Applied Surface Science 257 (2011) 7714–7718

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Graphene/silicon photoelectrode with high and stable photoelectrochemical response in aqueous solution

Kedi Wu[a,1], Wenying Quan[a,1], Hongtao Yu[a,b,*], Huimin Zhao[b], Shuo Chen[b]

[a] School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China
[b] School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

*Article history:*
Received 2 December 2010
Received in revised form 15 March 2011
Accepted 2 April 2011
Available online 12 April 2011

*Keywords:*
Graphene
Silicon
Interface
Anneal
Photoelectrochemical Stability

ABSTRACT

The graphene (Gr)/Si electrodes were fabricated by electrophoresis method and then following an annealing process. The p-Si surface was found to be covered completely with successive and transparent Gr sheets, and thus the impairment of aqueous solution on the photoelectrochemical capability of silicon could be avoided. This annealing process was a key process for improving the adhesion of Gr/Si interface. After annealing at 400 °C, the Gr/Si electrodes displayed high photoresponse ability and high stability in aqueous solution. The carriers transfer between Gr and Si is discussed on the basis of the semiconductor energy band theory. The results demonstrated that the Gr/Si electrodes would be a promising candidate as solar energy materials using in aqueous solution.



## 1. Introduction

Graphene (Gr) is a zero band gap semimetal [1] with extraordinary properties of high specific surface area, high carrier mobility [2] and optical transparency [3]. Because of these advantages, Gr is considered particularly to be a promising material for using as transparent electrode [4].

Some heterojunction solar cells built by a Gr transparent top layer and photoresponse materials (such as $TiO_2$ [5], ZnO [6] dye-sensitized $TiO_2$ [7] and P3HT [8,9]) have displayed their abilities to enhance photoconversion efficiency. It is suggested when Gr (as a top layer) is combined with photoresponse materials to build a heterojunction, the incident light would transmit through the Gr layer to induce electron–hole pairs of the sublayer materials. The photogenerated electrons and holes would then transfer to the opposite directions driving by the built-in electric field of this heterojunction. The carriers reaching Gr layer would be transferred rapidly due to the superhigh carrier mobility of Gr. Consequently, the photoconversion efficiency of photoresponse materials would be improved. Compared with these mentioned photoresponse materials, silicon materials show better photoelectrochemical performance owing to its excellent capability for photoresponse, non-toxicity and ease of passivation and texturing. It is expected, therefore, Si would exhibit more attractive advantages as photoresponse materials than the other photoresponse materials when it combines with Gr.

Several approaches for fabrication of Gr/Si composite materials have been reported. A common method is transferring prepared Gr sheets to the top of the Si wafer and then drying [10–12]. The spin-casting is another method reported [13]. However, the binding force between Gr and substrate is usually weak from these methods. The adhesion energy of the typical Gr–Si interface in the high vacuum condition is measured to be only $151 \pm 28\ mJ/m^2$. This value decreases when the Gr/Si samples are exposed to a humid environment because water molecules are able to diffuse into the blister via the Gr–Si interface and then reduce the adhesion strength [14]. Due to the weak adhesion, Gr layer exfoliates commonly from Si sublayer when these Gr/Si materials are used in aqueous solution. Consequently, the reported Gr/Si composite materials are difficult to be applied in many processes such as water splitting and water treatment. Although the Gr/macroporous silicon heterojunction prepared via electrophoresis depositing Gr layer on the rough surface of macroporous silicon then annealing is demonstrated in our previous work to be stable in aqueous solution [15]. However, the pristine silicon wafer, which is of much more interest in most of academic fields than macroporous silicon, could not form enough stable adhesion with Gr layer under the experimental conditions in that work, and thus its application in the aqueous solution is inhibited to some extent.

* Corresponding author at: School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China. Tel.: +86 411 84706265; fax: +86 411 84706263.
*E-mail address:* yuhongtao@dlut.edu.cn (H. Yu).
[1] These authors contributed equally to this work.

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.04.015

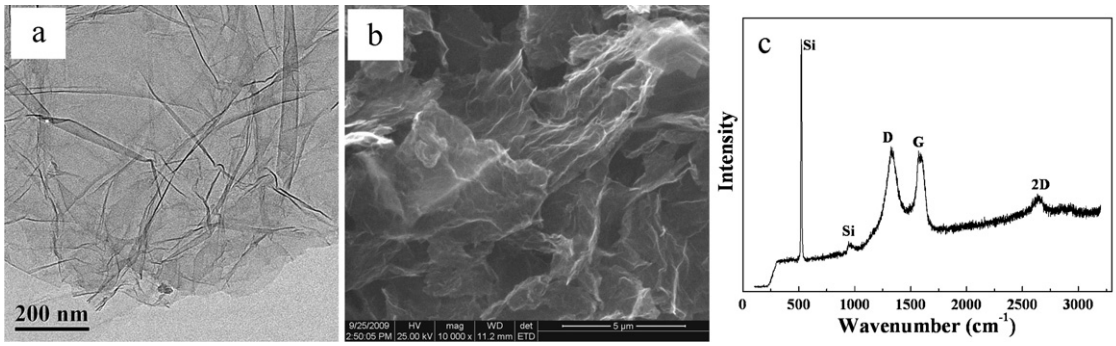


**Fig. 1.** (a) TEM image of Gr, (b) SEM image of Gr/Si and (c) Raman spectroscopy of Gr/Si.

In order to take the advantages of Gr/Si heterojunctions that can involve the reactions in aqueous solutions, development of proper methods for fabricating Gr/Si composite with sufficient mechanic and chemical stability is a critical issue. Herein, we optimize the fabrication method involving electrophoresis and anneal process. Suitable Gr/Si photoelectrode was successfully fabricated to be employed in aqueous solutions. The obtained Gr/Si photoelectrode displayed high photoresponse and good stability in aqueous solutions.

