Enhanced Electron Transport in Epitaxial Annealed Graphene Titanium Dioxide Heterojunction

Nelson Mugambi¹, James Mbiyu Ngariya¹, Simon Waweru Mugo¹

¹Jomo Kenyatta University of Agriculture and Technology
P. O. Box 62 000 – 00200, Nairobi, Kenya

DOI: 10.22178/pos.92.1

INTRODUCTION

Rising energy demand has dramatically led to rapid development and interest in photovoltaic (PV) technology – progress exploitation towards reduction of cost and improvement of efficiencies of solar cells [1]. TiO₂ draws significant attention among many semiconductors (such as SnO₂, TiO₂, ZnO, CdS, WO3 etc.) due to its high activity, low toxicity, and superchemical stability [2, 3]. In addition, further potential applications are being investigated for sensor devices, electro-optical, micromechanical and photovoltaic [4]. Common polymorphs of TiO₂, naturally occurring, includes; brookite, rutile, or anatase. Anatase nanosized TiO₂ is easily obtained with short diameters of less than 14 nm. Both rutile and anatase absorb the ultraviolet and are transparent in their visible region [5]. The band gap of anatase TiO₂ is 3.18 eV, while that of rutile is 3.08 eV. Both absorb only 5% of sunlight in the UV region, limiting their applications due to their low quantum yield [6].

Two TiO₂ bottlenecks include a lack of visible light response, high charge recombination rates, and short free path of electrons that hinder its applications [7, 8]. Researchers have classified two practical approaches to overcome these shortages: surface sensitization and internal doping [8, 9]. By annealing TiO₂ film morphology, crystallinity, surface porosity, and electrical resistivity are altered [10].

Different approaches to improve the photocatalytic performances of TiO₂ have been investigated, including loading with noble metal parti-

Abstract. Titanium dioxide (TiO₂) photocatalyst is a widely acceptable photocatalyst candidate due to its environment friendliness, cost-effectiveness, intrinsic electronics, photostability, good surface properties, and non-toxicity. However, TiO₂ faces significant challenges for commercial exploitations, including high recombination rates, low quantum yield, and low visible light photoconversion efficiency. In this research, the optical properties of graphene TiO₂ heterojunction were evaluated in measurements of Transmittance and Reflectance. Optical parameters in terms of WDD dispersion energy and dielectric constants were studied by annealing the films in the air up to 450 °C at 1 step, 2 °C/min and 1 °C/min annealing rates. Transmittance for the film annealed at 1 °C/min showed the highest transmittance of 86.57% and 74.07% for graphene and graphene TiO₂, respectively. SCOUT software modelled Transmittance data to obtain refractive index. Refractive indices for pristine, 1 step, 2 °C/min, and 1 °C/min TiO₂ films obtained at 550 nm were found to be 0.51, 0.53, 0.40 and 0.49, respectively. Porosity and dispersion energy for the lowest annealing rates (1 °C/min) was found to be 49 % and 12.7 eV in that order. Real and imaginary Interband transition (2.33–4.04) x 10⁵ and (0.23–2.73) x 10⁴ in that order, linear and nonlinear optical susceptibility (1.42–2.18) x 10⁻¹ and (4.12–22.50) x 10⁻⁹, optical conductivity (2.51–13.2) x 10⁻¹³ and electrical conductivity (3.89–4.60) x 10⁻¹⁵ were enhanced with decreasing annealing rates. This is due to pole filing, film densification, increased lattice absorption and scattering centres and improved crystallinity of the films due to heat treatment and large-area graphene anchoring. The findings revealed that annealing graphene – TiO₂ passivates its surface, reducing its boundary traps owing to quantum confinement effects and improving the electron transport throughout the heterojunction.

