

## The Property and Photocatalytic Performance Comparison of Graphene, Carbon Nanotube, and C<sub>60</sub> Modified TiO<sub>2</sub> Nanocomposite Photocatalysts

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A series of carbon nanotube, C<sub>60</sub>, and graphene modified TiO<sub>2</sub> nanocomposites were prepared by hydrothermal method. X-ray diffraction, N<sub>2</sub> adsorption, UV-Vis spectroscopy, photoluminescence, and Electrochemical impedance spectra were used to characterize the prepared composite materials. The results reveal that incorporating TiO<sub>2</sub> with carbon materials can extend the adsorption edge of all the TiO<sub>2</sub>-carbon nanocomposites to the visible light region. The photocatalytic activities were tested in the degradation of 2,4,6-trichlorophenol (TCP) under visible light. No obvious difference in essence was observed in structural and optical properties among three series of carbon modified TiO<sub>2</sub> nanocomposites. Three series of carbon materials modified TiO<sub>2</sub> composites follow the analogous tentative reaction mechanism for TCP degradation. GR modified TiO<sub>2</sub> nanocomposite exhibits the strongest interaction and the most effective interfacial charge transfer among three carbon materials, thus shows the highest electron-hole separation rate, leading to the highest photocatalytic activity and stability.

**Key Words** : Carbon nanotube, C<sub>60</sub>, Graphene, TiO<sub>2</sub>, Visible light

### Introduction

TiO<sub>2</sub>, as a charming heterogeneous photocatalyst, has been widely investigated because of its optical-electronic properties, low-cost, chemical stability, and non-toxicity. However, there are two aspects limiting its application. TiO<sub>2</sub> can be activated only by ultraviolet (UV) irradiation, the energy of which makes up only 3-5% of the solar light. On the other hand, over 90% photoexcited electrons and holes recombine, making most of the excitation useless.<sup>1</sup> Therefore, it is highly desirable to develop TiO<sub>2</sub>-based photocatalysts with high electron/hole separation rate and visible light activity.

The composite of TiO<sub>2</sub> and carbon materials, particularly carbon nanotube (CNT), has attracted much attention in recent years.<sup>2</sup> Hoffmann *et al.*<sup>3</sup> proposed that the photo-generated electrons in the space-charge regions may be transferred into CNT, and the holes remain on TiO<sub>2</sub>, thus retarding the recombination of electrons and holes. Besides, CNT can provide high surface area and peculiar functional groups for the efficient adsorption of reactants and may act as photosensitizer. The formation of Ti-O-C bonds between TiO<sub>2</sub> and CNT can shift the absorption edge into visible light region which obviously promote the photocatalytic performance under visible light. Furthermore, CNT could function for controlling the morphology of TiO<sub>2</sub> nanoparticles.<sup>4</sup> It is known that C<sub>60</sub> possesses high electron affinity and its electronic structure is similar to carbon nanotube.<sup>5</sup> One of the most attractive properties of C<sub>60</sub> in electron-transfer processes is that it can arouse a rapid photoinduced charge separation effectively and restrain charge recombination.<sup>6</sup>

Thus, the combination of TiO<sub>2</sub> and C<sub>60</sub> can provide an ideal system to achieve the enhanced charge separation by photo-induced electron transfer.

Graphene (GR), as a new allotrope of carbon, has attracted an enormous amount of interest from both theoretical and experimental scientists since its discovery in 2004 by Geim and co-workers.<sup>7</sup> GR is a two-dimensional sp<sup>2</sup>-hybridized carbon nanosheet, which possesses many unique properties such as a very high theoretical specific surface area (~2600 m<sup>2</sup>·g<sup>-1</sup>), high mobility of charge carriers, and good mechanical strength.<sup>8-10</sup> Very recently, GR-based nanocomposites have been widely explored in many fields, including biosensors, nanoelectronics, intercalation materials, drug delivery, catalysis, supercapacitors, and polymer composites.<sup>9-14</sup> With regard to the region of photocatalysis, GR also catches the eyes of researchers in this field and promotes great interest to synthesize GR-semiconductor nanocomposites as photocatalysts for target applications.<sup>15,16</sup> It is shown that CNT, C<sub>60</sub>, and GR have many similar structure and electronic properties in common. Therefore, it is reasonable to raise a fundamental question: are they similar in promoting the photocatalytic performance of semiconductors when we use them to assemble carbon-semiconductor composite photocatalysts? In this work, the CNT, C<sub>60</sub>, and GR modified TiO<sub>2</sub> nanocomposites were prepared by a hydrothermal method. The properties and photocatalytic performances of prepared nanocomposites were compared each other. It is hoped that this work could promote more objective understanding on the analogy and difference of these three carbon allotropes, CNT, C<sub>60</sub>, and GR on the rational synthesis and photo-activity improvement of semiconductor-carbon composites.

