Int. J. Electrochem. Sci., 12 **(2017)** 448 – 454, doi: 10.20964/2017.01.05

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Role of rGO on Structural, Optical, and Photocatalytic Properties of Cu_2O/rGO

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Received: 8 September 2016 / *Accepted:* 12 October 2016 / *Published:* 12 December 2016

The composite photocatalysts composed of Cu_2O and reduced graphene oxide (rGO) were prepared using a simple chemical method. The SEM, XRD and Raman spectrum indicate that graphene is well loaded to the surface of Cu_2O. The UV-vis DRS spectra results reveal that the Cu_2O had absorbed more visible light by recombination with graphene. The PL intensity of pure Cu_2O is decreased by the loading with rGO. The BET of pure Cu_2O is enhanced 3.6 times via the loading with rGO. The obtained Cu_2O/rGO composites exhibit higher photocatalytic activity that is 4.32 times larger than that of Cu_2O. The enhanced photocatalytic property of the rGO/ Cu_2O composites is ascribed to the increasing of charge transfer and specific surface area.

Keywords: Photocatalyst, Cuprous oxide, Graphene, Visible light

1. INTRODUCTION

With industrial development, environmental pollution problem is becoming more and more serious [1]. Over the past period of time, the semiconductor compounds have used to degrade organic pollutants, such as TiO_2, ZnO, BiOCl, and so on [2-6]. However, these semiconductor compounds have a large band gap, resulting in the ineffective utilization of the solar energy. Therefore, much research have been focused on the semiconductor compounds with a narrow band gap, for instance, $BiPbO_2Cl$ [7], $BiVO_4$ [8], Cu_2O [9], Bi_2WO_6 [10,11], and $BiLa_{1.4}Ca_{0.6}O_{4.2}$ [12]. Among the compounds, cuprous oxide (Cu_2O) is a bright red inorganic semiconductor compound with a band gap of 2.4 eV [9], which may be an effective photocatalyst for visible light. Nevertheless, pure Cu_2O has low photocatalytic activity owing to its less adsorptive performance, low conductivity and fast electron-hole recombination. In order to solve these problems, several studies have been performed regarding the composition of Cu_2O and other materials, for example, Ni/Cu_2O [13], Cu/Cu_2O [14], BiOCl/Cu_2O [15], Cu_2O/CuO [16], rGO/Cu_2O [17].

As a member of the carbon family, graphene, is a single layer of sp^2 hybridized carbon atoms, has large specific surface area, fast electron transportation, exceptional thermal conductivity, and excellent optical transmittance [18]. The conjugation of semiconductor compounds with graphene can effectively increase the separation rate of holes and electrons, the specific surface area, the adsorption capacity for pollutants [19]. Wang et al. [20] showed that the compound of $BiVO_4$ and graphene has improved photocatalytic activity, which was caused by the construction of excellent rGO/$BiVO_4$ interfaces.

Here, a new composition of Cu_2O and reduced graphene oxide (rGO) has been prepared by a simple chemical method, which displays superior photocatalytic activity of organic dye degradation. The effects of rGO on the micro-morphology, structure, optical properties, and photocatalytic properties of Cu_2O are studied. The photocatalytic property of Cu_2O is increased by combining with rGO.

2. EXPERIMENTAL

2.1. Synthesis of Cu_2O/rGO

The Cu_2O/rGO composites were prepared via a simple chemical method. 1g Cu_2O and 0.01g graphene oxide were dispersed for 2 hours in 50 mL deionized water and 50 mL ethyl alcohol respectively. After that, the above two solutins were mixed together. Moreover, Na_2SO_3 was put in the mixing solution (0.1 mol/L) as a reducing agent, and then stirred continuously for 6 hours in dark. Then, the suspension was irradiated under 500W high pressure mercury lamp for 8 hours. Finally, the precipitates were collected and washed with deionized water and absolute ethyl alcohol several times, and then heated at 70 ^oC for 12 h.

