Graphene covered SiC powder as advanced photocatalytic material

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Graphene covered SiC powder (GCSP) has been fabricated by well established method of high temperature thermal decomposition of SiC. The structural and photocatalystic characteristics of the prepared GCSP were investigated and compared with that of the pristine SiC powder. Under UV illumination, more than 100% enhancement in photocatalystic activity is achieved in degradation of Rhodamine B (Rh B) by GCSP catalyst than by pristine SiC powder. The possible mechanisms underlining the observed results are discussed. The results suggested that GCSP as a composite of graphene based material has great potential for use as a high performance photocatalyst. © *2012 American Institute of Physics*. [doi:10.1063/1.3676042]

Graphene, a novel two dimensional material, has intrigued enormous research interests[1–4] owing to its fascinating physical properties such as the existence of massless Dirac fermions[1] and the observation of quantum hall effect[2,5] since its discovery in 2004.[6] Meanwhile, another research branch on graphene based nano heterogeneous composite materials is rapidly expanding in the field of materials science recently to explore interesting photocatalystic materials.[7–10] For example, Zhang *et al.* reported the synthesis of graphene-P25 TiO_2 composites and showed their enhanced photocatalysis for degradation of methylene blue in aqueous solutions.[10] Among the researches, graphene acts as electron conductive channels to separate the photogenerated charge carriers and, consequently, to enhance the corresponding photocatalytic activity. However, it should be noted that the compositions of graphene and relevant photocatalyst are synthesized through physical or chemical methods where contact of photocatalyst and graphene is randomly happened on partial surface of the catalyst and photogenerated carrier transfer is critically depending on the synthesizing method and procedure.[7–10]

SiC is a harmless environment-friendly material, remarkable for its very high physical and chemical stability and very large difference between its conduction band and the chemical potential of the redox systems, which renders SiC an outstanding photocatalystic activity.[11,12] On the other hand, epitaxial graphene on SiC wafer has been rapidly progressing recently since SiC offers an exclusive choice for graphene potential applications such as RF devices[4,13] and IC systems.[14] An enormous amount of research has been concerning on growth mechanisms,[15,16] structural,[17,18] and electronic characteristics[19–21] of graphene grown on SiC wafers. However, graphene covered SiC powder (GCSP) or grains, as a micro-size graphene-SiC heterojunction powder, has not reported on its structural nor photocatalystic characteristics. GCSP as a composite of graphene and SiC, prepared by high temperature thermal annealing as used in growing graphene on SiC wafer, possesses heterojunction interface between inner SiC and outer graphene layers. On the exposed SiC facets, the graphene layers are continuously covered on the outer surface of SiC powder. Especially on the exposed Si-face facets, the neighboring carbon layer (usually named as buffer layer) is covalently bonding with the SiC.[21–23] Thus, photogenerated electrons in conduction band of SiC are more efficiently transferring to graphene through the near perfect heterojunction interface, which facilitates separation of electrons and holes in space and leads to an enhanced photocatalytic activity. Therefore, the GCSP is completely different from the reported graphene based heterogeneous composite materials. In this letter, we report the photocatalytic characteristics of GCSP by showing the degradation of Rh B in aqueous solution, which is a popular used dye for studying photocatalystic activity of a material.[24] An enhancement more than 100% in photocatalytic degradation of Rh B was observed using the GCSP under UV light irradiation compared with the pristine SiC powder. The results indicate that the GCSP as a photocatalystic material has potential for photocatalystic applications ascribed to its high performance photocatalystic activity, relatively mature fabrication method, and low cost of pristine SiC powder.

In a typical run, the GCSP is synthesized by high temperature annealing SiC powder at about 1600 °C under pressure of 10^{-3} Pa for about 10 min. Before fabrication of GCSP, n-type 6H-SiC powder of 150-300 mesh (in size about 60-120 μm, TankeBlue, Beijing) was carefully cleaned according to a standard degrease cleaning process for semiconductor wafer by using acetone, ethanol, and deionized water in sequence. Then, the SiC powder was heated to 130 °C in a bake oven over night to remove the absorbed water on the surface of the SiC powder. After the cleaning process, SiC powder was loaded into a graphite crucible and put them together into the furnace for GCSP fabrication. Finally, the heater was turned off and the samples were allowed to cool down to room temperature naturally.

The obtained GCSP was characterized and analyzed by using field emission scanning electron microscopy (SEM) for surface morphology, high-resolution Raman scattering

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spectra for checking typical scattering peaks of the graphene (Raman spectrometer is HR800 with a 532 nm laser focused to a spot with diameter about 1 μm), and optical absorption spectrum for monitoring the photocatalytic activities of the as-prepared GCSP under UV light irradiation emitted from a 150 W high-pressure Hg lamp.

