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Bipolar Carrier Transfer Channels in Epitaxial Graphene/ SiC Core-Shell Heterojunction for Efficient Photocatalytic **Hydrogen Evolution**

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Various nanosized semiconductors combined with a noble metal have been explored to develop highly efficient photocatalytic materials for hydrogen production.^[1,2] Because of limited metal resources and potential harmful effects on the environment and human health, graphene has been selected as a potential alternative to noble metals as a cocatalyst to improve the performance of semiconductor photocatalysts.^[3-6] Such application of graphene stems from its remarkable advantages for hydrogen generation by water splitting, which, in turn, are a consequence of its excellent carrier transport properties and its reduction potential being more negative than that of noble metals. However, few examples of graphene-assisted photocatalysts that match or surpass the performance of noble-metalassisted photocatalysts have been reported.[1,2,6,7] Therefore, graphene is suspected to be an effective cocatalyst instead of noble metals, although a large amount of researches are still in progress based on the wet chemical preparation of graphene (WCG) such as reduced graphene oxide (RGO), which exhibit properties that differ substantially from the intrinsic properties of graphene.^[8–10] To obtain a clearer understanding, epitaxial graphene (EG) has advantages over WCG to reveal intrinsic properties of graphene as a highly efficient cocatalyst for hydrogen evolution. Thermal decomposition on surface of SiC single-crystal wafer is a mature technique to prepare EG with great potential applications in high-performance graphene-based devices.^[10,11] By application of this method to SiC

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particles, graphene-covered SiC particles (GCSPs), where graphene is intimately wrapped around an SiC particle to form a stable core-shell heterojunction structure with a controllable graphene layer in the shell, has been developed.^[8,9]

Here, in situ EG growth on the surface of micrometer-sized SiC particles was used to demonstrate EG as an advanced cocatalyst for efficient H₂ evolution, where the GCSP possesses a perfect heterointerface between the EG and SiC. In addition, the quality and purity of the EG are obviously high compared to that of the CG.^[10] Therefore, GCSP is an ideal platform for exploring the intrinsic properties of graphene as a cocatalyst. In this paradigm, a high hydrogen evolution rate of 472.4 μ mol g⁻¹ h⁻¹ was achieved using the GCSP under a xenon light source illumination corresponding to a half AM-1.5 solar irradiation. The photocatalytic activity of the optimized GCSP exceeded the corresponding activity observed on pristine SiC particles by more than 33 times and that observed on optimized Ptdecorated SiC particles by more than four times. To the best of our knowledge, this activity is the highest enhancement factor observed for graphene as a sole cocatalyst, which confirms that graphene is superior to noble metals as a cocatalyst.^[1,2,6,7] The unusual enhancement of hydrogen evolution by our GCSP is due to the high graphene quality and, more importantly, the perfect graphene/SiC interface where the tunable energy bandmatching configuration induces both electron and hole transfer channels on the single core-shell structured particle. Our paradigm demonstrates that graphene has the potential to replace noble metals as a cocatalyst and that the GCSP is a superior metal-free eco-friendly photocatalyst for hydrogen evolution.

The parent material used in the present work is commercial 6H-SiC powder, which has a band gap (E_{α}) of $\approx 3 \text{ eV}$ with a conduction band edge (≈-1.5 V vs normal hydrogen electrode (NHE)) more negative than that of most photocatalysts, which most likely facilitates the reduction of H⁺.^[12,13] A detailed characterization of the SiC powder was performed using X-ray diffraction (XRD) and Raman scattering (Figures S1 and S2, Supporting Information). According to our previous study,^[9] the GCSPs, which consisted of two sizes and two graphene thicknesses, were chosen to test their photocatalytic performance for hydrogen evolution. These materials are ≈ 5 and 1–3 µm powders derived from \approx 5 and \approx 0.5 µm SiC powders, respectively; their scanning electron microscopy (SEM) images are shown in Figure 1a-f. At high temperature, the rough SiC particles become smooth and the small-sized particles tend to merge into large ones to decrease the surface energy.^[14,15] As the particle size decreased, the particles were more easily merged. The 0.5 µm particles were