2.2. Sample characterization

Powder XRD patterns were characterized via a PANalytical X' Pert Pro X-ray diffractometer with Cu Kα radiation (1.54178 Å). The surface micro-morphology of samples was studied using a scanning electron microscopy (SEM) (Model Hitachi S-4800). UV-vis diffuse reflectance spectra of the samples were measured with a Shimadzu UV-3600 Plus. The Raman spectra and photoluminescence emission spectra were characterized on a Horiba Jobin Yvon LabRAM. The Brunauer-Emmett-Teller (BET) specific surface area was measured with a V-Sorb 2800 apparatus.

2.3. Photocatalytic property test

During the experiment, 50 mg catalyst powders were put into 50 mL Rhodamine B (RhB) solution (RhB 20 mg/L), and stirred in the dark for 90 min continuously to establish adsorption/

desorption balance between the photocatalyst and the dye before illumination. The absorption spectra of RhB were measured via a Shimadzu UV-3600 Plus. The photocatalytic properties of the samples were evaluated from the absorption peak (at 553 nm) intensity ratio of the remnant RhB after visible light irradiation to that of the RhB in parent solution.

3. RESULTS AND DISCUSSION

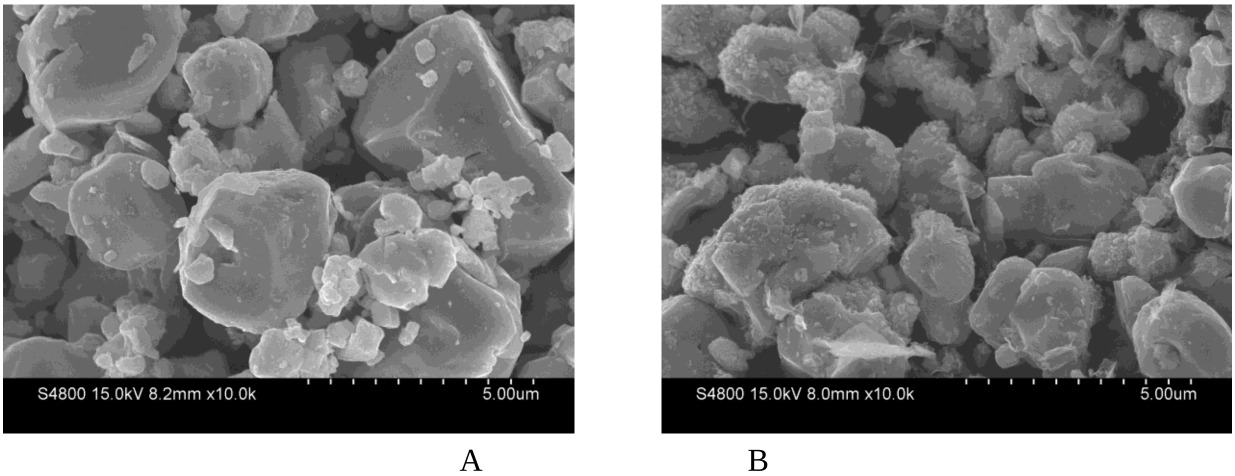


Figure 1. SEM images of Cu_2O (a) and Cu_2O/rGO (b).

The morphologies of Cu_2O/rGO composites are observed by SEM, where SEM morphology of Cu_2O (a) and Cu_2O/rGO (b) is shown in Fig. 1. It is clearly seen in Fig. 1a that the morphology of Cu_2O samples is lumpy, and the length is approximately 3.6 μm. As for Fig. 1b, Cu_2O samples are covered rGO sheet, which means that the addition of graphene tuned the Cu_2O samples and the rGO sheet were well distributed on the surface of Cu_2O samples.

