Ag-Ag_2S/Reduced Graphene Oxide Hybrids Used as Long-Wave UV Radiation Emitting Nanocomposites

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Abstract

We report a facile thermal decomposition approach to synthesize Ag-Ag_2S/reduced graphene oxide (Ag-Ag_2S/rGO), the Ag-Ag_2S nanoparticles uniformly dispersed on reduced graphene oxide with diameters of 10-20 nm. The photoluminescence spectra of Ag-Ag_2S/rGO showed two obvious emission peaks at 327 and 339 nm with the excitation wavelength at 287 nm. Compared with Ag-Ag_2S heterostructured clusters with two peaks at 407 and 430 nm, it showed a big blue shift and higher intensity, which makes it a novel candidate for long-wave UV radiation emitting nanocomposite.

Keywords

Ag_2S-Ag; Graphene; Hybrids; Radiation Emit

1. Introduction

In decays, the Janus nanoparticles (JNPs) with two or more different functional nanoparticles (NPs) contacting intimately have attracted great research interests owing to their novel properties which are not presented in individual component NPs.[1] In particular, as one of the most important JNPs, the noble metal-semiconductor composite systems have been investigated widely due to their well-known remarkable optical, electrical, magnetic and catalytic properties,[2] Considerable efforts have been devoted to synthesize noble metal–semiconductor composite, for instance, Au-ZnO,[3] Au-Ag_2S,[4] and Ag-Ag_2S.[5], Among these noble metal–semiconductors, Ag-Ag_2S nanohybrids were reported with excellent properties in resistive switches,[6] photodegradation of pollutants,[7] and water splitting [8]. Owing to its excellent photoelectric and photocatalytic properties, it is still necessary to explore a facile and rational synthetic strategy to synthesize Janus Ag-Ag_2S heterostructures and investigate their novel properties and potential applications.

Graphene, carbon atoms bonding through sp^2 hybridization, which possesses unexceptionable optical, mechanical, and electrical properties [9-10]. All its salient traits contribute to its widely used as a substrate to disperse and stabilize nanomaterials [11-15]. Nowadays, various kinds of graphene-based nanocomposites have been synthesized. Because of the excellent electron transmission capacity of graphene, the graphene-based nanomaterials possess enhanced electrical conductivities, improved electrochemical activities, high photocatalyzed performance, and other outstanding properties [10,16-17]. Among these nanocomposites, recent reports were concerned about the photoluminescence behavior change of the specific semiconductors. So far, there is no report around the synthesis of Ag-Ag_2S/rGO nanocomposite, the exploration of a mild and easy-to-implement method to prepare Ag-Ag_2S/rGO nanocomposite and research of its available properties become necessary.

Herein, we reported a facile thermal decomposition method to prepare Ag-Ag_2S/rGO nanocomposites. The Ag-Ag_2S heterojunctions were dispersed on rGO uniformly with the diameters of 10-20 nm. The photoluminescence spectra of Ag-Ag_2S/rGO showed obvious emission peaks at 327 and 339 nm with the excitation wavelength at 287 nm. Compared to Ag-Ag_2S heterostructured clusters with two peaks at 407 and 430 nm, it showed a big blue shift, which makes it a novel candidate for long-wave UV radiation emitting nanocomposite.

2. Experiment

Synthesis of the graphite oxide (GO) and reduced graphene oxide (rGO) can be found in supporting information.

Synthesis of Ag-Ag_2S/rGO nanocomposites and Ag-Ag_2S heterostructures

Typically, three kinds of precursors should be prepared at first. Precursor A, containing 15 mg of GO and 60 mL of ethylene glycol, was dispersed under sonicating for 30 min. Precursor B, including 34 mg of $AgNO_3$, 15 mL ethylene glycol and 5 mL ammonia water, was stirred for 10 min. Precursor C, containing 114 mg of thiocarbamide, 15 mL of ethylene glycol and 5 mL of deionized water, was stirred for 15 min. A mixed reactant was formed by transferring precursor A to a three-necked flask and stirring and heating to the temperature of 120 °C with a protection ambience of nitrogen, after which precursor B was injected into it quickly. The mixed reactant was kept stirring for 2 min under 120 °C with protection of nitrogen. Then precursor C was infused to the mixture immediately, stirred under the ambience of nitrogen at 120 °C for 20 min. At last, the resulted solution was cooled to room temperature naturally, and then washed by deionized water and ethanol alternately and the final powders were dried in vacuum at 60 °C for 6h. Ag-Ag_2S heterostructures were synthesized through the same procedures without adding GO.

