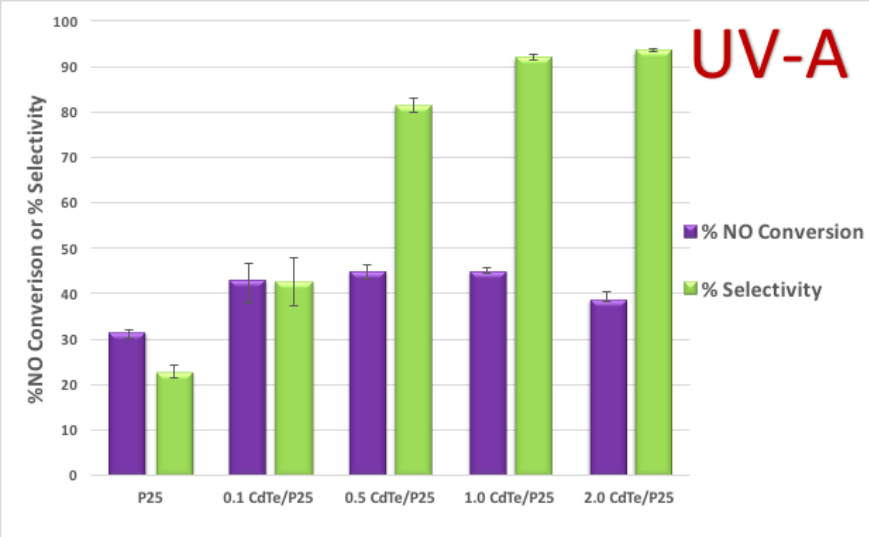


Figure 9. % NO Conversion & % Selectivity results for CdTe/P25 composites under UV-A light.

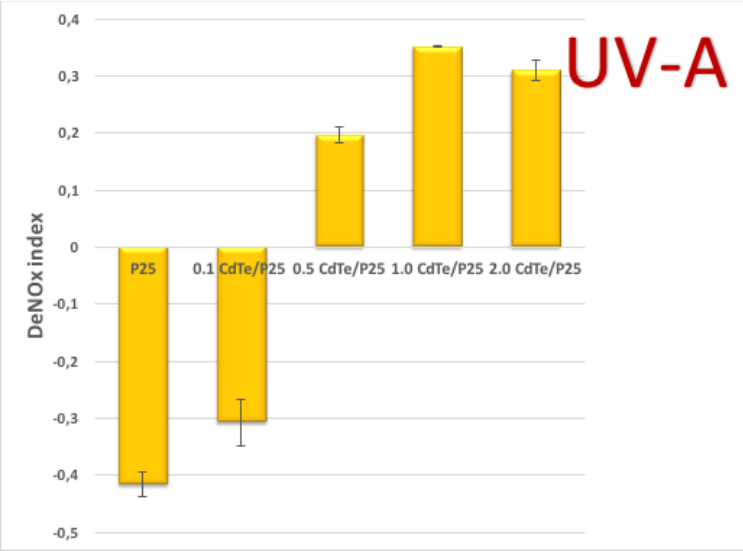


Figure 57. DeNOx index results for CdTe/P25 composites under UV-A light.

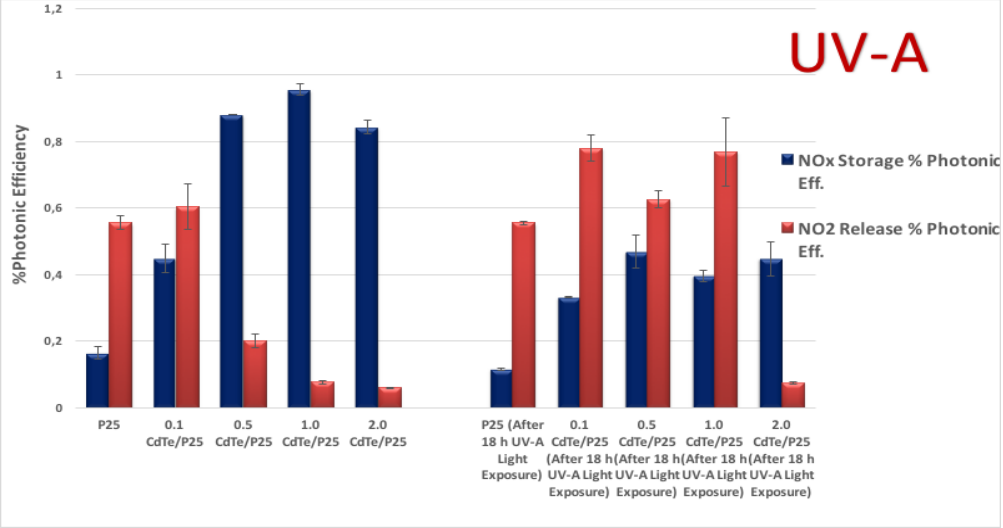


Figure 58. %Photonic efficiency results for fresh and aged CdTe/P25 composites under UV-A light.

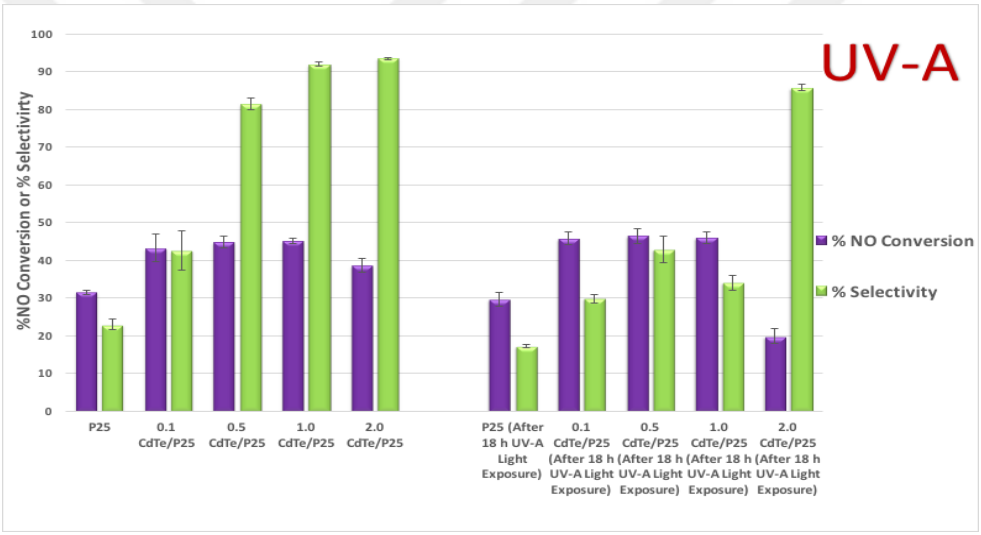


Figure 59. NO Conversion & % Selectivity results for fresh and aged CdTe/P25 composites under UV-A light.

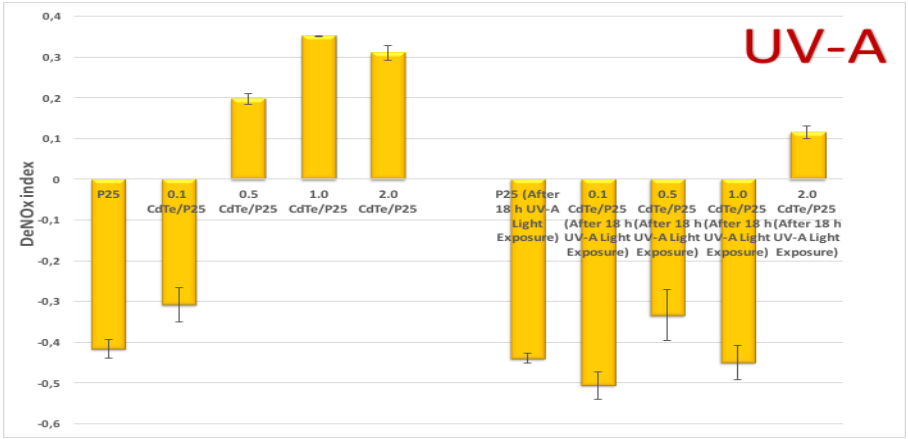


Figure 60. DeNOx index results for for fresh and aged CdTe/P25 composites under UV-A light.

In Figure 60, it can be noticed that the aged catalysts do not perform as good as their fresh forms. There is a decrease in the NO_x storage values and an increase in the NO_2 release after the aging of the catalyst. It should be pointed out that even after aging, CdTe/P25 composite materials outperform the bare titanium dioxide photocatalyst. Figure 59 demonstrates that % NO conversion stays almost constant for all CdTe loadings after aging except for the sample 2.0 CdTe/P25, while % selectivity decreases drastically as compared to the fresh forms. This is an indication that after aging, under UV-A light irradiation, CdTe/P25 catalysts start to deactivate. It is worth mentioning that for high CdTe loadings such as 2.0 CdTe/P25, even after 18 h UV-A aging photocatalyst still outperforms P25 benchmark and reveals a positive $DeNO_x$ index.

The effect of VIS light irradiation on CdTe/P25 composite materials were also examined. Figure 61 shows the % photonic efficiency results of different loadings of CdTe/P25 samples. Similar to UV-A light case, upon incorporation of CdTe onto P25 titania, a great increase in NO_x storage and a drastic drop in the amount of NO_2 gas release are observed. Figure 62 shows that there is a volcano plot with a maximum at 1.0 CdTe/P25 sample. As compared to pure P25, CdTe/P25 catalysts reveal a slight increase in %NO conversion; however, % selectivity values can reach up to 97%. Therefore, positive DeNOx index values are obtained (Figure 63). Thus, fresh CdTe/P25 composite materials can be regarded as a 'preferable catalyst' under VIS light illumination.
Figure 64 exhibits the effect of aging on the % photonic efficiency results of CdTe/P25 composite materials. A drastic decline in NO_x storage % photonic efficiencies and a slight change in NO_2 release % photonic efficiencies were observed.

In order to understand the origin of the higher NO_x storage capacity of CdTe/P25, some control experiments were conducted. These experiments were geared towards identifying the catalytic functionality of the individual structural components of the catalyst architecture as well as the influence of the QD dispersant medium (i.e. H_2O). In order to understand the effect of the dispersant (H_2O), H_2O/P25 samples were prepared and tested with the same volumes used in the CdTe/P25 preparation. These experiments are discussed in the next section.

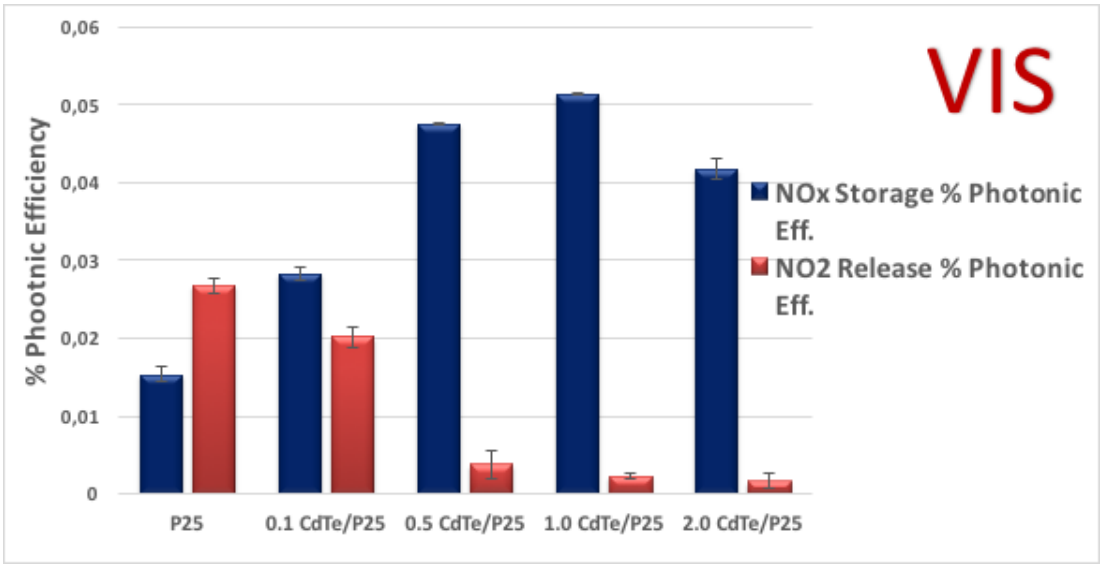


Figure 61. %Photonic efficiency results for CdTe/P25 composites under visible light.

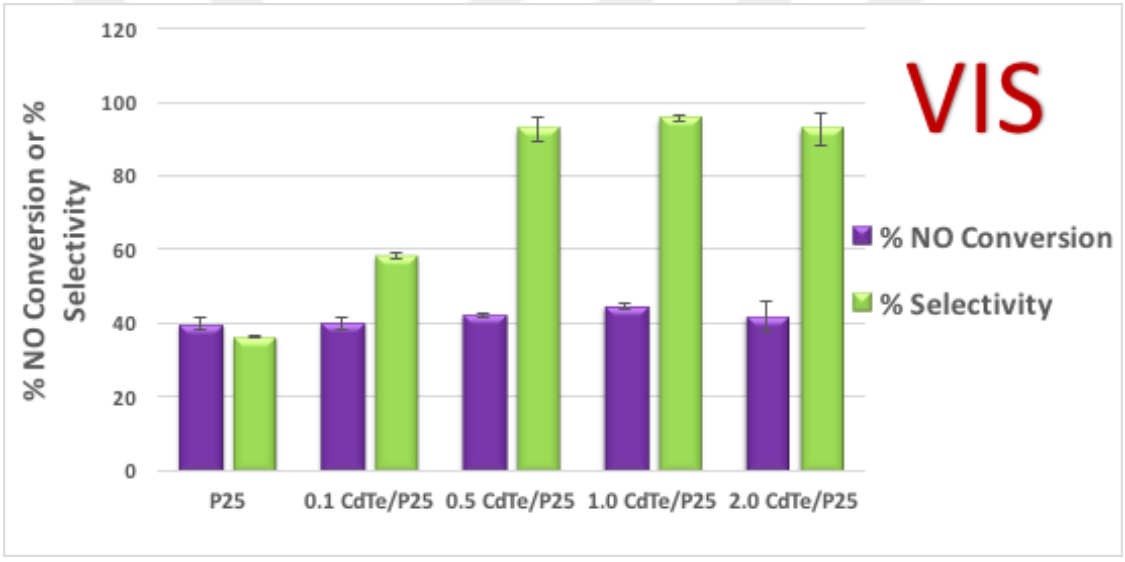


Figure 62. % NO Conversion & % Selectivity results for CdTe/P25 composites under visible light.

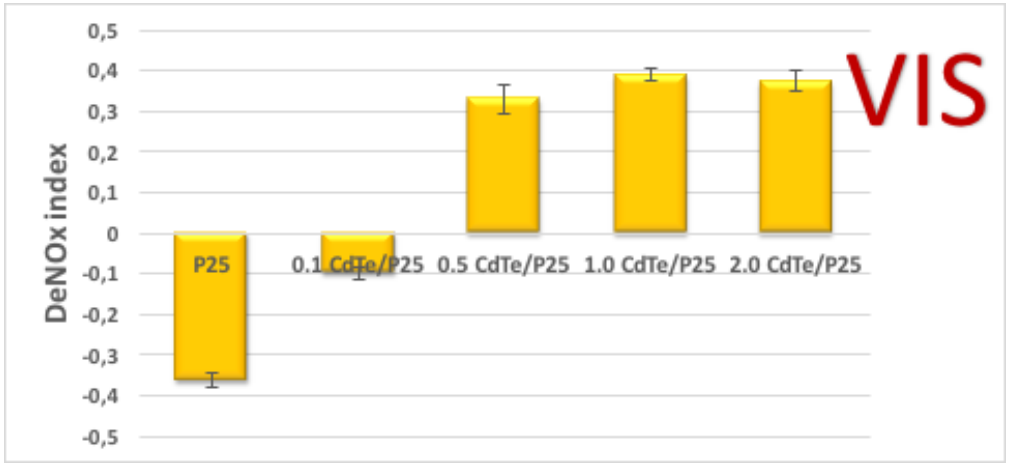


Figure 63. DeNOx index results for for CdTe/P25 composites under visible light.

