

GRAPHENE BASED OPTOELECTRONICS IN THE VISIBLE SPECTRUM

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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 Doctor of Philosophy.

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ABSTRACT

GRAPHENE BASED OPTOELECTRONICS IN THE VISIBLE SPECTRUM

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Graphene, a two dimensional crystal of carbon atoms, emerges as a viable material for optoelectronics because of its electrically-tunable broadband optical properties. Optical response of graphene at visible and near infrared frequencies is defined by inter-band electronic transitions. By electrical tuning of the Fermi energy, the inter-band transitions can be blocked due to Pauli blocking. However, controlling inter-band transitions of graphene in the visible and near infrared wavelengths, has been an outstanding challenge. We developed a new device to control optical properties of graphene in the visible spectra. Our device relies on a graphene supercapacitor which includes two parallel graphene electrodes and electrolyte between them. Mutual gating between graphene electrodes enables us to fabricate optical modulators which can operate in the visible and near-infrared. Single layer graphene, however, has performance limits due to its small optical absorption defined by fundamental constants. We extend our method and we developed a new class of electrochromic devices using multilayer graphene. Fabricated devices undergo a reversible color change with the electrically controlled intercalation process. The electrical and optical characterizations of the electrochromic devices reveal the broadband optical modulation up to 55 per cent in the visible and near-infrared. Integration of semiconducting materials on unconventional substrates enables optoelectronic devices with new mechanical functionalities that cannot be achieved with wafer-based technologies. As a novel application, we demonstrate ultra thin electronic paper displays using the multilayer graphene as a reconfigurable optical medium. We anticipate that the developed devices would find wide range of applications in optoelectronics.

Keywords: Graphene, optical modulator, optoelectronics, supercapacitor, smart window, electrochromic devices, electrolyte.

ÖZET

GÖRÜNÜR SPEKTRUMDA GRAFEN TABANLI OPTOELEKTRONİK

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İki boyutlu bir karbon kristali olan grafen, elektriksel olarak değiştirebilir geniş spektrum optik tepkisiyle optoelektronik için uyarlanabilir bir malzemedir. Görünür ve yakın kızılötesi spektrumda grafenin optik tepkisi bantlar arası geçişler tarafından belirlenir. Grafenin Fermi seviyesinin elektriksel olarak ayarlanması, bantlar arası geçişlerin engellenmesine neden olur. Fakat bantlar arası geçişlerin görünür ve yakın kızılötesi bölgede kontrol edebilmek büyük bir zorluktur. Grafenin optik özelliklerini kontrol etmek için yeni bir aygıt geliştirdik. Önerilen aygıt, superkapasitör yapısı kullanan paralel grafen elektrotlar ve bunların arasına hapsedilmiş sıvı elektrolitten oluşmaktadır. Grafen elektrotların karşılıklı elektriksel ayarlanması, görünür ve yakın kızılötesi spektrumda çalışabilen optik modülatörleri üretmemize olanak sunmaktadır. Fakat tek katmanlı grafenin temel sabitler tarafından belirlenen sınırlı optik soğurması nedeniyle performansı limitlidir. Kullandığımız tekniği geliştirerek çok katmanlı grafen tabanlı, yeni bir tür elektrokromik aygıt ürettik. Üretilen aygıtlar, elektriksel olarak kontrol edilen araya ekleme metoduyla, geri çevrilebilir renk değişimine uğramaktadır. Yapılan elektriksel ve optik karakterizasyonlar, çok katmanlı grafen tabanlı elektrokromik aygıtların görünür ve yakın kızılötesi bölgeyi kapsayan geniş bir spektrumda %55'e varan optik modülasyon sağladığını göstermiştir. Yarı iletken malzemelerin geleneksel olmayan alttaşlar üzerine entegrasyonu, yarı iletken alttaş kullanan teknolojilerle elde edilemeyecek optoelektronik aygıtların üretimine olanak sunmaktadır. Yeni bir uygulama olarak; geliştirdiğimiz kağıt alttaşlar üzerine aktarılmış çok katmanlı grafeni ayarlanabilir optik ortam olarak kullanan, ultra ince ekran aygıtları sunuyoruz. Geliştirdiğimiz aygıtların optoelektronikte geniş bir uygulama alanı bulacağını umuyoruz.

Anahtar kelimeler: Grafen, optik modülatör, optoelektronik, süperkapasitör, elektrokromik aygıtlar, elektrolit.

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Chapter 1

Introduction

Graphene is a two dimensional crystal of carbon atoms arranged in a honeycomb lattice. This atomically thin carbon crystal is a basic building block of other carbon allotropes such as one dimensional carbon nanotube, zero dimensional fullerene and three dimensional graphite [1]. Starting with the first observation of strong ambipolar electric field effect in the graphitic films [2] by Andre Geim and Kostya Novoselov, there has been a tremendous amount of effort from scientist and researchers to explore and enhance the electronic properties of graphene in the last decade. Groundbreaking discoveries such as experimental observation of the half integer quantum hall effect [3, 4], constant minimum conductivity in vicinity of charge carriers [5], ballistic transport at room temperature [1] and Klein paradox [6] open a gate through the graphene based basic science and fabrication of future electronic devices.

Graphene also has some unusual optical properties. Even if it is a one-atom-thick material, it can be seen on certain dielectric layer thickness [7] which provides an easy optical characterization even with the optical microscope. The main optical properties of the graphene such as the transmittance and reflectance are defined by the fine structure constant [8]. Furthermore, graphene has a gate tunable broad optical response [9] and one can simply control the absorption mechanism of graphene via electrostatic doping [10]. That intriguing optical properties make the graphene valuable for optical investigation and photonic devices.

The aim of this thesis is to develop the graphene based optoelectronic devices working in visible spectra. We will present active optical devices using the unconventional electronic and optical properties of this two dimensional carbon crystal.

After giving the fundamentals of graphene electronics and optics, we will demonstrate an efficient gating scheme using graphene supercapacitors which controls the absorption mechanism of graphene by Pauli blocking of interband

transitions. By using this gating scheme we will perform some electro-optic characterizations in visible and infrared spectra revealing the light-matter interaction in graphene in a broad spectrum. To show the promises of the method, we will also demonstrate the applications such as graphene based flexible electrochromic devices and graphene based e-papers by further expanding our investigation into multilayer graphene.

1.1 Outline

This thesis presents the new gating scheme which allows the graphene based optical devices to operate in visible spectra. Furthermore, it demonstrates the first practical graphene devices working in visible spectra using the presented gating scheme.

In chapter 1 we will provide the fundamental knowledge about graphene synthesis and transfer methods. We will briefly explain the methods that we used to obtain graphene layers and compare them to the previously used ones. Then, we will give the theoretical background for the electronic and optical properties of graphene which is required for the better understanding of the working mechanism and characterization of our fabricated graphene based devices.

Chapter 2 presents “controlling optical properties of single layer graphene” which contains the brief explanation about the physical mechanism and electro-optic characterization steps of the transparent graphene supercapacitors working as an optical modulators.

Chapter 3 includes the “optical properties of multilayer graphene” which demonstrate the first application of active reversible color change in the flexible multilayer graphene electrodes. In this chapter we will introduce the multilayer graphene as a new class of electrochromic material having key parameters for high contrast and broadband operation by using our proposed gating scheme.

Chapter 4 introduces an interesting practical application. “Graphene on paper”. In this chapter we demonstrate electronic paper display using graphene transferred on printing paper as the reconfigurable optical medium. The presented graphene based ultrathin electronic paper display provides large optical contrast in the visible spectra with fast response speed.

Chapter 5 includes the conclusion of our studies and provides an outlook of the presented devices.

1.2 Graphene synthesis and transfer techniques

In order to study the physical properties of the graphene one should isolate the two dimensional graphene layer. This is a challenging procedure due to the atomic thickness of graphene. However during the last decade several consistent methods have been developed to obtain the one-atom-thick single layer graphene which was previously thought to be instable. In the followings we will give a short review by explaining the advantages and disadvantages of these methods.

Mechanical exfoliation from bulk graphite [2] (also known as scotch-tape method) yields a non uniform thickness carbon film having fragments of different number of graphene layers. That makes the identification of single graphene layers difficult over the transferred substrate, yet it is still a simple method to study the fundamental electronic properties of graphene over very limited area (Fig. 1.1 (a)). This method gives the highest carrier mobilities ($200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in graphene based field effect transistors [11, 12].

Graphitization of SiC planes by annealing is another prominent method to obtain the two dimensional graphene. Epitaxial growth of graphene on SiC substrates (Fig. 1.1 (b)) and the promises of the method such as patterning the as grown graphene into the quantum confined structures was demonstrated [13]. By using this method, growth of relatively large area graphene samples are possible and devices using epitaxially grown graphene on SiC can operate in high frequency regime [14]. On the other hand, some handicaps such as high cost of the SiC substrates and requirement of ultra-high vacuum chambers still remain as disadvantages in the technique.

Isolating graphene layers chemically from the bulk graphite is an alternative method in which the intercalation of atoms or molecules through the graphite [15] yields the separation of graphene layers. However partial separation of the bulk graphite yields a dispersion that contains variety of graphene fragments and graphitic films [16]. To overcome this non-uniformity of the resulting graphene layers, chemical reduction of graphene oxide [17] and chemically functionalized graphene [18] were introduced (Fig. 1.1 (c)). However since these materials are suffer from low conductivity, achieving the conductivity order of the pristine graphene with this method is a handicap to date.

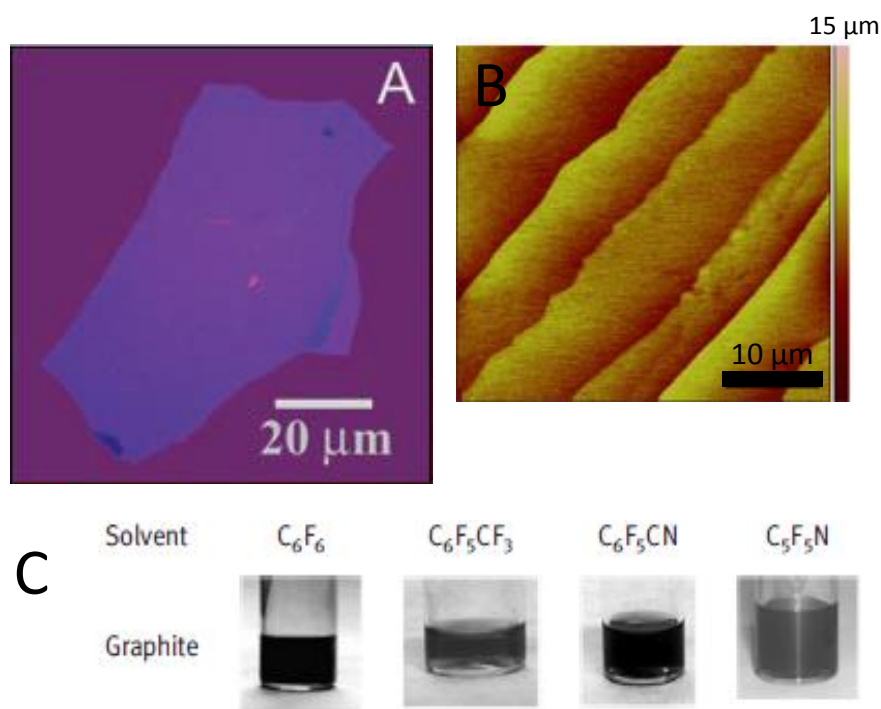


Figure 1.1: Techniques to obtain graphene. (a) Mechanically exfoliated graphene on oxidized Si dielectric surface. Reprinted with permission from Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. Science, 2004. 306(5696): p. 666-669. Copyright © 2004, American Association for the Advancement of Science. (b) Atomic force microscope image taken from the surface of graphitized SiC substrate. Reprinted with permission from Kim, J., et al., *Principle of direct van der Waals epitaxy of single-crystalline films on epitaxial graphene*. Nature Communications, 2014. 5. Copyright © 2014, Nature Publishing Group. (c) Liquid phase graphene dispersions prepared by using various chemical agents. Reprinted with permission from Bourlinos, A.B., et al., *Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes*. Small, 2009. 5(16): p. 1841-1845. Copyright © 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Today one of the most commonly used synthesis technique in graphene science is chemical vapor deposition (CVD). The advantages of the CVD synthesis over other techniques are scalability to large area, being low cost and effortless, and the consistent quality of the resulting graphene layers. Very large area CVD synthesized graphene samples were demonstrated and used as transparent electrodes in functional touch screen panel [19]. To form a graphene layer via CVD synthesis, a catalyst substrate is needed for the decomposition of carbon atoms from the carbon feedstock gas flowing through the CVD chamber. Nickel and copper substrates are frequently used as catalyst substrates, however usage of transition metals such as, Ir [20], Au [21], Ru [22], Pd [23] in CVD synthesis have also been demonstrated. The transport properties of the CVD synthesized graphene films are not superior compared to the mechanically exfoliated ones. This is due to the polycrystalline structure of the metal

substrates on which the graphene forms. However with the efficient controls of the gases flowing through the CVD chamber, large area single crystal graphene has already been reported [24]. For large area electronic applications, high quality samples with uniform transport properties are essential. Many breakthrough improvements on the quality of resulting graphene films in CVD synthesis have been reported [19, 25, 26]. Because of the low solubility limit of carbon in copper, graphene growth procedure is self-limited on copper substrates [25]. That property of copper provides the advantage of straightforward synthesis of single layer graphene. Copper foils are low cost and scalable substrates for graphene growth. The surface quality of the copper foils and the transfer printing process determine the performance and reliability of the graphene transistors. Commercially available copper foils, however, have very rough surfaces due to the rolling process. Deep scratches on the rough copper foil due to the rolling process, yield detrimental effects especially during the transfer printing process.

Previous works have showed that the morphology of the copper surface is one of the key parameters to have better quality graphene films [27]. To achieve the full surface coverage of the high quality graphene film; impurities, defects, grain boundaries and other surface features that can serve as a nucleation seed should be carefully engineered [27]. For that purpose, variety of techniques for smoothing the copper surfaces have been reported. Luo et al. [28] used standard electropolishing technique to smooth the copper surfaces. Their Raman spectroscopy investigation implied better quality graphene film with high surface coverage compared to the unpolished copper samples [28]. Similar electrochemical polishing technique was used in the work by Yan. et al [29]. Together with the high pressure annealing, they produced hexagonal single crystal graphene domains nearly 2mm in size [29]. Alternatively, melted copper surfaces were also used to form these single crystal hexagonal graphene flakes in previous works [30, 31]. Apart from these techniques, Vlassiounk et al.[32] reported the role of hydrogen gas as a surface activator and etchant. The shape and size of the single crystal graphene domains can be controlled precisely by adjusting the partial pressure of hydrogen gas [32]. In addition, Robertson et al. [33] showed the formation of few layer, single crystal, graphene flakes by changing the growth conditions.

Another prominent technique to form a smooth copper surface is the thin film deposition of copper on rigid substrates[34]. Howsare et al. [34] showed that adding a barrier layer between the deposited Cu and Si interface can further increase the quality of the graphene film by suppressing the interdiffusion between these layers. Moreover, Zhao et al. [35] investigated the effect of single crystal copper substrates on growth of the graphene layers. They reported the atomic structure of the graphene film and the grain orientations shows different properties going in different lattice directions [35].

It is known that the quality of the copper surface directly effects the transport properties of the resulting graphene layer [36]. Orofeo et al. [36] demonstrated the hole mobility of the graphene grown on the Cu film is nearly 10 times greater than that of the graphene grown on the Cu foil by chemical vapor deposition. In addition to surface morphology, crystallography of copper substrate also plays a crucial role in the formation of the graphene film [37]. Wood et al. [37] reported that, because of the carbon's higher diffusion rates at (111) surface, it is more likely to have monolayer graphene on that surface compared to other surfaces

In our experiments we used the high quality single layer graphene on commercially available ultra-smooth copper foils. In the industry, copper foils have been used as negative electrodes for lithium-ion batteries. For these applications surface quality plays a critical role in the performance of the batteries. Recent progress of large scale production of smooth copper foils can also provide opportunities to improve performance of graphene transistors.

We used relatively rough *Alfa Aesar* foil (*item #13382*) which is commonly used for CVD graphene growth (Fig. 1.2 (a-c)) and commercially available ultra-smooth surface copper foils (*Mitsui mining and smelting co., LTD, B1-SBS*) (Fig. 1.2 (d-f)). To investigate the effect of the surface roughness to the quality of the graphene layer, both the ultra smooth copper and the rough copper foils were placed in the same growth chamber to be exposed to same growth conditions. We also investigated the surface topography of the ultra-smooth copper foils with SEM and AFM. The ratio of the partial pressure of hydrogen and methane gases define the growth rate and shape of the graphene flakes. By sending the methane gas into the chamber with different intervals we obtain both the graphene flakes (Fig 1.3(a), (b)) and full coverage graphene film (Fig. 1.3 (c)) on the ultra-smooth copper foils. Figure 1.3 (a) shows the SEM images of copper surface partially covered by graphene flakes. The surface roughness of the copper is around 100nm. However, after the growth, graphene flakes form ripples (Fig. 1.3 (c)) likely because of physical instability of perfectly flat graphene layer [38-41].

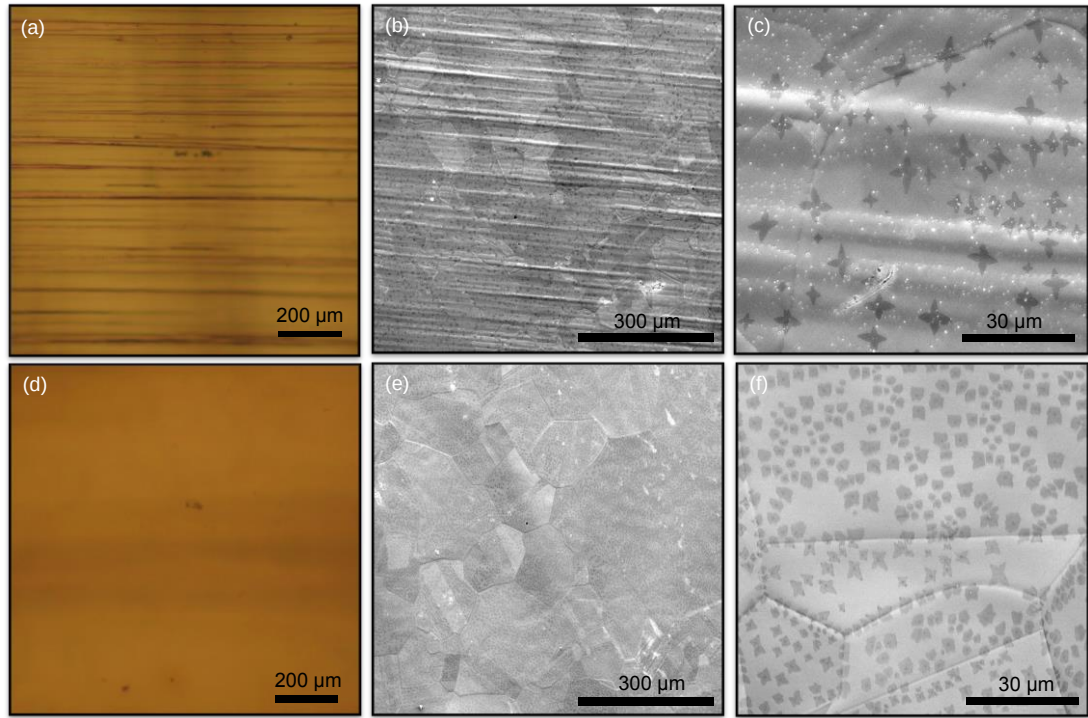


Figure 1.2: Effects of copper surface morphology to graphene growth. (a) Optical microscope image of rough copper foil (*Alfa Aesar* foil (*item #13382*)). Deep scratches on the rough copper foil due to the rolling process, are clearly visible (b) Scanning electron microscopy (SEM) image of the rough copper surface. (c) The magnified SEM image of the rough copper foil surface. The growth was terminated after 10 sec. to obtain dispersed graphene flakes. (d) Optical microscope image of ultra-smooth copper foil (*Mitsui mining and smelting co. LTD., B1-SBS*) and (e) SEM image of ultra smooth copper surface, after the graphene growth. (f) Ultra smooth copper surfaces with graphene flakes. The density and shape of the graphene flakes are different on the rough and smooth foils. The averaged grain size of the smooth copper foil after the growth is around 200 μm .

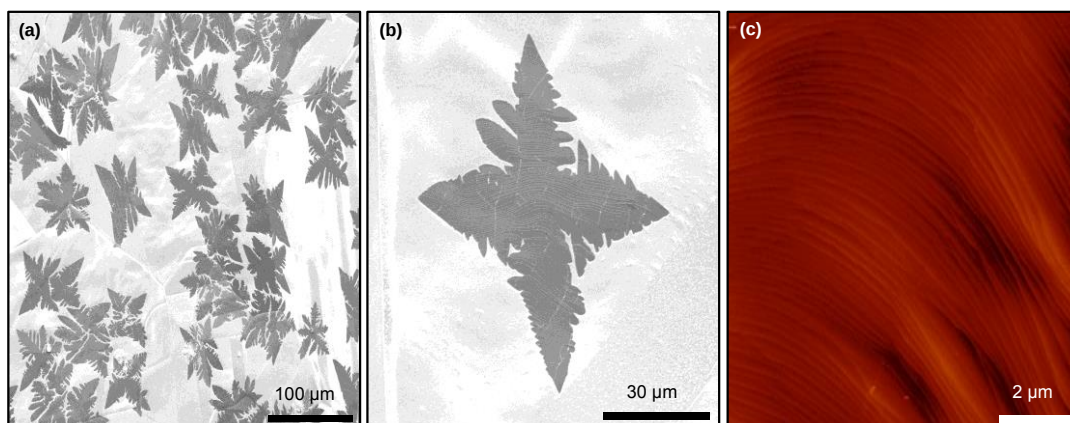


Figure 1.3: Graphene flake formation at early stages of growth. (a,b) SEM images of the surface of the ultra smooth copper partially covered by graphene flakes. To achieve $\sim 60\mu\text{m}$ flakes, methane gas was flushed into chamber for 5 seconds then left to cooling to room temperature. Smoothness of the surface and size of the grain boundaries of the copper are clearly visible. (c) AFM image showing the surface topography of full graphene layer on the ultra smooth copper foil. Graphene ripples, which are formed from the graphene flakes, are clearly seen.

Since electronic and optical properties of the graphene can't be examined on conducting metal substrates, the transfer printing of graphene layers to insulating substrate are essential in CVD synthesis. There are two commonly used transfer printing method for CVD synthesized graphene; namely the polymer-assisted transfer printing and roll-to-roll transfer printing [42].

PDMS (polydimethylsiloxane) is a silicon elastomer which is generally used for molding of microchannels [43] or as an optical mask for soft lithography [44]. Due to the low surface energy [45] and the hydrophobic nature of the PDMS [46] one can easily attach and retrieve graphene on PDMS surface (Figure 1.4). By using the PDMS stamping method, dry transfer of large area patterned multilayer graphene samples has been demonstrated [47]. However, formation of cracks along the graphene layer during the stamping and removal of PDMS to the insulator surfaces breaks up the uniformity of the transfer printed graphene layer by using PDMS stamping method.

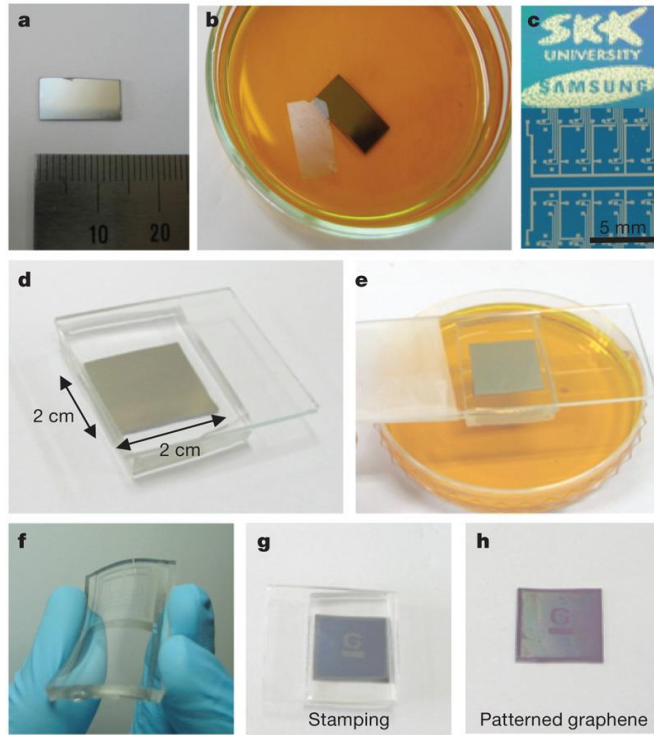


Figure 1.4: Graphene transfer by using PDMS stamping. (a,b) The nickel substrate is etched in FeCl_3 solution to obtain the floating graphene on liquid surface. (c) Then direct transfer to the rigid substrates by fishing out the graphene layer floating on the surface. (d-f) PDMS stamping to graphene holding nickel substrate and etching the metal foil in FeCl_3 solution to obtain graphene on PDMS. (g,h) Stamping the graphene holding PDMS to the dielectric surface to have conformal contact which results in the transfer of graphene layer on dielectric layer. Reprinted with permission from Kim, K.S., et al., *Large-scale pattern growth of graphene films for stretchable transparent electrodes*. Nature, 2009. 457(7230): p. 706-710. Copyright (2009) Nature Publishing Group.

Another polymer-assisted graphene transfer printing method is using PMMA (polymethyl methacrylate). Being highly conformal and having low density compared to PDMS, PMMA is able to cover and embed the surface structures when baked [48]. Basically, spin coating of PMMA and etching the graphene holding metal substrates results in graphene holding PMMA [49]. Putting the graphene holding PMMA on the target substrate and removing the PMMA with acetone yields the graphene on desired target substrate. Disadvantages of the method can be mentioned as the unsuccessful removal of the whole PMMA along the graphene layer which affects the transport measurements by introducing scattering points [50]. In addition, PMMA transfer method could remain random cracks on the surface. However, it has been reported that applying another layer of PMMA before the removal of PMMA could prevent the formation of cracks during the transfer [51].

To obtain a non-residual and crack-free transfer of CVD synthesized graphene layers we developed the photoresist drop casting method (Fig. 1.5). In this method, we poured thick droplets of photoresist (S1813) on graphene grown smooth copper surfaces and waited overnight at 70 °C. After a photoresist layer was hardened on smooth copper surfaces, they were immersed into nitric acid solution (~%22) for non-residual etching of copper film. Then graphene holding photoresist layer was placed on the 100 nm thick SiO₂ coated on Si wafer. Reflowing mechanism of the photoresist layer at 120 °C left the graphene layer on the substrate. Removal of the remaining photoresist layer yielded large area graphene films with high surface coverage.

