Photoconversion

DOI: 10.1002/anie.200907173

A Structured Macroporous Silicon/Graphene Heterojunction for Efficient Photoconversion**

Hongtao Yu, Shuo Chen, Xinfei Fan, Xie Quan, Huimin Zhao, Xinyong Li, and Yaobin Zhang*

Improvement of conversion efficiency of solar energy to electricity or chemical energy has attracted extensive attention due to the increasing need for clean and renewable energy.[1] Silicon has successfully been applied in photoelectric conversion,[2] but it is difficult to employ Si in converting solar energy to chemical energy due to rapid formation of an insulating oxide layer.[3] This problem could be overcome by coating the surface of Si with a transparent charge collector serving as a protective layer. Noble metals,[4] wide-gap semiconductors,[5] and polymer films were commonly employed as protective layers.[6] The high price (noble metal), relatively low conductivity (wide-gap semiconductor), and limited thermal and chemical stability (polymer) restricted practical application of these materials in conversion of solar to chemical energy.

Graphene (Gr), discovered in 2004,[7] is a promising protective material due to its good stability, extremely high electron mobility, and excellent optical transparency.[8] Moreover, Gr is an ideal two-dimensional ultrathin material with comparatively fewer defects than film constructed from nanoparticles.[9] Thus, it is a favorable material for charge transfer. In fact, Gr has found applications as the electron acceptor in dye-sensitized solar cells and polymer solar cells.[10,11] However, no work has been reported Gr protective layers. We have now built a macroporous Si (MPSi)/Gr heterojunction by depositing Gr on the surface of MPSi and demonstrated that Gr can be used as protective layer for MPSi to improve its ability to convert solar to chemical energy. Macroporous Si was selected as the substrate because it can offer higher surface area and lower reflection than planar Si wafer.

The MPSi was fabricated by chemically etching p-type Si wafer ((100) orientation, 3–4 Ω cm resistivity). The etching electrolyte was composed of 5 M NH_4F and 0.02 M $AgNO_3$. Graphene was obtained in two steps: fabricating graphite oxides by the Hummer method,[12] and then reducing them to Gr by pyrolysis at 1050 °C. To deposit Gr on the surface of MPSi, an MPSi cathode was immersed in a Gr suspension, and electrophoresis was performed. The stable Gr suspension was composed of 0.01 g of Gr, 100 mL of isopropyl alcohol, and 0.005 g of $Mg(NO_3)_2{\cdot}6H_2O$,[13] and the applied voltage and deposition duration of electrophoresis were 160 V and 10 s, respectively. After electrophoresis, annealing was carried out to improve the adhesion between the Gr layer and MPSi.

As shown in Figure 1 a, the longest part of the as-prepared Gr sheets is shorter than 2 μm, and ripples can be observed. The typical thicknesses of the ripples were measured from different sections marked by the rectangular frames in Figure 1 b. According to their line profiles, the average thickness of the ripples is 2.35 nm, which indicates that the sample as prepared is few-layer Gr (4–6 layers). According to Liu et al.,[14] few-layer Gr is less reactive but more stable than monolayer Gr in aqueous solution. Therefore, few-layer Gr is a suitable choice as protective layer.

