Effect of Graphene oxide Loading on TiO$_2$: Morphological, Optical, Interfacial Charge dynamics–A Combined Experimental and Theoretical study

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Abstract:

Reduced graphene oxide (rGO)-TiO_2 composites are prepared using photo-reduction method by varying GO to TiO_2 weight ratio from low (rGOT-0.001, 0.01, & 0.1) to high (rGOT-1, 3 & 10) range and its effect on morphological, optical and mechanism of fast charge dynamics at the interface are investigated. Experimental analysis confirm that reduction process improves as TiO_2 amount increases in rGO-TiO_2 but leads to aggregation of TiO_2 nanoparticles. rGOT-3 composite displayed the highest photocatalytic activity for degradation of phenols compared to TiO_2, GO and other composites. This was achieved due to uniform dispersion of TiO_2 nanoparticles over rGO surface, which enables distinct formation of Ti-O-C bond between each TiO_2 nanoparticle and rGO surface, and results in slight red shift in the band edge. This Ti-O-C bond facilitates fast electron transfer from TiO_2 to rGO and reduces recombination rate as revealed by photoluminescence and time resolved photoluminescence spectroscopy. The experimental findings were further investigated using Density Functional Theory simulations. Band structure calculation confirms high mobility states induced within the band gap due to formation of Ti-O-C bond in rGO-TiO_2 model which assists in fast electron transfer from TiO_2 to rGO during the photocatalytic process and hence reduces recombination rate.

Keywords: reduced graphene oxide, TiO_2, density functional theory, Ti-O-C, recombination rate.

1. Introduction:

TiO$_2$ is one of the most exhaustively studied material as it is a potential candidate for various applications such as photocatalytic degradation of organic pollutants for water treatment, H$_2$ production by photocatalytic bacteria deactivation, water-splitting, gas sensors, photovoltaics and Li ion batteries [1-4, 5]. TiO$_2$ gained interest in these applications owing to its low-cost, non-toxic nature, suitable band edge positions, earth-abundance and long-term photo- and chemical stability in all pH media. For photocatalytic application, the efficiency of TiO$_2$ is limited due to its wide bandgap, which restricts light absorption within UV range (5% of solar spectrum), and high bulk and surface recombination rates of the produced electron hole pairs. Former limitation can be circumvented by reducing the electronic bandgap of TiO$_2$ through metal [6] or non-metal doping [7,8], which improves its absorbance in visible spectrum. The latter issue of bulk recombination can be suppressed using high valence dopants (such as W^{6+}) that lead to formation of an impurity level just below the conduction band of TiO$_2$ and acts as a trap site for electron carriers, thereby improving charge carrier lifetime [9]. On the other hand, formation of heterojunction of TiO$_2$ with other semiconductors (C$_3$N$_4$, WO$_3$ etc) [10, 11], carbonaceous materials (carbon nanotubes, fullerene, graphene, reduced graphene oxide (rGO) and graphene oxide (GO)) and metal nanoparticles has proven to be very effective in decreasing the surface recombination rate [12-14].

Recently, rGO has gained great interest in photocatalytic water-treatment, as a supporting material for TiO$_2$, owing to its high surface area, superior electron mobility, tuneable bandgap and easily changeable surface properties [15]. It was found that combining rGO with TiO$_2$ leads to improvement in photo-induced charge separation by transfer of excited electrons to rGO through interface. During the synthesis of composite, the amount of rGO loading and proper coupling at the interface in rGO-TiO$_2$ composite plays a key role in deciding the photocatalytic performance

of the resulting composite. Generally, past literature on rGO-TiO$_2$ composites are divided into two categories where (1) TiO$_2$ particle is decorated by a small amount of rGO and (2) TiO$_2$ particles are well dispersed over 2D rGO sheet. To realize the former strategy, weight ratio between 0.1-5 wt% of rGO were used while for latter case, nearly equal amount of rGO were used. Optimum concentration of rGO is determined in both cases of rGO-TiO$_2$ composites. Depending upon the size of TiO$_2$ nanoparticles and the method adopted for synthesis of the composite, the optimum concentration of rGO that shows superior photocatalytic performance also varies. Lower amount of rGO acts as an electron sink over TiO$_2$ particles to reduce recombination process. In this case, though light is not shielded by rGO, the interaction area between TiO$_2$ and rGO is at minimum level. Iqbal et al. [16] fabricated rGO-TiO$_2$ composite using solvothermal method with GO to TiO$_2$ mass ratios of 0, 2.5, 5 and 10 wt% and found the mass ratio of 5 wt % as optimum ratio for the photodegradation of Rhodamine B dye and phenol due to efficient charge transportation and separation at the interface with enhanced visible light absorption. Liu et al. [17] also reported rGO-TiO$_2$ composite and observed that superior photodegradation performance is achieved when amount of rGO in the composite is 2 wt% compared to pure TiO$_2$ and 1 and 5 wt% rGO-TiO$_2$ composites. Similar study by Yu et al. [18] also demonstrated that when GO amount was controlled to 1wt % in rGO-TiO$_2$ composite, it has shown highest photocatalytic performance for degradation of methylene blue. Several other reports have also shown that when rGO is combined with TiO$_2$ to obtain composite with rGO weight ratio in the range of 0.1-10 wt%, then significant improvement towards photocatalytic activity under UV illumination can be achieved [15, 19, 20]. Using equal amount of rGO and TiO$_2$ provides better scenario for strong interaction between TiO$_2$ and rGO in form of Ti-O-C bonds at interface. These bonds not only provides channel for fast transfer of electrons but also create energy levels within the band gap of TiO$_2$ to improve the

