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Sonophotocatalytic Performance of Ag_2Se-Graphene Hybrid Nanomaterials Synthesized by Hydrothermal Method†

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In this article, we report a novel Ag_2Se-graphene nanocomposites synthesis *via* a facile hydrothermal method. The structural and physico-chemical properties of Ag_2Se-graphene composite are further characterized by X-ray diffraction, scanning electron microscopy with an energy dispersive X-ray analysis. The sonophotocatalytic activity of Ag_2Se-graphene was evaluated by measuring degradation of organic pollutants such as methylene blue, rhodamine B under visible light combined ultrasonic irradiation. The sonophotocatalytic degradation was analyzed using UV/visible spectrophotometer. The sonophotocatalysis was faster due to the more formation of reactive radicals as well as the increase of the active surface area of Ag_2Se-graphene composites.

Keywords: Graphene, Ag_2Se, Ultrasonics, Visible light, Organic pollutants.

INTRODUCTION

Semiconductor photocatalysis has been previously described as a promising option to remove persistent pollutants from contaminated water. Photocatalysis involves the *in situ* generation and use of highly oxidizing agents, mainly hydroxyl radicals. The hydroxyl radical possesses natural properties that enable it to degrade organic pollutants in water to obtain a complete mineralization into CO_2, water and mineral acids such as sulfuric, hydrochloric and nitric acids. Silver selenide exists as a low-temperature phase (β-Ag_2Se) and a high-temperature phase (α-Ag_2Se) with the phase transition point at 1331 °C[1]. α-Ag_2Se is a well-known superionic conductor that is useful as the solid electrolyte in photochargeable secondary batteries. β-Ag_2Se is a narrow-band-gap semiconductor and has been widely used for a photosensitizer in photo-graphic films or thermal chromic materials. Cao *et al.*[2] reported synthesized single-crystalline Ag_2Se complex nanostructures *via* a solvothermal route and characterization its photocatalytic activity by photodegradation of rhodamine B (Rh.B) dye under ultraviolet (UV) light irradiation.

Several approaches has been reported that graphene can be used as good support for semiconductor nanocrystals due to unique electronic, mechanical, physical and chemical properties[3,4]. Flat monolayer structure and charge transferring ability of graphene make it suitable candidate to anchor Ag_2Se nanocomposite and will help to improve the photocatalytic activity to overcome recombination process. Many approaches, such as hydrothermal methods[5], sol-gel methods[6], have been developed to decorate graphene sheets with nanoparticles. Ultrasonication is an effective technique for attachment of nanoparticles on grephene sheet. Ultrasonication involves the use of ultrasound as a source of high energy at a frequency range of 18-100 kHz causing the creation of a phenomenon called acoustic cavitations. It involves the formation, growth and collapse of cavity bubbles that entraps dissolved gases or vapors surrounding water[7,8]. Ultrasonication has been found important in using for initiation or enhancement of catalytic reaction in both homogeneous and heterogeneous cases[9].

In this manuscript Ag_2Se-graphene composite are prepared *via* a relatively facile hydrothermal method. The objective of this paper is to experimentally prove that the sonophoto-catalytic degradative ability of Ag_2Se decorated graphene composites is superlative using methylene blue and rhodamine B.

EXPERIMENTAL

Synthesis of Ag_2Se-graphene composites: Ag_2Se-graphene nanocomposite were prepared with hydrothermal method. In a typical synthesis procedure, about 300 mg of

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graphene oxide and 22 mg $AgNO_3$ were dispersed in 100 mL water by ultrasonication for 1 h using a digital sonifer to obtain an even graphene oxide nanosheets (GONS)/Ag^+ solution. In addition selenium powder and 6 mL NH_4OH (28 wt %) were added to the solution, the mixture was stirred rapidly at 100 °C for 8 h. and then transferred to a Teflon-lined stainless steel autoclave that was sealed. The contents were then warmed to 160 °C for 12 h. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water five times and dried in a vacuum oven.

