Synthesis of tunable core-shell nanostructures based on TiO₂-graphene architectures and their application in the photodegradation of rhodamine dyes

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Abstract

We present the synthesis of core-shell nanostructural materials with multi-component architectures based on TiO₂ and graphitic layers. The composites have been synthesized by chemical vapor deposition with methane as the carbon source, for 5, 10, 30 and 45 minutes. The final products were characterized by a combination of analytical approaches which include: electron microscopy, Raman, FT-IR and UV-Vis spectroscopy as well as thermogravimetric analysis. The amount of graphene shells covering the TiO₂ surfaces was found to vary linearly with the reaction time. Furthermore, the compounds were shown to have excellent stability and photocatalytic activity towards the UV degradation of rhodamine (RhB) dye solution at room temperature. These composites could have major applications in the area of environmental cleaning of various pollutants, electrochemistry or nanomedicine.

Keywords: Tunable core-shell nanostructures, TiO₂-graphene composites, photodegradation, organic dyes

Introduction

First reported in 2004, graphenes are bi-dimensional carbon nanostructures [1] with fascinating physical, chemical, and mechanical properties that have generated tremendous scientific interest. These materials have been proposed as the key components in a number of applications: nanoelectronics [2,3], photovoltaic devices [4,5], supercapacitors [6], bio-devices [7], and sensors [8]. Currently, for the synthesis of graphene, two primary methods are employed: chemical exfoliation of graphite and catalytic chemical vapor deposition (CCVD). Each of these methods has advantages and disadvantages. Nonetheless, CCVD remains, just as with carbon nanotubes, the preferred method for synthesizing graphene structures with one or multiple carbon sheets, in particular by using Cu [9] or Ni [10] substrates. CCVD with inductive heating (CCVD-IH) has been successfully applied for the synthesis of few layer-graphenes over bimetallic catalysts with acetylene as the carbon source [11,12] or over Fe-Mo/MgO with methane as the carbon source [13].

One of the most significant disadvantages of using such bi-metallic catalysts is that, even after purification, the final product still contains certain amounts of metallic impurities that can adversely affect the outcome of the applications for which the graphene structures will ultimately be used. As a result, various processes have been reported in which the graphenes were synthesized by CCVD over oxides, without using metals as the active catalytic centers. For example, SWCNTs have been synthesized over Al_2O_3 out of ethanol at temperatures ranging between 1073-1123K [14] on SiO_2 , out of methane at 900 °C [15], or SWCNTs and MWCNTs on ZrO_2 out of methane, acetylene, and ethylene in variable conditions of temperature and pressure [16]. Furthermore, few-layer graphenes have been synthesized by CCVD over MgO out of acetylene at 325 °C [17]. Recently, the synthesis of carbon-coated TiO_2 ($\text{TiO}_2@\text{C}$) core-shell nanocrystals out of acetylene at 500 °C was also reported [18].

In this contribution, we report the synthesis of complex multistructural composites of graphene/ TiO_2 by CCVD-IH out of methane at 900 °C and their successful use for the photodegradation of Rhodamine B (RhB) dye solution at room temperature under UV light illumination. These core-shell architecture nanostructures, with variable carbon content, were found to have a strong photocatalytic effect, which could lead to their use in various environmental applications that are related to the degradation of organic molecules and the purification of water.

