Editorial

Is Graphene Brand New in Carbon-Based Semiconductor Photocatalysts for Organic Pollutants Degradation?

Xincun Dou*

Laboratory of Eco-Materials and Sustainable Technology (LEMST), Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China

Graphene-based semiconductor photocatalysts have been extensively studied for the photocatalytic degradation of organic compounds and have proven more efficient than the bare semiconductor photocatalysts [1-5]. However, graphene, as a "rising star" material and another allotrope of carbon (activated carbon, fullerenes, and carbon nanotubes), is it really superior to other carbon materials when combined with semiconductor photocatalysts, or just because graphene is a newly discovered "weirdie" and people are blindly keen on? To get a comprehensive but still open answer to this question, the unique properties of graphene and the physical and chemical factors that matters the photodegradation activity of carbon-semiconductor photocatalysts should be addressed. In addition, the characteristics of different carbon-semiconductor system should be emphasized.

Graphene has many exceptional properties, such as high electron mobility, theoretically high surface area of 2600 m^2g^{-1}, and high transparency [6]. For the synthesis of graphene-based semiconductor photocatalysts, the most widely used technique to obtain graphene is Hummers' method [7]. The exfoliated graphite oxide (GO) sheets which are the intermediate products in the synthesis process usually possess a rich assortment of oxygen-containing groups, such as carboxylic, hydroxyl, and epoxide functional groups [4]. The presence of oxygen functionalities in GO allows interactions with the cations and provides reactive sites for the nucleation and growth of nanoparticles, which results in the rapid growth of various graphene-based composites. Furthermore, high quality graphene sheets permit ballistic transport, making them potentially ideal electron sinks or electron transfer bridges [8]. Based on these intrinsic physical and chemical characteristics, the enhanced photocatalytic degradation of organic compound for Graphene-TiO$_2$ system could be attributed to the following reasons: (1) the interactions between organic molecules and the aromatic regions of graphene enhance the adsorption on photocatalysts, (2) the formation of the Ti–O–C chemical bonds narrows the band gap of TiO$_2$ and extends the photoresponse range, (3) the transfer of excited electrons from TiO$_2$ to graphene suppresses the charge recombination [3]. It is also found that the electrons in the upper valence band could be directly excited from graphene to the conduction band of TiO$_2$ under visible light irradiation [9], thus graphene acts as the sensitizer to TiO$_2$. It is unassailable that the photocatalytic activity of TiO$_2$-Graphene composite is higher than that of TiO$_2$ alone. However, to compare graphene's superiority over other carbon, on one side, it was advocated that graphene is superior than carbon nanotubes (CNTs) in carbon-TiO$_2$ composites [5]. On the other side, it is strongly argued that TiO$_2$-Graphene composite is in essence the same as other TiO$_2$-carbon (activated carbon, fullerenes, and carbon nanotubes) composite materials on enhancement of photocatalytic activity of TiO$_2$ [10].

To clarify whether graphene provides brand new insights into carbon-semiconductor photocatalysts, the role of graphene's forebear should be addressed. Activated carbon (AC) has been extensively studied as a support for heterogeneous catalysis due to its high surface area (typically 900~1200 m^2g^{-1}) structure over which TiO$_2$ particles may be distributed and immobilized [11]. AC–TiO$_2$ mixtures/composites can improve the photocatalytic activity due to the high adsorption capacity and ready passage of reacting species to the TiO$_2$ particles [12]. Besides, AC support itself is capable of a significant level of self-photocatalytic activity, out-performing the AC–TiO$_2$ composite under UV light irradiation [13]. C60 has unique electronic properties and it absorbs moderately the visible light and strongly the UV light [14,15]. In C60-TiO$_2$ photocatalysts, the fullerene can act as an electron acceptor to minimize the electron–hole recombination or as an electron donor to sensitize TiO$_2$ [16]. CNTs can provide large amounts of surface reaction sites due to the large surface area (200~900 m^2g^{-1}). In addition, the surface chemistry of CNTs may be tailored to promote specificity towards adsorbents. CNTs may act as extremely effective electron sinks since they exhibit high electrical conductivity and high electron storage capacity (one electron for every 32 carbon atoms). As a result, they can synergistically enhance the photocatalytic activity of TiO$_2$ through the retardation of electron–hole recombination. The presence of the C-O-Ti bond in the system has been proven to extend light absorption to longer wavelengths. CNTs may also enhance TiO$_2$ photocatalytic activity by acting as a photosensitizer, transferring electrons to TiO$_2$ [17]. The mid band gap states introduced by defects or CNT oxidation also result in higher photocatalytic activity [9].

