Bi$_2$S$_3$ microspheres grown on graphene sheets as low-cost counter-electrode materials for dye-sensitized solar cells†

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In this work, we synthesized 3D Bi$_2$S$_3$ microspheres comprised of nanorods grown along the (211) facet on graphene sheets by a solvothermal route, and investigated its catalytic activities through $I$–$V$ curves and conversion efficiency tests as the CE in DSSCs. Although the (211) facet has a large band gap for a Bi$_2$S$_3$ semiconductor, owing to the introduction of graphene into the system, its short-circuit current density, open-circuit voltage, fill factor, and efficiency were $J_{sc} = 12.2$ mA cm$^{-2}$, $V_{oc} = 0.75$ V, FF = 0.60, and $\eta = 5.5\%$, respectively. By integrating it with graphene sheets, our material achieved the conversion efficiency of 5.5%, which is almost triple the best conversion efficiency value of the DSSCs with (211)-faceted 3D Bi$_2$S$_3$ without graphene (1.9%) reported in the latest literature. Since this conversion-efficient 3D material grown on the graphene sheets significantly improves its catalytic properties, it paves the way for designing and applying low-cost Pt-free CE materials in DSSC from inorganic nanostructures.

1. Introduction

Due to having a single-layered structure of sp$^2$-hybridized carbon atoms, monolayer graphene displays similar electronic properties to a zero-bandgap semiconductor and thus is promising for electronic transportation and storage. Various attractive properties of monolayer graphene such as its high electrical conductivity, low weight, great mechanical strength and structural flexibility make it an ideal substrate for the growth and anchoring of insulating materials. In fact, the formation of nanostructures on graphene sheets can improve the electrochemical stability and conductivity of nanomaterials. For instance, metallic oxide nanomaterials such as Mn$_3$O$_4$, Co$_3$O$_4$, and Fe$_3$O$_4$ grown on graphene have displayed augmented specific capacities and rate capabilities, thereby raising their performances as anode materials for lithium ion batteries (LIBs). In addition, recent work has shown a better storage performance of LIBs using SnSe$_2$ nanoplate–graphene composites as anode materials as oppose to using SnSe$_2$ nanoplatelets or graphene alone. Moreover, researchers of late have developed a porous nanoarchitecture from 2D graphene–SnS$_2$ (G–SnS$_2$) units, which allows the high-rate transportation of electrolyte ions and electrons throughout the electrode matrix, thus giving rise to its promising electrochemical properties as an anode material for LIBs.

Bismuth sulfide (Bi$_2$S$_3$), which is a type of semiconductor with a direct band gap, exhibits a layered structure and crystallizes in the orthorhombic system (Pbnm space group). It has attracted great research attention as it has a reasonably low band gap of 1.7 eV, an absorption coefficient on the order of $10^4$ to $10^5$ cm$^{-1}$, and an incident photon to electron conversion efficiency of ~5%, which makes it suitable for PEC applications. At present, various types of Bi$_2$S$_3$ nanostructure materials such as nanowires, nanorods, and nanotubes have been synthesized by methods including colloidal chemistry routes, hydrothermal reactions, solvent-free syntheses, solvothermal reactions, aerosol assisted chemical vapor depositions (AACVD), and vapor position methods. The aforementioned methods raise the performances of Bi$_2$S$_3$ in photo detectors and optoelectronic type nanodevices; as well as in biomolecule detectors and H$_2$ sensors.

Owing to their ordered nanostructures and complex morphologies, current trends in nanoscience and nanotechnology point toward the fabrication of 3D assemblies, which show promise in catalysis, Li-ion batteries, solar cells, water treatment, etc. In particular, fabrications of semiconductor materials that manipulate crystal facets have drawn increasing attention since the photoelectric properties of the semiconductors can be further enhanced for highly-economic replacement of the scarce Pt counter-electrode (CE) in dye-sensitized solar cells (DSSCs). For example, Zhang et al.
compared the catalytic activities of the (130), (211), (221) and (040) facets within Bi$_2$S$_3$ through DFT computations and experimental validations. The computations suggest that the (130) facet within Bi$_2$S$_3$ has the highest surface energy, the best electrical conductivity and the highest position of the conduction band minimum of the four facets, suggesting the most effective electron transfer path is from Bi$_2$S$_3$-130 CEs to the I$_3^-$/C$_3$O$_4$.