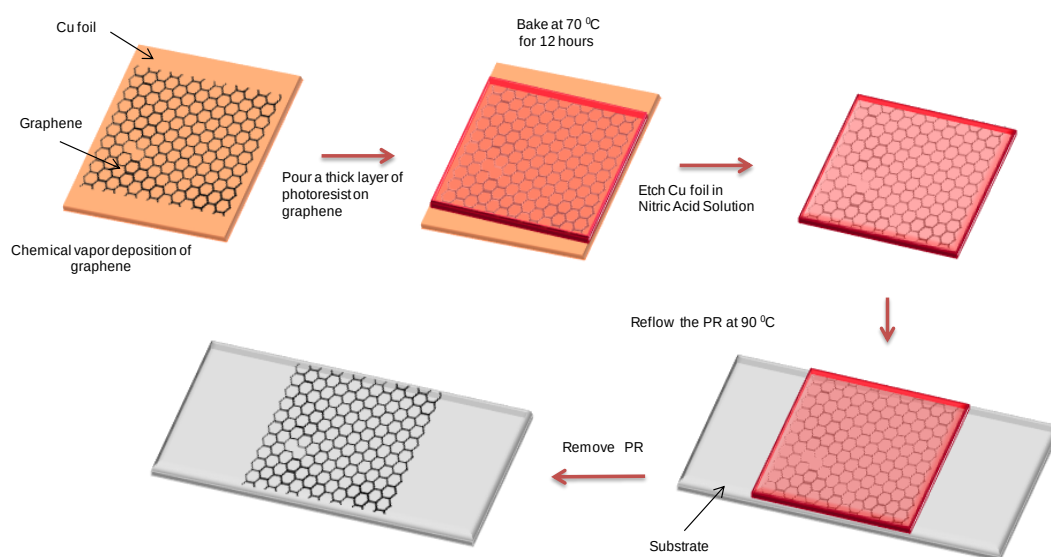


Figure 1.5: Transfer printing via photoresist drop casting. Reprinted with permission from Polat E.O., Kocabas C., *Broadband optical modulators based on graphene supercapacitors*. Nano Letters, 2012. 12(11): p. 5598-5602.). Copyright (2013) American Chemical Society

For the applications requiring larger area graphene, roll to roll transfer printing is the most efficient way compared to polymer assisted transfer techniques. Recently graphene based transparent electrodes is a great interest for the next generation flexible optoelectronic devices. In this method, CVD synthesized graphene on metal substrates is attached to a adhesive polymer film. To obtain a conformal contact between the graphene holding metal substrate and the adhesive polymer film, generally cylindrical hot rollers are used [19, 52]. Etching metal substrate in solution yields the the graphene holding polymer film. This process can be easily scaled up to very large dimensions [19]. Since the process requires flexible films, using rigid substrates can cause damages in the transferred graphene film. To transfer the large area graphene on rigid substrates such as wafers or glass, hot-pressing technique was also demonstrated [53].

Raman spectroscopy provides clear finger prints of graphene layers. Raman spectrum of the graphene samples was measured using a confocal microraman system (Horiba Jobin Yvon) in back-scattering geometry. A 532 nm diode laser was used as an excitation source and the Raman signal was collected by a cooled CCD camera. Figure 1.6 shows Raman spectra of the graphene on gold foils. Figure 1.6 (a) shows the Raman spectrum of the graphene synthesized on gold surface. The inset in Figure 1.6 (a) shows the optical micrograph of the graphene on the gold foil. The grain boundaries and wrinkles on the polycrystalline gold surface are clearly seen. Figure 1.6 (b) and (c) show the Raman spectrum of the graphene as grown on gold and after the transferring to silicon wafer.

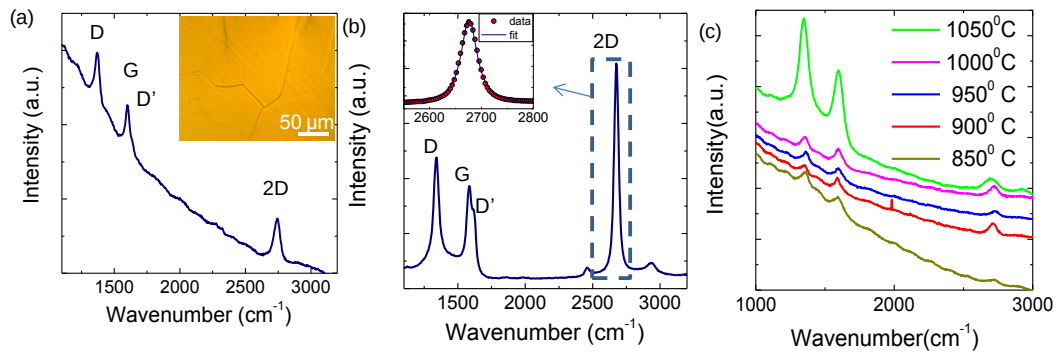


Figure 1.6: Raman spectroscopy of graphene. (a) Raman spectrum of the graphene as grown on gold surface. The inset shows the optical micrograph of the same area. (b) Raman spectrum of the graphene on SiO₂/Si substrate. The inset shows the zoomed spectrum of the 2D peak and a Lorentzian fit. The width of the Lorentzian is around 37 cm⁻¹. (c) Raman spectra of the graphene samples grown at a range of temperatures between 850 °C and 1050 °C. Reprinted with permission from Oznulner, T., et al., *Synthesis of graphene on gold*. Applied Physics Letters, 2011. 98(18). Copyright © 2011 AIP Publishing LLC

The expected Raman peaks of D, G, D', and 2D can be seen on the graph. The position of D, G, D', and 2D peaks are 1371, 1600, 1640, and 2743 cm⁻¹ on gold and 1339, 1584, 1620 and 2676 cm⁻¹ on SiO₂/Si substrate. There is a significant red shift after the transfer process, likely due to the release of compressive strain on the graphene film. The inset in Figure 1.6 (c) shows the zoomed 2D peak and the Lorentzian fit. The fit has a symmetric Lorentzian shape with a width of 37 cm⁻¹. The shape and the width of the 2D peak is a good indication of single layer graphene layer or noninteracting a few layers of graphene. The Raman D-band signal of graphene on gold is relatively more intense than the graphene grown on copper. This intense D band is likely due to the large lattice mismatch between gold and graphene. The lattice constant of bulk graphite and hexagonally closed-packed gold surface.

1.3 Electronic properties of graphene

As we mentioned in previous parts, graphene is a two dimensional carbon crystal with unusual physical properties. Since any material's electronic and optical properties is directly dependent on the crystal structure here we first study the crystal structure of graphene. Carbon, being a source element of life, has four valance bonds. In the ground state, it has 6 electrons dispersed to the shells with the configuration as $1s^2 2s^2 2p^2$. Graphene has sp^2 hybridization of carbon atoms. In this kind of hybridization s , p_x , p_y orbitals forms the σ bonding by combining [54]. σ bonds are strong covalent bonds between the carbon atoms in the two dimensional x-y plane of graphene which are responsible for the amazing mechanical properties of graphene such as extremely high young modulus and breaking strength[55]. On the other hand, the remaining p_z orbitals, which are perpendicular to the x-y plane, forms the formation of delocalized π bonds by lateral interaction [54]. Carbon atoms in graphene are arranged as a honeycomb lattice. Figure 1.7 is a ball and stick model showing the crystal structure of graphene. The unit cell of graphene is represented by basis vectors $\vec{a}_1$ and $\vec{a}_2$. There are two carbon atoms per unit cell (A and B). The carbon-carbon distance is graphene is 1.42 Å and represented by a_{cc} in Fig 1.3.

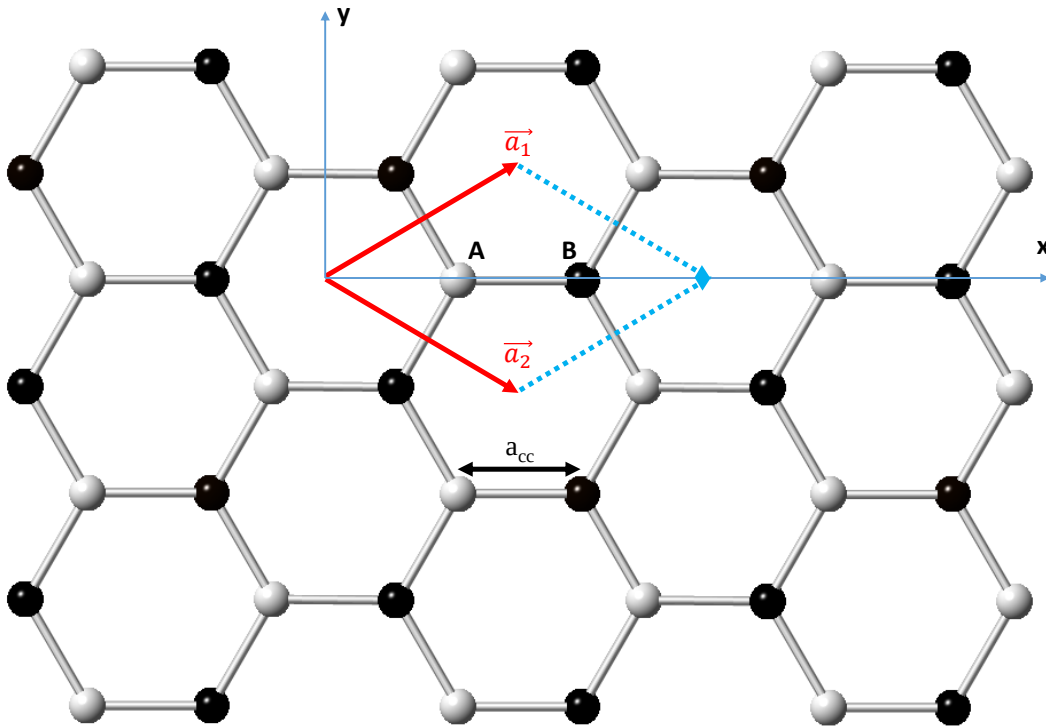


Figure 1.7: Crystal structure and basis vectors of graphene hexagonal lattice.

Therefore, by using the simple geometry, the basis vectors of graphene lattice can be written as

$$\vec{a}_1 = \sqrt{3}a_{cc} \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) \quad (1.1)$$

And,

$$\vec{a}_2 = \sqrt{3}a_{cc} \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) \quad (1.2)$$

Magnitude of these vectors denoted with a ,

$$a = |\vec{a}_1| = |\vec{a}_2| = \sqrt{3}a_{cc} \quad (1.3)$$

By using orthogonality condition,

$$\vec{a}_i \cdot \vec{a}_j = 2\pi\delta_{ij} \quad (1.4)$$

Reciprocal lattice vectors $\vec{b}_1$ and $\vec{b}_2$ are,

$$\vec{b}_1 = b \left(\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \quad (1.5)$$

And,

$$\vec{b}_2 = b \left(\frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \quad (1.6)$$

Where,

$$b = \frac{4\pi}{3} a \quad (1.7)$$

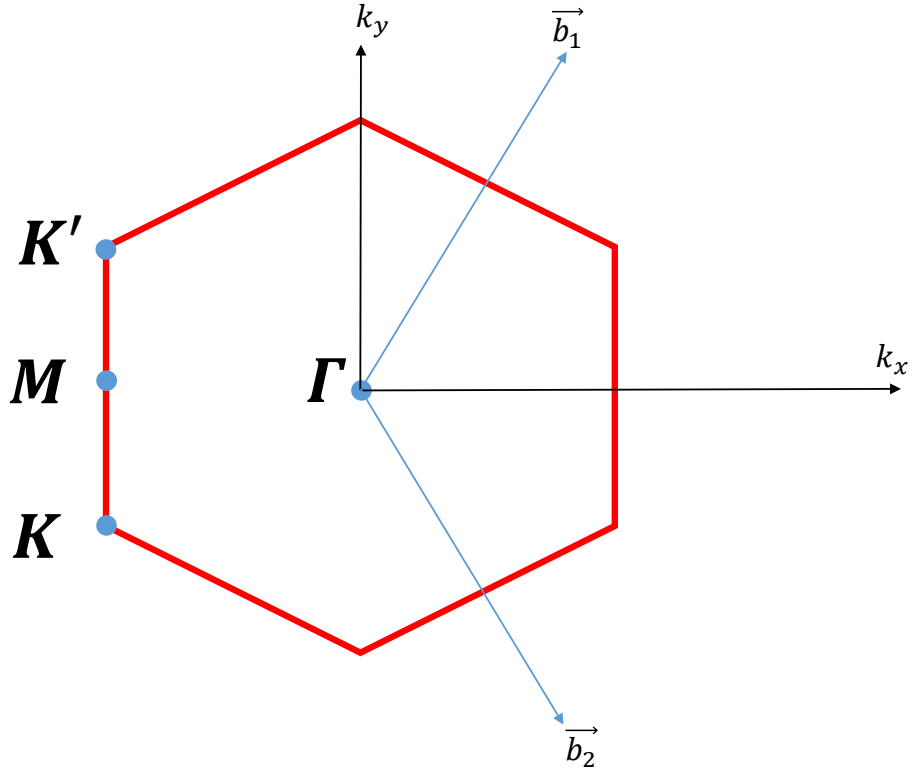


Figure 1.8: Brillouin zone and reciprocal basis vectors of graphene lattice.

The electronic band structure of graphene is first calculated by P. R. Wallace at 1947 [56]. Assuming the electrons can hop to only nearest neighbor atoms and next nearest neighbor atoms, one can determine the corresponding vectors for three nearest neighbor atoms in real space as,

$$\vec{c}_1 = a \left(\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \quad (1.8)$$

$$\vec{c}_2 = a \left(\frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \quad (1.9)$$

$$\vec{c}_3 = a(-1, 0) \quad (1.10)$$

For the six next-neighboring atoms, the real space vectors are;

$$\vec{c}_1' = \mp \vec{a}_1 \quad (1.11)$$

$$\vec{c}_2' = \mp \vec{a}_2 \quad (1.12)$$

$$\vec{c}_3' = \mp (\vec{a}_2 - \vec{a}_1) \quad (1.13)$$

Therefore the tight-binding Hamiltonian including only nearest and next-nearest terms [57];

$$H = -t \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + H.c) - t' \sum_{\langle i,j \rangle, \sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + b_{\sigma,i}^\dagger b_{\sigma,j} + H.c) \quad (1.14)$$

where $a_{\sigma,i}$ and $b_{\sigma,j}$ are the annihilation operators for the electrons of different sublattices having spin σ . Also t and t' stands for the nearest neighbor and next nearest neighbor hopping energy [57]. To obtain the electronic band structure of graphene, Schrödinger equation needs to be solved for the Bloch wavefunctions with the Hamiltonian given in the equation (1.14). The resulting energy eigenvalues appears in the form [58];

$$E_{\mp}(\mathbf{k}) = \mp t \sqrt{3 + f(\mathbf{k})} - t' f(\mathbf{k}) \quad (1.15)$$

Where,

$$f(k) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right) \quad (1.16)$$

Plotting equation (1.15) for $t = 2,7 \text{ eV}$ and $t' = -0,54 \text{ eV}$ yields;

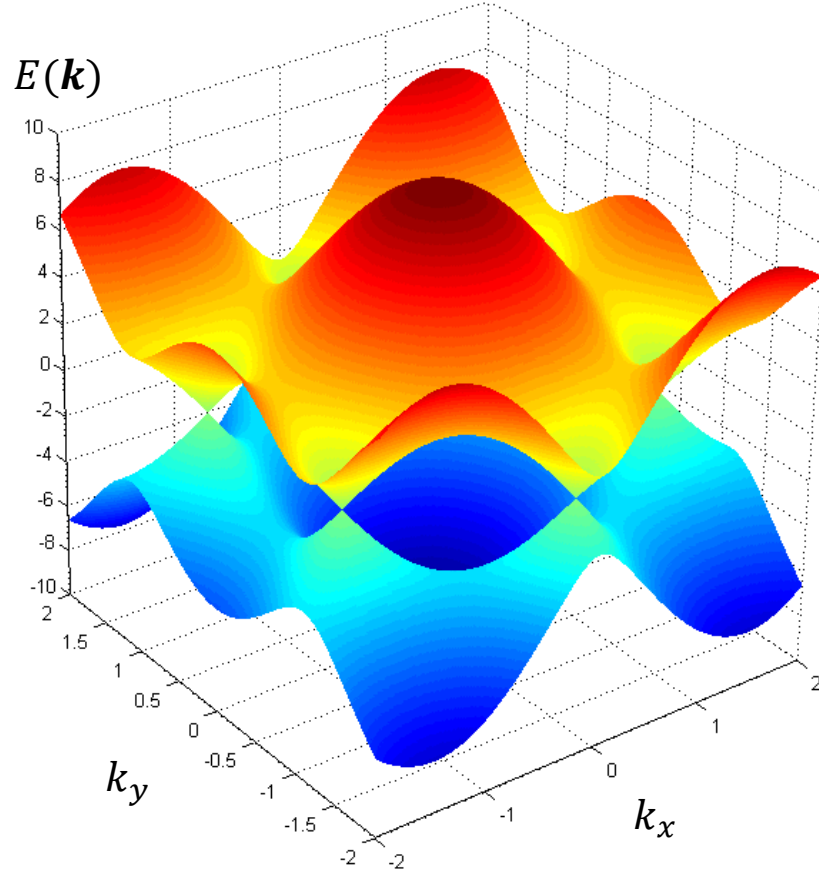


Figure 1.9: Electronic band structure of graphene.

Figure 1.9 shows the electronic band structure of graphene. The low lying band represents the valance band while the above band stands for the conduction band. They are crossing each other at the corners of the Brillouin zone (See Fig. 1.8 K and K' points). These are so called “Dirac points” or “charge neutrality points”. Graphene’s band structure represents the zero band gap semi-metal. At low energies, near to the charge neutrality points, the band structure shows the linear behaviour. This is similar to photon dispersion relation with a Fermi velocity $v_F \approx 10^6 \text{ ms}^{-1}$ instead of speed of light. Expanding (1.15) near a Dirac point $\mathbf{K}$ yields,

$$E_{\mp}(\mathbf{q}) \approx \mp \hbar v_F |\mathbf{q}| \quad (1.17)$$

where $\mathbf{q} \ll \mathbf{K}$ with the assumption $\mathbf{k} = \mathbf{K} + \mathbf{q}$ [57].

Plotting eq (1.15) with the above approximation, Figure 1.9 turns out to be,

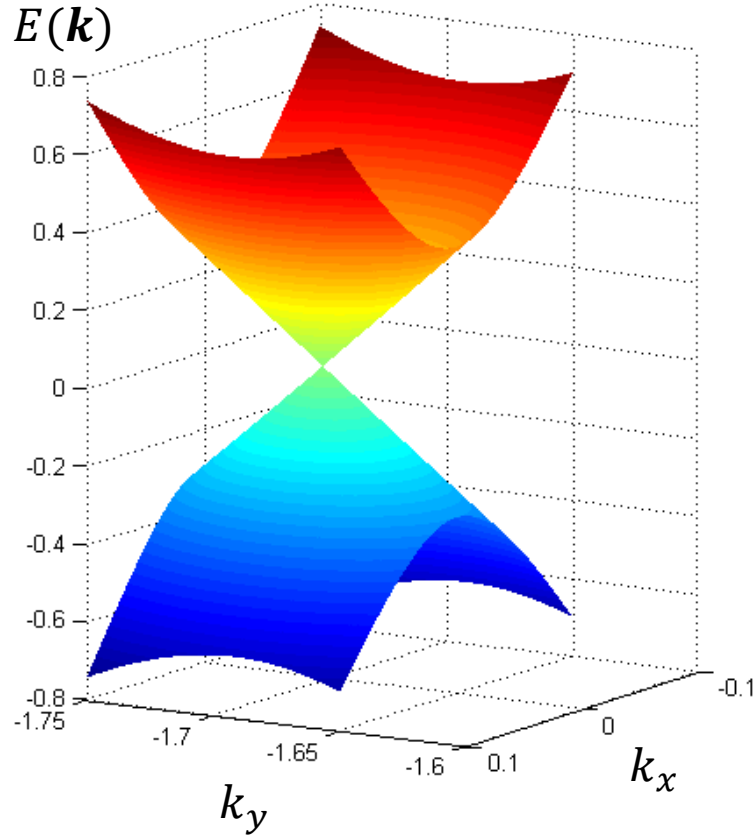


Figure 1.10: Linear dispersion of graphene at low energies.

In that sense, the band structure of graphene can be referred as relativistic-like. Many of the unusual electronic properties of graphene are sourced from this linear band structure (Fig. 1.10). One of them is cyclotron mass of charge carriers in graphene.

The effective mass of charge carriers in graphene depends on the square root of the charge density [5, 57, 59].

Cyclotron mass in solids is by definition,

$$m^* = \frac{\hbar}{2\hbar} \left(\frac{\partial A(E)}{\partial E} \right) \quad (1.18)$$

With the the area that is travelled by an the an electron in k space,

$$A(k) = \hbar k^2 \quad (1.19)$$

Inserting eq. (1.19) in eq. (1.18) yields

$$m^* = \hbar^2 k \left(\frac{\partial E}{\partial k} \right)^{-1} \quad (1.20)$$

For an electron under the application of external field, eq (1.20) leads to,

$$m^* = \frac{e H}{c w_c} \quad (1.21)$$

Therefore, considering the linear dispersion of graphene (eq 1.17), the cyclotron mass for graphene is [57]

$$m^* = \frac{\sqrt{\pi}}{v_F} \sqrt{n} \quad (1.22)$$

The effective mass in graphene is dependent on the charge density (eq 1.22) and is a different version of the cyclotron mass given in the eq (1.21).

The density of states of graphene is given by [60]

$$\rho(E) = \frac{4}{\pi^2} \frac{|E|}{t^2} \frac{1}{\sqrt{Z_0}} F \left(\frac{\pi}{2}, \sqrt{\frac{Z_1}{Z_0}} \right) \quad (1.23)$$

where F stands for the elliptic integral [60]. With the same approximation used above to find the linear dispersion for low energies, $\mathbf{q} \ll \mathbf{K}$ and $\mathbf{k} = \mathbf{K} + \mathbf{q}$, the density state for 4 fold degenerate case turns out to be [57],

$$\rho(E) = \frac{2A_c}{\pi} \frac{|E|}{v_F^2} \quad (1.24)$$

With the hexagonal unit cell area A_c and Fermi velocity v_F .

One can simply change the electronic properties of the graphene by electrostatic doping. Applying external fields tune the conductivity or resistivity of the graphene layer by changing the charge carrier concentration. Since the transistor is a main

element in variety of the electronic circuits, first devices to control the conductivity of graphene was field effect transistors (FETs) [2]. It is found that the conductivity of the mechanically cleaved graphene linearly changes with the applied gate voltage and the behaviour symmetrical to both polarities around charge neutrality point [5]. A graphene based FET is a three terminal device. These terminals, namely the source, drain and gate electrodes, are required for the application of the external field while maintaining a current flow on the graphene layer. In the graphene based field effect transistors a moderately or highly doped silicon substrate is used for gating the graphene. An oxide or nitrate layer which is deposited on Si substrate serves as a dielectric layer to prevent the electrical shortage between the graphene and the Si gate. After the transfer printing of graphene on this dielectric surface, graphene is shaped via lithographic techniques to isolate the channels defined by source and drain electrodes (Fig. 1.11 (a)).

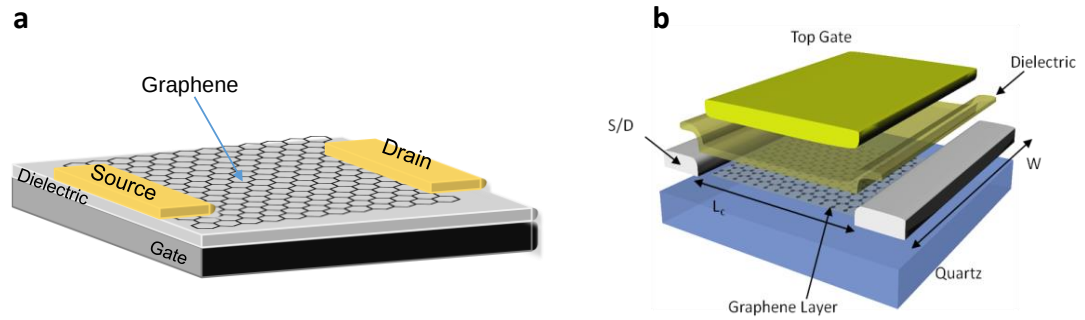


Figure 1.11: Graphene based field effect transistors (FETs). (a) A schematic showing the back-gate FET with a graphene layer aligned between source and drain electrodes on the dielectric layer. (b) Three dimensional exploded view of a top-gate graphene based FET. Thin dielectric layer is deposited on graphene layer to apply the gate voltage from top of the device. Reprinted with permission from “Pince, E. and C. Kocabas, *Investigation of high frequency performance limit of graphene field effect transistors*”. Applied Physics Letters, 2010. 97(17) Copyright (2010) American Institute of Physics.

The biggest advantage in fabricating a graphene based FET is obtaining high carrier mobilities. For mechanically exfoliated graphene samples, carrier mobilities around $15,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ have been reported in different works [2, 5, 61]. Terminating the scattering mechanisms in graphene yields extreme carrier mobility values such as $200,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in graphene based field effect transistors [11, 12].

Devices using top gate electrode (Fig 1.11 (b)) need a thin dielectric layer deposited on the graphene layer to fabricate the gate electrode on top. This situation had some disadvantages decreasing the carrier concentration in previous works [62, 63] . However the demonstration of high mobility top gate device [64] and the comparison with the back gate devices [65] provides the different device schemes for various electronic measurements [66].

We compared the electronic transport performance of graphene transistors that we fabricated by using graphene grown on ultra-smooth and rough copper foils. We used CVD to form the graphene layer on ultra smooth copper substrates (Mitsui mining and smelting co. LTD, B1-SBS). After 20 mins of annealing of smooth Cu substrates at 1035 °C, methane gas was sent into chamber in company with hydrogen. 15 mins of growth yielded single layer graphene on smooth Cu surfaces and then the samples were left to fast cooling down to room temperature. And we transfer printed the single layer graphene from copper to 100 nm SiO₂ on Si surfaces by photoresist drop casting method (See Section 1.2).

In order to fabricate the graphene based FETs, first conventional UV-photolithographic techniques were used to shape the source and drain electrodes on graphene. Then, thermal evaporation technique was used for metallization of the electrodes. After lift-off step, we isolated the graphene layer by using reactive ion etching so that the graphene layers would be aligned only between the source and drain electrodes to define the channels.

Schematic drawing of the fabricated back-gated transistors are given in Figure 1.12 (a). Optical microscope images of the devices are given in Fig. Figure 1.12 (b) and (c). Transistors fabricated on rough copper foils have cracks due to deep scratches on the copper. These cracks result in the large variation in the device performance especially for long channel length. The transfer characteristics of the fabricated graphene transistors on smooth and rough copper are given in Figure 1.12 (d) and (e), respectively. The channel length scaling of the devices are summarized in Figure 1.12 (d) and (h). The variation of on-current is significantly larger for the FETs based on the graphene grown on rough copper surface. The calculated field effect mobility of the devices (Fig. 1.12 (h)) scales with the channel length due to the contact resistance.

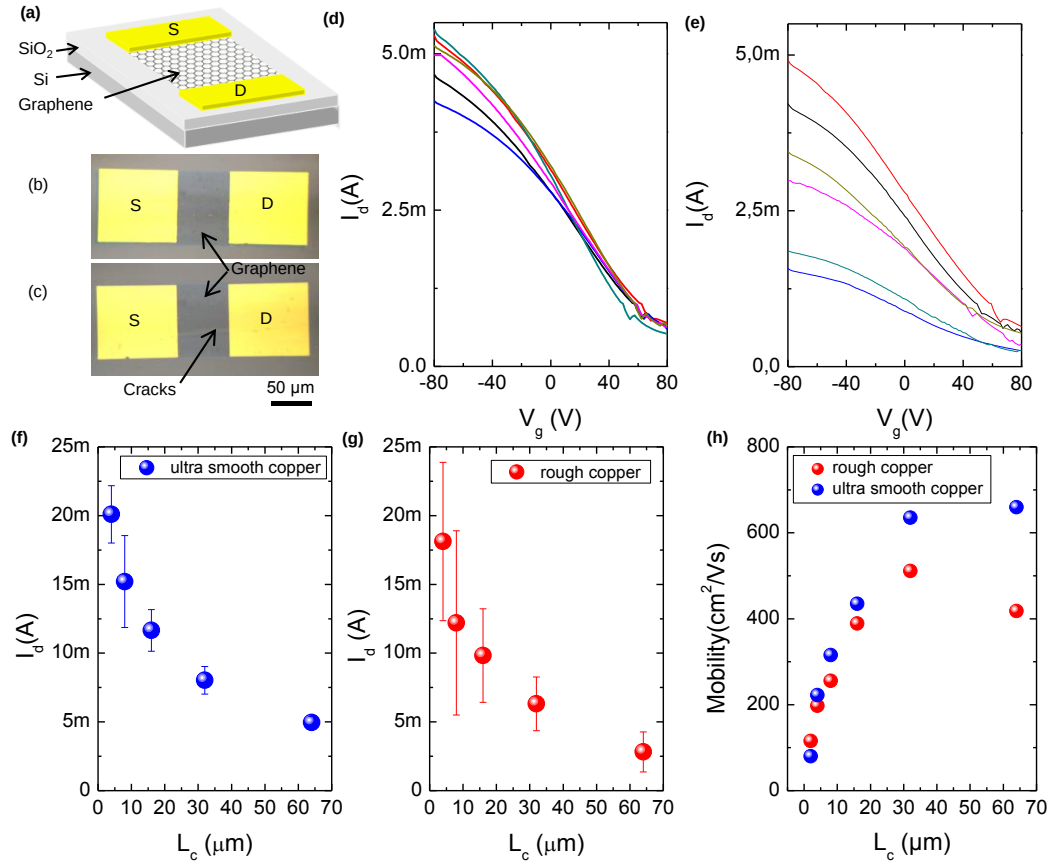


Figure 1.12 : Transport properties of fabricated graphene based transistors. (a) Schematic drawing of the fabricated graphene field effect transistor. The transistors use 100 nm thick SiO₂ as a dielectric and highly doped Si as a back gate electrode. The source/drain electrodes are 50 nm thick gold. (b,c) Optical microscope images of the fabricated transistors based on the graphene grown on ultra-smooth copper foils, and rough copper foils respectively. The deep scratches on the copper foils results in visible cracks in transferred graphene. (d,e) Transfer curves of the transistors with a channel length of 64 μm, based on the graphene grown on the ultra smooth and rough copper foils, respectively. (f,g) The scaling of the drain current with the channel length of transistors. The scattered plot shows the averaged value of the drain current measured from 10 identical transistors. The error bars show the standard deviation of the drain current. The transistors based on rough copper foils show significantly larger variation in the drain current than the ones based on ultra smooth copper foils. (h) The channel length scaling of the calculated field effect mobility of the transistors.

