Enhanced Photocatalytic Performance of ZnO through Coupling with Carbon Materials

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Photocatalytic degradation of organic pollutants is an effective way to overcome environmental pollution. During the past few years, carbon materials have demonstrated great potential to improve photocatalytic performance of ZnO nanomaterials. This review will comment on recent developments of carbon materials (including fullerene, carbon nanotube, graphene) coupling to improve photocatalytic performance of ZnO for photodegradation of organic pollutants. The effects of carbon materials on enhancing photocatalytic performance of ZnO include enhancing structure stability, increasing amounts of active sites of pollutant adsorption, boosting electron acceptor formation and transport, enhancing photosensitization, narrowing band gap, etc. Moreover, basic mechanisms how carbon materials enhance photocatalytic activity of ZnO materials are discussed according to the interaction between ZnO and carbon materials. Finally, concluding remarks and current challenges are highlighted with perspectives for future developments of ZnO-based carbon photocatalysts. This review aims at recent research advances on ZnO-based carbon photocatalysts developed for photocatalysis of organic contaminant degradation.

Keywords ZnO, photocatalysis, carbon materials, coupling, organic pollutants

Introduction

With marching of industrialization, environmental pollution becomes more and more serious, especially organic pollutants in water.[1-3] Various physical, chemical and biological treatments have been used to remove the organic pollutants.[4-6] Since 1972, Fujishima and Honda[7] observed the phenomenon of photoelectrochemical water splitting on semiconductor-based photocatalysts, the photocatalysis technology has been regarded as one of the promising ways to resolve organic pollutants. The basic requirement of photocatalysis is light absorption of photocatalysts. For instance, ZnO,[8-10] TiO2,[11,12] CdS,[13] ZnS,[14,15] SrTiO3,[16] BiOCl[17] can be excited by light to excite electron (e-) in the conduction band and leave a hole (h+) in the valence band, which in turn triggers photoredox reaction.

Zinc oxide (ZnO), as an important photocatalyst, has received much attention due to its excellent properties such as low cost, high redox potential, nontoxicity, and environmental friendliness.[18-22] ZnO has wide band gap (3.37 eV) and large exciton binding energy (60 meV).[23] Therefore, the main drawback that restricts its application is its fail to absorb visible light (~43% of solar spectrum), only absorbing UV light (~4% of solar spectrum).[24] The fast recombination of photogenerated electron-hole pairs also decreases the photocatalytic activity of ZnO. During the past decades, great efforts have been devoted to improving ZnO to extend the response into visible-light domain and suppress the recombination of electron-hole pairs,[25-31] such as doping metals or nonmetals,[34,35] depositing noble metals, constructing heterojunctions[36, etc. Recently, coupling carbon materials (for example, fullerene, carbon nanotube, graphene) with ZnO has been reported successfully for improving the photocatalytic performance of ZnO.[37-41] However, until now, few reviews focus on ZnO-based carbon photocatalysts. This paper affords recent developments on photocatalytic applications of ZnO-based carbon composites. The carbon materials include fullerene (C60), carbon nanotube, and graphene. The growing interests of ZnO-based carbon composites are evidenced by increasing number of relevant publications from 2012 to 2016 (Figure 1). The statistics of publications reflect that carbon materials play an important role in the research area of nanoscience. This review aims particularly at recent research developments on ZnO-based carbon composites to further develop effective photocatalysts for degradation of organic pollutants.

Figure 1 Statistics of papers published year by year relevant to ZnO-based carbon composites. Data analysis is based on the Web of Science as of January 2017.
Mechanisms of ZnO photocatalysis

Figure 2 shows the mechanism of photocatalytic degradation of organic pollutants by ZnO nanoparticles. The photocatalytic process occurs when ZnO is irradiated by the light with the energy equal to or greater than the band gap energy of ZnO. The absorption of light will cause charge carriers separation, and the excited electrons ($e^-$) transfer from the valence band (VB) to the conduction band (CB), and the holes ($h^+$) are left in the VB.[42] Then, the charge-carriers ($e^-$ and $h^+$) will move to the surface of ZnO nanoparticles. However, this process is unavoidably along with the unwanted recombination of electrons and holes, which will reduce the quantum yield of the charge carriers.[43,44] The active electrons and holes arriving at the ZnO surface will take part in reduction and oxidation reactions of common aqua solutions to produce hydroxyl radicals (•OH) and superoxide anion radicals (•O$_2^-$), respectively. Finally, the highly reactive radical groups (•OH, •O$_2^-$) will oxidize dye pollutant molecules contained in solution.