Keywords: graphene; titanium dioxide; annealing rates; transition; heterojunction.
cles, use of co-catalysts, metallic or nonmetallic doping and dye [11-13]. The photocatalytic activity of TiO2 enhancement utilizing visible light has been modified to form carbon-TiO2 using carbonaceous substances such as graphene, fullerenes and carbon nanotubes [14–16]. Graphene is a 2D honeycomb carbon sheet with excellent properties such as zero band gap and prolonged electron mobility (200,000 cm2 V–1 s–1), high visible light transparency, high thermal (≈ 5000 W m–1 K–1), and high electrical conductivity, which endow it as a beautiful photo catalyst modifier [17–19].

Transmittance and Reflectance of graphene TiO2 films were characterized by UV-VIS spectroscopy [20] and optical parameters such as refractive index, extinction coefficient, absorption coefficient, and dielectric constants analysis done by Scout software [21]. The optical properties of TiO2 were enhanced by shifting the absorption edge toward a longer wavelength once graphene is incorporated to form graphene TiO2 nanocomposite [22].

In the present work, TiO2 thin films were coated on graphene on a glass substrate, and the composite was studied holistically. This is to evaluate the influence of annealing and graphene on electron transport and crystallinity of TiO2 films by exploring dispersion parameters, porosity and dielectric characterization.

**Experimental Procedure**

Graphene monolayer grown with Roll-to-roll (R2R) chemical vapour deposition (CVD) and wet transfer synthesis on glass substrate were sourced from Charm Graphene CO., limited.

The graphene on the glass was then cleaned gently for about 5 minutes in analytical acetone grade 99.5% purity using cotton swamps, dipped in ethanol, and then rinsed with deionized water for about five minutes. The substrates were then dried by blowing them onto pressurized warm air and stored in a desiccator.

A scotch magic tape was placed on graphene on a glass substrate, leaving a 1 x 1 cm2 window to control TiO2 thickness. T/SP, 18% wt, 15-20 nm TiO2 nanocrystalline, sourced from Solaronix, Switzerland) was coated on the graphene 50 Ω/sq, using a clean tapered glass rod by sol-gel doctor-blading technique [23]. Uniform press-

sure was applied on the pasted region to obtain the desired film thickness. The films were free for about 20 minutes to enhance homogeneity.

The freshly prepared samples were annealed using KL 420 muffle furnace at 2 and 1 °C/min annealing rates up to 450 °C followed by 30 minutes of sintering to enhance the roughness and crystallinity of the films [24]. A few films were left pristine while others were subjected to 1 step annealing up to 450 °C, left to sinter for about 30 minutes, and then allowed to cool to room temperature.

Optical transmittance was measured using Shimadzu UV VIS Probe 1800 Spectrophotometer at 200–1100 nm. Optical parameters such as refractive index (n), absorption coefficient (α), extinction coefficient (k), real and imaginary dielectric constant (ε1, ε2) were obtained with SCOUT software.

Relative density, Porosity, Dispersion energy, interband transition, Energy losses, linear and nonlinear optical susceptibility, and optical and electrical conductivity were obtained. The data collected was processed using version 8.5 Origin Pro software.

**RESULTS AND DISCUSSION**

Figure 1 shows the transmittance spectra of annealed graphene samples and graphene TiO2 composite in the wavelength ranging from 300 to 800 nm.

Figure 1 – A graph Transmittance versus Wavelength

The optical transmittance spectra of thermally treated films were found to vary with decreasing annealing rates – a drastic decrease in transmittance in the UV region, which is the ab-
sorption edge. Transmittance enhanced significantly with a reduction in annealing rates with 1 °C per minute, showing the highest transmittance of 86.57 and 74.07 % for graphene and graphene TiO$_2$ respectively, at 500 nm wavelength. As prepared and annealed, graphene exhibits peaks at 500 nm, whereas graphene – TiO$_2$ was found at 713.5 nm wavelength. All the films displayed high transmittance within the visible light. It is worth noticing a blue shift in the transmittance of graphene and graphene – TiO$_2$ films as annealing rates decreased. The graphene monolayer is not expected to change its optoelectronic properties with annealing. Therefore, we report a variation in graphene transmittance at varying annealing rates. This is due to the removal of hydrocarbons and the decrement of wettability and polymer residues. A slight reduction in transmittance with increased annealing rates can be attributed to increased surface roughness or to alleviating oxygen defects [25]. When TiO$_2$ is annealed at lower annealing rates, oxygen vacancies are formed due to releasing oxygen into the environment. The transmittance values corresponding to $\lambda = 500$ nm within the transparent region were recorded in Table 1.