To show the promises of the ultra smooth copper foils, we fabricated macro-scale graphene based field effect transistors for the large scale applications and tested some of the charge carrier transport properties. Figure 1.13 (a) shows the fabricated transistors having cm-scale channel length. We used conductive carbon tapes as a contact electrodes.

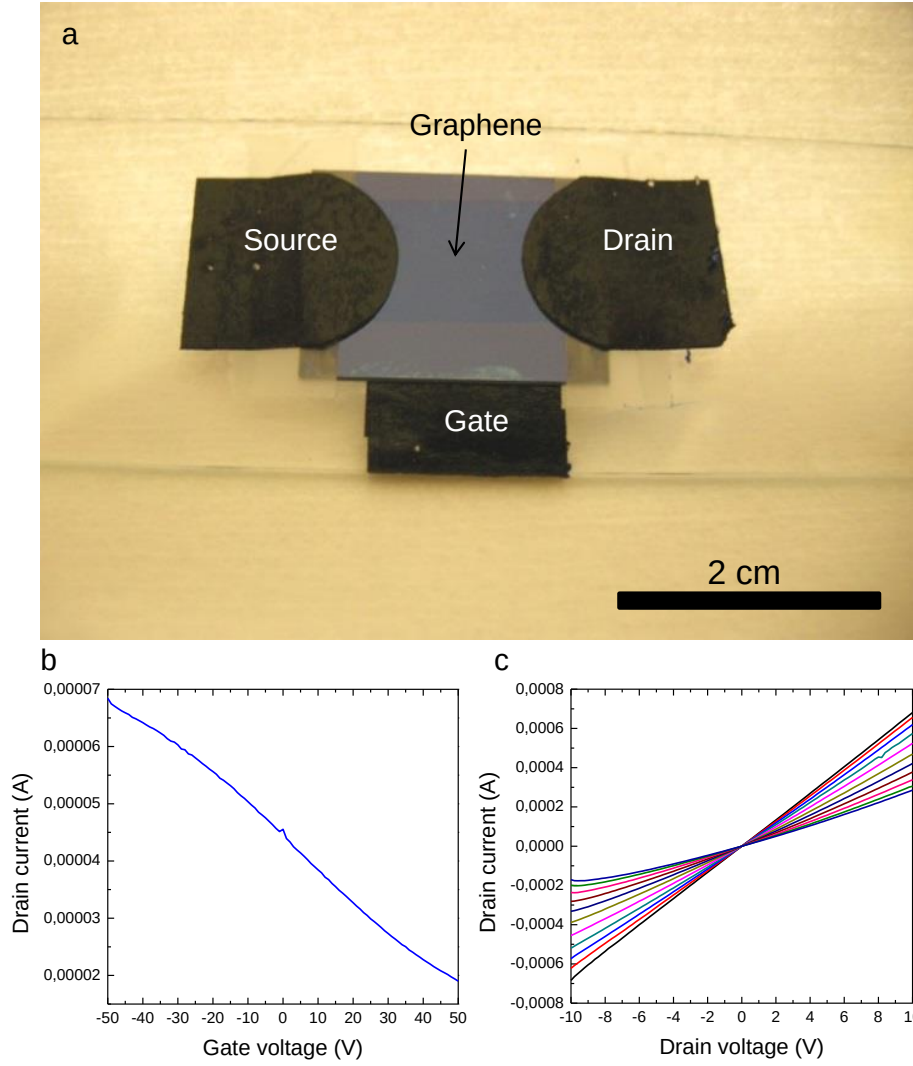


Figure 1.13 Macro scale graphene based FET and transport properties. (a) Photograph of the macro scale graphene based FET. Conductive carbon tapes are used as a contact electrodes. (b) Drain current vs. drain voltage characteristics of the device. (c) Modulation of the drain current with respect to applied gate voltage.

Figure 1.13 (b) shows the drain current modulation with respect to applied drain voltage. We scan the gate voltage from -50 to +50 and with 10 V steps to observe the modulation of drain current against drain voltage. Device shows p-type doped behavior due to the substrate doping. In Figure 1.13 (c) is a modulation of drain current against applied gate voltage plot. Because of the high p-type characteristics of the device Dirac point shifted to the positive voltages and we can see only the p-type tail of the total ambipolar behavior of the graphene. Gate voltages higher than 50 V causes dielectric breakdown and creates leakage current between the gate and the source. Therefore the breakdown voltage of the dielectric layer is another limiting factor to see the ambipolar behavior which is symmetric to both polarizations.

Since the graphene has no bandgap the graphene based FETs cannot be switched on an off like any semiconductor. However confining the charge carriers in small graphene structures yields the opening of a small band gap required for the operation of transistors and diodes [67-69]. Graphene nanoribbons (GNRs) are narrow graphene strips formed by cutting the graphene in certain direction. Some of the prominent techniques to shape the graphene as a nanoribbons are e-beam lithography [67], unzipping carbon nanotubes [70, 71], and chemical gas phase etching [72]. Y.Han et al. used the e-beam lithography method to tear the graphene layer into nanoribbons. They also demonstrated that the electronic transport in the graphene ribbons can be modified with changing ribbon width [67]. Another prominent technique is unzipping carbon nanotubes [70, 71]. Jiao et al. presented the polymer protected plasma etching method[70]. They obtained the aligned GNRs having different widths by longitudinal unzipping of single walled carbon nanotubes [70]. On the other hand, Kosynkin et al. used a solution-based oxidative process to obtain GNRs from multiwalled carbon nanotubes. In a similar way to ref [70], they provided longitudinal opening of carbon nanotubes to GNRs [71]. Alternatively, Wang et al. developed a controlled chemical process to narrow the graphene from the edges[72]. After a lithographic patterning they applied isotropic etching by using an oxidation reaction to obtain GNRs.

We demonstrated the fabrication of ~ 150 nm wide graphene ribbons on large area (1 cm^2). To that end we used the phase shift lithography to shape the cm^2 scale graphene area as a submicron ribbon array. By using the elastomeric masks in photolithography, sub 100 nm features can be created over the large areas [73-75]. If the thickness of the pattern on the elastomer mask is integer multiple of the UV radiation wavelength, the edges of the pattern induces a phase shift to the incident light [75]. This yields destructive interference at the edges of the patterns on mask and when exposed to UV light it transfers the patterns down to 50 nm in width [73]. Preparing the phase masks in desired patterns is an effortless process. Casting and curing PDMS on the previously patterned master Si results in the transfer of the replica of the pattern to the PDMS [75].

To shape the graphene layer as a ribbon array, we first generated a phase mask. To that end, we prepared a master as a mold for phase mask by using standard photolithography. Spin coating of S1805 photoresist on Si wafer at 5000 rpm for 1 min. yielded approximately 500 nm film thickness which is optimum thickness for a phase mask pattern to induce a phase shift to incident UV light. In that way, 2μ width photoresist lines with 2μ spacing were fabricated on surface. Casting and curing PDMS on this photoresist pattern resulted in the transfer of the replica of the pattern to contact surface of the PDMS phase mask. Removing PDMS from the master makes the phase mask ready to use in phase shift lithography.

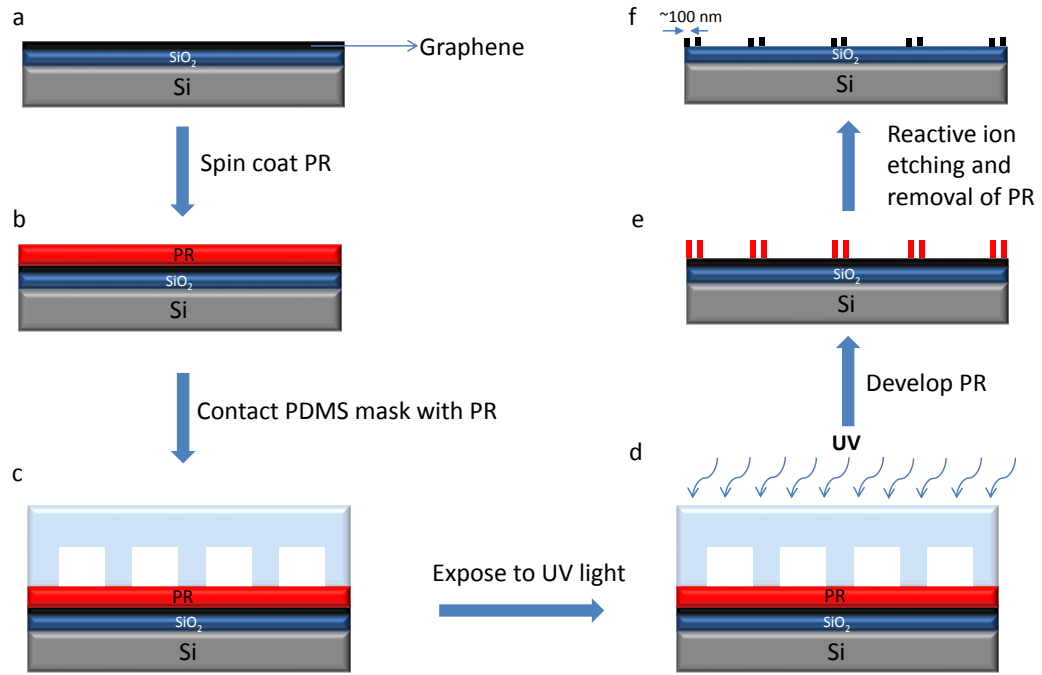


Figure 1.14: Fabrication steps of graphene ribbons via soft lithography

After the phase mask was ready, the phase shift lithography procedure was done by using these elastomer mask. We first spin coated ~500 nm thick photoresist (S1805) on the graphene transferred SiO₂ substrate (Fig. 1.14 (a-b)). Providing a conformal contact between the substrate and the elastomer mask and exposing to UV light shapes the photoresist layer as a ribbon array (Fig. 1.14 (c-e)). We used oxygen plasma to shape the graphene layer as a sub-micron wide ribbons. Using the photoresist ribbon array as a protective layer in reactive ion etching to remove the remaining underneath graphene resulted in ~100 nm wide ribbon array with ~2 μm spacing (Fig.1.14 (f)).

We examine the structural quality of the fabricated sub-micron graphene ribbons. Figure 1.15 (a) shows the atomic force microscopy (AFM) image of the individual ribbon having thickness of ~ 150 nm. The height of the many individual ribbons are measured as ~ 2 nm which is due to the residual chemicals stuck to the graphene nanoribbons during the fabrication procedure. The defects on the edges are sourced from the chemical treatment to remove the residual photoresist layer. Figure 1.15 (b) shows the scanning electron microscope (SEM) image of graphene ribbons. Due to the electrostatic charging, the graphene ribbons seem to be thicker than the original ones. We also investigated the Raman mapping of the fabricated structures to examine the quality of the resulting graphene structures. Figure 1.15 (c) shows the Raman mapping of the 2D peak proving the fabricated structures are graphene based.

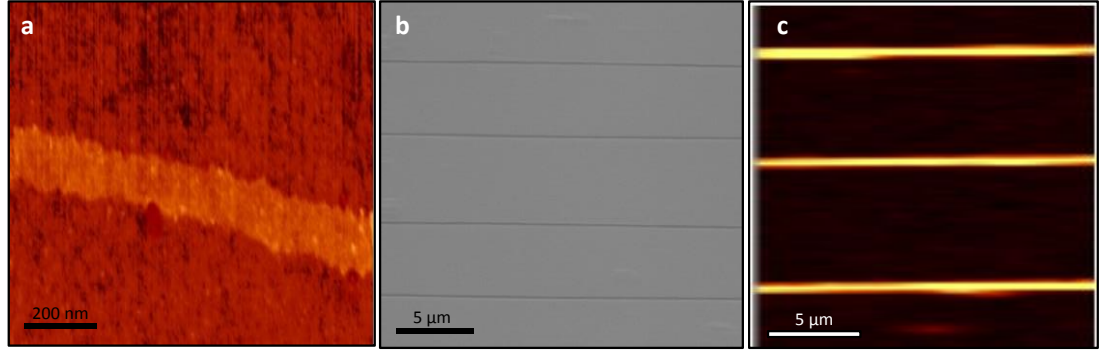


Figure 1.15: Structural characterization of fabricated graphene ribbons. (a) Atomic force microscope image of an individual ribbon. Ribbon height is measured as 2 nm on average. Due to the chemical process, the width of the ribbon varies between 150 nm to 200 nm in 1 μm ribbon length. (b) Scanning electron microscope image of fabricated graphene ribbons on SiO₂ surface. (c) Raman mapping of submicron graphene ribbons on large area.

We also measured the transport properties of graphene ribbons produced via soft lithography. We fabricated graphene ribbon based field effect transistors by aligning the ribbons between source and drain electrodes. We used the back gated FET structure. By scanning gate voltage from -80 V to +80 V, we observed the modulation of drain current with respect to drain voltage. We didn't observe a remarkable bandgap opening from the electronic measurements. This is due to the width of the ribbons. One should obtain sub 10 nm ribbons to effectively confine the charge carriers and create the band gap. Our graphene ribbon study could be more beneficial for graphene plasmonics where the submicron ribbon arrays are used for tuning the plasmonic resonances in graphene. In that way many breakthrough works has been reported about the plasmon excitation in graphene [76-81]. Chen et al. used 1 μ wide ribbons to collect the backscattering of the infrared light from the ribbon edges [76]. They used an AFM tip as a scatterer to couple the graphene plasmons with infrared light [76]. Similar work has been done by Fei et al. [77]. By gating the whole structure they showed that the plasma frequency of graphene can be varied by applied external field [77]. Moreover, Ju et al. investigated the plasmon resonances in graphene at terahertz frequency regime by using 4 μ width microribbon array [80]. They also revealed that the plasmon resonance frequency is inversely proportional to the square root of the ribbon width [80]. We will further investigate these improvements in the next section.

1.4 Optical properties of graphene

For the theoretical background of the optical properties of graphene¹, here we revisit the previously constructed model by Falkovsky [82].

Full expression for the optical conductivity of graphene is given by [82];

$$\sigma(w) = \frac{e^2 w}{i\pi\hbar} \left[\int_{-\infty}^{+\infty} d\varepsilon \frac{|\varepsilon|}{w^2} \frac{df_0(\varepsilon)}{d\varepsilon} - \int_0^{+\infty} d\varepsilon \frac{f_0(-\varepsilon) - f_0(\varepsilon)}{(w + i\delta)^2 - 4\varepsilon^2} \right] \quad (1.25)$$

Where

$$f_0(\varepsilon) = \left(e^{\frac{(\varepsilon - \mu)}{T}} + 1 \right)^{-1} \quad (1.26)$$

And therefore,

$$f_0(-\varepsilon) - f_0(\varepsilon) = \frac{\sinh\left(\frac{\varepsilon}{T}\right)}{\cosh\left(\frac{\mu}{T}\right) + \cosh\left(\frac{\varepsilon}{T}\right)} \quad (1.27)$$

There are mainly two physical mechanism contributing to the optical conductivity of graphene. The interband and intraband transitions. The first term of the eq 1.25 represents the intraband transitions while the second term stands for the interband transitions. Therefore we can express the the eq (1.25) as a superposition of two terms such as,

$$\sigma(w) = \sigma_{intra}(w) + \sigma_{inter}(w) \quad (1.28)$$

Integrating the first term of eq (1.25) to gives,

$$\sigma_{intra}(w) = \frac{2ie^2 T}{\pi\hbar(w + i\tau^{-1})} \ln\left(2\cosh\left(\frac{\mu}{2T}\right)\right) \quad (1.29)$$

With the assumption $\mu \gg T$, eq (1.27) reduces to,

$$\sigma_{intra}(w) = \frac{ie^2 |\mu|}{\pi\hbar(w + i\tau^{-1})} \quad (1.30)$$

Following the same procedure for the second term of eq (1. 25) for $T = 0$,

¹ Copyright © 2015 Pan Stanford Publishing Pte. Ltd. This subsection is reprinted with permission from S. Balci, E. O. Polat and C. Kocabas, "Chapter 11: Graphene based plasmonics," in the book "Introduction to Plasmonics: Advances and Applications," Pan Stanford Publishing 2015.

$$\sigma_{inter}(w) = \frac{e^2}{4\hbar} \left\{ \theta(w - 2\mu) - \frac{i}{2\pi} \ln \left(\frac{(w + 2\mu)^2}{(w - 2\mu)^2} \right) \right\} \quad (1.31)$$

Where $\theta(w - 2\mu)$ is a step function which is given by [82];

$$\theta(w - 2\mu) \rightarrow \frac{1}{2} + \frac{1}{\pi} \arctan \left[\frac{(w - 2\mu)}{2T} \right] \quad (1.32)$$

This form of interband conductivity (eq. 1.30) is not useful for the numerical calculations. However using eq. (1.27) in second term of eq. (1.25) yields;

$$\sigma_{inter}(w) = \frac{e^2}{4\hbar} \frac{\sinh\left(\frac{\hbar w}{2kT}\right)}{\cosh\left(\frac{\mu}{kT}\right) + \cosh\left(\frac{\hbar w}{2kT}\right)} \quad (1.33)$$

Noting that $\mu = \varepsilon_F$, this equation can be used as a model in the numerical calculations of interband conductivity of graphene. Plotting the eq (1.33) with respect to wavelength,

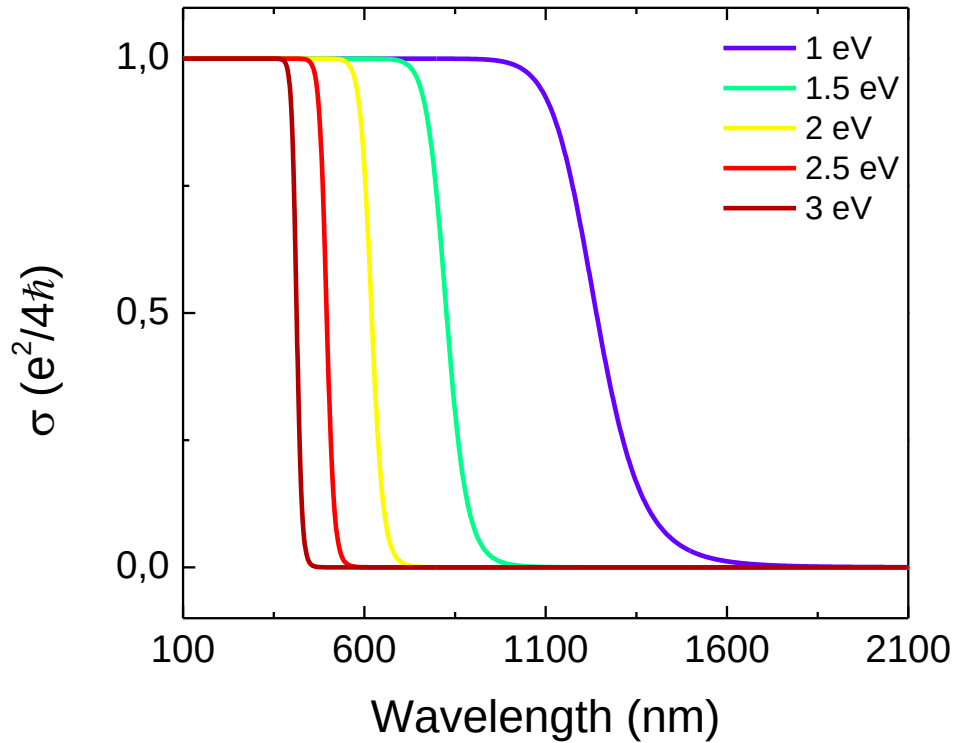


Figure 1.16: Interband conductivity of graphene with respect to wavelength.

The above plot of interband conductivity in graphene (Fig. 1.16) shows the required Fermi energy to manipulate the incident light at corresponding wavelength. Therefore one should effectively dope the graphene to obtain more than 500 meV Fermi energy to modulate the light in visible region. Conventional graphene based FETs can not achieve such high carrier concentrations. Therefore in the following chapters we will introduce liquid electrolyte based graphene supercapacitors working as optical modulators in the visible regime of the electromagnetic spectrum.

Setting $w = 0$ in the total expression of conductivity for practical conditions ($\varepsilon_F \gg kT$) we obtain the theoretical universal minimum conductivity value of graphene,

$$\sigma_0 = \frac{e^2}{4\hbar} \quad (1.34)$$

The transmittance of graphene can be expressed in terms of fine structure constant of the graphene lattice by using the minimum conductivity (1.34) as [83],

$$T = \left(1 + \frac{2\pi\sigma_0}{c}\right)^{-2} \approx 1 - \pi\alpha \quad (1.35)$$

Where the α is the fine structure constant and c is the speed of light. Inserting the value of fine structure constant for hexagonal graphene lattice,

$$\alpha = \frac{e^2}{\hbar c} \quad (1.36)$$

Transmittance of the single layer graphene defined by eq (1.35) takes the value,

$$T \approx 1 - \pi\alpha = 0,977 \quad (1.37)$$

Therefore for the few layer graphene having N layers of graphene,

$$(1 - T) = N\pi\alpha \quad (1.38)$$

Equation (1. 38) gives the opacity of the few layer graphene including N layers [8].

Many of the optical features of graphene can be tuned by electrostatic doping. For example, optical absorption, plasma frequency, and electron-phonon coupling in graphene can be tuned by electrostatic gating [77, 78, 80, 81, 84-86]. These tunable physical properties provide possibilities for new optical devices based on tunable light-matter interactions.

Graphene interacts with light through inter-band and intra-band electronic transitions (Figure 1.17). The gate dependence of the optical response of graphene varies with the wavelength of light, for example, in the visible region; the inter-band electronic transitions are dominant and yield a constant optical conductivity. By shifting the Fermi energy, one can block the inter-band transitions via Pauli blocking and reduce the optical conductivity (Figure 1.17 (a)).

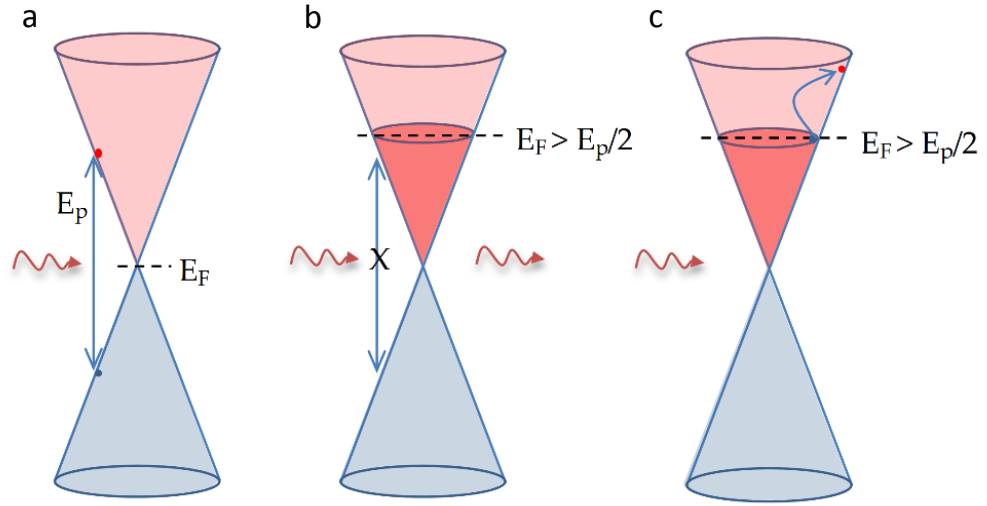


Figure 1.17: Interband and intraband transitions in graphene. (a) Interband electronic transition on the Dirac cone of graphene. (b) For doped graphene when the Fermi energy is larger than half of the excitation energy, inter-band transitions are blocked due to Pauli blocking. (c) Intraband electronic transitions, which define the optical properties of graphene at far-infrared spectrum. Graphene behaves like a Drude metal.

Ability to tune the optical conductivity yields new optical modulators [87]. At far-infrared regime, however, graphene behaves like a Drude metal with tunable charge density [88]. By tuning the charge density on graphene, one can tune the plasma frequency. Two recent studies have shown the gate tunable plasma oscillations on graphene.

In the first study Chen et al. launched and detected propagating optical plasmons in tapered graphene nanostructures using near-field scattering microscopy with infrared excitation light [76]. They used infrared laser and sharp AFM tip to launch plasmons on graphene and detected the standing wave patterns. They also tuned the charge density on graphene with a back-gate electrode. They found that the extracted plasmon wavelength is very short—more than 40 times smaller than the wavelength of illumination.

In the second work, Fei et al. measured the gate-tuning of graphene plasmons using infrared nanoimaging [77]. They integrated an infrared spectrometer with a sharp

AFM tip and measured the scattering cross-section of the tip. The scattering cross-section provides the amplitude of the excited plasma waves. They have succeeded in altering both the amplitude and the wavelength of these plasmons by varying the gate voltage. Active plasmonic devices operating in NIR spectrum are also possible. Kim *et al.* demonstrated a gate-tunable graphene-nanorod hybrid device by integrating gold nanorods in a graphene transistors [89]. Figure 1.16 shows the used device geometry and the SEM image of the gold-nanorods. They used ionic-liquid as an electrolyte to tune the electronic transition of graphene. Ionic liquids provide an efficient gating with charge densities larger than 10^{13} 1/cm² and Fermi energies of 1 eV. By electrostatic gating of graphene, they blocked interband optical transitions of graphene; they are able to significantly modulate both the resonance frequency and quality factor of gold nanorod plasmon. Their analysis showed that the plasmon–graphene coupling for graphene-nanorod structure is unexpectedly very high and they speculate that even a single electron in graphene at the plasmonic hotspot could yields an observable effect on plasmon resonance. Such hybrid graphene–nanometallic structure provides a powerful way for active plasmonic devices.

Patterning of graphene into nanometer sized ribbons or discs provide an additional level of control on the plasmonic response of graphene for new types of tunable metamaterials. Figure 1.17 shows various approaches to control the plasma resonance of graphene by patterning. Ju *et al.* explored plasmon excitations in engineered graphene micro-ribbon arrays [80]. They showed that graphene plasmon resonances can be tuned over a broad terahertz frequency range by varying the micro-ribbon width and in situ electrostatic doping.