3. Results and discussion

Fig. 1 showed the schematic of preparing Ag-Ag_2S/rGO. Obviously, carbon double bonds can be easily oxidized under strong oxidation conditions, thus the oxygen-containing functional groups (e.g. Epoxy, carboxyl group and hydroxy) that on the surface of graphene sheets are available for Ag^+ to interact with graphene via electrostatic attraction [18]. Then, thiocarbamide was added in excess (mole ratio of Ag to S is 1:7.5), part of which reacted with Ag^+ precursor to convert it into Ag-Ag_2S heterostructures. The rest thiocarbamide was to reduce GO to rGO. Eventually, Ag-Ag_2S/rGO nanocomposites were obtained.

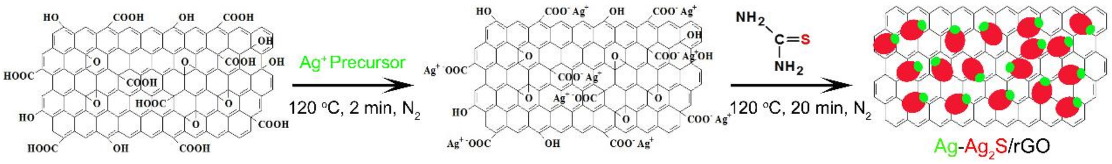

Fig. 1 Schematic illustration of the formation of Ag-Ag_2S/rGO nanocomposite.

Fig. 2a showed XRD patterns of as-obtained samples. A relatively wide peak at ~ 25° corresponded to the (002) lattice plane of rGO [10]. A few incisive peaks at ~ 34.6°, ~ 53.4°, ~ 36.9° were due to $(\bar{1}21)$, $(\bar{2}13)$ and (121) lattice planes of monoclinic structure of Ag_2S (JCPDS no.65-2356). While the peaks at ~ 37.9°, ~ 44.3°, and ~ 63.7° were related to (111), (200) and (220) lattice planes of face-centered cubic Ag crystals (JCPDS no. 65-8428). All of the diffraction peaks can be reflected Ag-Ag_2S/rGO nanocomposites were synthesized successfully. SEM image of Ag-Ag_2S/rGO (Fig. 2b) showed that the Ag-Ag_2S heterojunctions were dispersed and anchored on rGO favorably. The red cycles in Fig. 2b showed the thin flexible graphene were on the bottom of Ag-Ag_2S nanoparticles. TEM image of Fig. 2c presented that the diameters of the Ag-Ag_2S heterojunctions on rGO are ten to twenty nanometers. Ag gathered at one patch of Ag_2S and occupied one third to a half of the whole heterojunction. However, for Ag-Ag_2S heterostructures without rGO, they aggregated and formed clusters with high density of nanoparticles and with diameters of nanometer to micrometer (Fig. S1). The mechanism of formation of Ag-Ag_2S nanoparticles can be explained as follow: Ag^+ was reduced partly at first and Ag_2S was generated subsequently when adding thiocarbamide and could be deposited on the surface of Ag nucleus to form the Ag@Ag_2S core/shell nanostructures, while it is a metastable structure because of the different lattice spacings between Ag and Ag_2S thus inducing Ag to diffuse from the core of the Ag@Ag_2S nanoparticle and gather at the surface of the Ag_2S nanocrystal to form a patch according to Ostwald ripening effect process [19]. Fig. 2d is the HRTEM image of the juncture of Ag-Ag_2S. A measured interplanar d-spacings of ~ 0.238 nm on the dark side corresponded to the (111) plane separation of a face-centered cubic phase of Ag crystal, while d-spacings of ~ 0.283 nm and ~ 0.226 nm on the brighter side matched well with the $(\bar{1}12)$ and (120) lattice separation of a monoclinic phase of Ag_2S crystal, respectively.