Experimental Details

Graphene/TiO₂ (Gr/TiO₂) composites were synthesized by CCVD with inductive heating [19, 20] using a reactor built out of two concentrically positioned quartz tubes (length of 50 cm and the diameter of the internal tube of 3 cm). Cold water was passed in between the two quartz walls to ensure that the reactor walls would remain at a low temperature [21]. For each reaction, 50 mg of titanium dioxide (TiO₂) (Degussa-P25) were evenly distributed over the flat bottom of a graphite susceptor placed in the middle of the internal quartz tube, which was then positioned in the center of a water-cooled inductive coil connected to a high-frequency generator (1.2 MHz, 5KW). After being closed, the reactor was purged with Ar (300 mL/min) for 10 minutes, after which the graphite susceptor was inductively heated to 500 °C and maintained at this temperature for 10 minutes. Then, the temperature was raised to 900 °C (reaction temperature), and methane was introduced as the carbon source –at a flow rate of 100 mL/min. The reaction times (t_r) were 5, 10, 30, and 45 minutes. At the completion of the reactions, the methane was shut off, the generator was turned off, and the susceptor was allowed to cool to room temperature in Ar flow. Since, for all of the resulting samples, the only variable was the reaction time t_r , we will refer to the samples as follows: “Gr/TiO₂ - t_r ”. As an example, Gr/TiO₂ – 30, represents the sample synthesized over TiO₂ for a reaction time of 30 minutes. During the entire synthesis process, an infrared thermometer (Impac, IGA 8 plus) was used to monitor the temperature of the graphite susceptor in order to ensure a constant temperature throughout the entire reaction time. The temperature of the susceptor was maintained at the desired values by manually adjusting the RF generator power level, based on a pre-determined calibration curve, and the corresponding temperature values were continuously monitored for accuracy with the infrared thermometer.

Morphological characterization of the reaction products was performed by transmission electron microscopy (TEM – JEOL JEM-2100F), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray –photoelectron spectroscopy (XPS), and BET surface area analysis.

The total surface area (S_t) and porosity (pores medium radius – R_m) of the TiO₂ and Gr/TiO₂ samples were obtained from N₂ adsorption–desorption isotherms (measured at – 196°C) using the BET model for S_t determination and Dollimore – Heal method for R_m . The isotherms were recorded using a Sorptomatic 1990 apparatus (Thermo Electron Corporation). Prior to S_t and R_m determination, the samples (approximately 400 mg) were degassed at 200°C for 4h at a pressure of ~2Pa in order to remove the physisorbed impurities from the surface. In all cases, no pressure variation was observed during 1h at the end of sample degassing.

TGA studies were performed using a Mettler Toledo TGA/SDTA 851e instrument in air flow (50 mL/min), at a heating rate of 5 °C/min over the temperature range of 25 – 850 °C. A JASCO tip NRS 3300 spectrophotometer arranged in a back-scattering geometry and equipped with a CCD detector (-69 °C) and a 600 l/mm grid was used to collect Raman spectra at room temperature. The incident laser beam (approx. 1 μm^2) was focused using an Olympus microscope and a 100X objective. The calibration was made based on the Si 521 cm^{-1} peak. A laser with a wavelength of 633 nm and a power at the sample surface of 1.2 mW was used to perform the excitation. The spectra were collected with a spectral resolution of 10 cm^{-1} . Fourier Transform Infrared Spectroscopy (FT-IR) was performed using a Nicolet 6700 (ThermoScientific) Instrument. The chemical status of graphene was studied by X-ray Photoelectron Spectroscopy (XPS) (K alpha, Thermo Scientific). The data were collected at a background pressure of 2×10^{-9} torr, using a monochromated Al K α ($h\nu = 1436.6$ eV) x-ray source. The x-ray beam used was 36W, 400 μm in diameter. Survey scans (0 - 1350 eV) were taken for each sample at a pass energy (CAE) of 200 eV and 1 eV step size. The collected data were referenced to the C1s' peak at 284.5 eV based on the data obtained for adventitious carbon grown on a glass slide. Narrow scans (25 - 40 eV width) of the peaks of interest (C1s) were taken at a pass energy of 50 eV and 0.1 eV step size to provide higher resolution analysis of the peaks. Curve fitting was performed, using Shirley, Powell, and simplex models, on the narrow scans using Avantage V. 5.38 software.

The UV–vis absorption spectra were recorded using a Spectrophotometer JASCO V570 UV–vis–NIR equipped with an absolute reflectivity measurement JASCO ARN-475 accessory. The transformation of reflectance spectra in the absorbance spectra was obtained with the intern software of the spectrometer. The band gap energy of the samples was calculated from $(\alpha E) = A(E - E_g)^{1/2}$ by extrapolation of the linear part of the curve $(\alpha E)^2$ vs. E, where E is the photon energy, E_g the direct band gap, $\alpha = A/d'$ (A - the measured absorbance and d' - thickness of sample in the UV–VIS cell) is the optical absorption coefficient.