Figure 1. a-c) SEM images corresponding to the pristine SiC, GCSP-L, and GCSP-M particles that are $\approx 5 \ \mu m$ in size and d-f) corresponding to 0.5 μm pristine SiC, GCSP-L, and GCSP-M particles derived from 0.5 μm SiC. g) The mechanism for the transformation from the pristine SiC particle to GCSP.

nearly fused into balls $\approx 1 \ \mu m$ in diameter and further coalesced into even larger clusters (Figure 1e,f). Because of the loss of Si atoms and the reconstruction of the C atoms, the annealed SiC particles were tightly wrapped with fewer than three layers of smooth graphene (referred to as GCSP-L) or with 4–9 layers of smooth graphene (referred to as GCSP-M) to form nearly perfect core–shell-type heterojunctions. This structure was confirmed by X-ray photoelectron spectroscopy and Raman spectroscopy (Figures S3–S5, Supporting Information). Figure 1g schematically illustrates how the pristine SiC particle developed into GCSP.

Their Raman spectra (Figures S4 and S5, Supporting Information) indicated that nearly all of the GCSP samples exhibited a weak D peak. The mean intensity ratio (I_D/I_G) between the D and G peaks was ≈ 0.13 .^[9] much smaller than the ratios typically reported for CG, which tend to be 1 or greater.^[16-20] This result indicates that our graphene contained few defects. In addition, the EG growth process helped to reduce the occurrence of interfacial defects that typically act as recombination centers and decrease the photocatalytic performance.^[21] This behavior was indicated by the steepened absorption edges (Figure S6, Supporting Information) and narrowed photoluminescence band (Figure S7, Supporting Information) compared to that of the pristine SiC. This perfect core-shell heterojunction can efficiently separate the photogenerated carriers, as confirmed by the decreased photoluminescence compared to that of the pristine SiC (Figure S7, Supporting Information) and by the improved photocurrent and photoconductance.^[9]

To achieve a high efficiency carrier separation and transportation, both electron and hole channels are required on each

photocatalytic particle to sustain charge conservation. Nevertheless, this condition is difficult to achieve in common core-shell composites because of the fixed energy configurations. Thus, relatively low photocatalytic activities are usually achieved.^[21,22] Fortunately, unlike general materials, the work function of graphene is susceptibly affected by the polarity of the substrate as well as by the graphene defects, strain, morphology, and environment.^[23-30] Here, the surface of the SiC particle is a series of continuous facets that possess substantially different polarization fields, which would result in EG with different doping compared to that observed in graphene grown on differently oriented SiC substrates.^[27,28] Furthermore, the graphene grown on the same facet usually exhibits substantial fluctuation in its work function, sometimes leading to opposite doping.^[11,29,30] A charge-doping map of EG grown on an Si face of SiC (Figure S8, Supporting Information) confirms that opposite charge doping (bipolar charge) regions coexist on the same surface. These factors, coupled with the complex morphology and possible defects in our GCSP, result in bipolar doping in the graphene shell, as schematically shown in Figure 2a. In addition, the SiC particle is considered undoped compared to doped SiC in binding energies (Figure S3, Supporting Information),^[31] its Fermi level nearly equals to the Dirac point of graphene.^[12,32] In this case, two inverse energy band configurations of the Schottky junction would be created between the graphene and SiC, which would serve as the transfer channels for photogenerated electrons and holes because of the built-in potential (V_{bi}) and the Schottky barrier height (f_{SBH}), as shown in Figure 2b,c. This differs from that of typical core-shell composites. Therefore, we anticipate that GCSP may significantly





Figure 2. Schematic energy band diagrams of graphene and the SiC heterojunction a) before equilibration, b) after equilibration, and c) under UV illumination, where the interface field at the p (n)-doped graphene/SiC interface results in a hole (electron) transfer channel on top (bottom). The E_C , E_V , E_{FSIC} , and E_{FG} are the edges of the conduction band, edges of the valence band, the Fermi level of SiC, and the Fermi level of graphene, respectively.

improve the photocatalytic performance of pristine SiC for hydrogen evolution.