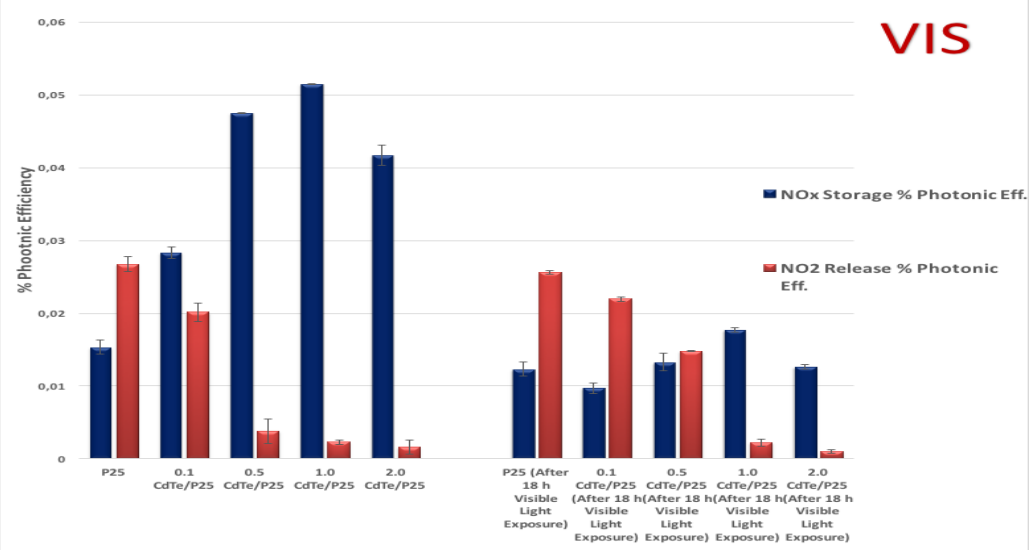


Figure 64. %Photonic efficiency results for fresh and aged CdTe/P25 composites under visible light.

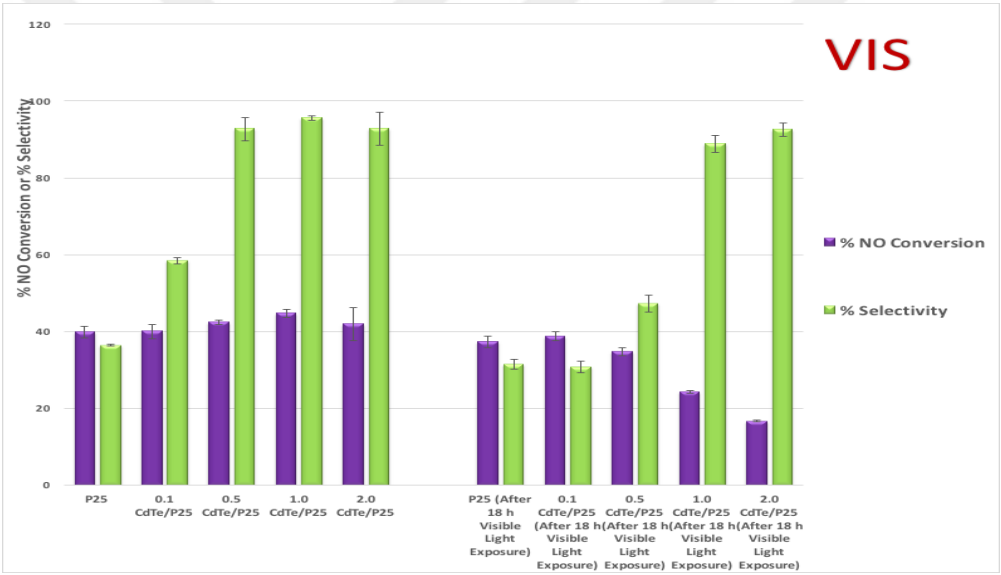


Figure 65. X20. NO Conversion & % Selectivity results for fresh and aged CdTe/P25 composites under visible light.

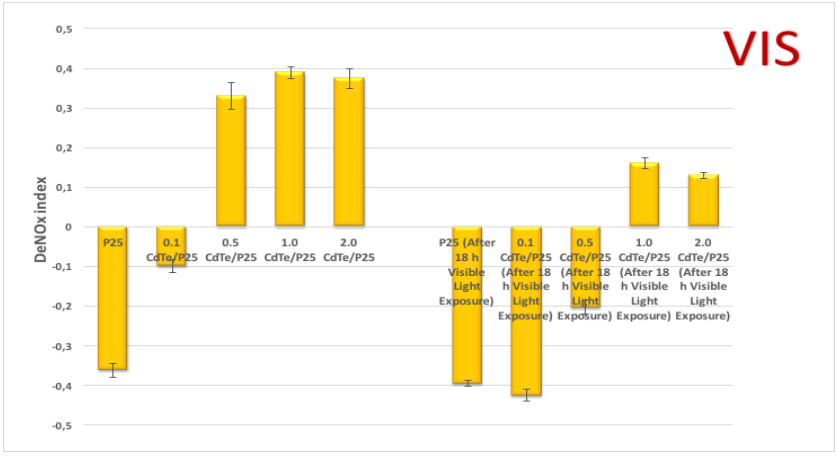


Figure 66. DeNOx index results for for fresh and aged CdTe/P25 composites under visible light.

3.2.3. EFFECT OF ADSORBED-WATER ON TiO_2 PHOTOCATALYSIS

The CdTe quantum dots are suspended in aqueous medium, therefore in order to understand the effect of the dispersant; the effect of water on titania photocatalysis should also be studied. As mentioned before, water is crucial for the photocatalytic NO_x oxidation and storage because it acts as the electrolyte of this photoelectrochemical process [19].

Another important function of water is that it can fill the oxygen vacancies on the titania surface created by UV light exposure. Hence a hydrophobic titania surface can turn into a hydrophilic surface upon UV exposure as shown in Figure 67 [26].

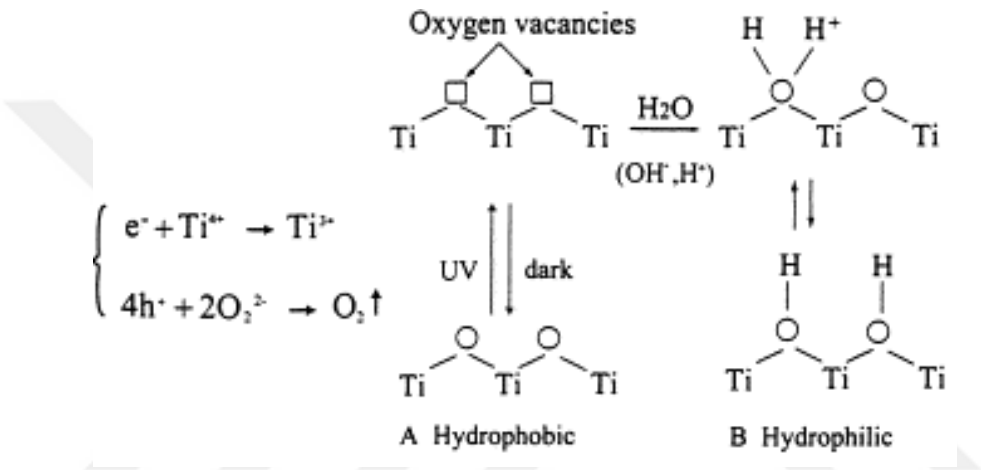


Figure 67. Mechanism of photo-induced hydrophilicity of titanium dioxide surfaces. Reprinted from Ref. 26 Copyright 2018 with permission from Elsevier [26].

Hence with the addition of water molecules on titania surface, there will be more hydroxide and hydrogen ions, which would be expected to enhance the photocatalytic activity of titanium dioxide.

Figure 68 demonstrates the effect of adsorbed water on titania photocatalysis under UV-A light irradiation. There seems to be a proportional increase of NO_x storage with the added volume of H_2O. However, addition of water also increases the amount of released NO_2 as well. Concomitant increase in the % NO conversion values can also be seen in Figure 69, as well as an increase in terms of % selectivity. This is an indication that hydroxide anions can be utilized both for NO oxidation and NO_x storage. When different volumes of added H_2O are compared, it can be argued that water molecules facilitate NO conversion and higher amounts of water expedite NO_x storage.

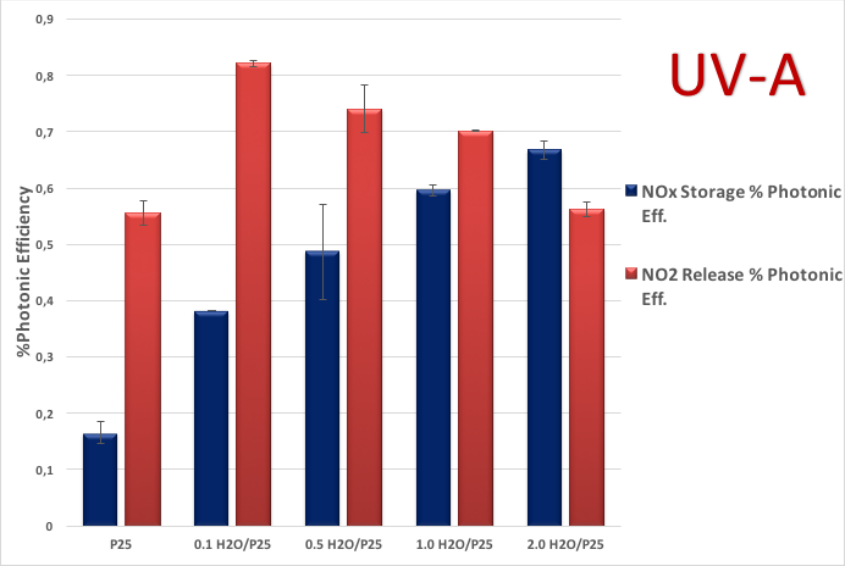


Figure 10. %Photonic efficiency results for H_2O/P25 samples under UV-A light.

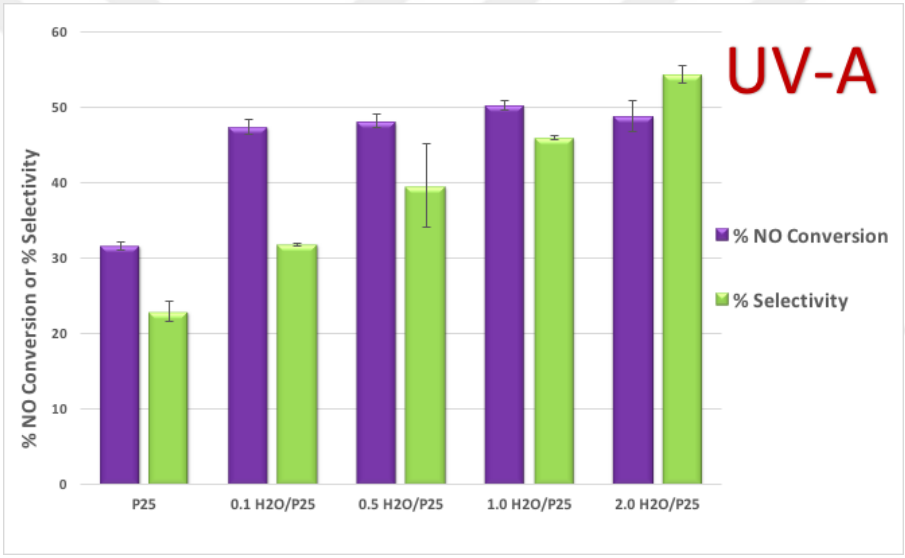


Figure 69. % NO Conversion & % Selectivity results for H_2O/P25 samples under UV-A light.

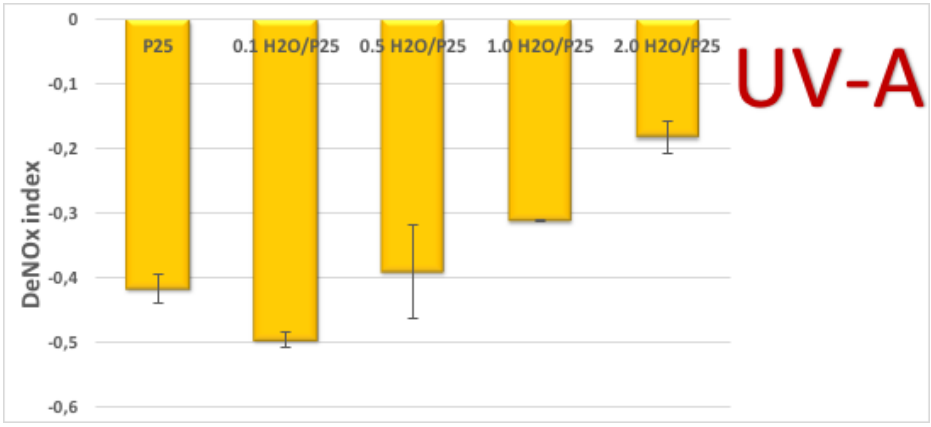


Figure 70. DeNOx index results for H_2O/P25 samples under UV-A light.

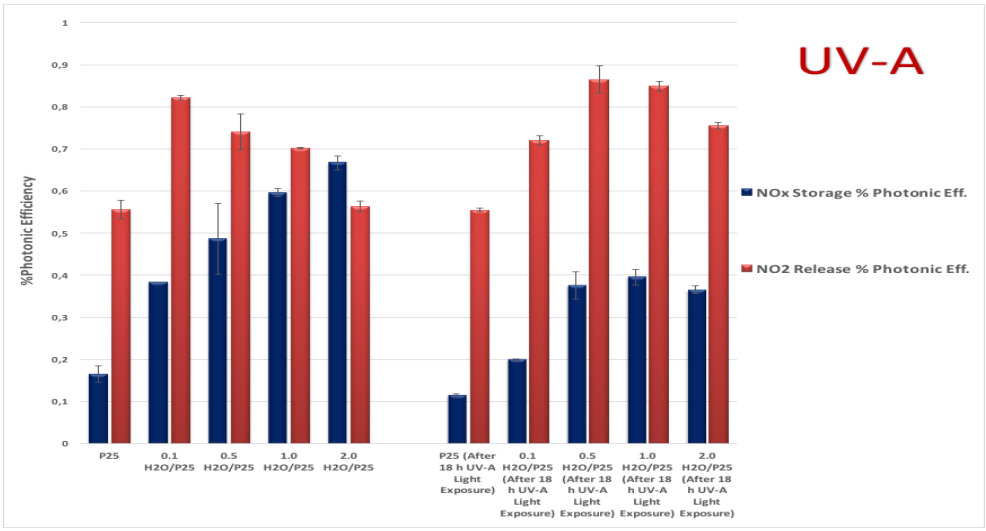


Figure 71. %Photonic efficiency results for fresh and aged H_2O/P25 samples under UV-A light.

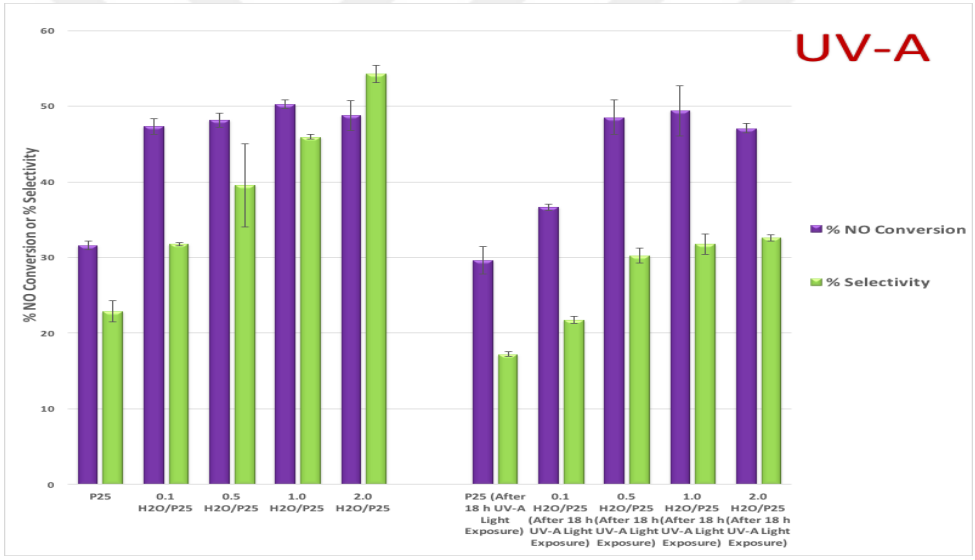


Figure 72. NO Conversion & % Selectivity results for fresh and aged H_2O/P25 samples under UV-A light.

