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Improved photoelectrochemical properties of TiO$_2$-graphene nanocomposites: Effect of defect induced visible light absorption and graphene conducting channel for carrier transport

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**ABSTRACT**

Use of heterojunctions between two materials having favorable optical and electronic properties can lead to increased photon absorption and charge separation resulting in enhanced photo-electro-chemical energy conversion. In the present study, graphene monolayer nano-flakes are mixed with TiO$_2$ nanoparticles to form nanocomposites having different weight percentages of graphene. The microstructural, morphological and structural properties of the composite samples are investigated using X-ray diffraction, Raman spectroscopy and transmission electron microscopy techniques. Raman studies carried out on samples annealed at different temperatures show the interfacial interaction between TiO$_2$ and graphene, although Anatase TiO$_2$ and graphene maintain their phase integrity. PEC measurements show higher photo-electro-chemical activity in TiO$_2$-graphene nanocomposite at an optimized concentration (2.0 weight percent) due to increased surface area, higher optical absorption in the visible part of the solar spectrum and favorable carrier transport due to increased concentration of defect states and graphene acting as a charge carrier medium.

1. Introduction

A large increase in global energy consumption has led to the depletion of the natural energy sources as well as the increase in pollution levels leading to potentially threatening environment effects of climate change. Thus, there is a strong need for alternate and sustainable sources of energy. Photo-electro-chemical method utilizes solar energy and water which are one of the most abundantly available and uniformly distributed resources in nature [1,2]. The photo-electro-chemical splitting of water to produce hydrogen energy fuel seems to be an ideal process as it produces zero emission of environmentally harmful gases [1]. Photo-electro-chemical (PEC) water splitting utilizes photo-electrode and electrolyte system producing both electricity and hydrogen directly from sunlight, which is produced during water redox reactions at the anode and cathode, respectively [1,3]. Stability in the liquid electrolyte, high visible light absorption, favorable band edge alignment with respect to water redox levels are the main characteristics required for a semiconductor material to be used as a photoelectrode [3,4]. As it is difficult for a single material to satisfy all these requirements, the synthesis of a suitable photo-electrode material in the form of a composite material with modified and improved properties is very important [5-8]. A variety of materials have been studied for their suitability for photo-electro-chemical activity [5-9]. Titanium oxide (TiO$_2$) is the most favored oxide material. This is mainly due to its stability. Other oxide-based materials such as ZnO, Cu$_2$O, CuO are the other photo-electrode materials, although these are not very stable in liquid electrolyte [10-12]. In general, metal oxides have their energy band edges straddling the water redox potentials. For efficient water splitting, the conduction band of the material must lie above the water redox potential, which is 0 V vs normal hydrogen electrode (NHE) and valence band must lie below the water oxidation potential, which is 1.23 V vs NHE [13,14]. Therefore, increase or decrease in the conduction and valence band edges with respect to water redox levels affect the charge carrier transport from conduction band to water redox level and from...
Methods including nanoparticle formation, bilayers, heterojunctions, transportation within the material itself [9]. In this regard, various alloys and composites have been employed to increase the efficiency [9, 15, 16, 22]. Graphene monolayer with its atomic layer thickness has large surface area. Its structural and electronic properties can be tailored by controlling the number of layers. Its conducting nature can help in the charge transfer process, which is an essential part of the photo-electro-chemical process [25]. Synthesis of nanocomposites of TiO$_2$ and graphene and study of its optical, structural and electronic properties and optimizing the composition for improved visible light absorption and favorable charge transfer for achieving enhanced photo-electro-chemical performance forms the central objective of the present study. It may be mentioned here that there are number of studies reported in literature in which TiO$_2$-G nanocomposites have been studied. In the literature, TiO$_2$ has been prepared from Titanium sources which result in reduced form of TiO$_2$ i.e TiO$_{2-x}$. Sriramoju et al. [26] has carried out synthesis of TiO$_{2-x}$ (called it brown TiO$_2$) using hydrothermal method where titanium tetrachloride (TiCl$_4$) has been used as the main precursor. Also, Gao et al. [27] have reported biphasic defective TiO$_{2-x}$/reduced graphene oxide (RGO) nanocomposites synthesized by simple hydrothermal reactions. In these studies, the photocatalytic performance of nanocomposites in terms of degrading various synthetic dyes have been investigated.

