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Preparation of C_{60} Nanowhiskers-ZnS Nanocomposites and Photocatalytic Degradation of Methylene Blue

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Liquid-liquid interfacial precipitation (LLIP) method was used to prepare C_{60} nanowhiskers. Zinc sulfide nanoparticles were synthesized by zinc nitrate hexahydrate and thiourea under microwave irradiation. C_{60} nanowhiskers-ZnS nanocomposites were prepared by a reaction of C_{60} nanowhiskers and ZnS nanoparticles in an electric furnace. The C_{60} nanowhiskers-ZnS nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV-visible spectrophotometry. The C_{60} nanowhiskers-ZnS nanocomposites were evaluated as a photocatalyst in the photocatalytic degradation of methylene by UV-visible spectrophotometry under ultraviolet light at 254 nm.

Keywords: ZnS, C_{60} nanowhiskers-ZnS nanocomposites, Photocatalytic degradation, Methylene blue, UV-visible spectrophotometry.

INTRODUCTION

Fullerenes have attracted considerable attention for their novel carbon chemical and physical properties, since their discovery in 1985[1,2]. C_{60} has been examined for applications in composite materials, semiconductors, medicine and superconductors[3]. Crystals composed of C_{60} fullerene molecules have been synthesized in a distinctive form of different forms[4]. Recently, liquid-liquid interfacial precipitation (LLIP) method was used to obtain a new type of needle-like C_{60} crystal[5]. This method resulted the nucleation of C_{60} molecules to the interface between toluene solution of C_{60} and isopropyl alcohol to form a needle-like arrangement of C_{60} molecules at the liquid-liquid interface[6-8]. The resulting of the needle-like C_{60} crystals had a size distribution ranging from sub-micrometers to several hundred micrometers[9]. This discovery is important for applications in fuel cells, solar cells and catalysts, *etc.*[10].

Zinc sulfide (ZnS) is an essential semiconductor utilized in forms of applications, such as optical coatings, photoconductors, photocatalysis and electro-optic modulators owing to its wide band gap and novel physical properties[11-13]. Zinc sulfide has attracted considerable interests because the properties in nanostructures differ significantly from those of their bulk[14]. Over the last few decades, ZnS nanoparticles have been synthesized *via* various chemical routes including hydrothermal, solvo-thermal methods, sonochemical method, sol-gel process, template method and direct elemental reaction route[15-21]. The microwave-assisted hydrothermal technique is useful technique for obtaining inorganic materials[22]. Generally, microwave synthesis is fast, simple and energy saving[21]. Furthermore, it has several advantages, such as a higher reaction rate, rapid volumetric heating and energy efficient[23-25].

Contaminated waste containing dyes from various laboratories and factories is toxic to microorganisms, aquatic life and humans[26]. Therefore, an effective and frugal treatment of these organic dyes has become an essential issue in many developed countries[27]. An effective method for the decomposition of organic dyes from domestic and industrial wastewater is photocatalysis technology[28]. In addition, it is a nontoxic, cost-effective, highly stable and environmentally-friendly technology[29].

This paper reports the preparation of C_{60} nanowhiskers, ZnS nanoparticles and C_{60} nanowhiskers-ZnS nanocomposites. The C_{60} nanowhiskers-ZnS nanocomposites were heated to 700 °C in an electric furnace under an inert Ar gas atmosphere for 2 h[30]. The photocatalytic effects of C_{60} nanowhiskers-ZnS nanocomposites on the photocatalytic degradation of methylene blue was examined under ultraviolet light at 254 nm using a UV-visible spectrophotometer.

EXPERIMENTAL

Zinc nitrate hexahydrate, tetrahydrofuran (THF), isopropyl alcohol (IPA), benzene and ethanol were obtained from Samchun Chemicals. Methylene blue (MB) and thiourea were purchased from Sigma-Aldrich. C_{60} was supplied by Tokyo Chemical Industry Co., LTD.