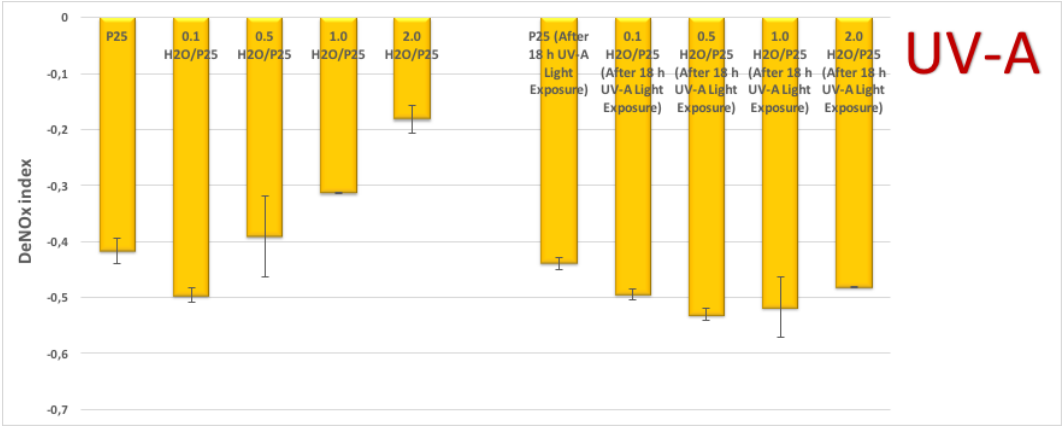


Figure 73. DeNOx index results for fresh and aged H_2O/P25 samples under UV-A light.

When the photocatalytic activity of H_2O/TiO_2 samples were examined after 18 h of UV-A irradiation, a slight decrease in NO conversion and a drastic drop in % selectivity can easily be observed (Figure 72). This indicates the surface saturation with oxidation products during 18 h of irradiation in air. As a result, with almost constant NO conversion and much less NO_x storage, the $DeNO_x$ index of spent catalyst is much more negative (Figure 73).

Switching the light source to visible light does not have as obvious influence as in UV-A light case. There is still a slight increase in terms of NO conversion and % selectivity and with increasing volume of added H_2O, the % selectivity increases (Figure 75). Similar to the results under UV-A light irradiation, 0.1 H_2O/TiO_2 sample has the most negative DeNOx index (Figure 76).

For the spent catalysts under visible light irradiation, there is a noticeable decrease in terms of NO conversion and selectivity results (Figure 78). This can be also attributed to the surface saturation with oxidation products during 18 h of visible light irradiation. The impact of water amount is not as prominent as in the UV-A light case. Therefore it can be claimed that hydroxide anions cannot do much chemically unless they are used by photo-generated excitons or transport to oxygen deficiencies on the catalyst surface. Since P25 has a band gap greater than 3.0 eV, excitons generation in VIS light irradiation is limited. Hence these lesser number of VIS photo-generated excitons can utilize a limited amount of hydroxide anions. As expected, the DeNOx index values are negative.

As the overall assessment of the control experiments associated with the effect of water, it can be stated that water alone cannot be solely responsible for the positive DeNOx index values obtained for CdTe/P25 samples under UV or VIS light irradiation. Thus, as the next step the effect of the capping agent (i.e. thioglycolic acid) on the PHONOS activity is investigated.

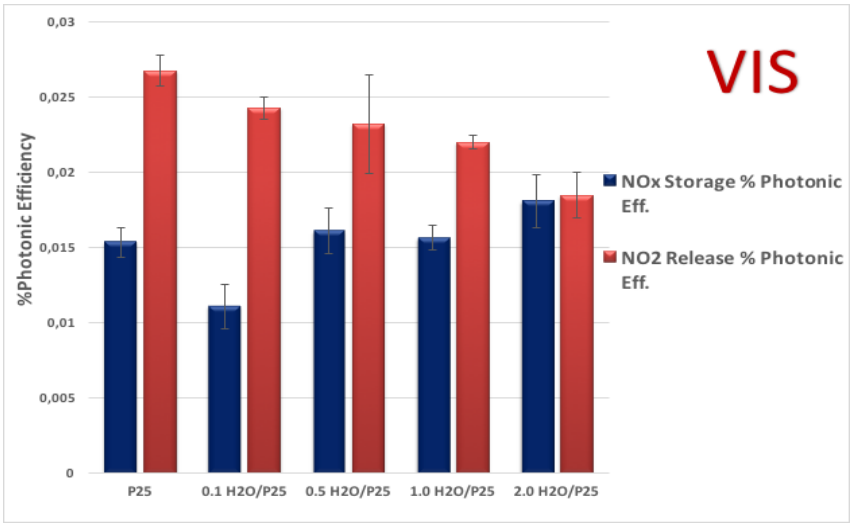


Figure 74. %Photonic efficiency results for H_2O/P25 samples under visible light.

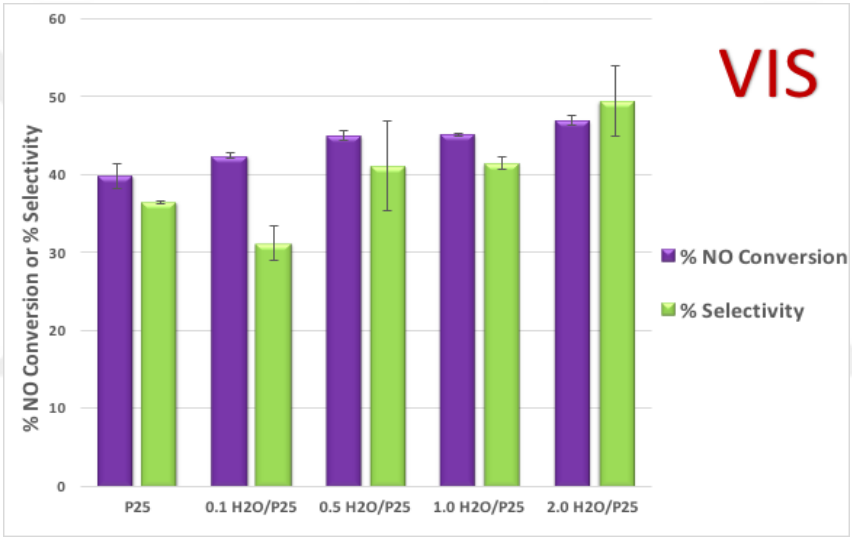


Figure 75. % NO Conversion & % Selectivity results for H_2O/P25 samples under visible light.

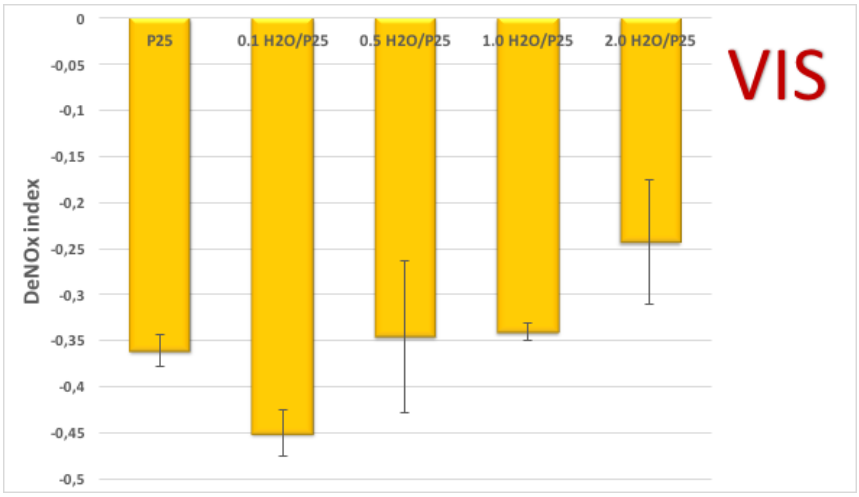


Figure 76. DeNOx index results for H_2O/P25 samples under visible light.

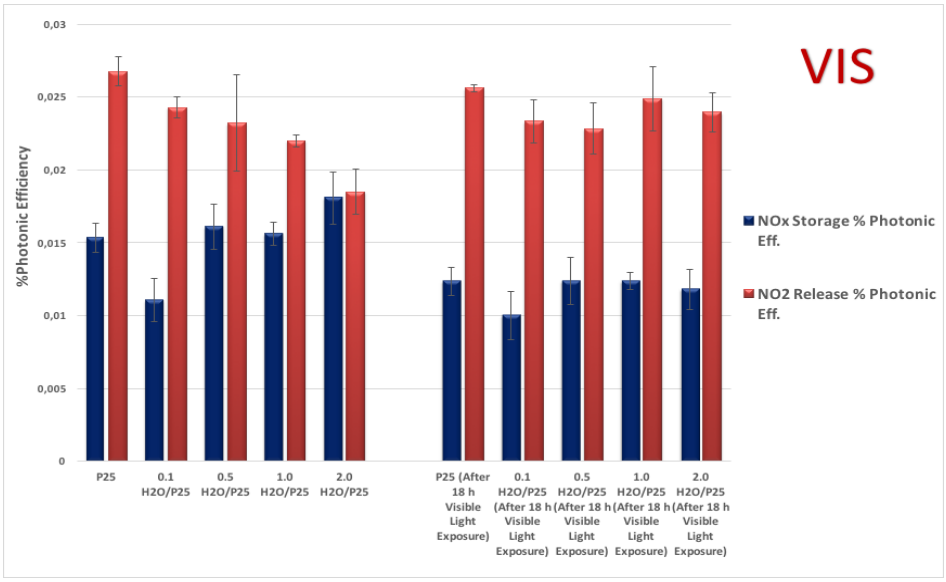


Figure 77. %Photonic efficiency results for fresh and aged H_2O/P25 samples under visible light.

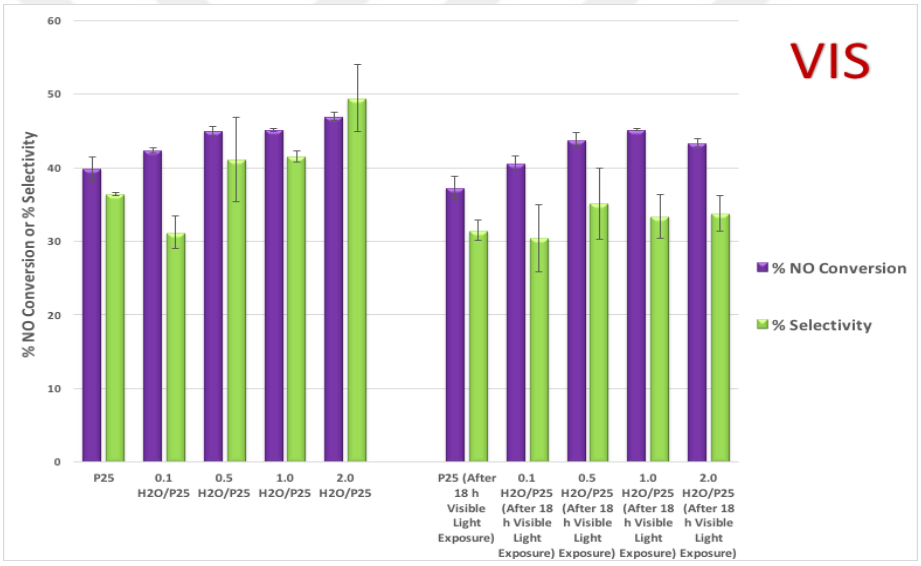


Figure 78. % NO Conversion & % Selectivity results for fresh and aged H_2O/P25 samples under visible light.

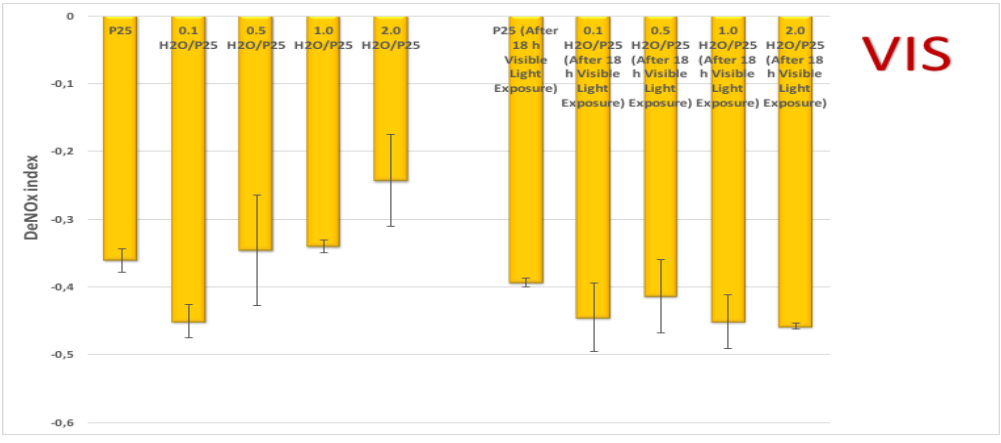


Figure 79. DeNOx index results for fresh and aged H_2O/P25 samples under visible light.

3.2.4. EFFECT OF THIOGLYCOLIC ACID ON TiO_2 PHOTOCATALYSIS

As CdTe quantum dots were capped with thioglycolic acid, the effect of this ligand on titania photocatalysis should also be studied. For this study, varying volumes of thioglycolic acid are dropcasted on titanium dioxide.

Figure 80 clearly demonstrates that under visible light irradiation, thioglycolic acid (TGA) poisons the titanium dioxide and blocks its active sites completely. Under these conditions, DeNOx index is not relevant and approaches as there is no NO conversion inside the reactor.

Similarly, under UV-A light irradiation, addition of thioglycolic acid also poisons the active sites of titanium dioxide. It is surprising that even a tiny amount of 0.1 ml of thioglycolic acid can be sufficient to completely suppress the active sites of titania. Figures 83, 84 and 85 demonstrate clearly that titania can no longer convert NO in the presence of TGA. However, it does not suggest that thioglycolic acid cannot adsorb/store NO_2. In the experiments associated with Figures 80-85, as there is no conversion from NO to NO_2, it is not possible to observe any NO_2 storage.

Therefore, a new control group was prepared by using a mixture of thioglycolic acid and water. The mixture was prepared by using the same concentration of thioglycolic acid as its initial concentration in the reaction suspension of CdTe quantum dots. By using a mixture of thioglycolic acid and water, the TGA concentration can be diluted so that it does not poison titanium dioxide and addition of water can enhance the NO conversion slightly.

The mixture of thioglycolic acid and water is labeled as TGA(aq). Figure 86 demonstrates clearly that once NO is converted to NO_2 by titania, TGA can adsorb and store NO_2. Although the % NO conversion increases by the addition of TGA/water mixture, this increase is caused by water molecules as discussed previously. Increasing the volume of the TGA(aq) mixture from 0.1 ml to 0.5 ml, suppresses the photocatalytic activity. Under UV-A light exposure, using the TGA(aq) mixture, a positive DeNOx index cannot be achieved (Figure 88).

Under visible light irradiation, introducing TGA(aq) mixture decreases the % NO conversion slightly, whereas it increases the % selectivity (Figure 90). Nonetheless, similar to UV-A case, increasing the volume of the TGA(aq) mixture on titania results in a drastic drop in terms of % NO conversion. Although at low amounts of TGA(aq) (e.g. 0.1 ml) a positive DeNOx index can be achieved, it is not possible to sustain it after 18 h of light irradiation (Figure 91).

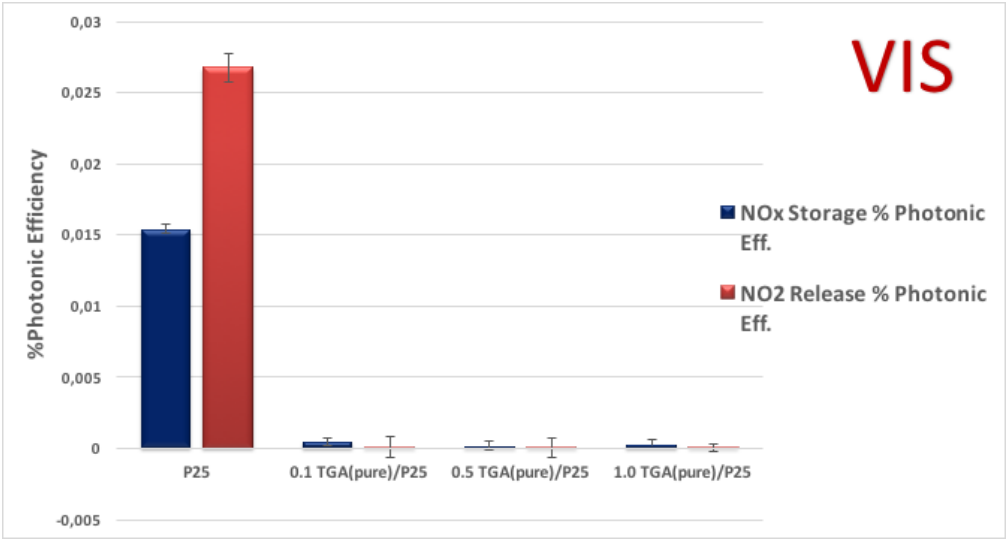


Figure 80. %Photonic efficiency results for TGA(pure)/P25 samples under visible light.