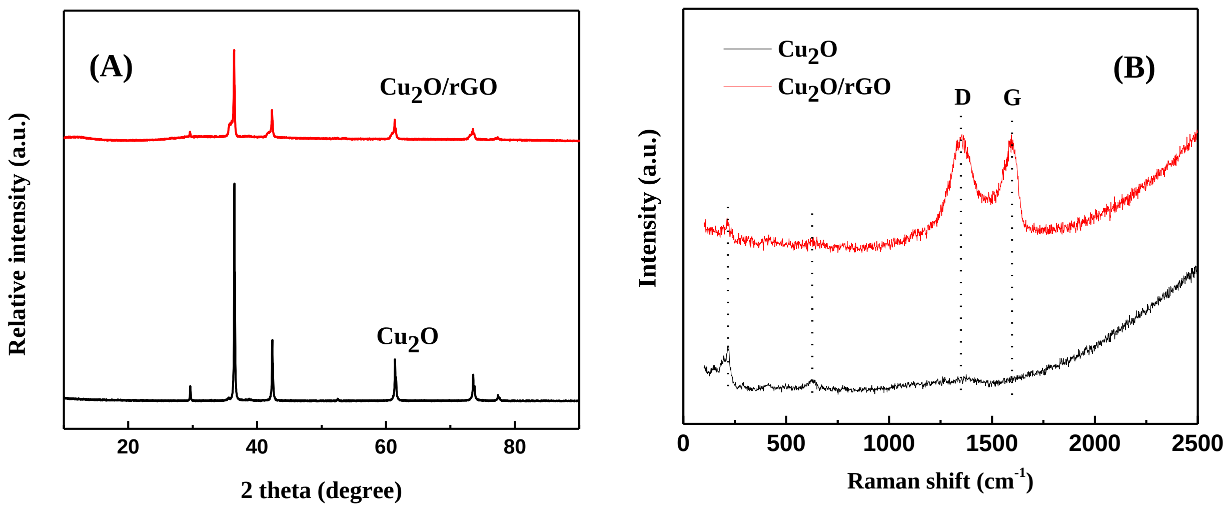


Figure 2. XRD patterns (a) and Raman spectra (b) of samples.

In order to confirm the crystal structure, XRD was conducted on the Cu_2O samples. Fig. 2a shows that the Cu_2O has a cubic phase (JCPDS No.05-0667). The sharp XRD peaks indicate that the crystallinity of Cu_2O is high. The XRD pattern of samples is similar between Cu_2O/rGO composite and Cu_2O, indicating there is no other phase. Raman spectrum is also used to detect the graphene. Fig. 2b shows the Raman spectra of Cu_2O/rGO composite and Cu_2O. From Fig. 2b, one can see that there are more two peaks in Cu_2O/rGO composite with respect to Cu_2O. The two characteristic peaks at 1358 and 1595 cm^{-1}, corresponding to the D band and G band of graphene [21], respectively. The results of SEM, XRD and Raman spectrum indicate that graphene is well loaded to the surface of Cu_2O.

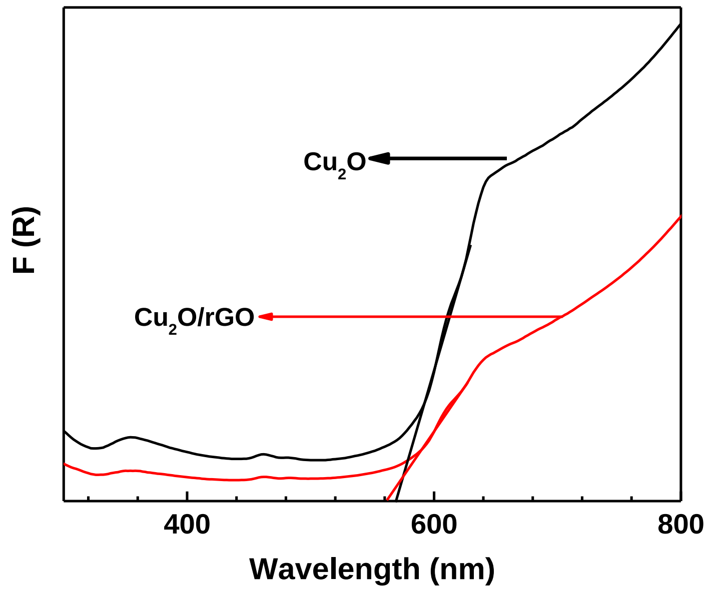


Figure 3. UV-vis DRS of Cu_2O and Cu_2O/rGO.