Table 1 – Transmittance and optical parameters of TiO$_2$ thin films at various annealing rates

<table>
<thead>
<tr>
<th>Samples</th>
<th>Transmittance, %</th>
<th>Refractive index, n</th>
<th>Relative density, %</th>
<th>Porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Prep</td>
<td>55.71</td>
<td>1.99</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>1 Step</td>
<td>65.47</td>
<td>1.67</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>2 °C/min</td>
<td>70.55</td>
<td>1.78</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>1 °C/min</td>
<td>74.07</td>
<td>1.90</td>
<td>49</td>
<td>51</td>
</tr>
</tbody>
</table>

To obtain the complex optical refractive index, $n$, of the film, we used relation (1)

$$\tilde{n} = n(w) + ik(w)$$

where the genuine part gives the refractive index $n$, whereas the imaginary part gives extinction coefficient $k$, the refractive index values of graphene and graphene TiO$_2$ films can be obtained from equation (2):

$$n = \left\{ \frac{4R}{(R-1)^2} \right\}^{1/2} - \frac{R+1}{R-1}$$

where $R$ is the reflectance and $k$ is the extinction coefficient [26].

Figure 2 presents plots of the refractive index $n$, of graphene and graphene TiO$_2$ films as a function of wavelength.

The refractive index spectra decrease with increasing wavelength revealing a normal dispersion behaviour. However, the refractive index varies with varying annealing rates. For both graphene and graphene TiO$_2$ films, refractive index spectra increase with decreasing annealing rates, which can be attributed to an increase in packing density and improvement in crystallinity [27]. A decreased refractive index with wavelength can be associated with the resonant effect between irradiated photons and electronic polarization due to film equality between irradiated photons and plasma frequency [27]. The refractive index at $\lambda = 500$ nm was recorded in Table 1.

The refractivity of films affects the porosity (the volume of pores per volume) of TiO$_2$ films. Porosity expressed as a percentage is estimated by the expression (3):

$$Porosity = (1 - \frac{n_p^2 - 1}{n_0^2 - 1}) \times 100$$

where $n_p$ is the refractivity of the anatase porous films, and $n_0 = 2.52$ is the refractivity of bulk TiO$_2$ [28, 29].
Porosity was obtained using the refractive index within the transparent region corresponding to a wavelength equal to 500 nm, recorded in Table 1. Porosity decreased with decreasing annealing rates, a phenomenon associated with reduced pore size due to film densification and compaction. Therefore, a high refractive index led to the lowest porosity. Film annealed at 1 °C per minute showed the lowest porosity, at 51%. Decreased annealing rates significantly increase TiO₂ densely packed particles overlap, reducing porosity. Overlap of particles at low porosity causes an increment in the internal surface area of the material. As porosity decreases, the coordination number (CN) of TiO₂ increases. For densely packed particles with a maximum CN=6, the porosity was found to be 0.41 (41%) [30, 31]. Expression (4), shown below, was used to determine the relative values of films [32].

\[
Relative\ density = \frac{n^2-1}{n_0^2-1} \times 100
\]  

(4)

Figure 3 displays a graph of relative density versus photon energy.

![Figure 3](image)

Figure 3 – A graph of refractive index versus annealing rate

The relative density of the annealed films rose with a rise in photon energy. The relative density of the films increased with decreasing annealing rates, which is attributed to the gradual improvement of the quality of the film, film densification, and film crystallization.