The samples were heat treated in an electric furnace (Ajeon Heating Industry Co., Ltd). Microwave irradiation was performed by continuous heating at the maximum power in a domestic oven (2450 MHz, 700 W). The crystal structure of the synthesized C_{60} nanowhiskers and ZnS nanoparticles was examined by X-ray diffraction (XRD, Bruker, D8 Advance) using CuK_α (λ = 1.5406 Å) radiation. The morphology and particle size of the samples were examined by transmission electron microscopy (TEM, JEOL Ltd., JEM-2010) at an acceleration voltage of 200 kV. The surface of all the samples was examined by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an acceleration voltage ranging from 0.5 to 30 kV. The UV-visible spectra of the samples were obtained using a UV-visible spectrophotometer (Shimazu, UV-1601 PC). An UV lamp (8 W, 254 nm, 77202 Marne La Valee-cedex 1 France) was used as the ultraviolet light irradiation source.

Preparation of C_{60} nanowhiskers: 7 mg of C_{60} powder was dissolved in 2 mL of benzene, ultrasonicated for 0.5 h and filtered to remove the undissolved C_{60} powder. The C_{60}-saturated benzene solution was poured into a 20 mL vial and 10 mL of isopropyl alcohol was added slowly to the C_{60}-saturated benzene solution to form a liquid-liquid interface. The solutions of the vial were then mixed manually and stored in a refrigerator at 5 °C.

Synthesis of ZnS nanoparticles under microwave irradiation: 0.2 M zinc nitrate hexahydrate and 0.2 M thiourea solutions were prepared separately in 20 mL of distilled water. The two solutions were then mixed in a 100 mL beaker and the mixture solution was stirred vigorously for 0.5 h. The resulting solution was exposed to microwave irradiation for 10 min to yield a yellow color powder.

Preparation of C_{60} nanowhiskers-ZnS nanocomposites: To synthesize C_{60} nanowhiskers-ZnS nanocomposites, 10 mg of synthesized C_{60} nanowhiskers and 10 mg of ZnS nanoparticles were dissolved separately in 5 mL of tetrahydrofuran. The two solutions were mixed and stirred vigorously for 0.5 h. The mixed solution was poured into a vessel and dried for 1 h to vaporize the organic solvent. The vessel was heated in an electric furnace to 700 °C under an Ar atmosphere for 2 h. The sample was then cooled down to room temperature under an Ar atmosphere for 5 h.

Evaluation of the photocatalytic degradation of methylene blue with ZnS nanoparticles and C_{60} nanowhiskers-ZnS nanocomposites: The synthesized ZnS nanoparticles and C_{60} nanowhiskers-ZnS nanocomposites were used as a photocatalyst for the degradation of methylene blue. 5 mg of synthesized ZnS nanoparticles and 5 mg of C_{60} nanowhiskers-ZnS nanocomposites were placed separately in a vial containing 10 mL of an aqueous methylene blue solution. The vial was irradiated with 254 nm light using a UV-lamp. The level of methylene blue degradation by the photocatalysts was analyzed by UV-visible spectrophotometry.

RESULTS AND DISCUSSION

The synthesized C_{60} nanowhiskers were characterized by UV-visible spectroscopy. Fig. 1 (a) shows the optical properties of C_{60} nanowhiskers dispersed in toluene at λ_{max} = 542, 597 and 622 nm. Fig. 1 (b) shows the optical properties of synthesized ZnS nanoparticles dispersed in ethanol at λ_{max} = 285 nm.