Coupling carbon materials

The photocatalytic performance of ZnO can be improved by coupling with carbon materials such as fullerene, carbon tube and graphene (Figure 3), which can serve as a photoelectron reservoir to store and shuttle the photogenerated electrons from ZnO to substrates, or act as photosensitizer just like an organic dye.[45-50] Fullerene (C$_{60}$) has received great interests by researchers due to its unique electronic and structural properties. C$_{60}$ contains a conjugated $p$ orbital system, which is beneficial for electron transfer in the photocatalytic process. Moreover, C$_{60}$ has superior electron conductivity, which also contributes to photon-energy conversion.[51-53] Compared with pure ZnO, ZnO-C$_{60}$ composites not only extend the absorbance in the visible light region, but also increase the absorption intensity of ZnO-C$_{60}$ composites with increase of C$_{60}$ loading amounts, particularly, from 0.5% to 1.5% (Figure 4A). The light absorbance of ZnO-C$_{60}$ composites at the wavelength of 600 nm changes with the mass ratio of ZnO-C$_{60}$ composites (the inset of Figure 4A).[54] Compared with pure ZnO, ZnO-C$_{60}$ composites possess a higher photocatalytic activity for degradation of methylene blue (MB) (Figure 4B).[54] The most optimum condition appears at the C$_{60}$ loading amount 1.5% with the rate constant 0.0569 min$^{-1}$, which is 3 times higher than that of pure ZnO (0.0188 min$^{-1}$). The enhanced photocatalytic activity of ZnO-C$_{60}$ composite is due to the high migration efficiency of photoexcited charge carriers across the interface of C$_{60}$ and ZnO. The high migration efficiency is attributed to the strong interaction between ZnO and C$_{60}$ for the conjugative $p$ orbital system of C$_{60}$. Furthermore, C$_{60}$ can be easily adsorbed on the ZnO surface, which will protect the oxygen vacancies on the ZnO surface from the ZnO corrosion by O$_2$ in solution. Therefore, C$_{60}$ adsorption will inhibit ZnO photocorrosion and step up the photostability of ZnO.
Carbon nanotube (CNT), with one-dimensional (1D) structure, is a potential candidate for anchoring semiconductor particles to construct high efficient CNT-based photocatalysts.[55-59] Previous works have confirmed that combining CNT with ZnO is an efficient way to enhance photocatalytic performance.[60-63] Because of the flexible sp²-hybridized conjugated bonding structure, the 1D CNT has roomy molecular orbital and ultrafast and long distance electron transport capability for storing and shuttling electrons. The special property will bust the recombination of photogenerated electron-hole pairs.[55,64] Moreover, the improved photocatalytic performance of ZnO-CNT results from improving dispersion of photocatalysts and increasing exposure of more active sites.[65] Because adsorbed CNT can alter the band structure of ZnO, CNT can also act as a photosensitizer to sensitize ZnO. For example, multi-walled CNT (MWCNT) modified ZnO exhibits visible light photocactivity for photodegradation of MB.[32] Figure 5A shows that the MB degradation rate constant is 0.00387 mol min⁻¹ for ZnO-MWCNT composites under visible light irradiation, whereas the photodegradation of MB is not observed for pure ZnO at the same condition. This photocatalysis result is consistent with the UV-DRS results (Figure 5B), and the MWCNT modification expands the visible light response of ZnO. Under UV-irradiation (Figure 5C), the rate constant of ZnO-MWCNT composites is much higher (0.01445 min⁻¹) than that of pure ZnO (0.00286 min⁻¹). Figure 5D shows the proposed photocatalytic mechanism.[66] Under visible light irradiation, MWCNT absorbs visible irradiation and transfers the photogenerated electron into the conduction band of ZnO. The organic dye was degraded on the ZnO surface, and the positively charged CNTs removed an electron from the valence band of ZnO and left a hole. Under UV light irradiation in the ZnO-MWCNT composites, the photogenerated electrons from ZnO move toward MWCNT and leave holes remain in ZnO valance band. The possibility of e⁻-h⁺ pair recombination is reduced, and the photocatalytic activity of MB degradation is enhanced under UV light.

