Chapter 7

Graphene oxide-TiO₂ nanocomposite*

In this chapter we discuss that metal oxide semiconductors thin films are the favourable candidates as an electron transport layer for perovskite solar cell applications. Nevertheless, due to low conductivity and a very high recombination rate at the interface of the electron transport layer and the light absorber (perovskite), hampers the efficiency of the solar devices. To address these issues, the graphene oxide-titanium dioxide (GO-TiO₂) nanocomposite thin films were prepared. The thin films of GO-TiO₂ nanocomposite were prepared by spin coating on indium tin oxide (ITO) substrates followed by annealing at 150 °C. The X-ray diffraction studies showed the rutile phase of TiO₂ nanostructures. The band gap of pure TiO₂ in thin film form was found to be 3.5 eV, which reduced to 2.9 eV for GO-TiO₂ nanocomposites showing a red shift towards higher wavelength. Further the post thermal annealing at 400 °C showed the improvement in transparency in the visible region and low sheet resistance. Our study demonstrates a facile, low-temperature solution processing approach to form a rGO-TiO₂ composite material which can serve as the electron transport layer in perovskite solar cells.

7.1 Introduction

Titanium dioxide (TiO$_2$) is a well-known semiconductor material and has been extensively investigated for the past couple of decades for a broad canvas of applications. TiO$_2$ is a non-toxic, chemically stable, cheap and easily available material, having a band gap of 3.2 eV which lies in the ultraviolet (UV) region.$^{[1]}$ This wide band gap makes it a suitable candidate to be used as electron transport layer for pervoskite solar cells. One of the architectures of these types of cells is the mesostructured solar cell with a mesoporous electron transport layer (ETL) composed of semiconducting metal oxides such as TiO$_2$, ZnO, etc. Metal oxide semiconductor charge transport layers have been widely used with the additional advantages of resistance to oxygen and moisture as well as optical transparency. Researchers have shown that the electron diffusion length is found to be shorter than the hole diffusion length in TiO$_2$-based ETLs.$^{[2]}$ The electron-hole recombination is very high in the mesoporous TiO$_2$ ETL and this is one of the serious issues that hinders electron transport due to grain boundary scatterings.$^{[3-5]}$ This recombination further reduces the energy conversion efficiency in solar cells. Therefore, improving charge transport has gained considerable interest. For the mesostructured cells, a number of efforts have been made to facilitate charge transport by employing modified TiO$_2$, such as substitutional doping of Y$^{3+}$, Al$^{3+}$, or Nb$^{5+}$ into TiO$_2$.$^{[6-11]}$

Recently graphene has received much attention due to its extraordinary electrical, optical, mechanical, and thermal properties.$^{[12]}$ This two-dimensional (2D) sp$^2$-hybridized carbon sheet emerged as an attractive candidate for energy applications, since its discovery in 2004 by A. K. Geim through micromechanical cleavage.$^{[13-21]}$ However, graphene sheets without functionalization are insoluble and infusible with limited practical applications. Current efforts have headed to solution-processable graphene oxides (GO) from exfoliation of graphite powders with strong oxidizing reagents. The availability of reactive carboxylic acid groups at the edge and epoxy/hydroxyl groups on the basal plane of GO sheets facilitates functionalization of graphene, allowing tunability of optoelectronic properties while holding the good solubility in polar solvents.$^{[22,23]}$
Moreover, GO can be produced and processed in solution at large scale with low cost, which is particularly attractive for massive applications. GO-based materials have been used in every part of polymer solar cell devices, namely as electrode, charge extraction layers, and in active layer.\textsuperscript{[24-27]}

In this study, we report on a cost effective and facile method to synthesize GO and TiO\textsubscript{2} nanoparticles and their composite films on ITO substrates. These thin films were synthesized by integrating TiO\textsubscript{2} nanoparticles with different wt\% of GO using solution processing. The structural, optical, morphological and electrical properties of GO-TiO\textsubscript{2} nanocomposite films were probed thoroughly. Hybridization of TiO\textsubscript{2} with graphene can significantly tune the energy band gap.\textsuperscript{[28]} Due to this hybridization the absorption threshold shifts from the UV to the visible range edge. Because of the electrostatic repulsion between GO flakes as well as random wrinkling and folding in the film-formation process, the GO film is usually more porous than the film processed directly from reduced graphene oxide (rGO). After the formation of the GO film, all GO flakes are locked in place and do not have much freedom to move during the reduction process.\textsuperscript{[29]} In this work, we also devised a simple method to produce the GO/TiO\textsubscript{2} composite and studied the post thermal annealing effects by the optical transmission and IV measurements.

