



A visible-light-sensitive siloxene-based composite material with enhanced photocatalytic activity

Hyoo Ji Kang, Sunhye Lee, Hyuk Joon Jung, Hee Jung Yang, Kyu Hyung Lee, Nam Hwi Hur*

Department of Chemistry, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul, 04107, Republic of Korea

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ABSTRACT

A novel layer-stacking approach that produces a layered composite of siloxene and reduced graphene oxide (RGO) sheets is presented. This method is based on the assembly of siloxene and graphene oxide sheets, followed by reduction at low temperature using solid hydrazine. High-resolution transmission electron microscopy reveals that the resulting siloxene-RGO composite has a layered structure with sheets that appear to be alternately stacked in a face-to-face fashion. This composite exhibits excellent photocatalytic activity under visible-light irradiation, with a photocurrent density that is about 40 times higher than that of the siloxene sheets alone. It is evident that the RGO sheets stacked on the siloxene surfaces are the key elements that increase the photocatalytic activity of the layered composite. This layer-stacking approach enhances siloxene properties in many ways, rendering ample opportunities for the development of new siloxene-based composite materials with novel functionalities.

1. Introduction

Graphene sheets composed of two dimensional (2D) layers of sp^2 -bonded carbons have unique electronic, optical, and mechanical properties [1–12]. In contrast to pristine graphite, the basal planes of graphene sheets are easily functionalized, which facilitates the preparation of a wide range of graphene-based materials and their utilization in a variety of applications. [13–15] Recent advances in our understanding of graphene sheets has evoked new interest in the ordered planar 2D sheets composed of other moieties such as silicon [16–22], germanium [23–26], boron nitride [27–32], metal carbides [33–37], and metal dichalcogenides and nitrides [38–47].

Siloxene is a layered silicon sheet with a nominal stoichiometry close to $Si_6H_3(OH)_3$, in which the Si atoms in the puckered layer are alternately terminated by hydrogen (H) and hydroxyl (OH) groups [48–51]. Siloxene sheets are typically prepared by immersing calcium silicide ($CaSi_2$) in concentrated HCl solution. The Zintl-type $CaSi_2$ phase is composed of 2D puckered $[Si^-]_2$ layers that are separated from each other by Ca^{2+} cations [52–55]. The cations are removed by Cl^- anions while maintaining the anionic $[Si^-]_2$ structure. The Si atoms in the puckered $[Si^-]_2$ layers are terminated by H- and OH- groups. The terminating groups in siloxene not only make the planar structure stable but also render the siloxene sheet dispersible in water. Unlike bulk silicon, siloxene has a direct band gap, which produces very efficient

photoemission in the visible region [56–59]. A drawback, however, is that the siloxene sheets are not conductive, which limits their electronic and photocatalytic applications. An alternative way of exploiting the 2D properties of siloxene is through the preparation of composites with conductive graphene sheets, such as reduced graphene oxide (RGO). The incorporation of RGO components into the siloxene matrix would improve its conductivity and enhance its mechanical strength.

Here, we report a novel method for the preparation of siloxene-RGO composites via the complete linking of siloxene and graphene oxide (GO) sheets through the use of 3-amino propyl-trimethoxy-silane (APTMS), followed by the solid-state reduction of the linked planar composite with solid hydrazine ($NH_3^+NHCO_2^-$). The siloxene-RGO composite, synthesized by this method, exhibits excellent photoelectrochemical properties and produces high photocurrents under visible-light irradiation compared to the parent siloxene sheets. This layer-by-layer assembly approach enhances the properties of siloxene, rendering ample opportunities for the development of new siloxene-based composite materials with novel functionalities.

2. Materials and methods

2.1. Materials

All chemicals were obtained from commercial suppliers and were

* Corresponding author.

E-mail address: nhhur@sogang.ac.kr (N.H. Hur).

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used without further purification. Silicon (powder, 99.999%), 3-aminopropyltrimethoxysilane (APTMS, 97%), graphite (powder, < 20 μm), potassium permanganate (99%), hydrazine monohydrate ($\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$), and ninhydrin (ACS reagent) were purchased from Sigma Aldrich (St. Louis, MO, USA). Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and 35% hydrochloric acid (HCl) were purchased from Jin Chemical Pharmaceutical Co (Seoul, Korea). $\text{N,N}'$ -dicyclohexylcarbodiimide (DCC, $\geq 99.0\%$) was obtained from Honeywell Research Chemical (Leicestershire, UK). Calcium silicide (CaSi_2 , Kojundo Chemical Laboratory Co) was used as the starting material for the synthesis of siloxene. Solid hydrazine ($\text{H}_3\text{N}^+\text{HCO}_2^-$) was purchased from FutureChem (Seoul, Korea).

2.2. Synthesis of siloxene sheets

A three-neck round-bottom flask with a magnetic stirring bar was charged with 1.0 g of CaSi_2 in an argon-filled glove box. After moving the flask into a fume hood, the flask was filled with N_2 , after which 100 mL of concentrated HCl (35%) was slowly added under N_2 . The mixture was stirred at room temperature for 10 h. A yellow precipitate gradually formed at the bottom of the flask. The mother liquor was removed by cannulation and the green solid residue was washed several times with water and ethanol to remove CaCl_2 . The resulting solid was dried under vacuum for 4 h to yield 0.63 g of siloxene ($\text{Si}_6\text{H}_3(\text{OH})_3$) sheets.