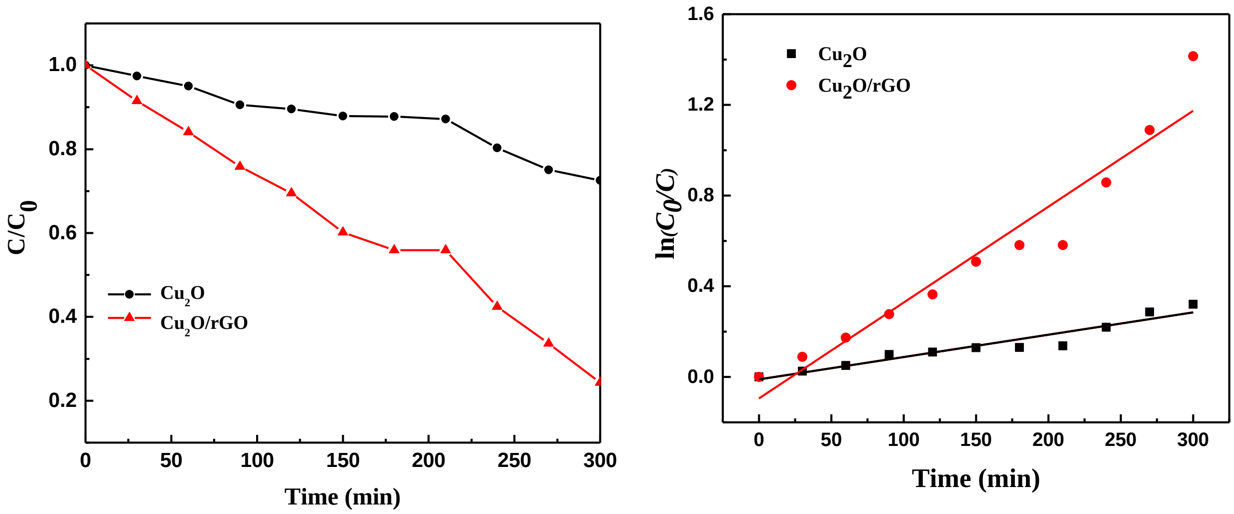


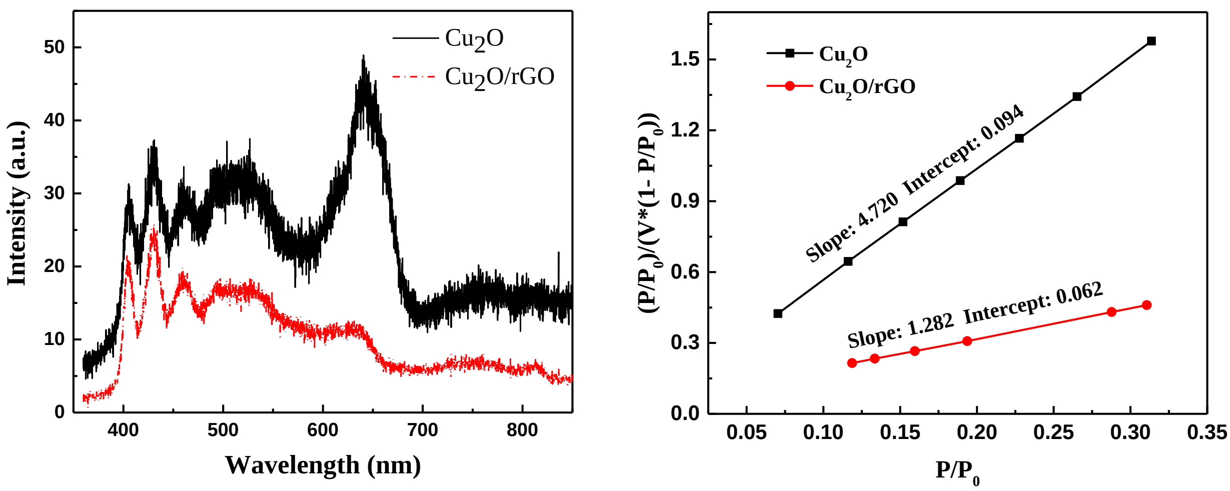
Figure 4. (A) Photocatalytic activites of samples under visible light, (B) The first order Kinetics of degradation of RhB in solution.