## Experimental

**Preparation and Characterization.** Carbon nanotubes and C<sub>60</sub> were purchased from Shenzhen Nanotech Port Co., Ltd., China and Yongxin Chemical Reagent Company. Graphene oxide (GO) was synthesized from natural graphite powder by a Hummers' method.<sup>17</sup> The preparation of carbon (GR, CNT, and C<sub>60</sub>) modified TiO<sub>2</sub> nanocomposite photocatalysts is as follows. A certain amount of carbon materials (0.2, 0.5, 1.5, and 3 wt %) was sonicated in a mixed solution of 10 mL ethanol and 20 mL deionized water for a long time to ensure the thorough dispersion of carbon materials. Then, another solution (1.7 mL tetrabutyl titanate and 10 mL ethanol) was added dropwise to the above solution of carbon materials under stirring. After 3 h, the suspension was transferred into a 50 mL Teflon-lined autoclave and kept at 200 °C for 15 h. During the hydrothermal process, GO is reduced to GR.<sup>18,19</sup> The obtained precipitates were centrifuged and washed with deionized water until the pH value was neutral. After that, the solid samples were dried at 60 °C in oven and noted as GR-x, CNT-x, and C<sub>60</sub>-x, where x stands for the weight ratio of carbon material to TiO<sub>2</sub>. For comparison, neat TiO<sub>2</sub> was prepared following the same procedure without addition of carbon material.

XRD patterns of the prepared TiO<sub>2</sub> samples were recorded on a Rigaku D/max-2400 instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Nitrogen adsorption was measured at -196 °C on a Micromeritics 2010 analyzer. All the samples were degassed at 393 K before the measurement. BET surface area was calculated according to the adsorption isotherm. UV-Vis spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using BaSO<sub>4</sub> as the reference sample. PL spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using an Xe lamp as excitation source. Electrochemical impedance spectra (EIS) made from these as-made materials were measured via an EIS spectrometer (EC-Lab SP-150, BioLogic Science Instruments) in a three-electrode cell by applying 10 mV alternative signal versus the reference electrode (SCE) over the frequency range of 1 MHz to 100 mHz. The cyclic voltammograms were measured in 0.1 M KCl solution containing 2.5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] (1:1) as a redox probe with the scanning rate of 20 mV/s in the same three electrode cell as EIS measurement.

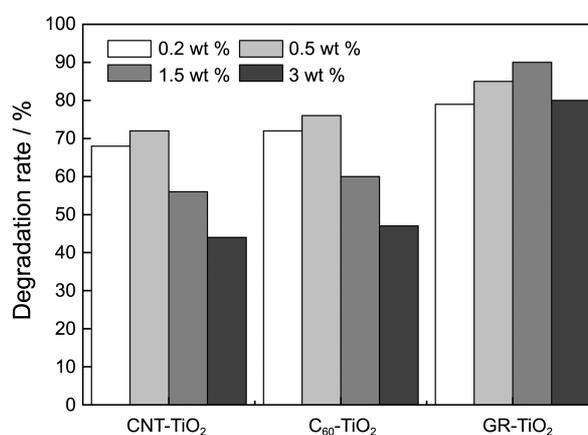
**Photocatalytic Reaction.** Photocatalytic TCP degradation was performed as follows. In a typical procedure, 0.1 g TiO<sub>2</sub> powders were dispersed in 100 mL solution of TCP (initial concentration  $C_0 = 60 \times 10^{-6} \text{ g}\cdot\text{mL}^{-1}$ ) in an ultrasound generator for 10 min. The suspension was transferred into a self-designed glass reactor, and stirred for 30 min in darkness to achieve the adsorption equilibrium. The concentration of TCP at this point was considered as the absorption equilibrium concentration  $C_0$ . The adsorption capacity of a catalyst to TCP was defined by the adsorption amount of TCP on the photocatalyst ( $C_0 - C_0'$ ). In the photoreaction under visible light irradiation, the suspension was exposed to a 400 W high-pressure sodium lamp with UV cutoff filter ( $\lambda$

> 420 nm), and air was bubbled at 130 mL/min through the solution. All runs were conducted at ambient pressure and 30 °C. The conversion of TCP was determined using an Agilent 1100 series HPLC operated in isocratic mode under the following conditions: methanol-water (80% : 20%); flow rate 1 mL·min<sup>-1</sup>; temperature 25 °C; Column Phenomenex Luna 10  $\mu$  Phenyl-Hexyl, 4.6 mm  $\times$  250 mm; detector UV at 254 nm; injection volume 5  $\mu$ L.