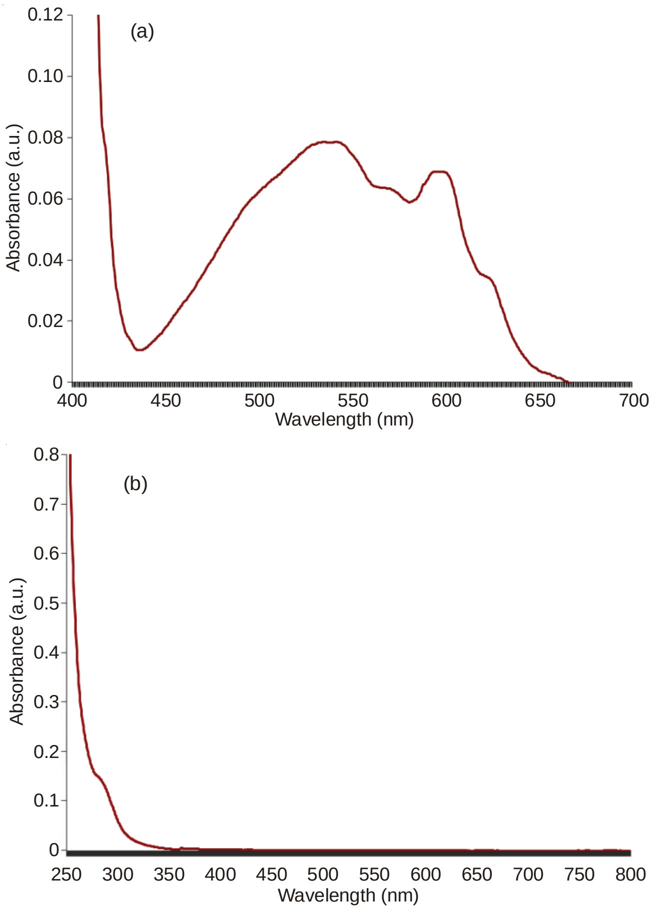

Fig. 1. UV-visible spectra of (a) synthesized C_{60} nanowhiskers and (b) ZnS nanoparticles

Fig. 2 shows XRD patterns of (a) synthesized C_{60} nanowhiskers and (b) ZnS nanoparticles. The characteristic peaks of synthesized C_{60} nanowhiskers were observed at 10.79°, 17.70°, 20.72°, 27.98°, 30.76° and 32.63° 2θ. The characteristic peaks of ZnS nanoparticles were observed at 27.01°, 28.60°, 30.60°, 39.75°, 47.65°, 51.86° and 56.55° 2θ.

Fig. 3 shows TEM images of (a) synthesized C_{60} nanowhiskers, (b) ZnS nanoparticles and (c) C_{60} nanowhiskers-ZnS nanocomposites. The synthesized C_{60} nanowhiskers had a rod and needle-like shape [Fig. 3 (a)]. The thickness of the C_{60} nanowhiskers ranged from 100 nm to 2 μm. The synthesized ZnS nanoparticles had a quasi-spherical shape and agglomeration. The mean size of the synthesized ZnS nanoparticles was 70 nm [Fig. 3 (b)]. The ZnS nanoparticles were attached to sides of the C_{60} nanowhiskers [Fig. 3 (c)].

Fig. 4 shows SEM images of (a) synthesized C_{60} nanowhiskers, (b) ZnS nanoparticles and (c) C_{60} nanowhiskers-ZnS nanocomposites. The SEM image of synthesized C_{60} nanowhiskers showed a rod and needle-like shape (Fig. 4 (a)). The surface of synthesized ZnS nanoparticles had many pores. Because of this structure, the synthesized ZnS nanocomposites had a large surface area [Fig. 4 (b)]. C_{60} nanowhiskers were broken into smaller size [Fig. 4 (c)]. And the surface of some C_{60} nanowhiskers was coated with collapsed ZnS nanoparticles. As a result, the surface of synthesized C_{60} nanowhiskers-ZnS nanocomposites was widened.

Fig. 5 shows the UV-visible spectra of the degradation of methylene blue using the (a) synthesized ZnS nanoparticles