Graphene (GR) sheets, with two-dimensional (2D) structures, are used as coupling materials to anchor semiconductors for constructing effective photocatalysts with high solar energy conversion.[67,78] Due to excellent properties of GR, wide range of researches have been performed to hybridize GR with ZnO to enhance its photocatalytic performance.[79-81] Figure 6A shows photocatalytic degradation of MB over GR, blank ZnO, mechanical mixture of ZnO/GR and ZnO-GR composite (graphene 2.0 wt%) under UV light irradiation, which demonstrates that ZnO-GR composites have the highest photocatalytic activity.[45] From Figure 6B, it can be seen that graphene sheets are not perfectly flat but have some wrinkles. The tight adsorption between ZnO and graphene makes electronic interaction possible and improves separation efficiency of photo-induced electrons and holes, which is verified by photocurrent measurement. Figure 6C indicates that the photocurrent of graphene hybridized ZnO is about 3.5 times higher than that of pure ZnO. The enhanced photocatalytic activity of ZnO-GR composite is due to the coupling of GR and ZnO, which can promote photon-generated carrier separation and increase life time of photo-induced e⁻-h⁺ pairs, or suppress charge carrier recombination (Figure 6D). Additionally, the presence of GR in the ZnO-GR composite could enhance adsorption affinity toward MB, which also contributes to improvement of photocatalytic activity of ZnO-GR composite.[62-85] Consequently, the improvement of photocatalytic activity of ZnO-GR composites is also attributed to other factors such as raising the amount of electron acceptor and transport channel, increasing specific surface area of reactive sites, increasing light harvesting, and so on.[73,75,86-88]
Figure 6  (A) The rate constant of MB photodegradation under UV light on graphene, ZnO, mechanical mixture of ZnO and graphene (2.0 wt%), and the ZnO-GR (graphene 2.0 wt%) composite. (B) TEM images of ZnO-GR composite (2.0 wt%). (C) Photocurrent transient responses of ZnO and ZnO-GR electrodes. (D) Charge transfer mechanism of ZnO-GR composite under UV light irradiation.\[45\]

Conclusions and outlook

ZnO-based carbon composites are promising photocatalysts to photodegrade organic pollutants. Carbon materials including C_{60}, carbon tube, and graphene for improving photocatalytic performance of ZnO are comprehensively overviewed. A systematical understanding of the effects of carbon materials on enhancing the performance of ZnO photocatalysts for photodegradation of organic pollutants is summarized, for example, how to enhance structure stabilities, increase active adsorption sites, rise amounts of electron acceptor and transport channel, improve photosensitization, narrow the band gap, and so on. The basic mechanism behind the effects is discussed according to electron interaction between ZnO and carbon materials. Compared with CNTs, GR has some advantages in photocatalysis. Firstly, the theoretical specific surface area of GR is much higher than that of CNTs, resulting in more adsorption centers and active centers on the surface of GR. Secondly, the 2D structure of GR can assure better dispersion of ZnO nanoparticles on its surface in comparison with 1D CNTs. Thirdly, electrical conductivity and electron mobility of GR are much higher than that of CNTs due to flatter extended π-aromatic structure of GR, which is beneficial for electron capture and migration during photocatalytic process. Compared with CNTs and GR, C_{60} is excellent electron acceptors and electron donors, which enrich functionality of carbon materials in photocatalysis. Despite great accomplishment has demonstrated extraordinary potential of ZnO-based carbon composites in the field of photocatalytic degradation of organic pollutants, big challenges is still remained. It is expected that further progress in understanding properties and applications of carbon modified ZnO nanomaterials will be accelerated in coming years.

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References

[1] Gogate, P. R.; Pandit, A. B. Adv. Environ. Res. 2004, 8, 501.
[2] Low, J.; Yu, J.; Ho, W. J. Phys. Chem. Lett. 2015, 6, 4244.
[3] Wang, Y.; Li, T.; Bie, S.; Qi, K.; Cao, Z.; Zhang, K.; Wu, S.; Wang, D. Int. J. Hydrog. Energy 2016, 41, 276.
[4] Liu, M.; Xu, J.; Cheng, B.; Ho, W.; Yu, J. Appl. Surf. Sci. 2015, 332, 121.
[5] Dong, F.; Wu, L.; Sun, Y.; Fu, M.; Wu, Z.; Lee, S. C. J. Mater. Chem. 2011, 21, 15171.
[6] Martinen, S. K.; Kettunen, R. H.; Sormunen, K. M.; Soimiasuo, R. M.; Rintala, J. A. Chemosphere 2002, 46, 851.
[7] Fujishima, A.; Honda, K. Nature 1971, 238, 37.
[8] Liu, T.; Li, Y.; Zhang, H.; Wang, M.; Fei, X.; Duo, S.; Chen, Y.; Pan, J.; Wang, W. Appl. Surf. Sci. 2015, 357, 516.
[9] Wu, C. Appl. Surf. Sci. 2014, 319, 237.
[10] Sankal, R. T.; Shinde, S. S.; Mahadik, M. A.; Mohite, V. S.; Waghmode, T. R.; Govindwar, S. P.; Rajpure, K. Y.; Bhosale, C. H. Journal of Photochemistry and Photobiology B: Biology 2012, 114, 102.
[11] Qi, K.; Zasada, F.; Piskorza, W.; Indyka, P.; Gryboś, J.; Trochowski, M.; Buchalska, M.; Kobielus, M.; Macyk, W.; Soja, Z. J. Phys. Chem. C 2016, 120, 5442.
[12] Schneider, J.; Matsushita, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D. W. Chem. Rev. 2014, 114, 9919.
[13] Yu, J.; Yu, Y.; Zhou, P.; Xiao, W.; Cheng, B. Appl. Catal. B: Environ. 2014, 156–157, 184.
[14] Hong, Y.; Zhang, J.; Huang, F.; Zhang, J.; Wang, X.; Wu, Z.; Lin, Z.; Yu, J. J. Mater. Chem. A 2015, 3, 13913.
[15] Baran, T.; Wojtyla, S.; Dibenedetto, A.; Arena, M.; Macyk, W. Appl. Catal. B: Environ. 2015, 178, 170.
[16] Plaza, M.; Huang, X.; Ko, J. Y. P.; Shen, M.; Simpson, B. H.;
Improving Photocatalytic Performance of ZnO