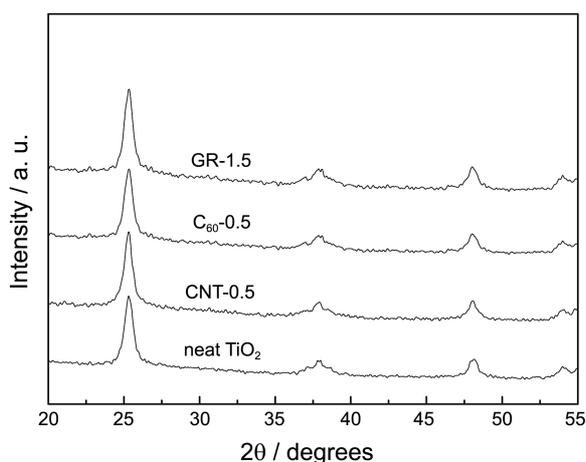
## Results and Discussion

Figure 1 shows the photocatalytic activities of prepared TiO<sub>2</sub> nanocomposites under visible light. It is noted that dark condition without illumination or illumination in the absence of catalyst did not lead to the TCP decomposition, indicating the presence of both illumination and catalyst was necessary for efficient photocatalytic degradation. Unsurprisingly, neat TiO<sub>2</sub> exhibited very low photocatalytic activity because of the low visible light absorption (not shown). For carbon materials modified TiO<sub>2</sub> catalysts, TCP degradation rate improved obviously. CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5 exhibited the highest degradation rates for three series of carbon materials modified TiO<sub>2</sub> catalysts (72%, 76%, and 90%). It is indicated that CNT and C<sub>60</sub> modified TiO<sub>2</sub> catalysts exhibited comparable activity, which is lower than that of GR modified TiO<sub>2</sub>. In order to clear what cause the activity difference among three series of carbon materials modified TiO<sub>2</sub> catalysts, CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5 were selected for the further analysis.

The XRD patterns of the as-prepared neat and carbon materials modified TiO<sub>2</sub> catalysts are shown in Figure 2. It is shown that all of the TiO<sub>2</sub>-carbon nanocomposites exhibit similar XRD patterns. The diffraction peaks of all samples match well with the anatase TiO<sub>2</sub> (JCPDS No. 21-1272). Compared with the standard card of anatase TiO<sub>2</sub>, it is obvious that three different kind of carbon materials modification have no obvious influence on the TiO<sub>2</sub> characteristic peaks, which can be ascribed to two reasons. On the one hand, the addition amounts of carbon materials in the nanocomposites are very low. On the other hand, the main



**Figure 1.** Photocatalytic performances of prepared samples in the degradation of TCP under visible light irradiation.



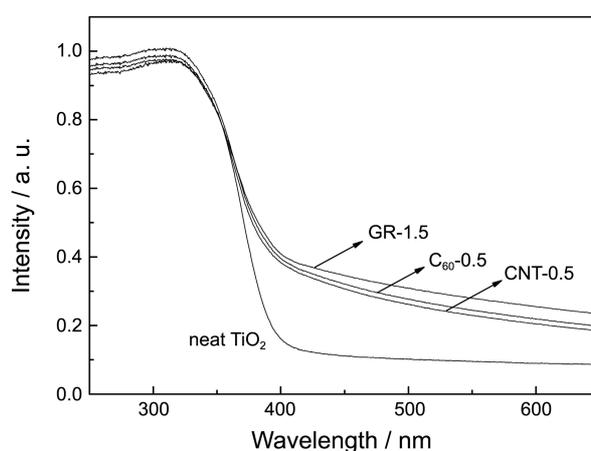
**Figure 2.** XRD patterns of the as-prepared neat and carbon materials modified TiO<sub>2</sub> catalysts.

