Fabrication of TiO$_2$ Nanosheet Aarrays/Graphene/Cu$_2$O Composite Structure for Enhanced Photocatalytic Activities

Jinzhao Huang*, Ke Fu, Xiaolong Deng, Nannan Yao and Mingzhi Wei

Abstract
TiO$_2$ NSAs/graphene/Cu$_2$O was fabricated on the carbon fiber to use as photocastalysts by coating Cu$_2$O on the graphene (G) decorated TiO$_2$ nanosheet arrays (NSAs). The research focus on constructing the composite structure and investigating the reason to enhance the photocatalytic ability. The morphological, structural, and photocatalytic properties of the as-synthesized products were characterized. The experimental results indicate that the better photocatalytic performance is ascribed to the following reasons. First, the TiO$_2$ NSAs/graphene/Cu$_2$O composite structure fabricated on the carbon cloth can form a 3D structure which can provide a higher specific surface area and enhance the light absorption. Second, the graphene as an electron sink can accept the photoelectrons from the photoexcited Cu$_2$O which will reduce the recombination. Third, the TiO$_2$ nanosheet can provide more favorable carrier transportation channel which can reduce the recombination of carriers. Finally, the Cu$_2$O can extend the light absorption range.

Keywords: TiO$_2$ nanosheet arrays, Graphene, Cu$_2$O, Heterostructure, Photocatalysis

Background
Recently, application of semiconductor photocatalyst titanium dioxide (TiO$_2$) in environmental purification has attracted great attention owing to its tremendous advantages, such as stability, nontoxicity, and low cost [1–3]. Based on the fact that photocatalytic reactions mainly take place on the surfaces of the photocatalysts, the morphology is the crucial factor to determine the efficiency [4]. Up to now, many efforts have been made to fabricate TiO$_2$ nanocrystals, nanowires, nanorods, and nanotubes [5–8]. However, the application of TiO$_2$ nanosheet arrays with larger specific surface area in photocatalytic degradation is rarely reported. Especially, TiO$_2$ nanosheet arrays grown on the carbon cloth can construct three-dimensional (3D) structures to improve the specific surface area.

Unfortunately, the wide bandgap of TiO$_2$ limits the effective absorption of visible light [9]. In order to overcome the shortcoming, one strategy is to modify TiO$_2$ with narrow bandgap semiconductors [10–12]. Among them, cuprous oxide (Cu$_2$O) with narrow bandgap can be a promising candidate for expanding the absorption spectra range. [13–18] Moreover, the built-in electric field between P-type Cu$_2$O and N-type TiO$_2$ can accelerate the separation of carriers. However, the poor interfacial feature between different semiconductors directly influences the separation efficiency of carriers. Therefore, the interfacial optimization is an effective way to enhance photocatalytic degradation efficiency [19, 20]. The previous researches indicate that graphene (G) shows excellent interfacial optimization function between different semiconductors due to its high conductivity and two-dimensional structure, which facilitates the interfacial contact and carrier transportation [21–25]. However, it is difficult to make graphene well disperse between different semiconductors. In this paper, a modified method is applied to fabricate the homogeneously dispersed G between TiO$_2$ nanosheet and Cu$_2$O.

In this study, the composite structure of TiO$_2$ NSAs/G/Cu$_2$O has been prepared (Fig. 1). The significant enhancement of photocatalytic activities was observed, and the corresponding results were analyzed. The
proposed mechanism of the photocatalytic degradation was also discussed. As we know, there are no related reports on TiO$_2$ NSAs/G/Cu$_2$O photocatalysts up to now, so and thus it will be a meaningful reference for designing and fabricating this kind of photocatalyst used in photocatalytic degradation.

**Methods**

**Preparation of TiO$_2$ NSAs/G/Cu$_2$O**

The fabrication of TiO$_2$ NSAs is the following. TiO$_2$ sol was prepared using a previously reported method [10]. In brief, TiO$_2$ seed layer was deposited on carbon cloth (2 cm × 3 cm) by immersing in TiO$_2$ sol for 10 min. Then, the seed layer was calcined at 400 °C for 1 h. The Teflon-lined stainless steel autoclave (100 mL in volume) filled with 40 mL of aqueous solution of 10 M NaOH and 0.2 g of activated carbon was placed in an oven at 180 °C for 24 h. After the autoclave cooled down to room temperature, the prepare samples were rinsed with DI water to remove the residual activated carbon, followed by soaking with 0.1 M hydrochloric acid for 1 h, then washed to neutral with DI water.

