A Facile One-Pot Hydrothermal Method to Produce SnS/Reduced Graphene Oxide and Its Application in Removal of Dyes from Aqueous Solution†

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In this work, we report a novel one-pot synthesis of SnS/reduced graphene oxide nanocomposites *via in situ* reduction of graphene oxide by Sn^{2+} under ethylene glycol assisted hydrothermal conditions. The morphology and structure of the obtained product were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy with energy dispersive X-ray analysis, transmission electron microscopy and UV-visible diffuse reflectance spectrophotometer. The as-synthesized graphene-SnS composite efficiently catalyzed the photodegradation of methyl orange with high concentration in aqueous solutions under visible light irradiation. Based on the high photocatalytic activity, the graphene-SnS composite can be expected to be a practical visible light photocatalyst.

Keywords: Graphene, SnS, Visible light, Photocatalytic activity.

INTRODUCTION

The graphene-metal sulfide composites was traditionally prepared using graphene oxide as staring material, the oxygen containing groups in graphene oxide controlled the decoration of nanoparticles without aggregation. Besides, the reduction of graphene oxide led to graphene based composites with well charge. SnS is an orthogonal IV-VI group semiconductor material and has been proved to have potentially excellent properties for application in various areas, such as photovoltaic material[1] *etc.* Jayalakshmi *et al.*[2] investigated hydrothermally prepared nano SnS as an electrode active material for supercapacitor. Nano SnS electrode has good cycling stability and the capacitance is impressively higher in both alkali and neutral solutions. Peisong *et al.*[3] reported synthesized SnS using a low cost and less toxic $SnCl_2$ as the precursor and demonstrated that SnS nanomaterials possess high photocatalytic activity under visible light, which may be ascribed to the strong visible-light absorption and its efficient multiple exciton generation under the excitation of light irradiation with the higher energy than the band gap. However, up to date, less literatures report on the ethylene glycol assisted synthesis of graphene based SnS nanocomposite and applications for visible light photodecomposition of organic dye solution.

EXPERIMENTAL

Synthesis of graphene-SnS nanocomposites: In a typical experiment, about 20 mg graphene oxide was dispersed in 100 mL ethylene glycol and then exfoliated to generate GONS dispersion solution by ultrasonication for 1 h. Subsequently, 0.29 g of tin(II) chloride dihydrate powder was added to the GONS aqueous dispersion, followed by ultrasonication for 20 min. Afterwards, anhydrous sodium thiosulfate and 10 mL ammonium hydroxide were added to the mixture under various stirring for 0.5 h. which was in favour of the uniform distribution of SnS on GNS. After that, an amount of PVP powder was slowly added into the solution with vigorous stirring at 100 ºC for another 4 h. The final product was rinsed with distilled water and ethanol for several times and dried at 60 ºC for 12 h.

Photocatalytic studies: In order to analysis of the photocatalytic effect, the degradation reaction of methylene orange in water was followed. For irradiation system, the visible light (λ > 420 nm, LED lamp) was used at the distance of 100 mm from the solution in darkness box, respectively. The clean transparent solution was analyzed by UV-visible spectroscopy. Details of methyl orange is given in Table-1.

TABLE-1 MOLECULAR STRUCTURE AND ABSORBANCE MAXIMUM (λ_{max}) OF METHYL ORANGE		
Organic dyes	Molecular structure	λ_{max}
Methyl orange		465 nm