The photocatalytic activities of different samples were performed by measuring the degradation rate of Rhodamine B (RhB) dye solution at room temperature under UV light illumination. The UV-irradiation was provided by two 15W UV lamps with a peak wavelength of 365nm. 6 mg of catalyst were suspended in 10 mL aqueous solution of RhB (1.0×10^{-5} mol L^{-1}); next, the mixture was put into a beaker and agitated by magnetic stirring in the dark to achieve the adsorption/desorption equilibrium on the catalyst surface in order to

eliminate the electrons and holes pre-produced by the environmental light. The dye solution with samples was illuminated for 270 min, and the mixture (3.5 mL) was withdrawn for analysis every 30 min. After separating the photocatalyst from the dye solution by centrifuging, the dye concentration was determined by taking the absorption spectra using a UV-VIS spectrophotometer. The photodegradation rate (PhR) was calculated using the following equation: $\text{PhR (\%)} = \frac{A_t}{A_0} \times 100$, where A_0 and A_t represent the initial and the instantaneous absorbance of RhB at 553 nm, respectively.

Results and Discussions

The TEM images for the Gr/TiO₂-5 (a) and Gr/TiO₂-45 (b) samples, as well as the two high magnification TEM images for Gr/TiO₂-45 (c and d), are shown in Figure 1. The TEM analysis indicates that the TiO₂ particles are covered uniformly over their entire surfaces with at least two graphene-like graphitic layers. We presented the representative images for the samples obtained after 5 and 45 minutes of reaction; however, the same observations were found to be true for the composites obtained after 10 and 30 minutes of reaction time. A further analysis of Figures 1 (c) and (d) indicated that the graphitic layers were spaced about 0.34 nm apart, representing typical graphene architectures. For the TiO₂ particles, (Figure 1 (c)), the distance between 8 consecutive layers was found to be 2.55 nm, which means a distance of 0.32 nm between two adjacent layers. This distance represents the inter-planar distance (110) of the rutile TiO₂ [22].

The N₂ adsorption – desorption isotherms of all of the Gr/TiO₂ samples have very similar profiles. The total surface area and pore radius are presented in Table 1. The total surface area of Gr-TiO₂ samples has lower values compared to the starting TiO₂ samples, indicating an obstruction of titania pores by graphene formation. A direct relationship between the surface area of the samples obtained at an increasing synthesis time and their corresponding lower surface areas could be observed only for samples obtained for 5, 10, and 30 min reaction time. The very high values of pore radius obtained for the Gr/TiO₂ samples indicate that this material does not have an intrinsic porosity, as opposed to the starting TiO₂ material which had a classic mesoporous structure. This is possibly due to the formation and deposition of graphene layers on the titania surface, followed by pores obstruction either by their filling with carbon, or by the blockage of the gas access inside the pores by the graphene layers deposited on their entrances. The high nitrogen uptake observed at high p/p₀ relative