UV-vis diffuse reflection spectra (DRS) are applied to describe the optical properties of Cu_2O/rGO composite and Cu_2O (Fig. 3). It is distinct that Cu_2O exhibits an absorption edge at around 570 nm, showing fine absorption of visible light.

For the Cu_2O/rGO composite, the absorption edge slightly red-shifted to about 590 nm, and the light reflection capability in the range of 420-800 nm is also decreased because of the absorption of rGO. However, Cu_2O/rGO composites indicate slightly lower reflection intensities than that of Cu_2O in the visible light region, which is possibly resulted from the addition of the black-body properties of graphite-like materials [22]. Similar result has been presented in other report [23].

The photocatalytic activities of the samples have been performed under the excitation of visible light (Fig. 4a). From Fig. 4a, it is clearly that the photocatalytic property of Cu_2O has been enhanced by the loading with rGO. The reaction kinetics of RhB degradation under visible light was carried out to display the removal rates by the photocatalysts. Fig. 4b presents photocatalytic reaction kinetics of RhB degradation in solution. From Fig. 4b, the RhB removal rate over Cu_2O/rGO composite (0.00423 min^{-1}) is about 4.32 times of the Cu_2O (0.00098 min^{-1}).

In order to understand the reason for increasing of photocatalytic activities, we measured the room temperature photoluminescence (PL) emission spectra (Fig. 5a) and specific surface area (BET) (Fig. 5b) of the Cu_2O and Cu_2O/rGO composite. A lower PL intensity is usually representative of a lower recombination rate of photo-generated charge carriers [24]. From Fig. 5a, the PL spectra of the samples exhibit emission peaks in the 400-750 nm range under the excitation at 320 nm, the PL intensity of pure Cu_2O is decreased by the loading with rGO, indicating that the Cu_2O/rGO composite have lower recombination rate of photo-generated hole and electron. On the other hand, after the Cu_2O is covered by rGO, the specific surface area is improved by 3.6 times, which increases from 0.90 m^2/g to 3.24 m^2/g [25].



A **B**

Figure 5. Photoluminescence emission spectra (a) and BET (b) of samples.

On the base of above results, there are three reasons for the enhancing of samples. Firstly, due to the excellent electron mobility of graphene, photo-generated electrons in the excited Cu_2O can be transferred to the rGO surface, which results in effective separation of photo-electron and hole [23]. Secondly, in Cu_2O/rGO, the charge transfer and the specific surface area are improved, which lead to the enhanced photocatalyst activity. Lastly, the Cu_2O had absorbed more visible light by recombination with graphene.

4. CONCLUSION

In summary, Cu_2O/rGO composites were prepared with a simple chemical method. The results of SEM, XRD and Raman spectrum indicate that graphene is well loaded to the surface of Cu_2O. The UV-vis DRS shows that Cu_2O/rGO composites show slightly lower reflection intensities than that of Cu_2O in the visible light region. The PL intensity of pure Cu_2O is decreased by the loading with rGO. The BET of pure Cu_2O is enhanced 3.6 times via the loading with rGO. Compared to Cu_2O, the photocatalytic property of the Cu_2O/rGO composite is improved as large as 4.32 times. The improved photocatalytic property of the rGO/ $BiPbO_2Cl$ composites is ascribed to the increasing of charge transfer and specific surface area.

ACKNOWLEDGEMENTS
This work is partly supported by the National Natural Science Foundation of China (Grants No. 51572183), Zhejiang Provincial Natural Science Foundation of China (Grant No. LQ14E020004), Zhejiang Province Education Department Scientific Research Projects (Grant No. Y201533230). Zhejiang Provincial Key Laboratory for Cutting Tools (Grant No. ZD201303).