To confirm this concept, the H_2 evolution reactions were performed under a xenon light source illumination corresponding to a half AM-1.5 solar irradiation using GCSPs and related SiC materials as photocatalysts with/without sacrificial reagents. In pure water, the GCSPs exhibit H_2 evolution ability clearly, and no discernible H_2 was evolved over SiC particles (**Figure 3**a,b). With Na₂S/Na₂SO₃ as sacrificial reagents, the low energy holes were effectively consumed, which further reduced the electron–hole recombination. Therefore, the H₂ evolution rates of GCSPs were substantially enhanced and much higher than that of pristine SiC and even optimized Pt/SiC composites containing an ~0.2 wt% of Pt loading on SiC via photodeposition (Figure 3c,d).^[33] The highest rate of 472.4 µmol g⁻¹ h⁻¹ was obtained in the case of 5 µm GCSP-M; this rate is high compared to the rates observed for some popularly used nanocatalysts such as TiO₂- and CdS-based composites.^[3,6,22,34,35]



Figure 3. Time profiles of H₂ evolution in 100 mL of deionized water over 100 mg of photocatalyst consisting of pristine SiC particles and GCSPs derived from a) 5 and b) 0.5 μ m SiC particles (the dashed lines show the linear fits) and in a 0.1 mmol L⁻¹ Na₂S/Na₂SO₃ aqueous solution over pristine 6H-SiC particles, GCSPs and 0.2 wt% Pt/SiC derived from c) 5 and d) 0.5 μ m SiC particles under xenon lamp illumination (\approx 50 mW cm⁻²).

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Figure 4. Schematics of the Schottky bands of GCSPs with thinner (left) and thicker (right) graphene layers under UV illumination in Na₂S/Na₂SO₃ solution, where E_{eb} is the equivalent field induced by the specific adsorbed anions that results in a shift in E_{FG} and E_{FSiC} (yellow lines) from the equilibration level (gray dashed line) and the flat band potential of SiC; corresponding changes in $T_{i(i = e, h)}$ were observed.

These results suggest that H_2 evolution can be greatly improved if the micrometer-sized GCSP is reduced to a scale of nanometer size due to contribution of increased specific surface area. Notably, in Figure 3, irrespective of the presence or absence of sacrificial reagents, the H_2 evolution over the catalysts derived from the 0.5 µm SiC particles was at least one time lower than that of the 5 µm catalysts, which is a consequence of the poor crystal quality of the 0.5 µm SiC particles confirmed by XRD measurement (Figure S1, Supporting Information). The poor quality of the SiC particles results in more recombination centers for photogenerated carriers. In addition, differing with the performance of the catalysts in pure water, the H_2 evolution rates significantly increased with EG thickness when sacrificial reagents were added as shown in Figure 3c,d.

To gain insight into the mechanism of H₂ evolution over GCSP as a function of the EG thickness in the presence of sacrificial reagents, the interaction between ions and the potential configuration was considered. The photogenerated carriers that are transferred from SiC to graphene rely on the following potential: $T_{i(i = e, h)} = E_g/e + V_{bi} - f_{SBH}$. According to the law of charge conservation, the smaller value between T_e and T_h in weighted average determines the actual total efficiency of the carrier transfer. Thus, the case of $T_{\rm e}$ and $T_{\rm h}$ approaching equilibrium will favor improved photocatalytic performance. In pure water, they are nearly fixed (because $V_{\rm bi}$ and $f_{\rm SBH}$ are only dependent on the work function difference between SiC and graphene) and should be near equal in probability if the graphene is not intended doped (but a low H₂ evolution activity is because the transferred holes are hardly captured and consumed by OH- without sacrificial reagent that breaks charge conservation). Therefore, GCSP-Ls and GCSP-Ms exhibit similar performances.