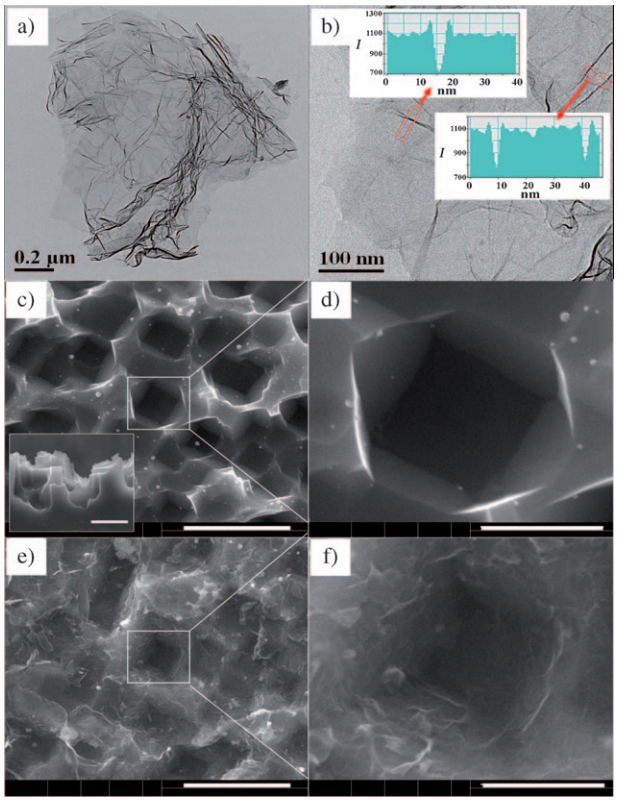

Figure 1. a) TEM image of a typical Gr sheet. b) Magnification of (a) and insets showing line profiles of the rippled parts. c,d) SEM images of MPSi (inset of (c): profile). e,f) SEM images of MPSi/Gr. Scale bars: 10 μm for (c), including its inset, and (e); 3 μm for (d) and (f).

[*] Dr. H. T. Yu, Dr. S. Chen, X. F. Fan, Prof. Dr. X. Quan, Dr. H. M. Zhao, Prof. Dr. X. Y. Li, Dr. Y. B. Zhang
School of Environmental Science and Technology
Key Laboratory of Industrial Ecology and Environmental Engineering (MOE), Dalian University of Technology
Dalian 116024 (P. R. China)
Fax: (+86) 411-8470-6263
E-mail: quanxie@dlut.edu.cn

[**] This work was supported by National Natural Science Foundation of China (No. 20837001, No. 20525723), Education Department of Liaoning Province (No. 2008T224), and Program for Changjiang Scholars and Innovative Research Team in University (IRT0813).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200907173.

The morphologies of MPSi are displayed in Figure 1c and d. After etching, the surface of Si wafer is covered with macropores all over. The size of a macropore is about 3 × 3 μm, and the depths of these macropores are in the range of 10–20 μm (the inset of Figure 1c). The size of these macropores is comparable to that of Gr sheet, which is favorable for close association between Gr sheets and MPSi. Figure 1e and f show the morphology of MPSi/Gr. The MPSi/Gr samples fabricated by depositing Gr on MPSi substrates are clearly different from naked MPSi. The surface of MPSi is covered completely by successive and uniform Gr sheets, while the shape of macropore is retained. With regard to suitable size of the macropores, MPSi is even better than Si-based nanostructures when combined with Gr.

The Raman spectrum recorded from MPSi/Gr (Figure 2a) exhibits five intense bands located at 520, 974, 1339, 1574, and 2669 cm^{-1}. The first two are assigned to the MPSi substrate, while the other bands agree well with the D band, G band, and 2D bands of Gr. In general, the strong D band at 1350 cm^{-1} is activated by intrinsic defects[15] such as vacancies, grain boundaries, or edges. In the present work, the D band comes from the exposed Gr edges, which can be seen in Figure 1f.

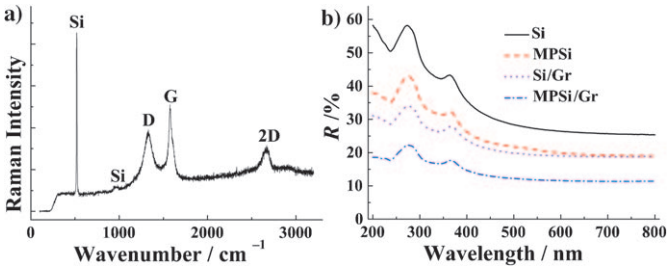

Figure 2. a) Raman spectrum of MPSi/Gr. b) Reflectance spectra of Si, MPSi, Si/Gr, and MPSi/Gr.