In the present study, investigation of the PEC performance of TiO$_2$-G nanocomposite samples has been carried out. Graphene was added to the matrix of TiO$_2$ in different weight percentages (0.2 %, 0.4 %, 1.0 % and 2.0 %) by solid state method. The obtained materials were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photo-electron spectroscopy (XPS) for studying structural and morphological properties. Results show that 0.2 wt. % G-TiO$_2$ nanocomposite samples have better PEC response in comparison to the pristine and other samples. The results have been explained in terms of improvement in the optical, surface area and charge transfer properties of the nanocomposite.

![Schematic representation of synthesis method for TiO$_2$-G nanocomposites](image)

Fig. 1. Schematic representation of synthesis method for TiO$_2$-G nanocomposites by solid state mixing and sonicating method. A schematic of the possible microstructure of nanocomposite comprising of 0D nanoparticles and 2D nanoflakes is also shown.

2. Experimental Section

2.1. Synthesis of TiO$_2$-graphene nanocomposites

In the present study, the commercially available TiO$_2$ nanoparticles and single layer graphene (SLG) (analytical grade) nano-sheets have been used to synthesize the nanocomposite samples. We have purchased TiO$_2$ NP (CAS number 1317-80-2, 100G) and single layer graphene sheets (EC number 231-955-3, 500MG) from sigma Aldrich. For the synthesis of TiO$_2$-G nanocomposite samples in pallet form, the powder in required quantities is mixed using a magnetic stirrer followed by sonication. This growth method has several advantages due to its relative simplicity and easy processing of nanocomposite samples and the concentration can be conveniently varied while maintaining the uniformity of mixing. A fixed amount of TiO$_2$ nanoparticles powder (2 mg) was used as initial reagent and different amounts of single layer graphene nano-sheets (0.2 wt. %), 0.4 wt. %, 1 wt. % and 2 wt. %) with a known weight percent of TiO$_2$ NPs were added into 20 ml of ethanol solution, magnetically stirred for 30 mins and finally ultrasonicated for 90 minutes. The mixture was dried at 80 °C. The obtained composites were denoted as “PTiO$_2$, TG(0.2), TG(0.4), TG1, TG2 “(‘P’ indicates pristine TiO$_2$ nanoparticles and ‘TG’ indicate the nanocomposite samples with numerals 0.2, 0.4, 1 and 2 indicating the weight percent of graphene). This synthesis method, as expected, resulted in large contact between the 1D TiO$_2$ nanoparticles and 2D graphene layers, as illustrated in Fig. 1. It may be mentioned that it was not possible to prepare nanocomposite samples having more than 2 % of graphene, as the sample became flaky and characterization of the samples with this concentration was not possible. Therefore, the present investigation is carried out on nanocomposite samples having a maximum graphene concentration of 2%.

2.2. Characterisation techniques

X-ray diffraction (XRD) patterns of all samples were collected in the range 20 = 20–80° using Panalytical X-Ray diffractometer (Cu K radiation, 1.5406 Å), operated at 40 kV and 100 mA. The sample morphology was characterized by high resolution transmission electron microscopy (HRTEM, JEM2000EX) and field emission scanning electron microscopy (FESEM) techniques. Kratos XSAM 800 kit having dual anode X-ray source was used for X-ray photoelectron spectroscopy (XPS) studies. Mg Kα (1253.6 eV) X-ray source was used for all samples, along with the pressure in the analyzing chamber which was in the range of 4–8×10$^{-9}$ mbar.

XPS analysis of samples was carried out using Kratos XSAM 800 Kit
Fig. 2. (a) XRD Plots for different sample. Raman spectra of pristine TiO$_2$ and TiO$_2$-graphene nanocomposite (TG0.2, TG0.4, TG1, TG2) sample at (b) RT, (c) 200°C, (d) 300°C and (e) 400°C.
equipped with dual anode X-ray source. All sample spectra were analyzed using the CasaXPS software and the peak shift due to any apparent charging were calibrated with respect to Mo3d peak set to 227 eV (corresponding to signal from Molybdenum sample holder). The shift of the binding energy due to relative surface charging was corrected using the C1s level which was observed to be at 284.4 eV as a reference. In Carbon C1s spectra, sp\(^3\) hybridization corresponds to adventitious Carbon (C-C) bonding, whereas sp\(^2\) hybridization corresponds to Graphene (C-C) bond. Raman measurements were carried out using Horiba scientific Raman spectrometer instrument having excitation wavelength of 514 nm.