Charge transport in a solid-state lattice site is a hopping-like movement that results in electron recombination. Flat, dense TiO₂ electron transfer improves due to better light absorption, pore filling and charge compensation because of a reduction in porosity [33].

A single oscillator model by [34, 35] can examine refractive index dispersion in low absorption regions using the relation (5):

\[
(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \frac{1}{E_0 E_d} (hv)^2
\]

(5)

where \(E_0\) is the single oscillator energy, and \(E_d\) is the dispersion energy, \(h\) – Planck’s constant, \(v\) – frequency, \(hv\) – photon energy.

Representation spectra of \((n^2-1)^{-1}\) as a function of \((hv)^2\) for pristine and annealed graphene and graphene TiO₂ films are presented in Figure 4.

![Figure 4](image)

Figure 4 – The plot of \((n^2-1)^{-1}\) versus \((hv)^2\) of annealed graphene and graphene TiO₂ coatings

\((n^2-1)^{-1}\) decreases with increasing photon energy. For all the films, \((n^2-1)^{-1}\) disperses at lower points and clusters together as we approach higher photon energy attributed to the lattice absorption due to impurities and structural defects contained in the inter-crystallite’s boundaries containing and increased scattering centres in the films [35].

They fit linearly in Figure 4 and yield straight lines illustrated in Figure 5 ranging from 3.5 to 6.5 \((eV)^2\) chosen from the obtained curvature.
Lattice vibrations contribute negatively to the refractive index, so a positive curvature deviation is observed linearly from long wavelengths [35].

\[
E_d = \beta N_c Z_a N_e
\]  

where \(\beta\) is a covalent or ionic value = 0.37 eV [35] for covalent materials, the formal valence of anion \(Z_a=2\), and the adequate number of valence electrons per anion \(N_e\), for TiO\(_2\) equals 8.

The particle coordination numbers calculated are displayed in Table 2. These values are seen to increase with decreasing annealing rates. 1 °C per minute achieves a higher particle coordination number attributed to improvement in percolation pathways. For an electron residing on a particular particle, a higher particle coordination number implies that it can percolate in a three-dimensional lattice to another particle.

According to [38], the nonlinear polarizability parameter, also known as nonlinear optical susceptibility \(\chi^3\) and the linear optical susceptibility \(\chi^1\) can be determined using the Miller rule (7), which is very convenient for visible and near infra-red frequencies.

\[
\chi(3) = C\left(\chi(1)^2\right)^4 = \frac{E_0 E_d}{4\pi E_0^2 - (\hbar v)^2} = \frac{C}{(4\pi)^4 (n^2 - 1)^4}
\]

where \(C\) is a constant, \(C=10^{-10}\) esu.

This shows the highest values attributed to the film having better excitation energy for electronic transition and appealing strength of interband optical change. High specific surface area and many chemical defects on graphene monolayers make them have high dispersion. This, in return, causes high dispersion when it scaffolds TiO\(_2\) which can probably enhance dye adsorption in DSSC applications.

Dispersion energy, \(E_d\) can be related by a relation (6) to determine the coordination number \((N_c)\) [36, 37].