Reflection measurements on MPSi/Gr (Figure 2b), performed in comparison to flat Si, MPSi, and flat Si with the same thickness of Gr layer (Si/Gr), showed that, compared to the planar Si, the macroporous texture of MPSi and the Gr coating layer of Si/Gr can reduce reflection of light. In MPSi/Gr, the combined effects of the macroporous texture of MPSi and Gr layer result in high antireflective performance.

The results of photoelectrochemical measurements in 0.05 M H_2SO_4 solution are shown in Figure 3a–c. For MPSi electrode (Figure 3a), the photoresponse can be observed at both positive and negative bias potentials. It is well known that the photocurrent of p-Si at negative bias potential results from hydrogen evolution,[16] while at positive bias potential it is probably due to dissolution of Si.[17] These photocurrents decrease with increasing number of test scans because the surface of Si is passivated by oxidation of Si to SiO_2 in the electrolyte. In the case of MPSi/Gr electrode (Figure 3b), no anodic photocurrent is observed because dissolution of Si at the positive bias potential is prevented by the Gr protecting layer. Furthermore, the photocurrents at MPSi/Gr are almost unchanged over three scans, that is, the MPSi/Gr electrode is

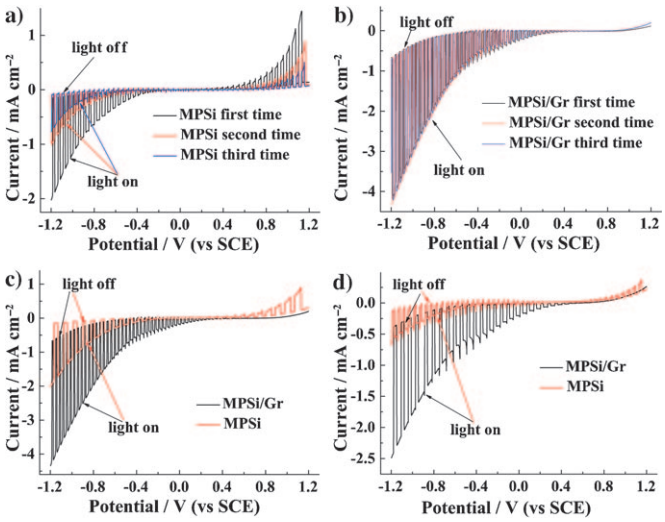

Figure 3. Stabilities of MPSi (a) and MPSi/Gr (b) in 0.05 M H_2SO_4. Photoelectrochemical behavior of MPSi and MPSi/Gr in 0.05 M H_2SO_4 (c) and 0.01 M Na_2SO_4 (d).

very stable in this electrolyte under the protecting Gr layer. The photocurrents of MPSi/Gr and MPSi in the first scan are compared in Figure 3c. The cathodic photocurrent at the MPSi/Gr electrode is about twice that of MPSi. This high photocurrent is ascribed to effective separation of photogenerated electrons and holes at the interface of MPSi and Gr. Another advantage of MPSi/Gr heterojunction can also be observed in Figure 3c: The photocurrent onset shifts from −0.24 V for MPSi to +0.30 V for MPSi/Gr, which means the hydrogen evolution on MPSi/Gr electrode could be easier than on MPSi electrode. This implies that Gr has potential in hydrogen production through water splitting by utilizing solar energy.

The depletion layer formed at the electrode/electrolyte interface can also provide the driving force for separation of photogenerated carriers.[18] This force would be affected by the properties of electrolyte (e.g., pH value). As shown in Figure 3d, for MPSi photocathode in 0.01 M Na_2SO_4 (pH 7), the photocurrent density at −1.2 V bias is 0.49 mA cm^{-2}, which is only 25% of the value in 0.05 M H_2SO_4 (pH 1). The result shows that the driving force from the electrode/electrolyte interface is weakened markedly in neutral electrolyte, while for MPSi/Gr photocathode the photocurrent density at −1.2 V bias in 0.01 M Na_2SO_4 is almost 60% of that in 0.05 M H_2SO_4. Thus, the MPSi/Gr electrode is resistant to the effect of the pH value of electrolyte because of protection by Gr. This property is significant for converting solar energy under moderate conditions.