Based on the above discussion, it is clear that although graphene is much more popular than its forebears at present, the graphene-based semiconductor photocatalysts basically exhibit four positive factors that can potentially enhance the photocatalytic activity (provision of high quality highly adsorptive active sites, minimization of electron-hole recombination, band gap tuning, and photosensitization). All the four factors were well established in other carbon semiconductor photocatalysts. Nevertheless, it is still too early to get a decisive answer for graphene's superiority to other carbon materials when combined with other semiconductor photocatalysts. Graphene is a new carbon material applied for photocatalysis, it is still too young since it was only born in 2004. Although the number of the reports on graphene-

*Corresponding author: Prof. Xincun Dou, Laboratory of Eco-Materials and Sustainable Technology (LEMST), Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China, Tel: +86-991-367-7875; Fax: +86-991-383-8957; E-mail: xcdou@ms.xjb.ac.cn

Citation: Dou X (2012) Is Graphene Brand New in Carbon-Based Semiconductor Photocatalysts for Organic Pollutants Degradation? J Thermodyn Catal 3:e104. doi:10.4172/2157-7544.1000e104

semiconductor photocatalysts is increasing unprecedentedly, the fully understanding of the role of graphene to the photocatalytic properties and mechanisms of graphene-based photocatalysts still need more evidence. Furthermore, as pointed by Leary and Westwood [8] the development and endorsement of standardized testing methods is needed for the investigation of photocatalysis activity.

References

1. Huang X, Qi X, Boey F, Zhang H (2012) Graphene-based composites. Chem Soc Rev 41: 666-686.

2. Machado BF, Serp P (2012) Graphene-based materials for catalysis. Catal Sci Technol 2: 54-75.

3. An X, Yu JC (2011) Graphene-based photocatalytic composites. RSC Adv 1: 1426-1434.

4. Xiang Q, Yu J, Jaroniec M (2012) Graphene-based semiconductor photocatalysts. Chem Soc Rev 41: 782-796.

5. Zhang H, Lv X, Li Y, Wang Y, Li J (2010) P25-Graphene Composite as a High Performance Photocatalyst. ACS Nano 4: 380-386.

6. Rao CNR, Sood AK, Subrahmanyam KS, Govindaraj A (2009) Graphene: The New Two-Dimensional Nanomaterial. Angew Chem Int Ed 48: 7752-7777.

7. Hummers WS, Offeman RE (1958) Preparation of Graphitic Oxide. J Am Chem Soc 80: 1339-1339.

8. Leary R, Westwood A (2011) Carbonaceous nanomaterials for the enhancement of TiO2 photocatalysis. Carbon 49: 741-772.

9. Woan K, Pyrgiotakis G, Sigmund W (2009) Photocatalytic Carbon-Nanotube–TiO2 Composites. Adv Mater 21: 2233-2239.

10. Zhang Y, Tang ZR, Fu X, Xu YJ (2010) TiO2−Graphene Nanocomposites for Gas-Phase Photocatalytic Degradation of Volatile Aromatic Pollutant: Is TiO2−Graphene Truly Different from Other TiO2−Carbon Composite Materials? ACS Nano 4: 7303-7314.

11. Rodríguez-reinoso F (1998) The role of carbon materials in heterogeneous catalysis. Carbon 36: 159-175.

12. Lee DK, Kim SC, Kim SJ, Chung IS, Kim SW (2004) Photocatalytic oxidation of microcystin-LR with TiO2-coated activated carbon. Chem Eng J 102: 93-98.

13. Velasco LF, Parra JB, Ania CO (2010) Role of activated carbon features on the photocatalytic degradation of phenol. Appl Surf Sci 256: 5254-5258.

14. Guldi DM, Prato M (2000) Excited-State Properties of C60 Fullerene Derivatives. Acc Chem Res 33: 695-703.

15. Apostolopoulou V, Vakros J, Kordulis C, Lycourghiotis A (2009) Preparation and characterization of [60] fullerene nanoparticles supported on titania used as a photocatalyst. Colloids Surf A Physicochem Eng Asp: 349: 189-194.

16. Park Y, Singh NJ, Kim KS, Tachikawa T, Majima T, et al. (2009) Fullerol–Titania Charge-Transfer-Mediated Photocatalysis Working under Visible Light. Chemistry 15: 10843-10850.

17. Wang W, Serp P, Kalck P, Faria JL (2005) Visible light photodegradation of phenol on MWNT-TiO2 composite catalysts prepared by a modified sol–gel method. J Mol Catal A Chem 235: 194-199.