pressures combined with the type T3 hysteresis on the desorption branch is more likely due to the gas condensation between Gr/TiO₂ particles rather than in the particles' pores. This conclusion is sustained also by the TEM images which show small Gr/TiO₂ particles of about 100 nm (Figure 1 (a)) enveloped in graphene layers (Figure 1 (b)). Figure 2 presents the Raman spectra for the original TiO₂ particulate material: as purchased (a), TiO₂ particles after they were heated in Ar at 900 °C (b), as well as for the Gr/TiO₂ -5 (c) and Gr/TiO₂ -45 (d) samples, respectively. All the spectra were obtained by averaging three measurements in different location and each measurement averaged three acquisitions for each location. It is rather well-known that both crystalline phases corresponding to TiO₂ (anatase and rutile) have been used for photochemical applications [23, 24]. Figure 2 (a) shows the Raman spectrum (0-1000 cm⁻¹) of the TiO₂ materials, as purchased, and indicates the presence of six peaks corresponding to the anatase phase: 638.6 cm⁻¹, 515.1 cm⁻¹, 394.4 cm⁻¹, 195.9 cm⁻¹, and 142.2 cm⁻¹. Figure 2 (b) shows the Raman spectrum of the TiO₂ sample after it was heated for 20 min at 900 °C in Ar environment. The analysis of these figures indicated the presence of three Raman bands at 611.5 cm⁻¹, 447.1 cm⁻¹, and 242.1 cm⁻¹, which are characteristic of the rutile crystalline phase. As a result, we can conclude that, during this thermal treatment, the anatase phase converted to rutile [25]. The presence of the 445.4 cm⁻¹ band in Figure 2 (a), indicates that, in the original sample, in addition to the anatase phase, there is also a small proportion of rutile. Figure 2 (c,d) shows the Raman spectra, normalized at the G band, for the Gr/TiO₂ - 5 (c) and Gr/TiO₂ - 45 (d), respectively. The analysis of these spectra indicated the presence of two groups of Raman bands: the first one at approximately the values of 607, 436, and 252 cm⁻¹, and the second one at ~ 1326, ~ 1607, and ~ 2630 cm⁻¹. The first group represents the bands characteristic of the TiO₂ rutile phase, while the second one corresponds to few-layer graphenes when excited with 633 nm (1.96 eV) laser irradiation.

In general, three important bands are reported: the D band at ~1320 -1330 cm⁻¹, G band at ~1600 cm⁻¹, and 2D band at ~2630 – 2640 cm⁻¹. The G band is characteristic of all sp²-type graphitic structures, while the D band provides information structural defects in the graphitic layers, its intensity being proportional to the number of sheets that compose the few-layer graphene. The ratio between the intensities of the G and D bands (I_G/I_D) of the graphitic sheets [26-28] provides a measure of the degree of defects. Furthermore, the I_G/I_D ratio provides information regarding the in-plane crystallite sizes (L_a) for the graphitic structures through the following relationship: $L_a = 560/E_l^4(I_G/I_D)$, where E_l is the energy of the laser excitation in eV [29]. The 2D band is sensitive to the number of graphitic sheets that form the few-layer graphene structure and can be used to calculate this number, if it is not higher than

4 [30]. Both D and 2D bands have a dispersive character with their position being dependent upon the energy of the excitation laser, with an approximately $50 \text{ cm}^{-1}/\text{eV}$ shift for the D band and $100 \text{ cm}^{-1}/\text{eV}$ for the 2D band, respectively [31]. Figure 2 (c and d) shows, for the Gr/TiO₂ - 5 and Gr/TiO₂ - 45 samples, the presence of the Raman bands corresponding both to the TiO₂ rutile phase (608, 436, and 252 cm^{-1}), as well as for crystalline graphene-like structures (~ 1326 , ~ 1607 and $\sim 2630 \text{ cm}^{-1}$). It can be concluded that the synthesis process results in the generation of graphene structures of the rutile phase of TiO₂; this observation was also confirmed by the HRTEM images. Additionally, it was observed that the positions of the bands corresponding to the TiO₂-rutile (as purchased and for those that resulted after the graphene synthesis) (Figure 2 c and d) had shifted. For the $\sim 445 \text{ cm}^{-1}$ band, we observed a blue shift of $\sim 11 \text{ cm}^{-1}$, while, for the $\sim 242 \text{ cm}^{-1}$ band, there was a red-shift of about $\sim 10 \text{ cm}^{-1}$. These shifts can possibly be explained by the complex interactions that take place between the TiO₂ - rutile and the graphene structures during the synthesis process. Table 2 shows the I_G/I_D values, as well as the size of the in-plane crystallites, L_a , for the graphenes that were synthesized over the surface of the TiO₂ - rutile. No correlations between these values and the synthesis times were observed.