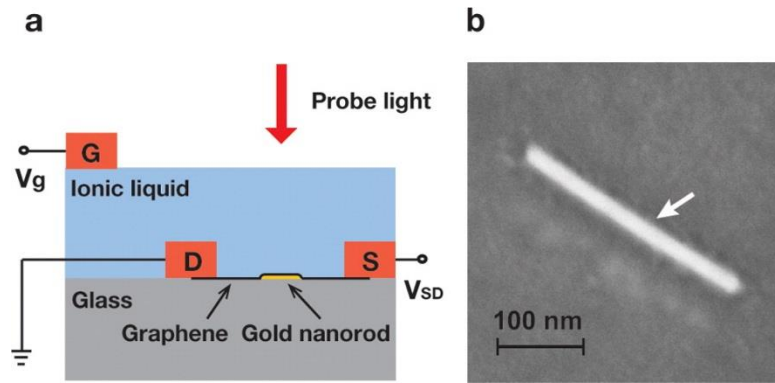


Figure 1.18: Electrical Control of Optical Plasmon Resonance with graphene. (a) Electrolyte gated graphene-gold-nanorod hybrid structure. A top electrolyte gate with ionic liquid is used to control the charge density and optical transitions on graphene. (b) A SEM image of the single gold nanorod covered by graphene. Reprinted with permission from Kim, J., et al., *Electrical Control of Optical Plasmon Resonance with Graphene*. Nano Letters, 2012. 12(11): p. 5598-5602. Copyright (2012) American Chemical Society

Patterning graphene into ribbons yields remarkably large oscillator strengths, and enhances room-temperature optical absorption peaks. Their results are the first for realization of tunable graphene-based terahertz metamaterials. Another approach to control plasma resonance of graphene is to use graphene/insulator stacks, which are formed by depositing alternating wafer-scale graphene sheets and thin insulating layers [90]. Yan et al. have patterned the graphene/insulator stacks into photonic-crystal-like structures. They showed that the plasmon in such stacks is non-classical due to direct consequence of the unique carrier density scaling law of the plasmonic resonance of Dirac fermions. Their work could lead to the development of new types of photonic devices such as detectors, modulators, and three-dimensional metamaterial systems. However, graphene has inherently weak optical absorption at visible and infrared wavelengths, which limits realistic applications. To overcome this challenge Fang et al. introduced nanopatterning of a graphene layer into an array of closely packed graphene nanodisks [91].

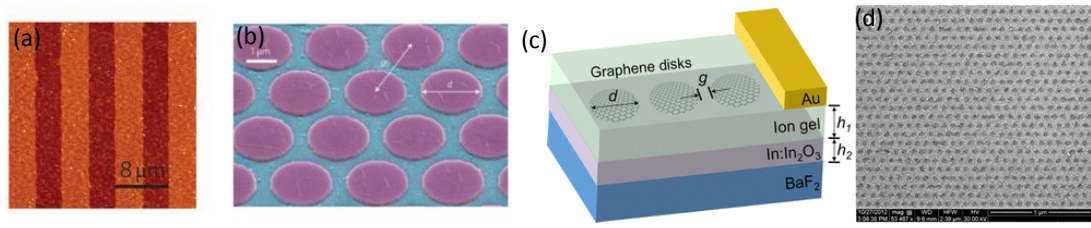


Figure 1.19: Controlling the plasma frequency of graphene by patterning graphene. (a) Patterning into graphene ribbons. Reprinted with permission from Ju, L., et al., *Graphene plasmonics for tunable terahertz metamaterials*. Nature Nanotechnology, 2011. 6(10): p. 630-634. Copyright © 2011 Nature Publishing Group (b) Making graphene/insulator stacks. Reprinted with permission from Yan, H.G., et al., *Tunable infrared plasmonic devices using graphene/insulator stacks*. Nature Nanotechnology, 2012. 7(5): p. 330-334. Copyright © 2012 Nature Publishing Group (c,d) Graphene nano disks. Electrostatic doping of these patterned graphene introduces an additional control on the plasma frequency. Reprinted with permission from Fang, Z.Y., et al., *Active Tunable Absorption Enhancement with Graphene Nanodisk Arrays*. Nano Letters, 2014. 14(1): p. 299-304. Copyright © 2013 American Chemical Society

The optical absorption of these arrays can be increased from less than 3% to 30% in the infrared region of the spectrum. Furthermore, they studied the dependence of the enhanced absorption on nanodisk size and interparticle spacing. By integrating the patterned disk in transistor geometry, they were able to tune plasma frequency with the gate voltage. These active plasmonic devices highlight possible ways for realization of novel devices using gate-tunable nature of graphene.

Chapter 2

Graphene Based Optical Modulators

Optical modulators are commonly used in communication and information technology to control intensity, phase or polarization of light. Electro-optic, electroabsorption and acousto-optic modulators based on semiconductors and compound semiconductors have been used to control the intensity of light. Due to gate tunable optical properties, graphene introduces new potentials for optical modulators. The operation wavelength of graphene based modulators, however, is limited to infrared wavelengths due to inefficient gating schemes.

In this chapter, we report a broadband optical modulator based on graphene supercapacitors formed by graphene electrodes and electrolyte medium.² The transparent supercapacitor structure allows us to modulate optical transmission over a broad range of wavelengths from 450 nm to 2 μ m under ambient conditions. We also provide various device geometries including multilayer graphene electrodes and reflection type device geometries that provides modulation of 35%. The graphene supercapacitor structure together with the high modulation efficiency can enable various active devices ranging from plasmonics to optoelectronics.

² Copyright © 2013 American Chemical Society. This chapter is reprinted with permission from E. O. Polat and C. Kocabas, "Broadband Optical Modulators Based on Graphene Supercapacitors," *Nano Letters*, vol. 13, pp. 5851-5857, 2013/12/11 2013.

2.1 Controlling the Optical Properties of Single Layer Graphene

Monoatomic thickness, optical transparency and broad-band absorption of graphene together with gate-tunable carrier density, provide unique platform for electro-optical devices [9, 10, 92-94]. As we mentioned in the introduction graphene interacts with light through inter-band and intra-band electronic transitions [93] (See section 1.4). Optical response of graphene at visible and near infrared frequencies is defined by inter-band transition where the momentum of light is not sufficient to create electron-hole pair in the same band. . Due to the linear band structure of the graphene, the inter-band transitions yield broadband optical response with constant optical conductivity [95] (eq 1.34). At long wavelengths (far infrared and terahertz frequencies), the inter-band transitions are blocked due to unintentional doping, therefore the optical response is dominated by the low energy intra-band transition.

These transitions yield gate-tunable Drude-like optical conductivities [88].

$$\sigma(w) = \frac{\sigma_{DC}}{(1 - iw\tau)} \quad (2.1)$$

Where the σ_{DC} is the low frequency conductivity (Drude conductivity), w is the angular frequency of light and τ is the electron scattering time.

Active optical devices such as detectors [96], modulators [94, 97], tunable antennas [89] and meta-materials [80] working at far infrared and terahertz wavelengths have been demonstrated based on gate-tunable intra-band transition. Controlling inter-band transitions of graphene in the visible and near infrared wavelength, however, requires much higher carrier concentrations [98]. By electrical tuning of the Fermi energy (E_F), the inter-band transition with energies less than $2|\varepsilon_F|$ can be blocked due to Pauli blocking resulting transparent graphene.

Liu et al. [87] demonstrated an electroabsorption modulator using graphene integrated on an optical waveguide working at near infrared (NIR) wavelengths. In their work, the Fermi energy of graphene is tuned up to 0.5 eV through a dielectric capacitor. Similar device structures, usually back gated transistors, have been implemented to tune photonic and plasmonic cavities operating at NIR. The electrical breakdown of the dielectric layer of the capacitor limits the operation in the visible and NIR spectra. The working wavelength can be reduced down to 700 nm by electrolyte gating of graphene layer [98-100]. In the electrolyte gating schemes, application of a gate voltage polarizes the electrolyte and forms an electrical double layer (EDL) near the graphene surface. Since the thickness of EDL is around a few nanometer, EDL generates very large electric fields and associated Fermi energies.

The electrochemical potential window of the electrolyte limits the maximum bias voltage and the carrier concentration.

2.2 Graphene Supercapacitors Working as Optical Modulators

As an alternative gating scheme, we propose to use supercapacitors instead of dielectric capacitors. Supercapacitors, also called ultracapacitor or electric double-layer capacitors, store charges at the electric double-layers formed at the electrolyte-electrode interface. Carbon based electrodes provides very large surface area which enhances energy storage capacity [101-103]. Recent studies indicate that graphene electrodes provide scalable approach for ultrahigh energy densities [101-103]. Here, we report uses of graphene supercapacitors as broadband optical modulators. The proposed device consists of two parallel graphene electrodes and electrolyte between them. The modulator has simple parallel plate geometry, yet, with a very efficient device operation. The graphene supercapacitors operate as electroabsorption modulators over a broad range of wavelengths from 450 nm to 2 μm under ambient conditions. We also studied various device geometries to increase the modulation amplitude. We were able to obtain modulation of 35 % using a few layer graphene with an ionic liquid electrolyte.

Figure 2.1 (a) shows the schematic drawing of the graphene capacitor used as an optical modulator. We transferred large area graphene layers on double-side-polished quartz wafers (1x2 cm graphene layers are grown by chemical vapor deposition on copper foils, see Section 1.2). Graphene coated quartz wafers were put together by a 100- μm thick spacer. The gap between the graphene electrodes were filled with an electrolyte solution. We used 5 mM solution of Tetrabutylammonium tetrafluoroborate (TBA BF₄) in DI water as the electrolyte because of its large electrochemical potential window.

Application of a voltage bias between the top and bottom graphene electrodes polarizes the electrolyte and generates double layer formation at the interface of graphene electrodes with different polarities. The double layers with different polarities electrostatically dope the graphene electrodes and shift the Fermi energy of graphene electrodes in the opposite directions. The schematic band structure of the top and bottom graphene electrodes are shown in Figure 2.1 (b) and (c). Unlike dielectric capacitors where the voltage drops linearly between the electrodes, in supercapacitors, the voltage drops sharply at the double layers (in a few nanometers) which generates very large electric fields.

The equivalent circuit of the graphene supercapacitor is shown in Fig.1d. Superscript “T” and “B” represent the top and bottom electrodes, respectively. In the circuit, the arrows represent the voltage dependent circuit elements. The charge density of graphene layers defines the resistance R_G^T, R_G^B and the quantum capacitance C_Q^T, C_Q^B of electrodes.

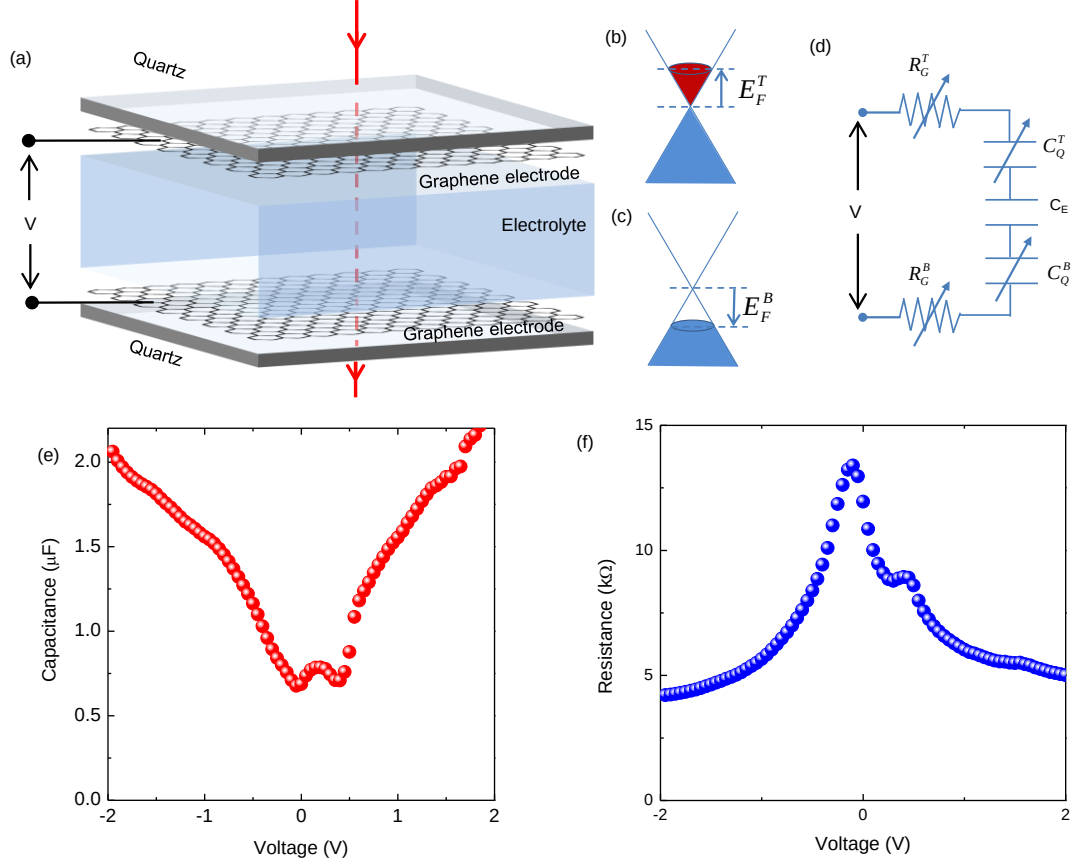


Figure 2.1: Electronic properties of the graphene supercapacitor. (a), Schematic exploded view of the optically transparent double layer capacitor formed by two parallel graphene electrodes transfer-printed on quartz substrates and the electrolyte medium (5 mM TBA BF salt in DI water) between them. (b), (c) Schematic representation of the electronic band structure of the top and bottom graphene layers under a voltage bias. (d), Equivalent circuit of the supercapacitor. Superscript “T” and “B” represent the top and bottom electrodes, respectively. The arrows indicate the voltage-variable elements. (e), (f), The variation of the capacitance and resistance of the device as a function of bias voltage, respectively.

At room temperature, the quantum capacitance [104] of graphene is expressed as [105, 106];

$$C_Q = e^2 D = \frac{2e^2}{\hbar v_F} \sqrt{\frac{n}{\pi}} \quad (2.2)$$

where D is the density of states, n is the charge concentration and v_F is the Fermi velocity.

To extract the voltage dependence of the circuit elements (quantum capacitance and resistance of graphene electrodes), we measured the impedance of the graphene supercapacitor as a function of bias voltage. We used an excitation signal of 100mV

at 20 Hz and measured the phase and amplitude of the generated alternating current through the capacitor. Figure 2.1 (e) and (f) show the measured capacitance and the serial resistance of device. Both the capacitance and the resistance show profound voltage dependence. The capacitance-voltage curve in Figure 2.1 (e) shows two distinct minima at -0.1 and 0.4 V, corresponding the charge neutrality points of graphene electrodes where the quantum capacitance is minimum. Similarly, the voltage dependence of the resistance (Fig. 2.1 (f)) shows two distinct peaks at the charge neutrality points of graphene electrodes. The total resistance including top and bottom graphene electrodes, varies from 14 k Ω to 4 k Ω as the bias voltage changes from 0 V to 2V.

The value of minimum carrier concentration also defines the maximum resistance and the minimum quantum capacitance. The minimum value of the capacitance depends on the residual charge density however; the maximum value of the resistance depends on both residual charge and carrier mobility. The mobility difference between the graphene electrodes is likely the cause of different resistance values at Dirac points.

C_E represents the electrostatic capacitance of the double layers. We measured the value of C_E as 30-40 $\mu\text{F}/\text{cm}^2$ (Fig. 2.2 (a)) which is much larger than the quantum capacitance of the graphene electrodes at low doping concentrations (2 $\mu\text{F}/\text{cm}^2$). Therefore, the total capacitance of the optical modulator is limited by the quantum capacitance of the electrodes (For capacitors connected in series; the equivalent of the circuit is defined by the smallest capacitance.)

At high carrier concentrations the quantum capacitance of the graphene electrodes increases up to 20 $\mu\text{F}/\text{cm}^2$ and becomes comparable with the capacitance of the ionic double (Fig. 2.2 (b)). This causes flattening of the total capacitance at high carrier concentrations.

The optical transmission through the graphene supercapacitor can be modulated by blocking the inter-band optical transition. In the fabricated graphene supercapacitor each graphene electrodes has broad band optical absorption around 1.5 to 2 % (Figure 2.3).

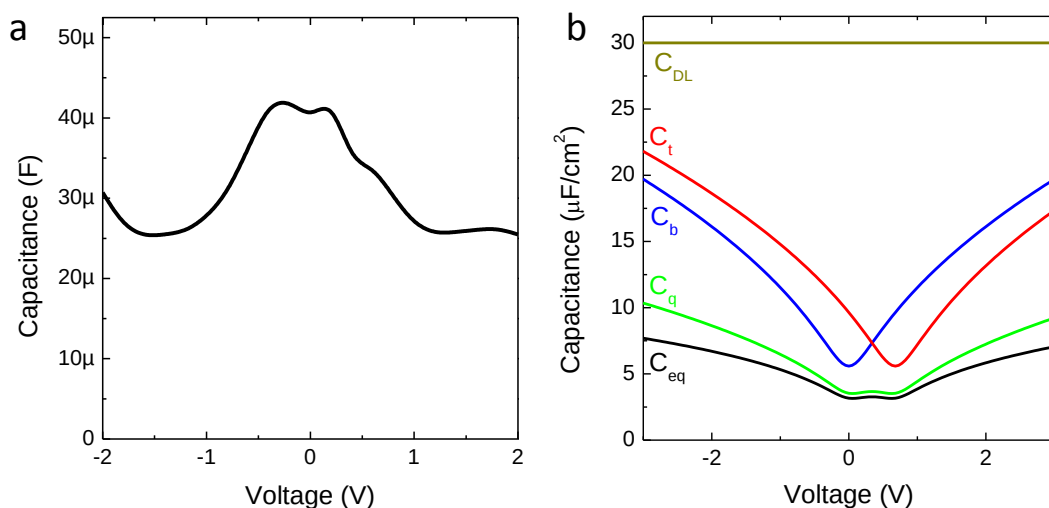


Figure 2.2: Comparison of electrostatic capacitance and quantum capacitance.(a) Electrostatic capacitance of the electrical double layer of aqueous electrolyte (5mM of TBA BF₄ in DI water) measured using gold electrodes. (b) Calculated capacitance of the top (C_t) and bottom (C_b) graphene electrodes (Dirac point of the bottom graphene is shifted by 0.7 V), electrostatic double layer (averaged value of 30 μ F/cm² calculated from the previous measurement) and the equivalent capacitance (C_{eq}) of the super capacitor. C_q represents the total quantum capacitance of the graphene electrodes. The difference between C_q and C_{eq} shows the contribution of the double layer capacitance. At low carrier concentration, the capacitance is limited by the quantum capacitance and at high concentrations, the contribution of double layer capacitance flattens the total capacitance.

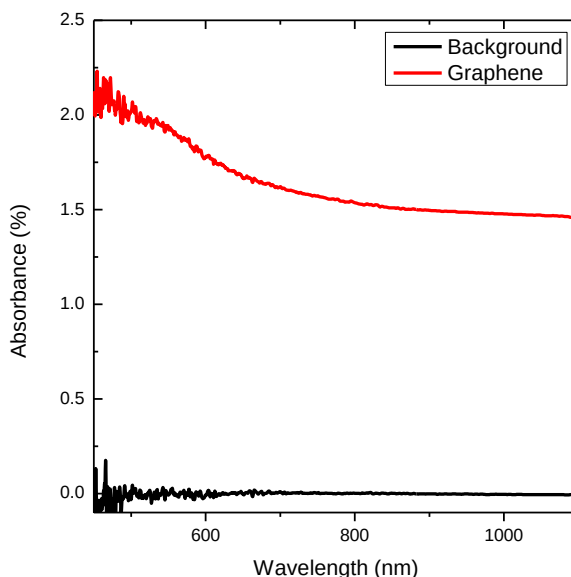


Figure 2.3: Optical absorption of graphene electrodes in graphene supercapacitor.

2.3 Electro-optic Response

After the electrical characterizations, we measured electro-optical response of the graphene supercapacitor (Fig. 2.4 (a)). By shifting the Fermi energy ε_F of the graphene, one can block the optical absorption for wavelength with energies less than twice the Fermi energy ($h\nu < 2|\varepsilon_F|$). We measured the optical transmission of the capacitor in the visible and near infrared wavelength (between 500 nm to 1200 nm) using a FTIR spectrometer. Figure 2.4 (b) shows the change of the transmission against the wavelength and bias voltage between -2.4 V to 2.4 V. The change of the transmission is normalized by the transmission recorded at 0V.

We observed a symmetric change in the transmission around 2% in the positive and negative voltages indicating that absorption of only one electrode is modulated. The spectral distribution of the change of the transmission has a step-like behavior with transition center at $2|\varepsilon_F|$ for positive voltages is shown in Figure 2.4 (c). The variation of $2|\varepsilon_F|$ with the bias voltage is shown by the scatted plot in Figure 2.4 (d).

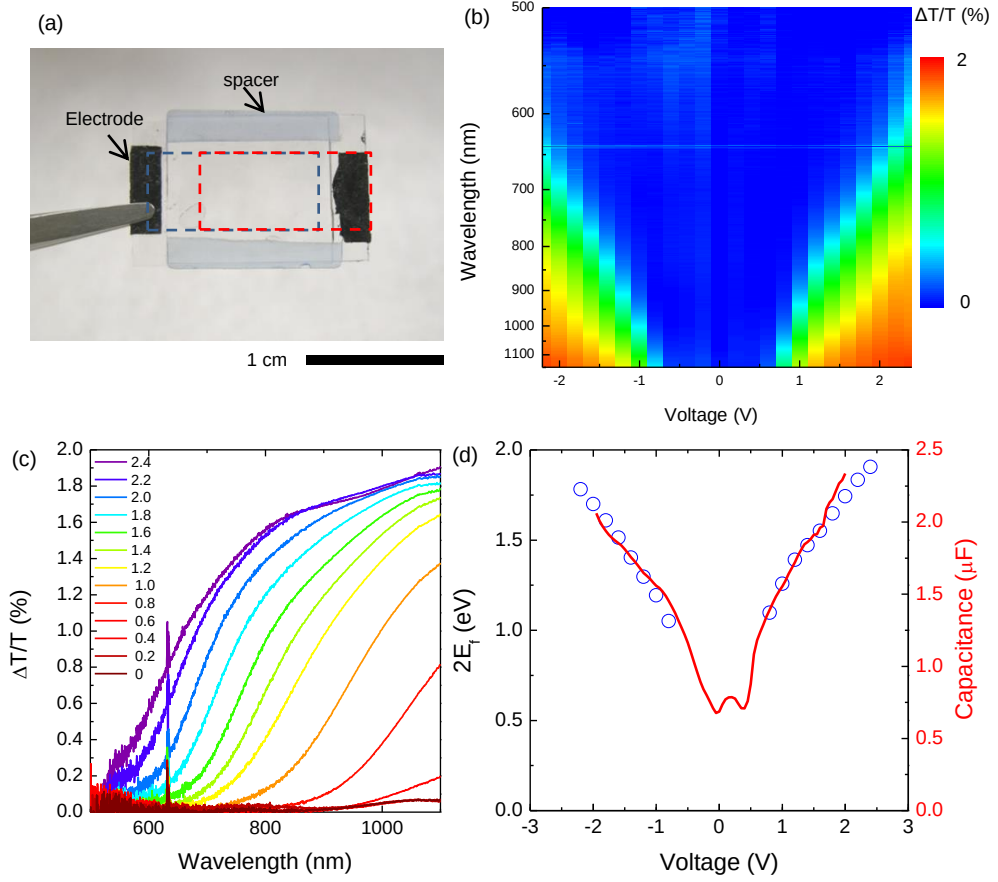


Figure 2.4: Electro-optic characterization of graphene supercapacitor based optical modulators. (a) Picture of the fabricated graphene supercapacitor. The black regions are carbon electrodes that are used to make electrical contact to graphene. (b) The normalized change of the transmission of the capacitor plotted against wavelength and bias voltage. (c) The variation of the normalized change of the transmission versus the wavelength for various bias voltages. (d) Fermi energy (scattered plot) extracted from the electro-optical response of the capacitor and measured capacitance (solid red curve). Both Fermi energy and the capacitance show $\sim\sqrt{n}$ dependence.

With the aqueous electrolyte, we were able to achieve $2|\varepsilon_F|$ values as large as 1.8 eV. The maximum value of the bias voltage is limited by the electrochemical window of the electrolyte. Application of a bias voltage outside of the voltage range (between -2.5 V to 2.5 V) induces irreversible structural deformation on the graphene and reduces the modulation strength. With the electrostatic doping, both Fermi energy and capacitance scales as $\sim\sqrt{n}$ where n is the total charge density on graphene. To show the agreement, we plot the measured capacitance (red solid curve) and $2|\varepsilon_F|$ on the same graph (Fig. 2.4 (d)).

The minimum value of capacitance ($0.6 \mu\text{F}$) and Fermi energy ($\sim 250 \text{ meV}$, (Fig. 2.5)) is determined by the unintentional doping on graphene due to charged impurities on the substrate and electrolyte.

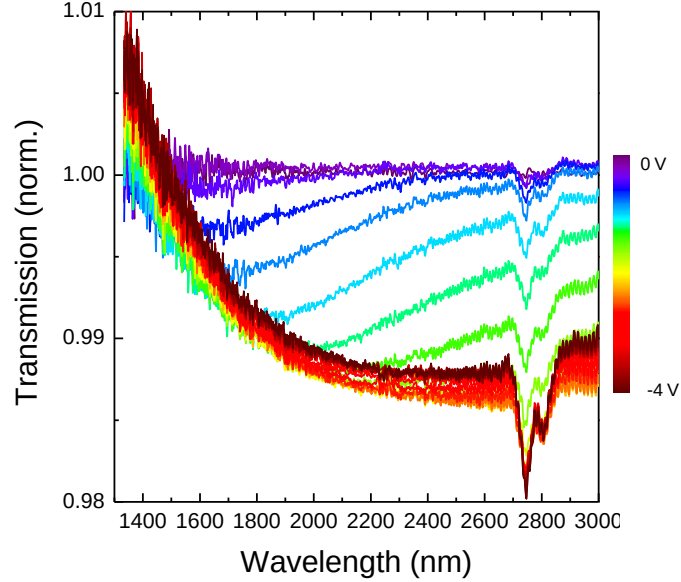


Figure 2.5: Near-infrared respond of graphene supercapacitor based optical modulators. Modulation of the normalized transmission of graphene supercapacitor at near-infrared regime. The Fermi energy of undoped graphene is estimated as 250 meV.

The parallel plate geometry allows us to measure the Raman spectra of graphene electrodes to monitor the electrostatic doping as function of bias voltage. The 2-dimensional map of Raman intensity is plotted in Figure 2.6 (a) against the Raman shift and the bias voltage. We observed strong voltage dependent Raman spectra indicating strong electrostatic doping. Figure 2.6 (b) and 2 (c) shows the voltage dependence in Raman frequency and Raman intensity of G and 2D bands, respectively, obtained from the fitting of the Raman peaks. The G-band shows a profound change in the Raman frequency; on the other hand, 2D-band shows strong change in the Raman intensity. The physical mechanisms behind these behaviors are different. The frequency change of the G-band can be understood by tunable electron-phonon coupling [107, 108]. However, the mechanism of the intensity change of 2D-band is due to change of possible inelastic light scattering pathways at large Fermi energies [98]. Furthermore, we observed a distinguished asymmetry between electron and hole doping. Electron doping (at negative bias voltages) is significantly larger than hole doping (at positive bias voltage) likely because of different gating-strength of anions (BF_4^{-1}) and cations ($((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^{+1})$) of the electrolyte [109]. The results obtained from the Raman spectra suggest that under

a bias voltage, the Fermi energy of the top and the bottom graphene electrodes are different owing to the asymmetric doping levels, therefore, we could only modulate absorption of one graphene electrode that results around 2% modulation. Raman spectra of graphene electrodes under large bias voltages (Fig. 2.6 (d)) shows strong defect mode (D-band). The appearance of D-band is irreversible indicating structural damages of graphene due to a redox reaction.

