FULL LENGTH ARTICLE

One pot environmental friendly nanocomposite synthesis of novel TiO₂-nanotubes on graphene sheets as effective photocatalyst

Heba H. El-Maghrabi a,*, Engy Ahmed Nada b, Fathi S. Soliman a, Yasser Mohamed Moustafa a, Alaa El-Sayed Amin b

a Egyptian Petroleum Research Institute, 11727 Cairo, Egypt
b Faculty of Science Benha University, Cairo, Egypt

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Abstract A nanocomposite synthesis of TiO₂NT-graphene was prepared from titanium dioxide nanotubes and graphene oxide (GO) by a simple environmental friendly method (green method). The structure, surface morphology and chemical composition were characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffract meter (XRD), Raman, energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). XRD results confirm the interaction of TiO₂-NT with graphene. A fast decomposition of the phenol was observed with a degradation efficiency of 70.6% within 180 min.

1. Introduction

During the last decades, urgent need on environment protection has substantially promoted the development of nanotechnology for the synthesis of neoteric photocatalysis nanomaterial systems, such as TiO₂, WO₃ and ZnO, which has been explored to degrade recalcitrant organic pollutants [1,2]. In spite of TiO₂ being a popular and universally recognized catalyst and the most considerably employed photocatalyst, many researchers were motivated to explore the properties of modified TiO₂ in photocatalytic reactions [3,4]. Ultimately, TiO₂ nanotubes have been receiving inclusive interest due to the fact that they integrate the properties of conventional 1-dimensional (1-D) [5]. TiO₂ nanoparticles (TNPs) (e.g., chemically stable, inexpensive, nontoxic, and abundant in nature) with their distinguishing features (e.g., one dimensional (1-D) nano-structure, large specific surface area, good electron/proton conductivity, high aspect ratio, and ion exchange) [6–8]. Due to the large band gap such as band gap of TiO₂ (anatase: 3.2 eV; rutile: 3.0 eV), many semiconductors ordinarily used can generate electron–hole pairs only when illuminated by ultraviolet light, which is a limit to the photo-electronic transition efficiency of solar photo catalysis because the portion of UV-light in the solar spectrum is only about 3–5% of total sunlight [9,10]. Therefore, the development of visible-light-driven photocatalysts is indispensable.

* Corresponding author.
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to make adequate use of solar energy in decontaminating water[11]. The significant improvements in TNP photocatalytic performance have been demonstrated by incorporating novel carbonaceous nanomaterials, such as carbon nanotubes (CNTs) [12,13], graphene and fullerenes [14], to form carbon TiO2 nanocomposite photocatalysts. In particular, Graphene, a sp²-bonded carbon sheet with a thickness of single atom as a newly discovered two-dimensional (2-D) carbonaceous material, possesses high electron mobility, high transparency, flexible structure, and large specific surface area, and many researchers have been devoted to studying the several applications of GO or reduced graphene oxide (RGO) as a high performance support or an efficacious co-catalyst [15]. In TiO2NT–graphene hybrids, graphene can slow the electron-hole pairs, increasing charge transfer rate of electrons and surface-adsorbed amount of chemical molecules through π–π interactions [16,17]. Moreover, the formation of Ti–O–C bonds can expand the light absorption to longer wavelengths [18]. Thus the integration of nanosized anatase TiO2 with two-dimensional graphene nanosheets offers a great opportunity to design and synthesize TiO2NT–graphene hybrid materials with improved visible-light photocatalytic activity.

In this work, we report the preparation of TiO2NT–graphene nanocomposites by environmental friendly method, which is used as an effective photocatalyst for photocatalytic degradation of phenol compound under solar irradiation.

2. Experimental

2.1. Materials

Graphite powder (99 wt%), potassium permanganate (KMnO4, 98 wt%), sulfuric acid (H2SO4, 98 wt%), hydrogen peroxide (H2O2, 98 wt%), sodium nitrate (NaNO3, 99 wt%), and titanium dioxide (TiO2, 98 wt%), sodium hydroxide (NaOH), Hydrochloride (HCl) were purchased from, Fisher chemical, Piochem, Scharlow, Adwic, longlive, Adwic, Sigma-aldrich, Honey Well respectively. All reagents used in this research were superior to chemically pure and used without further purification.