Direct reduction of GO films by annealing in nitrogen environment can minimize the re-stacking of the graphene sheets and allow for the formation of an rGO film with much better porosity, lower oxygen content and the higher carrier mobility. Moreover, the photoelectrons are transferred from the TiO\textsubscript{2} conduction band to graphene, which improves the electron-hole pair separation and prevents recombination. This in turn would reduce the interfacial resistance and thus improves the charge transport efficiency. Our study demonstrates a low-temperature solution processing approach to the composite films with better porosity, enhanced carrier mobility and the resistance to oxygen and moisture for better ETL in perovskite solar cells.
7.2 Experimental details

7.2.1 Materials and sample preparation

The following materials were all purchased from Sigma Aldrich and Merck for the synthesis of graphene oxide and titanium dioxide nanoparticles: Titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$), hydrogen peroxide ($\text{H}_2\text{O}_2$), potassium permanganate (KMNO$_4$), graphite powder, sodium nitrate (NaNO$_3$), sodium hydroxide pellets (NaOH), polyvinyl alcohol (PVA), hydrochloric acid (HCl, purity 35%), hydrofluoric acid (HF, reagent grade, 48%), indium tin oxide (ITO, sheet resistance 7-15Ω/sq.), and sulphuric acid (H$_2$SO$_4$, purity 97.99%).

The TiO$_2$ nanoparticles were prepared by hydrothermal synthesis technique by using $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ as precursor. The 10 ml of precursor material was added in 100 ml deionized water, after 5 min stirring 0.6 g NaOH pellets and 0.5 g PVA were added into the solution. The resulting white solution was sonicated for 1 h and then put into an autoclave at 100 °C for 8 h followed by cooling to room temperature. For graphene oxide (GO) preparation, as received graphite flakes powder (Sigma 97%) were purified with HF treatment followed by washing with distilled water for several times to get to a neutral PH. The resulting material was once washed with acetone and dried in an oven at 100 °C to get pure graphite flakes. GO was prepared by using a modified Hummer’s method.$^{[30]}$ 1 g of purified graphite flakes and 0.5 g of NaNO$_3$ were mixed together and put in a round bottom flask; 23 ml of concentrated H$_2$SO$_4$ was added into the mixture under constant stirring at 60 rotations per min (rpm) for 1 h while keeping the temperature at 5 °C by using an ice-water bath; 3 g of KMnO$_4$ was added gradually to the resulting homogeneous solution to prevent overheating and explosion and to maintain the temperature below 20 °C. The resulting dark greenish mixture was stirred for 12 h at 35 °C using an oil bath. Next 500 ml distilled water was added slowly to dilute the resulting solution under strong stirring. After 1 h this suspension was further diluted with 5 ml H$_2$O$_2$ solution and further stirred for 2 h. The resulting suspension was washed with 125 ml solution of 10 % HCl and distilled water and then dried in an oven for 6 h at 90 °C. Dark black GO sheets were finally obtained.
7.2.2 Preparation of GO-TiO$_2$ composites films on ITO substrates

ITO coated glass substrates with a sheet resistance of 15-25 Ω/sq purchased from Sigma Aldrich were cut into 2 cm x 1 cm size and cleaned by sequential ultra-sonication in detergent mixed into distilled water, acetone and isopropyl alcohol (IPA) for 15 min each. The cleaned substrates were then dried in a hot and dry air flux. Nanocomposite sample with composition xGO-TiO$_2$ (x=0, 2, 4, 8, 12 wt%) were prepared in the following three steps: first a TiO$_2$ nanoparticle dispersion was made by adding 50 mg of TiO$_2$ nanoparticles in 1 ml of ethanol and sonicating for 1 h; secondly, a GO solution were prepared by sonicating the chosen weight % of GO in 2 ml of isopropanol; in the final step the two prepared suspensions were mixed together and sonicated for another 3 h to get a homogenous suspension.