RESULTS AND DISCUSSION

Characterization: Fig. 1a is the illustration of deposition of SnS on the GONS. Fig. 1b shows the XRD pattern of the product obtained from the above procedure. It can be seen that the diffractogram of graphene exhibits the typical peaks at 25.9 and 42.7°, corresponding to the graphite (002) and (100) reflections (Joint Committee for Powder Diffraction Studies (JCPDS) No. 01-0646)[4], respectively. In graphene-SnS composite all the diffraction peaks could be indexed to a simple cubic lattice with the cell constant a = 4.3284 Å, that is consistent with the reported data for SnS[5]. However, no signal for any other phases about graphene oxide (001) or graphene (002) can be detected in graphene-SnS composite.
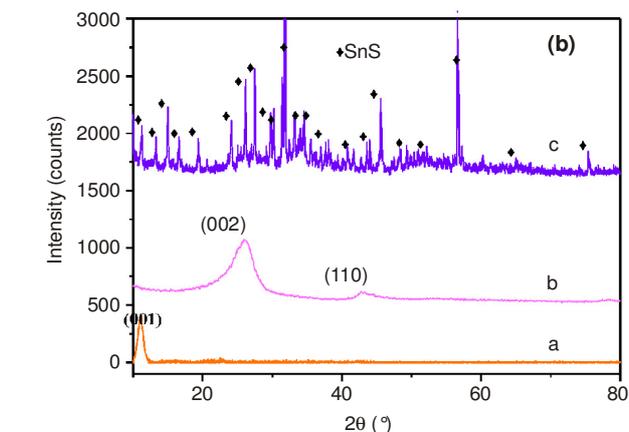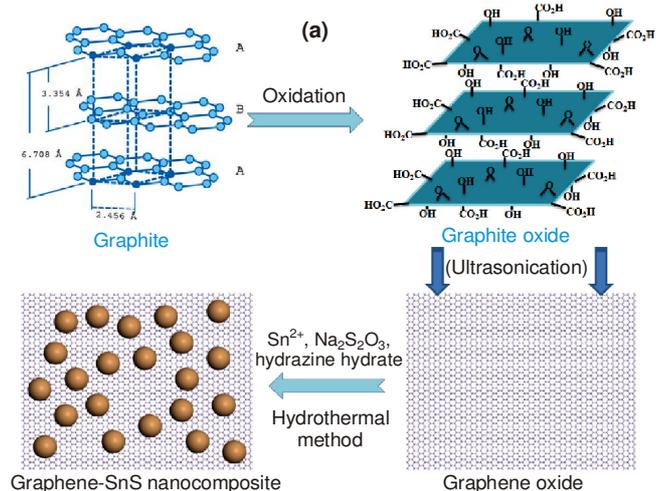
Fig. 1. (a) Schematic illustration of deposition of SnS on the graphene, (b) XRD pattern of graphene oxide, graphene and graphene-SnS composite

In Fig. 2a, it can be clearly seen that the pure graphene oxide sheets naturally aggregate and stack to multilayers with

numerous edges. Moreover, the surface of graphene oxide was very smooth compared with graphene sheets doped with SnS nanoparticles in Fig. 2b. In Fig. 3, it could be seen that SnS nanospheres were uniformly distributed on a single layered graphene sheets, no apparent aggregation of the SnS spheres was discerned. The size of SnS spheres was calculated to be around 5-15 nm.
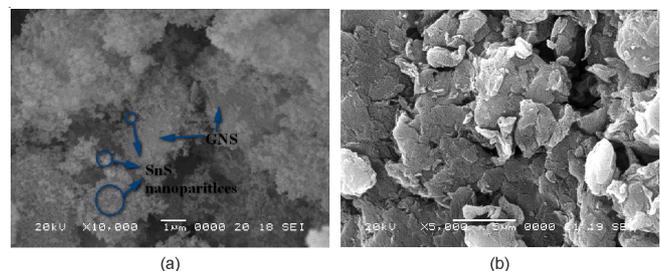
Fig. 2. SEM images of as-prepared composites: (a) graphene oxide, (b) graphene-SnS composite
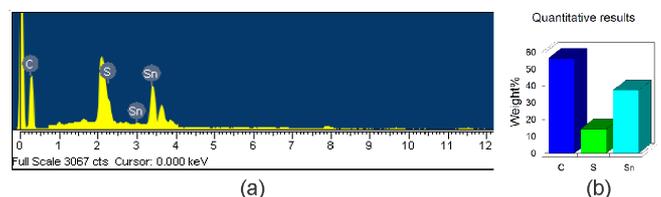
Fig. 3. EDX microanalysis (a) and element weight % (b) of graphene-SnS composite

To get information about change in elements and element weight %, the prepared graphene-SnS composite were examined by EDX. Fig. 3 shows the EDX microanalysis and element weight % of graphene-SnS composite. Main elements such as C, Sn and S are existed. The strong C signal should mainly originate from graphene nanosheets. The Sn and S peak comes from the precursor materials $SnCl_2\cdot 2H_2O$ and $Na_2S_2O_3$.