characteristic peaks of GR and CTN are located at 25.0° and 26.2° which probably shadowed by the (101) peak anatase TiO<sub>2</sub> (25.3°), which is consistent with the previous reports.<sup>20</sup> The particle sizes of the as-prepared nanocomposites were calculated by their XRD patterns according to the Debye-Scherrer equation and shown in Table 1.<sup>21</sup> Obviously, carbon materials modified TiO<sub>2</sub> catalysts exhibit the similar particle size with neat TiO<sub>2</sub>. Generally, the ability of adsorption, desorption, and diffusion of reactants and products are mainly determined by the S<sub>BET</sub> and pore volume of catalyst.<sup>22</sup> Therefore, a catalyst with high specific surface area (S<sub>BET</sub>) and big pore volume is significant to the enhancement of catalytic performance.<sup>23</sup> The S<sub>BET</sub> and pore volume of neat TiO<sub>2</sub> are 168 m<sup>2</sup>g<sup>-1</sup> and 0.37 cm<sup>3</sup>g<sup>-1</sup>, which are very close to that of carbon materials modified TiO<sub>2</sub> catalysts (Table 1). This is reasonable because, with such a small carbon amount, the surface area and porosity are mainly dominated by TiO<sub>2</sub> ingredients. Based on above results, it is concluded that three series of carbon modification did not change the crystal phase, particle size, and structural property of TiO<sub>2</sub> catalyst.

To study the optical properties of as-prepared neat and carbon materials modified TiO<sub>2</sub> catalysts, UV-Vis spectra were measured, as shown in Figure 3. It is shown obviously that the addition of CNT, C<sub>60</sub>, and GR all induce the significant increased light absorption intensity in the whole visible light region. Such phenomenon were reported by previous literatures.<sup>24,25</sup> The absorption curves of three series of carbon materials modified TiO<sub>2</sub> are almost the same,

**Table 1.** Particle sizes, S<sub>BET</sub>, Pore volume, and TCP adsorption amount of prepared TiO<sub>2</sub> catalysts

Sample	Size (nm)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Adsorption amount (ppm)
Neat TiO <sub>2</sub>	12.2	168	0.37	5.2
CNT-0.5	12.5	172	0.35	5.5
C <sub>60</sub> -0.5	11.8	169	0.36	5.4
GR-1.5	12.6	174	0.37	5.5

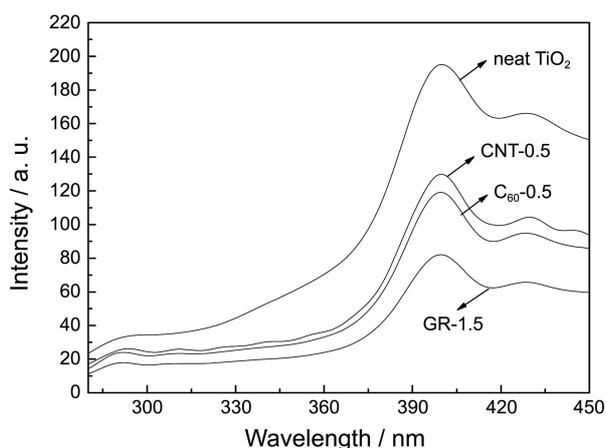


**Figure 3.** UV-Vis diffuse reflectance spectra of as-prepared neat and carbon materials modified TiO<sub>2</sub> catalysts.

indicating that the optical properties have no essential difference among them. The absorption intensity starts to increase rapidly at 400 nm for neat TiO<sub>2</sub>, corresponding to the intrinsic band gap absorption of anatase TiO<sub>2</sub>. For carbon materials modified TiO<sub>2</sub> catalysts, the red shifts of the absorption edges are observed, which is consistent with previous reports.<sup>26-28</sup> This is proposed to correspond to the formation of Ti-O-C bond between TiO<sub>2</sub> and carbon materials similar to that observed for the carbon-doped TiO<sub>2</sub> composites.<sup>29</sup> The band-gap energies calculated according to the method of Oregan and Gratzel were 3.1, 2.9, 2.9, and 2.86 eV for neat TiO<sub>2</sub>, CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5, indicates that carbon materials modified TiO<sub>2</sub> catalysts exhibited much narrowed band-gap energies.<sup>30</sup> Such slight narrowed band-gap energy of GR-1.5 compared with other carbon modified TiO<sub>2</sub> catalysts suggests that the interaction between TiO<sub>2</sub> and GR was the strongest among three series of carbon modified TiO<sub>2</sub> nanocomposites.<sup>25</sup> The absorption of carbon materials modified TiO<sub>2</sub> composites in the visible light region is of great importance for its practical application since it could be activated by visible light.