visible light absorption. Although better dispersion of TiO_2 is obtained here, provided by higher surface area of rGO, however a portion, also relevant, of light reaching the TiO_2 particle is blocked by surface covering of rGO. Even the surface exposure of TiO_2 to reactant and product of the catalytic reaction is also reduced drastically. Gao et al. [21] reported that GO to TiO_2 weight ratio of 3:2 has the highest degradation rate towards methylene orange under UV irradiation as compared to pure TiO_2 and other weight ratios (0:1 and 0.1:1). Similarly, a microwave-assisted combustion method was developed to synthesize GO-TiO_2 composite with GO to TiO_2 weight ratios between 0.25-2.0 [22]. The weight ratio of 1.5 was found to be the best for degradation of methylene orange dye and beyond this value, absorption and scattering of light takes place by rGO which leads to significant reduction in photocatalytic activity. To avoid the agglomeration, Lee et al. [23] reported that hydrothermally synthesized graphene wrapped TiO_2 composite, using GO and amorphous TiO_2 nanoparticles results in formation of Ti-C bond, which helps in efficient photo-charge transfer from TiO_2 to graphene to enhance the photocatalytic performance. It was noted that graphene wrapping also results in less exposed TiO_2 active sites for photo-oxidation of pollutants and thus reducing the photocatalytic performance. Recently, Williams et al. demonstrated a facile and chemical free reduction process of GO via UV-assisted photoreduction method in presence of TiO_2 nanoparticles which also results in formation of rGO-TiO_2 composite [24]. This provides a simple method to synthesize uniformly dispersed TiO_2 nanoparticles decorated over rGO sheets by just varying the weight ratio of GO to TiO_2. Though extensive research has been carried out in past for both strategies, it is still unclear which range of rGO is best suited for photocatalytic activity. Also, none of them explains the effect of variation of GO loading on the morphological properties, charge dynamics and degree of functionalization of the resulting composite, which was taken up in this work.

Thus, in the present work, rGO-TiO$_2$ composite is studied in a holistic manner by synthesizing different weight ratio of both the ranges namely 0.001:1, 0.01:1, 0.1:1, 1:1, 3:1 and 10:1. For an intimate interaction between TiO$_2$ and rGO, photo-reduction technique was used for synthesizing the composite. Effect of weight ratio on the properties of the composite samples were explored using various characterization techniques. The developed composites were tested for photocatalytic degradation of para-Nitrophenol under Xenon and UV irradiations. The experimental results were co-related with theoretical data by constructing a model of rGO-TiO$_2$ bilayer and performing calculations using DFT. The reasons for the higher photocatalytic performance of rGO-TiO$_2$ composites were investigated and explained.

2.   Experimental Methods

2.1   *Synthesis of TiO$_2$, GO and rGO-TiO$_2$ nanocomposite*

TiO$_2$ nanoparticles were synthesized by sol-gel method using Titanium (IV) n-butoxide (Ti(OC$_4$H$_9$)$_4$) as a precursor. In a typical procedure, a mixture of Ti(OC$_4$H$_9$)$_4$ with ethanol was prepared to obtain TiO$_2$ sol. To this precursor sol, a mixture of ethanol, double distilled water (DDW) and HNO$_3$ was added slowly and stirred for 2 hours for homogeneous mixing. The ratio of titanium butoxide/DDW/ethanol/HNO$_3$ was maintained at 1/30/20/0.1. After stirring, the solution was kept overnight for gelation, at room temperature. The resulting gel was thoroughly washed with DDW and ethanol followed by drying for 3 hours at 120 ℃ in open atmosphere. A pale white TiO$_2$ powder was obtained which was grinded and calcined at 400 ℃ for 2 hours to obtain crystalline TiO$_2$ powder

Synthesis of GO was carried out by modified Hummers method, as discussed by Kalambate et al. [25]. The synthesis procedure involves oxidation of graphite using a strong oxidizing agent

like KMnO$_4$ along with NaNO$_3$, which acts as supporting oxidizing agent. 1g graphite powder was exfoliated using 48 ml 98% H$_2$SO$_4$ in presence of 0.5 g NaNO$_3$ at 0 ⁰C under ice bath, followed by gradual addition of 5 g KMnO$_4$ in small parts. After the addition of KMnO$_4$, the solution was stirred for 2 hours under water bath at room temperature. The reaction was terminated by addition of 240 ml DDW, followed by 5 ml H$_2$O$_2$ (30%) solution. The obtained solution was filtered and washed several times with 10% v/v HCl solution, DDW and ethanol, and later dried under vacuum. The dried powder obtained here is GO.

A composite of the synthesized TiO$_2$ and GO powders was made by photo-reduction method, as reported by Williams et al. [24]. With this method, aqueous solutions of TiO$_2$ and GO were made separately and ultrasonicated for one hour. The two dispersion solutions were mixed together and were again ultrasonicated for one hour to obtain homogeneous mixture. The final mixture was irradiated under UV light for 24 hours under constant stirring at room temperature to complete the photo-reduction process. After the process, black powder is obtained which indicates reduction of GO to rGO. The solution is then filtered and washed with water followed by drying under vacuum to obtain rGO-TiO$_2$ composite. By varying the weight ratio of GO in the aqueous mixture, samples with different rGO:TiO$_2$ weight ratios (0.001:1, 0.01, 0.1:1, 1:1, 3:1 and 10:1) were prepared and hereafter are denoted by rGOT-0.001, rGOT-0.01, rGOT-0.1, rGOT-1, rGOT-3, rGOT-10, respectively. For all the samples, the weight of TiO$_2$ was fixed (100 mg) while that of GO was varied.