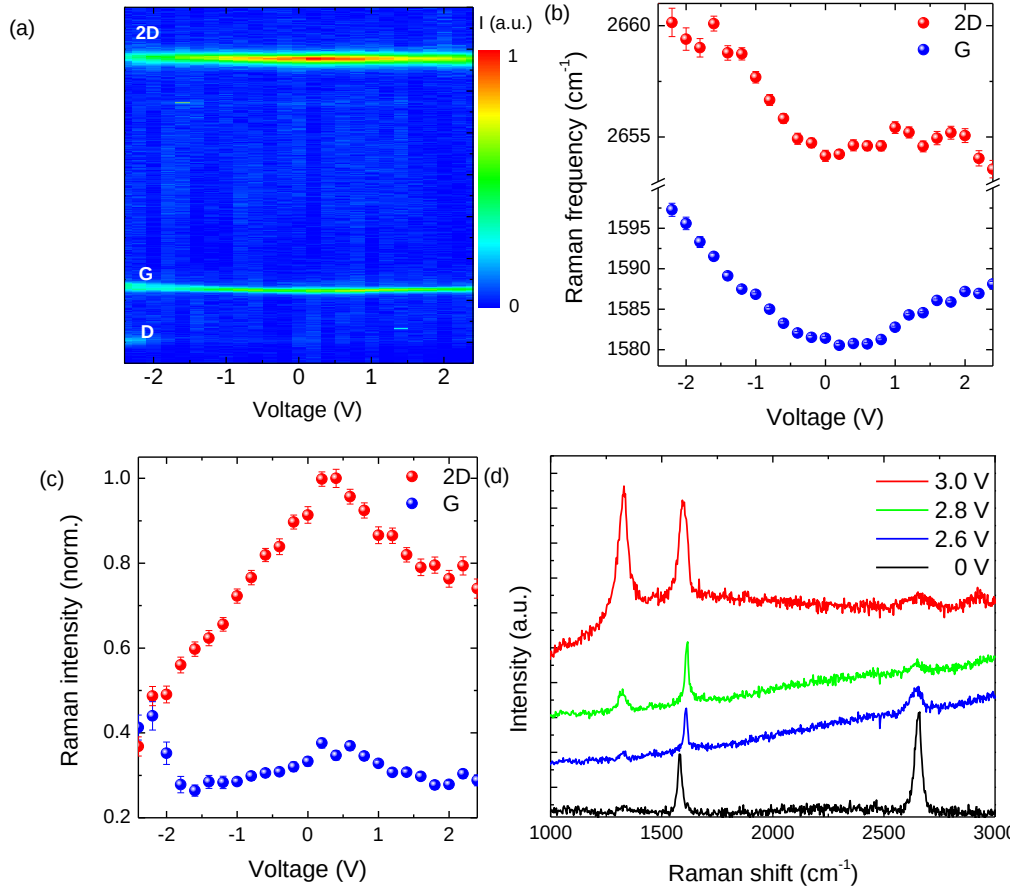


Figure 2.6: Raman spectroscopy of graphene supercapacitor based optical modulators. (a) Intensity map of Raman scattering of the graphene electrode as a function of Raman shift and applied voltage. The labels indicated the D, G and 2D Raman peaks of graphene. (b,c) Variation of Raman frequency and intensity of 2D and G bands as a function of bias voltage. (d) Raman spectra of defected graphene electrodes after application of bias voltages larger than the electrochemical window of the electrolyte.

With the aqueous electrolyte, we were able to reach $2|\varepsilon_F|$ values up to 1.8 eV. This upper limit is defined by the electrochemical window of the electrolyte. To overcome this limitation, we used a special ionic liquid (Diethymethyl (2-methoxyethyl)

ammonium bis (trifluoromethylsulfonyl) imide) with large electrochemical window (from -3.5 V to +3 V). Ionic liquids have superior performance as an electrolyte owing to their large electrochemical window, higher ion concentrations, and low vapor pressures. Furthermore, the double layer capacitance of ionic liquids are larger than aqueous electrolyte due to very thin (<1 nm) Helmholtz layer [109].

We measured the electro-optical response of the ionic liquid based graphene supercapacitor. The modulation of the optical transmission is plotted in Fig. 2.7 (a). We were able to apply bias voltages in the range of -5 V to +3.5 V which yields $2|\varepsilon_F|$ values of 2.3 eV (Fig. 2.7 (b)) without detrimental effects on the graphene electrodes. Interestingly, for high negative bias voltages ($V_b < -3.5$ V), we observed an additional shoulder of modulation at long wavelength likely due to blocking the interband transition of the second graphene electrodes. For aqueous electrolyte we usually observed modulation strength around 2% owing to the doping of only one graphene electrode. In the case of ionic liquid, we observed the same asymmetry; however, at high voltages we observed the modulation of the second electrode. The illustration of the optical modulation mechanism of the capacitor is shown in Fig. 2.7 (c). The bias voltage drops unevenly at the quantum capacitance of the top and bottom graphene layers owing to the asymmetric charge doping. Maximum charge density achieved with ionic liquid electrolyte is around $7 \times 10^{13} \text{ 1/cm}^2$ which yields Fermi energy of 1.15 eV.

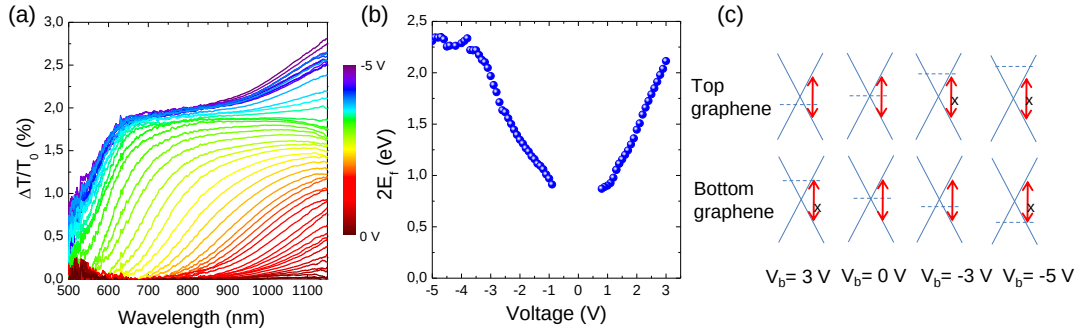


Figure 2.7: Ionic liquid performance in the graphene supercapacitor. (a) Normalized change of the transmission of a graphene supercapacitor that uses ionic liquid as an electrolyte for bias voltage in the range of -5V to 0 V. (b) The cut-off energy ($2E_f$) as a function of bias voltage. (c) Illustration of gate-induced change of Fermi energy for top and bottom graphene for different bias voltage.

At a certain wavelength, we first observe optical modulation due the one electrode, at large bias voltages the inter-band transition of the second graphene is blocked resulting additional modulation. The measured capacitance and extracted $2|\varepsilon_F|$ do not match exactly for the ionic liquid electrolyte. There are two reasons that could cause this deviation. The first one is the high level of unintentional doping. From the transport measurement of the supercapacitor structure with ionic liquid electrolyte, we observed that the Dirac point is shifted to +1 V and -1 V (Fig. 2.8). This shift is larger than the aqueous electrolyte likely due to the unintentional doping of ionic

liquid which induces more residue charges on graphene. The second one is the low interfacial capacitance of the double layer of ionic liquid. Even the ionic density is very high for the ionic liquid, the mobility of ions are much slower than the aqueous electrolyte. Therefore the measured capacitance (at 20 Hz) underestimates the actual capacitance of the device.

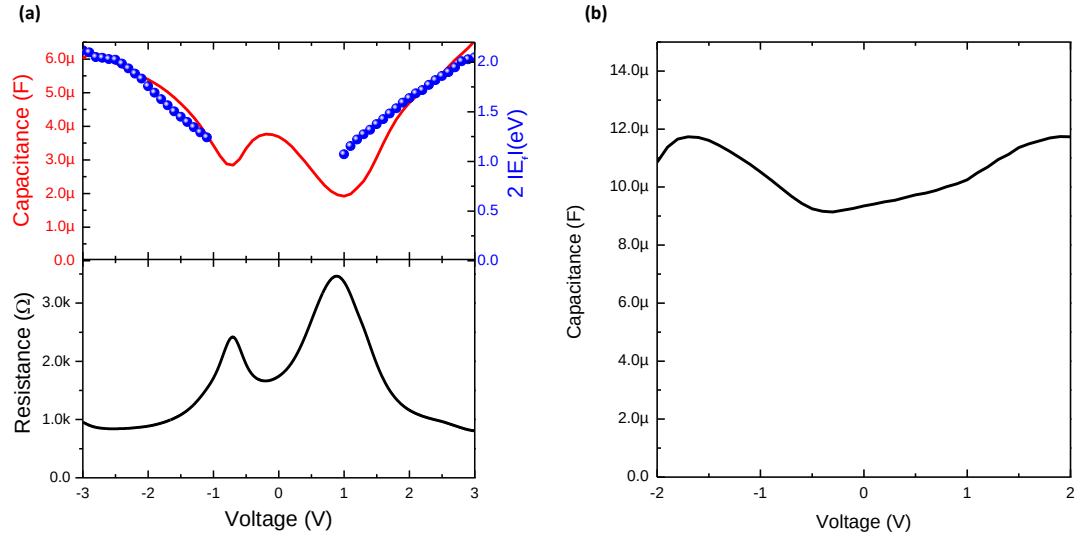


Figure 2.8: Electrical properties of graphene supercapacitor with ionic liquid electrolyte (a) The measured capacitance and resistance of graphene supercapacitor with ionic liquid electrolyte. The scattered plot shows the extracted Fermi energy. The deviation of the measured capacitance from $\sqrt{n}$ dependence is likely due to the large contribution of capacitance of the ionic double layer. (b) The measured capacitance at frequency of 20Hz for 1cm² capacitor with gold electrodes and the ionic liquid electrolyte. The capacitance is significantly less than the aqueous electrolyte due to low ionic mobility of ions in the ionic liquid.

2.4 Switching Performance

Ionic liquid electrolyte allows us to shift the optical modulation down to visible spectra. We studied the switching performance of the modulator at the wavelength of 635 nm using a diode laser. Fig. 2.9 (a) shows spectra of the normalized modulation at bias voltages of -3 V and -2 V. The red vertical line shows the working wavelength. We monitored the transmitted intensity while switching the bias voltage with a time trace given in Fig. 2.9 (b). The recorded time trace of the normalized modulation is given in Fig. 2.9 (c). The time response of the capacitor is limited by the charging time which is defined by the resistance of the graphene electrodes and the total capacitance of the modulator. The measured RC time constant of the capacitor is around 200 ms. Since the overlapping area of graphene electrodes is around 2cm^2 , the RC time constant is quite high. We also measured the frequency dependence of the total capacitance (Fig. 2.9 (d)). The differential capacitance at high frequencies decays significantly due to the low ionic conductivity of the ionic liquid.

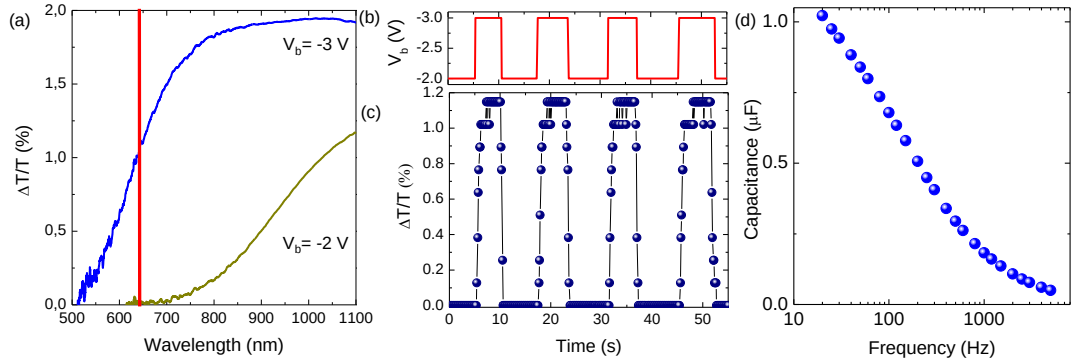


Figure 2.9: Switching performance of graphene optical modulators. (a) Normalized transmittance of the capacitor at bias voltages of -2 V and -3 V. The vertical red line indicated the working wavelength (635 nm) (b) Time trace of the bias voltage applied between graphene electrodes. (c) Time trace of the normalized transmittance. (d) The variation of the total capacitance as a function of frequency at a bias voltage of 0V.

2.5 Device Schemes

Optical absorption of a single layer graphene limits the modulation efficiency around 2% (Fig. 2.10 (a)). We proposed device strategies to increase the modulation efficiencies by increasing the interaction of light with graphene electrodes. Figure 2.10 provides the illustration of the supercapacitor structures to increase the modulation strength. In the first approach (Fig. 2.10 (b)) we increase the number of graphene layers. We grew multilayer graphene (~ 7 -10 layers) on copper foils and transferred them on glass substrates (Fig 2.11 (a, b)). Figure 2.10 (d) shows the measured normalized transmittance of the capacitor with multilayer graphene electrodes.

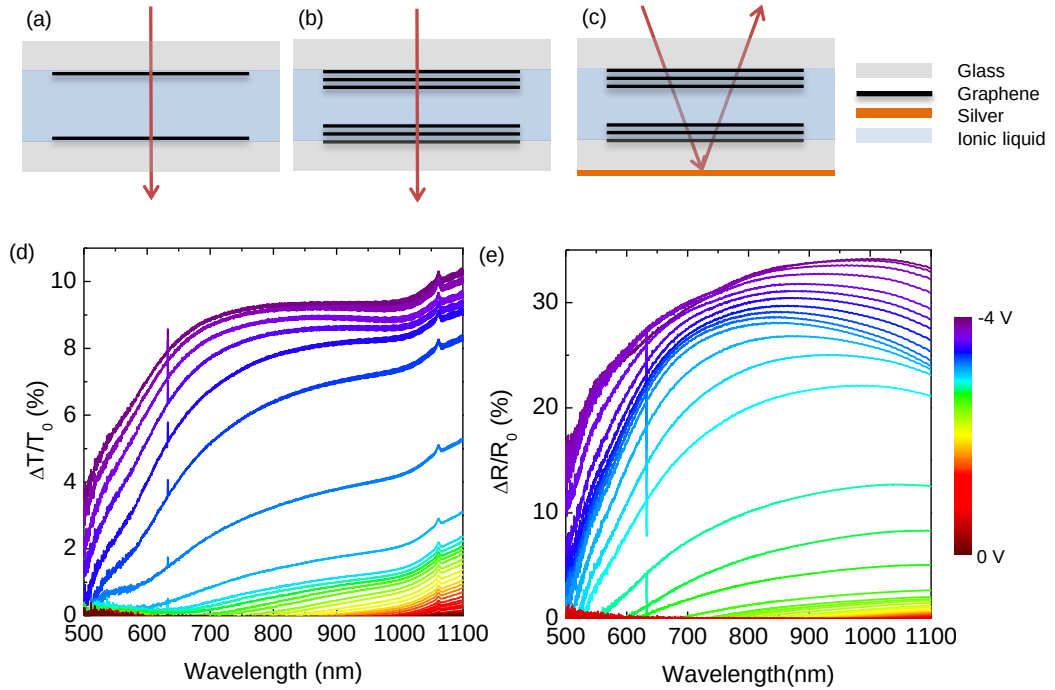


Figure 2.10: Various device schemes to increase the modulation efficiency. Graphene supercapacitors using (a) single layer and (b) multilayer graphene electrodes, (c) Reflection type graphene optical modulator. (d) Normalized transmittance of the graphene supercapacitor with multilayer graphene electrodes. (f), Normalized reflectance of the graphene supercapacitor with a reflecting surface.

We obtained a modulation around 10%. Unlike single layer graphene electrode, multilayer graphene yield more abrupt changes at large bias voltages. Furthermore, we tested the multilayer graphene electrodes formed by layer-by-layer transfer printing process. However, we do not obtained significant increase in the modulation strength (around 2-4%) likely because of air gap or organic residues remain between the graphene layers which prevent efficient gating of underneath graphene layers.

For CVD grown multilayer graphene, however, layers stack by van der Waals forces, therefore, the underneath graphene layers can be gated by the field of the ionic liquid electrolyte. Note that, due to the low density of states of graphene, top graphene layer cannot completely screen the penetration of electric field of the electrolyte [110].

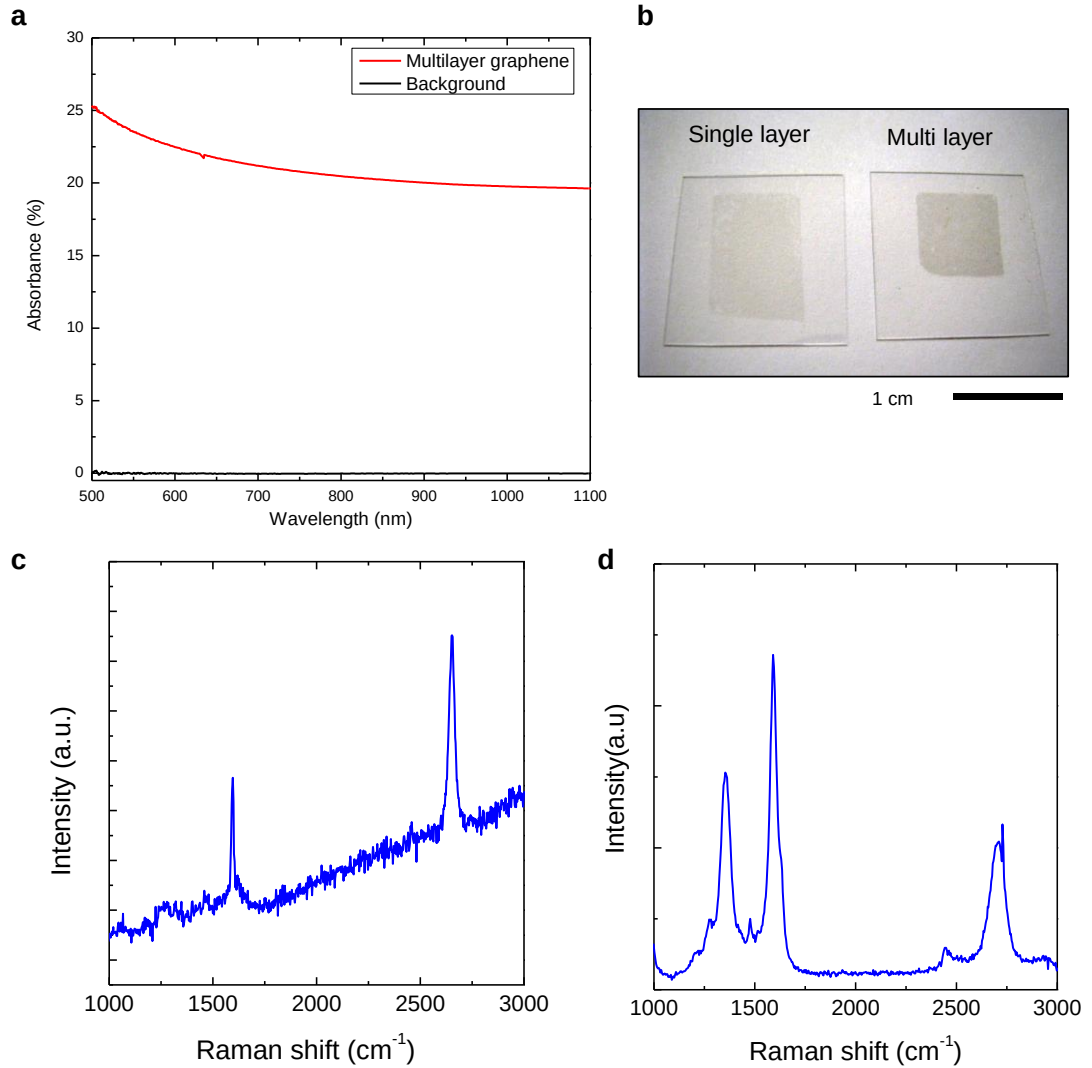


Figure 2.11: Single and multilayer graphene based optical modulators. (a) Broadband absorbance of multi layer graphene on glass substrate (The red curve). The black curve shows the background signal. (b) Photographs of large area single layer graphene and multilayer graphene transfer-printed on glass substrates. (c) Raman spectra of single layer graphene (d) Raman spectra of multi layer graphene.

We observed that ionic liquid electrolyte can block the optical transition of graphene up to 5-7 layers. In the second design, we used a reflecting surface (the external side of the substrates is coated with 100 nm Ag) to double the interaction of light with graphene electrode. With this reflection type device geometry, light passes through the graphene layers by two times. We measured the reflectance from the sample for

various bias voltages (Fig. 2.10 (e)). We obtained a modulation strength of around 35% in the near-infrared and around 20% modulation in the visible. The modulation strength can be further increase by multiple reflections or placing the super capacitor in an optical cavity.

Since the supercapacitor structure has parallel plate geometry, it can provide polarization independent modulation which is a common drawback for optical modulators (Fig. 2.12). Large area device geometry with polarization independent operation in the visible spectra yields a unique combination that can find many applications in optoelectronics.

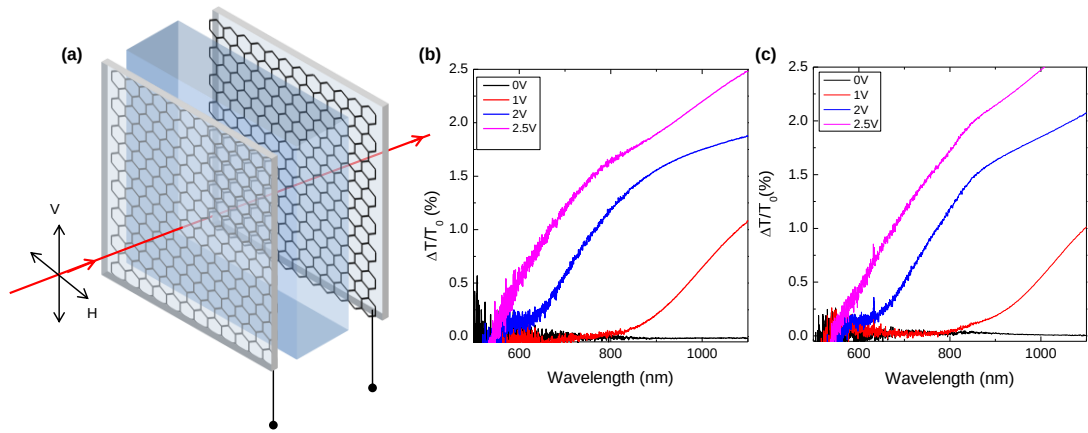


Figure 2.12: Polarization independent operation of graphene based optical modulators. (a) Schematic diagram of the graphene supercapacitor and the polarization of light with respect to the device geometry. Normalized transmittance of the supercapacitor for vertical (b) and horizontal (c) polarizations. The device shows polarization independent operation.

Furthermore, graphene supercapacitor can be fabricated on flexible substrates (Fig. 2.13) that can be used as electrically reconfigurable flexible coatings or smart windows. The supercapacitor structure with ionic liquid electrolyte (they have very low vapor pressures) is also compatible with ultrahigh vacuum systems which could enable optical measurements at cryogenic temperatures to reveal the fundamental properties of graphene.

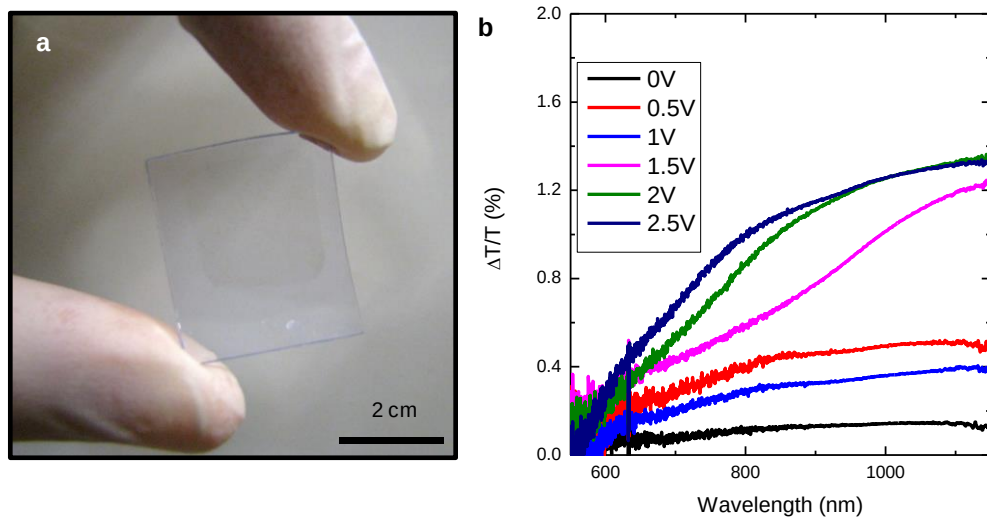


Figure 2.13: Graphene supercapacitors using flexible substrates. (a) Single layer graphene transfer printed on a flexible PET substrate. **(b)** Normalized transmission of the flexible graphene supercapacitor for various bias voltages.

We anticipate that the simplicity of the device geometry together with the efficient gating scheme will enable new graphene based active optical devices ranging from plasmonics to optoelectronics.

Chapter 3

Electrochromism in Multilayer Graphene

Graphene emerges as a viable material for optoelectronics because of its broad optical response and gate-tunable properties. For practical applications, however, single layer graphene has performance limits due to its small optical absorption defined by fundamental constants. In this chapter we demonstrate a new class of flexible electrochromic devices using multilayer graphene (MLG) which simultaneously offers all key requirements for practical applications; high-contrast optical modulation over a broad spectrum, good electrical conductivity and mechanical flexibility.³ Our method relies on electro-modulation of interband transition of MLG via intercalation of ions into the graphene layers. The electrical and optical characterizations reveal the key features of the intercalation process which yields broadband optical modulation up to 55 per cent in the visible and near-infrared. We illustrate the promises of the method by fabricating reflective/transmissive electrochromic devices and multi-pixel display devices. Simplicity of the device architecture and its compatibility with the roll-to-roll fabrication processes, would find wide range of applications including smart windows and display devices. We anticipate that this work provides a significant step in realization of graphene based optoelectronics.

Electrochromism provides electrically-controlled color change [111-113]. Color of an electrochemically active material with strong optical absorption can be bleached by electron-transfer reaction (redox). For example, a deep absorption which generates blue color can be switched to transmissive state with white or orange color.

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Various material systems such as metal oxides [114], polymers [113], nanocrystals [115, 116] and carbon nanotubes [117-119] have been used as electro-active materials [120].

The advantages of ECDs over the well-established liquid crystal display technologies, are their low material cost and compatibility with nonplanar and flexible surfaces. However many of these devices require fragile transparent and conducting electrodes which hinder the realization of the full potential of electrochromic materials for flexible applications. Various synthetic approaches [116, 121] have been developed to integrate conducting polymer and coloring molecules in a multilayer structure for flexible applications, however, low conductivity of polymers and interfacial mismatched between the layers degrades the performance.

The tradeoff between high contrast ratio and broad spectral response is another technical challenge. High contrast ratio requires strong optical absorption which limits the efficiency of the bleaching process. The full potential of flexible electrochromic devices has yet to be realized [122, 123]. These technologies would benefit from a material which is mechanically flexible, electrically conductive and optically tunable in a broad spectrum. In this chapter we show that multilayer graphene (MLG) provides all these challenging requirements and yields a new perspective for optoelectronic devices.

3.1 Multilayer Graphene Electrodes

Gate-tunable optical properties of graphene have been the subject of an active research in optoelectronics [2, 8, 10, 84, 87, 89, 100, 124-129]. The interband electronic transition of single and bilayer graphene can be blocked by electrostatic doping [10, 130]. In previous chapter we presented a new type of optical modulation scheme using graphene supercapacitors. We showed that optical transmittance of single layer graphene electrode can be modulated by 2% via electrostatic doping [10, 87, 93]. However, controlling interband transition of thick multilayer graphene is not possible by electrostatic doping due to screening of the top layers. In this chapter we show that fast and reversible intercalation process can control optical absorption of multilayer graphene which yields a tunable optical transmittance with high-contrast.