## 2. Material and methods

### 2.1. Fabrication of graphene

The graphite oxide was produced by the Hummer's method [16]. Initially, 1 g graphite and 23 mL of $H_2SO_4$ were mixed and strongly stirred at 0 °C. Then 3 g $KMnO_4$ was added carefully to the solution in 40 min, followed by 60 min sonication. Afterwards, the suspended solution was stirred continuously for 1 h, and 46 mL water was added slowly to the suspension in 15 min. Subsequently, the suspension was diluted by 140 mL water and 10 mL $H_2O_2$ (30%), and separated by centrifugation. Finally, the deposition was washed with hydrochloric acid (5%), filtered, washed with deionized water, and dried at room temperature to obtain dry graphite oxide. Gr was obtained by pyrolyzing graphite oxide at 1050 °C in a tube furnace under the protection of Ar flow.

### 2.2. Preparation of Si substrate

P-type one-side polishing silicon wafer (Boron doped, (1 0 0) orientation, 3–4 Ω cm resistivity, 500 μm thickness), was purchased from China Electronics Science & Technology Group No. 46 Institute. The process of cleaning Si wafers involved firstly rinsing in ultrasonic bath with acetone (5 min), ethanol (5 min) and deionized water (10 min), sequentially; secondly chemical etching by immersing in a mixture of $H_2SO_4$ and $H_2O_2$ (3:1 in volume) for 30 min; and lastly dipping into a solution of HF (5%) for 1 min and drying in Ar flow at room temperature.

### 2.3. Fabrication of Gr/Si electrode

Firstly, a stable Gr suspension was prepared via dispersing 0.01 g Gr in 100 mL isopropyl alcohol by sonication for 3 h and then adding 0.005 g $Mg(NO_3)_2{\cdot}6H_2O$ into this initial suspension with an ultrasonic dispersion for 1 h [17]. In succession, the clean Si wafer (as cathode) with its unpolished side facing to stainless steel anode was immersed into this suspension, and an electrophoresis process was performed at 160 V for 10 s. After electrophoresis, Gr/Si was put in Ar stream to dry at room temperature. The dried sample then was transferred into a quartz tube in a tube furnace to be annealed for 30 min in Ar flow with heating rates of 2 °C $min^{-1}$. At last, Gr/Si sample was cooled to room temperature under the protection of Ar flow.

### 2.4. Characterization

The morphologies of samples were observed by environmental scanning electron microscopy (ESEM Quanta 200 FEG) and transmission electron microscopy (TEMFEI-Tecnai $G^2$ 20). The Raman spectra were obtained using a Renishaw Micro-Raman System 2000 Spectrometer. Surface photovoltage (SPV) measurements were carried out using a system composed of a monochromator (model Omni-k 3005) and a lock-in amplifier (model SR830-DSP) with an optical chopper (model SR540). X-ray photoelectron spectroscopy (XPS) analyses were performed using ESCALAB250 spectrometer (Thermo VG, America) with Al Kα source, operating at an accelerating potential of 15 kV and a power of 150 W.

### 2.5. Photoelectrochemical measurements

Photoelectrochemical measurements were performed in 0.05 M $H_2SO_4$ electrolyte using a three-electrode cell that was connected to a CHI 650B electrochemical station (CH Instruments, Shanghai Chenhua, China), where the Gr/Si acted as the working electrode, a platinum foil as the counter electrode and the SCE as the reference electrode. Incident light intensity was 100 mW $cm^{-2}$ supplied by a high pressure Xe short arc lamp (CHF-XM35-150 W, Beijing Changtuo Co., China).

## 3. Results and discussion

### 3.1. SEM and Raman characterization

The TEM image of Gr as prepared is shown in Fig. 1a. A paper-like nanosheet character of Gr is displayed. As shown in Fig. 1b, after electrophoresis and annealing, the successive and uniform Gr sheets cover completely the p-Si substrate. Fig. 1c shows the Raman spectrum of Gr/Si. Five peaks located at 521 $cm^{-1}$, 974 $cm^{-1}$, 1324 $cm^{-1}$, 1596 $cm^{-1}$ and 2634 $cm^{-1}$ can be observed. The highest peak (521 $cm^{-1}$) and the peak at 974 $cm^{-1}$ belong to the Si substrate. The peaks at 1324 $cm^{-1}$ (D band) and 1596 $cm^{-1}$ (G band) represent the in-plane bond-stretching motion of the pairs of C sp3 and sp2 atom orbital hybridization, respectively. The strong D band is generally ascribed to the intrinsic defects [18], such as vacancies, grain boundaries or edges. D band comes from the exposed Gr edges, which could be found in Fig. 1b. Meanwhile, 2D band is also observed at the wavenumber of 2634 $cm^{-1}$.