General Chemistry

Rodríguez-López, J.; Ritzert, N. L.; Letchworth-Weaver, K.; Gunceler, D.; Schlom, D. G.; Arias, T. A.; Brock, J. D.;Abrutha, H. D. J. Am. Chem. Soc. 2016, 138, 7816.

[11] Li, C.; Cao, J.; Lin, H.; Wang, Y.; Chen, S. Mater. Lett. 2016, 166, 267.

[18] Chen, X.; Zhai, Y.; Li, J.; Fang, X.; Fang, C.; Xu, W.; Wei, Z.; Wang, X. Appl. Surf. Sci. 2014, 319, 216.

[27] Zhang, H.; Zhu, J.; Qian, L.; Wu, G.; Xu, J.; Zhu, J. Chem. Eng. Chem. 2016, 2, 31.

[29] Liu, S.; Chen, Z.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J.

P. Sci. 2015, 335, 98.

[50] Guo, Y.; Lin, S.; Li, X.; Liu, Y.

[47] Cao, S.; Yu, J.

[46] Bai, X.; Wang, L.; Zhu, Y.

[22] Cheng, J.; Zhang, H.; Zhu, J.; Qian, L.; Lu, Q.; Wu, G.; Xu, J.; Zhu, J. Gen. Chem. 2016, 2, 31.

[25] Calzolari, A.; Ruini, A.; Catellani, A.

[26] Liu, X.; Huang, W.; Cheng, H.; Huang, B.; Bai, D.; Fu, F.; Wu, H.; Li, L.

[31] Rehman, S.; Ullah, R.; Butt, A. M.; Gohar, N. D.

[20] Jing, W.; Qi, H.; Shi, J.; Jiang, Z.; Zhou, F.; Cheng, Y.; Gao, K. Appl. Surf. Sci. 2015, 355, 403.

[35] Shi, R.; Yang, P.; Song, X.; Wang, J.; Che, Q.; Zhang, A.

[34] Shrivastav, A.; Gupta, R. K.; Singh, P.; Tripathi, R. M.; Bhadwal, A. S.

[50] Liu, S.; Chen, Z.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J.; Yang, M.-Q.; Weng, B.; Xu, Y.-J.

[49] Yang, M.-Q.; Weng, B.; Xu, Y.-J. Mater. Ch. A 2014, 2, 1710.

[48] Yang, M.-Q.; Weng, B.; Xu, Y.-J. Mater. Chem. A 2014, 2, 1710.

[50] Liu, S.; Chen, Z.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. Phys. Chem. C 2013, 117, 8251.

[51] Qi, K.; Selvaraj, R.; Al Fahdi, T.; Al-Kindy, S.; Kim, Y.; Wang, G.-C.; Tai, C.-W.; Sillanpää, M. Appl. Surf. Sci. 2016, 387, 750.

[52] Guldik, D. M. Chem. Commun. 2000, 321.

[53] Jens Czerny, P. B.; Martinj M. Wienk, Rene A. J. Janssen Chem. Mater. 2006, 18, 5832.

[54] Fu, H.; Xu, T.; Zhu, S.; Zhu, Y. Environ. Sci. Technol. 2008, 42, 8064.

[55] Kauffman, D. R.; Star, A. Angew. Chem., Int. Ed. 2008, 47, 6550.

[56] Gooding, J. J. Electrochem. Acta 2005, 50, 3049.