**Table 2 – Dispersions and dielectric parameters of TiO\(_2\) thin films at various annealing rates**

| Samples       | \(E_d\) | \(E_0\) | \(N_c\) | \(\chi^3\) \(
\times 10^{-13}\) | \(\chi^1\) \(
\times 10^{-1}\) | \(\varepsilon_1\) | \(\varepsilon_2\) | \(\tan \delta\) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Prep</td>
<td>45.6</td>
<td>15.8</td>
<td>7.70</td>
<td>30.50</td>
<td>2.35</td>
<td>0.62</td>
<td>0.26</td>
<td>0.41</td>
</tr>
<tr>
<td>1 Step</td>
<td>6.38</td>
<td>4.66</td>
<td>1.08</td>
<td>4.12</td>
<td>1.42</td>
<td>0.28</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>2 °C/min</td>
<td>9.77</td>
<td>5.46</td>
<td>1.65</td>
<td>8.70</td>
<td>1.72</td>
<td>0.36</td>
<td>0.13</td>
<td>0.38</td>
</tr>
<tr>
<td>1 °C/min</td>
<td>12.7</td>
<td>5.76</td>
<td>2.15</td>
<td>22.50</td>
<td>2.18</td>
<td>0.48</td>
<td>0.32</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Figure 6 displays a graph of the nonlinear optical susceptibility of annealed graphene TiO\(_2\) as a function of photon energy. \(\chi^3\) spectra increase with increasing photon energy. Linear and nonlinear optical susceptibility was enhanced with decreased annealing rates attributed to the quantum confinement effect. \(\chi^3\) values were obtained at a corresponding \(h\nu = 2.26\) eV, and corresponding \(\chi^1\) values were calculated using equation 7. The values are listed in Table 2.

The lowest annealing (1 °C per minute) exhibited a much higher nonlinear optical susceptibility due to the enhanced crystallinity of TiO\(_2\) on graphene through the possible existence of C-O-Ti bonds associated with facile charge separation [39].
The complex refractive index (1) contributes to the dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) [40] generates real \( \varepsilon_1 \) and imaginary \( \varepsilon_2 \) parts of the dielectric constant given by equations (8)-(9).

\[
\varepsilon_1 = n^2 - k^2 \tag{8}
\]

\[
\varepsilon_2 = 2nk \tag{9}
\]

Both natural and imaginary parts variations for all graphene \( \text{TiO}_2 \) films (pristine and annealed) as a function of wavelength are presented in Figure 7.

Complex interband can be generated from the real and imaginary part of the dielectric constant using relation (11):

\[
J_{cv} = J_{cv1} + J_{cv2} = \frac{m_o^24\pi^2}{e^2h^2} \frac{(hv)^2}{2} (\varepsilon_1 + i\varepsilon_2) \tag{11}
\]

where \( h \) is the Plank’s constant, \( e \) is the electron charge; \( m_o \) is the mass of an electron.

Dielectric transition strength is proportional to the genuine part interband transition \( J_{cv1} \) and imaginary part interband transition [44].

Pre multiplier \( \frac{m_o^24\pi^2}{e^2h^2} \) is used as \( 8.289 \times 10^{-6} \text{ gcm}^{-3}(\text{ev})^{-2} \) for convenience computation. The dependence of \( J_{cv1} \) and \( J_{cv2} \) on the photon energy is displayed in Figure 8a. Interband transition strength increases with photon energy. \( J_{cv} \) shows enhancement with decreasing annealing rates associated with improved electronic transition probability.
There is a significant increase in $J_{cv}$ at $(h\nu)^2 > 5.0 \text{ (eV)}^2$, which implies high absorption elevating the excitation of the electrons. This enables electron movements from the valence band to the conduction band. A Greater $J_{cv}$ ratio of 1 °C per minute reveals low dielectric loss of graphene TiO$_2$ annealed at the lowest annealing rate, demonstrating an increase in electron density of the film associated with a reduction in charges recombination.

Surface energy loss function (SELF) and volume energy loss (VELF) expresses the energy transferred to and from the topmost atom layer of a compound semiconductor due to electrons’ excitation in the surface and bulk. Relations (12) and (13) respectively evaluated both SELF and VELF losses [45].

$$S_{elf} = \left\{ \frac{-1}{\varepsilon} \right\} = \frac{\varepsilon_2}{(1+\varepsilon_1)^2+\varepsilon_2^2}$$

$$V_{elf} = \left\{ \frac{-1}{1+\varepsilon} \right\} = \frac{\varepsilon_2}{\varepsilon_1^2+\varepsilon_2^2}$$