In order to compare the interaction between TiO<sub>2</sub> and three carbon materials, 0.1 g CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5 were dispersed in 10 mL water and sonicated for 10 min respectively, and then the suspensions were obtained. For GR-1.5, the as-prepared nanocomposite in suspension began to sink to the bottom after resting for a while. After 2 h, the solution became clear, indicating that the simultaneous subsiding of TiO<sub>2</sub> and GR. This suggests that the GR in the solution are completely coupled on the surface of TiO<sub>2</sub> nanoparticles to form a TiO<sub>2</sub>-GR nanocomposite. However, for CNT-0.5 and C<sub>60</sub>-0.5 suspensions, partial carbon materials rose up to the surface immediately. The formed TiO<sub>2</sub>-carbon nanocomposites sink to the bottom within 1.5 h, leaving the partial colloidal TiO<sub>2</sub> suspension. This hints a stronger interaction between the TiO<sub>2</sub> and GR compared with other carbon materials.

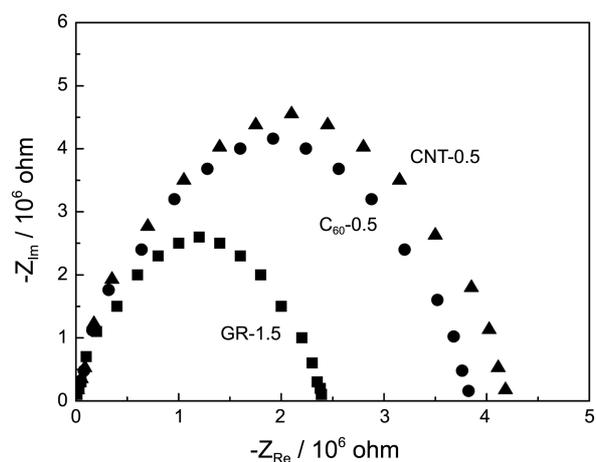
During the recombination process of photo-induced charge carriers, a certain amount of chemical energy is released,



**Figure 4.** Photoluminescence emission spectra of as-prepared neat and carbon materials modified  $\text{TiO}_2$  catalysts.

following by transform to heat or light energy. The light energy is dissipated as radiation, which results in a luminescence emission of semiconductor, called the PL phenomenon. PL is a highly sensitive technique used to provide information on charge separation/recombination of photo-induced charged carriers.<sup>31</sup> In general, the lower PL intensity, the higher separation rates of photogenerated  $e^-/h^+$  pairs, thus the higher the photocatalytic activity. Figure 4 presents a comparison of PL spectra of as-prepared neat and carbon materials modified  $\text{TiO}_2$  catalysts. It is shown that all the catalysts exhibit the similar PL curves. Carbon materials modified  $\text{TiO}_2$  exhibit the lower PL intensities compared with neat  $\text{TiO}_2$ . This should be due to the interaction between  $\text{TiO}_2$  and carbon materials which cause the charge transfer occurred between them, leading to the lower electron-hole recombination rate. It is known that most of the electrons and holes recombine within a few nanoseconds in the absence of scavengers. If scavengers, such as CNT,  $\text{C}_{60}$ , and GR, are present to trap the electrons or holes, the electron-hole recombination can be suppressed, leading to a photoluminescence quenching. Besides, GR-1.5 exhibits much lower PL intensity than that of CNT-0.5 and  $\text{C}_{60}$ -0.5. This is probably due to that stronger interaction between  $\text{TiO}_2$  and GR than CNT and  $\text{C}_{60}$  causes its charge transfer more effectively, which is consistent with UV-Vis result.