To obtain films of xGO-TiO$_2$ (x = 0, 2, 4, 8, 12 wt%) films, the composite solutions were dropped on the conducting ITO substrate with the help of syringe and spin-coated at 3000 rpm for 40 s. The prepared films were annealed at 150 °C for 1 h. The post thermal treatment of xGO-TiO$_2$ (x= 12 wt%) film in nitrogen environment at 400 °C for 20 minutes was also carried out.

7.3 Results and discussions

The XRD patterns of as synthesized GO and TiO$_2$ nanoparticles is shown in figure 7.1 (a). The layer spacing was calculated using the Bragg’s equation, $\lambda=2d\sin(\theta)$, where $\lambda$ is the wavelength of the X-ray beam ($\lambda = 0.154$ nm), d is the distance between GO or reduced graphene oxide (rGO) adjacent sheets. For GO, the peak at 10.2° assigned to the (001) plane, corresponds to an interlayer spacing of 0.44(2) nm. The very weak diffraction peak observed in the XRD pattern of reduced graphene oxide (rGO) around 26.0° corresponds to an interlayer distance of 0.18 (2) nm and there is also a weak diffraction peak at ~ 42.57° (d ~ 0.077(2) nm). The weak diffraction peak observed at 42.50° is associated with the incomplete oxidation of graphite. The higher value of the interlayer spacing for GO is due to the oxidation of graphite.
Figure 7.1: (a) X-ray diffraction patterns of as synthesized GO and TiO$_2$ nanoparticles, (b) as prepared thin films composites ITO/x(GO)-TiO$_2$ (x=2, 4, 8, 12wt%).

The XRD pattern of pure TiO$_2$ nanoparticles in powder form is shown in figure 7.1 (a). The pattern confirms the formation of TiO$_2$ rutile phase nanoparticles matched with reference card ICSD 01-076-0726. The main
peak at 27.1° corresponds to (110) plane for rutile phase. The other peaks with corresponding planes are shown in table 7.1. The average crystallite size was calculated to be around ~ 43 nm.

The XRD patterns xGO-TiO$_2$ (x= 2, 4, 8, 12 wt%) nanocomposite films deposited on ITO are shown in figure 7.1 (b). As explained above, GO was obtained by exfoliation of graphite and used as intercalation matrix in the synthesis of composites. The XRD analysis of the composites shows a pure crystalline TiO$_2$ rutile phase, with characteristic peaks corresponding to the planes (110), (200), (220), (002) and (221) and. There are two extra peaks appearing, which are related to tin oxide (SnO$_2$) from ITO substrate, indexed as SnO$_2$ (101) and SnO$_2$ (211). Furthermore, in the composites another very weak diffraction peak at ~ 10°-12° is observed. This weak peak with very low intensity indicates the presence of GO in the composites. The GO peak is very weak and has low intensity because the concentration of GO in the composites was very low. In the composites x=2, 4, 8 wt%, the main peak associated to (110) plane has shifted slightly towards lower 2θ value at 26.3° while for x= 12 wt % peaks has shifted to a higher 2θ value of 26.6°.

The rGO peak observed around 26.0° in the XRD diffraction pattern in figure 7.1 (a) get overlaps with TiO$_2$ peak in the XRD patterns of composites resulting a very intense peak around 26.3°.

<table>
<thead>
<tr>
<th>Miller indices</th>
<th>Peak position</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>27.1°</td>
<td>44.66</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>38.2°</td>
<td>45.96</td>
</tr>
<tr>
<td>(0 0 2)</td>
<td>62.2°</td>
<td>37.99</td>
</tr>
<tr>
<td>(2 2 1)</td>
<td>66.1°</td>
<td>44.36</td>
</tr>
</tbody>
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Table 7.1: XRD peak positions and corresponding crystallite size of TiO$_2$ nanoparticles.