2.2   Materials Characterization

The phase and crystalline structure of all the samples were identified by X-ray diffraction (Rigaku Ultima IV) using Cu Kα radiation (λ = 1.5414 Å) in θ-2θ mode. Optical absorbance of the

synthesized samples was determined using UV-Vis-NIR spectrophotometer (Shimadzu) in diffused reflectance mode in the wavelength window of 200 – 800 nm. Transmission electron microscope (TEM, JEM 2100, 200 kV) was used to determine the morphology of all samples. Raman microscopy was used to gain information of the degree of reduction of GO in rGO-TiO$_2$ composites. Raman spectra were recorded on a HORIBA LabRAM HR 800 spectrometer using 532 nm solid-state laser source with a power of 50mW. FTIR spectroscopy was used to identify the functional groups on GO and rGO-TiO$_2$ composites using JASCO FT-IR-660 plus spectrometer, operated at room temperature. X-ray photoelectron spectroscopy (XPS) measurement was performed using an AXIS Supra (Kratos Analytical) instrument equipped with a monochromatic Al Kα (1486.6 eV) X-ray source to analyze the surface electronic states and composition. The binding energy (BE) positions were referenced to standard C 1s (284.8 eV) peak for all elements. XPS analysis was performed using ESCApe software from Kratos where the background was corrected using Shirley method. For deconvolution and fitting of XPS peaks, a combination of 50% Lorentzian and 50% Gaussian distribution functions were used. Radiative recombination of photogenerated charge carriers was determined with the help of photoluminescence (PL) emission spectra, measured using a Fluorescence spectrophotometer (Varian, Cary Eclipse) at an excitation wavelength of 385 nm. Time-resolved photoluminescence (TRPL) spectra were obtained using an ISS Chronos BH fluorometer. The charge carriers were excited to higher energy level using excitation pulse of wavelength 405 nm with a pulse width of 70 ps obtained from a pulsed diode laser (Hamamatsu). To obtain PL and TRPL spectra, a homogeneous dispersion of 2 mg powder in appropriate amount of double distilled water was prepared.

2.3   *Photocatalytic activity measurement*

The photocatalytic measurements for water purification was carried out in a lab-made photoreactor assembly. The set up consists of a top-down assembly of 150 W collimated Xenon arc lamp (Hamamatsu) and a borosilicate photoreactor (250 ml) provided with constant stirring system. The distance between source of light and reactor was kept fixed for all the measurements and was measured to be 47 cm. At this distance, the light flux was measured to be 8.6 mW/cm^2. This distance was also found to be ideal to maintain uniform illumination over the samples. The whole setup was kept in dark atmosphere to avoid any errors due to stray lights. For each measurement, 10 mg of photocatalyst was uniformly dispersed in 50 ml p-Nitrophenol (p-NP) solution by ultrasonication for 5 min. Prior to photo-irradiation, the solution was kept in dark under constant stirring for about 30 min, in order to achieve adsorption/desorption equilibrium between the photocatalyst surface and pollutant in the solution. Once the equilibrium condition was established, the solution was illuminated by light under constant stirring, at room temperature. During photo-catalytic reaction, after an interval of 30 minutes, 5ml of the solution was collected in a quartz cuvette and absorbance spectra was recorded using UV-vis spectrometer (Implen Nano Photometer). A control experiment was also performed by irradiating the pollutant solution under the same conditions, in absence of the photocatalyst. The photo-degradation rate was determined by measuring the variation in characteristic UV-Vis absorbance peak of p-NP at 320 nm with irradiation time. All the samples were tested at least 3 times to establish the consistency of the obtained results.

3. Computational details

All the spin-polarized first principles calculations (ionic relaxation and electronic structure) were performed within the framework of density functional theory (DFT), using the projector augmented wave (PAW) method for the core-valence interaction as implemented in the VASP code [26-29]. The generalized gradient approximation (GGA) [30] for the exchange-correlation functional correction to the local density approximation has been employed and an energy cut-off of 400 eV for the plane-wave basis expansion was considered. The supercell contains 4x4 graphene layer containing 32 C and a vacuum of 20 Å were taken to avoid interaction between periodic images in the Z direction (perpendicular to graphene plane). A systematic adsorption of 12 hydroxyl (OH) and 4 epoxy (-O-) groups were carried out to obtain graphene oxide model. In rGO, there are 8 OH and 2 epoxy resulting a C:O ratio of 3.2, which matches with experimental samples. For rGO-TiO$_2$ model (101) surface of TiO$_2$ was considered. A Monkhorst-Pack grid of 3x3x1 k-points was taken to sample the Brillouin zone [31] during the relaxation whereas 11x11x1 k- points were considered for accurate calculations of Density of States(DOS).The self-consistent field convergence threshold was taken as 10^{-5} eV, while the Hellmann-Feynman forces were less than 0.01eV/Å in the structural relaxation.

In order to avoid mismatch between surface area of rGO layer and 101 TiO$_2$ layer due to different lattice parameter value, rotation of top layer was done with respect to lower layer about an axis perpendicular to the plane of both the layers. To minimize compression and expansion with respect to each other, bilayer of hexagonal 4x4 rGO layer was combined with hexagonal 2x2 101 TiO$_2$ layer, as this constitutes the smallest possible combination of two layers.

4.   Results and Discussion:

To understand the effect of loading of GO on TiO_2 and subsequent formation of $rGO-TiO_2$ composite, samples with different weight ratios of $GO:TiO_2$ were synthesized such that it covers the whole possible range of GO from low (0.001, 0.01, 0.1) to high ratio (1,3,10). Fig. 1 displays X-ray diffraction pattern of TiO_2 nanoparticles, GO and the series of $rGO-TiO_2$ nanocomposites with different weight ratios. XRD pattern of bare GO shows a major diffraction peak around 11.26^o and a minor peak at 43.9˚ corresponding to the reflections from (002) and (100) planes of GO, respectively, consistent with previous reports [32, 33]. XRD pattern of pure TiO_2 displays nine diffraction peaks at 25.3^o, 37.7^o, 48.1^o, 53.8^o, 55.1^o, 62.7^o, 68.8^o, 70.3^o and 75.3^o ascribed to the reflections from (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes, respectively of pure anatase phase. Crystal size of 5-9 nm was calculated from the main peak (25.3^o) of TiO_2 for all the samples. In composite, the peaks assigned to both materials are observed but with different intensities depending on its weight ratio. From the figure, it is clear that as the weight ratio of GO to TiO_2 decreases, the intensity of main characteristic peak of GO at 11.26^o also decreases, suggesting improvement in reduction of GO to rGO with increasing amount of TiO_2. The existence of both diffraction peaks at 11.26^o and 43.9˚ of GO in rGOT-10 and rGOT-3 composite could be ascribed to the absence of sufficient amount of TiO_2 nanoparticles in the composite to reduce GO to rGO. However, when TiO_2 and rGO are in equal amount (rGOT-1), merely a broad signal of both peaks are detected, which implies that TiO_2 nanoparticles are in sufficient quantity to reduce majority of GO to rGO, during photoreduction but not fully. The reduction in the intensity of main characteristic peak at 11.26^o is attributed to the disruption of stacked (002) planes of GO. On further decreasing the amount of GO in composite, only the peaks attributed to anatase TiO_2 are visible. Furthermore, on comparison of the XRD pattern of all the