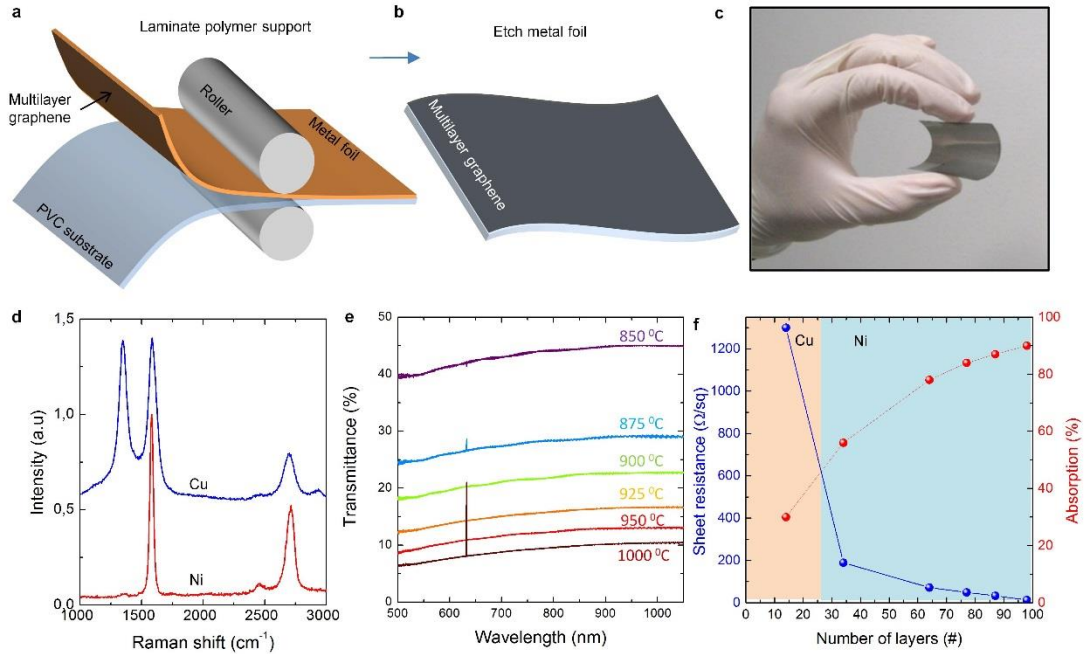


Figure 3.1: Synthesis and characterization of multilayer graphene on flexible substrates. (a) Transfer printing of large area multilayer graphene on flexible PVC substrates by lamination process. Multilayer graphene electrodes were synthesized on metal foils (copper or nickel), then 75 μm thick PVC film was laminated on graphene coated side. (b) Etching the metal foils yields flexible multilayer graphene electrodes on the PVC support. (c) Photograph showing the flexible multilayer graphene electrodes. (d) Raman spectra of the samples synthesized on copper and nickel foils. (e) Optical transmittance spectra of the MLG electrodes using grown on nickel at different temperatures. (f) Variation of the sheet resistance (blue curve) and optical absorption (red curve) of MLG electrodes with the layer number.

Figure 3.1 (a) and (b) show the preparation steps of multilayer graphene electrodes on flexible substrates. We synthesized large area multilayer graphene on metal foils using chemical vapor deposition. Multilayer graphene samples were synthesized on 25 μm thick copper and nickel foils (*Alfa Aesar item #13382 and Alfa Aesar item #12722 respectively*) by chemical vapor deposition at various temperatures ranging from 850 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ at the ambient pressure. H_2 , Ar and CH_4 gases were used during the growth process. CH_4 gas served as a carbon feedstock and only sent during the growth. Flow rates of the CH_4 , H_2 , and Ar were set as 30 sccm, 100 sccm, 100 sccm respectively. Growth times were 30 min for copper foils and 5 min for nickel foils. After terminating the growth, the samples were left for fast cooling to room temperature. By controlling the growth time and temperature, we obtained series of multilayer graphene samples having various thickness (10 to 250 layers according to the growth temperature.)

After the growth, we used lamination technique to transfer the multilayer graphene on transparent PVC substrates. At 120 $^{\circ}\text{C}$, we laminated 75 μm thick PVC film on the graphene coated side of metal foils conformably and etched the foils from back side in %30 hydrochloric acid solution (Figure 3.1 (a,b)). When the metal foils was completely etched in an hour, the PVC support holding multilayer graphene was rinsed in DI water and left to fast air drying. Etching the foils with diluted hydrochloric acid solution yields large area graphene films on transparent and flexible substrate (Figure 3.2 (c)). The multilayer graphene remains stable on the flexible PVC even after bending the substrate (Figure 3.1(c)).

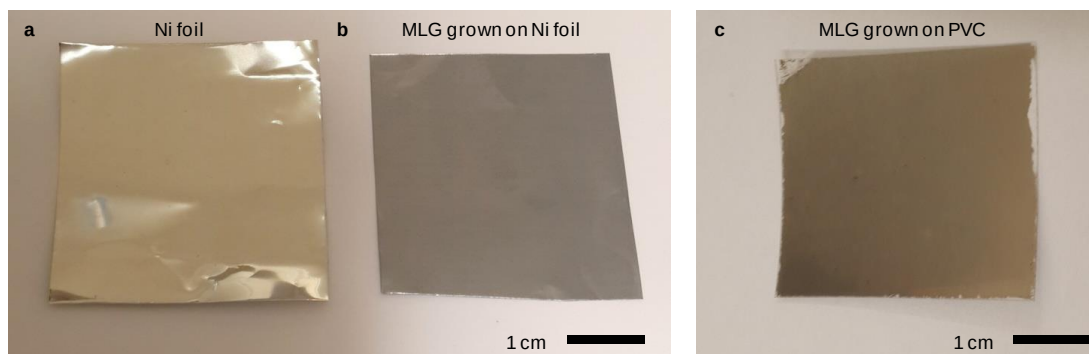


Figure 3.2: Multilayer graphene on metal and polymer substrates. (a,b) Photographs of the bare nickel foil and graphene grown on nickel foil respectively. (c) Photograph of graphene on PVC substrate.

We used copper and nickel foils as a growth substrate in chemical vapor deposition of graphene layers. Figure 3.1 (d) shows the Raman spectra of graphene samples grown on nickel and copper foils. The multilayer graphene samples grown on copper foils are more defective (intense D-band) than the ones grown on nickel foils. This is because of the different growth mechanisms; the growth mechanism on copper is based on surface adsorption which yields defective multilayer graphene, however,

the growth mechanism on nickel is based on precipitation of the dissolved carbon in the foil [131].

The growth time and the temperature determine the number of graphene layers grown on nickel and copper foils, respectively. We estimated the thickness of the synthesized MLG from the transmittance spectra and measured the sheet resistance of the MLG electrodes using transfer length method (TLM) (Figure 3.3).

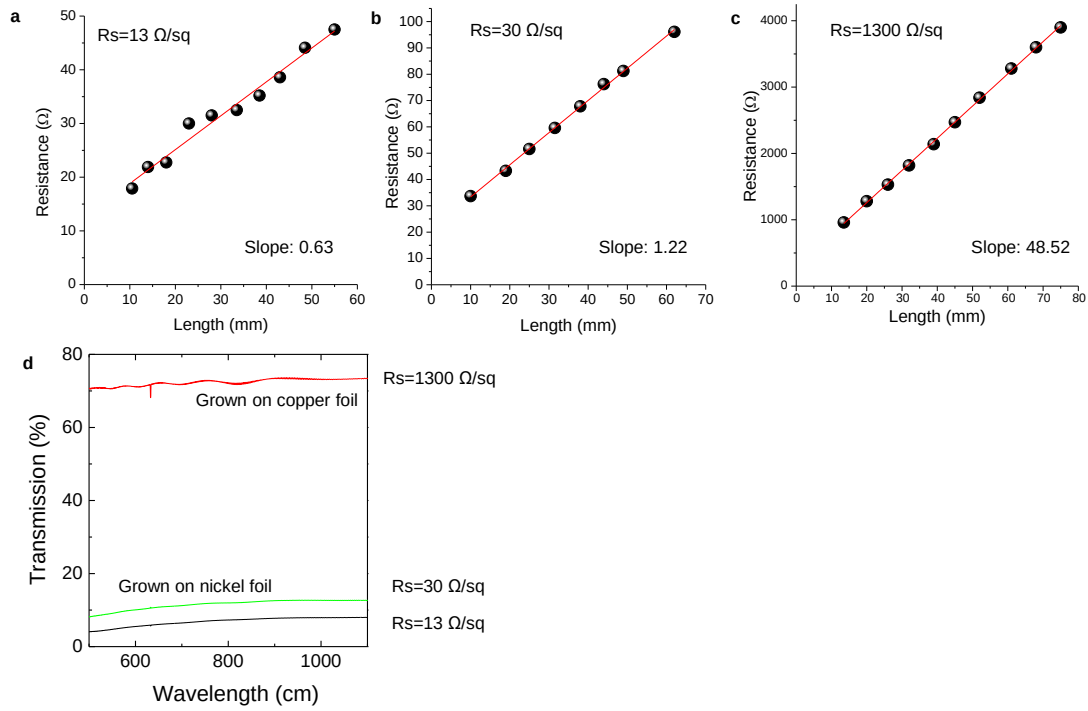


Figure 3.3: Resistivity and transmittance of various thickness graphene samples. (a-c) Transfer line measurements for three different MLG. The slope yields the sheet resistance of the electrodes. The sheet resistance varies between 13 Ω/sq to 1300 Ω/sq. (d) Optical transmission spectra of the MLG electrodes used for transfer line measurements.

Figure 3.1 (e) shows the optical transmittance spectra of various samples that have MLG grown on nickel at temperatures from 850 to 1000°C. On copper foils, we were able to grow MLG up to 20 layers, however MLG grown on nickel foils, were much thicker between 30-100 layers. The variation of the sheet resistance and optical absorption with the layer number is given in Figure 3.1 (f). The sheet resistance decreases from 1300 to 13 ohm/sq as the number of layers increases from 14 to 98. At the same time optical absorption increases from 30 to 90 %.

The MLG electrodes on PVC have mechanical flexibility with bending radius down to 2 mm with a constant the sheet resistance (within 1%, Figure 3.4).

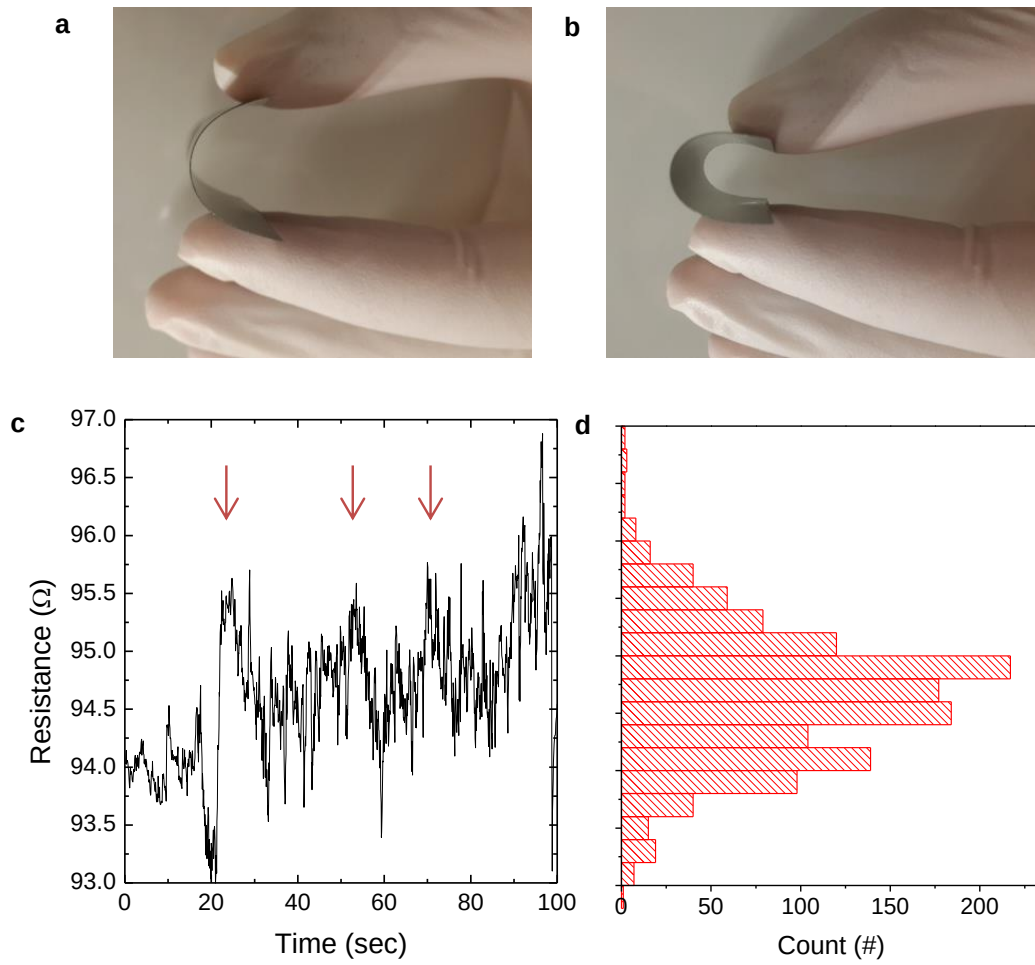


Figure 3.4: Bending test for the graphene electrodes. (a,b) photographs of the MLG electrodes on flexible PVC substrates. (c) Variation of resistance of MLG electrode as the electrode is deformed. (d) The histogram of the resistance.

3.2 Graphene Based Electrochromic Devices

To fabricate the electrochromic devices, we attached two graphene coated PVC substrates with a spacer and filled the gap with an ionic liquid electrolyte. The spacer is a 250 μm thick frame containing 50 μL ionic liquid electrolyte (Diethylmethyl(2-methoxyethyl)ammoniumbis(trifluoromethylsulfonyl)imide). Figure 3.5 (a) shows the schematic exploded view of the device. We started our investigation by measuring the optical transmittance of the device.

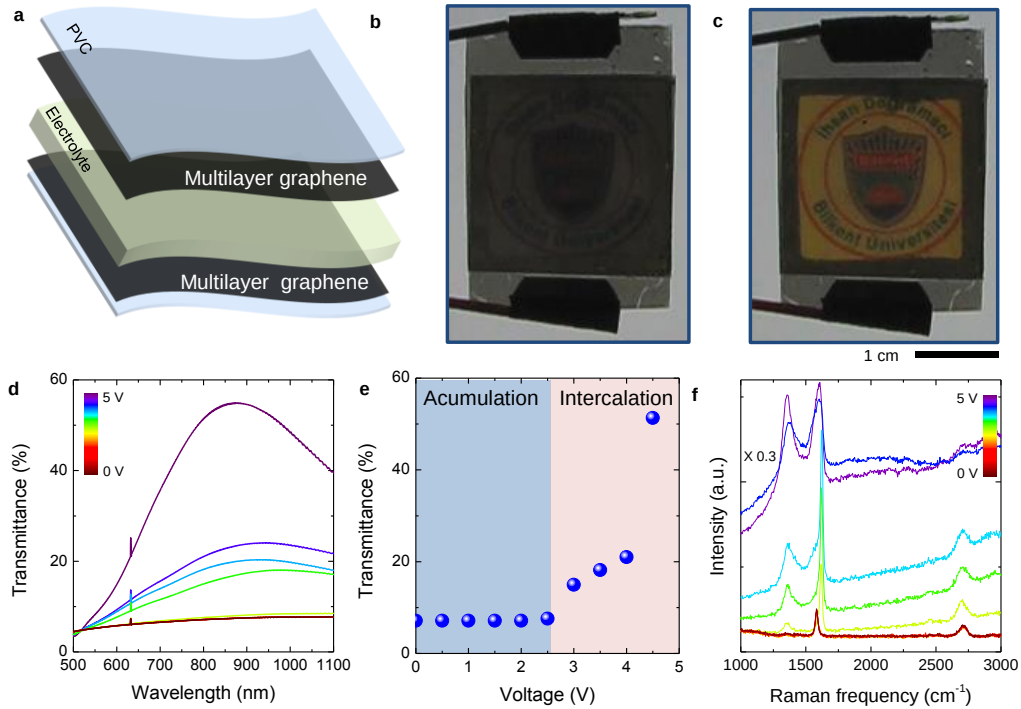


Figure 3.5: Graphene electrochromic devices. : (a) Exploded-view illustration of the graphene electrochromic device. The device is formed by attaching two graphene coated PVC substrates face to face and imposing ionic liquid in the gap separating the graphene electrodes. (b,c) Photographs of the devices under applied bias voltages of 0 V and 5 V, respectively. The image of Bilkent University logo [copyright permission from I.D. Bilkent University] appears at 5 V. Demonstrated device is composed of two multilayer graphene electrodes synthesized at 925 $^{\circ}\text{C}$ each having ~ 78 layers. (d) Transmittance spectra of the device under applied voltage between 0 V to 5 V. e, Variation of the transmittance (at 800 nm) with the applied voltage. (f) Variation of the Raman spectra of graphene electrodes under the applied voltage. (g-i) Schematic representation of the proposed operating regimes, i.e. neutral, charge accumulation, and intercalation, respectively.

For the voltage range from 0 to 2.5 V, we do not observe a significant change in the transmittance however, as we increase the voltage further, the transmittance

increases rapidly and the device become more transparent at 5 V (<http://www.nature.com/srep/2014/141001/srep06484/extref/srep06484-s1.mov>).

(<http://www.nature.com/srep/2014/141001/srep06484/extref/srep06484-s2.mov>)

Figure 3.5 (b) and (c) show the photographs of the device at 0, and 5 V, respectively. We put the logo of our university behind the device with a backlight illumination. At 5 V, the logo appears clearly through the device (Figure 3.5 (c)). The transmittance spectra under applied voltage from 0 V to 5 V are shown in Figure 3.5 (d). At 0 V, the transmittance is only 8% and slightly varies with the wavelength. At 5 V, the transmittance increases sharply to 55 % at 900 nm. Figure 3.5 (e) shows the variation of the transmittance at 800 nm with the applied voltage. The modulation of the spectra originates from the blocking of interband transitions of the graphene layers via electrostatic doping. However, this requires effective doping of underneath layers. Surprisingly, the above layers can be doped when we applied large bias voltages. We propose that the efficient doping of above layers is due to intercalation of ions into the graphene layers. According to our observation, using thicker spacer which contains more ionic liquid (~100 μ L) didn't affect the device operation in terms of transmittance modulation or charging time. However using thinner spacer, which contains less volume of ionic liquid, can cause electrical shortage between the top and bottom graphene layers in large scale devices due to the sagging of the flexible substrate.

3.3 Operation Mechanism

To understand the mechanism behind the optical modulation, we measured the Raman spectra of the graphene electrode under the applied voltage (Figure 3.5 (f)). For applied voltages less than 2.5 V, Raman spectra show no significant change, however, after 2.5 V, the intensity of G-band significantly increases, and D-band appears. Furthermore we observed a strong fluorescence background. The enhancement of G-band and the background fluorescence indicate strong electrostatic doping of graphene layers while appearance of D-band shows formation of defects in graphene layers [98].

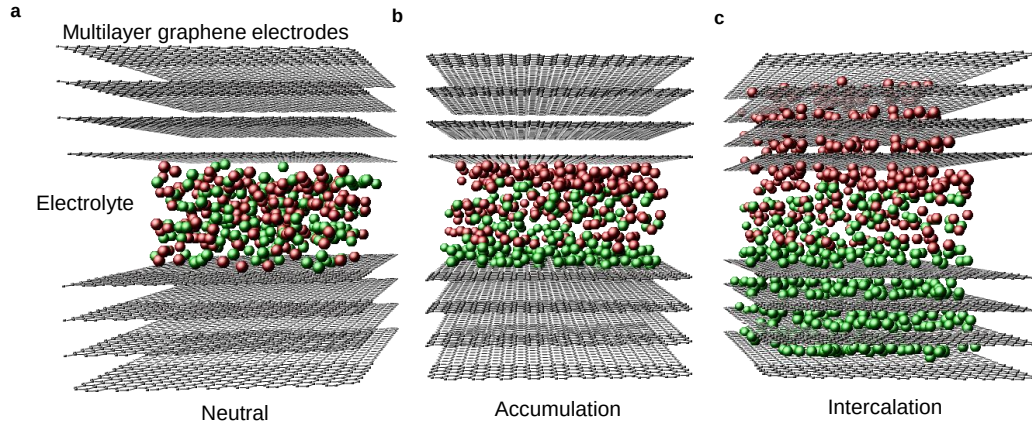


Figure 3.6: Mechanism for the electrochromism in multilayer graphene. Schematic representation of the proposed operating regimes, (a) neutral, (b) charge accumulation, and (c) intercalation, respectively.

These observations suggest that after a threshold voltage which is around 2.5 V, ions can intercalate into the multilayer graphene through the induced defects and provide effective doping on the above layers. The schematic drawings in Figure 3.6 demonstrate proposed mechanism for the observed electrochromism. Applied voltage less than 2.5 V, polarizes the ionic liquid and charges accumulate at the graphene-electrolyte interface. We named this range as “accumulation” which results in a very small optical modulation (around 2 % of the initial transmittance) due to doping of the graphene layer at the electrolyte interface (Figure 3.6 (b)).

Applied voltage larger than 2.5 V induces structural defects and initiates intercalation of ions into the graphene layers (Figure 3.6 (c)). Appearance of intense D-band in the Raman spectra after 2.5 V indicates the formation of defects on the graphene which enhances the intercalation process.

We have tested various electrolytes including water based electrolytes and ionic liquids. The electrochemical window of the electrolyte is a key parameter to achieve effective doping of the graphene layers via intercalation process. We observed that, water based electrolytes do not yield effective intercalation due to narrow electrochemical window. We obtained the best performance with ionic liquid [DEME][TFSI] which have an electrochemical window between -3.0 to 3.5 V.

At the very first cycle, we also observed that color change initiates at the edge and propagates along the device (Figure 3.7). The color change of multilayer graphene is reversible and can be cycled many times. Intentionally created structural defects on graphene with the applied voltage has only long term effects on device operation. We showed that the devices are stable for 70 cycles of switching between on and off states. (~ 50 minutes of continuous operation) (Figure 3.8).

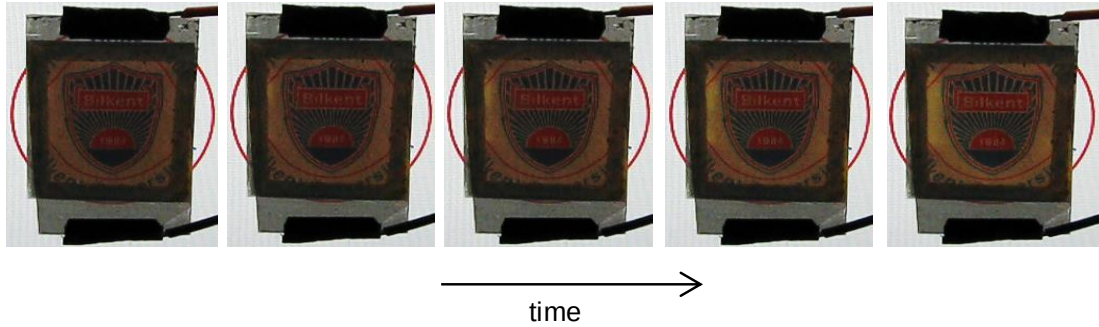


Figure 3.7: The variation of the optical transmittance of the device at +4 V. The intercalation process starts from the edge of the sample and propagates along the device.

We also measured a change in the resistance of MLG electrodes. For applied voltages of less than 5 V, the resistance of electrode decreases from 180 to 110 Ω . When MLG is transparent, its resistivity is less than the neutral state. These experiments suggest that the observed electrochromic effect is not because of a chemical reaction that oxidizes the graphene electrodes [132, 133] but it is because of the intercalation process which electrostatically dopes the graphene layers.

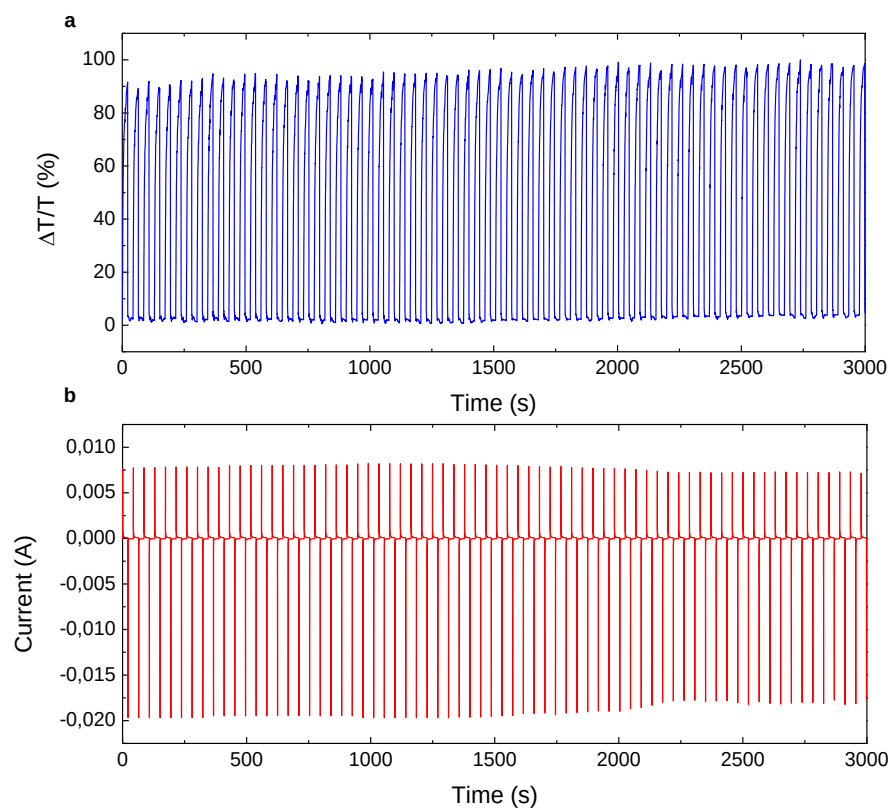


Figure 3.8: Switching performance of the graphene electrochromic device. Time trace of the (a) percentage transmittance and (b) charging current.

3.4 Transmittance Modulation

Since the observed optical contrast is defined by the efficiency of the intercalation process, the thickness of MLG determines the device performance. We fabricated a series of devices using MLG with varying thickness. Figure 3.9 shows the voltage controlled transmittance modulation of 6 representative devices that have MLG electrodes with various thickness. Devices shown in Figure 3.9 (a-c) were fabricated by using MLG grown on copper while the devices shown in Figure 3.9 (d-f) were fabricated by using MLG grown on nickel foils.

The insets in Figure 3.9 (a-f) show the estimated number of graphene layers (number of graphene layers are calculated through the transfer length method given in Figure 3.10). Since the graphene quality affects the device operation in terms of transmittance modulation, MLG grown on copper or nickel foils yields some differences in the device performance. Nickel foils produce more crystalline graphene than copper foils. This significantly enhances the device characteristics. For the devices using MLG grown on copper, we observed a flat optical response over a broad spectrum (Figure 3.9 (a-c)), however, for the devices using MLG grown on nickel, the modulation spectra show a broad peak centered at 850 nm (Figure 3.9 (d-f)).

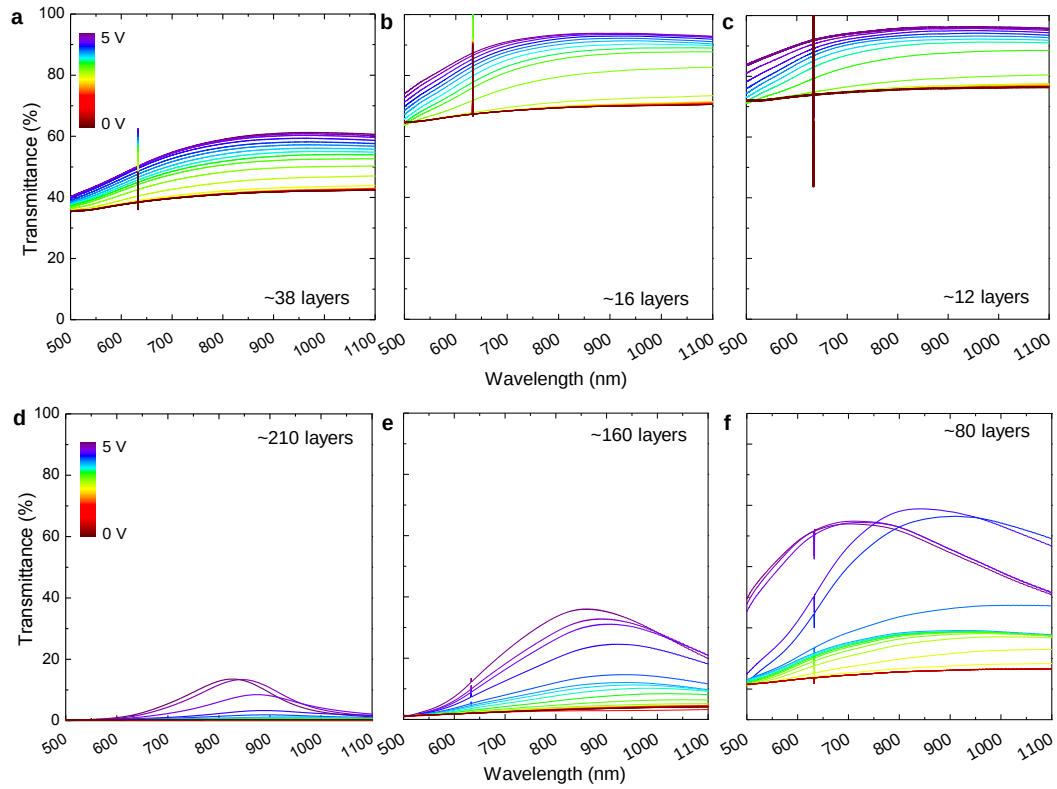


Figure 3.9: Effect of thickness and quality of graphene on the device performance. Transmittance spectra (under applied voltage ranging from 0 V to 5 V) of electrochromic devices using various thicknesses of MLG. Devices shown in (a-c) use MLG grown on copper foils while devices shown in (d-f) use MLG grown on nickel foils, respectively. The inset shows the estimated number of graphene layers. The color bar shows the applied voltage.