Photocatalytic studies: In an ordinary photocatalytic test performed at room temperature, 0.03 g of composite sonophotocatalyst was added to 50 mL of 3.0×10^{-5} mol/L methylene blue and rhodamine B solution. In addition, the sonophotocatalytic activities were determined using methylene blue and rhodamine B decomposition in aqueous solution under visible light ($\lambda > 420$ nm, LED lamp) combined with ultrasonic generators (Ultrasonic Processor VCX 750, Korea) operated at a dixed frequency of 20 kHz and output power of 750 W through manual adjusting. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the rhodamine B concentration in solution after dark adsorption, which was hereafter considered as the initial concentration (C_{ads}). Samples were then withdrawn regularly from the reactor by an order of 30, 60, 90, 120 and 150 min. The clean transparent solution was analyzed by using a UV-visible spectrophotometer (Optizen POP) at wavelength from 250 to 800 nm.

RESULTS AND DISCUSSION

Characterization: Fig. 1a is the illustration of deposition of Ag_2Se 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), respectively. XRD pattern of Ag_2Se exhibit the characteristic (002), (112), (121), (103), (031), (200), (213) and (134) crystal planes originated from the orthorhombic Ag_2Se phase, which were in accordance with the results reported by Zhang *et al.*[5] with the lattice parameters were close to a = 4.331 Å, b = 7.061 Å and c = 7.763 Å (JCPDS card no. 14-0072). However, no signal for any other phases about graphene oxide (001) or graphene (002) can be detected in Ag_2Se-graphene composite.

In Fig. 2a, it can be clearly seen that the pure graphene oxide sheets naturally aggregate and stack to multilayers with numerous edges. The morphology of the graphene observed is a flaky texture reflecting its layer structure. Agglomarted Ag_2Se nanoparticles can be observed which were distributed on graphene sheets in Fig. 2b. The graphene sheets act like a bridge for Ag_2Se nanoparticles which may be benificial to provide a path for the photogenerated electron and hence will enhance the sonophotocatalytic performance.

To get information about change in elements and element weight %, the prepared Ag_2Se-graphene composite were examined by EDX. Fig. 3 shows the EDX microanalysis and element weight % of Ag_2Se-graphene composite. Main

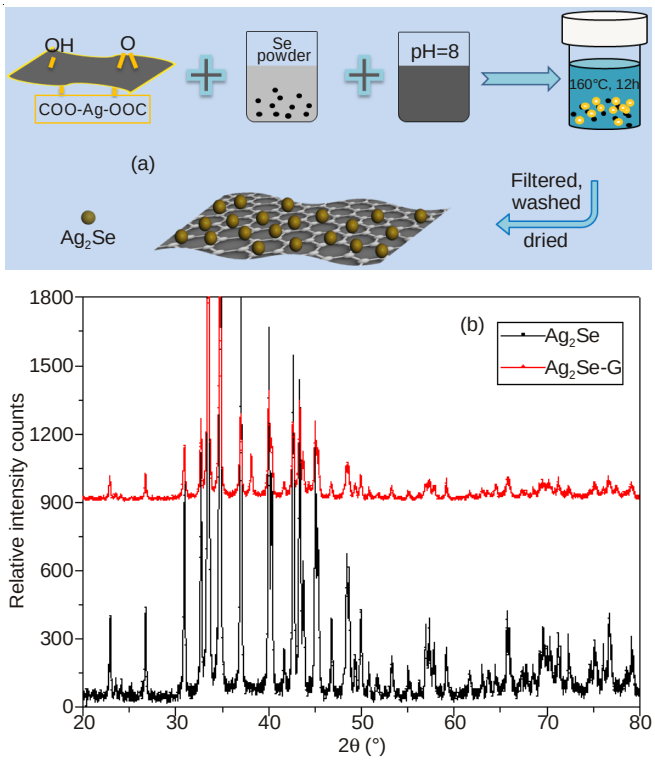

Fig. 1. (a) Schematic illustration of deposition of Ag_2Se on the graphene, (b) XRD pattern of Ag_2Se and Ag_2Se-graphene composite