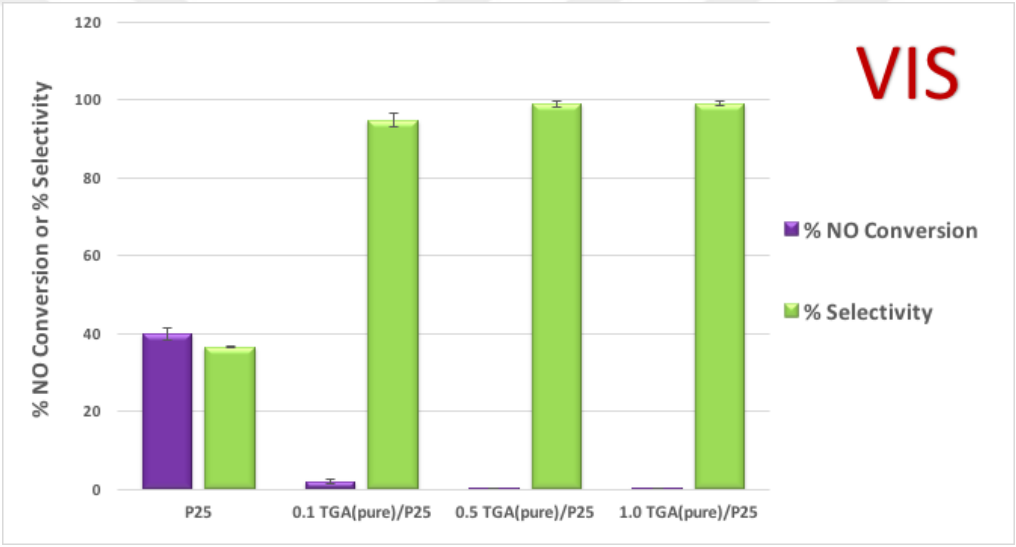


Figure 81. % NO Conversion & % Selectivity results for TGA(pure)/P25 samples under visible light.

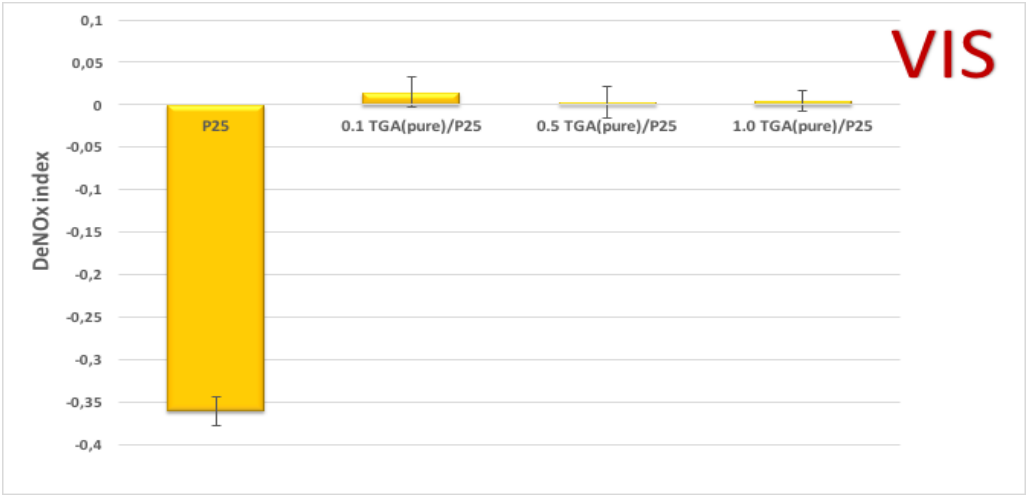


Figure 82. DeNOx index results for TGA(pure)/P25 samples under visible light.

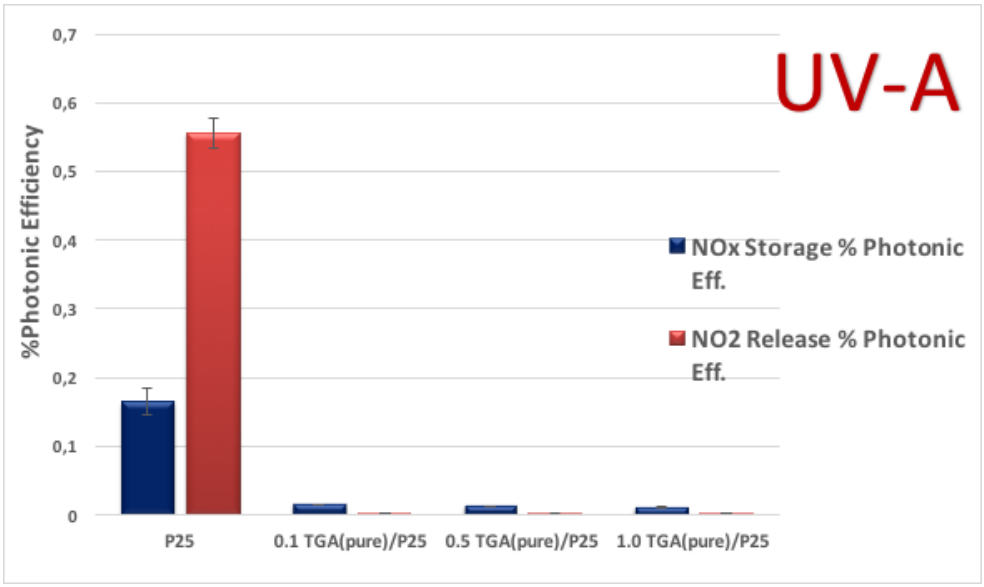


Figure 83. %Photonic efficiency results for TGA(pure)/P25 samples under UV-A light.

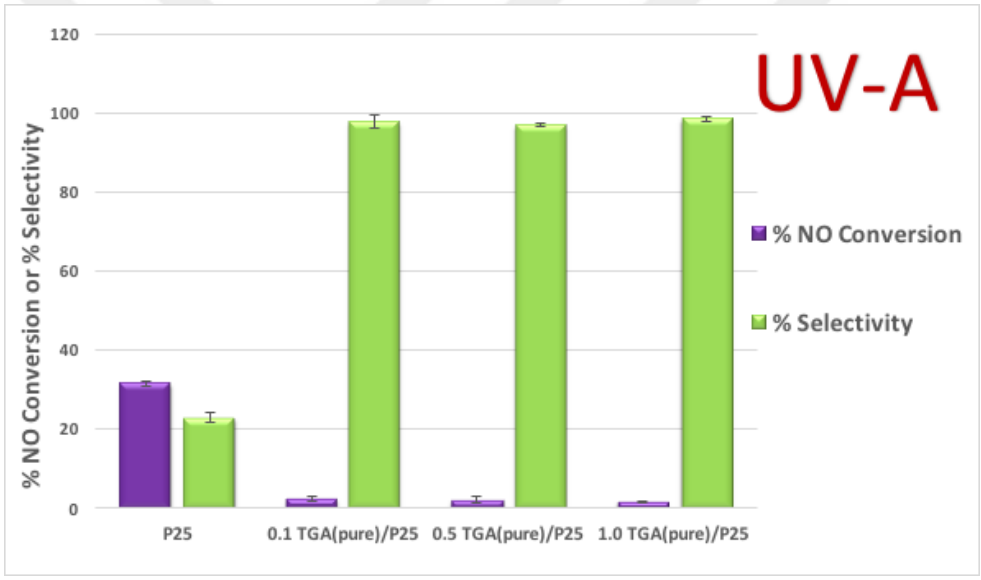


Figure 84. % NO Conversion & % Selectivity results for TGA(pure)/P25 samples under UV-A light.

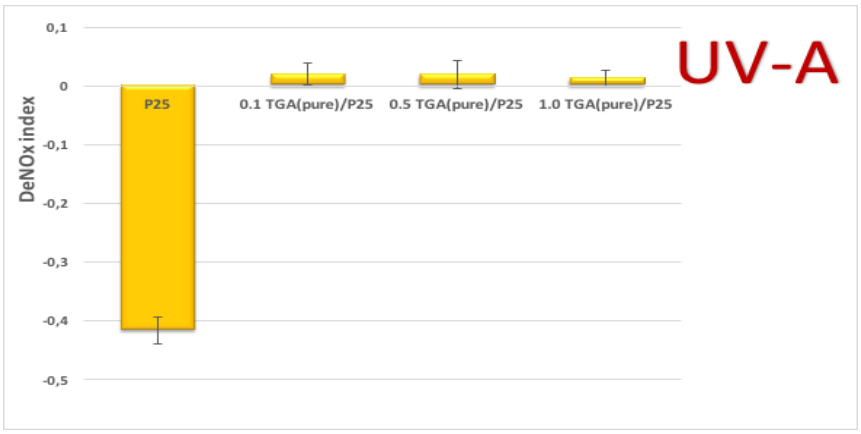


Figure 85. DeNOx index results for TGA(pure)/P25 samples under UV-A light.

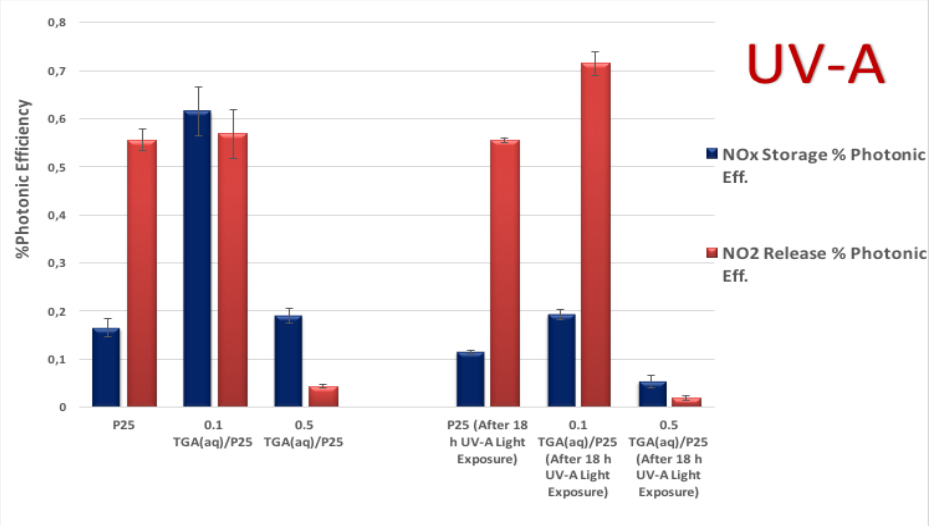


Figure 86. %Photonic efficiency results for fresh and aged TGA(aq)/P25 samples under UV-A light.

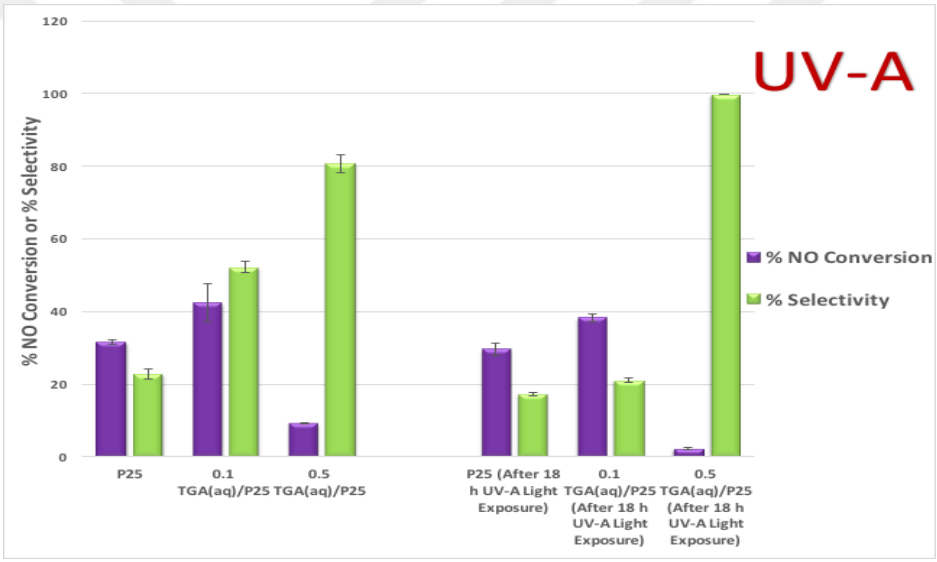


Figure 87. % NO Conversion & % Selectivity results for fresh and aged TGA(aq)/P25 samples under UV-A light.

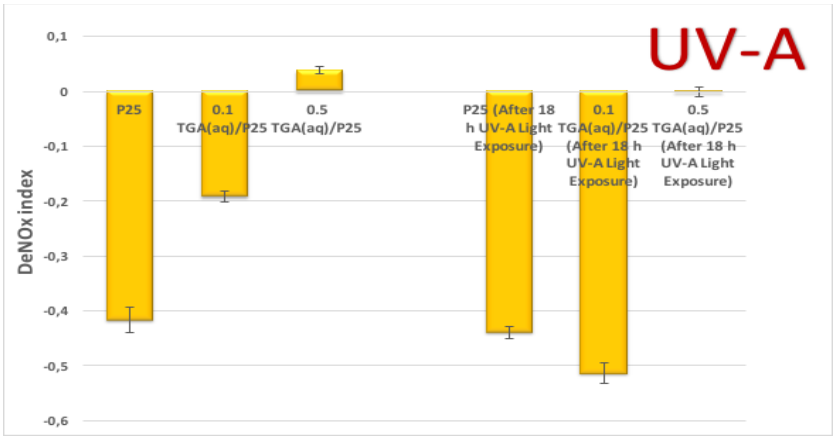


Figure 88. DeNOx index results for fresh and aged TGA(aq)/P25 samples under UV-A light.

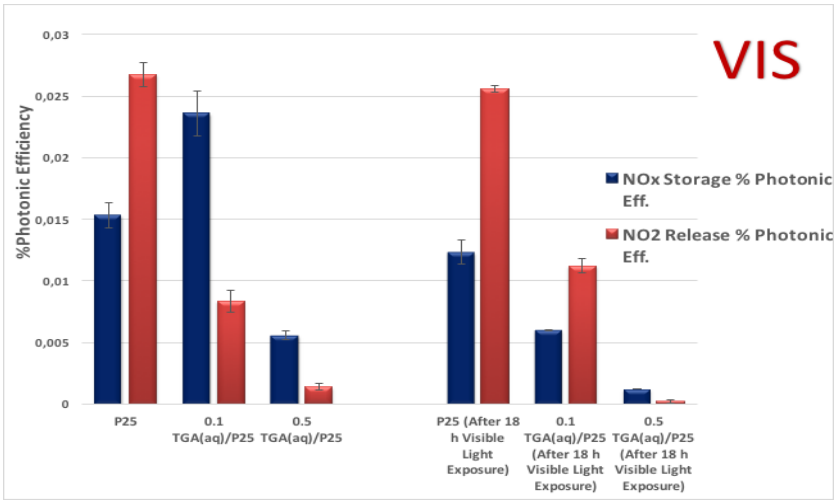


Figure 89. %Photonic efficiency results for fresh and aged TGA(aq)/P25 samples under visible light.