However, with scavengers, strong specific adsorption of S^{2-} and SO_3^{2-} induces a preferential change at the energetic configurations of the bipolar channels. Specifically, it may

be equivalent to adding a negative bias to the Schottky junction, which results in a downward shift of the flat band corresponding to SiC and an upward shift for the Fermi level and Dirac point of graphene.^[36] Thus, an increase (decrease) in $V_{\rm bi}$ and a decrease (increase) in f_{SBH} occur at the p (n)-doped EG/ SiC interface, and the electrons (holes) transferring potential $T_{\rm e}$ ($T_{\rm h}$) is reduced (enhanced) (Figure 4). When less EG layers are involved in the bias division, a more substantial variation in T_i occurs. As the EG thickness was limited increased, because of the constant adsorptive surface, the changes were moderate and nearer to equilibrium. Therefore, GCSP-M with thicker EG exhibits greater activity than GCSP-L in an Na2S/Na2SO3 solution. However, the activity will decrease in the case of GCSP with more thicker EG because of the evident buffering of incident-light and carriers transportation, which has been previously confirmed by our group.^[9]

Because the activity of GCSP is strongly affected by the EG thickness in the Na₂S/Na₂SO₃ solution, a more homogeneous EG thickness should further promote H₂ production. By optimizing the EG homogeneity of GCSP-M derived from 0.5 µm SiC, we obtained GCSP-Mo, and ≈95% of the EG was concentrated in 4–8 layers, which is ≈27% improvement in graphene homogeneity compared to GCSP-M (Figure 5a). Correspondingly, the H₂ evolution rate over GCSP-Mo increased by \approx 33% compared to GCSP-M (Figure 5b). The quantum efficiency (QE) of ≈5.6% was determined under irradiation with 380 nm light (Figure S9, Supporting Information). Speculatively, the QE of 5 µm GCSP-Mo (not prepared) should be ≈11.7% on the basis of the ratio of H₂ evolution over the GCSP-Ms catalysts. They are large values for the micrometer particles, because only the thin surface layer of the SiC particle can effectively participate in the photocatalytic reactions.

In addition to the interface structure, the graphene quality should also significantly affect the photocatalytic efficiency

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Figure 5. a) Dispersions of the EG layer number on GCSP-M and GCSP-Mo. b) Comparison of H_2 evolution over GCSP-M, GCSP-Mo, and GCSP-Mod derived from 0.5 μ m SiC. c) Enhancement factors for H_2 evolution activity over Pt/SiC and GCSPs. d) Continuous reaction test of H_2 evolution over GCSP-Mo.

because of defects such as scattering and/or recombination centers of carriers.^[10] To study the influence of the graphene quality, GCSP-Mod was prepared with the same homogeneity of graphene as GCSP-Mo but poor quality, as indicated by its Raman spectrum (Figure S10, Supporting Information), in which the average I_D/I_G ratio is ≈ 1 . Using Cançado's method,^[18] we estimated the defect densities of graphene in GCSP-Mod and GCSP-M/Mo to be $\approx 10^{11}$ and 10^{10} cm⁻², respectively. Therefore, GCSP-Mod exhibits an H₂ evolution rate that is $\approx 23.5\%$ lower than that of GCSP-Mo (Figure 5b). In comparison to the atom density of graphene ($\approx 4 \times 10^{15}$ cm⁻²), the defect densities are low, therefore, the decrease in the graphene quality has relatively little effect on H₂ evolution.