Moreover, we also observed a tradeoff between initial optical absorption (at 0 V) and transmittance modulation efficiency. The thickness of a multilayer graphene electrode defines the maximum transmittance modulation efficiency that the electrochromic device can have. For thin MLG (~ 20 layers), the optical absorption can be blocked, however for very thick MLG (> 50 layers), the intercalation process is inadequate that yields diminishing optical modulation. The variation of the transmittance at 800 nm is plotted in Figure 3.11 (a) (for the devices using MLG grown on copper foils) and Figure 3.11 (b) (for the devices using MLG grown on nickel foils). Graphene grown on copper yield less modulation but smooth variation with the applied voltage, however, graphene grown on nickel yield larger modulation with steep variation with the applied voltage.

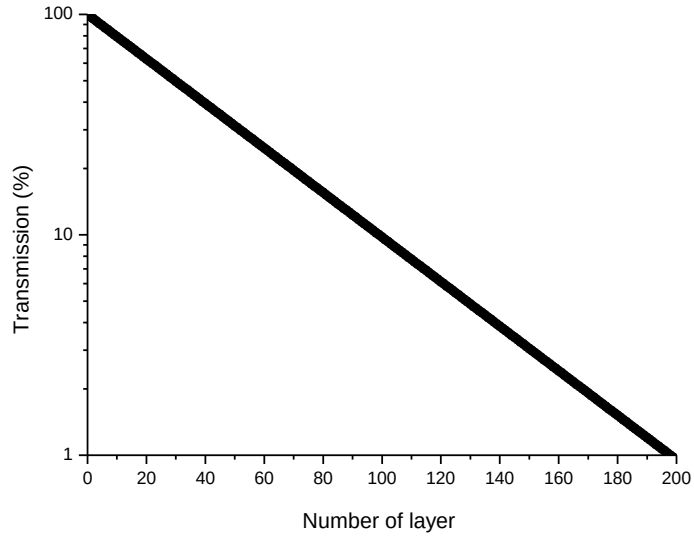


Figure 3.10: Calculated optical transmission of MLG plotted against the number of layers. $T = (1-\alpha)^N$, where T is the transmission, α is the absorption of single layer which is around 2.3 % and N is the number of graphene layers.

The measured optical modulation is plotted in Figure 3.11 (c) against the estimated number of graphene layers. Maximum modulation of 30% can be obtained with 25 layers of MLG electrodes grown on copper foil, whereas, MLG grown on nickel foils yield modulation of 55 % and decays as the number of graphene layers increases.

To understand the charging and discharging dynamics of the graphene electrochromic devices, we performed simultaneous electrical and optical characterization. Figure 3.12 (a) shows the experimental configuration used to measure current-voltage (Figure 3.12 (b)) and transmittance-voltage curves (at 635 nm wavelength) (Figure 3.12 (c)).

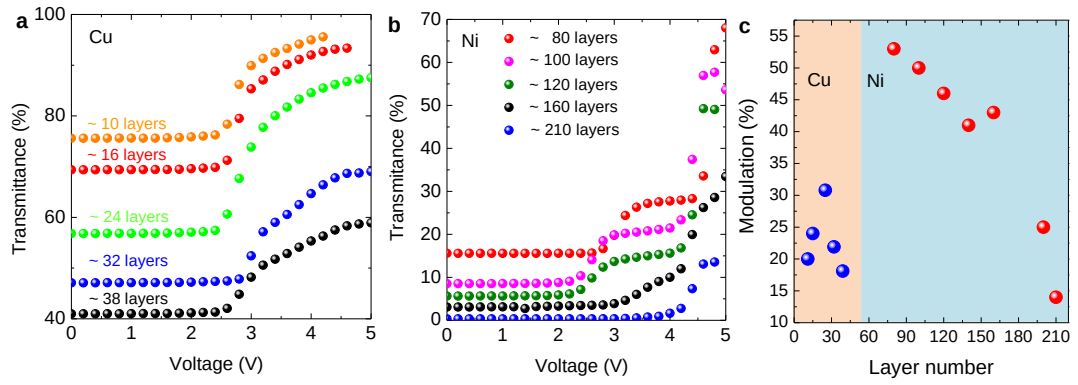


Figure 3.11: Transmittance modulation of graphene electrochromic devices. Variation of the transmittance (at 800 nm) of ECD using MLG grown on (a) copper and (b) nickel foils, respectively. (c) Maximum optical modulation plotted against the estimated number of graphene layers.

The electrical current and optical transmittance was measured simultaneously, as we swept the voltage between -5 V to 5 V with a scan rate ranging from 0.5 V/sec to 5 V/sec.

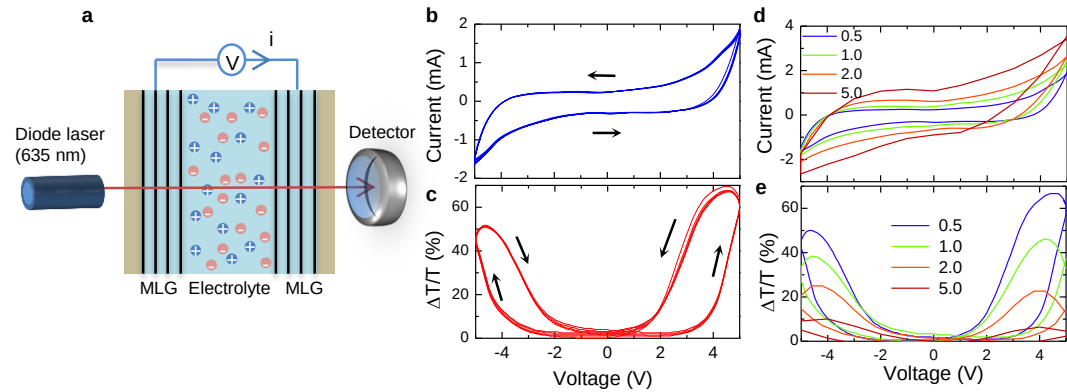


Figure 3.12: Charging and discharging characteristics of graphene electrochromic devices. (a) Schematic illustration of the experimental setup used for the simultaneous electrical and optical characterization of the graphene electrochromic devices. (b) Current-voltage and c, transmittance-voltage curves at 635 nm at a scan rate of 0.5 V/s. (d) Current-voltage and (e) transmittance-voltage for different scan rates.

We observed a profound hysteresis in both current and optical transmittance. The arrows represent the scan direction of the voltage. Interestingly, these devices provide optical bistability. For example, at 4 V bias voltage, the device has two distinct optical transmittance depending on the scan direction. The level of hysteresis varies with the scan rate (Figure 3.12 (d) and (e)). As we increase the scan rate, the

charging current increases (Figure 3.13 (a)) whereas the optical modulation diminishes sharply (Figure 3.13 (b)).

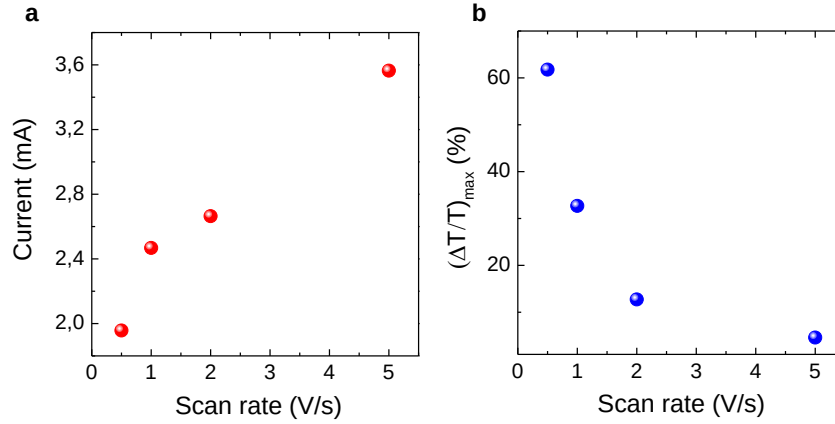


Figure 3.13: Scan rate characteristics of graphene electrochromic devices. (a) Maximum current and (b) maximum optical modulation versus the scan rate.

The hysteresis is a characteristic behavior of supercapacitors due to the formation of electric double layers. We also observed an asymmetry between the charging and discharging cycles. To further characterize charging and discharging time scales, we applied 5 V and 0 V in a sequence and recorded the time trace of the optical transmittance and charging current (Figure 3.14 (a)). The charging time (3.5 sec) is significantly larger than the discharging time (0.25 sec). This difference is clearly seen in Figure 3.14 (b) which shows the optical modulation during a single cycle. The current during charging and discharging cycles are also different. When we applied 5 V, the charging current starts from 5 mA and decays exponentially. During the discharging, we measured a current of 20 mA which decays much faster (Figure 3.14 (c)). This asymmetric behavior is likely due to the variation of the electrical conductivity of the graphene electrodes. In the charged state, the conductivity is larger than its value in the discharged state because of electrostatic doping.

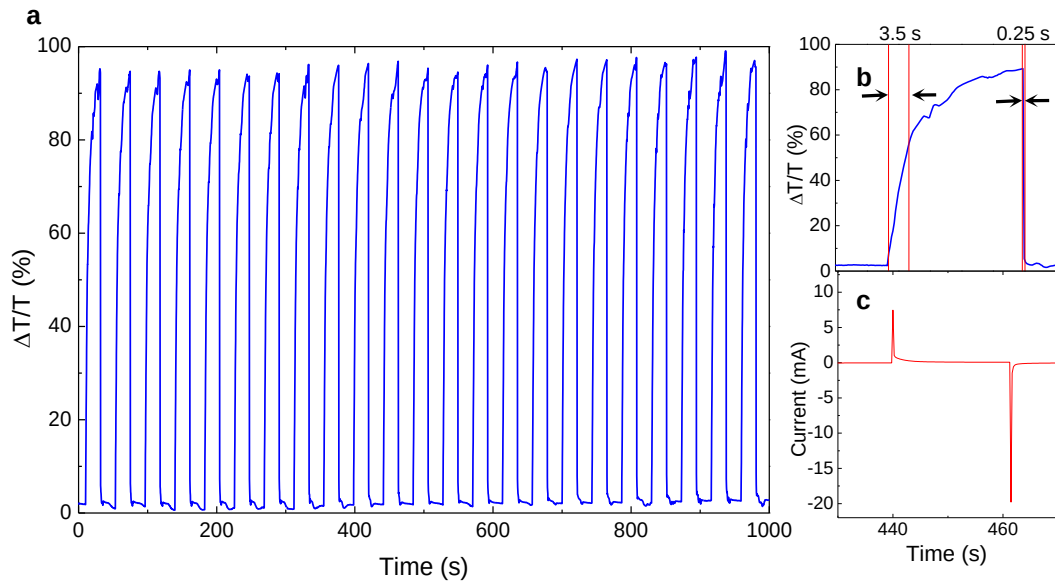


Figure 3.14: Optical switching characteristics of the device at 635 nm. (a) Transmittance modulation of the graphene electrochromic device with respect to time. Time variation of (b) transmittance and (c) charging current for a single switching cycle. The extracted RC time constants of the electrochromic device (3.5 seconds for charging and 0.25 seconds for discharging respectively) are illustrated on the single switching cycle with intervals defined by the red bars.

In order to test the stability of the device, we measured the time trace of optical transmittance for 70 cycle and plotted the histogram of the intensity of the transmitted light at the on-state (Figure 3.15 (a) and (c)) and off-state (Figure 3.15 (b) and (d)). The variation of the transmittance in the off-state is much less than the variation of the transmittance in the on-state which is likely due to inhomogeneous charging.

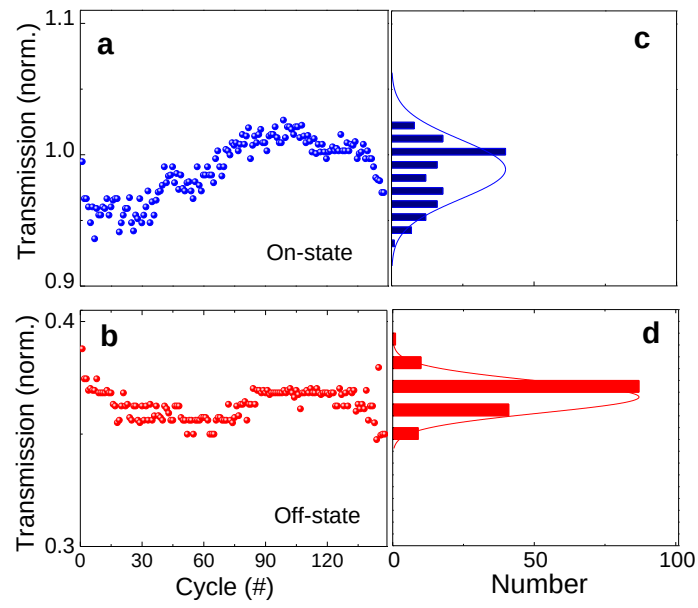


Figure 3.15: Stability test for graphene electrochromic devices. Long term stability of the transmittance in the (a) on-state (at 5 V) and (b) off-state (0 V). (c,d) The histogram of the transmittance in the on- and off-state.

3.5 Multi-pixel Displays

To show the promises of graphene electrochromic devices, we fabricated a multi-pixel flexible electrochromic display. We synthesized large area (5 cm x 5 cm) graphene electrodes and transferred them on a PVC support. The top and bottom graphene layers were patterned to form three 1 cm wide ribbons and placed face to face perpendicularly (Figure 3.16 (a)). The top and bottom graphene electrodes were separated by a thin spacer to prevent electrical shorting. Figure 3. 16 (b) shows the photograph of the fabricated device. The device is flexible and can be curved with 1 cm radius without any damage on graphene electrodes.

We first applied voltage to alternating electrodes to form a chessboard pattern (<http://www.nature.com/srep/2014/141001/srep06484/extref/srep06484-s3.mov>). We take the snapshots of the device at various voltages (Figure 3.16(c)). After 4 V, the chessboard pattern appears clearly. The transmittance of individual pixels can be reconfigured by changing the voltages applied to the rows and columns. Figure 3.16 (d) represents different patterns obtained at 5 V applied voltage. The performance of the individual pixels is similar to the single pixel devices. The pixel size of the display device can be easily scaled down by photolithography and etching process.

Furthermore, we fabricated reflective type graphene electrochromic devices. This device consists of electrolyte sandwiched between gold and graphene electrodes (Figure 3.17(a)). MLG was transferred on a PVC support by lamination process and 100 nm thick gold electrode was evaporated on another PVC support. Figure 3.17 (b) and (c) show the photograph of the device at 0 and 5 V applied voltages. When the device is unbiased, it looks black due to absorption of the MLG electrodes. Under an applied voltage of 5 V, MLG electrodes become transparent and the color of the device turns into yellow due to underneath gold layer. The reflection spectra at various applied voltages are shown in Figure 3.17 (d). This simple device architecture provides new possibilities for reconfigurable mirrors. As an example we fabricated multi-pixel reflective device, by patterning the gold and MLG electrodes (Figure 3.17 (e)). We isolated the pixels using a spacer with circular holes that contain the ionic liquid. Figure 3.17 (f) and (g) show the chessboard pattern appears on the device under 5 V applied voltage. The device is bendable and the pattern is reconfigurable.

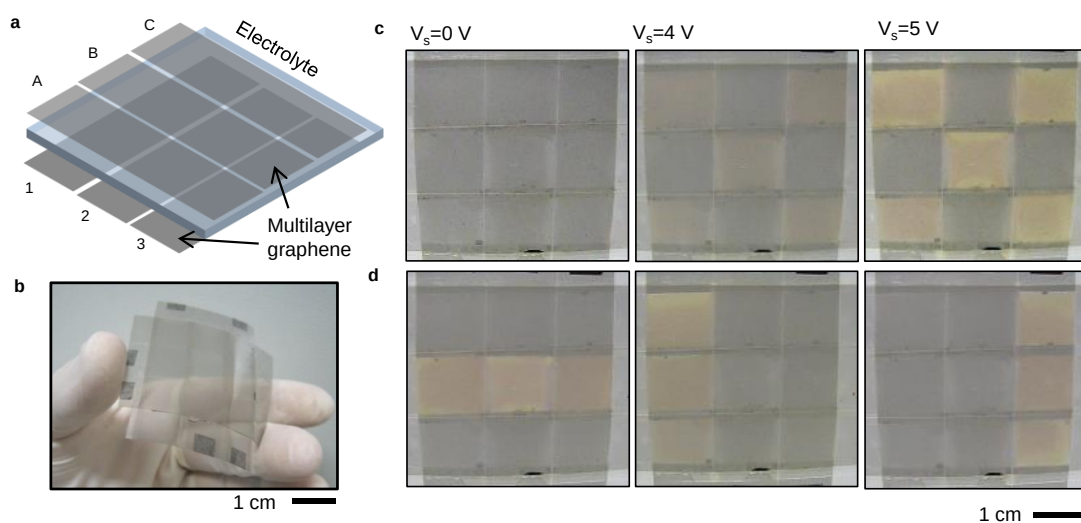


Figure 3.16: Multi-pixel display device. (a) Schematic illustration of the multi-pixel display device consisting of 3 x 3 arrays of flexible electrochromic device. (b) Photograph of the fabricated flexible multi-pixel device. (c) Photographs of the device under various bias voltages that generate chessboard pattern. (d) Photographs of the device under 5 V bias voltage with different reconfigurable patterns.

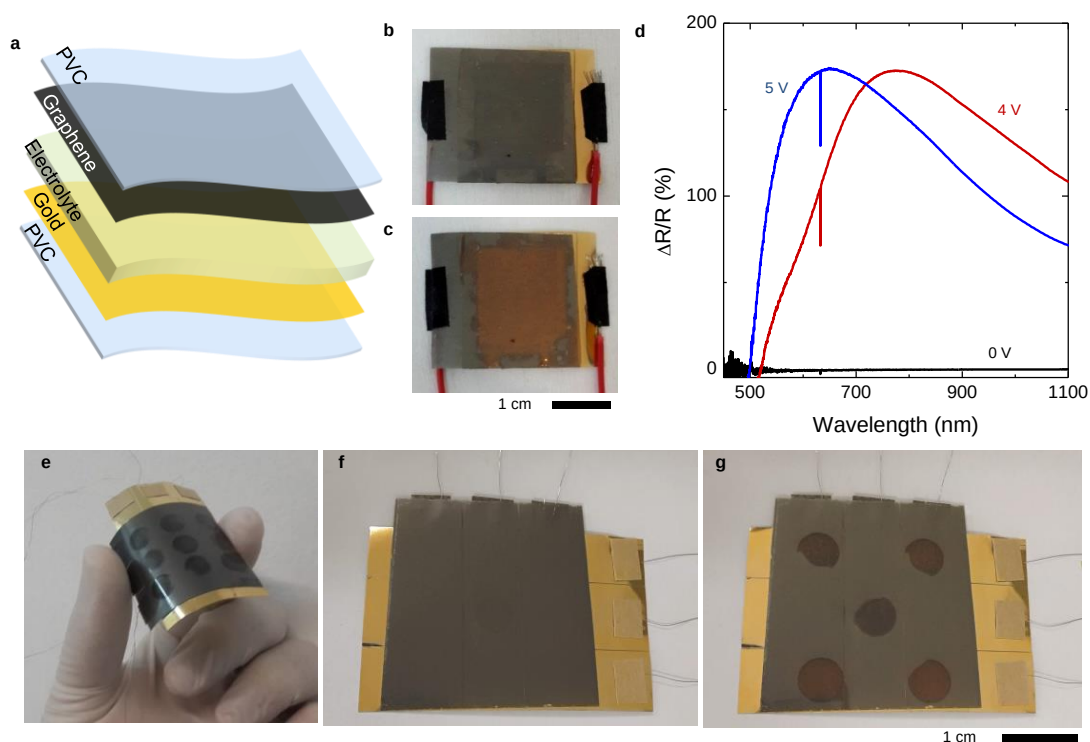


Figure 3.17: Graphene based reflective electrochromic devices. (a) Exploded-view schematic illustration of the reflective graphene-electrochromic device consisting of gold and multilayer graphene electrodes. (b,c) Photograph of the fabricated device at 0 V and 5 V applied voltage, respectively. (d) Modulation of the reflectance spectra of the devices under various applied voltages. (e) Photograph of the flexible multi-pixel reflective device. (f,g) Photographs of the reflective device under bias voltage of 0 V and 5 V that generate chessboard pattern.

Chapter 4

Graphene Based Paper Displays

Integration of semiconducting materials on unconventional substrates enables optoelectronic devices with new mechanical functionalities that cannot be achieved with wafer-based technologies. Electronic paper has been the most attractive application aiming to reconfigure the displayed information electronically on printing paper. Optoelectronics on printing paper, however, have been an outstanding challenge due to the large surface roughness and its incompatible nature with microfabrication techniques. In this chapter, using graphene as the reconfigurable optical medium, we demonstrate electronic paper display on a piece of printing paper. Our approach relies on electromodulation of optical properties of multilayer graphene-on-paper via blocking the interband electronic transitions. The presented ultrathin paper display yields large optical contrast in the visible spectra with fast response speed. Furthermore, we demonstrate a colour concept simply by printing colored ink on paper substrates. Our technique is compatible with roll-to-roll fabrication method. We anticipate that, the presented graphene-based electronic paper can be used for ubiquitous optoelectronics.

Paper-based substrates has been an ambition of research in various fields ranging from medical diagnosis to display technologies aiming to create low cost and ubiquitous devices. Paper based microfluidic devices [134], electronic circuits [135] even robotic systems [136] have been developed. Fabrication of display devices on printing paper has been a challenge [137, 138]. Several technologies based on electrophoretic motion of particles [139], thermochromic dye [140], electrowetting of liquids [141] and electrochromic materials [142] have been developed to realize electronic paper (e-paper) which has great potential for consumer electronics. Contrasting the primary aim of e-paper, these technologies, however are not compatible with conventional printing papers which is based on cellulose fibers. In the followings we will give the detailed fabrication and characterization steps of a new display technology directly on a conventional printing paper using multilayer graphene as an electrically reconfigurable optical medium.

Controlling interband electronic transitions of graphene by electrostatic doping yield electro-modulation of optical transmittance in a very broad spectrum [10, 87, 93]. Electro-modulation of atomically thin graphene is limited by the optical absorption of 2.3 % which is defined by fundamental constants [8]. This small absorption, however, is not suitable for display applications. In order to increase the optical modulation, graphene have been integrated on resonant optical cavities which leads enhanced light-matter interactions via multiple passes [99]. In another approach, increasing number of graphene layers provide very large optical absorption which can be modulated by intercalation of ions into the layers which results blocking of interband electronic transitions [52, 84, 143, 144].

4.1 Characterization of Multilayer Graphene on Paper

By integrating large area multilayer (ML) graphene on printing paper, we managed to fabricate electronic paper display based on electro-modulation of graphene layer via reversible intercalation process. In our approach, ML-graphene has a double role; first, it operates as an electrically reconfigurable optical medium, second it provides the electrically conductive electrodes. The paper substrate yields a mechanical support for the graphene layer and it holds the electrolyte in the network of hydrophilic cellulose fibers (Figure 4.1)

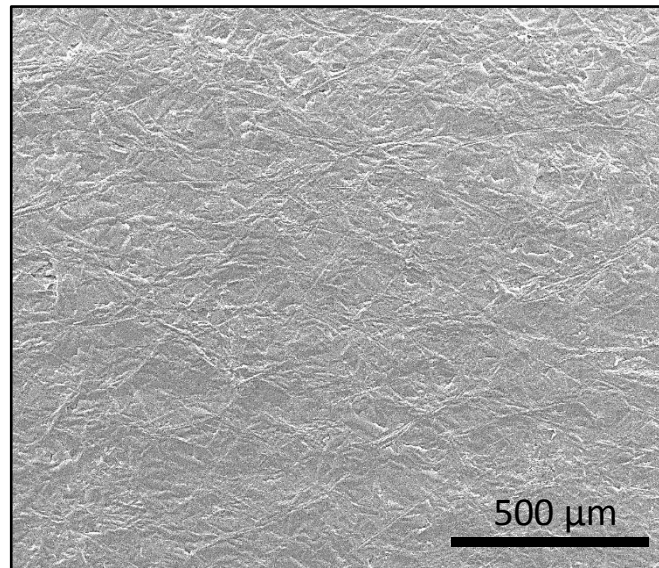


Figure 4.1: Scanning electron micrograph of paper surface coated with ML-graphene.

Figure 4.2 summarizes the structural and electrical properties of ML-graphene-on-paper. We synthesized ML-graphene on Ni foils using a chemical vapor deposition system that use methane as a carbon source. After the growth, we transferred graphene onto the paper surface by immersing the paper substrate into the liquid (see Figure 4.3). Figure 4.2 (a) shows a photograph of ML-graphene-on-paper. We used a piece of thick printing paper (Koehler Chamois Ivory Board, 246g/m^2) obtained from a local printing service. Figure 4.2 (b) shows the dark field microscope image of the corner of the ML-graphene layer. The RMS surface roughness of the paper is around $3\text{ }\mu\text{m}$ and the thickness is $300\text{ }\mu\text{m}$ (Figure 4.2 (c)). The scanning electron microscope image shows the rough surface consist of random network of fibers

(Figure 4.2 (d)). After the transfer process, we dried the paper at 70 °C and obtained conformal graphene coating on fiber network.

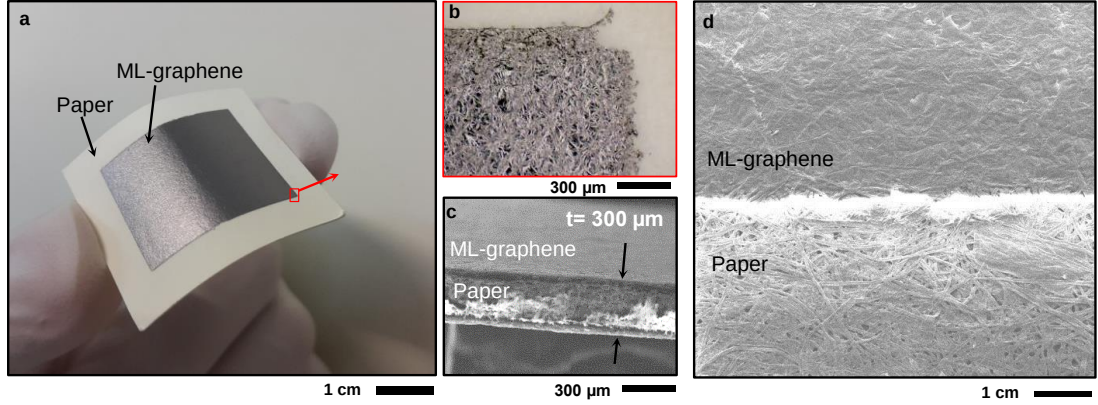


Figure 4.2: Multilayer graphene on paper. (a) Photograph of multilayer graphene transferred on printing paper. (b) Dark field optical micrograph of MLG on paper. (c,d) Scanning electron microscope of the cross section and edge of graphene layer on paper. The bright area is due to electrostatic charging of the paper. The RMS surface roughness is around 3 μm.