Figure 8b displays the dependence of photon energy and effective VELF/SELF ratio in the visible and ultraviolet regions of graphene TiO$_2$ pristine and annealed films. Practical VELF/SELF decreased with increasing photon energy Self and Velf values corresponding to values of $\varepsilon_1$ and $\varepsilon_2$ at $h\nu = 2.26 \text{ eV}$ are presented in Table 2. SELF and VELF values corresponding to $\varepsilon_1$ and $\varepsilon_2$ at $h\nu = 2.26 \text{ eV}$ are shown in Table 2. Volume energy losses are higher than surface energy losses, implying that an electron dissipates more energy as it traverses through the bulk than the surface. SELF and VELF increase with decreasing annealing rates, showing nearly identical behaviour as free charge carriers travel through the surface and size. Similarly, VELF/SELF decreased with decreasing annealing rates, indicating an improvement in the crystallinity of films due to increased surface mobility of adatoms on the surface of the glass substrate and a favourable anchor of TiO$_2$ on graphene. The earlier report shows that more energy is lost when a fast-moving electron passes through bulk than the surface of a medium due to the excitation of plasma oscillation of the electron [43, 46, 47].

Scattering energy losses and total absorption mainly affect a medium’s absorption coefficient ($\alpha$). Absorption coefficient values were obtained from scout software by simulating transmittance data. The absorption coefficient of graphene TiO$_2$ decreased with increasing wavelength. A low absorption coefficient at a high wavelength implies a low possibility of electron transition since the photon energy was insufficient to move the electron from the valence band to the conduction band of a semiconductor. There is a higher possibility for electron transition at a shorter wavelength since the photon energy is enough. The probability of an electron transition is higher where the values of $\alpha$ are $> 10^4 \text{ cm}^{-1}$. At $\alpha < 10^4 \text{ cm}^{-1}$, electron transition is indirect; therefore, the phonon maintains the electron momentum [48]. Values for $\alpha$ at $\lambda = 500 \text{ nm}$ within the transparent region were listed in Table 3.

### Table 3 - Electron transition and transport parameter of graphene TiO$_2$ thin films at various annealing rates

<table>
<thead>
<tr>
<th>Samples</th>
<th>$J_{cv}$ x 10$^{-6}$</th>
<th>$J_{cv}$ x 10$^{-6}$</th>
<th>Self x 10$^{-6}$</th>
<th>Velf x 10$^{-6}$</th>
<th>Velf / Self</th>
<th>$\sigma$ x 10$^{13}$</th>
<th>$\sigma$ x 10$^{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Prep</td>
<td>5.13</td>
<td>2.13</td>
<td>0.10</td>
<td>0.57</td>
<td>5.98</td>
<td>36.55</td>
<td>17.34</td>
</tr>
<tr>
<td>1 Step</td>
<td>2.33</td>
<td>0.23</td>
<td>0.02</td>
<td>0.35</td>
<td>20.64</td>
<td>5.92</td>
<td>2.51</td>
</tr>
<tr>
<td>2 °C/min</td>
<td>2.95</td>
<td>1.11</td>
<td>0.07</td>
<td>0.93</td>
<td>12.85</td>
<td>6.99</td>
<td>2.79</td>
</tr>
<tr>
<td>1 °C/min</td>
<td>4.04</td>
<td>2.73</td>
<td>0.14</td>
<td>0.95</td>
<td>6.75</td>
<td>28.58</td>
<td>13.20</td>
</tr>
</tbody>
</table>

$\alpha$ increased with decreasing annealing rates with 1 °C per minute, showing the highest $\alpha$, implying a higher probability of electron transition due to closeness in the top points of a valence band and bottommost moments of the
conduction band.

The optical conductivity ($\sigma_{opt}$), electrical conductivity ($\sigma_e$) and absorption coefficient are related by equations (14)-(15) in that order [42].

$$\sigma_{opt} = \frac{\alpha_n c}{4\pi}$$

(14)

$$\sigma_{opt} = \frac{\alpha_n c}{4\pi}$$

(15)

where $n$ is the refractive index and $c$ is the velocity of the radiation.

