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Colloidal nanocomposite of reduced graphene oxide and quantum dots for enhanced surface passivation in optoelectronic applications

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ABSTRACT

Colloidal graphene/PbS quantum dots (QDs) hybrid nanostructures are fabricated with chemical grafting in one-pot solution methods. In the hybrid nanocomposites, PbS QDs are decorated on the reduced graphene oxide (rGO) nanosheets (NSs). By employing X-ray photoelectron spectroscopy (XPS) analysis, it is shown that the rGO NSs are bonded to PbS nanocrystals through oxygen functional groups, leading to improved surface passivation and electrical conductivity in the hybrids. The results obtained by the recordings of time-resolved photoluminescence spectra, field effect mobility, and photovoltaic performance revealed that rGO grafted to PbS QD composite structures provided better charge transport by 16 times compared to PbS alone, which is attributed to suppressed charge recombination and improved interfacial charge transport processes. Thus, the developed hybrid photoactive film enhanced open circuit current (J_{sc}) and power conversion efficiency (PCE) by 12% and 14% correspondingly.

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1. Introduction

The formation of a colloidal QD composite with an appropriate host matrix can provide several advantages, such as the improved stability of QDs by the passivation effects of the matrix, and very efficient charge and energy transport between QDs with strong electronic interaction with the matrix [1,2]. In general, inorganic carbon matrices are known to have distinctive thermal and optical resistances compared with their organic or polymeric counterparts and could be good candidates for QD encapsulation [3–5].

Graphene-based composite materials with semiconductor QDs have shown to improve electrical and thermal conductivity [6–12]. The anchoring of semiconductor nanoparticles on graphene sheets potentially provides a new way to develop catalytic, magnetic, and optoelectronic materials. Encapsulation of semiconductor QDs inside multi-shell graphitic cages is usually achieved during carbon arc-discharge at high temperatures [13–15]. Similarly, interesting hybrid structures with carbon nanotubes [1,16] and graphitic oxide nanoplatelets [17] have been developed by incorporating semiconductor nanoparticles.

Here, we demonstrate a facile method to prepare the composite structure of rGO NSs and PbS QDs hybrids via one-pot solution synthesis. Efforts have also been made to synthesize semiconductor

particles protected by rGO sheets and assemble them as thin films using layer-by-layer self-assembly technique. The ability of rGO sheets to react with cationic defect sites on the surface of QDs via oxygen containing functional groups has enabled us to develop chemical synthetic strategies and tailor their properties with chemical functionalization. Chemical grafting and ligand exchange were used to control the interface of rGO/PbS nanohybrids and the PbS QD interparticle distance, respectively. The effects of the controlled interface on the optical and electrical properties are presented here. We find that the surface functionalization of PbS QDs via the rGO grafting gives rise to efficient surface passivation and trap removal, significantly improving their charge transport and photovoltaic performance.

2. Experimental section

2.1. List of materials

Lead oxide (99.999%), oleic acid (90%), 1-octadecene (90%), octane (anhydrous, ≥ 99%), hexamethyldisilathiane (TMS, synthesis grade), 1,2-ethanedithiol (EDT, ≥ 98%) were purchased from Sigma Aldrich for the synthesis of PbS QDs. Hexane and acetone used in QD purification were purchased from Merck. To prepare the reduced graphene oxide nanosheets the following list of materials were used such as natural graphite powder (Kanto Chemical, ≥ 80%), potassium permanganate (≥ 99%), sulfuric acid (extra pure, 95%), phosphoric acid (≥ 85%), hydrochloric acid

(32%), hydrogen peroxide (35%), hydrazine monohydrate (98%), N, N-dimethylformamide (DMF, anhydrous, 99.8%). Zinc acetate dehydrate ($\geq$ 98%), lithium hydroxide monohydrate ($\geq$ 98%) and absolute ethanol were used to prepare ZnO nanocrystal solution. To accomplish the device preparation gold (99.99%) and molybdenum (VI) oxide (metals basis, 99.9995%) is used as electrode materials.

2.2. Sol–gel synthesis of ZnO nanocrystals

The fabrication of nanocrystalline (NC) ZnO was performed according to the method reported in literature [18] with certain modifications. For the first step, 0.1 M solution of organometallic Zn precursor was prepared by making a mixture of 2 mmol zinc acetate dehydrate with 20 ml of absolute ethanol in 50 ml round shape 1-neck flask. The flask was connected to the reverse condenser and placed into an oil bath to maintain the temperature at 80 °C under atmospheric pressure. The mixture was stirred with magnetic bar vigorously for 1 h until the transparent solution was obtained. Next, 2.8 mmol of lithium hydroxide monohydrate powder was added to the solution. Finally, the suspension was placed into an ultrasonic bath at room temperature to accelerate the release of OH$^-$ ions, resulting in formation of stable solution of ZnO nanocrystals. The ZnO NCs were precipitated by adding hexane into the main solution with 1:3 volume ratio and centrifuged at 10,000 r.p.m. for 5 min. Then, the obtained ZnO nanocrystal precipitate was dispersed in anhydrous ethanol to obtain 80 mg/ml solution. The characteristics of ZnO NCs colloidal solution are presented in Supplementary material Figs. S1–S3. Finally, 0.20 µm pore size syringe filter was used to filtrate the NC solution before using it in PV cell structure.