[57] Kada, K.; Furuya, S.; Watanabe, K. Phys. Rev. B 2001, 63.

[58] Hasoboe, T.; Fukuzumi, S.; Kamal, P. Angew. Chem. 2006, 118, 769.

[59] Hu, Y. H.; Ruckenstein, E. Chem. Phys. Lett. 2006, 425, 306.

[60] Saleh, T. A.; Gondal, M. A.; Dmrosn, Q. A.; Yamani, Z. H.; Al-yamani, A. Chem. Eng. J. 2011, 166, 407.

[61] Mohamed, R. M.; Abdel Salam, M. Mater. Res. Bull. 2014, 50, 85.

[62] Liu, P.; Guo, Y.; Xu, Q.; Wang, F.; Li, Y.; Shao, K. Ceram. Int. 2014, 40, 5629.

[63] Dai, K.; Dawson, G.; Yang, S.; Chen, Z.; Lu, L. Chem. Eng. J. 2012, 191, 571.

[64] Weng, B.; Liu, S.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. J. Appl. Mater. Interfaces 2014, 6, 8560.

[65] Tripathy, N.; Ahmad, R.; Kul, H.; Lee, D. H.; Hahn, Y.-B.; Khang, G. J. Photochem. Photobiol. B: Biol. 2016, 161, 312.

[66] Yu, J.; Li, C.; Liu, S. J. Colloid Interface Sci. 2008, 326, 433.

[67] Ma, Q. L.; Xiong, R.; Zhai, B.-g.; Huang, Y. M. Appl. Surf. Sci. 2015, 324, 842.

[68] Rehman, S.; Ullah, R.; Butt, A. M.; Gohar, N. D. J. Hazard. Mater. 2009, 170, 560.

[69] Wang, B.; Liu, S.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. Appl. Surf. Sci. 2015, 355, 403.

[70] Yang, S.; Wang, J.; Li, X.; Zhai, H.; Han, D.; Wei, B.; Wang, D.; Yang, J. J. Appl. Surf. Sci. 2014, 319, 211.

[71] Son, D. I.; Kwon, B. W.; Yang, J. D.; Park, D. H.; Angadi, B.; Choi, W. K. J. Mater. Chem. 2012, 22, 816.

[72] Shi, R.; Yang, P.; Song, X.; Wang, J.; Che, Q.; Zhang, A. Appl. Surf. Sci. 2016, 366, 506.

[73] Guo, Y.; Lin, S.; Li, X.; Liu, Y. Appl. Surf. Sci. 2016, 384, 83.

[74] Sudheer Khan, S. J. Photochem. Photobiol. B: Biol. 2015, 142, 1.

[75] Yu, J.; Ma, T.; Liu, G; Cheng, B. Dalton Trans. 2011, 40, 6635.

[76] Ameen, S.; Shaheer Akhtar, M.; Seo, H.-K.; Shik Shin, H. Mater. Lett. 2013, 100, 261.

[77] Zhou, X.; Shi, T.; Zhou, H. Appl. Surf. Sci. 2012, 258, 6204.

[78] Wang, J.; Tsuzuki, T.; Tang, B.; Hou, X.; Sun, L.; Wang, X. ACS Appl. Mater. Interfaces 2012, 4, 3084.

[79] Fan, H.; Zhao, X.; Yang, J.; Shan, X.; Yang, L.; Zhang, Y.; Li, X.; Gao, M. Catal. Commun. 2012, 29, 29.

[80] Gupta, S. M.; Tripathi, M. Chin. Sci. Bull. 2011, 56, 1639.

[81] Kadam, A.; Dhabhe, R.; Gophane, A.; Sathe, T.; Garadkar, K. J. Photochem. Photobiol. B: Biol. 2016, 154, 24.

[82] Tripathi, R. M.; Bhadwal, A. S.; Gupta, R. K.; Singh, P.; Shrivastav, A.; Shrivastav, B. R. J. Photochem. Photobiol. B: Biol. 2014, 141, 288.

[83] Xu, T.; Zhang, L.; Cheng, H.; Zhu, Y. Appl. Catal. B: Environ. 2011, 101, 382.

[84] Bai, X.; Wang, L.; Zhu, Y. ACS Catal. 2012, 2, 2769.

[85] Cao, S.; Yu, J. J. Photochem. Photobiol. C: Photochem. Rev. 2016, 27, 72.

[86] Yang, M.-Q.; Weng, B.; Xu, Y.-J. Mater. Chem. A 2014, 2, 10549.

[87] Liu, S.; Chen, Z.; Zhang, N.; Tang, Z.-R.; Xu, Y.-J. Phys. Chem. C 2013, 117, 8251.