For the composite structure of TiO$_2$ NSAs/G, 0.2 g of graphene replacing activated carbon was added into the Teflon-lined stainless steel autoclave ethanol solution. Cu$_2$O layer was deposited by the following procedures. 2.3 mmol of Cu(CH$_3$COO)$_2$ and 2.3 mmol of CH$_3$CONH$_2$ were dissolved into 100 mL of diethylene glycol (DEG) under ultrasonication to prepare the reaction solution. Then, TiO$_2$ NSAs or TiO$_2$ NSAs/G substrate was immersed into the solution. Subsequently, it was heated to 120° under magnetic stirring and kept at this temperature for 6 h. After cooling down to room temperature in air, TiO$_2$ or TiO$_2$ NSAs/G substrate coated with Cu$_2$O was washed with absolute ethanol and DI water for five times in sequence and dried in air.

**Characterization**

The morphologies of the samples were investigated by a field emission scanning electron microscopy (FE-SEM, Quanta FEG250). The crystal structure of samples was examined by X-ray diffraction (XRD, D8 Advance) with Cu $K\alpha_1$ at $\lambda = 0.15406$ nm radiation. XPS spectra were recorded on a Thermo Fisher ESCALAB 250Xi system with Al $K\alpha$ radiation, operated at 150 W. The absorption spectrum of the samples was measured using a UV–vis spectrophotometer (TU-1901). The Raman spectrum of the sample was characterized by Raman spectroscopy (LabRAM HR800).
Photoelectrochemical Measurement

Photocurrent density was measured using an electrochemical workstation (CS2350) in a three-electrode electrochemical cell with 1 M Na₂SO₄ as the electrolyte, in which the as-prepared samples were acted as the working electrode, Pt and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The $I-t$ curve was recorded under Xe lamp (153 mW/cm²) irradiation.

Measurement of Photocatalytic Activity

The photocatalytic activity was evaluated toward the photodegradation of RhB. A 500 W Xe lamp was used as the light source. The samples with same size 2 cm × 3 cm were placed into 20 ml RhB solution (10 mg/L). After irradiation for a designated time (30 min), 3 mL of RhB solution was taken out to identify the concentration of RhB using UV–vis spectrophotometer (TU-1901). All of these measurements were carried out at room temperature.

Results and Discussion

Figure 2a–c, the obtained TiO₂ NSAs characterized by FE-SEM, shows that the uniform TiO₂ NSAs with about 40–60 nm in width and 1.5 μm in height vertically grew on the surface of carbon cloth. These results illustrate that the morphology in favor of the enhancement of photocatalytic performance. As shown in Fig. 2d–f, Cu₂O particles have been successfully deposited on the
surface of the nanosheets. Unfortunately, G cannot be directly observed in Fig. 1d, e, though it could be confirmed by XPS measurement.

XRD patterns were performed to investigate the crystal phase structure of photocatalyst. The XRD patterns of TiO$_2$ NSAs, TiO$_2$ NSAs/G, and TiO$_2$ NSAs/G/Cu$_2$O are shown in Fig. 3. For TiO$_2$ NSAs (curve a), five distinctive peaks match well with TiO$_2$. In curve b (for TiO$_2$ NSAs/G), there are the same diffraction peaks with curve a. The phase on G is not detected because the content is low. From the curve c (TiO$_2$ NSAs/G/Cu$_2$O), the diffraction peaks on Cu$_2$O are observed.

X-ray photoelectron spectroscopy (XPS) was used to confirm the existence of G. The XPS survey spectrum of TiO$_2$ NSAs/G composite shows the elements C, O, and Ti (Fig. 4a–c). The presence of these elements proves the method to fabricate TiO$_2$ NSAs/G composite is feasible. XPS spectrum of C1s located at 284.77 eV can be corresponded to carbon-containing species on the surface, which is the dominant existence form (Fig. 4a). Moreover, the 288.37 eV indicates the tiny existence of C–O bond. The peak located at 529.78 eV is related to the oxygen bonded with metal as Ti–O, and the 534.98 eV is the adsorbed oxygen or hydroxyl species (Fig. 4b). It can be seen that the spectra of catalysis showed two peaks at 458.38 and 464.03 eV. These peaks can be assigned to 3d5/2 and 3d3/2 spin orbital components of Ti$^{4+}$ species (Fig. 4c) [26, 27]. In order to confirm the existence of graphene, furtherly, the Raman spectrum was characterized. The typical Raman spectra of TiO$_2$ NSAs/G are shown in Fig. 4d. There are two typical Raman peaks corresponding to the typical D band and G band of graphene, respectively.