2.3. Synthesis of graphene oxide (GO) and APTMS-functionalized siloxene sheets

Graphene oxide (GO) was obtained by the oxidation of graphite powder according to a modification of Hummers method. The resulting GO sheets were dried under vacuum at room temperature for 24 h to give a dark-brown powder. Siloxene sheets were functionalized with APTMS as follows. Briefly, 0.5 g of siloxene was dispersed in 15 mL of ethanol and 0.8 mL of APTMS was added to the solution. The dispersion was stirred for 3 h at 40 $^\circ\text{C}$, after which the resulting APTMS-functionalized siloxene sheets were collected by centrifugation, washed with three times ethanol, and dried under vacuum. The presence of APTMS on the siloxene sheet was confirmed by the ninhydrin test.

2.4. Synthesis of siloxene-reduced graphene oxide (RGO) composites

To prepare the siloxene-GO composite, 0.2 g of the APTMS-functionalized siloxene was dispersed in 100 mL of ethanol while 0.065 g of GO was separately dispersed in 50 mL of ethanol. The two dispersions were mixed and stirred for 30 min. DCC (30 mg) was added to the solution, after which it was allowed to react at 70 $^\circ\text{C}$ for 3 h. The resulting dark-green powder was collected by centrifugation, washed three times with ethanol, and dried under vacuum to afford about 0.176 g of the dried siloxene-GO product. The conversion of siloxene-GO into siloxene-RGO was performed in two ways. First, GO and solid hydrazine was reacted in the solid-state as follows. Briefly, siloxene-GO (0.2 g) was mixed with solid hydrazine (0.1 g) and the mixture was ground using a mortar and pestle in a nitrogen-filled glove box. The ground powder was placed in a 50 mL-glass pressure bottle and allowed to react at 80 $^\circ\text{C}$ for 1 h. The second method is based on the conventional solid-state reaction, in which the siloxene-RGO composite was prepared by annealing the siloxene-GO sample at 300 $^\circ\text{C}$ under Ar/H_2 for 3 h.

2.5. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku DMAX 2500 diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 150 mA. High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL JEM-2100 F microscope (JEOL, Japan). The HRTEM specimens were

prepared by dispersing finely ground sample powders in anhydrous ethanol. A drop of the suspension was allowed to evaporate on a carbon-coated grid. High-resolution scanning electron microscopy analyses were carried out using a Hitachi S-5500 microscope (Hitachi, Japan). The SEM samples were prepared by dropping diluted samples in anhydrous ethanol on a lacey support grid. Samples were also chemically micro-analyzed using an INCA TEM 300 system (Oxford Instruments, Abingdon, UK) for energy dispersive X-ray (EDX) analysis. UV-vis absorption spectra were recorded using a Lambda 950 spectrophotometer (Perkin Elmer, USA). Powder spectra were recorded by the diffuse reflectance method using an integrating-sphere accessory. Thermogravimetric analysis was carried out using a TGA 2050 instrument (TA Instruments, USA). Samples were placed on a platinum pan and analyzed under nitrogen from 25 to 700 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. Raman spectra were obtained using a Jobin-Yvon Triax 550 spectrometer equipped with a liquid-nitrogen-cooled charge-coupled-device detector. The Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 205 FT-IR spectrometer in a KBr pellet, scanning from 4000 to 600 cm^{-1} at room temperature.

2.6. Photoelectrochemical testing

A potentiostat/galvanostat (Model 263A, Princeton Applied Research, USA) was used for the electrochemical experiments. Before preparation of the working electrode, the indium tin oxide (ITO) glass substrate was cleaned by sonication in ethanol and then acetone for 30 min, after which it was rinsed with distilled water and stored in isopropyl alcohol for 12 h. The composite sample (5 mg) was typically dispersed in 200 μL of dilute Nafion (0.5 wt%) in methanol, after which it was drop-casted onto a 1.0 cm^2 ITO glass substrate. The resulting electrode was dried in air at 100 $^\circ\text{C}$. Photoelectrochemical experiments were performed in a three-electrode cell system with Pt wire as the counter electrode, a Ag/AgCl electrode (3 M NaCl) as the reference electrode, and the sample-coated ITO glass as the working electrode. The three-electrode cell was immersed in a 15-mL Pyrex vial. A 300 W Xe arc lamp with a 420 nm cut-off filter was used as the source of visible light. The working electrodes were illuminated from the rear.

3. Results and discussion

Siloxene sheets were prepared by the HCl-promoted deintercalation of the Ca in CaSi_2 at room temperature, which is schematically illustrated in Fig. 1. After treatment with concentrated HCl for 10 h, the product was collected by filtration, washed with water and then ethanol to remove residual CaCl_2 , followed by drying in vacuo. The color changed from black, in the original CaSi_2 , to yellow in the dried solid, indicating that CaSi_2 has been converted into siloxene by HCl.

The siloxene prepared in this manner was examined by powder X-ray diffraction (XRD), as shown in Fig. 2. New reflections corresponding to siloxene are evident in the XRD profile of this material, which are well indexed to its hexagonal graphitic-like structure, with $a = 3.74 \text{ \AA}$ and $c = 6.44 \text{ \AA}$ [60–62]. They confirm the formation of siloxene with the nominal $\text{Si}_6\text{H}_3(\text{OH})_3$ composition. The broad peaks indicate that the formed siloxene is composed of numerous nanometer-scale siloxene sheets.

A typical high-resolution TEM image and elemental maps of the siloxene sheets are displayed in Fig. 3. The TEM image highlights the planar structure of this material, which is composed of a few-layered sheets, and is consistent with the corresponding XRD data provided in Fig. 1(b). This microstructural TEM image is analogous to that of individual RGO sheets obtained by the reduction of GO [63–65]. The elemental maps confirm the presence of Si and O. The Si image is very distinctive due to the strong scattering power of Si. On the other hand, the O map is blurred mainly because the scattering intensity of oxygen is relatively weak. These maps reveal that Si and O are evenly dispersed over the siloxene surface. Another notable feature is the sparseness of

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