Linear sweep voltammetry (LSV) measurements were performed under dark and light conditions in the AM 1.5 G solar simulator using a three-electrode cell with a working electrode (semiconductor photocatalyst coated over ITO substrates by sol–gel spin coating method), a Pt wire as the counter electrode, and a saturated silver chloride as the reference electrode and an electrolyte which is comprised of a 0.5 M \(\text{Na}_2\text{SO}_4\) solution. Electrodes were prepared in the form of thin film using sol gel (prepared via mixing TiO\(_2\)-graphene nanocomposites in 10 ml of ethanol solution) spin coating method. Conducting Indium doped tin oxide (ITO) coated glass was used as a substrate for film deposition. First conductivity of ITO sheet was measured by using a multimeter. ITO coated glass sheet shows resistivity of 14-18 ohms/sq. Thereafter, ITO substrates were ultrasonically cleaned by soap solution, DI water, acetone, and then propanol successively for 15 minutes. To deposit the film, the substrate was taken out from the propanol breaker and then rinsed with DI water. The last step is to blow the substrate with Ar gas to dry it. Then, a small portion of the substrate conducting side is left covered with Kapton tape to have contact using silver paste. Then, the substrate is mounted inside the spin coater for deposition. Electrodes were prepared by making the ohmic electrical contacts using silver paste and copper wire onto the undeposited area of conducting ITO substrate, and later the area was sealed to the glass tube by using the non-transparent and non-conducting epoxy resin then left it to dry for several hours. The dimension of the prepared electrode is 1×2 cm\(^2\).

3. Results and Discussion

3.1. X-ray diffraction studies

Fig. 2(a) shows the X-ray diffraction (XRD) spectra of pristine TiO\(_2\) (PTiO\(_2\)) nanoparticles and TiO\(_2\)-G nanocomposites (TG) having different weight percent concentrations of graphene i.e. 0.2 %, 0.4%, 1% and 2% namely as TG0.2, TG0.4, TG1 and TG2, respectively. The sharp diffraction peaks of pristine TiO\(_2\) nanoparticles observed at 2\(\theta\) values of 25.28\(^{\circ}\), 36.92\(^{\circ}\), 37.77\(^{\circ}\), 38.55\(^{\circ}\), 48.05\(^{\circ}\), 53.87\(^{\circ}\), 55.06\(^{\circ}\), 62.11\(^{\circ}\), 68.75\(^{\circ}\), 70.29\(^{\circ}\), 74.03\(^{\circ}\), 75.04\(^{\circ}\) and 76.04\(^{\circ}\) corresponding to (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), (215) and (301) planes of Anatase tetragonal phase of TiO\(_2\), respectively. These values match well with reported JCPDS data (Card No. 21-1272) and indicate high crystallinity of the nanoparticles. The respective XRD peak positions observed for TiO\(_2\)-G nanocomposite samples of TG0.2, TG0.4, TG1 and TG2 also confirm that the Anatase tetragonal phase of pristine TiO\(_2\) nanoparticles has not been altered on incorporation of graphene nano-sheets. XRD results confirm that the formation process of TiO\(_2\)-G nanocomposites does not affect the Anatase phase, which is similar to results reported earlier [28,29]. Raman spectroscopy measurements confirm the crystalline structure, phase purity and presence of graphene in the TiO\(_2\)-G nanocomposites. The results are shown in Fig. 2(b-e). The observed Raman vibrational bands at wavenumbers 141 (E\(_{\text{g}}\)), 193, 394 (B\(_{1g}\)), 515 (E\(_{\text{g}}\)+B\(_{1g}\)), 636 (E\(_{\text{g}}\)) cm\(^{-1}\) corresponds to Anatase tetragonal as the dominant crystalline phase of TiO\(_2\) in pristine and TiO\(_2\)-G nanocomposite samples [30].