To test the photocatalytic activities of the as-prepared GCSP, 0.1 g of the as-prepared GCSP was dispersed into 100 mL Rh B aqueous solution (0.02 mM). Prior to photocatalytic reactions, the suspension was vigorously stirred in the dark for 15 min, which was long enough to make the Rh B aqueous solution approach a stable absorption equilibrium to the dark ambience. The GCSP sample was then irradiated by UV light at room temperature and ambient pressure, while keeping the solution stirred. Blank experiments at the same conditions show that no photocatalystic activity is observed in the absence of catalyst or light irradiation. During UV light irradiation, about 3 mL of the suspension was taken out from the reaction cell at a given time intervals in sequence for subsequent analysis of target dye concentration after centrifuging. The photocatalytic activity of GCSP is evaluated from the intrinsic absorption band (centered at 552 nm) intensity ratio of the remnant Rh B after UV light illumination to that of the initial Rh B under the dark condition. The photocatalytic activity of the prinstine SiC powder was also tested under the same conditions as a reference.

Morphologies of the GCSP and the pristine SiC powder were analyzed by SEM as shown in Fig. 1. No discernible difference is observed in low magnified SEM images of Fig. 1(a) for pristine SiC powder and Fig. 1(b) for GCSP. However, a clear difference is observed in the magnified SEM images of Figs. 1(c) and 1(d). There are wrinkles on the surface of GCSP as shown in Fig. 1(d), which are usually observed on graphene grown on SiC surface[25,26] due to the large difference in thermal expansion coefficient between epitaxial graphene layers and SiC. Close examination of Fig. 1(d) reveals that the wrinkles are continuously curved across the SiC step edges. It thus can be indicated that the graphene layers are continuously covering on the SiC surface without interruption, which is similar to the case in graphene grown on a SiC substrate.[25]

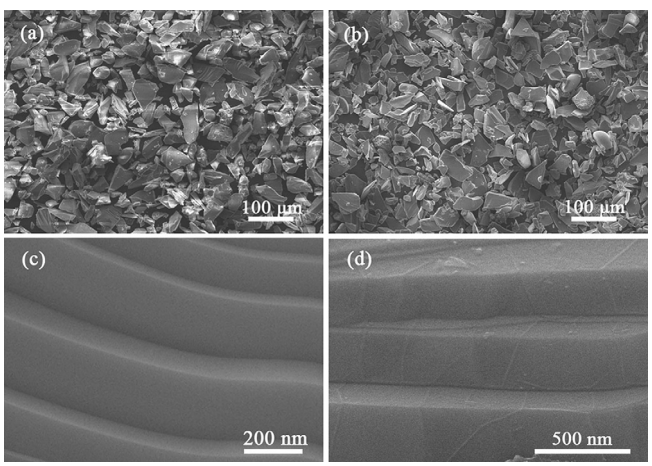

FIG. 1. SEM images of pristine SiC powder (a), Graphene covered SiC heterojunction powder (b), as well as magnified SEM images of SiC powder (c), and GCSP (d).

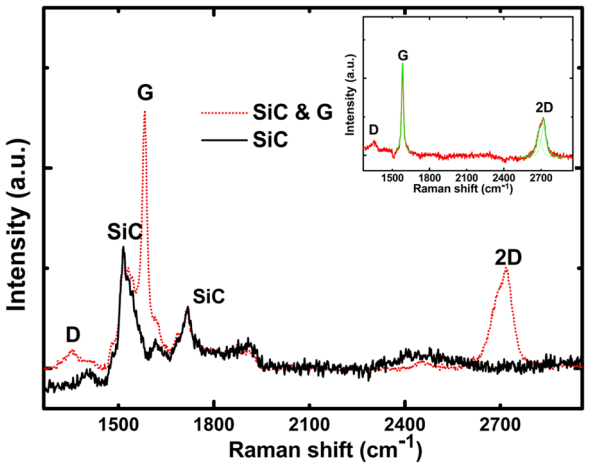

FIG. 2. (Color online) Raman spectra of pristine SiC powder (solid line) and GCSP (dotted line). The inset is Raman signal of graphene after subtracting SiC's signal from GCSP.