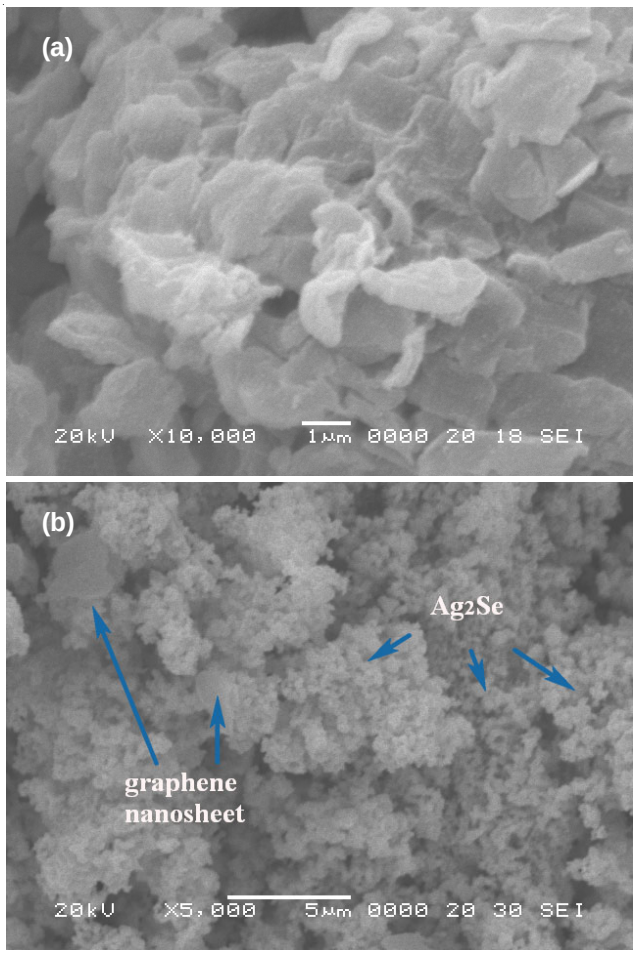

Fig. 2. SEM images of as-prepared composites: (a) GO, (b) Ag_2Se-graphene composite

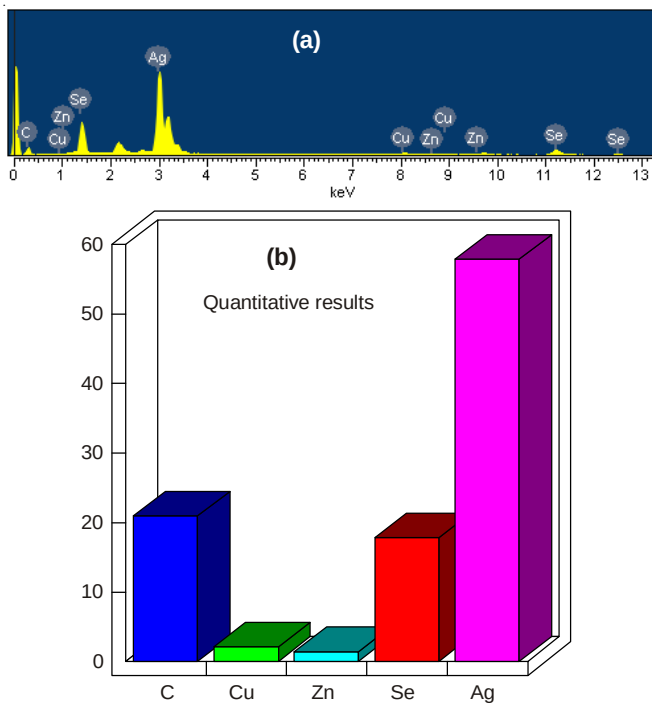

Fig. 3. EDX microanalysis (a) and element weight % (b) of Ag_2Se-graphene composite

elements such as C, Ag and Se are existed. The strong C signal should mainly originate from graphene nanosheets. Very low concentration of impurity was present which may be due to experimental procedure. This confirms that Ag_2Se-graphene hybrid has been synthesized successfully.