2.2. Preparation of TiO2 nanotubes (TiO2NT)

TiO2NT were prepared by the modified hydrothermal method [19]. In a typical run, 2 g TiO2 added into 50 mL of different concentration of NaOH aqueous solution and the suspension system was stirred for 1 h at room temperature to form a suspension. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave. The autoclave was heated statically at different temperatures and different time durations. After cooling naturally in air, the mixture was centrifuged at a speed of 4000 rpm and. The precipitates were collected. The white powder was thoroughly washed with different concentrations of HCl aqueous solution and then dried at 80 °C. All prepared samples were calcinated for 4 h at different temperatures.

2.3. Preparation of graphene oxide (GO)

GO was prepared by oxidizing the graphite powder in a mixture of concentrated sulfuric acid and KMnO4 according to modified Hummers method [20]. Briefly, graphite powder was stirred in 98% H2SO4 on a magnetic stirrer for 2 h. Then KMnO4 was gradually added into the above solution by maintaining the temperature at less than 20 °C. The mixture was then stirred at 35 °C for 2 h in an oil-bath. The resulting solution was diluted by adding double distilled water under vigorous stirring for 1 h. Then a dark brown suspension was obtained. The suspension was further treated by adding 30% H2O2 solution drop wise until the color of the solution became bright yellow. The resulting GO suspension was washed by repeated centrifugation, first with 5% aqueous HCl solution to remove excess of manganese salt followed by double distilled water until the pH of the solution became near neutral. The purified GO was finally dispersed in double distilled water ultrasonically to obtain a stable dispersion of GO (see Fig. 1).

2.4. Green preparation of binary TiO2NT-graphene nanocomposites

TiO2NT-graphene nanocomposite samples were prepared by a simple one-pot. In brief, titania powders were mixed with ultrasonically dispersed GO in aqueous solution of Ascorbic acid for 2 h, then the solution was subjected to stirring for 24 h at room temperature. The resulting nanocomposite was collected by centrifugation and washed with double distilled H2O followed by drying at 50 °C for 2 days. After that, the solid was collected. Different contents of graphene in TG-x (x: 10, 20 and 30 wt%, respectively) were also obtained to investigate the effect of graphene loading. The synthetic route of TG is shown in Fig. 2.

2.5. Characterization

Fourier-transform infrared spectroscopy (FT-IR) spectrum of sample was recorded between 4000 and 500 cm−1 with an FTIR spectrometer Perkin Elmer (model spectrum one FT-IR spectrometer, USA). Samples were prepared using the standard KBr pellets. The phase of the powders was identified by an X-ray diffractometer (XRD, Shimadzu XD-1) with a Cu Ka radiation at 40 kV and 30 mA over the 20 range of 4–80° at a scanning speed of 4°/min with a sampling angle interval of 0.04°. Raman test was carried out using the dispersive Raman microscope (Model Sentera, Bruker, Germany) instrument at laser wave length 532 nm [doubled Nd:YAG laser (neodymium-doped yttrium aluminum garnet)] and power 10 mW. UV–vis diffuse reflectance spectroscopy (UV–vis
Figure 2  The synthetic route of TG.

Figure 3  Raman spectra of TiO$_2$NT, GO and TGs nanocomposites.
DRS) was carried out on Jasco model V-570A. Transmission electron microscopy and Selected area electron diffraction (SAED) performed on JEOL JEM 2100 were used to characterize the crystallite size and shape of the photocatalysts.

2.6. Photocatalytic activity

Photocatalytic reactions were conducted in a commercial photo-reactor equipped with a 500 ml cylindrical Pyrex vessel irradiated directly with solar irradiated. For photocatalytic phenol degradation, 0.2 g of the catalyst was mixed with 500 ml of 50 mg/l phenol solution which was further stirred in the dark for 60 min to reach the adsorption equilibrium prior to the photocatalytic test. During the photocatalytic reaction, samples were collected at selected time intervals and the catalyst particles were removed by centrifugation. The residual phenol concentration was determined using HPLC (Agilent 1200, USA), equipped with an ultraviolet (UV) detector and a C18 reversed phase column (250 mm × 4.5 mm, Agilent, USA) at 30 °C. The mobile phase consists of water and acetonitrile (40/60, v/v) with a flow rate of 1.0 ml min⁻¹.