The enhancement factors of the photocatalytic activity for H₂ evolution over GCSPs and optimized Pt/SiC composites are summarized in Figure 5c. Notably, the rates over 5 and 0.5 μ m Pt/SiC are only \approx 2.8 and \approx 6.1 times greater than the rate over the corresponding pristine SiC. By the same optimization, the Pt/SiC composite reached a factor of ≈15 under other conditions in a previous study.^[33] Nevertheless, GCSP still exhibits better performance, and the enhancement factor of GCSP-Mo is more than 34 (Figure 5d). To the best of our knowledge, this factor is the highest value reported for a solely graphene-based cocatalyst;^[3,5,6] furthermore, this work is the first report of this factor dramatically surpassing those of highly efficient noble-metal cocatalysts. In fact, only a few studies have reported an enhancement factor that only slightly exceeds those of noble metals under the same conditions.^[7,37] In contrast, the optimized RGO/SiC composite improved the activities only by $\approx 30\%$.^[9,38] These results demonstrate that

properly prepared graphene can be a superior cocatalyst compared to noble metals on the basis of price as well as efficiency. In addition, the continuous reaction of GCSP-Mo observed in Figure 5d indicates that the evolution rate only decreased slightly because of the consumption of sacrificial reagents, and the Raman study did not determine a discernible difference between the fresh particles and those soaked in the solution for one month after the reaction, which demonstrates the good stability of GCSP.

In summary, the in situ EG-wrapped SiC particle photocatalyst (GCSP) enhanced the H_2 evolution activity of SiC to a remarkably high value even though the particles are micrometer-sized, and the activity of the GCSP is much higher than that observed for optimized Pt/SiC composites. This impressive performance is primarily due to the perfect EG/SiC coreshell structure including critical bipolar carrier transfer channels based on the matching energetic configuration of the heterojunction, suitable homogeneous graphene thickness, and tight and stable contact at the EG/SiC interface. In addition, the graphene quality also obviously influences the H_2 evolution over the catalyst. Our paradigm strongly suggests that graphene has the potential to replace noble metals as a cocatalyst and that GCSP has the potential to be an efficient, green, and economical photocatalyst for H_2 production.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.





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- [1] X. Zhou, G. Liu, J. Yu, W. Fan, J. Mater. Chem. 2012, 22, 21337.
- [2] F. E. Osterloh, Chem. Mater. 2008, 20, 35.
- [3] G. Xie, K. Zhang, B. Guo, Q. Liu, L. Fang, J. R. Gong, Adv. Mater. 2013, 25, 3820.
- [4] W. Tu, Y. Zhou, Z. Zou, Adv. Funct. Mater. 2013, 23, 4996.
- [5] N. Zhang, Y. Zhang, Y.-J. Xu, Nanoscale 2012, 4, 5792.
- [6] Q. Xiang, J. Yu, M. Jaroniec, Chem. Soc. Rev. 2012, 41, 782.
- [7] J. Zhang, J. Yu, M. Jaroniec, J. R. Gong, Nano Lett. 2012, 12, 4584.
- [8] K. Zhu, L. Guo, J. Lin, W. Hao, J. Shang, Y. Jia, L. Chen, S. Jin, W. Wang, X. Chen, Appl. Phys. Lett. 2012, 100, 023113.
- [9] W. Lu, L. Guo, Y. Jia, Y. Guo, Z. Li, J. Lin, J. Huang, W. Wang, RSC Adv. 2014, 4, 46771.
- [10] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, *490*, 192.
- [11] J. L. Tedesco, B. L. VanMil, R. L. Myers-Ward, J. M. McCrate, S. A. Kitt, P. M. Campbell, G. G. Jernigan, J. C. Culbertson, C. R. EddyJr., D. K. Gaskill, *Appl. Phys. Lett.* **2009**, *95*, 122102.
- [12] V. V. Afanas'ev, M. Bassler, G. Pensl, M. J. Schulz, E. S. von Kamienski, J. Appl. Phys. 1996, 79, 3108.
- [13] T. Inoue, A. Fujishima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637.
- [14] O. Gülseren, F. Ercolessi, E. Tosatti, Phys. Rev. B **1995**, 51, 7377.
- [15] J.-H. Shim, B.-J. Lee, Y. W. Cho, Surf. Sci. 2002, 512, 262.
- [16] A. C. Ferrari, J. Robertson, Phys. Rev. B 2000, 61, 14095.
- [17] D. S. Knight, W. B. White, J. Mater. Res. 1989, 4, 385.