Photodecolorization process: The effect of catalyst composition on methyl orange (3.00×10^{-5} mol/L, 100 mL) degradation efficiency was investigated under visible light irradiation with a catalyst amount of 0.03 g. According to the results, a plot of -ln (c/c_{ads}) *versus* t will yield a slope of k_{app}. The results are displayed in Fig. 4. The scheme of excitation and charge transfer process between SnS particles and graphene nanosheets under visible light irradiation is shown in Fig. 5.
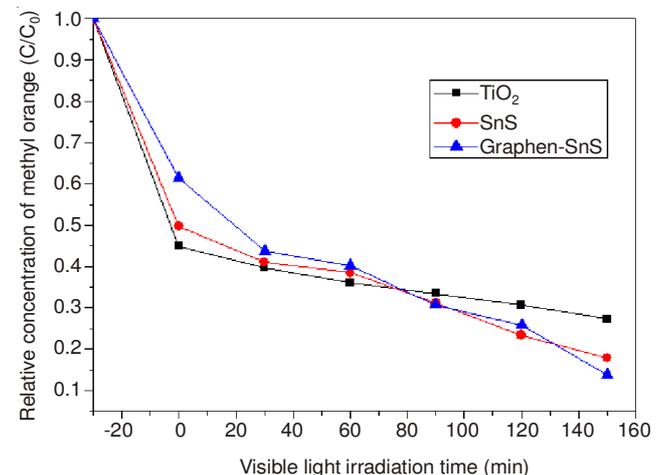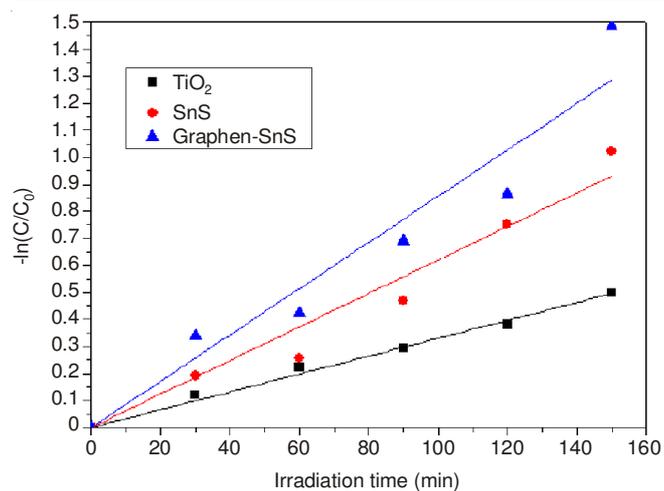
Fig. 4.   Effect of the methyl orange decolorization process and the apparent first order kinetics of methyl orange in presence of TiO₂, SnS and graphene-SnS photocatalysts
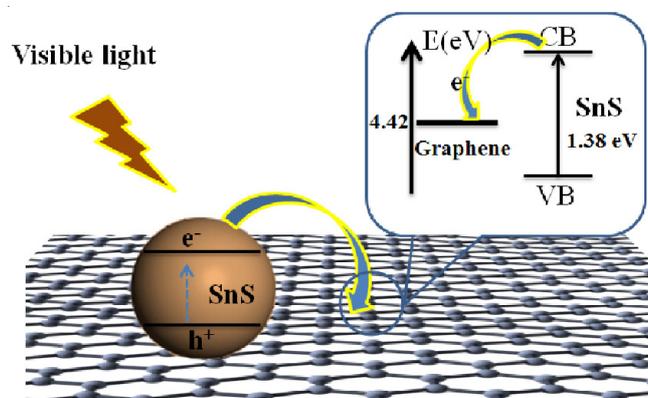
Fig. 5.   Schematic diagram of the charge transfer between graphene and SnS under visible light irradiation

Conclusion

In this study, we report the obtention of graphene-SnS nanocomposites were successfully synthesized by a facile ethylene glycol assisted hydrothermal method. SEM and TEM observation showed that SnS nanoparticles were triggered by precipitation reaction uniformly distributed on the graphene sheets. The results reveal that graphene-SnS composite exhibit the highest photocatalytic activity on the degradation of methyl orange solution under visible light irradiation.

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