3. Results and discussion

3.1. Characterization of the photocatalysts

Raman spectroscopy has been widely employed for the characterization of the electronic structure of carbonaceous materials. Fig. 3 shows the Raman spectra of GO and T/G samples. For TiO₂NT sample in Fig. 3, several characteristic Raman peaks at 153, 283, 519 and 705 cm⁻¹ (corresponding to the E_g(1), B_1g(1), A_1g + B_1g(2), and E_g(2) modes of anatase TNT, respectively) can be seen in the range of 50–800 cm⁻¹ [22,23,25]. No peaks corresponding to rutile or brookite phase are observed, which is consistent with the XRD results (see Fig. 5). The typical features of carbonous materials in Raman spectra are G band at 1603 cm⁻¹ and D band at 1345 cm⁻¹.
the in-plane vibration of sp² bonded carbon atoms, whereas D band is related to the edges, defects and structurally disordered carbons [24] and [27]. Generally, a smaller intensity ratio of the D and G bands \( I_D/I_G \) in a Raman spectrum can be assigned to lower concentrations of defects and disorders in the graphitized structures, smaller fraction of \(-sp^3/sp^2\)-bonded carbon, and/or larger size of inplane graphitic crystallite sp² domains [28,29]. In comparison with the D band and G band of GO, the observed D and G bands of GR are blue-shifted slightly with decreased intensities, confirming the reduction of GO via the green treatment [26,28]. Remarkably, the \( I_D/I_G \) intensity ratio of GR increases compared to that of GO, suggesting an increased level of defects and disorders, but along with a decrease in average size of sp² domains upon reduction of the exfoliated GO [25]. In the Raman spectrum of the TG10 composite, besides the predominant TiO2NT feature, the two additional characteristic peaks of GR still exist, showing the presence of GR after green reduction [28]. Also, a lower \( I_D/I_G \) intensity ratio of GR in the TG10 than pristine GR is observed, which is probably attributed to the presence of TiO2NT, benefiting the restoration of the aromatic structures by repairing defects.

The detailed characterization FTIR curves of the pure TiO2NT, graphene oxide and TiO2NT–graphene nanocomposites are demonstrated in Fig. 4. The pure TiO2NT, absorption peak located at 3400 cm\(^{-1}\) is attributed to the O–H stretching vibration and at 1600 cm\(^{-1}\) is attributed to the O–H bending of the surface hydroxyl from adsorbed water, while the absorption at 919, 621 and 477 cm\(^{-1}\) is assigned to the Ti–O–Ti vibration [30]. The FT-IR spectrum of graphene oxide showed the typical skeletal vibration adsorption band of C=C at about 1638 cm\(^{-1}\), C=OH at about 1387 cm\(^{-1}\), C=C-O stretching band at about 1742 cm\(^{-1}\) and C=O stretches at about 1073 cm\(^{-1}\) [31,32], demonstrating the abundant existence of the oxygen-containing functional groups on its surface. Compared to that of the pure TNTs and TiO2NT–graphene samples, the absorption band below 1000 cm\(^{-1}\) becomes wider for the TiO2NT–graphene with increase in graphene ratio. The wider absorption peak can be considered as a combination of Ti–O–Ti (690 cm\(^{-1}\)) and Ti–O–C vibrations (798 cm\(^{-1}\)) [33], demonstrating the formation of chemical bond between them [34].

The XRD patterns of pure GO, pure TiO2NT and TiO2NT–graphene nanocomposites are shown in Fig. 5. The GO sample prepared by modified Hummers method exhibits two characteristic diffraction peaks at 20 of 10.8° and 42.5° corresponding to (002) and (100) planes, respectively [21,30]. The (002) diffraction peak corresponds to a larger interlayer distance of approximately 0.82 nm than that of graphite (0.34 nm), implying that the GO sheets are separated by the covalently bonded oxygen atoms [21,27,35]. This endows GO with a good hydrophilicity, which is beneficial to an effective dispersion of GO as precursor in aqueous solution [35].