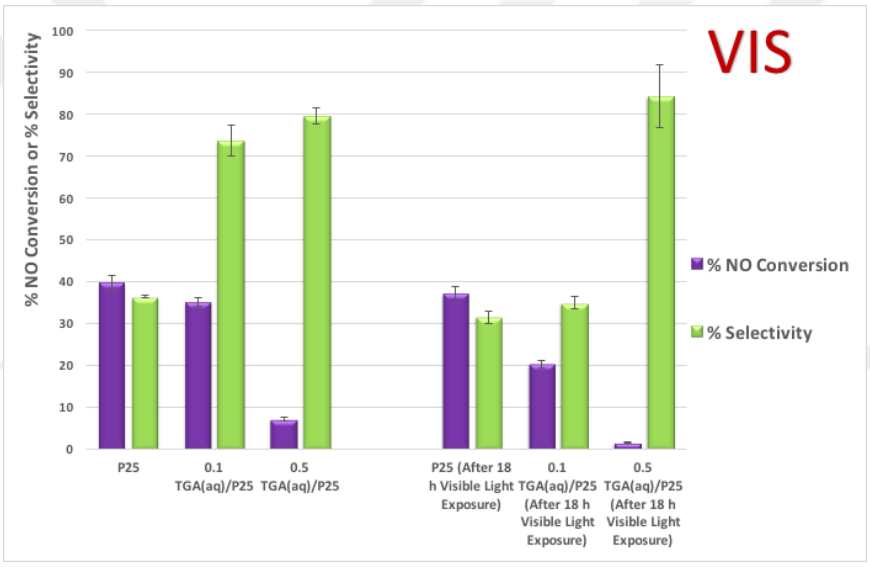


Figure 90. % NO Conversion & % Selectivity results for fresh and aged TGA(aq)/P25 samples under UV-A light.

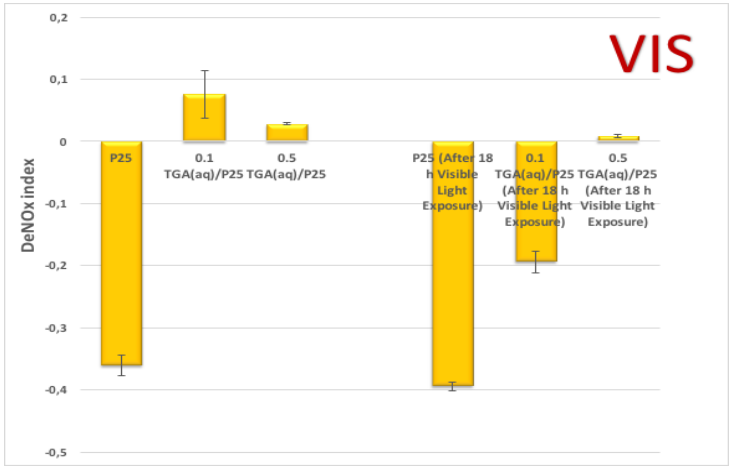


Figure 91. DeNOx index results for fresh and aged TGA(aq)/P25 samples under UV-A light.

3.2.5. CONTROL EXPERIMENTS WITH ALUMINA

In order to observe the photocatalytic effect of each structural component/additive in the absence of titania, titania was replaced with gamma alumina. Gamma alumina is preferred for control experiments as it has almost no photocatalytic activity towards NO conversion. Hence, it would be easier to show if the additives can do any photocatalysis without the base catalyst (i.e. titania).

Figure 92 clearly demonstrates that under visible light irradiation, the only material that can utilize the incoming photons is the CdTe/Alumina sample. It has a very high NO_x storage % photonic efficiency, which is more than two times of titanium dioxide's under visible light. For the rest of the samples, there seems to be no change. Analyzing Figure 93, it seems to be fair to claim that only CdTe quantum dots can oxidize NO to NO_2. As this conversion can only be observed under light irradiation, activity of the CdTe/Alumina sample cannot be attributed to simple chemical adsorption but associated with a photocatalytic process that employs the photo-generated electron-hole pairs. Water and thioglycolic acid neither can cause any photochemical process nor can bind to NO chemically. This indicates that for H_2O/TiO_2 and TGA(aq)/ TiO_2 samples, the photocatalytic NO conversion is done by titania. Once NO_2 is formed, TGA can chemically bind it to increase the % selectivity.

Under UV-A light irradiation, although there seems to be some NO conversion with TGA/alumina, the values are within the detection limits. For CdTe/alumina sample, there seems to be a very high NO conversion, which is caused by photo-generated electron-hole pairs by the quantum dots.

As a result, it can be argued that the enhancement of water on titania photocatalysis is not done by the hydroxide anions but by the radicals that are formed by photo-generated electron-hole pairs on titania. Moreover, as mentioned before, water can make the titania surface more hydrophilic so that it can utilize/adsorb more of the water vapor in the humidity and create more hydroxyl radicals to be used in photocatalytic reactions. Considering TGA alone, it is photocatalytically inactive and when placed on titania, it can poison titania even at low loadings. When its concentration is diluted with water, water can accelerate the conversion from NO to NO_2 and TGA can bind to NO_2. With CdTe QDs, there will be more photo-generated electron-hole pairs which can help conversion of NO to NO_2 and the resulting NO_2 can be oxidized further by these excitons or can bind to the capping on the QDs.

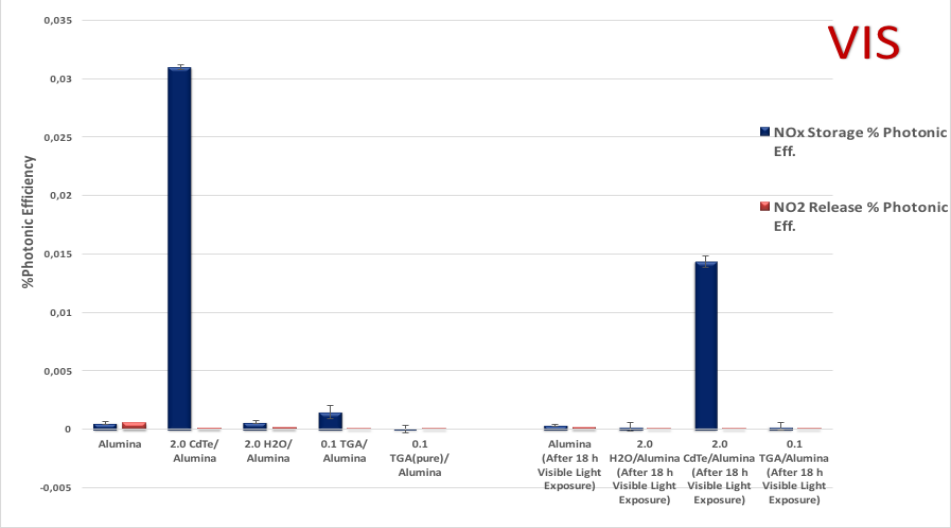


Figure 92. %Photonic efficiency results for alumina control samples under visible light.

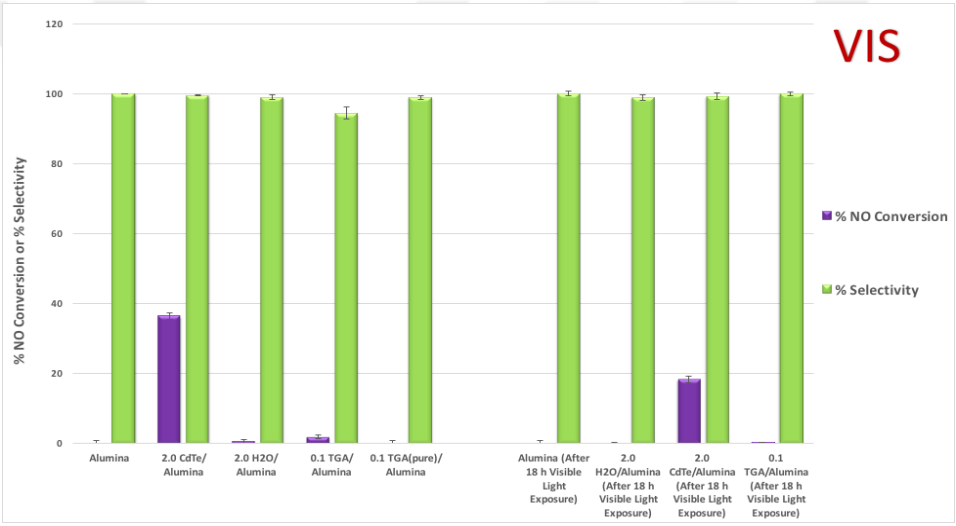


Figure 93. % NO Conversion & % Selectivity results for alumina control samples under visible light.

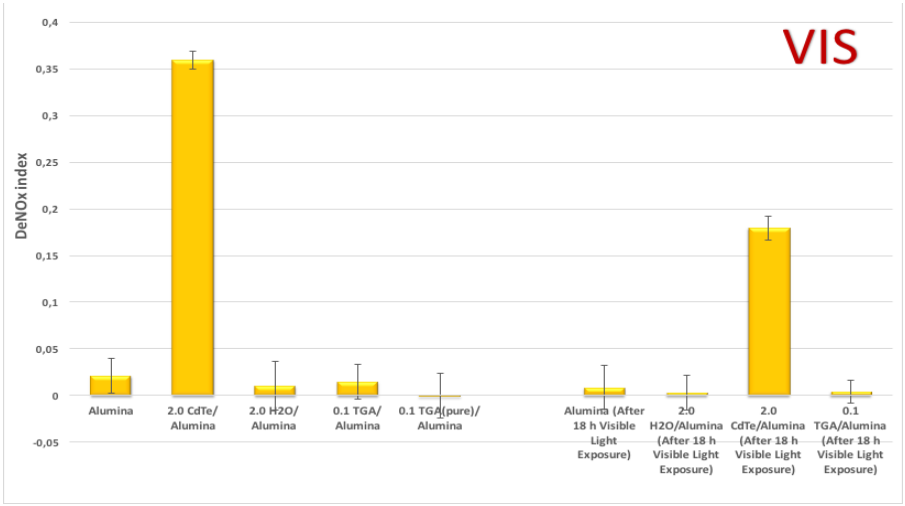


Figure 94. DeNOx index results for alumina control samples under visible light.

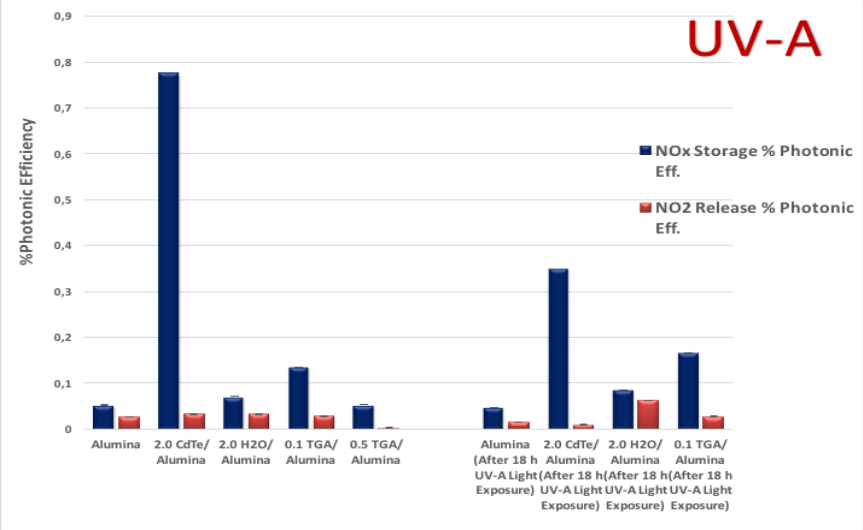


Figure 95. %Photonic efficiency results for alumina control samples under UV-A light.

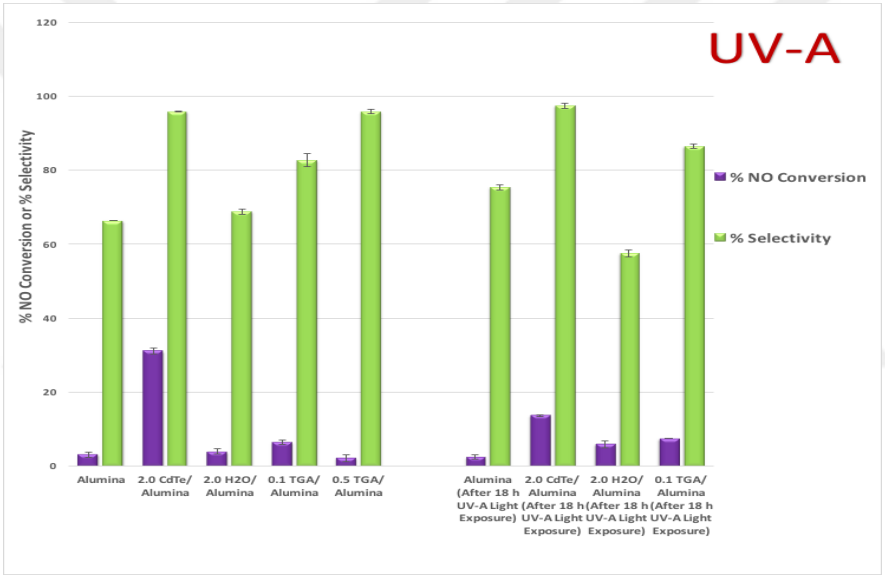


Figure 96. % NO Conversion & % Selectivity results for alumina control samples under UV-A light.

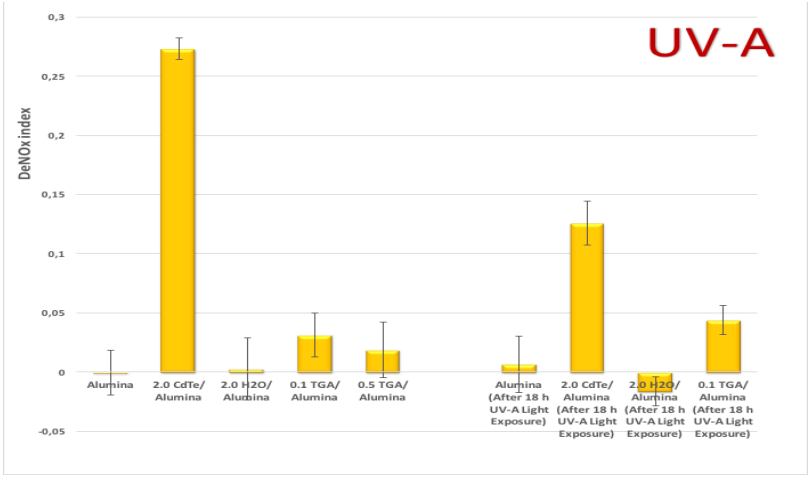


Figure 11. DeNOx index results for alumina control samples under UV-A light.

3.2.6. RE-USE MEASUREMENTS

In order to demonstrate the aging of the photocatalysts, repeated measurements were conducted without taking out the sample from the reactor. Under visible and UV-A light irradiation, the photocatalytic activity measurements for P25, 2.0 CdTe/P25 and 0.1TGA/P25 samples were conducted for 5 successive where each run lasted for 1 h. Although 1.0 CdTe/P25 is slightly better performing than 2.0 CdTe/P25; 2.0 CdTe/P25 is chosen for repeated measurements since it performs better after 18 h of light irradiation. Also, as it incorporates more CdTe QDs, it will be possible to preserve the activity for longer times. Along these lines, for TGA/P25 samples, the best performing catalyst in repeated measurements was 0.1 TGA/P25.

Under visible light irradiation, despite a slight decrease in terms of % selectivity, P25 seems to be very stable in terms of NO conversion (Figure 99). The NO conversion of the first run is higher for 2.0 CdTe than P25; however, it decreases for each run. In terms of selectivity, 2.0 CdTe/P25 seems to be the best photocatalyst. For 0.1 TGA/P25, there is a decrease in terms of both NO conversion and selectivity. Due to high selectivity values, 2.0 CdTe/P25 has always a positive DeNOx index. However, since TGA is only used for NO_2 storage, as it is being consumed, DeNOx index becomes negative similar to bare P25.

Under UV-A light irradiation, P25 seems to be still stable in terms of NO conversion (Figure 102); however, due to the saturation of the surface with oxidation products, the selectivity decreases. For 2.0 CdTe/P25, the starting NO conversion value is greater as compared to P25; however, it decreases with each run. For 0.1 TGA/P25, there is a different behavior due to the super hydrophilicity effect of P25 with water under UV-A illumination. Water can enhance the NO conversion as well as selectivity. TGA can be used for NO_2 storage but as it is being consumed, DeNOx index becomes much more negative similar to bare P25.

In Figures 104-109, 10 runs of 1 h measurements for 2.0 CdTe/P25 sample are demonstrated under both UV-A and visible light sources. It can be observed that after around the 5^{th} run, steady state can more or less be reached.