Scanning electron micrographs of xGO-TiO$_2$ nanocomposites (x=0, 2, 4, 8, 12 wt%) are shown in figure 7.2 (a, b, c, d, e). Figure 7.2 (b), (c) and (d) show TiO$_2$ nanoparticles on GO sheets. These results evidence that the voids are
reduced and quality of the film is improved with graphene oxide addition. The *Energy-dispersive X-ray spectroscopy* (EDS) mode of the scanning electron microscope was used for the determination of the elemental composition of the samples. Figure 7.3 (a) and 3(b) shows the EDS results of TiO$_2$ and GO-TiO$_2$ nanocomposite films respectively. The EDS spectrum and

*Figure 7. 2: SEM micrographs of (a) ITO/TiO$_2$, (b) ITO/xGO–TiO$_2$ (x = 2 wt%), (c) ITO/xGO–TiO$_2$ (x = 4 wt%), (d) ITO/xGO–TiO$_2$ (x = 8 wt%), and (e) ITO/xGO–TiO$_2$ (x = 12 wt%) nanocomposite thin films.*
Elemental composition shown in figure 7.3 (a) confirm the presence of titanium, oxygen, carbon and tin oxide in pure TiO$_2$ thin film. The appearance of the carbon peak in the spectra is due to adsorbed carbon species on the surface of sample, and the peaks of tin oxide are coming from substrate. Similarly, we observed the titanium, oxygen, carbon and tin oxide peaks in the EDS spectra and elemental composition of GO-TiO$_2$ composite shown in figure 7.3 (b). Also here the carbon peak contains contributions from adventitious carbon in addition to that from the rGO and it is therefore not possible to use these spectra for verifying that the wt% present in the suspension is also that of the film.
Figure 7.4: UV-visible transmittance spectra of ITO/x(GO)-TiO$_2$ ($x = 0, 2, 4, 8, 12$ wt%) nanocomposites

Figure 7.5: Band gap spectra of ITO/xGO–TiO$_2$ ($x = 0, 2, 4, 8$, and 12 wt%) nanocomposites.
To understand the electronic structure and optical properties of thin films, UV-visible spectroscopy was employed. Transmittance spectrum of TiO$_2$ and GO-TiO$_2$ is presented in Figure 7.4. The samples present a strong light absorption in the UV region. In comparison with pure TiO$_2$, the GO-TiO$_2$ nanocomposites showed a red shift to higher wavelength in the absorption region and a better visible light absorption in the wavelength range 400-800 nm. The increase in the photo absorption of nanocomposites is attributed to GO.

The line tangent to the point of inflection of the Kubelka Munk curve, calculated from the transmission spectrum and shown Figure 7.5, determines the optical band gap (E$_g$). For pure TiO$_2$ thin films the optical band gap was found to be at around 3.5 eV, while the nanocomposites showed reduced value, as low of 2.9 eV for the xGO-TiO$_2$ sample with x=12 wt%. The Ti-O-C bonding between TiO$_2$ and GO is responsible for this shift. Furthermore, it is observed that the narrowing of band gap increases with increase of GO content, which indicates that the interaction between TiO$_2$ and GO has increased. There is a hump at 3.25 eV in each Kubelka Munk plot in figure 7.5, which is due to the presence of defects. These defects introduce additional energy states within the bandgap of TiO$_2$.\[^{[33]}\]

The decrease in transmission due to GO addition is a disadvantage in the GO-based ETL, which is addressed by the thermal annealing of the xGO-TiO$_2$ (x = 12 wt%) film at higher temperature (400 °C) in an inert environment for 20 min. There an augmentation of 10-12 % in transmission (figure 7.4) and increase in band gap from 2.9 eV to 3.4 eV (figure 7.5) are observed after annealing. The high temperature treatment reduces the oxygenated graphene, resulting in better transmission and conductivity.\[^{[34]}\]

To study the electrical properties of xGO-TiO$_2$ (x = 0, 2, 4, 8, 12 wt%) thin films, we analysed the current-voltage (I-V) characteristics as shown in Fig. 7.6. For the pure TiO$_2$ nanoparticle film, the current is seen to increase linearly with voltage, which proves that the contact between the TiO$_2$ nanoparticles and the ITO substrate is ohmic. It is also observed that the
current flowing through the GO-TiO$_2$ nanocomposite films is smaller than that traversing the pure TiO$_2$ nanoparticle film and decreases with increasing GO concentration in the composites. This decrease in current is due to the presence of functional groups attached to the basal planes of the GO sheets. The functional groups present in the highly oxygenated GO disrupt the sp$^2$ hybridization of carbon atoms and hence make it insulating.