This is further substantiated by the superiority of the conversion efficiency of DSSCs with (130)-faceted Bi$_2$S$_3$ CEs (3.5%) over those with (211) faceted Bi$_2$S$_3$ CEs (1.9%). Controlled organization of the primary building units of Bi$_2$S$_3$ into curved structures on graphene sheets with a spherical configuration along a specific facet will further improve their electrical properties, though it remains a big challenge to grow nanocrystals on graphene sheets in solution for materials with more sophisticated compositions and structures.

Herein, we report the synthesis of 3D Bi$_2$S$_3$ comprising of nanorods with microsphere morphologies on graphene sheets along a specific facet through a solvothermal route. The decomposition of L-cysteine at temperatures of 150°C allowed S$^{2-}$ to efficiently diffuse, and graphene oxide sheets were used as a starting substrate for 3D Bi$_2$S$_3$ growth and anchoring, which were fully reduced to graphene during the solution step. Its electrical properties as a counter electrode in DSSCs are also investigated. This work suggests that it is possible to grow 1D nanorods into 3D microspheres on graphene sheets through a one-step solvothermal methodology under controlled conditions.

2. Results and discussion

The atomic force microscopy (AFM) image shown in Fig. S1† indicates the height of the graphene oxide to be 0.35‐1 nm, and reveals that the graphene sheets are either mono- or bi-layered.

Fig. 1 a shows a typical TEM image of a Bi$_2$S$_3$ nanorod-based superstructure, where microspheres are formed on graphene sheets. Fig. 1b shows a typical transmission electron microscopy (TEM) image of an isolated Bi$_2$S$_3$ nanorod-based superstructure. The edge portion of the superstructure is lighter than that of the center, and is comprised of rod-like 1D nanostructures. The high-resolution TEM (HRTEM) image of a single nanorod in the microsphere shows a single-crystalline structure (Fig. 1c and d), and the nanorods exhibit diameters of 10–15 nm and a shortest length of 250 nm. The lattice spacing of 0.23 nm corresponds to the d-spacing between adjacent (211) crystallographic planes of the Bi$_2$S$_3$ nanorods. The as-synthesized nanorods are elongated along the (211) direction; the lengthwise axes of the nanorods are parallel to the (211) direction, which indicates that the nanostructures indeed grow along a certain direction.

Low-magnification scanning electron microscopy (SEM) observations show that the as-obtained Bi$_2$S$_3$ samples are composed of many uniform, sphere-like architectures ranging from 0.65 to 2.5 μm in diameter (Fig. 2a). Higher-magnification SEM images reveal that the Bi$_2$S$_3$ microspheres are built from crystalline nanorods. These crystal rods, analogous to a dandelion, are aligned perpendicularly to the spherical surface, pointing toward their common center (Fig. 2b–d).

Powder X-ray diffraction (XRD) is used to characterize the phase structure of the products. It can be seen from Fig. 3 that the XRD pattern conforms with orthorhombic Bi$_2$S$_3$ (JCPDS: JCPDS no. 17-0320, red pattern in Fig. 3). No characteristic peak was observed for other impurities such as Bi, S, and Bi$_2$O$_3$. This indicates that pure crystalline Bi$_2$S$_3$ was formed via the solvothermal process. From Fig. 3, it can also be seen that the (130), (211), and (040) planes show the three strongest diffraction peaks, and the relative diffraction intensity of (211)/(130) is higher than the corresponding conventional values. The
resultant Bi$_2$S$_3$ products are mainly dominated by (211) facets, and therefore their (211) planes tend to be preferentially oriented parallel to the surface of the supporting substrate on graphene sheets in the experiment, which is consistent with the HRTEM analysis.