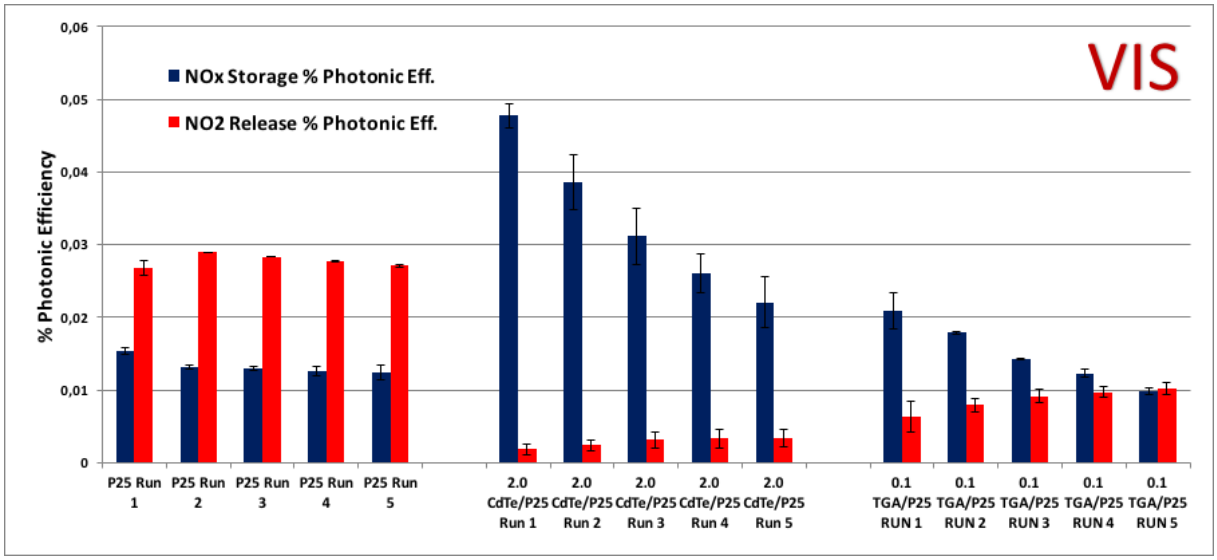


Figure 98. Re-use %photonic efficiency results for P25, CdTe/P25 and TGA/P25 samples under visible light.

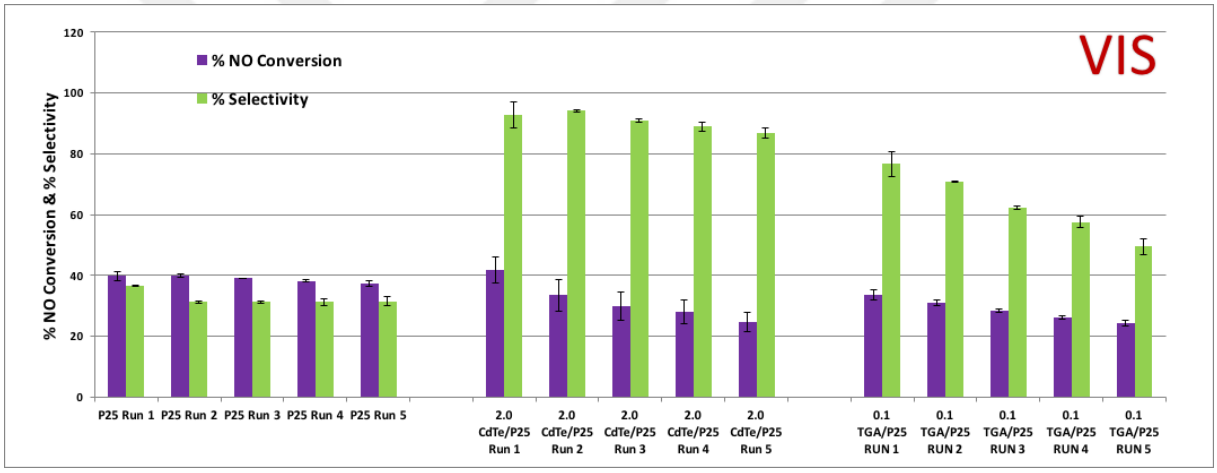


Figure 99. Re-use %NO conversion and % selectivity results for P25, CdTe/P25 and TGA/P25 samples under visible light.

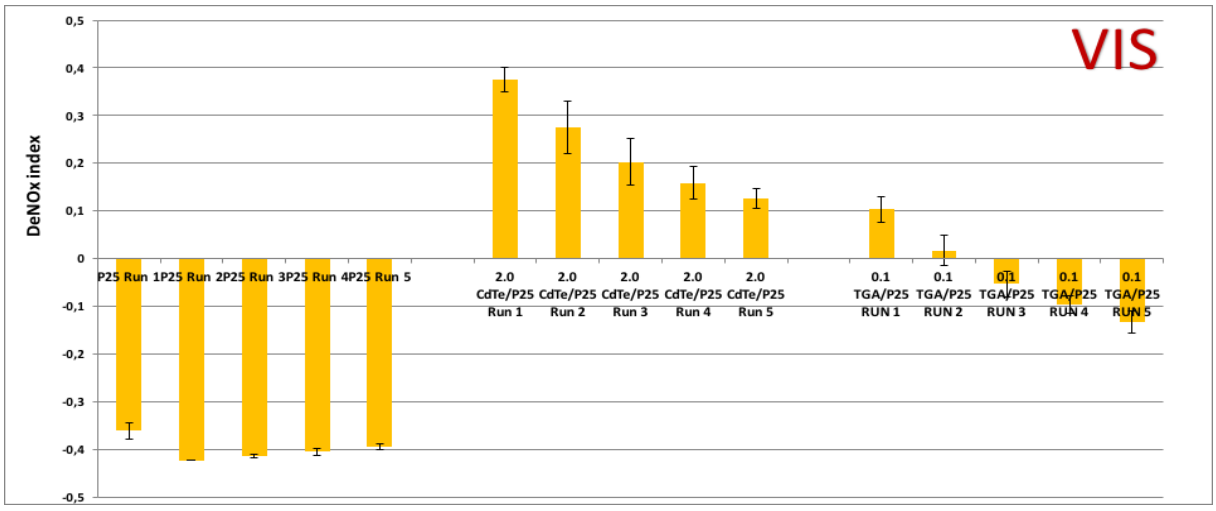


Figure 100. Re-use DeNOx index results for P25, CdTe/P25 and TGA/P25 samples under visible light.

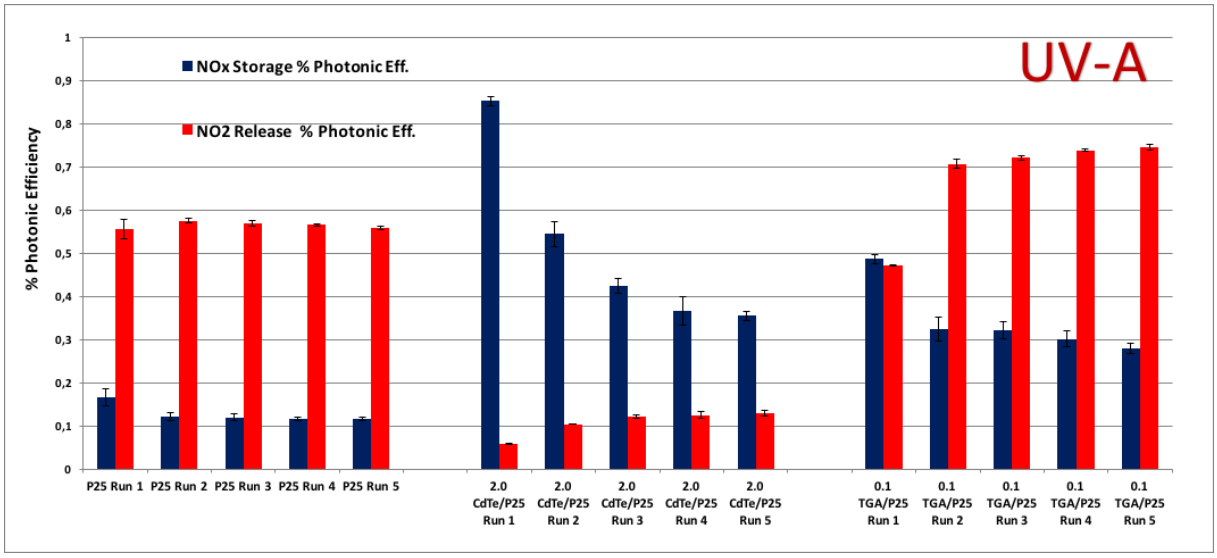


Figure 101. Re-use %photonic efficiency results for P25, CdTe/P25 and TGA/P25 samples under UV-A light.

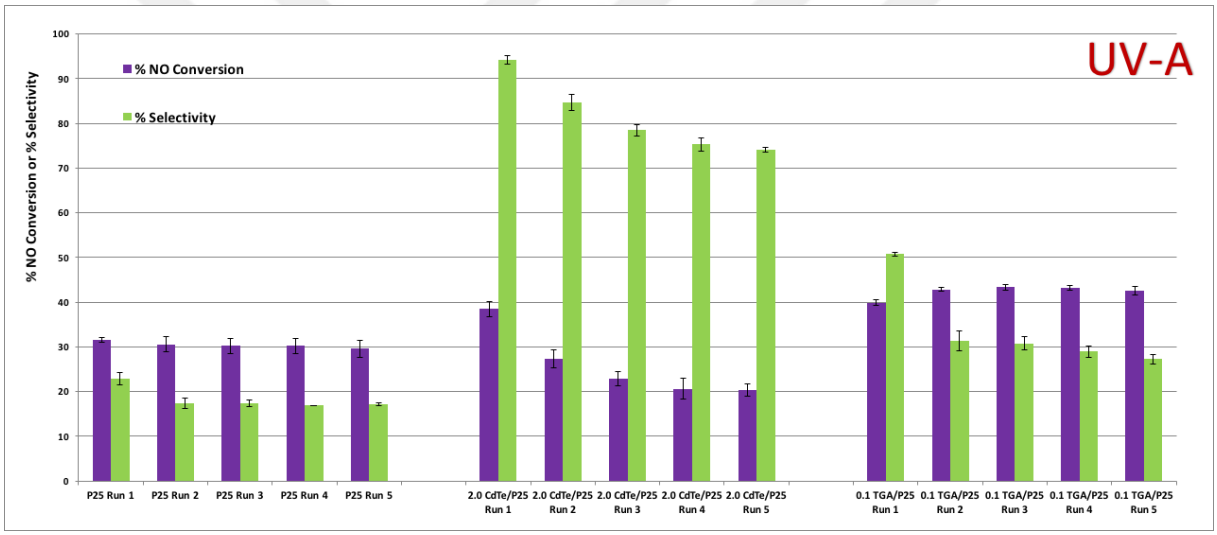


Figure 102. Re-use %NO conversion and % selectivity results for P25, CdTe/P25 and TGA/P25 samples under UV-A light.

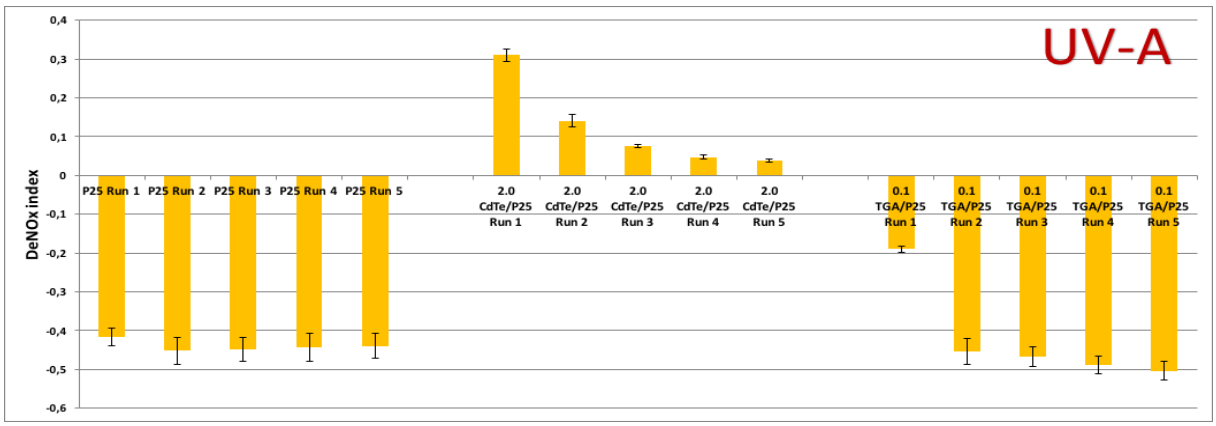


Figure 103. Re-use DeNOx index results for P25, CdTe/P25 and TGA/P25 samples under UV-A light.

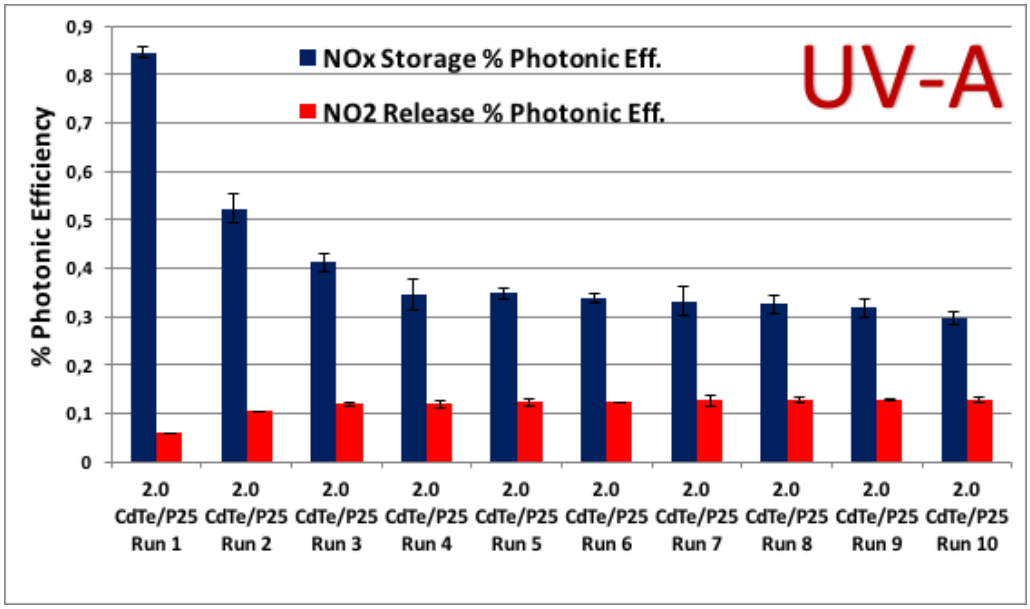


Figure 104. Re-use %photonic efficiency results for CdTe/P25 under UV-A light.

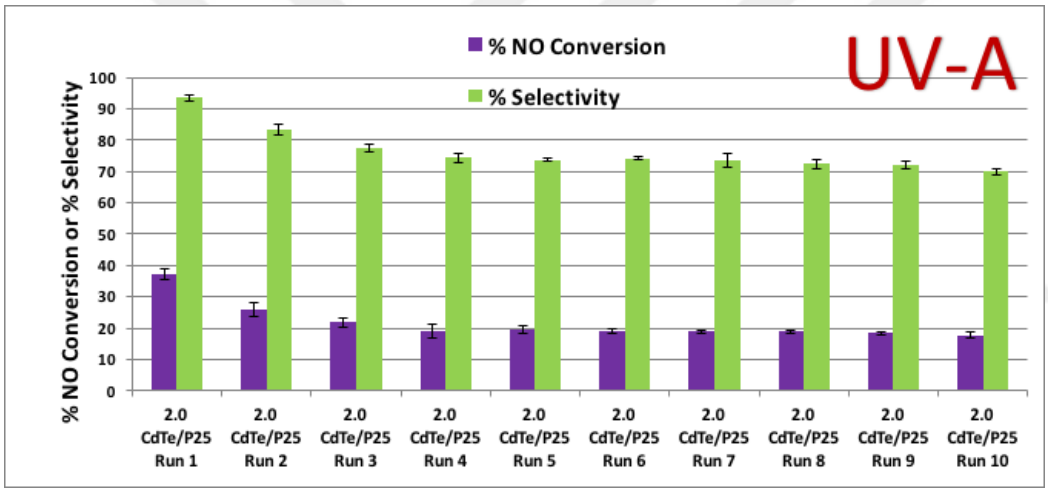


Figure 105. Re-use %NO conversion and % selectivity results for CdTe/P25 under UV-A light.