The work function of a free-standing Gr sheet is 4.5 eV,[19] so the Fermi level E_F of Gr, which can be calculated by the formula $E_F = E_0$(vacuum level)$-W$(work function), is −4.5 eV relative vacuum level, or 0 eV relative to the normal hydrogen electrode (NHE). Hence, it would be difficult for Gr itself to generate hydrogen. However, when the heterojunction structured by MPSi and few-layer Gr is illuminated by incident light, photogenerated electrons would transfer from the conduction band of MPSi to Gr. With

electrons accumulating on Gr, the Fermi level of Gr would shift upward and closer to the conduction band of MPSi due to the metallic behavior of Gr (for few-layer Gr flakes, stacking of multiple layers leads to some overlap of their carrier wave functions, and thus they show overall metallic behavior[20]). Therefore, it would be possible for MPSi/Gr heterojunction to generate hydrogen at the surface of Gr, although its Fermi level is not high enough for hydrogen evolution. This mechanism is analogous to that of hydrogen production on heterojunctions of semiconductors and noble metals (e.g., Pt or Au, whose Fermi levels are far lower than 0 eV vs. NHE).[21]

The percentage photoconversion efficiency of MPSi/Gr photocathode in 0.05 M H_2SO_4 electrolyte was calculated with the following formula: $\eta = [J_p(1.23 - E_{appl})/I_0] \times 100$ (open-circuit photopotential is 0.34 V). The maximum varied from 2.12 to 2.36% for five measurements (Figure 4). The efficiency is comparable to that of planar Si coated by Pt[22] and distinctly higher than that of silicon nanowire protected by TiO_2.[23] Moreover, it could be improved further by optimizing the thickness of Gr and the pore size of MPSi.

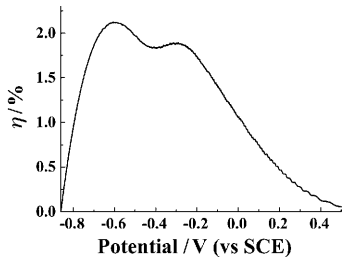

Figure 4. Photoconversion efficiency of MPSi in 0.05 M H_2SO_4 electrolyte.

The photoresponse of Gr was investigated by Dawlaty et al.,[24] who used a laser as light source to ensure photoexcitation of Gr. They showed that the lifetime of the excited carriers of Gr is in the 0.4–1.7 ps range. In view of the very short lifetime, capturing the hot electrons and holes of Gr would be extremely difficult. Therefore, low photoconversion ability of Gr is expected, especially when an Xe lamp instead of a laser is used as a simulated solar light source.

To evaluate the role of Gr in photoconversion while avoiding the effect of MPSi, the photoelectrochemical behaviors of ITO/Gr (deposition of Gr on ITO under the same conditions) and ITO in 0.05 M H_2SO_4 were studied in a control experiment, and the results are shown in Figure S1 of the Supporting Information. For ITO/Gr, the current under Xe lamp irradiation is almost superposed on the dark current, which confirms that Gr layer can not produce photocurrent under Xe lamp irradiation. Therefore, the markedly higher current under Xe lamp illumination compared to the dark current of MPSi/Gr (Figure 3b) is attributed to the photoresponse of MPSi. Compared with ITO electrode, ITO/Gr electrode displays higher cathodic current and more positive onset potential both under light illumination and in the dark due to the presence of the Gr layer. Moreover, the same results are observed with MPSi/Gr and MPSi. Thus, although no photocurrent is generated by the Gr layer, it plays an important role in shifting the onset potential of the substrate in the positive direction and makes hydrogen evolution easier.