The diversity of $\sigma_{opt}$ for pristine and annealed graphene TiO$_2$ films as a function of photon energy is represented in Figure 8c. It is seen from the figure that $\sigma_{opt}$ increases with the photon energy, which we attribute to the photon energy exciting the electrons. The optical conductivity of graphene TiO$_2$ was elevated with decreasing annealing rates attributed to TiO$_{1-x}$ oxygen deficit acting as donor defects due to oxygen vacancies and interstitial titanium states [49]. Maximum conductivity is experienced at one °C per minute, a phenomenon of the effect of oxygen vacancies on the film’s carrier density [50].

Figure 8d illustrates the dependence of electrical conductivity as a function of photon energy. It is noteworthy that $\sigma_e$ is significantly reduced with increased photon energy due to electrons trapping at the defect centres. Electrical conductivity increases with decreased annealing rates, which can be attributed to crystallinity and lattice absorption improvement.

Porosity, nonlinear susceptibility and optical conductivity correlation have been presented in Figure 9. Nonlinear susceptibility and visual conductivity increase with decreasing annealing rates. Moreover, porosity decreased with lowering annealing rates due to gradual quality improvement in film crystallization, film pore filling and densification due to the local migration of matter attributed to particle diffusive sintering.

Authors [51] found higher values of porosity for TiO$_2$ film anchored on FTO than the values we find of TiO$_2$ on graphene due to the large surface area of graphene that offer a scaffold anchor of TiO$_2$. Tiny gaps and voids at the FTO/TiO$_2$ interface cause higher porosity due to the uneven microstructure of FTO glass. According to [52], annealing time and temperature influence the porosity aggregate and quality of the films.

Graphene TiO$_2$ film’s significant nonlinear susceptibility of order $10^{-14}$ esu is attributed to the substantial enhancement of the local field. Nonlinear optical exposure increased with decreasing annealing rates attributed to the lattice’s vibration and dispersion effects due to grain size increase as the film transited from amorphous to crystalline. We associate the increase in $S_{EL}/V_{EL}$ with improving the crystalline quality of the TiO$_2$ films. The surface-to-volume ratio has the same trend as dispersion energy.

**CONCLUSIONS**

A UV VIS spectrophotometer has characterized graphene TiO$_2$ films prepared by Doctor Blade. Graphene and graphene TiO$_2$ have obtained in the range 300–800 nm, from which refractive index, relative density, porosity, dispersion, linear and nonlinear susceptibility, interband transition, energy losses, optical and electrical conductivity optical parameters were deducted. Graphene metal being a semimetal not expected to vary optoelectronic properties by annealing. A transmittance, porosity and dispersion parameters variation at different annealing rates was reported. This variation can be attributed to removing hydrocarbons, wettability decrement, and polymer residues. All the films exhibit high transmittance.
significant third-order susceptibility, (≈ 80–86% for graphene) and (≈ 56–74% for graphene TiO$_2$), decreasing porosity (66–49%), sizeable third-order susceptibility (4.12–30.50) x 10$^{-14}$ esu. Interband transition increased with decreasing annealing rates showing a higher probability of an electron transit from the valence band to the conduction band. The experimental results reveal the film for graphene TiO$_2$ annealed at 1 °C per minute is suitable for application in optoelectronic owing to its low porosity, significant third-order susceptibility, higher interband transition, low VEF/SELF-ratio, higher optical and electrical conductivity and good crystallinity.

Therefore, we have successfully evaluated the influence of anchoring TiO$_2$ on graphene and annealing temperature. The films annealed at 1 °C/min rate showed better diffusion rate, longer electron lifetime due to low recombination rate, and improved crystallinity that enhanced electron transport of the films.

REFERENCES