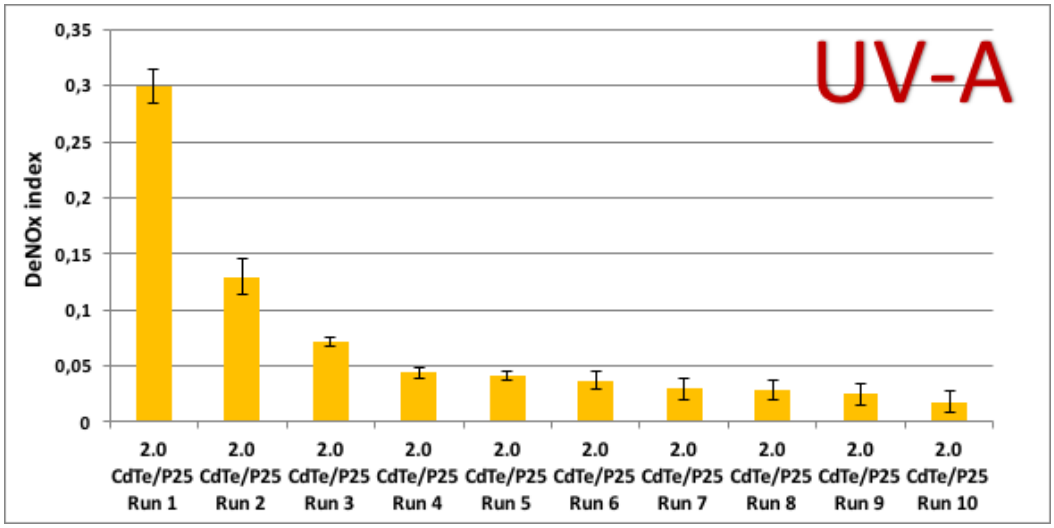


Figure 106. Re-use DeNOx index results for CdTe/P25 under UV-A light.

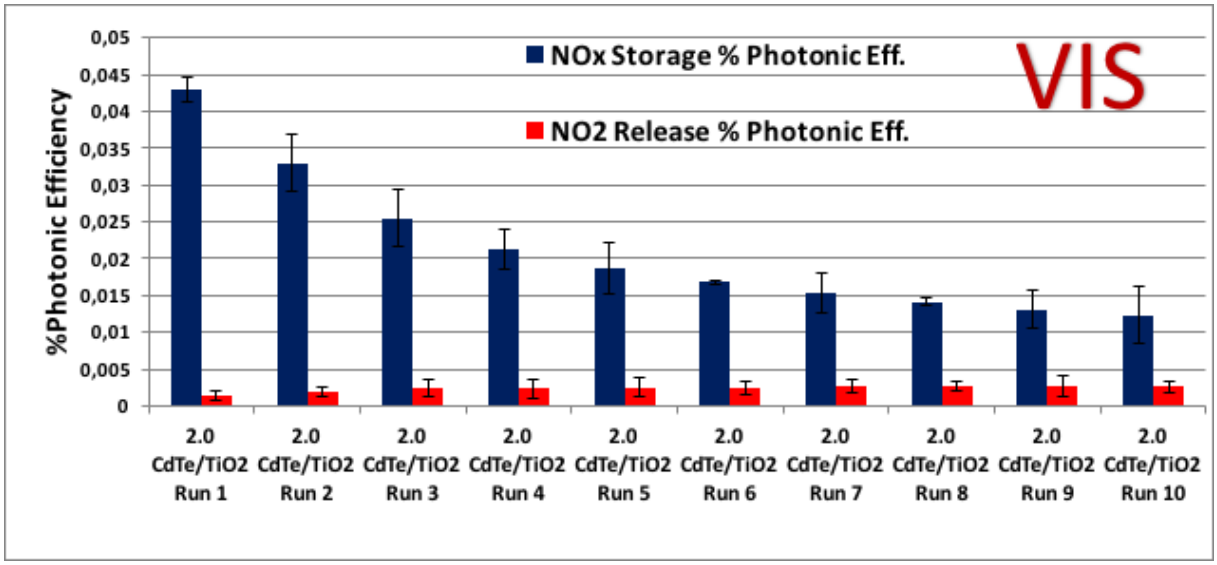


Figure 107. Re-use %photonic efficiency results for CdTe/P25 under visible light.

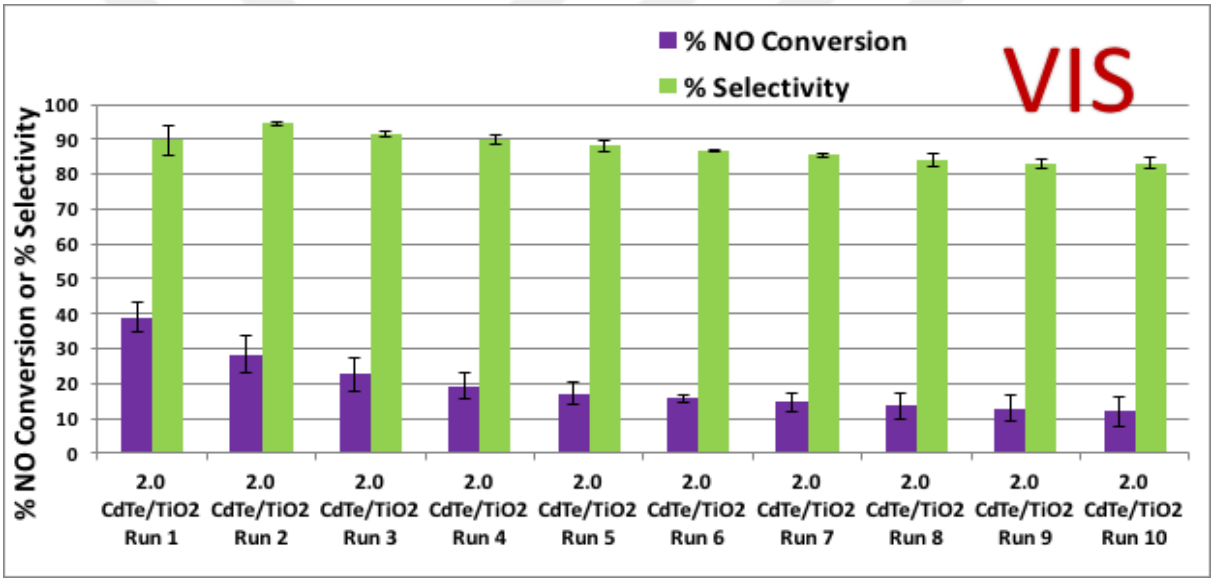


Figure 108. Re-use %NO conversion and % selectivity results for CdTe/P25 under visible light.

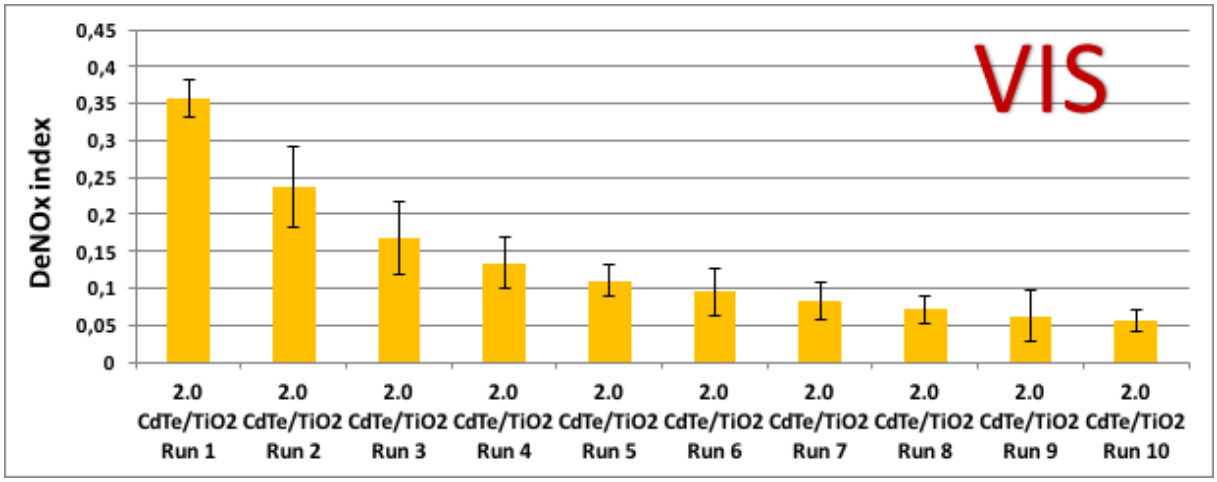


Figure 109. Re-use DeNOx index results for CdTe/P25 under visible light.

3.2.7. PROPOSED MECHANISM

Considering the currently provided photocatalytic measurements, a mechanism for the NO_x storage and NO conversion can be proposed. It is apparent that for the CdTe/P25 composite materials, both P25 and CdTe QDs can harvest photons to enhance the overall NO conversion and NO_x storage as shown in Figure 110. With the control experiments using alumina as the support, it was demonstrated that CdTe QDs can independently utilize the light even in the absence of titania.

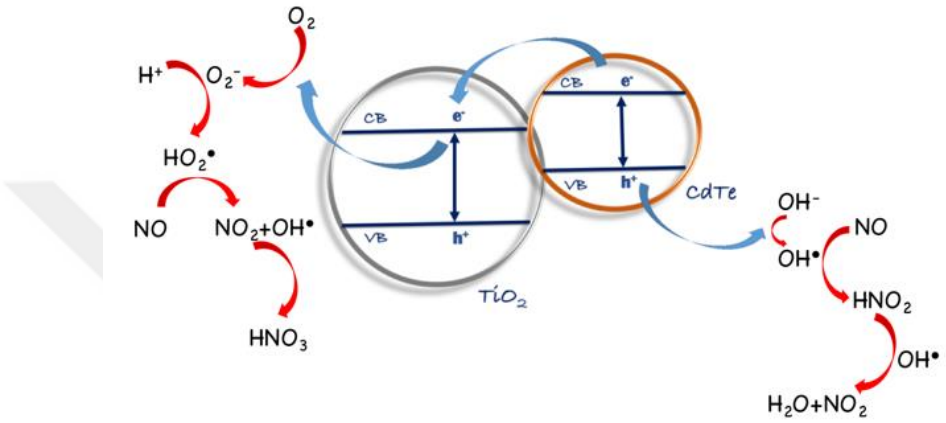


Figure 12. A possible mechanism for CdTe/P25 composites for NO_x oxidation and storage.

However, the reason why these composites cannot endure longer can be due to the oxidation/decomposition of the capping agent (thioglycolic acid) on titania surface. This can be observed as a color change of the material as well. Figure 111 demonstrates that when a red CdTe suspension is mixed with white titanium dioxide powder, the resulting slurry becomes pinkish. However, after the calcination, the material becomes grayish/blue which could be due to the polymeric/graphitic oxidation products of the thioglycolic acid. The final form of the material can keep its color in dark; however, when the material is exposed to light, the color fades away as shown in Figure 112. This can be due to the self-cleaning of titania under light irradiation. This kind of a color change cannot be observed when CdTe is placed on alumina. After calcination on alumina, the color becomes reddish brown and after light irradiation, it keeps the color but becomes slightly pale as shown in Figure 113. Hence, it can be claimed that due to the decomposition of the capping agent, CdTe becomes more vulnerable to get oxidized in a very oxidative reaction system. This would be the reason of activity loss for the spent catalyst.

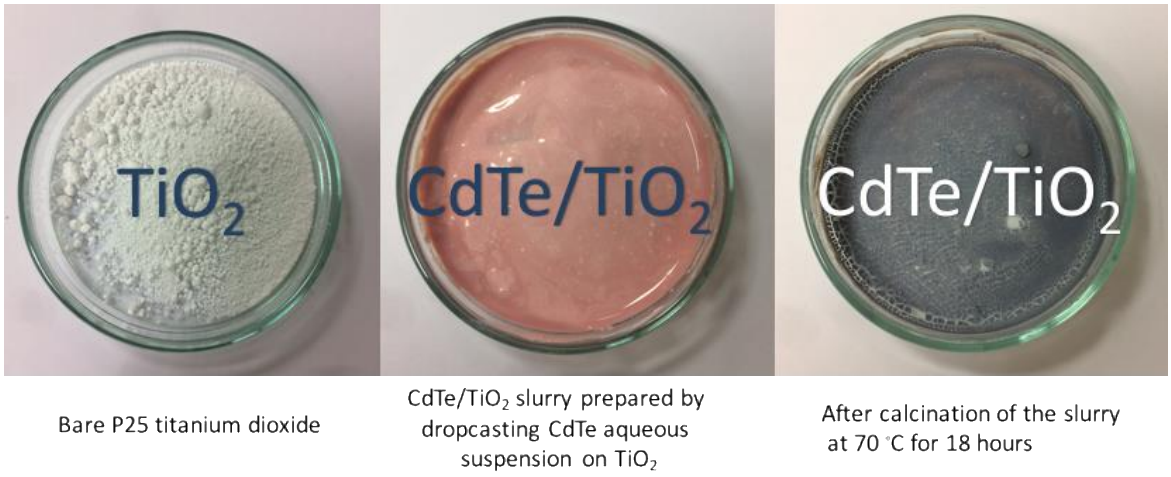


Figure 13. Color change of bare P25 titania (left) after dropcasting CdTe on titania (2.0 CdTe/P25, middle) and after calcination of the prepared slurry at 70°C for 18 h (right).

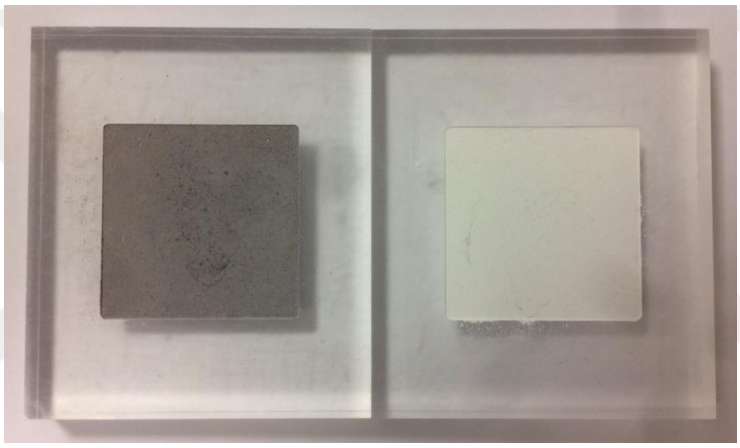


Figure 112. Color change of CdTe/P25 calcined at 70°C for 18 h (left) and after visible light exposure for 5 h (right).

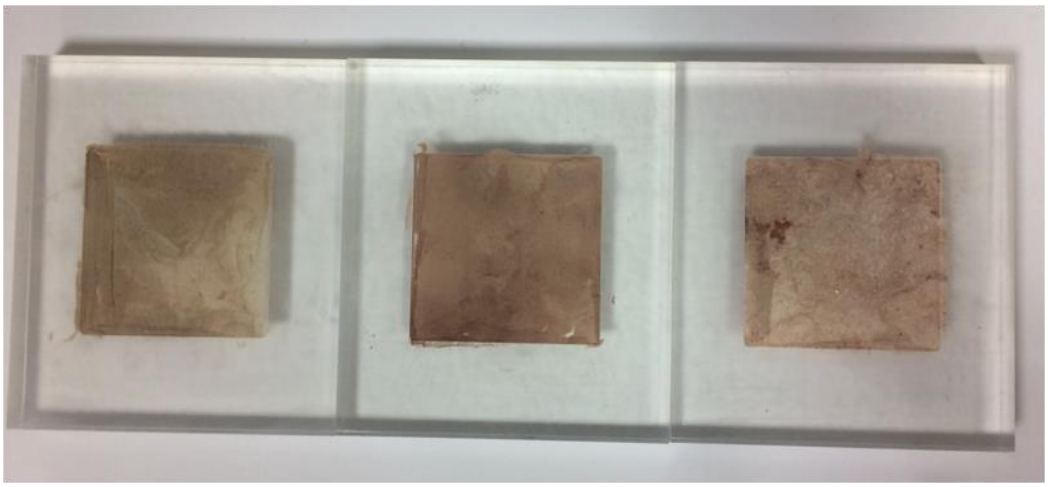


Figure 113. Color differences between CdTe/Alumina after UV-A exposure (left), fresh CdTe/Alumina (middle) and CdTe/Alumina after visible exposure (right).