Fourier Transform Infrared (FT-IR) spectroscopy was run using KBr pellet. The peaks are indicative of the graphene-TiO₂ nanocomposite (Figure 2 e). The characteristic broad peak obtained at 673 cm^{-1} is due to the stretching frequency of Ti-O bond in TiO₂. The peak at 422 cm^{-1} is attributed to Ti-O-Ti bond in TiO₂ [32]. The broad peak at 3442 cm^{-1} is due to the stretching frequency related to hydroxyl (OH) groups. TiO₂ can adsorb water or moisture from air very easily and the adsorbed water is responsible for the broad OH peak in the FT-IR spectrum. The peak observed at 1710 cm^{-1} is due to any carbonyl (CO) functionalities present in graphene. The peak at 1636 cm^{-1} is due to the presence of the hydroxyl group in molecular water in the sample. The peaks in the regions of $1636\text{-}1373 \text{ cm}^{-1}$ can also be assigned to C=C bond vibrations. The peak at around 1180 cm^{-1} is due to any C-O bond present in graphene. The peaks at 2921 cm^{-1} and 2848 cm^{-1} are related to any C-H stretching frequencies [33].

Figure 3 shows the TGA curves (for the temperature range of $30 - 850 \text{ }^\circ\text{C}$) for the Gr/TiO₂- t_r ($t_r = 5, 10, 30, 45 \text{ min}$) “as-grown” samples, as the average of three different measurements, along with the thermal decomposition curve for the TiO₂-rutile. Since the samples are represented by graphenes grown over the surfaces of TiO₂-rutile, the absolute quantity of graphene (efficiency of synthesis- η_s) can be determined from the TGA histograms for the “as-grown” compounds. After the thermal treatment in air at $850 \text{ }^\circ\text{C}$, the

remaining mass represents the amount of TiO_2 – rutile since the graphitic structures are expected to decompose thermally at lower temperatures [34].

Given the fact that graphitic crystalline nanostructures (SWCNT, MWCNT, graphenes) have thermal degradation temperatures superior to 400 °C [35], the mass loss that occurs below this temperature (100-400 °C) can be explained by the loss of adsorbed water and amorphous carbon [36], as well as the chemical surface functionalities (COOH, C=O, C-OH) attached to the graphene [37]. As a result, the percentage mass of graphene present on the surface of TiO_2 – rutile is given by the mass loss in the temperature interval of 400-850 °C, temperature domain where the TiO_2 -rutile doesn't show any significant mass variation, which could influence the values collected for the “Gr/ TiO_2 - t_r ” samples. These values, for all synthesis times, are presented on the TGA curves in Figure 3 and show a linear relationship with the reaction time, as indicated in the inset in Figure 3.

The same conclusions can also be reached on the basis of the XPS analysis - Figure 4. As the reaction time increased, we measured a decrease in the signal intensity corresponding to Ti_{2p} , explained by the increase in the graphitic mass with the reaction time. Graphene stabilizes with increasing reaction time as indicated by the increasing atomic percentage of C1s with increasing reaction time. The C1s narrow scan shows a strong presence of sp^3 bonds along with sp^2 bond for the reaction time of 5 min. This may be due to the presence of a large number of defects in graphene in the early stage of the reaction. As the reaction proceeds further, graphene becomes more stable and only the sp^2 bond prevails as seen in the C1s narrow scan for 45 min. reaction time. The evolution of graphene in the presence of the TiO_2 catalyst as a function of reaction time is summarized in Table 3.

The optical properties of TiO_2 (P25 and rutile) and Gr/ TiO_2 - t_r (t_r = 5, 10, 30, 45 min) samples were evaluated using the UV-Vis absorption spectra (Fig. 5). The initial TiO_2 (P25) and TiO_2 rutile samples showed absorption edges at approximately 305 and 325 nm, respectively, due to the electron transfer from the valence band to the conduction band. The observed red shift of the absorption edge for the TiO_2 rutile is due to thermal treatment of the sample which induces anatase-rutile phase transformation [38]. All Gr/ TiO_2 - t_r samples presented similar absorption and shifted to longer wavelengths with an increase in the reaction time. This behavior indicates that the absorption edge of these nanoparticles can vary from UV to green. The band gaps were determined from the absorption spectra for Gr/ TiO_2 -5, Gr/ TiO_2 -10, Gr/ TiO_2 -30 and Gr/ TiO_2 -45 are 2.90, 2.87, 2.76 and 2.75 eV, respectively, and were lower compared to the value measured for the initial TiO_2 samples (P25-3.22 eV and rutile-2.95 eV). The narrowing of the Gr/ TiO_2 - t_r band gap with increasing reaction times