samples, it is clear that TiO_2 present in the composite exhibits similar diffraction peaks as that of pristine TiO_2, suggesting that only GO is reduced to rGO, while TiO_2 phase remains preserved. This result suggests that GO and rGO-TiO_2 composite both are present in higher range loading, while GO is completely reduced to form rGO-TiO_2 composite in lower range loading.

To study the morphological differences between the series of rGO-TiO_2 composites, TEM was used and the corresponding images are presented in Fig. 2. Fig. 2a shows crumbled structure of bare GO sheet, confirming successful exfoliation of graphite into GO layers. Fig. 2b shows that TiO_2 nanoparticles are spherical in shape with a narrow size distribution ranging from 5-8 nm. From the morphological analysis of rGOT-0.001 (Fig. 2b) and rGOT-0.1 (Fig. 2c), it is revealed that the amount of TiO_2 nanoparticles, as compared to GO, is very high and hence most of the particles can be seen in the form of aggregates rather than uniformly distributed over the surface. Similar morphology is observed for rGOT-0.01 (figure not shown). In the case of rGOT-1 (Fig. 2d), although rGO is very well decorated and covered by TiO_2 nanoparticles, but still certain degree of agglomeration of TiO_2 nanoparticles is observed on the surface of rGO sheet. However, the agglomeration is lower as compared to that observed in smaller rGO concentration ratio. TEM images of rGOT-3 (Fig. 2e) and rGOT-10 (Fig. 2f) show uniform and well-separated TiO_2 nanoparticles decorated on rGO sheets. For lower concentration loading, though TiO_2 nanoparticles mostly covers rGO, they appears agglomerated on the surface, while contrary behaviour is observed for the higher concentration loading. Formation of a composite with uniform distribution over rGO and large spacing between the particles may result in more exposed active sites of TiO_2 for photocatalytic reactions, in contrast to rGO decorated with agglomerated TiO_2 nanoparticles. In addition, even dispersion is more likely to permit formation of an interface

between each TiO$_2$ nanoparticle and rGO which creates a channel for fast charge transfer between them. This is a very important feature to reduce the recombination process during photocatalysis.

The effect of variation in weight ratio of rGO-TiO$_2$ composites on their optical properties was studied using UV-Vis absorption spectra in diffuse reflectance mode. From Fig. 3, it is evident that TiO$_2$ possesses an absorption edge at 385 nm corresponding to a band gap of 3.2 eV [34], consistent for anatase phase. On formation of rGO-TiO$_2$ composite in lower concentration range, there is a very small shift in the absorption edge with significant increase in absorbance throughout the visible range. As the weight ratio of rGO to TiO$_2$ increases to higher value, absorption of photons in the visible spectrum also increases. This absorption of visible light is mainly attributed to the contributions from GO and rGO whose bandgap varies from 2.2eV to 0.5eV depending on the amount of oxygen containing groups on their surface. On the other hand, a slight red shift in the absorption edge of TiO$_2$ to 2.9 eV is observed for lower amount of GO. This is mainly due to the formation of impurity levels just above the valence band owing to Ti-O-C bond formation at the interface of TiO$_2$ and rGO, as confirmed by XPS and DFT calculation in later sections.

Raman spectroscopy was used to explore the effects of variation in the rGO:TiO$_2$ weight ratio on ordered and disordered structures of rGO and TiO$_2$ on surface. Raman spectra of graphite, GO, TiO$_2$ and rGO-TiO$_2$ with different weight ratio are displayed in Fig. 4 in the range of 1200 to 1700 cm^{-1} wavenumber, while low wavenumber range (100-800 cm^{-1}) is presented in Fig. S1. For graphite, peak measured at 1341 cm^{-1} and 1568 cm^{-1} (Fig. 4) corresponds to D and G band, consistent with previous results [35, 36]. D band is assigned to disordered mode, which may arise due to presence of sp^3 defects, disruption of hexagonal graphitic lattice, edge defects and dangling bonds. The observed G band is contributed by phonons of in-plane sp^2 C-C bonds. Raman spectra of unoxidized graphite shows highly intense G band and a weak D band [35] suggesting presence