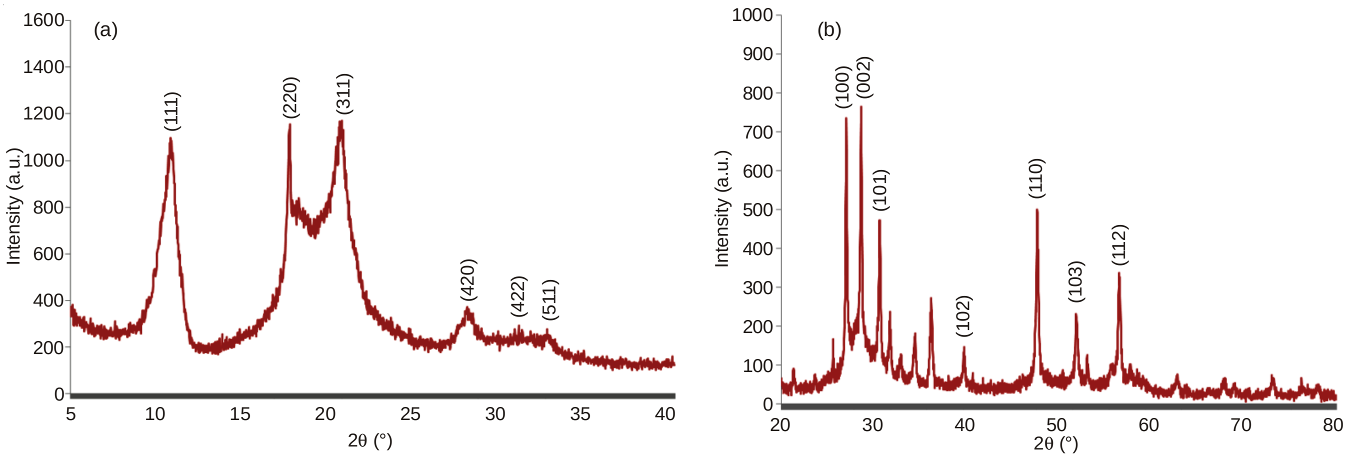

Fig. 2. XRD patterns of (a) synthesized C_{60} nanowhiskers and (b) ZnS nanoparticles

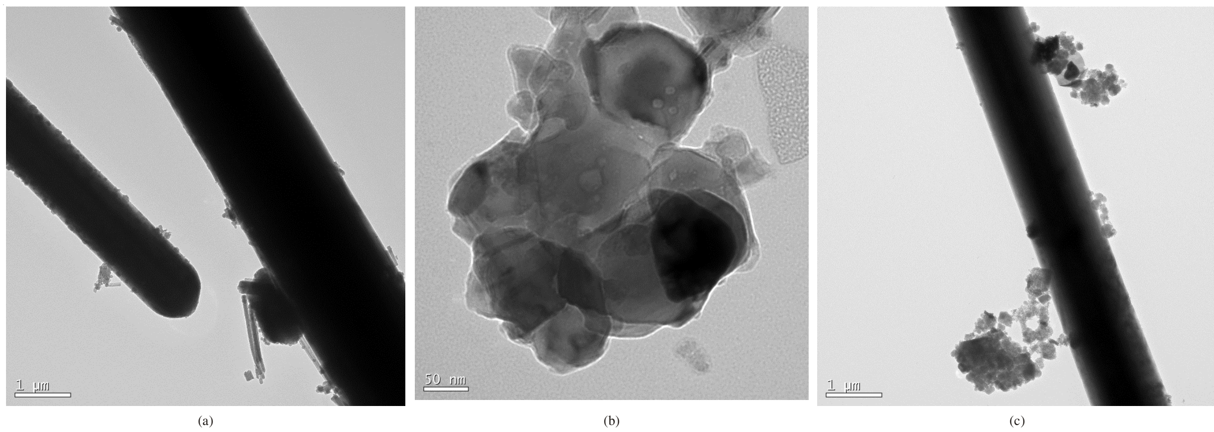

Fig. 3. TEM images of (a) synthesized C_{60} nanowhiskers, (b) ZnS nanoparticles and (c) C_{60} nanowhiskers-ZnS nanocomposites

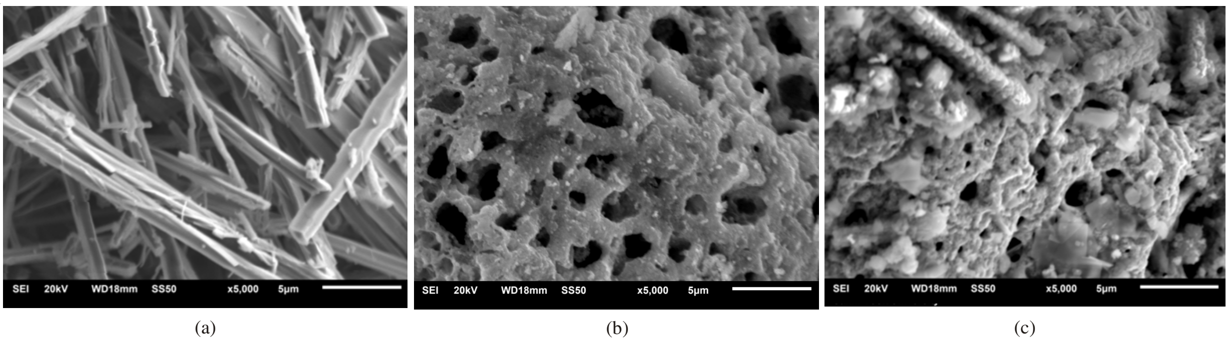

Fig. 4. SEM images of (a) synthesized C_{60} nanowhiskers, (b) ZnS nanowhiskers and (c) C_{60} nanowhiskers-ZnS nanocomposites