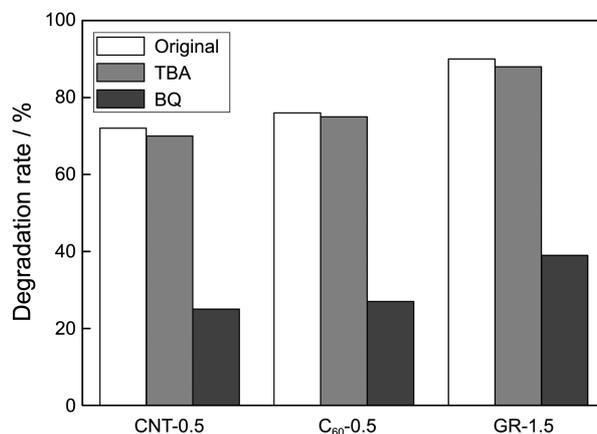
Electrochemical impedance spectroscopy (EIS) is a very useful tool to characterize the charge-carrier migration, thus was used to further confirm the interfacial charge transfer effect of as-prepared  $\text{TiO}_2$  nanocomposites. Figure 5 shows the EIS Nyquist plots of the as-prepared carbon materials modified  $\text{TiO}_2$  composites under visible light irradiation. GR-1.5 shows much decreased arc radius compared with CNT-0.5 and  $\text{C}_{60}$ -0.5. The reduced arc radius indicates diminished resistance of working electrodes, suggesting a decrease in the solid state interface layer resistance and the charge transfer resistance across the solid-liquid junction on the surface by forming hybrid structures of  $\text{TiO}_2$  with graphene.<sup>32</sup> Since the radius of the arc on the EIS spectra reflects the migration rate occurring at the surface, it suggests that a more effective separation of photogenerated electron-hole



**Figure 5.** EIS spectra of CNT-0.5,  $\text{C}_{60}$ -0.5, and GR-1.5.

pairs and a faster interfacial charge transfer occurs on GR-1.5 surface under this condition.<sup>33</sup> Combine with the PL results, it is concluded that the GR modified  $\text{TiO}_2$  nanocomposite exhibits the most effective interfacial charge transfer among three carbon materials, thus shows the highest electron-hole separation rate, leading to the highest photocatalytic degradation rate.

It is known that the adsorption capacity of catalyst is a key factor which influences its catalytic performance. The adsorption of TCP on neat  $\text{TiO}_2$ , CNT-0.5,  $\text{C}_{60}$ -0.5, and GR-1.5 were measured by the equilibrium adsorption capacity, and shown in Table 1. Obviously, the absorption amount of all the samples are very close, which should be due to their similar  $S_{\text{BET}}$  and pore volume values. In order to further understand the underlying reaction mechanism for the photocatalytic degradation of TCP over the as-prepared carbon modified  $\text{TiO}_2$  photocatalysts, a series of controlled experiments with addition of different scavengers for the photogenerated radical species have been investigated (Figure 6). When the hydroxyl radicals ( $\cdot\text{OH}$ ) scavenger,<sup>34,35</sup> tert-butyl alcohol (TBA), is added to the reaction system of the three carbon materials modified  $\text{TiO}_2$  nanocomposites, the TCP degradation only slight decreased compared with



**Figure 6.** Controlled experiments using different radical scavengers for the photocatalytic degradation of TCP under visible light.

the original experiments without the radical scavengers. This indicates hydroxyl radical is not the main active oxygen species for this oxidation reaction. However, when the radical scavenger, benzoquinone (BQ), for superoxide radical species (O<sub>2</sub><sup>•-</sup>) is added into the reaction system,<sup>36,37</sup> the degradation rate decreased dramatically, indicating O<sub>2</sub><sup>•-</sup> is mainly responsible for the TCP degradation. Therefore, it is deduced that the active oxygen species for TCP degradation over three series of carbon materials modified TiO<sub>2</sub> catalysts are the same.

For the practical application of photocatalysts, the mineralization ratio in the catalysis process is a key issue. The photocatalytic degradation of organic compound is a complex process, and many intermediate products are produced, especially when the initial substrate is complicated. Many intermediate products are more harmful to human health than the initial pollutant, so a thorough decomposition of the pollutant is necessary. The mineralization ability of prepared catalysts to TCP molecules was evaluated by monitoring the changes of TOC in the reaction systems. Figure 7 shows the evolution of TOC during the TCP degradation under visible light over prepared materials. The TOC removal rate follows the order: neat TiO<sub>2</sub> < CNT-0.5 < C<sub>60</sub>-0.5 < GR-1.5, which is consistent with degradation rate. The ratio of degradation rate of TCP to TOC removal rate represents the mineralization ratio. The calculated results indicated that the mineralization ratios for CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5 were very close (0.74, 0.76, and 0.77). Summing up the above discussion, we propose that three series of carbon materials modified TiO<sub>2</sub> composites follow the analogous tentative reaction mechanism for TCP degradation.