To investigate the stability of MPSi/Gr samples further, 20 cyclic voltammetry measurements were performed. The results indicate the MPSi/Gr samples fabricated by only electrophoresis have poor stability (Figure S2a): the photocurrent at −1.2 V in the first cycle is more than 4 mA cm^{-2}, but it decreases to 1.5 mA cm^{-2} after 20 cycles, while the MPSi/Gr samples annealed at 350 °C in Ar flow after the electrophoresis process display stable photocurrent in 20 cycles (Figure S2b). The origin of the strong adhesion between MPSi and Gr is not clear. A discussion of changes in the interface of MPSi and Gr during the annealing process can be found in the Supporting Information.

In summary, by constructing MPSi/Gr heterojunction and investigating its photoelectrochemical properties, three potential functions of Gr have been explored. Firstly, Gr as a protective layer can protect Si against dissolution or passivation. Secondly, Gr as a charge collector can promote separation and transfer of photogenerated carriers. Thirdly, Gr can make hydrogen evolution easier and show considerable photocurrent under moderate conditions. By profiting from these functions of Gr, the MPSi/Gr heterojunction shows remarkable photoconversion ability. We expect that these findings will be the starting point for Gr as a protective material not only for Si but also for other narrow-gap semiconductors and thus promote their application in conversion of solar energy to chemical energy.

Experimental Section

Graphite oxide was produced by Hummer's method. The detailed steps can be found in reference [12]. Gr was obtained by pyrolysis of graphite oxide at 1050 °C in a tube furnace under the protection of Ar flow.

MPSi was fabricated by chemically etching p-type silicon wafer (boron-doped, (100) orientation, 3–4 Ω cm resistivity, 500 μm thickness, purchased from China Electronics Science & Technology Group No. 46 Institute). The Si wafers were cleaned as described in reference [23]. The clean Si wafer was then put into the vessel containing the etching solution of 5 M NH_4F and 0.02 M $AgNO_3$. The etching reaction was performed for 90 min at 60 °C in a thermostatic water bath. After reaction, Ag was removed by placing the sample in a mixture of HNO_3/H_2O (1/1 by volume). An ohmic contact was provided by depositing the Al film on top of the back side of the MPSi.

The MPSi/Gr heterojunction was fabricated by electrophoresis. A stable Gr suspension was obtained by dispersing 0.01 g of Gr in 100 mL of isopropyl alcohol by sonication for 3 h, and then 0.005 g $Mg(NO_3)_2 \cdot 6H_2O$ was added to this initial suspension with ultrasonic dispersion for 1 h. The applied voltage and deposition duration of electrophoresis were 160 V and 10 s, respectively. MPSi and stainless steel electrodes were used as the cathode and anode, respectively, and their separation was 0.5 cm. After electrophoresis, the MPSi/Gr was placed in an Ar stream to dry at room temperature, and then transferred to a quartz tube in a tube furnace and annealed at 350 °C for 30 min in Ar flow with a heating rate of 2 °C min^{-1}, and remained in the furnace under Ar protection until cooling to room temperature.

Environmental scanning electron microscopy (ESEM Quanta 200 FEG) and transmission electron microscopy (TEMFEI-Tecnai G^2 20) were employed to characterize the morphologies of samples. Photoelectrochemical measurements were performed in electrolyte

in a three-electrode cell that was connected to a CHI 650B electrochemical station (CH Instruments, Shanghai Chenhua, China), in which the MPSi/Gr heterojunction (or MPSi) acted as the working electrode, a platinum foil as the counterelectrode, and saturated calomel reference electrode. A high-pressure Xe short-arc lamp (CHF-XM35-150W, Beijing Changtuo Co., China) was used as light source to simulate solar light. The light intensity was 100 mW cm^{-2}. The Raman spectra were obtained with a Renishaw Micro-Raman System 2000 Spectrometer operated with He–Ne laser excitation (wavelength 623.8 nm, laser power 35 mW) with a beam spot size of about 2 μm. The UV/Vis spectra were recorded on a Shimadzu UV-2450 UV/Vis spectrophotometer with an integrating sphere; $BaSO_4$ was used as a reference.