is attributed to the formation of Ti-O-C chemical bonding in the Gr/TiO₂-t_r samples [39]. The degradation of RhB under UV light irradiation was used to evaluate the photocatalytic activities of the samples, and the results are shown in Figure 6. Before the photodegradation experiments, the adsorption/desorption equilibrium of RhB on the surface of the initial TiO₂ (P25 and rutile) and Gr/TiO₂-t_r samples were studied. The adsorption was checked by mixing the photocatalyst with the RhB solution in dark. For our experiments, it took about 60 min to reach the adsorption-desorption equilibrium. The initial TiO₂ samples (P25 and rutile) showed a very small decrease in the dye concentration. On the contrary, in the case of Gr/TiO₂-t_r samples, an important decrease in the concentration of dye could be observed, reaching 55% for Gr/TiO₂-5 and about 45 % for the Gr/TiO₂-10, Gr/TiO₂-30, and Gr/TiO₂-45 samples. In our case, the BET measurements revealed a decrease in the surface area when the surface of TiO₂ was modified with graphene. Therefore, the high adsorption ability of the Gr/TiO₂-t_r samples could be explained based on the fact that more active sites (oxygen-containing groups, evidenced by XPS analysis) were available on the graphene surface [40] and through π - π stacking interactions between RhB and aromatic regions of the graphene [41]. During the UV irradiation process (Fig. 6), the strong absorption band of RhB located at 553 nm steadily decreases with increases in irradiation time and completely disappears after 270 min in the case of Gr/TiO₂-5 and Gr/TiO₂-10. After an irradiation time of 270 min, the photodegradation rate of Gr/TiO₂-30, Gr/TiO₂-45, TiO₂ Degussa-P25, and TiO₂ rutile is 9, 10, 14, and 21%, respectively. The photocatalytic activity of the TiO₂ (P25) sample is higher than that of the TiO₂ rutile. This behavior is generally recognized [42], and there are two possible explanations: (i) the longer electron-hole pair life in anatase than in rutile evidenced by transient photoconductivity measurements on single crystalline sample facilitate the participation of charge carriers in surface reactions [43]; and (ii) the larger band of the TiO₂ anatase may increase the valence band maximum to higher levels of energy relative to the redox potentials of adsorbed molecules, enhancing the oxidation ability of the electrons and facilitating the electron transfer process from the TiO₂ to the adsorbed molecules [44]. Combining the TiO₂ rutile with graphene resulted in a significant enhancement of the photocatalytic performance of all of the resulting composites of Gr/TiO₂-t_r as compared with that of TiO₂ (P25). The lower photocatalytic performance of Gr/TiO₂-30 and Gr/TiO₂-45 than Gr/TiO₂-5 and Gr/TiO₂-10 in the decomposition of RhB dye under UV light irradiation may be caused by a decrease in the effective light absorption. In the case of these samples, most of the light was probably absorbed by the graphene, which would undermine the effective utilization of light. This phenomenon is called the “shielding effect” and is common in

photocatalysis involving black materials [45,46]. Furthermore, with increasing exposure time, the intense pink color of the initial solution disappeared gradually—indicating that RhB was de-ethylated resulting in the destruction of its conjugated structure under UV light irradiation [47]. The performance of a photocatalyst depends on its light-response range, adsorption capacity, and the recombination kinetics of the photo-generated charge carriers [48]. The photocatalytic degradation process mediated by the Gr/TiO₂-tr samples can be explained as follows: under UV-light irradiation of the samples, the valence electrons (e⁻) of TiO₂ are excited into the conduction band (CB) and therefore forming holes (h⁺) in the valence band (VB). If the graphene is not present, it is believed that the majority of these charges recombine quickly, and a small percentage (less than 1%) of the electrons and holes will participate in the complex photocatalytic reaction [49]. When TiO₂ is in contact with graphene, however, the photo-induced electrons on the CB of TiO₂ can further transfer to the graphene sheets [50], which slows the recombination of the photo-induced electrons as well as holes. These isolated electrons and holes are then captured by the surface adsorbed molecules. The holes react with adsorbed water molecules to form hydroxyl radicals (•OH), while the electrons stored within the graphene structure are trapped by O₂ resulting in superoxide radical anions (•O²⁻) [51]. From all of the experimental outcomes presented above, it can be therefore proposed that graphene could have the ability to enhance the photo-induced catalytic activity of the TiO₂ nanostructures.