However, after thermal annealing of the xGO-TiO$_2$ (x = 12 wt%) film at 400 $^\circ$C the conductivity as shown in Fig. 7.6. In fact, the annealing favours the detachment of functional groups from carbon basal plane $^{[20]}$, restoring larger areas of sp$^2$ hybridized carbon, and consequently causing a decrease in the sheet resistance of the film.

To gain a detailed insight into their elemental composition, XPS spectra were collected from the GO-TiO$_2$ nanocomposite films. Figure 7.7 shows the spectra relative to the ITO/x(GO)-TiO$_2$ (x = 8wt%) nanocomposite; the survey spectrum (a) confirms the presence of carbon, oxygen and titanium. The C1s core level region shown in figure 7.7 (b) is deconvoluted into four
contributions located at 284.6 eV, 285.6 eV, 287.3 eV, and 289.0 eV in binding energy (BE). The first peak at 284.6 eV corresponds to C-C/C-H bonds. The contribution positioned at 285.6 eV can be assigned to C-OH groups, while the ones at 287.3 eV and 289.0 eV stem from C-O-C and >C=O groups respectively. These peak position assignments are also in good agreement with the reported studies.\textsuperscript{[35-37]} Since GO sheets typically contain –COOH groups\textsuperscript{[36]} we suggest that the latter react with TiO\textsubscript{2} to form –COO-Ti bonds.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.7.png}
\caption{XPS analysis of as synthesized ITO/xGO-TiO\textsubscript{2} (x = 8 wt\%) nanocomposite, survey scan (a), high resolution scans (b, c, d)}
\end{figure}

The O1s core level spectrum contains three contributions as depicted in figure 7.7 (c). The peak located at 529.9 eV is consistent with the binding energy of O\textsuperscript{2-} in the TiO\textsubscript{2} lattice. The other contributions at binding energies of 531.6 and 532.8 eV are attributed to oxygen bonded with carbon and OH\textsuperscript{-} on TiO\textsubscript{2} surface respectively.\textsuperscript{[38,39]} The detailed scan of the Ti2p core level is shown in figure 7.7 (d). The peaks at binding energies of 458.7 and 464.52 eV are the 2p\textsubscript{3/2} and 2p\textsubscript{1/2} components of the Ti2p spin-orbit doublet.\textsuperscript{[38,40]}
7.4 Conclusions

We demonstrated that spin coating is an inexpensive and facile way to synthesize the xGO-TiO$_2$ nanocomposite thin films as supported by the structural, morphological and elemental analysis. The characterisation of the electrical properties gave evidence for an ohmic contact between the xGO-TiO$_2$ thin films and the ITO substrate. When the film is annealed in nitrogen environment, the sheet resistance is found to decrease noticeably, which suggest the improved charge transport when incorporated in solar cells. The UV-Visible spectroscopy showed that there is a red shift in absorption spectrum of xGO-TiO$_2$ as compared to pure TiO$_2$, demonstrated that the band gap of the nanocomposite can be tailored with the choice of the amount of GO incorporated and with thermal treatment. In fact, the bandgap decreased from 3.5 eV for TiO$_2$ to 2.9 eV for xGO-TiO$_2$ (x=12 wt%) but increased again to 3.4 eV with thermal annealing at 400 °C for xGO-TiO$_2$ (x=12 wt%). Annealing is therefore associated with an increased transmission in the visible range and hence making these nanocomposites suitable as a window layer material for the electron transport properties. Our results suggest that post-thermal annealed GO-TiO$_2$ nanocomposites could form an efficient transport layer for perovskite solar cells.

References