The photocatalytic properties of the as-obtained samples were investigated by decomposition of RhB (Fig. 5a). Before irradiation started, the system was kept in dark for 1 h to reach the adsorption–desorption equilibrium. There is almost no change in the concentration of the solution when RhB solution is irradiated without any catalysts. After 180 min, the degradation ratio of RhB was almost 80% in the presence of TiO$_2$ NSAs/G/Cu$_2$O, whereas 50 and 40% of RhB was decomposed by TiO$_2$ NSAs and TiO$_2$ NSAs/ Cu$_2$O, respectively. All of these measurements show that TiO$_2$ NSAs/G/Cu$_2$O exhibits more prominent photocatalytic activity compared with other samples. A very important reason for the advantage of TiO$_2$ NSAs/Cu$_2$O on the photodegradation of RhB is that Cu$_2$O plays a significant role in extending light absorption spectrum. In addition, TiO$_2$ NSAs/G/Cu$_2$O exhibits a better photocatalytic activity than TiO$_2$ NSAs/Cu$_2$O which results from the presence of graphene. The graphene as an electron sink to accept the photoelectrons from the photoexcited Cu$_2$O will reduce the recombination of photoelectron-hole pairs, resulting in a higher photocatalytic activity. The stability of the TiO$_2$ NSAs/G/Cu$_2$O was carried out, and the results (Fig. 5b) show that TiO$_2$ NSAs/G/Cu$_2$O has good stability.
Generally, responding ability to light is one of the most important factors for evaluating photocatalytic performance. Therefore, UV–vis absorption spectra of samples were characterized as shown in Fig. 6. The absorption of TiO$_2$ NSAs is located in the UV region. Compared with TiO$_2$ NSAs, the absorption edge of TiO$_2$ NSAs/Cu$_2$O shows redshift. This larger absorption would result in the improvement of the photocatalytic property of TiO$_2$ NSAs/Cu$_2$O.

To further understand the improvement of photocatalytic activity, the $I$–$t$ response of TiO$_2$ NSAs, TiO$_2$ NSAs/Cu$_2$O, and TiO$_2$ NSAs/G/Cu$_2$O were observed, as shown in Fig. 7. It can be found that TiO$_2$ NSAs/G/Cu$_2$O exhibits enhanced photocurrents compared with TiO$_2$ NSAs and TiO$_2$ NSAs/Cu$_2$O. The higher photocurrent density of TiO$_2$ NSAs/G/Cu$_2$O indicates an enhanced light absorption and higher separation efficiency of photogenerated electrons and holes.

The improved photocatalytic property of TiO$_2$ NSAs/G/Cu$_2$O may be attributed to the following factors. First, the introduction of Cu$_2$O can extend the light absorption range, and thus, the photocatalytic activities are enhanced. Second, the limitation of carrier recombination is a key factor to enhance the photocatalytic property. The graphene as an electron sink can accept the photoelectrons from the photoexcited Cu$_2$O which will reduce the recombination. Besides, TiO$_2$ nanosheet structure can provide more favorable carrier transportation channel. Third, the better photocatalytic property can take advantage of large specific surface area. TiO$_2$ NSAs/G/Cu$_2$O structure fabricated on the carbon cloth can form a 3D structure which can provide a higher specific surface area. The high surface area of the 3D structure allows not only more surfaces to be reached by the incident light but also more sites on the surface for the adsorption and photodegradation of RhB, which results in enhanced photocatalytic performance. Finally, the 3D structure can enhance the photon utilization efficiency. The structure allows a great number of the photons to penetrate deep inside the photocatalyst, and most photons are trapped within the 3D structure until being completely absorbed.

The corresponding mechanism of electron transfer has been illustrated in Fig. 8. Both TiO$_2$ and Cu$_2$O can be photoexcited under the light irradiation. Because the $E_{VB}$ of TiO$_2$ is more positive than that of Cu$_2$O, holes in the VB of TiO$_2$ can migrate to the VB of Cu$_2$O by the interface. Similarly, the $E_{CB}$ of Cu$_2$O is higher than that of TiO$_2$, so the electrons in the CB of Cu$_2$O can transfer...
to the CB of TiO$_2$. More importantly, graphene as electronic exchange medium can promote electron transfer ability between Cu$_2$O and TiO$_2$.