The green strategy to \textit{in-situ} construct TiO2NT–graphene nanocomposites is feasible [28]. As shown in Fig. 5, the peaks at 20 values of 25.3°, 37.8°, 48.2°, 54.0°, 55° and 62.7° for pure TiO2NT and TiO2NT–graphene nanocomposites can be well indexed to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) crystalline planes of anatase TiO2 (JCPDS, card no: 21-1272), respectively [24,36,28]. Notably, no characteristic peaks (10.8°) of GO are observed for all TiO2NT–graphene nanocomposites samples, implying that the oxygen-containing functional groups of GO have been removed after green reduction. It should also be noted that no characteristic peaks for G (ca. 25.0°) are observed probably due to the shielding effect resulted from the strong peak of anatase TiO2NT at 20 of 25.3°. This is owing to the diffraction peak of RGO (ca. 25°) that overlaps with the reflections of the (1 0 1) peak of anatase TiO2NT. Similar results were reported previously [37,38]. It is obvious that the TiO2NT–graphene nanocomposites with different amounts of graphene exhibit similar XRD patterns.

The morphologies of the pure TiO2NT, graphene oxide (GO) and TiO2NT–graphene nanocomposites with different concentrations of graphene are observed by HR-TEM images. According to Fig. 6 GO displays the crumbled and re-stacked sheet-on-sheet structure with large surface area (about few micrometers in the diameter) which is an advantage for growing TiO2NT on their surface, the lattice fringe with 0.85 nm

![Figure 5](image-url)  
**Figure 5** XRD patterns of TiO2NT, GO and TGs nanocomposites.
(layer spacing), which is assigned to the (1 0 1) plane of GO, in which it is distinguished on uniform titanate nanotubes through RGO layers shape. The 1-D tubular morphology with the average diameter of TiO$_2$NT was estimated to be about 10 nm and 150 nm in length and it can be clearly seen. The TiO$_2$NT can be identified clearly in TG-10 and TG-20 because

Figure 6  HR-TEM images of TiO$_2$NT, GO and TGs nanocomposites.
of the low content of graphene (10 and 20 wt% respectively). On the contrary, the excess graphene (30 wt%) covered two sides of TiO$_2$NT, so no TiO$_2$NT was revealed obviously. The composition of the TG nanocomposites is determined by energy-dispersive X-ray (EDX) spectroscopy experiment, as is supplied in Fig. 7. As a result, C, O and Ti elements were identified. The semi-quantitative analysis indicates that the

![Figure 7](image)

**Table 1** The atomic ratio composition of the TGs nanocomposites.

<table>
<thead>
<tr>
<th>Element</th>
<th>TG-10</th>
<th>TG-20</th>
<th>TG-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>37.76</td>
<td>46.96</td>
<td>61.47</td>
</tr>
<tr>
<td>O</td>
<td>30.15</td>
<td>26.04</td>
<td>21.65</td>
</tr>
<tr>
<td>Ti</td>
<td>32.09</td>
<td>27</td>
<td>16.89</td>
</tr>
</tbody>
</table>

Nanocomposite synthesis
The atomic ratio between O and Ti element in TG nanocomposites is as shown in Table 1.

UV–vis diffuse reflectance measurement is a conventional approach used to analyze the light absorption spectrum and the band gap energy of a photocatalytic sample. Fig. 8 shows the results of reflectance measurements for pure TiO$_2$NT, and TiO$_2$NT–graphene nanocomposites with various GO contents from 10 to 30 wt%. It can be seen that the samples of TGs exhibited absorption in the visible region and the continuous absorption band in the range of 400–800 nm. This is due to the black color of our carbon samples. The wide visible-light absorption of the TGs composites becomes stronger with increasing GO content, which is consistent with their color change from white to gray. However, when GO was reduced on the TiO$_2$NT, a red-shift of ca. 22 nm was observed in the absorption edge. Extrapolation of the reflectance was used to obtain the band gap energy of the samples. Those corresponding to the band gap energy of TGs are shown in Table 2. This