The FT-IR spectra of graphene oxide (GO) and graphene supported Bi$_2$S$_3$ microspheres (G–Bi$_2$S$_3$) is shown in Fig. S3.† The three bands of GO appear at 1050 cm$^{-1}$, 1720 cm$^{-1}$, and 3450 cm$^{-1}$ and are due to the epoxide and carboxyl functional moieties, respectively. This result clearly reveals that functional groups are introduced into the carbon frameworks upon oxidation. However, in case of G–Bi$_2$S$_3$, the epoxide and carboxylate functional groups almost disappear, which confirms that GO has been reduced to graphene during the solution step, which is consistent with the XRD results (Fig. S2† and Fig. 3).

The relationship between the morphology of the Bi$_2$S$_3$ and synthesis time was also investigated. The SEM images of Bi$_2$S$_3$ at different synthesis times (1, 2, 4, and 24 h) are shown in Fig. 4a–c and Fig. 2 respectively. After 1 h of synthesis, irregular nanoparticles began forming on the graphene sheets. The sphere-like shapes and nanorod-composed microsphere formation became apparent after 2 h, followed by the formation of clearer nanorod-composed microspheres after 4 h. After 24 h, microspheres with narrowly distributed diameters were visible, as seen in Fig. 2. The results reveal that reaction time is one of the main factors in forming nanorod-based Bi$_2$S$_3$ microspheres with narrowly distributed diameters; that is, the Ostwald ripening process is indispensable. The formation process of Bi$_2$S$_3$ microspheres on graphene is shown in Fig. 5.

In a control experiment, the same synthetic steps without the addition of mildly oxidized graphene oxide (mGO) produced nanorod-based Bi$_2$S$_3$ microspheres (See ESI, Fig. S4†). Thus, the results suggest that mildly oxidized graphene sheets are a strong candidate for growing nanocrystals into well-defined morphologies. In this process, the functional groups on mGO allow the adsorption of cations and nanoparticle nucleation to achieve a uniform precursor coating in the first step of the reaction, the conjugated graphitic regions of reduced mildly oxidized graphene oxide (rmGO formed by the reduction of mGO under solvothermal conditions) weakly interact with the surface species to promote the formation of well-defined shapes of nanocrystals by anisotropy under reactive conditions. The resulting nanorod-based Bi$_2$S$_3$ microspheres can be bonded to rmGO by Bi–O–C bonds at the remaining oxygen sites and by Van der Waals interactions with the aromatic regions of rmGO.

By tuning the surface atomic structures, the photoelectric and photocatalytic properties of facet-controlled semiconductor materials can be further optimized for DSSC applications.$^{27-30}$ Electronic conductivity is one of the critical factors that influences the catalytic activity of CEs in DSSCs. In semiconductors, electrical conductivity increases with decreasing band gap. The periodic density functional theory (DFT) computations performed by a slab model revealed that the (040) facet for Bi$_2$S$_3$ crystalline has the largest band gap, and the continuing facet order from smaller to larger is (211) > (221) > (130), so electrons...
can transfer from Bi$_2$S$_3$ facets to I$_3^-$ in the following sequence: (130), (221), (211), (004). However, the conversion efficiency of all Bi$_2$S$_3$ 3D nanoproducts needs to be improved. To enhance their electronic conductivity, it is necessary to further adjust the band gap of the semiconductors.