of ordered structure. However, after oxidation of graphite, i.e. formation of GO, an intense D band centred at 1341 cm^{-1} was observed. An increase in relative intensity of D to G band implies disruption of symmetric hexagonal lattice due to introduction of oxygen containing groups (epoxy, hydroxyl & carboxyl). Simultaneous decrease in G band confirms reduction of in plane sp^2 C-C bond and formation of sp^3 bonds in C network with oxygen of epoxy or hydroxyl group. Also, a small shift in G band to higher wavenumber 1597 cm^{-1} indicates the formation of isolated double bond, which resonates at higher frequency compared to G band in graphite [35]. For low range of GO loading, D and G bands are merely visible due to large quantity of TiO$_2$ on the surface of covering rGO. The relative intensity of I_D/I_G is a good indication for the amount of reduction of GO in the composite. Thus, Table 1 summarizes the relative ratio of I_D/I_G for all the composite with different weight ratio and GO. In composite, I_D/I_G intensity ratio decreases from 1.17 (GO) to 0.73 (rGOT-0.1) indicating that level of reduction is enhanced with amount of TiO$_2$. Raman bands observed at 148 cm^{-1}, 397cm^{-1}, 518 cm^{-1} and 640cm^{-1} are assigned to Eg, B1g, A1g and E1g modes of anatase phase of pure TiO$_2$ nanoparticles (Fig. S1). Raman spectroscopy of rGO-TiO$_2$ composite with weight ratio 0.001, 0.01 and 0.1 does not show any significant shift in wavenumber of TiO$_2$ phase. However, Raman modes of TiO$_2$ in composites with higher weight ratio (1, 3 and 10) are suppressed due to the low concentration of TiO$_2$ on the surface as a result of covering by rGO.

FTIR spectra of GO and rGO-TiO$_2$ composites are illustrated in Fig. S2. In graphene oxide, a broad peak extending from 3700 cm^{-1} to 2700cm^{-1} corresponds to stretching and vibration of O-H bond and intercalated water molecules. The peak at 1614 cm^{-1} is assigned to skeletal vibration of C=C bond of unoxidized graphite. Additionally, the peaks centred at 1718, 1373, 1226, 1026 and 959 cm^{-1} are attributed to vibrations and stretching of C=C, C-OH, C-O-C and C-O (alkoxy)

groups, respectively [36, 35]. This result confirms that GO surface is mainly covered by hydroxyl, epoxy, carbonyl and carboxylic groups. However, after formation of rGO-TiO$_2$ composite, there is significant decrease in the peak corresponding to oxygen containing functional groups confirming reduction of GO to rGO and formation of rGO-TiO$_2$ composite for both the range of loading.

In order to investigate the chemical nature of bonding and interactions at the interface between rGO and TiO$_2$ after the formation of composite, XPS analysis of all the samples were conducted. The spectra of Ti $2p$ core level for TiO$_2$ and rGO-TiO$_2$ composites are shown in Fig.5. For pure TiO$_2$ (Fig. 5a), the two peaks located at 458.5eV and 464.2 eV are assigned to Ti^{4+} state in TiO$_2$ for Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels, respectively. Both these peaks are maintained for rGOT-0.001 (Fig. 5b) and 0.01 (Figure not shown) where the amount of rGO is low. However, in other rGO-TiO$_2$ composites, a positive shift by 1.1 to 1.2 eV was observed in both Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels (Fig. 5c-f). This shift is attributed to the strong interaction between rGO and TiO$_2$ caused by electron transfer from TiO$_2$ to rGO leading to the formation of Ti-O-C bonds. These Ti-O-C bonds are highly beneficial because they act as a channel for fast transfer of electrons from TiO$_2$ to rGO during photocatalytic process. For rGOT-10, where amount of rGO is the highest, the signal for Ti is merely detected, thus suggesting complete coverage of TiO$_2$ with rGO and GO.

XPS spectra of C 1s level (Fig. S3) of GO and the series of rGO-TiO$_2$ composites are deconvoluted into mainly three peaks with BE 284.8 eV, 286.1 – 286.7 eV and 288.2 – 288.6 eV, corresponding to sp^2 hybridized C-C bond, C-O-C bond and C=O bond, respectively. Comparison between all the composites and GO clearly indicates that after formation of the composite, peaks located at 286.1 – 286.7 eV and 288.2 – 288.6 eV reduces significantly due to removal of oxygen

functional groups attached on the surface of GO, in the presence of light and TiO_2 and subsequent conversion to rGO.

The core level of O $1s$ spectra of TiO_2, GO and all the composites are presented in Fig. 6. For pure TiO_2 nanoparticle (Fig. 6a), the main peak of O $1s$ can be deconvoluted into two peaks, centred at around 529.8 eV, corresponding to Ti-O-Ti bond [37] and at higher BE 531.0 eV is attributed to the Ti-OH bond. On the other hand, in GO (Fig. 6b), single peak located at 532.5 eV is assigned to the presence of hydroxyl and epoxy groups on the surface of GO layer. The intensity of this peak reduces considerably for all the composites except for rGOT-0.001 (Fig. 6c) and rGOT-0.01 (Figure not shown), where it is not visible. This again confirms that all oxygen containing groups on the surface of GO are reduced by introducing TiO_2 and the degree of reduction increases with increasing the TiO_2 concentration. For the sample with lower weight ratio (rGOT-0.001 and rGOT-0.01), the two peaks in O $1s$ level are exactly similar to that found in case of pure TiO_2. On the contrary, for composites with other weight ratios i.e. rGOT-0.1 (Fig. 6d), rGOT-1 (Fig. 6e) and rGOT-3 (Fig. 6f), the peak attributed to O in TiO_2 at 530.9 eV shows a positive shift of 1.1eV, similar to Ti $2p$ level. Therefore, it again validates the presence of strong bonding between rGO and TiO_2 created by electron transfer from latter to former. This peak of TiO_2 is completely absent in O $1s$ level of highest weight ratio rGOT-10 (Fig. 6g), suggesting absence of TiO_2 on the surface owing to complete coverage by GO. Additional peak is detected at 533.2-533.3eV for higher concentration range of GO which is, after deconvolution, is assigned to Ti-O-C bond formed at interface of TiO_2 and rGO. This channel in the form of Ti-O-C is highly useful for electron transfer during photocatalytic reaction. XPS results indicates that for lower GO loading (rGOT-0.001 and 0.01), TiO_2 is mainly present on the surface of the composite and even if interaction between rGO and TiO_2 occurs, this is not with the TiO_2 nanoparticles present on the

16

surface. On the other hand, for higher GO loading, TiO_2 nanoparticles on the surface display clear interaction with rGO present in form of Ti-O-C bond. At highest loading (rGOT-10), TiO_2 is mostly wrapped by the GO sheets.