The observed graphene layers are further confirmed by Raman scattering measurement. Fig. 2 shows the Raman scattering spectra of the pristine SiC powder and GCSP as presented by the solid and dot dashed curves, respectively. Raman fingerprint peaks of graphene, D, G, and 2D peaks are well identified located at 1353, 1582, and 2716 cm^{-1} on the curve of the GCSP. The weak D peak indicates few structural defects exist in the graphene. To determine the intensity ratio of the G and 2D peaks, we subtract the signal due to SiC from the measured Raman signal of GCSP. The inset of Fig. 2 shows the Raman signal of graphene. According to the intensity ratio of G and 2D peaks, number of the graphene layers is estimated to be about 5-6 layers.

The photo-degradation of Rh B was employed to evaluate the photocatalytic activities of the GCSP and the pristine SiC powder. The characteristic absorption band of Rh B at 552 nm is chosen as the monitoring parameter. Fig. 3 shows the absorption spectrum of the Rh B aqueous solution after different photocatalytic degradation durations in the presence of pure SiC powder (Fig. 3(a)) and GCSP (Fig. 3(b)). It is seen that the main absorption peak of Rh B at 552 nm is monotonically decreased with increasing irradiation time in the existence of the two kinds of photocatalysis materials. However, it is noted that the absorption peak intensity decrease even faster in presence of GCSP catalyst than in pristine SiC powder catalyst. As the UV exposure time approaches to 2.5 h, the absorption peak of Rh B disappeared completely in presence of GCSP catalyst, while remaining 30% intensity in presence of the pristine SiC powder. The result indicates graphene covered on the SiC surface improves and enhances the photocatalystic activity of the SiC powder.

The relative remnant concentration of the partly degradated Rh B aqueous solution under various UV irradiation durations is summarized in Fig. 4. The figure and the inset give the relative remnant concentration variation in linear and natural logarithmic form versus irradiation time, respectively. The relationship of $\ln(c/c_0)$ versus irradiation time fits 1st order reaction well, i.e., $\ln(c/c_0) = -k_i t$, where c is the remnant concentration of degraded Rh B, c_0 is the initial concentration of

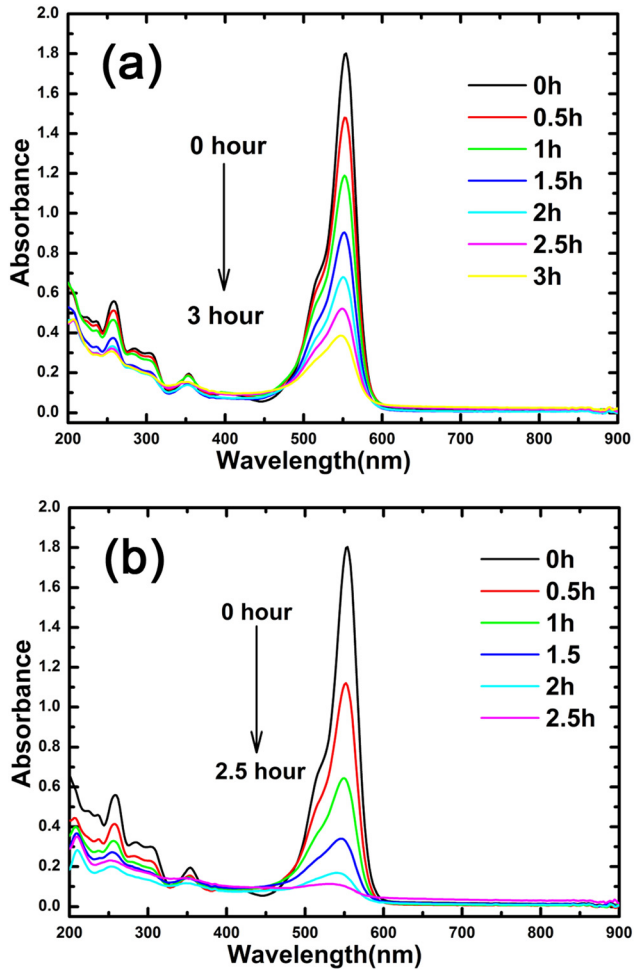

FIG. 3. (Color online) Absorption spectra of Rh B after different photo degradation durations by SiC powder (a) and GCSP (b).