3.2. Raman spectroscopy studies

For studying the interaction between TiO\(_2\) and graphene phases, Raman spectroscopy measurements were carried out on pristine TiO\(_2\)
(PTiO$_2$) and TiO$_2$-G nanocomposites (TG0.2, TG0.4, TG1 and TG2) at different annealing temperatures of RT, 200°C, 300°C and 400°C. Fig. 2(b-e) and insets show the Raman spectra of different samples at RT, 200°C, 300°C and 400°C, respectively. Raman modes at 144, 197, 393, 514, 643, 1340 and 1597 cm$^{-1}$ are observed in samples annealed at 200°C. Raman modes at 144, 194, 393, 515, 634, 1342 and 1598 cm$^{-1}$ are observed for samples annealed at 300°C. Raman modes at 143, 196, 398, 519 and 640, 1345 and 1594 cm$^{-1}$ are observed for samples annealed at 400°C. These modes are assigned to Anatase TiO$_2$ phase. The Raman analysis shows that there is a shift in the vibrational modes corresponding to TiO$_2$ in nanocomposites annealed at different temperatures with respect to that in pristine sample. This shift may be due to the interaction between graphene and TiO$_2$ phases. The presence of vibrational modes corresponding to TiO$_2$ along with graphene reveals the formation of TiO$_2$-graphene nanocomposite. Additionally, in Fig. 2(c-e), the G band of graphene was observed at ~1597, 1593 and 1594 cm$^{-1}$, which corresponds to the E$_{2g}$ phonon of the sp$^2$ hybridized C atoms and the D band was observed at 1340, 1342 and 1345 cm$^{-1}$. This indicates that there is some structural disorder due to vacancies or grain boundaries defects [23,24] or due to the presence of amorphous carbon species [25]. The intensity ratio (I_D/I_G) of the D and G peaks is an indicator of the crystalline quality of the graphene. As shown in Fig. 2(c) and 2(e), the intensity ratio (I_D/I_G) in case of TiO$_2$-G nanocomposites decreases, which indicates higher concentration of sp$^3$ carbon in unannealed nanocomposites as compared to samples annealed at 400°C. Thus, the structural analysis carried out using XRD and Raman spectroscopy measurements confirms Anatase tetragonal as a dominant crystal structure phase. Increase in defect density was observed with increase in the weight percent of graphene layers in nanocomposite samples or with increase in the annealing temperature.

3.3. Transmission electron microscopy studies

Transmission electron microscopy (TEM), selected area electron diffraction pattern (SAED) and high resolution transmission electron microscopy (HRTEM) techniques have been used to study the morphology properties of the pristine TiO$_2$ nanoparticles and TiO$_2$/G nanocomposite samples. TEM images in Fig. 3(a, b) show that TiO$_2$ nanoparticles and G nano-sheets are uniformly distributed and TiO$_2$ nanoparticles have size in the range of 20–100 nm. Furthermore, energy dispersive X-Ray analysis (EDX) is used for carrying out the elemental and compositional analysis of nanocomposite, as shown in Fig. 3(c). EDX spectrum shows the presence of C, Ti and O as the constituent elements in TG2 sample and also confirms Ti:O in the atomic ratio of 1:2. Fig. 3(d) shows the STEM elemental mapping of TiO$_2$ nanoparticles. Ti rich (purple) and O rich (green) elemental images demonstrate the uniform spatial distribution of the elemental constituents of TiO$_2$ nanoparticles, as shown in Fig. 3(d, e). Transmission electron microscopy (TEM) analysis was carried out using JEOL JEM 2100 instrument. HRTEM measurements were carried out to further study the interface between the two components (TiO$_2$ and Graphene), particle size and morphology of TiO$_2$-G nanocomposites. HRTEM images (Fig. 4) of TG2 nanocomposite sample shows elongated spherical nanoparticles of TiO$_2$ having size distribution of ~20-100 nano-meters and folded graphene nano-sheets interspersed within nanoparticles (Fig. 4a and 4b). Selected area electron diffraction (SAED) studies were carried out to investigate the crystalline nature of the nanocomposites. The SAED pattern (Fig. 4c) shows diffraction spots along with diffused rings which confirm the polycrystalline nature of pristine and TiO$_2$-G nanocomposite samples. The appearance of clear diffraction rings in SAED pattern (Fig. 4c) confirms the crystallinity of
the prepared sample and the inter-planar spacing is observed to be 1.25 nm and 0.75 nm corresponding to (301) and (303) crystallographic planes. The inter-planar spacing obtained using SAED pattern also confirms the Anatase tetragonal phase for TiO$_2$ nanoparticles. Hence, the results obtained are consistent with the results related to size, phase purity and polycrystalline nature of the nanocomposite samples observed from FESEM, XRD and Raman spectroscopy studies.