References

1. R.A. He, S.W. Cao, P. Zhou, J.G.Yu, *Chinese J. Catal.*, 35 (2015) 989.
2. Q.C. Xu, J.X. Zeng, X.Y. Li, J. Xu, X.Y. Liu, *RSC Adv.*, 6 (2016) 51888.
3. J.G. Yu, and X.X. Yu, *Environ. Sci. Technol.*, 42 (2008) 4902.
4. K.L. Zhang, C.M. Liu, F.Q. Huang, C. Zheng, W.D. Wang, *Appl. Cataly. B: Environ.*, 68 (2006) 125.
5. A. Y. Booshehri, S.C.-K. Goh, J.D. Hong, R.G. Jiang, R. Xu, *J. Mater. Chem. A*, 2 (2014) 6209.
6. Y.B. Wang, J.D. Hong, W. Zhang, R. Xu, *Catal. Sci. Technol.*, 3 (2013) 1703.
7. W.W. Zhong, D.D Li, S.F. Jin, W.J. Wang, X.A. Yang, *Appl. Surf. Sci.*, 356 (2015) 1341.
8. S.W. Cao, Z. Yin, J. Barber, F.Y.C. Boey, S.C. J. Loo, and C. Xue, *ACS Appl. Mater. Interfaces*, 4 (2012) 418.
9. M. Hara, T. Kondo, M. Komodo, S. Ikeda, J.N. Kondo, K. Domen, K. Shinohara and A. Tanaka, *Chem. Commun.*, 3 (1998) 357.
10. S.C. Zhang, C. Zhang, Y. Man, Y.F. Zhu, *Journal of Solid State Chemistry*, 179 (2006) 62.
11. H.B. Fu, C.S. Pan, W.Q. Yao, Y.F. Zhu, *J. Phys. Chem. B*, 109, (2005)22432.
12. W.W. Zhong, Y.F. Lou, S.F. Jin, W.J. Wang, L.W. Guo, *Scientific Reports*, 6 (2016) 23235.
13. X.L. Li, Y.J. Ma, Z. Yang, S.S. Xue, L.M. Wei, D. Huang, T. Wang, N.T. Hu, and Y.F. Zhang, *Dalton Transactions*, 45 (2016) 7258.

14. T.Y. Kou, C.H. Jin, C. Zhang, J.Z. Sun, Z.H. Zhang, *RSC Adv.*, 2 (2012) 12636.
15. C.H. Cao, L. Xiao, C.H. Chen, Q.H. Cao, *Appl. Surf. Sci.*, 357 (2015) 1171.
16. H.G. Yu, J.G. Yu, S.W. Liu, S. Mann, *Chem. Mater.*, 19 (2007) 4327.
17. X.Q. Liu, Z. Li, W. Zhao, C.X. Zhao, Y. Wang, and Z.Q. Lin, *J. Mater. Chem. A*, 3 (2015) 19148.
18. S. Chowdhury, R. Balasubramanian, *Appl. Cataly. B: Environ.*, 160-161 (2014) 307.
19. Y.H. Zhang, B. Shen, H.W. Huang,Y. He, B. Fei, F.Z. Lv, *Appl. Surf. Sci.*, 319, (2014) 272.
20. T. Wang, C.J. Li, J.Y. Ji, et al., *ACS Sustainable Chem. Eng.*, 2 (2014) 2253.
21. A. Chunder, T. Pal, S. I. Khondaker, and L. Zhai, *J. Phys. Chem. C*, 114 (2010) 15129.
22. E. Gao, W. Z. Wang, M. Shang and J. H. Xu, *Phys. Chem. Chem. Phys.*, 13 (2011) 2887.
23. Y. Zhou, X.J. Zhang, Q. Zhang, F. Dong, F. Wang, and Z. Xiong, *J. Mater. Chem. A*, 2 (2014) 16623.
24. J. Jiang, K. Zhao, X.Y. Xiao, and L.Z. Zhang, *J. Am. Chem. Soc.*, 134 (2012) 4473.
25. Y.F. Zhou, K. Bi, L. Wan, X. Ji, C. Wen, K. Huang, C. Liang, Z.B. Sun, D.Y. Fan, H.J. Yang, Y.G. Wang, M. Lei, *Mater. Lett.*, 154 (2015) 132.