Table 2 The band gap energy and surface area of TiO$_2$NT and TGs nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO$_2$NT</th>
<th>TG-10</th>
<th>TG-20</th>
<th>TG-30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ (eV)</td>
<td>3.2</td>
<td>2.4</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>$m^2/g$</td>
<td>190.937</td>
<td>456.418</td>
<td>535.868</td>
<td>625.968</td>
</tr>
</tbody>
</table>

Figure 9 The adsorption and Photocatalytic degradation of phenol over the TiO$_2$NT, GO and TGs nanocomposites under solar illumination.
narrowing in band gap might be attributed to the chemical bonding between TiO$_2$NT and graphene [39,40].

3.2. Catalytic activity of the photocatalysts

Phenol was adopted as the model pollutant to estimate the catalytic properties of the photocatalysts. Concentrations of the phenol over pure TiO$_2$NT, pure graphene oxide, and TiO$_2$NT–graphene nanocomposites samples as a function of solar irradiation time are shown in Fig. 9. Attributed to its wide band-gap, pure TiO$_2$NT can hardly decompose phenol under solar irradiation. Similarly, phenol cannot be degraded by pure graphene because graphene is not a photocatalyst. Contrarily, the degradation of the phenol under solar irradiation using the TiO$_2$NT–graphene is very high. Based on comparing the photocatalytic performances of the TiO$_2$NT–graphene of TG-10, TG-20 and TG-30 it can be inferred that chemical bond between the graphene and TiO$_2$NT is the precondition for the visible-light activity, while the excess graphene (30 wt%) on TG-30 has low activity. Moreover, the absorbability of these materials was analyzed in dark, and the results are shown in Fig. 7. The great absorbability of the TiO$_2$NT–graphene results from its large surface area as clarified in BET surface area data on Table 2. Therefore, the graphene really acts as a sensitizer in the photocatalyst.

2.2.1. The role of graphene on the photocatalytic activity

The photocatalytic mechanism of the TGs nanocomposites is suggested in Fig. 10 and in the following steps:

The first step: This is the adsorption of the phenol molecule on the high surface of graphene sheets. Upon interaction with graphene sheets, the oxidative species surrounding the catalyst can readily access the adsorbed phenol, making the photodegradation process more effective.

The second step: Under visible-light irradiation, $\pi$ state electrons were excited in the graphene by absorbing visible-light. Owing to the $\pi$–$d$ conjugate, the $\pi$ state electrons were subsequently injected into the conduction band of TiO$_2$NT [41–45]. The high carrier mobility of graphene makes the photogenerated electrons transfer to TiO$_2$NT quickly, which is in favor of utilizing efficiency of photogenerated electrons and high photoactivity. These electrons transferred to the surface of TiO$_2$NT and reacted with oxygen to yield superoxide and hydroxyl radicals.

The third step: In the presence of graphene, the excited electrons are quickly transferred through the sp$^2$-hybridized network of graphene sheets. If the electron–hole pairs are prevented from recombining, the excited electrons on the valence band will be available to reach the reaction points and generate oxidative species, thus enhancing the performance of photocatalytic processes.

4. Conclusion

In summary, nanocomposites of TiO$_2$NT–graphene photocatalysts (TGs) were prepared from TiO$_2$NT and GO by a simple green process. The obtained photocatalysts were characterized by Raman, FT-IR, XRD, EDS and TEM. The influences of GO content were investigated by measuring the photocatalytic performance for the degradation of phenol under solar irradiation. The degradation efficiency of phenol could be obtained 70.6% at a GO content of 20% within 180 min. The high photocatalytic activity of TGs is attributed to the decrease in band gap values increasing with the amount of graphene, for which graphene can slow the electron–hole pairs, increase charge transfer rate of electrons, and increase surface-adsorbed amount of chemical molecules through $\pi$–$\pi$ interactions. The obtained results indicated that the prepared TiO$_2$NT–graphene nanocomposite photocatalyst has a potential application for the industrial effluents wastewater treatment containing phenol.

References