From the results so far, it is now established that photo-reduction process helps in formation of rGO-TiO_2 composite and a channel is created in the form of Ti-O-C bond for fast transfer of electrons. This intimate interaction between TiO_2 and rGO through Ti-O-C bond is expected to hinder the recombination process in TiO_2. To investigate the recombination process in rGO-TiO_2 composites, photoluminescence (PL) studies were carried out. PL spectra (Fig. 7a) of all the composite samples including TiO_2 shows four peaks around 420, 438, 485 and 526 nm. The two peaks at 420 and 438 nm are due to relaxation from self-trap states whereas other two peaks at 485 and 526 nm are due to interband transitions [38]. From the PL spectra, it is revealed that as the rGO:TiO_2 ratio increases, peak intensity decreases and reaches a minimum for rGOT-10. The reduction in the peak intensity of PL spectrum confirms that addition of rGO reduces the recombination process in TiO_2 by immediate electron transfer from TiO_2 to rGO via Ti-O-C bond. To further confirm this result, time-resolved photoluminescence (TRPL) studies were performed for all the samples.

Fig. 7b shows the TRPL decay curves for pristine TiO_2 and rGO-TiO_2 composites and decay curves are fitted by two-exponential decay functions comprising two time components, τ_1 and τ_2 corresponding to fast and slow decay components respectively. The former arises by electron and hole relaxation near band edge of TiO_2 and latter originates from recombination of excitons which are self-trapped at various defect sites in lattice or surface (such as oxygen vacancies, surface hydroxy group and other defects). The values of these components with the corresponding fractions are summarized in Table 1 along with the average life time value. In pure TiO_2, the

average lifetime of 1.12 ns is mainly dominated by slow component with fraction of 79% as compared to fast component (21%). For lowest GO loading (rGOT-0.001) the time component values are nearly same but fraction of slow component decreases to 70% as compared to 79% of TiO_2 which results in slight decrease of overall lifetime to 1.084 ns. Similar decrease in average lifetime is also observed for rGOT-0.1 where the fraction of τ_2 further decreases to 67.8% but the value of τ_1 increases to 0.592 ns in comparison to TiO_2 (0.370 ns). TiO_2 nanoparticles are in form of agglomerated clusters for lower ratio GO loading, where only few nanoparticles on the outside of cluster interact with GO to form rGO-TiO_2 composite. In these interacting TiO_2 nanoparticles, photo-generated electrons before being trapped by the defect sites are transferred to rGO, leading to decrease in fraction of slow component. But majority of TiO_2 nanoparticles are not in contact with rGO, thus the overall lifetime is slightly lower or close to that of TiO_2. In case of the high range GO loading, mainly for rGOT-1 and rGOT-3, the average lifetime value is more than doubled than that of TiO_2 owing to the increase in τ_1 and τ_2 values by more than two times. This increase in lifetime values can be directly linked to the formation of Ti-O-C bond between TiO_2 and rGO, found for only higher ratio GO loading. Each TiO_2 nanoparticle is well dispersed on 2D sheet forming distinct interfacial channel with rGO in form of Ti-O-C bond. Since conduction band minima of TiO_2 (-4.2 eV) is higher than the work function of rGO (-4.4 eV), this Ti-O-C bond acts as a channel to immediately transfer the electrons from TiO_2 to rGO after its photo-generation. PL and TRPL results suggest that interaction between TiO_2 and rGO is an important factor to reduce recombination process in rGO-TiO_2 composite.

4.1   Photocatalytic activity:

To investigate the effect of loadings variation of GO in rGO:TiO_2 towards their photocatalytic performance, photodegradation of p-NP was carried out. For all measurements, the amount of

TiO$_2$ was kept constant (2.5 mg), so as to ensure that the amount of photocatalyst is same in all the samples. Fig. 8a shows the graph of photocatalytic degradation of p-NP under Xenon light irradiation for pure TiO$_2$ and rGO-TiO$_2$ composites. It is evident that rGO-TiO$_2$ composites show better photocatalytic activity as compared to unsupported pure TiO$_2$, irrespective of the weight ratio value. One can observe that as the weight ratio is increased, the photo-degradation efficiency increases until the value becomes 3:1. On further increasing the amount of GO (rGOT-10), photoactivity starts decreasing. This implies that rGOT-3 with GO:TiO$_2$ weight ratio of 3:1 portrays the most suitable scenario that assists in improving the photocatalytic performance by 3.5 times as compared to pure TiO$_2$.

To understand the reasons for better photocatalytic performance of rGO-TiO$_2$ composites, rGOT-3 in particular, one need to understand the differences in pristine TiO$_2$ and the composite samples. Two major modifications take place in the properties of composite samples when compared to pure TiO$_2$: (a) increase in the absorption of visible light spectrum and (b) decrease in the recombination of photogenerated charge carriers. The presence of rGO with a bandgap less than 2.2 eV is mainly responsible for absorption of visible light, as confirmed by UV-Visible spectroscopy. Additionally, in composite samples, marginal narrowing of TiO$_2$ bandgap was also observed, which is due to the formation of Ti-O-C level above the VB. This phenomenon also contributes to the improved utilization of visible spectrum. The reduced recombination rate is a consequence of the fast electron transfer from TiO$_2$ to rGO at the interface of the composite. According to XPS results, strong interaction between TiO$_2$ and rGO is developed at the interface due to the formation of Ti-O-C bonds. The conduction band minimum of TiO$_2$ (-4.2 eV) is higher than the work function of rGO (-4.4 eV) which assists the fast transfer of electrons from TiO$_2$ to

rGO through interfacial channel to reduce the recombination rate as also confirmed by PL and TRRL spectroscopy.