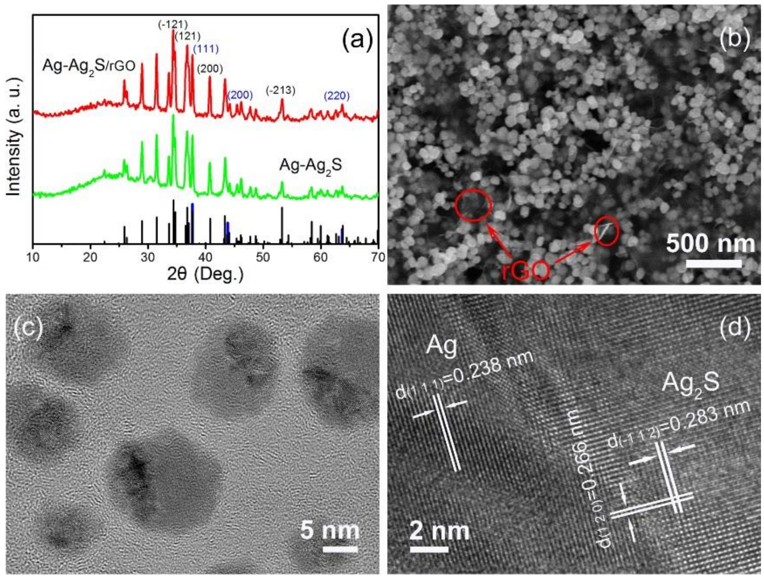

Fig. 2 (a) XRD patterns of Ag-Ag_2S and Ag-Ag_2S/rGO nanocomposites, respectively. (b) SEM image of Ag-Ag_2S/rGO. (c) TEM and (d) HRTEM images of the Ag-Ag_2S nanoparticles on rGO.

There are few reports about the PL spectra of nanostructured Ag_2S-zeolite A clusters, they presented an emission peak accompanied by a weaker shoulder peak, which could display the color of emission ranging from blue-green to red [20, 21]. Fig. 3 shows the photoluminescence spectrum of GO, Ag-Ag_2S heterostructures and Ag-Ag_2S/rGO. Fig. 3a, showed no apparent peak for the GO, while two peaks at 407 and 430 nm could be detected in case of Ag-Ag_2S heterostructures in Fig. 3b. With regard to Ag-Ag_2S/rGO in Fig. 3c, there are two peaks appeared at 327 and 339 nm, this phenomenon represented perfectly that Ag-Ag_2S/rGO was with a big blue shift compare with that of Ag-Ag_2S, which could be attributed to its smaller size of Ag-Ag_2S heterojunctions on rGO compared with clustered Ag-Ag_2S heterostructures. PL intensity of Ag-Ag_2S/rGO shows relative enhancement compared with our synthesized Ag-Ag_2S nanoparticles, which could be reflected from their corresponding integral area of peaks (Fig. S4). This phenomena can be explained by two factors. One is that rGO in Ag-Ag_2S/rGO possesses a few functional groups, which makes it much more easily to dissolve in ethanol compared with Ag-Ag_2S nanoparticles. The other is that electrons are excited from the valence band of the Ag-Ag_2S to the conduction band by incident light. Because of the interaction between the Ag-Ag_2S and rGO, the excited electrons can be transferred to rGO and get energy from the excitation levels of graphene, resulting in its transferring from the excited state of graphene to the Ag-Ag_2S and recombination with holes, [22] thus inducing the enhancement in the PL intensity of the Ag-Ag_2S/rGO composite.

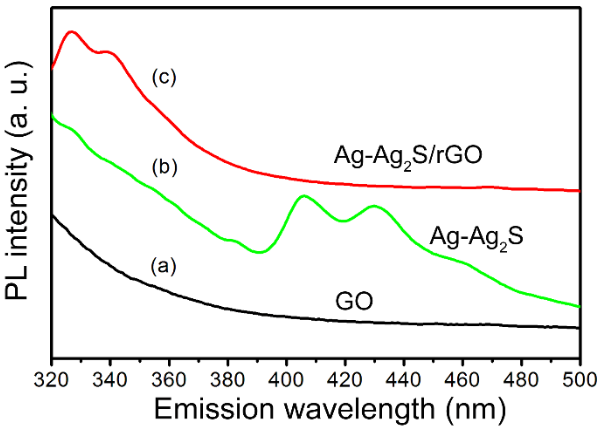

Fig. 3 Photoluminescence spectra of (a) GO, (b) Ag-Ag_2S and (c) Ag-Ag_2S/rGO

4. Conclusion

Ag-Ag_2S/rGO nanocomposites were synthesized via a facile thermal decomposition method. In our reaction system, silver ions were added to form nucleation precursors and interact with graphene via electrostatic attraction. Silver ions were reduced partly and the rest reacted with thiocarbamide to form Ag_2S. Ag diffused from the core and gathered at the surface to form a patch according to Ostwald ripening effect process. The photoluminescence spectra of Ag-Ag_2S/rGO showed two obvious emission peaks at 327 nm and 339 nm, respectively, with the excitation wavelength of 287 nm at room temperature, which makes it a novel candidate for long-wave UV radiation emitting nanocomposite.

Acknowledgements

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