Due to the electron transfer from the conduction band of the semiconductor to the graphene, we speculate that the electronic conductivity of the semiconductors will obviously increase, which grows along a specific facet for large band gaps. So we synthesized 3D Bi$_2$S$_3$ microspheres with assembled-nanorods grown along the (211) facet on graphene sheets, and investigated its photovoltaic properties in DSSCs. The Bi$_2$S$_3$ sample film was fabricated by the doctor blade method on FTO conductive glass and sensitized with N719 dye. The short-circuit current density, open-circuit voltage, fill factor, and efficiency were $J_{sc} = 12.2$ mA cm$^{-2}$, $V_{oc} = 0.75$ V, FF = 0.60, and $\eta = 5.5\%$, respectively, as shown in Fig. 6. In comparison with ref. 33, the conversion efficiency of our product has an advantage over that of Bi$_2$S$_3$ comprised nanorod-like microspheres, which grow along the same (211) facet and $\eta$ of which equals 1.9%. In fact, the conversion efficiency of the Bi$_2$S$_3$ microspheres grown along the (211) facet on graphene is more than that of the Bi$_2$S$_3$ microsphere grown along the (130) facet, which has the smallest band gap in ref. 26. Because graphene is a zero-bandgap semiconductor and shows highly electronically conductive properties for storing and transporting electrons, it is possible that the conversion efficiency of synthetic Bi$_2$S$_3$ microspheres along (130) facet on graphene as a counter electrode has the advantage over that of Pt in dye-sensitized solar cells, which are effective for the semiconductor to the graphene, and the interface between FTO and Bi$_2$S$_3$ layers, while those in the intermediate and low-frequency region offer information on the resistance at the Bi$_2$S$_3$/electrolyte interface and the finite layer Nernst diffusion impedance within the electrolyte, respectively. The equivalent circuit (shown in Fig. 8) consists of several components: ohmic resistance ($R_s$), charge transfer resistance at the FTO/Bi$_2$S$_3$ layers ($R_1$, 20.1 $\Omega$), charge transfer resistance at the photoelectrode/electrolyte ($R_2$, 9.2 $\Omega$), charge transfer resistance at the finite layer (Nernst diffusion impedance) ($R_3$, 5.5 $\Omega$), the constant phase element of capacitance corresponding to $R_1$ (CPE1), the constant phase element of capacitance corresponding to $R_2$ (CPE2), and the constant phase element of capacitance corresponding to $R_3$ (CPE3). For electrodes having a rough surface the semicircle is flattened and Cd is often replaced by a constant phase element (CPE), where CPE was defined by two parameters, CPE-p and CPE-t. Based on the formula: $Z = \frac{1}{T \cdot e^{\alpha t}} \left[ \cos \left( \frac{-\beta t}{2} \right) + j \sin \left( \frac{-\beta t}{2} \right) \right]$, when CPE-p = 1, and the CPE is pure Cd, generally, CPE-p is from 0.5 to 1.0. In our model circuit, the corresponding CPE-p is always less than 1.0, which demonstrates that the corresponding electrodes' surfaces are rough and the ideal Cd cannot describe them correctly; as a result, Cd needs to be modified and replaced by a CPE for better explaining them. By the EIS analysis, the largest impedance comes from the charge-transfer resistance ($R_1$, 20.1 $\Omega$), however, the good contact between the FTO/Bi$_2$S$_3$ layers has the benefit of reducing the main resistance ($R_1$). On the other hand, both $R_1$ and $R_3$ depend on ionic conductance from the electrolyte between the anode and the cathode. These internal impedances have a direct effect on the electron transport mechanism in DSSCs. As a consequence, the cell performance of the DSSCs is improved when the sum of the resistance components ($R_s$, $R_1$, $R_2$, and $R_3$) is small (Table 1).

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**Fig. 6** $I$–$V$ curve of the Bi$_2$S$_3$ sample.

**Fig. 7** Nyquist plots of the measured EIS spectra of the counter electrode.

**Fig. 8** Equivalent circuit of the symmetric device.
Table 1  Simulation value of equivalent circuit of the Fig. 8

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3. Conclusion

By introducing the graphene with its outstanding carrier transfer properties, the electronic conductivity of CEs should be dramatically enhanced and the electronic transfer from CEs to triiodine could be more efficient. We developed the first synthesis of complex single-crystalline nanomaterials on highly conducting mildly oxidized graphene sheets of a desired size and morphology along a specific facet. The resulting high electrical conductivity and catalytic activity led to excellent rate performance for the otherwise extremely insulating 3D Bi$_2$S$_3$ counter electrode material. This work opens the door to the design and engineering of complex hybrid materials with graphene for advanced energy materials for dye-sensitized solar cells.