To identify which of the two factors, absorption of visible spectrum or decrease in recombination rate, is dominant in improving the photocatalytic performance, more experiments were performed. As rGO is a low bandgap material, it is mainly responsible for enhancement in absorbance of visible spectrum in the composite samples. In order to investigate the possibility that GO absorbs visible light under xenon lamp and the enhancement in rGO:TiO_2 composite is due to extended absorption in visible region, the photo-degradation tests were carried out under UV light irradiation, as shown in Fig. 8b. In these measurements also, the amount of TiO_2 was kept constant (2.5 mg) to make a fair comparison. Even under UV irradiation, rGOT-3 shows the highest activity, similar to that under Xenon irradiation. This confirms the fact that TiO_2 is the dominant photocatalyst in the composite and visible light absorption is not the main reason for enhancement in their photocatalytic performance. Thus, charge separation at the interface is the major factor controlling the photocatalytic performance in rGO-TiO_2 composites. In rGOT-3, the amount of GO is 3 times that of TiO_2. This raises a concern that the observed photocatalytic activity can also have contributions from the excess amount of GO and not purely due to enhanced charge separation at the interface. To shed more light on this concern, GO powder in an amount equal to thrice the value of TiO_2 (i.e. 7.5 mg) was tested individually for photo-degradation under UV and Xenon light, as shown in Fig. 8b and 8a respectively. On comparing the activity graphs of rGOT-3 and GO, clear difference in their photo-degradation activity is observed, which indicates that enhancement in photoactivity is purely due to the interaction between rGO and TiO_2 at the interface, rather than due to excess amount of GO.

This result also indicates that higher GO loading (rGOT-1, 3 and 10) displays significantly improved photocatalytic activity as compared to lower GO loading (rGOT-0.001, 0.01 and 0.1). TEM and XPS results shows that for higher GO loading TiO_2 nanoparticles are well dispersed on the 2D sheet to form distinct interfacial channel with rGO in the form of Ti-O-C bond, for fast electron transfer. This effect is optimum for weight ratio of 3:1 thus leading to highest degradation rate with minimum recombination processes. For highest loading (rGOT-10), slight decrease in the activity is observed which is due to the wrapping of TiO_2 nanoparticles by excess amount of GO present in the composite as evidenced by the absence of TiO_2 peaks in XPS and Raman spectra of the surface. The surface coverage not only prevents light to reach on TiO_2 but also avoids the interaction between TiO_2 active sites and organic pollutants leading to reduce activity. In case of lower GO loading, TiO_2 nanoparticles are mostly in aggregate state on the surface out of which only fewer nanoparticles are able to interact with GO and form Ti-O-C channel for electron transfer. Thus all the above results are able to clarify the role played by the formation of interface between rGO and TiO_2 and establish as the most important factor in rGO-TiO_2 composite. To further elaborate and confirm the role of interface, DFT calculations were performed.

4.2 DFT Results

DFT simulations was carried out to qualitatively support our experimental observations to present theoretical insight for the interactions of TiO_2 on rGO through the analysis of Density of States, Partial Density of States, charge transfer and orbital interactions. Initially 4x4 graphene and rGO which contains 8 OH and 2 epoxy resulting a C:O ratio of 3.2 as per the experimental sample was built and relaxed. Bulk structure of TiO_2 having tetragonal structure (I41/amd) with unit cell containing 4titanium atoms and 8 oxygen atoms was constructed with optimized lattice parameters a=b=3.76 Å and c= 9.48 Å, which is in good agreement with the experimental results [39]. From

the relaxed structure of bulk TiO_2, (101) plane of TiO_2 was constructed keeping a vacuum of 20 Å and optimized the surface. We constructed hybrid rGO-TiO_2 bilayer by placing TiO_2 layer 3 Å above rGO layer. The relaxed structure of rGO, TiO_2 and rGO-TiO_2 bilayer are shown in Figure S4. During the relaxation TiO_2 layer comes closer to rGO and Ti of TiO_2 layer makes a bond with O from functional groups of rGO layer with a bond length of 2.3 Å. There may be charge transfer from Ti of TiO_2 to O of rGO. From the Bader charge analysis, the amount of charge transfer from TiO_2 surface to rGO is 0.0243e which is in agreement with XPS results. To explore the coupling between rGO and TiO_2 and its impact on the electronic and optical properties, total density of states for TiO_2 and rGO before and after formation of bilayer, was computed and displayed in Fig S5 and Fig. S6, respectively. It is noticed from Fig. S5 that the bandgap for TiO_2 surface is 2.57 eV, lower than experimental band gap of 3.2 eV which is expected as normal DFT underestimate the band gap [40]. In rGO, there is opening of band of 0.41 eV compared to zero band gap in pristine graphene as depicted in Figure S6. Due to interaction of rGO and TiO_2, intermediate states appears within the band gap region and the band gap becomes almost zero as shown in Figure S5(c). To further understand the orbital contributions of different elements in TiO_2 and rGO, partial density of states of Ti d and O p of TiO_2 and C p and O p of rGO as displayed in Figure S6. It can be notice that the upper valence band of TiO_2 is mainly composed of O $2p$ orbitals with a small contribution from Ti $3d$ states, whereas conduction band is mainly contributed by Ti $3d$ states. In the case of rGO (Fig. S6b), valence band and lower conduction band clearly shows hybridization between O $2p$ and C $2p$ orbitals. Figure 9 depicts partial density of states of Ti d, O p and C p for TiO_2, rGO and rGO-TiO_2 bilayer. It is infered that Ti $3d$, O $2p$ and C $2p$ states are mainly responsible for the formation of Ti-O-C bond. So here interaction is strong and not just weak vander Waals attraction as usually observed in the case of graphene and TiO_2 [41].