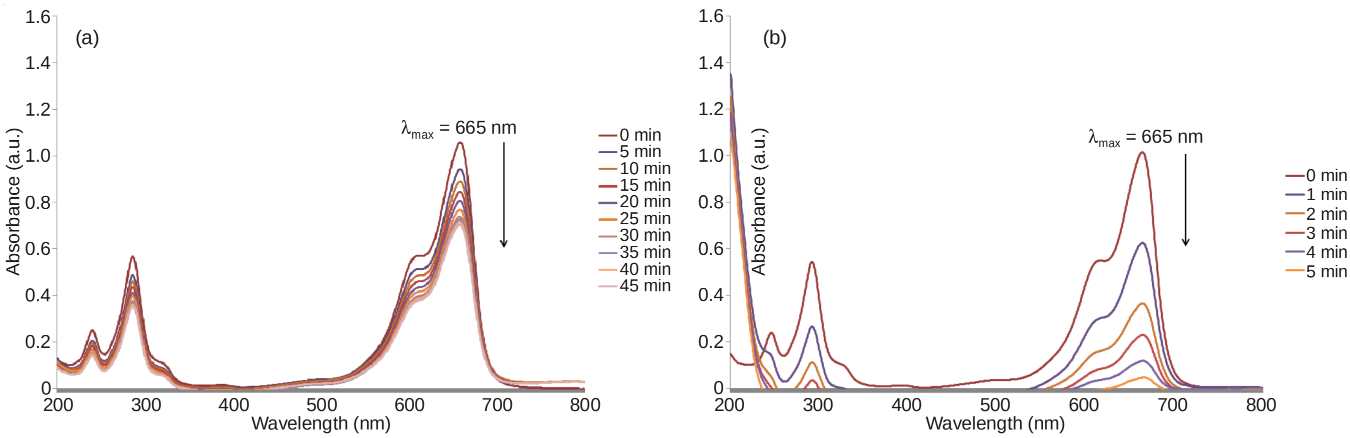

Fig. 5. UV-visible spectra of degradation of methylene blue with (a) synthesized ZnS nanoparticles and (b) C_{60} nanowhiskers-ZnS nanocomposites

under ultraviolet irradiation at 254 nm for 5 min and (b) C_{60} nanowhiskers-ZnS nanocomposites at 254 nm for 1 min. A comparison of two spectra in Fig. 5 showed that C_{60} nanowhiskers-ZnS nanocomposites were more efficient as a photocatalyst than ZnS nanoparticles. The C_{60} nanowhiskers had an important effect on the photo-catalytic degradation of methylene blue. The addition of nanocarbon material to the matrix of suitable semiconductor material (ZnS) can lead to a smaller band gap due to chemical bonding between semiconductor nanoparticles and nanocarbon material[31,32].

Conclusion

LLIP method was used to prepare C_{60} nanowhiskers. The synthesized C_{60} nanowhiskers had a rod and needle-like shape. Zinc sulfide nanoparticles were synthesized using a microwave irradiation technique. The synthesized ZnS nanoparticles had porous surface and large surface area. The C_{60} nanowhiskers-ZnS nanocomposites were prepared by heat treatment in an electric furnace at 700 °C under an Ar atmosphere for 2 h. The form of C_{60} nanowhiskers-ZnS nanocomposites displayed that ZnS nanoparticles were attached to sides of C_{60} nanowhiskers. Also, synthesized C_{60} nanowhiskers-ZnS nanocomposites had large surface area. The ZnS nanoparticles and C_{60} nanowhiskers-ZnS nanocomposites were examined as a photocatalyst for the degradation of methylene blue under UV-light at 254 nm. The degradation of methylene blue was effective using the synthesized ZnS nanoparticles and C_{60} nanowhiskers-ZnS nanocomposites as a photocatalyst. The C_{60} nanowhiskers-ZnS nanocomposites were superior to the ZnS nanoparticles. The addition of C_{60} nanowhiskers had a significant effect on the photocatalytic degradation of methylene blue.

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