4. Experimental section

Synthesis of GO nanosheets

Graphene oxide (GO) nanosheets were made by a modified Hummers method. In detail, graphite powder (2 g) was put into 100 mL of cooled (0 °C) concentrated H$_2$SO$_4$, followed by the slow addition of KMnO$_4$ (6 g), a slight exotherm may be produced in this process. The suspension was then stirred at 35 °C for 12–15 hours. Afterwards, 200 mL of distilled water was added and the temperature was kept at 96 °C for 2 h. The temperature was reduced to 60 °C, and 10 mL of H$_2$O$_2$ (30%, 10 mL) was injected into the suspension to completely react with the excess KMnO$_4$, which yielded a bright yellow mixture. The solid product was separated by centrifugation, and then washed with HCl (5%) several times and with water until the pH value of the supernatant was nearly 6, and graphene oxide was obtained. The collected precipitate was dispersed in water, then sonicated and subsequently concentrated to obtain a GO suspension, and kept at 50 °C for 10 h and GO powder was obtained.

Synthesis of Bi$_2$S$_3$–reduced graphene oxide hybrid

The concentration of the final GO water suspension was 0.05 g per 8 mL. A two-step approach for the synthesis of the hybrid is used in this process. In the first step of the synthesis, 0.1 g of GO powder was added into a 50 mL beaker with 40 mL of absolute ethanol, and then 1.0 g of Bi(NO$_3$)$_3$ was added stirred with a magnetic stirrer to form a homogeneous solution, then 0.8 g of L-cysteine was added. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 mL for solvothermal treatment at 150 °C for 15 h. In the second step of the synthesis, after the autoclave was allowed to cool to room temperature, 0.5 g of L-ascorbic acid was added to the autoclave and magnetically stirred. The mixture was then sealed in the autoclave for solvothermal reaction at 150 °C for another 9 hours. The precipitate was separated by centrifugation, after which it was washed with water and absolute ethanol to remove impurities, and the Bi$_2$S$_3$–reduced graphene hybrid was obtained.

Characterization

The phase of the samples was characterized using X-ray diffraction (XRD) with a Rigaku D/Max-2500 X-ray diffractometer employing Cu K$_\alpha$ radiation, with $\lambda = 1.54056$ Å. The morphologies and sizes of the samples were characterized by using a field emission scanning electron microscope (JEOL JSM-6700) and transmission electron microscopy (TEM, JEOL-2010, with an operating voltage of 200 kV), high-resolution TEM (HRTEM, JEOL-2010), and AFM (MultiMode8, Bruker). The Fourier transform infrared (FT-IR) spectrum was recorded using a GX spectrophotometer (Perkin-Elmer) with the KBr wafer technique.

Photovoltaic performance tests

Approximately 0.05 g of Bi$_2$S$_3$ powder was mixed with 0.5 mL of 2.5% PEG 20 000 solution and stirred until a fluid mixture formed. A film was then made using the doctor-blade method on FTO conductive glass (LOF, TEC-15, 15 W per square). The film was heated at 450 °C for 1 h under an argon atmosphere to obtain the Bi$_2$S$_3$ counter electrode. A commercial TiO$_2$ sol (Solaronix, Ti-Nanoxide T/SP) was used to prepare the TiO$_2$ film on FTO also through the doctor-blade method, and the film was soaked in an N-719 dye solution (in ethanol) for 24 h to obtain dye-sensitized TiO$_2$ electrodes. DSSCs were assembled by injecting the electrolyte into the aperture between the dye-sensitized TiO$_2$ electrode and the counter electrode. The liquid electrolyte was composed of 0.05 M I$_2$, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPH), and 0.5 M 4-tert-butylyl pyridine in acetonitrile. Surlyn 1702 was used as the separator between the two electrodes. The two electrodes were clipped together and solid paraffin was used as the sealant to prevent the electrolyte from leaking. The effective cell area was 0.25 cm$^2$. Photocurrent–voltage curves were measured using a Zahner IM6ex electrochemical workstation with a Trusttech CHF-XM-500W source under simulated sun illumination (Global AM 1.5, 100 mW cm$^{-2}$).

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References