3.4. Optical properties

The absorption edge and recombination rate of photo-generated charge carriers are important for understanding the changes in PEC performance of pristine and nanocomposite samples. UV-vis spectrophotometry technique has been used to measure spectral dependence of absorbance of nanocomposites samples. Absorption coefficient can be measured using the relation $\alpha = (2.303 \times A)/d$, where A is absorbance and d is the thickness of samples. The band gap value can be calculated from the absorption coefficient value by plotting Tauc’s plot [31]. The Tauc’s plot for the pristine TiO$_2$ sample shows an absorption edge at about 3.7 eV with a weak absorption tail at lower energy. The absorption spectrum shows increased light absorption in the visible region as graphene content is increased in TiO$_2$-G nanocomposite samples. This increased visible light activity is due to the increase in the density of surface oxygenated groups which interact with the TiO$_2$ nanoparticles on incorporation of graphene nano-sheets, as shown in Fig. 5(a). The intense tail present in the absorption spectra for the nanocomposite sample makes it difficult to estimate the absorption edge value in case of nanocomposite sample. The increase in the intensity of absorption tail below the band gap in nanocomposite samples is indicative of the presence of large concentration of defects on incorporation of graphene. 

3.5. X-ray photoelectron spectroscopy studies

XPS studies has been used to determine the chemical states of different elements and bonding between TiO$_2$ and graphene phases. Ti–C and Ti–O–C bond formation is clearly observed from the XPS...
results. XPS spectra of Ti 2p core level shows two peaks due to Ti 2p3/2 and Ti 2p1/2, respectively at binding energies of 458.5 and 464.2 eV attributed to Anatase phase [32]. For TiO2 nanoparticles, the spin-orbit splitting of Ti 2p orbital in 2p 3/2 and 2p 1/2 with an energy separation ($\Delta$) = 5.7 eV confirms the tetragonal Anatase phase of TiO2 in case of PTiO2 sample. A shift in the Ti 2p peaks towards higher binding values of 459.9 eV (for Ti 2p 3/2), 465.6 eV (for Ti 2p 1/2), is observed, as shown in Fig. 6 (a-d) is related to the perturbation of the Ti-O bonds on incorporation of graphene. The increase in the graphene content results in shift in the binding energy values for the C-C and C-O bonds, as also observed in an earlier study [33]. These results are consistent with the results of optical absorption studies, in which the presence of graphene was found to have led to increased absorption due to high concentration of defect states.

Increase in graphene concentration (2%) creates oxygen deficiency in TiO2 and therefore creates Ti$^{3+}$ species in TG2 nanocomposite sample, which is absent in pristine and samples with lower graphene concentration. TiO2-G nanocomposite samples with increased graphene concentration shows a decrease in chemisorbed water (Fig. 6b and d). This may be attributed to the hydrophobic nature of graphene. The deconvoluted spectrum of O1s shows gradual increase of Ti-OH/C-O with respect to increase in graphene concentration. XPS spectra for TG2 nanocomposite sample, shows a strong peak of C=O species which is absent in all other samples as shown in Fig. 6(d). Fig. 7(a and c) shows the survey spectrum of pristine and graphene incorporated nanocomposite (TG2) which confirms the presence of Ti, C and O in the samples. The deconvoluted spectra in Fig. 7(b and d) also show increase in the concentration of C-O-C species for nanocomposite samples wrt pristine sample.