2.3. Synthesis of reduced graphene oxide nanosheets

The rGO NSs were initially synthesized by modified Hummer's method using natural graphite powder [19]. Obtained graphene oxide NSs after multiple purification, were exposed to hydrazine-assisted reduction process to improve the conductivity by reducing the number of oxygen containing functional groups ($-$OH, H–C=O, O–C=O, and epoxy) on the surface [20]. The suspension of rGO NSs with a concentration of 1 mg/ml in DMF was used to fabricate rGO/PbS hybrid material.

2.4. Synthesis of rGO/PbS hybrid composite material

The synthesis of rGO/PbS hybrid material was performed by the hot injection method that is based on previously reported synthesis route for PbS QDs [21] with certain modifications. For this purpose, preliminary prepared suspension of rGO NSs in DMF was injected into the reaction vessel as lead precursor was transformed to the lead oleate complex, then reaction mixture was degassed for 17 h in 95 °C. TMS solution in ODE, which was preliminary degassed for 12 h at 80 °C, was injected to the reaction mixture to burst the nucleation. The heating mantle was turned off as nucleation induced (solution color changed to dark brown), and the solution was cooled down naturally. After reducing the solution temperature to 38 °C the crystal growth process was inhibited by injection of 20 ml of distilled acetone. To purify as-prepared QD solution it was centrifuged three times in the mixture of toluene/acetone (1:3 volume ratio) at the spin speed of 6000 r.p.m. for 5 min. After drying in a vacuum condition the obtained solid was dissolved in octane to obtain a solution with 60 mg/ml concentration and stored in N$_2$ atmosphere in glove box for further use. A reference PbS QD solution was also prepared without adding graphene.

2.5. Material characterization

The morphology and particle size of hybrid composite material was analyzed by transmission electron microscopy (JEOL, JEM-3010 (300 kV)). The portion area of rGO covered by PbS QDs (PA, %) was estimated statistically among the same scaled TEM images of different 24 rGO/PbS samples. First we assumed that single QD projection area is matched to its covered area. As so, the integrated area of the QD covered rGO is calculated as a sum of projection area of all QDs ($\sum QDA = n \cdot \pi r^2$, where n is the counted number of QDs, and r is the average radius of QD). Then this value is compared to the selected area of rGO NSs (rGOA) covered by those QDs as given in Eq. (1)

$$PA = \frac{n \cdot \pi r^2}{rGOA} \cdot 100\% \tag{1}$$

The X-ray diffraction analysis were carried out with RIGAKU, D/MAX-2500 diffractometer (Cu K$_\alpha$ radiation). The device cross-sectional view and the surface properties of all type of samples were by scanning electron microscope (Hitachi S-4800). The optical absorption features were investigated by Mecasys, Optizen POP, Korea, and the XPS analysis was carried out using Thermo VG Scientific, ESCALAB 200i spectrometer equipped with a micro-focused monochromator X-ray source. The luminescence lifetime values were evaluated using FLP920 (Edinburgh Instruments) fluorescence decay analysis software. For low temperature measurement the liquid nitrogen cryostat was used in combination with diaphragm vacuum pump (Edwards, RH 10 9LW) to maintain 2×10^{-4} mbar vacuum condition. EPL-785, picosecond pulsed diode laser (785 nm) was used as a light source, and the signals were detected by NIR-PMT detector with the range of 300–1400 nm. Samples were prepared on glass by drop casting in the case of OA-capped PbS and rGO–PbS films, or by layer-by-layer (LBL) deposition for EDT ligand exchanged ones. The fluorescent decay curve was fitted with triexponential decay fit. The goodness of fit was judged by χ^2 (1 ± 0.2) values. The average decay time (τ_{avg}) values of PbS QD and rGO/PbS composite films were analyzed using Eq. (2) [22]

$$\tau_{avg} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}, \tag{2}$$

where τ is the lifetime and α is the pre-exponential factor with subscripts 1, 2, and 3 representing various species.

2.6. Photovoltaic device fabrication

ITO-coated glass substrates were processed to three step sonication for 30 min in methanol, acetone and isopropyl alcohol solvents. Then, freshly synthesized ZnO NCs solution was spin coated on top of ITO to make a film with 90 nm thickness, then annealed in open air at 260 °C for 30 min to improve film crystallinity. The next steps of device fabrication were performed in N$_2$ filled glove box. On top of ITO/ZnO substrate the active layer was deposited by LBL spin coating of rGO/PbS hybrid material with EDT-assisted solid state ligand exchange procedure [23]. To perform the LBL deposition 4 drops of QD solution (60 mg/ml) for 20 s, 5 drops of EDT solution (1% vol. in acetonitrile), 9 drops of acetonitrile and 10 drops of toluene were spin coated for 5 s one by one at fixed spinning speed of 2500 r.p.m. Overall procedure results in formation of active layer with 280 nm thickness after 8 LBL cycle. Then, 10 nm of MoO$_3$ layer and 50 nm of Au top electrode were deposited by thermal evaporator under high vacuum condition (10^{-7} Torr) with 0.5 Å/s and 1 Å/s deposition rate correspondingly.