Conclusions

Here, we report the successful synthesis of core-shell, multi-structural composites formed of graphene/TiO₂ (rutile) out of methane at 900 °C using CCVD with inductive heating and a reactor with water-cooled walls. The starting material was the Degussa-P25 TiO₂ (anatase), and the reaction times were 5, 10, 30, and 45 minutes. TEM analysis highlighted that the TiO₂ particles were rather uniformly covered with graphitic layers (at least 2 with an inter-layer distance of 0.34 nm). Raman spectroscopy indicated the existence of graphene-like structures along with the TiO₂-rutile in the final composites. Both TGA and XPS showed that the amount of carbon increased relatively linearly with the reaction time. The band gap of Gr/TiO₂-tr samples narrowed with the reaction time. The band gap narrowing results confirmed the formation of Ti-O-C chemical bonding. The Gr/TiO₂-tr samples showed enhanced photocatalytic activity in the photodegradation of RhB compared with TiO₂ (P25).

The highest photocatalytic activity was obtained from the Gr/TiO₂-5 and Gr/TiO₂-10 samples. Graphene acts as a superb electron acceptor and transporter, and therefore reducing the recombination rate of the charge carriers and further enhancing the photocatalytic activity of the complex system.

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Figure Captions

Fig. 1. TEM images for the Gr/TiO₂-5 (a) and Gr/TiO₂-45 (b) samples. HRTEM images for the Gr/TiO₂-45 sample (c) and (d).

Fig. 2. Raman spectra for the as purchased TiO₂ Degussa-P25 (a), TiO₂ heated in Ar at 900 °C (b), Gr/TiO₂ - 5 (c) and Gr/TiO₂ - 45 (d), respectively. FT-IR spectrum of the Gr/TiO₂-45 sample (e).

Fig. 3. TGA curves for the TiO₂ (rutile) and the “as-grown” Gr/TiO₂-t_r (t_r = 5, 10, 30, 45 min) samples. The “inset” shows the relationship between the amounts of graphene grown over the TiO₂-rutile surfaces as a function of the synthesis time.

Fig. 4. XPS analysis of the Gr/TiO₂-t_r (t_r = 5, 40 min), wide scan (a and b), and narrow scan for C1s (c and d).

Fig. 5. UV-Vis absorption spectra for TiO₂ (P25 and rutile) and Gr/TiO₂-t_r samples.

Fig. 6. Photodegradation rate of RhB over TiO₂ (P25 and rutile) and Gr/TiO₂-t_r samples under UV light irradiation.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Table 1. Total surface area and mean pore radius of TiO₂ and Gr/TiO₂ samples.

	TiO₂ (P25)	TiO₂ (rutile)	Gr/TiO₂-5	Gr/TiO₂-10	Gr/TiO₂-30	Gr/TiO₂-45
S_t (m²/g)	50	24	12	9.8	7.3	9.6
R_m (Å)	190	190	830	750	825	950

Table 2. Raman experimental values for I_G/I_D and L_a for the composites graphene/TiO₂ obtained in various synthesis conditions.

Sample	I_G/I_D	L_a(nm)
Gr/TiO₂-5	0.508	74.8
Gr/TiO₂-10	0.532	71.4
Gr/TiO₂-30	0.601	63.2
Gr/TiO₂-45	0.584	65.1

Table 3. Atomic elemental percentage as measured by XPS for the graphene/TiO₂ composites obtained under various synthesis conditions.

Elements (atomic percentage)	Gr/TiO₂- 5	Gr/TiO₂- 10	Gr/TiO₂- 30	Gr/TiO₂- 45
Ti2p	21.18	17.25	16.78	11.8
O1s	43.71	40.28	39.86	30.41
C1s	35.11	42.47	43.92	57.78