Received: December 19, 2009
Revised: March 22, 2010
Published online: June 11, 2010

Keywords: energy conversion · graphene · photoelectrics · silicon · thin films

[1] a) M. Woodhouse, B. A. Parkinson, *Chem. Soc. Rev.* **2009**, *38*, 197; b) P. V. Kamat, *J. Phys. Chem. C* **2007**, *111*, 2834.
[2] M. A. Green, *Prog. Photovoltaics.* **2009**, *17*, 183.
[3] Y. Nakato, T. Ueda, Y. Egi, H. Tsubomura, *J. Electrochem. Soc.* **1987**, *134*, 353.
[4] N. Koshida, K. Echizenya, *J. Electrochem. Soc.* **1991**, *138*, 837.
[5] H. Morisaki, T. Watanabe, M. Lwase, K. Yazawa, *Appl. Phys. Lett.* **1976**, *29*, 338.
[6] R. Noufi, A. J. Frank, A. J. Nozik, *J. Am. Chem. Soc.* **1981**, *103*, 1849.
[7] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
[8] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.
[9] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, *Angew. Chem.* **2009**, *121*, 7890; *Angew. Chem. Int. Ed.* **2009**, *48*, 7752.
[10] X. Wang, L. Zhi, K. Mllen, *Nano Lett.* **2008**, *8*, 323.
[11] a) Z. Liu, Q. Liu, Y. Huang, Y. Ma, S. Yin, X. Zhang, W. Sun, Y. Chen, *Adv. Mater.* **2008**, *20*, 3924; b) X. Wang, L. Zhi, N. Tsao, Ž. Tomović, J. Li, K. Müllen, *Angew. Chem.* **2008**, *120*, 3032; *Angew. Chem. Int. Ed.* **2008**, *47*, 2990; c) Y. Wang, X. Chen, Y. Zhong, F. Zhu, K. P. Loh, *Appl. Phys. Lett.* **2009**, *95*, 063302.
[12] W. S. Hummers, Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
[13] Z. S. Wu, S. Pei, W. Ren, D. Tang, L. Gao, B. Liu, F. Li, C. Liu, H. M. Cheng, *Adv. Mater.* **2009**, *21*, 1.
[14] H. Liu, S. Ryu, Z. Chen, M. L. Steigerwald, C. Nuckolls, L. E. Brus, *J. Am. Chem. Soc.* **2009**, *131*, 17099.
[15] a) C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, K. S. Novoselov, D. M. Basko, A. C. Ferrari, *Nano Lett.* **2009**, *9*, 1433; b) A. K. Gupta, T. J. Russin, H. R. Gutiérrez, P. C. Eklund, *ACS Nano* **2009**, *3*, 45.
[16] D. C. Bookbinder, N. S. Lewis, M. G. Bradley, A. B. Bocarsly, M. S. Wrighton, *J. Am. Chem. Soc.* **1979**, *101*, 7721.
[17] X. G. Zhang in *Electrochemistry of Silicon and Its Oxide (Chinese edition)*, *Vol. 1* (Eds.: Z. Duan, L. Liu), Chemical Industry Press, Beijing, **2004**, p. 208.
[18] S. Licht, *J. Phys. Chem. B* **2001**, *105*, 6281.
[19] P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. van den Brink, P. J. Kelly, *Phys. Rev. B* **2009**, *79*, 195425.
[20] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132.
[21] a) V. Subramanian, E. E. Wolf, P. V. Kamat, *J. Am. Chem. Soc.* **2004**, *126*, 4943; b) M. Jakob, H. Levanon, *Nano Lett.* **2003**, *3*, 353.
[22] I. Lombardi, S. Marchionna, G. Zangari, S. Pizzini, *Langmuir* **2007**, *23*, 12413.
[23] H. T. Yu, X. Y. Li, X. Quan, S. Chen, Y. B. Zhang, *Environ. Sci. Technol.* **2009**, *43*, 7849.
[24] J. M. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, M. G. Spencer, *Appl. Phys. Lett.* **2008**, *92*, 042116.