In order to check the photocatalytic stability of prepared carbon-TiO<sub>2</sub> nanocomposites, the photocatalytic performances of fresh and reused catalysts were investigated (Figure 8). No obvious decrease in activity was observed for GR-1.5 after three cycles, indicating its good stability. However, for CNT-0.5 and C<sub>60</sub>-0.5, the activities decreased obviously. This is probably due to that the interaction between TiO<sub>2</sub> and CNT or C<sub>60</sub> is not strong enough, leading to the structural

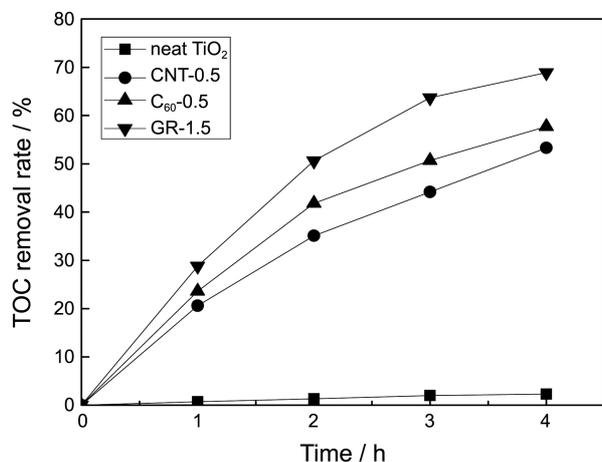


Figure 7. Evolution of TOC during the course of TCP degradation under visible light over prepared materials.

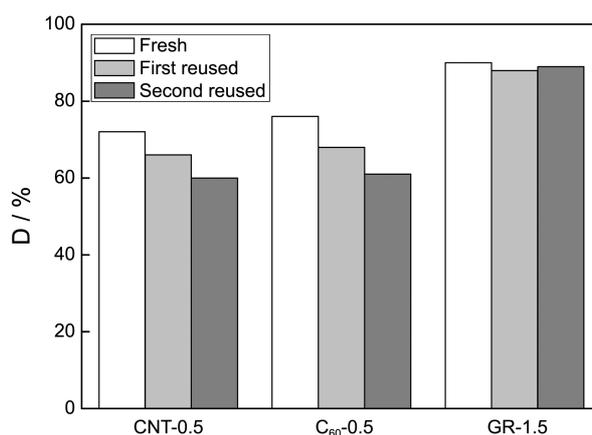


Figure 8. Photocatalytic stability of CNT-0.5, C<sub>60</sub>-0.5, and GR-1.5.

damage during the reaction. In order to confirm our point of view, we observed the suspensions of fresh and reused CNT-0.5 and C<sub>60</sub>-0.5 carefully. It was found that, compared with fresh CNT-0.5 and C<sub>60</sub>-0.5, more carbon materials rose up to the surface for reused catalysts. This indicates that the structural damage of nanocomposite occurred, leading to more TiO<sub>2</sub> and carbon materials separated from each other. Therefore, it is confirmed that the structures of CNT-0.5 and C<sub>60</sub>-0.5 are not as stable as that of GR-1.5.

## Conclusion

A series of carbon nanotube, C<sub>60</sub>, and graphene modified TiO<sub>2</sub> nanocomposites were prepared by hydrothermal method. The results reveal that incorporating TiO<sub>2</sub> with carbon materials can extend the adsorption edge of all the TiO<sub>2</sub>-carbon nanocomposites to the visible light region. The optimal carbon amounts were 0.5, 0.5, and 1.5 wt % for carbon nanotube, C<sub>60</sub>, and graphene modified TiO<sub>2</sub> nanocomposites. No obvious difference in essence was observed in structural and optical properties among three series of carbon modified TiO<sub>2</sub> nanocomposites. Three series of carbon materials modified TiO<sub>2</sub> composites follow the analogous tentative reaction mechanism for TCP degradation. GR modified TiO<sub>2</sub> nanocomposite exhibits the strongest interaction and the most effective interfacial charge transfer among three carbon materials, thus shows the highest electron-hole separation rate, leading to the highest photocatalytic activity and stability. It is hoped that this work could promote more objective understanding on the analogy and difference of these three carbon allotropes, CNT, C<sub>60</sub>, and GR on the rational synthesis and photoactivity improvement of semiconductor-carbon composites.