Sonophotodecolorization process: Fig. 4(a) and 4(b) represent the degradation of methylene blue and rhodamine B with Ag_2Se-graphene under visible light combined with ultrasonic irradiation from which it is clear that the concentration of methylene blue and rhodamine B gradually diminishing with increasing time for all of samples. Moreover, the dye solution increasingly lost its colour intensity as the dye concentration continued to decrease. The decrease in concentration was evaluated at the λ_{max} values of the dyes which were determined from the absorption spectra of the dyes. The λ_{max} values of methylene blue and rhodamine B were found to be 665 nm and 554 nm, respectively. The scheme of excitation and charge transfer process between Ag_2Se particles and graphene nanosheets under visible light combined with ultrasonic is shown in Fig. 5.

Conclusion

In this study, Ag_2Se-graphene composite sonophotocatayst were prepared by hydrothermal method. XRD pattern of the Ag_2Se-graphene composite suggests the Ag_2Se particles appear as the predominant crystalline phase of acanthite. SEM images shows that Ag_2Se nanoparticles were attached on graphene sheet. From the EDX data, the main elements like Ag, Se, C existed in the composites. The catalytic activity of Ag_2Se-graphene composites were examined by degradation of methylene blue and rhodamine B in aqueous solutions under visible light combined with ultrasonic irradiation. These results reveals the exceptional feature of graphene that make it an excellent supporting material for semiconductor nanoparticles as an electron acceptor and transporter.

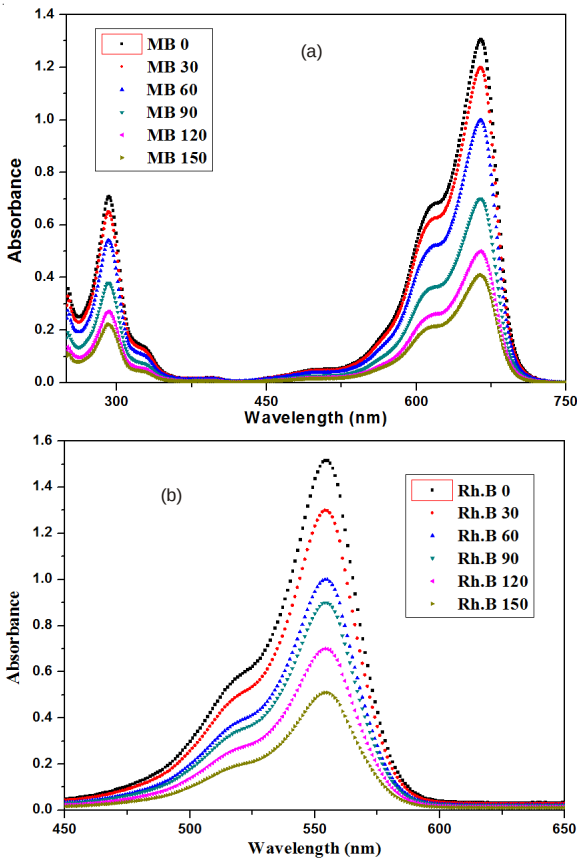

Fig. 4. Effect of the methylene blue and rhodamine B decolorization process in presence of Ag_2Se-graphene sonophotocatalysts

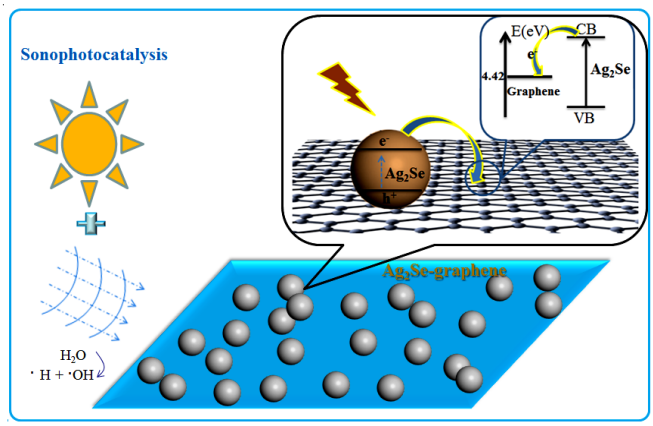

Fig. 5. Schematic diagram of the charge transfer between graphene and Ag_2Se under visible light combined ultrasonic irradiation

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