Rh B, t is the irradiation time, and k_i is the photocatalystic reactive rate constant. The lower index i in k_i is 1 or 2 corresponding to rate constant of GCSP or SiC powder, respectively. It is inferred from the inset that the rate constant k_1 is 0.021/min and k_2 is 0.008/min, which indicates the degradation rate constant of GCSP is about 2.6 times of that of pristine SiC powder. Clearly, more than 100% improvement in photocatalystic activity is achieved by using GCSP catalyst than pristine SiC powder. In the inset of Fig. 4, it is noted that the data point for irradiation 2.5 h is little deviated from the quasi-linear variation trace. The reason is that the remnant concentration of the degraded Rh B is too low (about 5% of its initial concentration) to be degraded effectively by the catalyst. The phenomena had been observed in other photocatalyst experiment.[27]

The enhanced photocatalytic activity of the GCSP could be schematic illustrated by Fig. 5. Under UV illumination, the photons are absorbed majorly by SiC inside of the GCSP and scarcely by graphene layers outside of the GCSP, because band gap of the 6H-SiC is about 3.0 eV (corresponding to an absorption edge about 410 nm) and optical absorption of the few-layer graphene is less than 15% since a monolayer graphene absorption is about 2.3% to the irradiated light no mater what wavelength the irradiated light is. Accompanying the absorption of photons by SiC, electrons (e^-) are excited from the valance band (VB) to the conduction band (CB) of SiC, remaining holes (h^+) in the VB. In

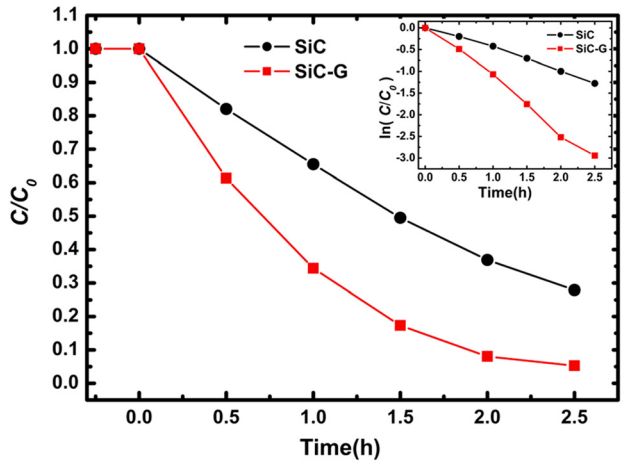

FIG. 4. (Color online) The relative remnant concentration of the partly degradated Rh B versus irradiation duration. The inset is the natural logarithm of the ratio between the remnant concentration and the initial concentration of Rh B versus irradiation time.

the absence of the graphene layers, most of these excited electrons recombine quickly with holes. Usually, only a small portion of electrons or holes participate in the photocatalytic reactions,[28] resulting in low reactivity. It is know that the electron affinity of 6 H-SiC is about 3.45 eV (Ref. 29) and electron work function of graphene is about 4.5 eV,[30] taking vacuum level as a reference. The large difference between conduction band of SiC and Fermi level of graphene allows quick transferring of the photogenerated electrons from SiC to graphene, avoiding recombination of electrons and holes in SiC. Furthermore, the perfect hererojunction interface and large contact area between SiC and graphene result in a strong coupling between SiC and graphene, which also benefits the photogenerated carrier transfer. The advantages of GCSP are well supported by the enhanced photocatalytic activity of GCSP than pristine SiC powder as shown in Fig. 4. We attributed the advantages of the GCSP to the perfect combination of graphene and SiC, where interface contact is completely different from that of the graphene based nano heterogeneous materials which is becoming one of the hot topics of materials physics currently,[7–10] where surface of nano particles is partly contacted with graphene through van der Waals force or other interactions and the contact coupling critically depends on synthesized technique and procedure. These important structural and energy band

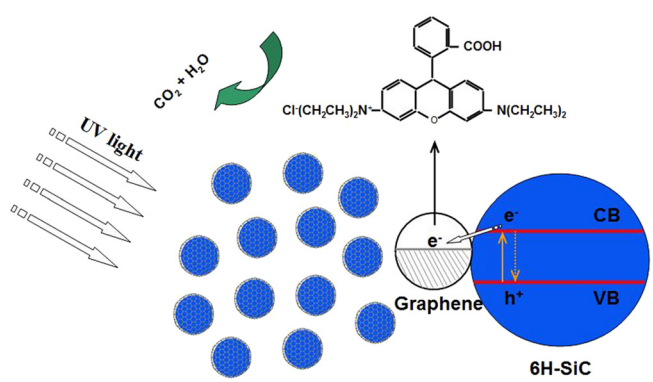

FIG. 5. (Color online) Schematic mechanism of photocatalystic process of GCSP for degradation of Rh B.

properties of the GCSP, combined with the graphene's advantages of high carries mobility and strong absorption to other molecules together, make the GCSP have great potential in photocatalystic applications. We believe that further decreasing SiC powder size (increasing redox reactive surface) and optimizing graphene layers will render the GCSP an outstanding photocatalyst activity.