Conclusions

In summary, the novel 3D TiO$_2$ NSAs/G/Cu$_2$O structure is prepared via a simple and efficient method. Importantly, the composite structure exhibits excellent photocatalytic degradation properties. The enhanced performance can be ascribed to its extended light absorption range, large specific surface area, enhanced photon utilization efficiency, improved charge transfer efficiency and suppressed photoelectron-hole recombination. Furthermore, the photocatalysts grown on carbon cloths make the collection and recycle of photocatalysts much easier.

Acknowledgements

This work was supported by the Natural Science Foundation of Shandong Province (Grant Nos. ZR2016FM30, ZR2016JL015), the Science-Technology Program of Higher Education Institutions of Shandong Province (Grant No. J14LA01), the Graduate Innovation Foundation of University of Jinan, GFLUN, (Grant No. YCXS15006), the Open Project Program of Key Laboratory for Photonic and Electric Bandgap Materials, Ministry of Education, Harbin Normal University (Grant No. PEBIM201505), and National Natural Science Foundation of China (Grant Nos. 51672109, 61504048, 21505050).

Authors’ contributions

Y.N.N. and H.J.Z. designed the experiments. Y.N.N. and FK performed the experiments. D.X.L. performed the SEM observations. Y.N.N., H.J.Z., D.X.L., and Y.N.N. and H.J.Z. designed the experiments. Y.N.N. and F.K. performed the experiments. W.M.Z. discussed and commented on the experiments and results and wrote the paper. All authors read and approved the final manuscript.

Competing interests

The authors declare that have no competing interests.

Publisher’s Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Author details

1School of Physics and Technology, University of Jinan, Jinan 250022, Shandong Province, People’s Republic of China. 2School of Material Science and Engineering, Qilu University of Technology, Jinan 250353, Shandong Province, People’s Republic of China.