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## References

1. Wang, X. D.; Caruso, R. A. *J. Mater. Chem.* **2011**, *21*, 20.
  2. Woan, K.; Pyrgiotakis, G.; Sigmund, W. *Adv. Mater.* **2009**, *21*, 2233.
  3. Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
  4. Xu, Y. J.; Zhuang, Y.; Fu, X. *J. Phys. Chem. C* **2010**, *114*, 2669.
  5. Joumet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; de la Chapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756.
  6. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
  7. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
  8. Geim, A. K.; Novoselov, K. S. *Nature Mater.* **2007**, *6*, 183.
  9. Geim, A. K. *Science* **2009**, *324*, 1530.
  10. Allen, M. J.; Tung, V. C.; Kaner, R. B. *Chem. Rev.* **2010**, *110*, 132.
  11. Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K. S.; Govindaraj, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 7752.
  12. Guo, S.; Dong, S. *Chem. Soc. Rev.* **2011**, *40*, 2644.
  13. Xiang, Q.; Yu, J.; Jaroniec, M. *Chem. Soc. Rev.* **2012**, *41*, 782.
  14. Liang, Y. T.; Hersam, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 17661.
  15. Zhao, D.; Sheng, G.; Chen, C.; Wang, X. *Appl. Catal., B* **2012**, *111-112*, 303.
  16. Zhang, J.; Xiong, Z.; Zhao, X. S. *J. Mater. Chem.* **2011**, *21*, 3634.
  17. Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.
  18. Zhang, Y.; Tang, Z. R.; Fu, X.; Xu, Y. J. *ACS Nano* **2011**, *5*, 7426.
  19. Pan, X.; Zhao, Y.; Liu, S.; Korzeniewski, C. L.; Wang, S.; Fan, Z. Y. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3944.
  20. Zhang, Y.; Tang, Z. R.; Fu, X.; Xu, Y. J. *ACS Nano* **2010**, *4*, 7303.
  21. Lin, J.; Lin, Y.; Liu, P.; Mezziani, M. J.; Allard, L. F.; Sun, Y. P. *J. Am. Chem. Soc.* **2002**, *124*, 11514.
  22. Liu, S. W.; Yu, J. G.; Jaroniec, M. *J. Am. Chem. Soc.* **2010**, *132*, 11914.
  23. Yu, J. G.; Wang, G. H.; Cheng, B.; Zhou, M. H. *Appl. Catal. B* **2007**, *69*, 171.
  24. Zhang, L. W.; Wang, Y. J.; Xu, T. G.; Zhu, S. B.; Zhu, Y. F. *J. Mol. Catal. A: Chem.* **2010**, *331*, 7.
  25. Fan, W. Q.; Lai, Q. H.; Zhang, Q. H.; Wang, Y. J. *J. Phys. Chem. C* **2011**, *115*, 10694.
  26. Zhu, P. L.; Nair, A. S.; Yang, S. Y.; Peng, S. J.; Elumalai, N. K.; Ramakrishna, S. *J. Photochem. Photobiol. A* **2012**, *231*, 9.
  27. Mu, S.; Long, Y. Z.; Kang, S. Z.; Mu, J. *Catal. Commun.* **2010**, *11*, 741.
  28. Shah, Md. S. A. S.; Park, A. R.; Zhang, K.; Park, J. H.; Yoo, P. J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3893.
  29. Sakthivel, S.; Kisch, H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4908.
  30. Oregan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
  31. Nakajima, H.; Mori, T.; Shen, Q.; Toyoda, T. *Chem. Phys. Lett.* **2005**, *409*, 81.
  32. He, B. L.; Dong, B.; Li, H. L. *Electrochem. Commun.* **2007**, *9*, 425.
  33. Huang, Q. W.; Tian, S. Q.; Zeng, D. W.; Wang, X. X.; Song, W. L.; Li, Y. Y.; Xiao, W.; Xie, C. S. *ACS Catal.* **2013**, *3*, 1477.
  34. Zhang, N.; Fu, X.; Xu, Y. J. *J. Mater. Chem.* **2011**, *21*, 8152.
  35. Zhang, N.; Liu, S.; Fu, X.; Xu, Y. J. *J. Phys. Chem. C* **2011**, *115*, 22901.
  36. Styliadi, M.; Kondarides, D. I.; Verykios, X. E. *Appl. Catal., B* **2004**, *47*, 189.
  37. Raja, P.; Bozzi, A.; Mansilla, H.; Kiwi, J. *J. Photochem. Photobiol. A* **2005**, *169*, 271.
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