Due to the surface roughness, paper provide an ideal Lambertian-view characteristics. Figure 4.4 (a) shows the angular dependence of the scattering cross section of paper surface (red line) and the Lambertian cosine model (black curve). The good agreement between the model and scattering data indicates angular independent appearance of the paper surface. The graphene coated surface (Figure 4.4 (a), blue curve) yields more specular reflection than bare paper due to the metallic like surface.

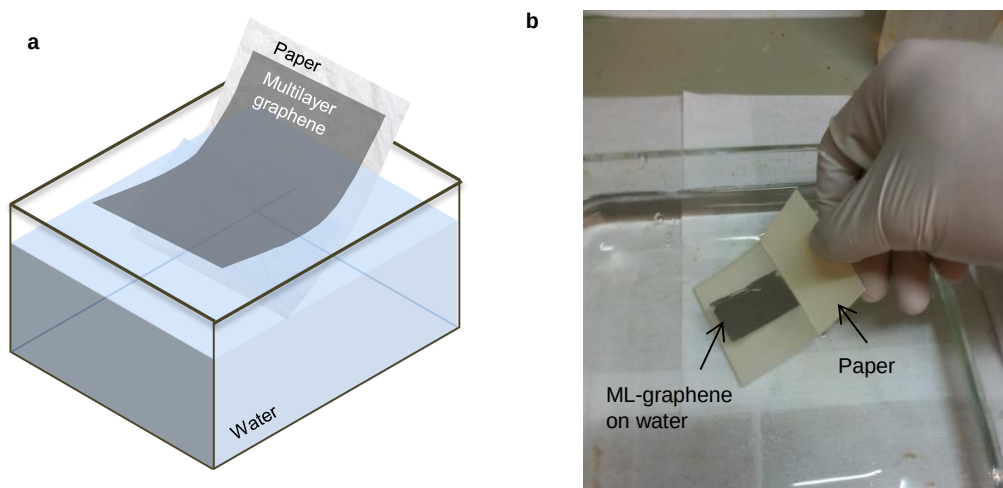


Figure 4.3: Transferring ML-graphene on paper. (a) Schematic drawing of the transfer process. Due to the hydrophobic nature of the graphene surface, ML-graphene stay on the water surface. (b) Photograph taken during the transfer process.

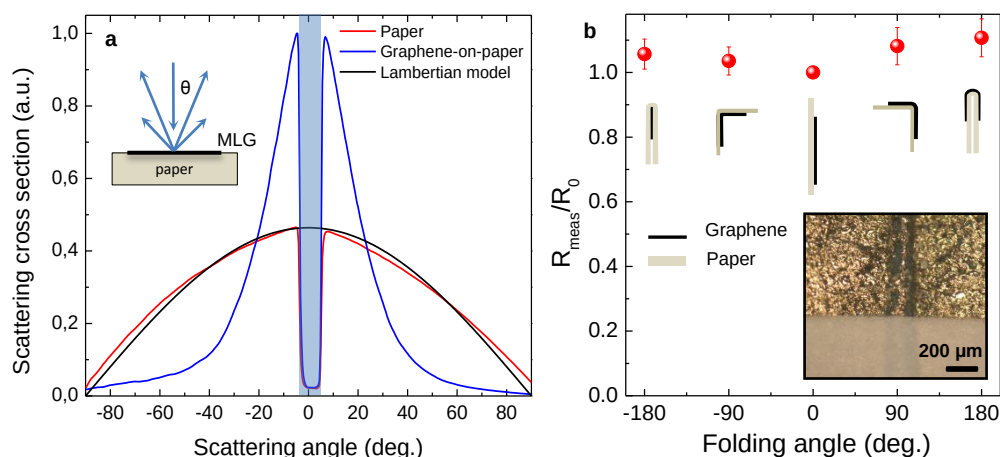


Figure 4.4: Scattering cross section and resistance measurements. (a) Scattering cross section (at 650 nm) of bare paper surface (red curve) and graphene coated surface (blue curve). The black curve shows the Lambertian cosine model. The inset shows the configuration. (b) Resistance of graphene for various folding configurations.

The characteristics of the diffuse reflectance varies from metallic-like to paper-like as the thickness of ML-graphene layer gets thinner (Figure 4.5). Besides its ideal-lambertian view, the paper substrate yields a flexible and foldable support. Figure 4.4 (b) shows the variation of resistance of ML-graphene layer after various acute and obtuse folding schemes. We observed only 10% increase in the total resistance after

acute folding which yields structural defects on graphene (see the inset in Figure 4.4 (b)).

Furthermore we perform 10 successive acute and optuse folding to observe the resistivity change under continuous folding (Figure 4.6). In the case of optuse bending we observed that the resistance deviation is higher due to the created fractures on the graphene surface under the tensile stress. We also showed that the device operation is stable when folded (Figure 4.7). Due to the resistance stability under compressive/tensile stress, and the continuos device operation during folding, fabricated graphene on paper devices would find diverse applications in foldable electronics.

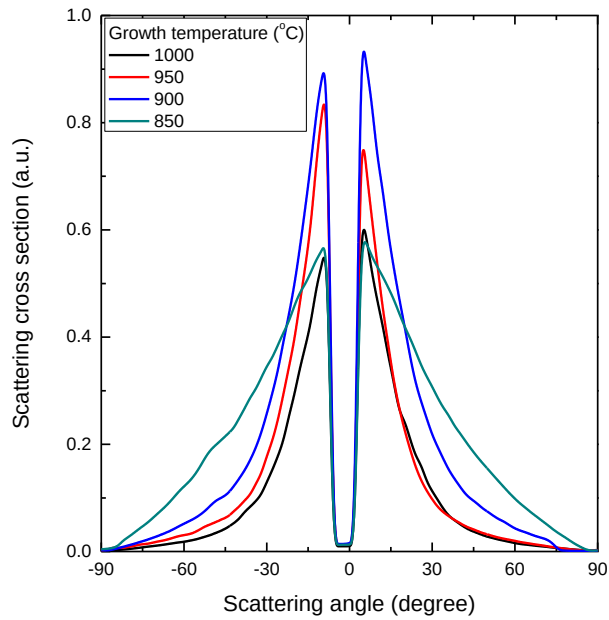


Figure 4.5: Angular dependent normalized scattering cross section of paper coated with ML-graphene grown at different temperature.

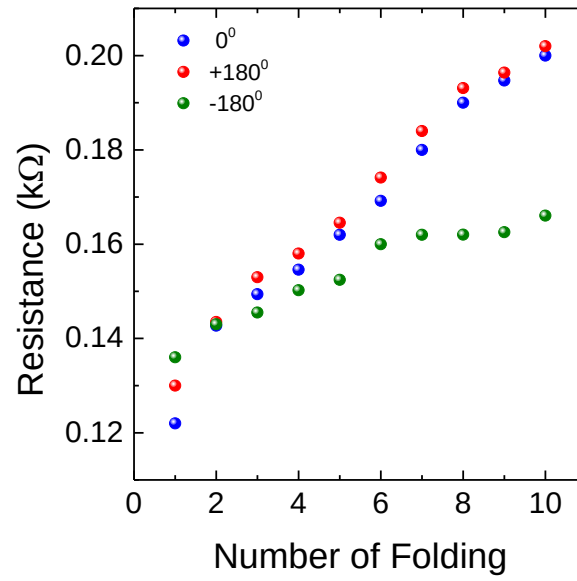


Figure 4.6: Variation of the resistance of ML-graphene as we continuously fold the paper substrate.

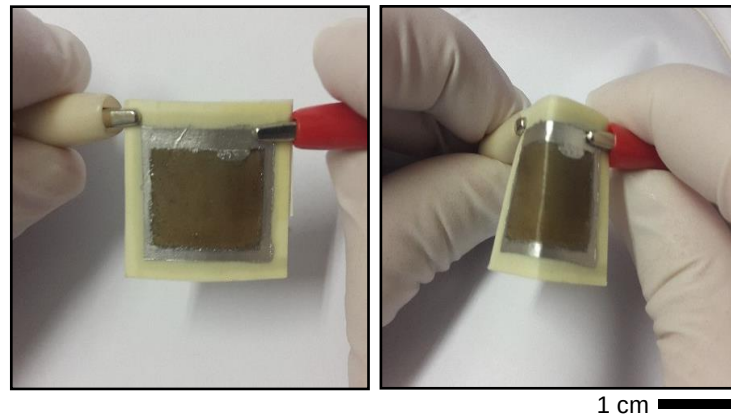


Figure 4.7: Continuos device operation during folding.

4.2 Electrically Controlled Colour Change

We would like to demonstrate electrically controlled colour change of ML-graphene-on-paper. Figure 4.8 (a) shows the schematic drawing of the device. We transferred two ML-graphene layers on both side of the paper and soaked ionic liquid electrolyte into the paper. We used conductive paint (Electrofix conductor paint kit) to make electrical contact to the ML-graphene electrodes. Figure 4.8 (b,c) shows photographs of the fabricated device at different bias conditions. When we applied bias voltage larger than 3 V, we observed a significant change in the colour and then graphene gets semitransparent. Figure 4.8 (d,e) shows the optical microscope image of the edge of ML-graphene. Initially ML-graphene looks shiny metallic, under a voltage bias it first gets dark and turn into transparent. This transparency is associated with the blocking of interband transitions as the Fermi level shift to larger energies.

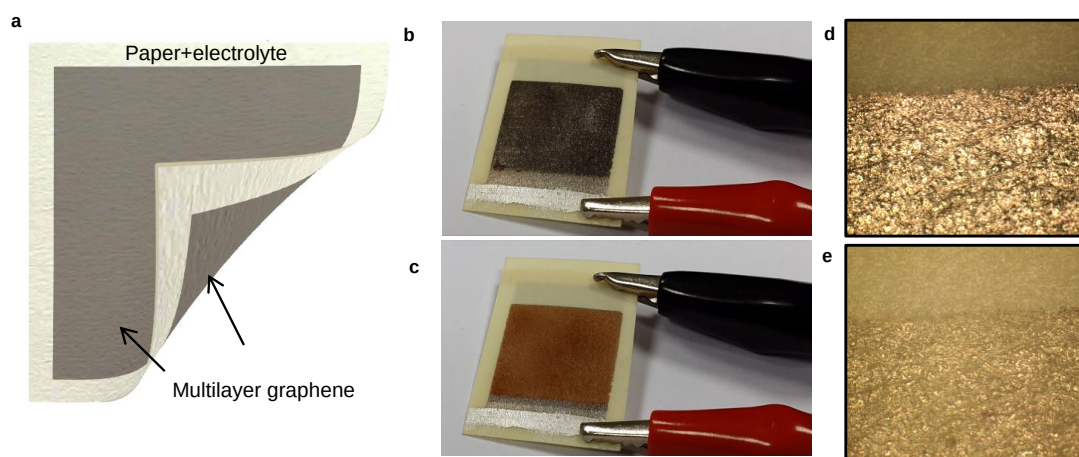


Figure 4.8: Optoelectronic property of ML-graphene on paper. (a) Schematic representation of the graphene based electronic paper. (b,c) Photographs of the fabricated e-paper at various bias voltages. (d,e) Optical microscope image of the edge of ML-graphene at various bias voltages.

We measured the scattering cross section of graphene coated paper surface as we tuned the voltage from 0 to 5 V (Figure 4.9 (a)). At 0 V, device yield a significant specular reflection, however, as the voltage increases, the back scattered intensity is suppressed resulting more near-lambertian view due to the underneath paper surface. We observed colour change in a very broad spectrum covering nearly all visible spectra (Figure 4.9 (b)). To understand the mechanism, we performed a Raman spectroscopy on the ML-graphene on paper at different bias voltages (Figure 4.9 (c)).

We observed a significant enhancement and blue-shift in G-band, whereas the intensity of the 2D-band diminishes. These behaviors indicate a very strong electrostatic doping of graphene layers. Our results suggest that ML-graphene-on-paper can be used as a reconfigurable optoelectronic material which yields substantial color change in the visible spectra.

We also tested the switching characteristics of the graphene-on paper ultra-thin displays. Figure 4.10 shows the scattering intensity-time and current-time behaviors of the device for multiple times of switching between on (5 V) and off (0 V) states. Due to the the intentional damaging of below graphene layers during the voltage controlled intercalation process small degradation from the on state is visible after multiple times of switching (Figure 4.10 (a)). Device shows typical electrolytic capacitor behavior with a fast discharge and relatively slow charge time (Figure 4.10)

To show the reliability of the method we demonstrate the same color change by using normal printing paper and conductive carbon tapes as contact electrodes (Figure 4.11).

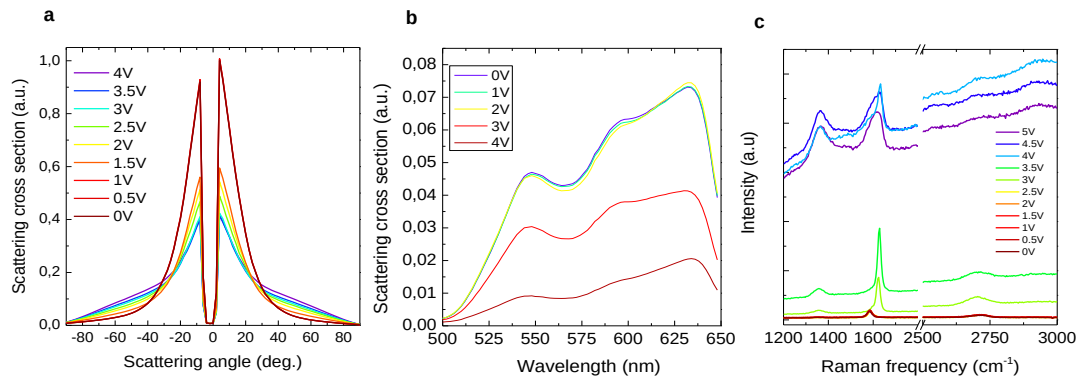


Figure 4.9: Electrical control of optical properties. (a) Scattering cross section (at 650 nm) from the ML-graphene measured at bias voltages between 0 V to 5 V. (b) Spectrum of the scattered light from the ML-graphene at various bias voltages. (c) Evolution of the Raman spectra of ML-graphene with the bias voltage.

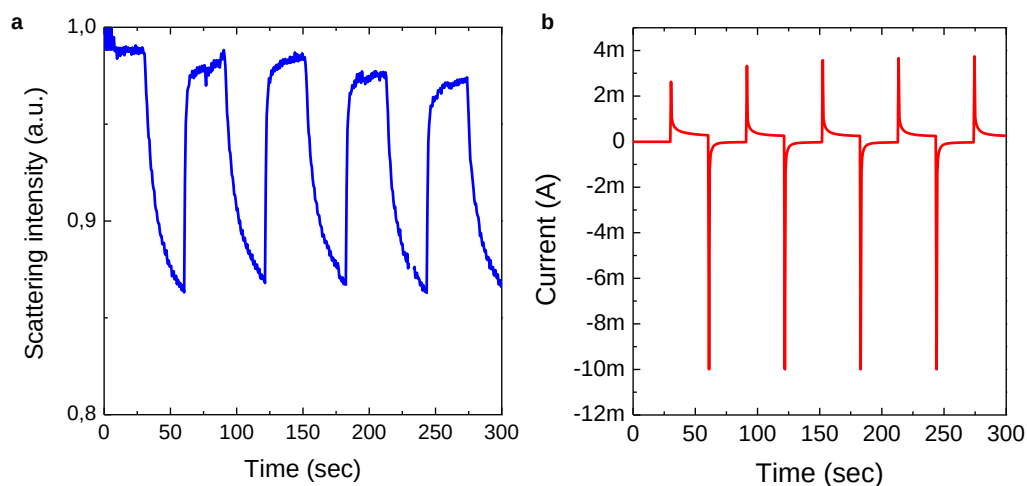


Figure 4.10: Switching characteristics of the device. (a) Scattering intensity against time, (b) current versus time behaviour during switching between on and off states.

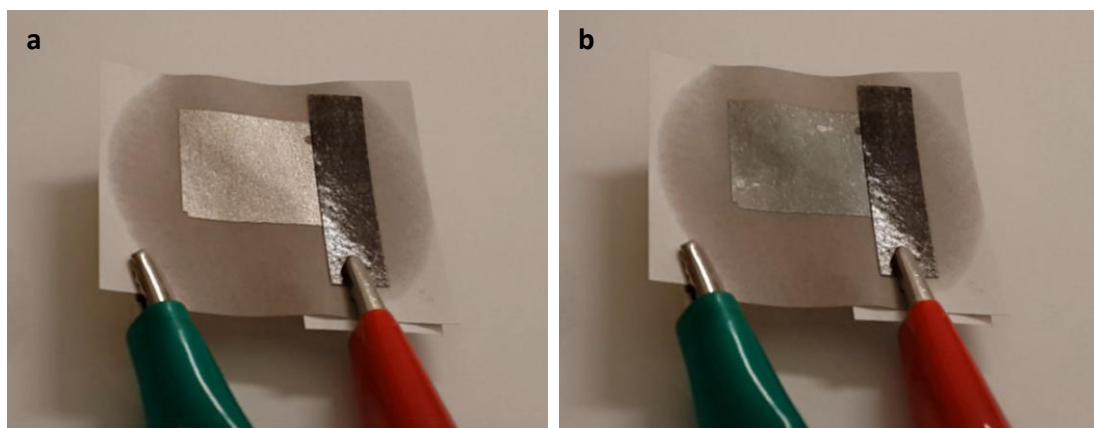


Figure 4.11: Controlling colour of ML-graphene on normal printing paper. (a) In the off-state of the device graphene looks reflective. Conductive carbon tapes are used as the contact electrodes. (b) Applying 4V bias voltage yields the reversible color change of multilayer graphene on normal printing paper.

4.3 Ultra-thin Displays on Paper

To show the promises of graphene based electronic paper, we demonstrated a multipixel paper display device. Figure 4.12 (a) shows the schematic drawing of the device formed by two patterned ML-graphene electrodes registered in perpendicular directions. To address a pixel, we used passive matrix addressing by applying various voltage bias of 0, 2.5 and -2.5 V to the rows and columns. When we applied 2.5 V to a column and -2.5 V to the row, the colour of the intersecting area changes from metallic to reddish paper-view (Figure 4.12 (b)). Using a manual switch box, we were able to reconfigure the pattern by manually adjusting the voltage configuration. The migration of the boundary of the colour change illustrates the intercalation process.

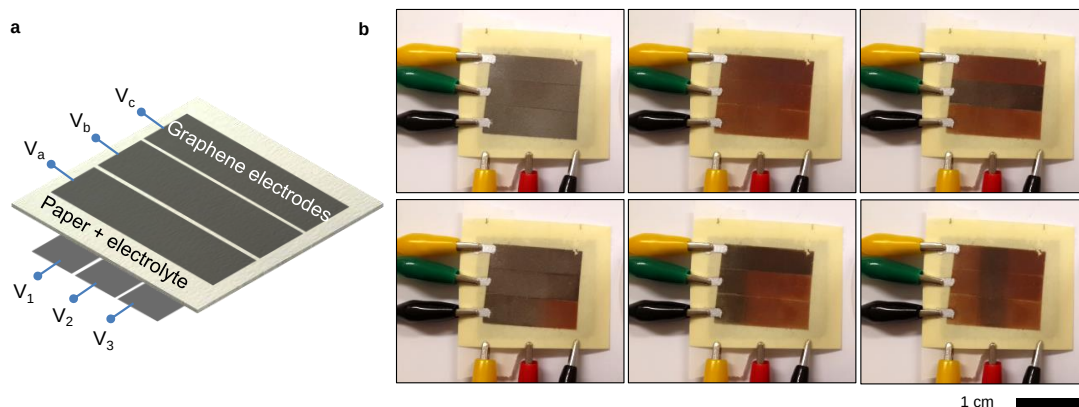


Figure 4.12: Multipixel e-paper display. (a) Schematic representation of multipixel paper display using 3x3 array of patterned graphene electrodes. The width and the length of graphene electrodes are 7 mm and 3 cm, respectively. (b) Photograph of the reconfigurable pattern on paper using passive matrix addressing at various voltage configurations.

We were able to reconfigure the pattern on paper many time, however, we observed that after a 10 minutes the graphene layer gets oxidized and turn into dark back. Degradation of the performance is likely due to the very reactive nature of highly doped graphene which is exposed to oxygen in air. Undoped graphene is very stable however, highly doped graphene can oxidize in ambient conditions. To reduce the oxidation, we first tested our device in vacuum. We observed that, we can apply more voltages (> 5 V) and the device can provide similar color change. Our results suggest that the degradation of the device performance is due to the oxygen in the

atmosphere and water content in the electrolyte. The performance of the device increases when we bake the ionic liquid in vacuum before we inject it into the paper.

Furthermore, we would like to demonstrate a colour principle on our paper display. Simplicity of the device architecture allows us to realize the colour principle by simply printing colour toner on the paper. Figure 4.13 (a) shows the schematic of the colour paper display. We printed a mosaic pattern using halftone colour (Figure 4.13 (b)). Halftone colors consisting of separated dots allows ions to intercalate the graphene layers. Under the voltage bias, graphene gets transparent and makes the color pattern on the paper visible. Figure 4.13 (c) and (d) shows the photograph of the device at 0 and 5V bias voltages. Printed colours can be seen clearly through the doped ML-graphene layer.

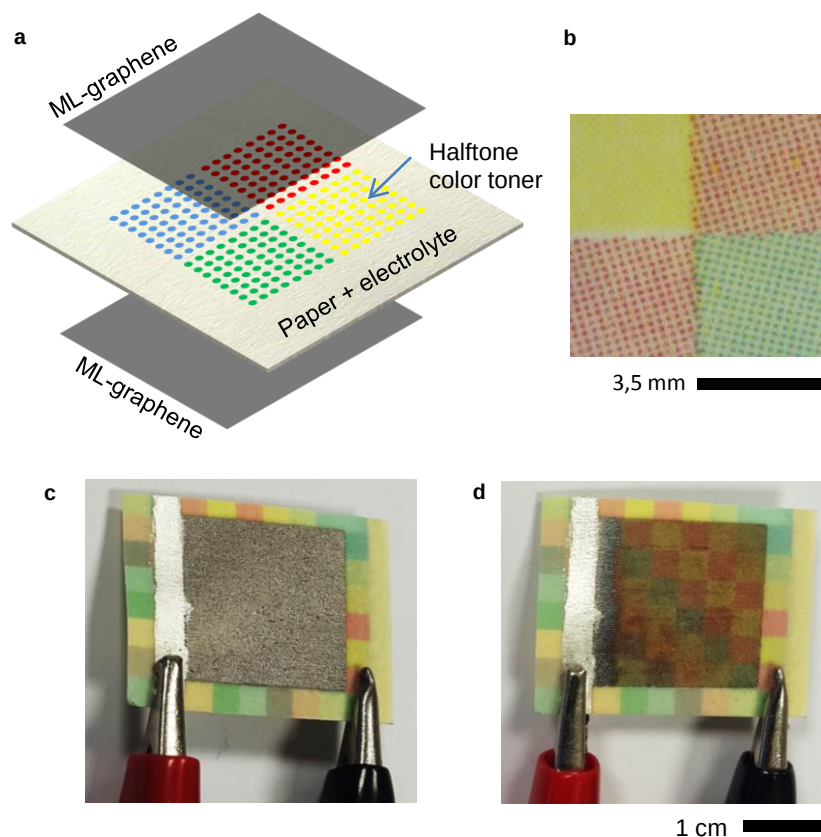


Figure 4.13: Demonstration of colour principle. (a) Schematic representation of colour e-paper formed by printing halftone colour toner on paper sandwiched between two ML-graphene electrodes. (b) Optical microscope image of colour toner dots printed on paper. (c,d) Photograph of the working device at 0 and 5 V bias voltage.

Electronic devices on conventional rigid substrates become problematic during disposal procedures. Fabricated on-paper devices are easily disposable. Figure 4.14 shows the quick burning-away of graphene on paper device and the resulting ashes.

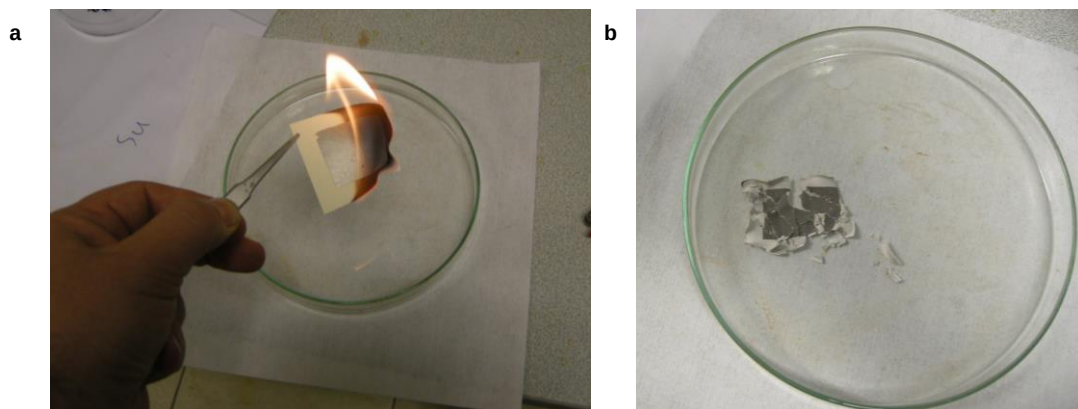


Figure 4.14: Disposable the e-paper. (a) A photograph of a burning device. The paper substrate burns very fast however, the ML-graphene layer does not burn. (b) The ashes of the device. The remaining graphene layer on the paper ash is visible.

Chapter 5

Conclusions

This thesis focuses on the graphene based active optical devices operating in the visible spectrum.

We first developed the optical modulators operating over a broad range of wavelengths from 450 nm to 2 μ m based on graphene supercapacitors. The demonstrated device has simple parallel-plate geometry, yet, with a very efficient device operation. We also studied various device geometries to increase the modulation amplitude. We were able to obtain 35 % modulation using a few layer graphene with an ionic liquid electrolyte. Another advantage of the supercapacitor structure is the symmetry of the device with respect to the polarization of light. Large area device geometry with polarization independent operation in the visible spectra yields a unique combination that can find many applications in optoelectronics.

By further expanding our investigation to multilayer graphene, we demonstrated a new class of flexible electrochromic devices using multilayer graphene electrodes. We showed that the optical transmittance of MLG can be controlled by electrostatic doping via reversible intercalation of charges into the graphene layers. Simultaneous electrical and optical characterizations of the graphene electrochromic devices reveal the mechanism behind electrochromic operation. The demonstrated reflective/transmissive multipixel electrochromic display device and reflection type device highlight the promises of the method. The key attributes of our flexible devices are the simplicity of device architecture, high optical contrast and broad band operation.

As a novel application of the presented gating scheme for multilayer graphene, we developed electronic paper display on a piece of printing paper which using graphene as the reconfigurable optical medium. Our approach relies on electromodulation of optical properties of multilayer graphene-on-paper via blocking the interband electronic transitions. The presented ultrathin paper display yields large optical

contrast in the visible spectra with fast response speed. Furthermore, we demonstrate a colour concept simply by printing colored ink on paper substrates.

The novelty of our thesis is fourfold:

- (1) We provide, for the first time, a graphene based optical modulators working in the visible spectra. It operates as polarization independent and provides large area optical modulation.
- (2) We demonstrated the active and reversible color change in multilayer graphene which is a new class of electrochromic device without using extra conducting coating or polymers. Compatibility of the devices with roll-to-roll fabrication processes enables scalable approaches for large area applications.
- (3) With the presented devices very high optical modulation strength was obtained up to 55% in the visible and near infrared region.
- (4) The presented graphene-based electronic paper can be used for ubiquitous optoelectronics and also have the potential to open new possibilities in adopting the conventional optoelectronics on paper.

We conclude that, the proposed devices can be used to modulate the other parts of the electromagnetic spectrum than the visible and near-infrared wavelengths. Presented devices are compatible with various spectroscopic techniques to study the open parts of light-matter interaction in graphene. As discussed, the performance of the devices can be further increased by using different electrolytes with various device schemes. We believe that this work will guide the fabrication and testing of future active optical devices using two dimensional materials to control the light matter interaction in various regions of the electromagnetic spectrum.

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