Received: 8 March 2017 Accepted: 18 April 2017

Published online: 26 April 2017

References

1. Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiiuchi Y, Anpo M, Bahnemann DW (2014) Understanding TiO2 photocatalysis: mechanisms and materials. Chem Rev 114:9919–9986
2. Zhang Z, Huang Y, Liu K, Guo L, Yuan Q, Dong B (2015) Multichannel-improved charge-carrier dynamics in well-designed hetero-nanostructural plasmonic photocatalysts toward highly efficient solar-to-fuels conversion. Adv Mater 27:5906–5914
3. Fu K, Huang J, Yao N, Xu X, Wei M (2015) Enhanced photocatalytic activity of TiO$_2$ nanorod arrays decorated with CdSe using an upconversion TiO$_2$: Yb$^{3+}$, Er$^{3+}$ thin film. Ind Eng Chem Res 54:659–665
4. Tian J, Hao P, Wei N, Cui H, Liu H (2015) 3D Bi$_2$MoO$_6$ nanosheet/TiO$_2$ nanobelts heterostructure enhanced photocatalytic activities and photoelectrochemical performance. ACS Catal 5:4530–4536
5. Wang J, Ji G, Liu Y, Gondal MA, Chang X (2014) Cu$_2$O/TiO$_2$ heterostructure nanotube arrays prepared by an electrodeposition method exhibiting enhanced photocatalytic activity for CO$_2$ reduction to methanol. Catal Commun 46:17–21
6. Yan W, He F, Gai S, Gao P, Chen Y, Yang P (2014) A novel 3D structured reduced graphene oxide/TiO$_2$ composite: synthesis and photocatalytic performance. J Mater Chem A 2:3605–3612
7. Huang J, Fu K, Yao N, Deng X, Ding M, Shao M, Xu X, Wei M (2016) Enhanced photocatalytic performance using one dimensional ordered TiO$_2$ nanorods modified by graphene oxide. J Nanosci Nanotechnol 16:14771482.
8. Wei X, Shao C, Li X, Lu N, Wang K, Zhang Z, Liu Y (2016) Facile in situ synthesis of plasmonic nanoparticle-decorated g-C$_3$N$_4$/TiO$_2$ heterojunction nanofillers and comparison study of their photosynthetic effects for efficient photocatalytic H$_2$ evolution. Nanoscale 8:11034–11043
9. Yao N, Huang J, Fu K, Liu S, Deng X, Wang Y, Xu X, Zhu M, Cao B (2014) Efficiency enhancement in dye-sensitized solar cells with down conversion material ZnO: Eu$^{3+}$, Dy$^{3+}$. J Power Sources 267:405–410
10. Fu K, Huang J, Yao N, Deng X, Xu X, Li L (2016) Hybrid nanostructure of TiO$_2$ nanorod arrays/Cu$_2$O with a CH$_3$NH$_3$Pbi$_x$, interlayer for enhanced photocatalytic activity and photoelectrochemical performance. RSC Adv 6: 57695–57700
11. Huang J, Liu S, Huang J, Fu K, Yao N, Li L (2016) Enhanced photocatalytic activity of quantum-dot-sensitized one-dimensionally-ordered ZnO nanorod photocatalyst. J Environ Sci 25:1043–1050
12. Dutta SK, Multemot SK, Pradhan N (2015) Metal semiconductor heterostructures for photocatalytic conversion of light energy. J Phys Chem Mater 6:935–944
13. Li H, Kondo T, Komoda M, Ikeda S, Kondo J, Domen K, Hara M, Shinohara K, Tanaka A (1998) Cu$_2$O as a photocatalyst for overall water splitting under visible light irradiation. Chem Commun 3:357–358
14. Paracchino A, Laporte V, Sivula K, Grätzel M, Thimsen E (2011) Highly active oxide photocathode for photoelectrochemical water reduction. Nat Mater 10:456–461
15. Li C, Li Y, Delaunay J (2013) A novel method to synthesize highly photocative Cu$_2$O microcrystalline films for use in photocatalytic. ACS Appl Mater Interfaces 6:480–486
16. Tilley S, Schreier M, Azevedo J, Stefini M, Graetzel M (2014) Ruthenium oxide hydrogen evolution catalysis on composite cuprous oxide water-splitting photocathodes. Adv Funct Mater 24:303–311
17. Li C, Hisatomi T, Watanabe O, Nakabayashi M, Shibata N, Domen K, Delaunay J (2015) Positive onset potential and stability of Cu$_2$O-based photocathodes in water splitting by atomic layer deposition of a Ga$_2$O$_3$ buffer layer. Energy Environ Sci 8:1493–1500
18. Li C, Hisatomi T, Watanabe O, Nakabayashi M, Shibata N, Domen K, Delaunay J (2016) Simultaneous enhancement of photovoltage and charge transfer in Cu$_2$O-based photocathode using buffer and protective layers. Appl Phys Lett 109:033902
19. Fan W, Yu X, Lu H, Bai H, Zhang C, Shi W (2016) Fabrication of TiO$_2$/RGO/ Cu$_2$O heterostructure for photoelectrochemical hydrogen production. Appl Catal Environ 181:7–15
20. Fu K, Huang J, Yao N, Xu X, Wei M (2016) Enhanced photocatalytic activity based on composite structure with down-conversion material and graphene. Ind Eng Chem Res 55:1559–1565
21. Li X, Yu J, Jaroniec M (2016) Hierarchical photocatalysts. Chem Soc Rev 45: 2603–2636
22. Li J, Wu N (2015) Semiconductor-based photocatalysts and photoelectrochemical cells for solar fuel generation: a review. Catal Sci Technol 5:1363–1384
23. Li X, Yu J, Wageh S, Al-Ghamdi AA, Xie J (2016) Graphene in photocatalysis: a review. Small 12(6):6636–6660
24. Ge M, Li S, Huang J, Zhang K, Al-Deyab SS, Lai Y (2015) TiO$_2$ nanotube arrays loaded with reduced graphene oxide films: facile hybridization and promising photocatalytic application. J Mater Chem A 3:3491–3499
25. Li Q, Li X, Wageh S, Al-Ghamdi AA, Yu J (2015) CdS/graphene nanocomposite photocatalysts. Adv Energy Mater 5:1500010
26. Bhosale RR, Pujari SR, Muley GG, Patil SH, Patil KR, Shaikh MF, Gambhire AB (2014) Solar photocatalytic degradation of methylene blue using doped TiO$_2$ nanoparticles. Sol Energy 103:473–479
27. Alsawat M, Althali T, Gulati K, Santos A, Losic D (2015) Synthesis of carbon nanotube–nanotubular titanias composites by catalyst-free CVD Process: insights into the formation mechanism and photocatalytic properties. ACS Appl Mater Interfaces 7:28361–28368