- [18] L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, *Nano Lett.* **2011**, *11*, 3190.
- [19] J. A. Arcibar-Orozco, T. J. Bandosz, J. Mater. Chem. A 2015, 3, 220.
- [20] T. J. Bandosz, S. Wang, D. Minami, K. Kaneko, Carbon 2015, 87, 87.
- [21] S. Bai, J. Ge, L. Wang, M. Gong, M. Deng, Q. Kong, L. Song, J. Jiang, Q. Zhang, Y. Luo, Y. Xie, Y. Xiong, Adv. Mater. 2014, 26, 5689.
- [22] Q. Zhao, M. Ji, H. Qian, B. Dai, L. Weng, J. Gui, J. Zhang, M. Ouyang, H. Zhu, Adv. Mater. 2014, 26, 1387.
- [23] D. Tomer, S. Rajput, L. J. Hudy, C. H. Li, L. Li, Appl. Phys. Lett. 2014, 105, 021607.
- [24] J. E. Lee, G. Ahn, J. Shim, Y. S. Lee, S. Ryu, Nat. Commun. 2012, 3, 1024.
- [25] Md. W. K. Nomani, R. Shishir, G. Tompa, N. Sbrockey, M. G. Spencer, R. A. Webb, G. Koley, *Appl. Phys. Lett.* **2012**, *100*, 092113.
- [26] U. Starke, C. Riedl, J. Phys.: Condens. Matter 2009, 21, 134016.
- [27] C. Riedl, C. Coletti, U. Starke, J. Phys. D: Appl. Phys. 2010, 43, 374009.
- [28] N. Camara, B. Jouault, A. Caboni, A. Tiberj, P. Godignon, J. Camassel, Nanosci. Nanotechnol. Lett. 2011, 3, 49.
- [29] O. Renault, A. M. Pascon, H. Rotella, K. Kaja, C. Mathieu, J. E. Rault, P. Blaise, T. Poiroux, N. Barrett, L. R. C. Fonseca, J. Phys. D: Appl. Phys. 2014, 47, 295303.
- [30] J. Hicks, A. Tejeda, A. Taleb-Ibrahimi, M. S. Nevius, F. Wang, K. Shepperd, J. Palmer, F. Bertran, P. Le Fèvre, J. Kunc, W. A. de Heer, C. Berger, E. H. Conrad, *Nat. Phys.* **2013**, *9*, 49.
- [31] Th. Seyller, K. V. Emtsev, F. Speck, K.-Y. Gao, L. Ley, Appl. Phys. Lett. 2006, 88, 242103.
- [32] H. Hibino, H. Kageshima, M. Nagase, J. Phys. D: Appl. Phys. 2010, 43, 374005.
- [33] J. J. Yang, *Ph.D. Thesis*, University of Science and Technology, Beijing, China **2013**.
- [34] C. Liu, L. Wang, Y. Tang, S. Luo, Y. Liu, S. Zhang, Y. Zeng, Y. Xu, Appl. Catal., B 2015, 164, 1.
- [35] J. Zhang, Z. Zhu, Y. Tang, K. Müllen, X. Feng, Adv. Mater. 2014, 26, 734.
- [36] S. Tongay, M. Lemaitre, X. Miao, B. Gila, B. R. Appleton, A. F. Hebard, *Phys. Rev. X* 2012, 2, 011002.
- [37] L. Ye, Z. Li, Appl. Catal., B 2014, 160, 552.
- [38] J. Yang, X. Zeng, L. Chen, W. Yuan, Appl. Phys. Lett. 2013, 102, 083101.

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