Band structure calculations of rGO, TiO$_2$, and rGO-TiO$_2$ bilayer were carried out to understand the position and nature of new electronic levels due to formation of Ti-O-C bond. Fig. 10 shows electronic band structure of rGO (Fig. 10a), TiO$_2$ (Fig. 10b) and rGO-TiO$_2$ bilayer (Fig. 10c). The conduction band minima (CBM) of TiO$_2$ appears at Gamma point while valence band maxima (VBM) is near Gamma point and lies on G-Y line, suggesting indirect band nature of TiO$_2$, consistent with previous results [39, 42]. CBM and VBM of rGO layer lies at Gamma point with bandgap of 0.4 eV consistent with our DOS results. After formation of rGO-TiO$_2$ bilayer, there are noticeable changes in the band structure of rGO-TiO$_2$ composite. From the plot, it can be noticed that there is a slight decrease in the band gap due to formation of new states in the bandgap of rGO-TiO$_2$. The decrease in bandgap is consistent with the absorbance spectra (Fig. 3), which showed shift in the absorption edge of TiO$_2$ towards higher wavelength. It is very interesting to notice that the new states are formed within the bandgap of TiO$_2$. It seems there appear some Dirac point like pattern, usually observed in the case of pristine graphene. These observed new states are high mobility states, which may be one of the reasons for fast transfer of electrons from TiO$_2$ to rGO during photocatalysis reaction. Presence of these states is one of the important results that explains the observed enhancement in photocatalytic process. Thus, the fast charge transfer from TiO$_2$ to rGO through high mobility Ti-O-C channel is the key factor for improved photocatalytic performance in rGO-TiO$_2$ composite system.

5. Conclusion

rGO-TiO$_2$ composites with different GO loading from low to (rGOT-0.001, rGOT-0.01 and rGOT-0.1) to high GO (rGOT-1, rGOT-3 and rGOT-10) concentration range were synthesized using photoreduction method to investigate the effect of GO loading on morphological, interfacial,

structural, optical and electron transfer dynamics in resultant composite. The following differences in various properties are listed below.

Techniques	High concentration (rGOT-1, 3 and 10)	Low concentration (rGOT-0.001, 0.01and 0.1)
XRD, Raman, FTIR, XPS	Incomplete reduction of GO to rGO due to insufficient amount of TiO_2 nanoparticles.	Complete reduction to rGO.
TEM	Well dispersed TiO_2 nanoparticles on rGO sheets.	Agglomerated clusters of TiO_2 nanoparticles covering over rGO.
XPS	Each nanoparticle is strongly interacting with rGO in form of Ti-O-C bond at interface.	No visible sign of Ti-O-C bond is observed.
UV-Vis	Visible light absorption in whole range due to presence of low band gap rGO and GO.	Slight red shift in the absorption edge of TiO_2.
PL, TRPL	The amount of recombination processes significantly reduced with prolonged carrier lifetime due to fast transfer of electron through Ti-O-C channel.	Amount of recombination process is lower than TiO_2 nanoparticles but carrier lifetime slightly decreases.

All the above mentioned properties led to higher photocatalytic activity for degradation of phenol for higher concentration GO loading as compared to TiO_2 as well as lower range composites. Among all, the weight ratio, rGOT-3 showed the best performance under both Xenon and UV lamp owing to better dispersion of each nanoparticles which allows to form strong interaction with rGO creating Ti-O-C channel at interface. Marginal decrement in activity at the highest weight ratio of 10:1 is due to excess amount of GO which results in wrapping of TiO_2 active sites for photo reaction as well as blocking of light. Computationally designed rGO-TiO_2 bilayer also verified the formation of Ti-O-C bond at interface which leads to improved optical absorbance by

formation of intermediate states. Band structure calculations reveal that these Ti-O-C states are high mobility levels which assist in charge separation through fast transfer of electrons at the interface. Holistic studies of variation in GO content clearly suggests that Ti-O-C states play a key role in improving photocatalytic activity of rGO-TiO$_2$ composite.

Acknowledgement

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Figure caption:

Figure 1: XRD pattern of GO, TiO_2 and rGO-TiO_2 nanocomposite with different weight ratios.

Figure 2: TEM images of (a) GO; (b) rGOT-0.001; (c) rGOT-0.1; (d) rGOT-1; (e) rGOT-3; (f) rGOT-10.

Figure 3: UV-Visible absorption spectra (in diffused reflectance mode) of pure TiO_2, GO and rGO-TiO_2 nanocomposites with different weight ratio.

Figure 4: Raman spectra of GO and rGO-TiO_2 nanocomposites in the higher wavenumber region.

Figure 5: XPS spectra of Ti 2p states for (a) TiO_2, (b) rGOT-0.001, (c) rGOT-0.1, (d) rGOT-1, (e) rGOT-3 and (f) rGOT-10.

Figure 6: XPS spectra of O 1s states for (a) TiO_2, (b) GO, (c) rGOT-0.001, (d) rGOT-0.1, (e) rGOT-1, (f) rGOT-3 and (g) rGOT-10.

Figure 7: (a) Photoluminescence emission spectra and (b) Time-resolved photoluminescence decay curve of pure TiO_2 and rGO-TiO_2 nanocomposites with different weight ratio.

Figure 8: Comparison of photocatalytic degradation of p-NP under (a) Xenon irradiation and (b) UV light irradiation for pure TiO_2, GO and rGO-TiO_2 nanocomposites.

Figure 9: Partial DOS plot of Ti *s*, *p* and *d* states of (a) TiO_2 and (b) rGO-TiO_2 bilayer; O *s* and *p* states of (c) rGO layer and (d) rGO-TiO_2 bilayer; C *s* and *p* states of (e) rGO layer and (b) rGO-TiO_2 bilayer

Figure 10: Bandstructure plot of (a) rGO (b) TiO_2 and (c) rGO-TiO_2 bilayer.

Table 1: Ratio of intensities of D and G band (I_D/I_G) and average lifetime values along with fitting parameters (τ_1 and τ_2 with their corresponding fractions f_1 and f_2) of the total decay, for pure TiO_2, GO and rGO-TiO_2 nanocomposites with different weight ratio.