As water can add more protons and hydroxyl radicals to the titania system, there is more NO oxidation on the surface. Nonetheless, since the storage rate of the system cannot keep up with the NO oxidation rate; despite an increase in % selectivity, the DeNOx index values are still negative.

The capping agent thioglycolic acid plays a significant role in terms of % selectivity. It can be suggested that most of the generated NO_2 can be captured by the capping gent, which drastically increases the selectivity. It was shown in Figures 80-85 that pure TGA on titania cannot adsorb or oxidize NO. Moreover, it even suppresses the activity of titania by blocking/poisoning the active sites on titania even at low loadings. When TGA is diluted in water, there is less TGA to block titania. When titania can oxidize NO to NO_2, TGA can adsorb the NO_2 to increase the selectivity of the system. Although there is some increase in terms of NO conversion as well, this increase is mostly due to the addition of water rather than TGA.

Overall, for CdTe/P25 photocatalyst system, it can be argued that NO is oxidized to NO_2 by titanium dioxide and CdTe QDs using photo-generated electron-hole pairs. The resulting NO_2 can be stored partially by these photo-induced reactions but mostly by the capping agent thioglycolic acid as shown in Figure 114.

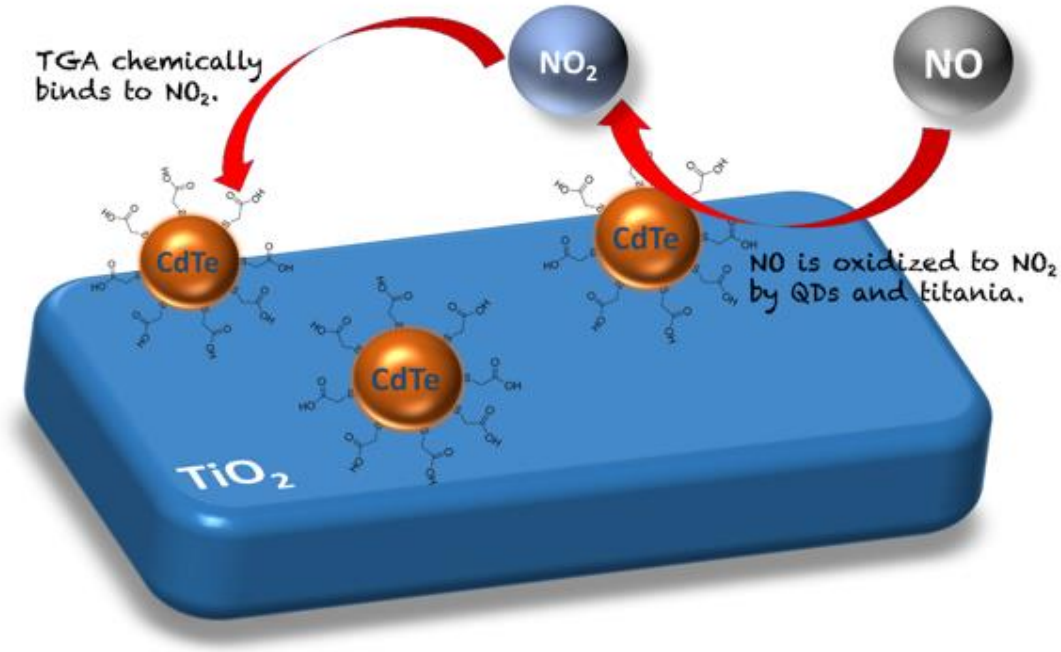


Figure 114. A possible scheme for CdTe/P25 composites for NO_x oxidation and storage.

Even though the capping agent is harmed after the calcination of the CdTe/P25 composite material, it can be claimed that the quantum dots can still harvest light. This statement can be proved by the UV-Vis spectrum of the CdTe/P25 sample as shown in 112. It can be observed easily that there is an absorption of titanium dioxide in the UV region and an absorption of CdTe QDs in the visible region.

Yu et al. studied the thermal oxidation of TGA on titania. Figure 115 demonstrates that one of the characteristic peaks of TGA at 2565 cm^{-1} (S-H vibration) is missing for QDs and QDS-TGA-TiO_2 samples, which is an indication of Cd-S bond formation between the capping agent and QDs. The presence of the peaks at 1583 cm^{-1} (COO asymmetric stretch) and 1388 cm^{-1} (CH_2 flexural vibrations) for QDs and QDS-TGA-TiO_2 sample indicates 'successful anchoring' onto titania surface. Moreover, as the QDS-TGA-TiO_2 sample is calcined from 80°C to 200 °C, these peaks perish and become similar to bare titania spectrum. Yu et al. claims that this is an 'evidence of complete decomposition of TGA' [79].

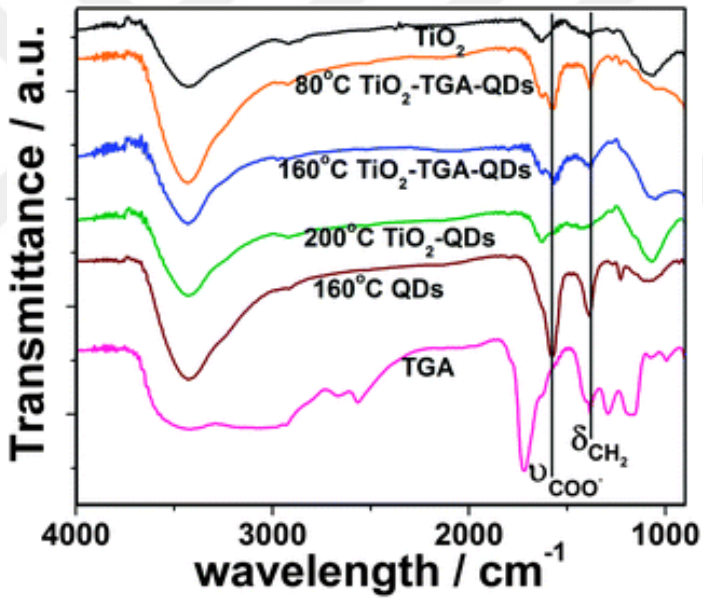


Figure 115. FTIR spectra of bare titania, capping agent TGA, CdTe/CdS core/shell QDs prepared at 160 °C, and QD-sensitized electrodes prepared at different temperature. Reprinted from Ref. 79 Copyright 2018 with permission from Royal Society of Chemistry [79].

As a result, incorporating CdTe QDs to the titania system can firstly boost the utilization of solar irradiation. Secondly, it can be a good tool for increasing the loading of thioglycolic acid without introducing negative/posioning effects on titania active sites. As TGA is bound to the quantum dots, it cannot block the active sites on titania easily. Hence, its loading can be increased further to enhance NO_2 storage.

4. CONCLUSIONS

In this study, an aqueous suspension of thioglycolic acid capped CdTe quantum dots was incorporated into titania photocatalysis in an attempt to enhance the photocatalytic activity and selectivity of the NO_x photo-abatement system. Prepared CdTe/TiO_2 composite materials were tested using a chemiluminescent NO_x analyzer under both UV-A and visible light sources. Aside from the fresh synthesized composites, aged catalysts were also tested. The results of the photocatalytic activity measurements were reported in terms of % photonic efficiency, % NO conversion, % selectivity and DeNOx index parameters.

The activity results revealed much higher solid state NO_x storage capabilities and enhanced NO conversion values. Although titanium dioxide benchmark catalyst P25 has a negative DeNOx index, incorporation of CdTe quantum dots eventually resulted in a positive index. Although this indicates that the proposed CdTe/P25 system can actually clean the air in terms of NO_x pollution; considering the cost and toxicity of these quantum dots, this system can be regarded as a 'Proof of Principle' rather than an actual commercial photocatalyst system.

In order to understand the mechanism of the QD enhancement on titania photocatalysis, reference materials were prepared in order to observe the effect of each component. As the QDs are suspended in an aqueous medium, the effect of water was also studied. It is concluded that water can contribute more protons and hydroxyl radicals to titania, which improves both the NO conversion and the selectivity. However, as the NO_x storage rate cannot keep up with the NO oxidation rate, the resulting DeNOx index becomes more negative.

Moreover, as the quantum dots are capped with a ligand which is thioglycolic acid, the influence of the capping agent was also studied. The activity measurements demonstrated when thioglycolic acid (TGA) is used alone on titania, even small amounts of it can cause poisoning of the titania active sites. TGA alone cannot oxidize NO. However, when TGA is diluted in water and then mixed with titania, at lower loadings it does not significantly block the active sites of titania. Hence, when titania can freely oxidize NO to NO_2, TGA can capture the generated toxic NO_2 gas, increasing selectivity.

Unfortunately, the CdTe/P25 composite system cannot sustain its good photocatalytic activity. Due to the oxidation/decomposition of TGA on titania, the quantum dots become more vulnerable to get oxidized.

In overall, utilizing CdTe quantum dots are advantageous for exploiting more of the solar irradiation; however, they suffer from low stability and short catalytic life time.

Appendix

As there was an issue about the thermal heating of the visible lamp, the distance of the lamp from the reactor was adjusted to the highest position. With the regular position of the lamp, the flux values were recorded on average around 500 μmol/m^2s; however, the temperature inside the reaction chamber increases by 20°C. This difference is high enough to influence the kinetics of the system. Adjusting the level of the visible light source to the highest position, this temperature difference dropped to ~5°C. Since the distance between the light source and the reactor is inversely proportional with the incoming photon flux; using the highest position of the light source results in a decrease in the number of incoming photons to the surface of the photocatalyst. The photon flux at the highest position was recorded on average around 90 500 μmol/m^2s. Figure 117 demonstrates that decreasing the photon flux results in lower NO conversion values; however, it can be clearly seen that using CdTe quantum dots increases both NO conversion and selectivity. The increase in NO conversion is more prominent at the lower photon flux measurements. Figure 116 shows the % photonic efficiency results where

2.0 CdTe/P25 sample at lower photon flux (~88 μmol/m^2s) exhibits an outstanding performance in terms of NO_x storage % photonic efficiency results. It can not only outperform P25 at higher and lower photon flux measurements but also can utilize the incoming photons more efficiently compared to high photon flux measurements of 2.0 CdTe/P25. Considering the DeNOx index in Figure 118, it can be claimed for both high and low photon flux measurements, introducing CdTe quantum dots to titania system results in a positive index value.

Considering these particular measurements, it can be said that the enhancement of the photocatalytic activity with CdTe quantum dots is not a thermal enhancement rather a photocatalytic one. It can be further claimed, considering higher NO_x storage results at lower photon flux values, that thermal heating of the visible lamp has a negative influence on the proposed CdTe/P25 photocatalyst system.

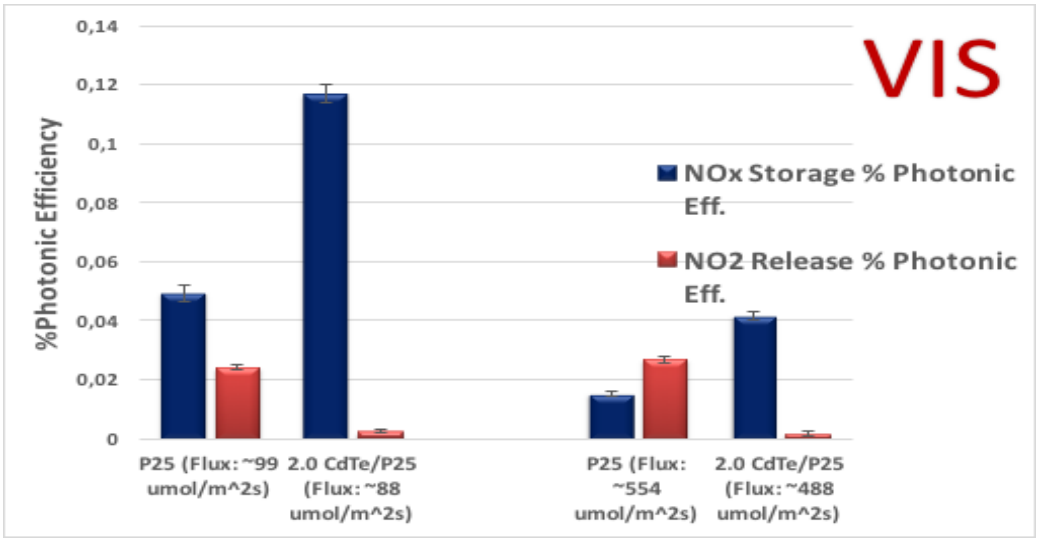


Figure 116. % Photonic efficiency results showing the effect of photon flux on 2.0CdTe/P25 and P25.

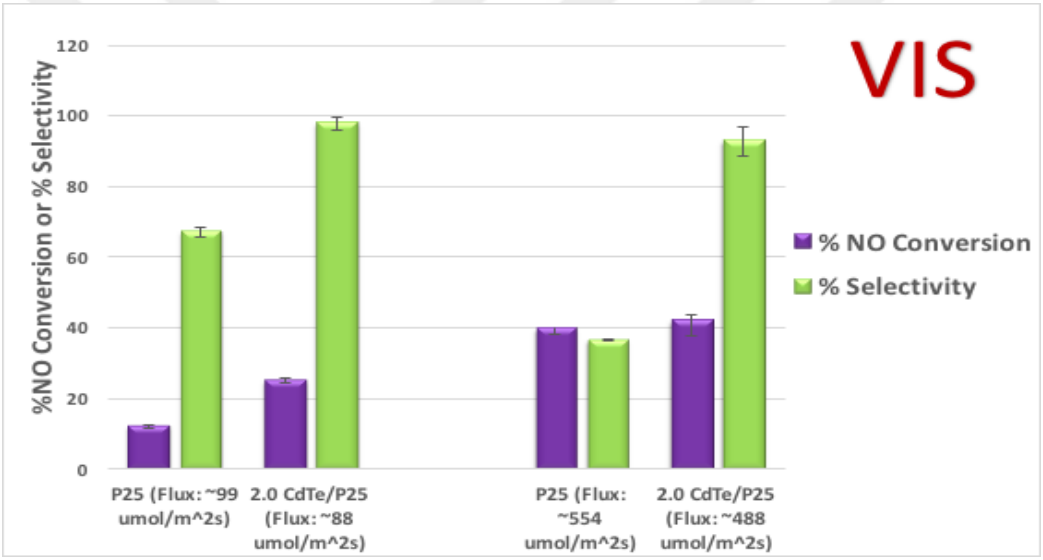


Figure 117. % NO Conversion and % Selectivity results showing the effect of photon flux on 2.0CdTe/P25 and P25.

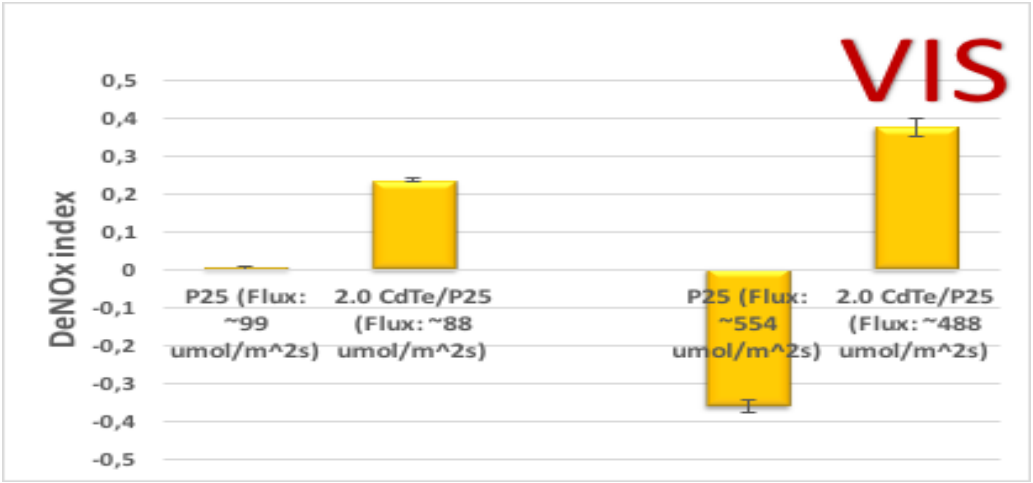


Figure 118. DeNOx index results showing the effect of photon flux on 2.0CdTe/P25 and P25.

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