### 3.6. Photo-electro-chemical and interface studies

PEC measurements were carried out for measuring the photocurrent density of the pristine and TiO2-G nanocomposites in a three electrode PEC cell configuration comprising of a working electrode (in the form of TiO2 nanoparticles or TiO2-G nanocomposite sample with Ag contact and a polymer protection layer), a reference electrode (Ag/AgCl) and a counter electrode in the form of Pt mesh). 0.5M Na$_2$SO$_4$ aqueous solution was used as an electrolyte. Enhanced photocurrent density values were observed for TiO2/Gr nanocomposite sample (TG2) i.e. ~2.94 mA/cm$^2$ in comparison to the pristine TiO2 nanoparticle samples (0.22 mA/cm$^2$) at an applied potential of 0.63 V vs Ag/AgCl (Fig. 8a). The observed value of photocurrent density for sample TG2 is nearly an order of magnitude higher (13 times) as compared to the pristine TiO2 nanoparticles (sample PTiO2). The enhanced values of photocurrent density in the nanocomposite is attributed to an increased visible light activity on incorporation of graphene in the nanocomposite samples. Increased photon absorption below the TiO2 band gap was observed in the absorption spectra of nanocomposite sample, as described earlier. The
incorporation of graphene and surface interaction of graphene monolayer with TiO$_2$ nanoparticles results in the formation of defect in the matrix and corresponding defect states in the forbidden gap. The XPS and Raman spectroscopy results described earlier confirms graphene-TiO$_2$ interaction. Similar results on the enhanced optical absorption due to defect generation has been reported for interaction of TiO$_2$ nanoparticles with carbon nanoparticles [34–36]. In the present study, the 2D nature of graphene is expected to increase the interaction of C (from graphene) with TiO$_2$ nanoparticles due to increased surface area of graphene. The increased optical absorption below the band gap value of TiO$_2$ due to defects states formed by graphene-TiO$_2$ interaction, which increases with increase in the graphene concentration, is an important result of the present study. As mentioned earlier, at higher concentration of graphene (more than 2 weight percentage), samples attain flaky structure and it was not possible to take PEC measurements.

Mott-Schottky measurements were performed to study the flat band potential ($V_{FB}$) at the semiconductor-electrolyte interface and charge carrier density ($N_D$) of the pristine and TiO$_2$-G nanocomposites. The positive slope shows n type conductivity for all the samples. The observed flat band potential is observed to shift to negative values in graphene nanocomposites as compared to pristine PTiO$_2$ Nanocomposite sample (Fig. 8b). This indicates improved charge transfer across the interface in nanocomposite sample.

EIS measurements were performed to find out recombination rate of the photo-generated charge carriers at the photo-electrolyte interface. The addition of graphene to pristine TiO$_2$ nanoparticles results in smaller semicircle in Nyquist plots (as shown in Fig. 8c), which indicates that there is a decrease in the charge transfer resistance in case of TiO$_2$-G nanocomposites samples. The decrease in charge transfer resistance is due to a large surface area of graphene and graphene acting as an transport medium for electrons from the conduction band of TiO$_2$ to graphene due to sp $[2]$ carbon network of graphene. Therefore, the presence of graphene in the nanocomposites decreases the recombination rate leading to an increase in carrier lifetime and improvement in the overall photo-electro-chemical (PEC) performance of the nanocomposites [28,32,35,37].

4. Conclusions

Structural, optical and electronic properties of TiO$_2$-G
nanocomposite samples having varying graphene concentrations are investigated in the present study. A large enhancement (about 13 times) in photo-current density at an optimized value of 2.0 % of graphene in comparison to pristine TiO₂ nano-particles was observed. The enhancement is attributed to increased visible light absorption due to defect states on incorporation of graphene in the nanocomposite arising due to interaction of TiO₂ and Graphene. Mott-Schottky measurements confirm that all TiO₂-graphene nano-composite samples have a type conductivity with shifting of flat band potential to negative values with increase in graphene concentration. This indicates that graphene network acts as a conducting path resulting in improved charge transfer process across anode-electrolyte interface in case of nanocomposite samples. The addition of graphene monolayers into TiO₂ nanoparticle samples results in increase of defect induced optical absorption, large surface area and a favorable conducting channel thus improving photo-electro-chemical performance in the nanocomposite samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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