In summary, we have synthesized graphene covered SiC heterojunction powder by high temperature thermal annealing. This composite of heterogeneous material shows an over 100% improvement in photocatalystic activity compared with that of its parent SiC powder. The great enhancement in photocatalystic activity is ascribed to the advantageous carrier transferring in this unique structured material. Our results suggest that GCSP has great potential for use as a photocatalystic material.

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[1]K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature **438**, 197 (2005).
[2]Y. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim, Nature **438**, 201 (2005).
[3]E. McCann, Phys. Rev. B **74**, 161403(R) (2006).
[4]Y. W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett **97**, 216803 (2006).
[5]K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, and A. K. Geim, Science **315**, 1379 (2007).
[6]K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science **306**, 666 (2004).
[7]K. K. Manga, Y. Zhou, Y. Yan, and K. P. Loh, Adv. Funct. Mater. **19**, 3638 (2009).
[8]Q. Xiang, J. Yu, and M. Jaroniec, J. Phys. Chem. C **115**, 7355 (2011).
[9]Y. Liang, H. Wang, H. S. Casalongue, Z. Chen, and H. Dai, Nano Res. **3**(10), 701 (2010).
[10]H. Zhang, X. Lv, Y. Li, Y. Wang, and J. Li, ACS Nano **4**, 380 (2010).
[11]T. Inoue, A. Fujishima, S. Konishi, and K. Honda, Nature **277**, 637 (1979).
[12]B. R. Eggins, P. K. J. Robertson, E. P. Murphy, E. Woods, J. T.S. Irvine, J. Photochem. Photobiol. A: Chem. **118**, 31 (1998).
[13]J. S. Moon, D. Curtis, M. Hu, D. Wong, C. McGuire, P. M. Campbell, G. Jernigan, J. L. Tedesco, B. VanMil, R. Myers-Ward, C. Eddy, Jr., and D. K. Gaskill, IEEE Electron Devices Lett. **30**, 650 (2009).
[14]Y. M. Lin, A. Valders-Garcia, S. J. Han, D. B. Farmer, I. Meric, Y. Sun, Y. Wu, C. Dimitrakopoulos, A. Grill, P. Avouris, and K. A. Jenkins, Science **332**, 1294 (2011).
[15]H. Huang, W. Chen, S. Chen, and A. T. S. Wee, ACS Nano **2**, 2513 (2008).
[16]M. Hupalo, E. H. Conrad, and M. C. Tringides, Phys. Rev. B **80**, 041401(R) (2009).
[17]L. B. Biedermann, M. L. Bolen, M. A. Capano, D. Zemlyanov, and R. G. Reifenberger, Phys. Rev. B **79**, 125411 (2009).
[18]S. Tanaka, K. Morita, and H. Hibino, Phys. Rev. B **81**, 041406(R) (2010).
[19]T. Ohta, A. Bostwick, T. Seyller, K. Horn, and E. Rotenberg, Science **313**, 951 (2006).
[20]V. W. Brar, Y. Zhang, Y. Yayon, T. Ohta, J. L. McChesney, A. Bostwick, E. Rotenberg, K. Horn, and M. F. Crommie, Appl. Phys. Lett. **91**, 122102 (2007).
[21]F. Varchon, R. Feng, J. Hass, X. Li, B. N. Nguyen, C. Naud, P. Mallet, J. Y. Veuillen, C. Berger, E. H. Conrad, and L. Magaud, Phys. Rev. Lett. **99**, 126805 (2007).
[22]A. Mattausch and O. Pankratov, Phys. Rev. Lett. **99**, 076802 (2007).
[23]K. V. Emtsev, F. Speck, Th. Seyller, and L. Ley, Phys. Rev. B **77**, 155303 (2008).
[24]H. Fu, C. Pan, W. Yao, and Y. Zhu, J. Phys. Chem. B **109**, 22432 (2005).
[25]Z. G. Cambaz, G. Yushin, S. Osswald, V. Mochalin, and Y. Gogotsi, Carbon **46**, 841 (2008).
[26]W. Norimatsu, J. Takada, and M. Kusunoki, Phys. Rev. B **84**, 035424 (2011).
[27]J. Du, X. Lai, N. Yang, J. Zhai, D. Kisailus, F. Su, D. Wang, and L. Jiang, ACS Nano **5**, 590 (2011).
[28]N. Serpone, D. Lawless, R. Khairutdinov, and E. Pelizzetti, J. Phys. Chem. **99**, 16655 (1995).
[29]S. Y. Davydov, Semiconductors **41**, 696 (2007).
[30]G. Giovannetti, P. A. Khomyakov, G. Brocks, V. M. Karpan, J. van den Brink, and P. J. Kelly, Phys. Rev. Lett. **101**, 026803 (2008).