



Preparation of C₆₀ Nanowhiskers/NiS₂ Nanocomposites and Photocatalytic Degradation of Organic Dyes

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Received: 1 May 2014;

Accepted: 13 July 2014;

Published online: 20 February 2015;

AJC-16896

[C₆₀]Fullerene nanowhiskers/NiS₂ nanocomposites were prepared by a reaction of NiS₂ nanoparticles and C₆₀ nanowhiskers. The C₆₀ nanowhiskers (FNWs) were synthesized by a liquid-liquid interfacial precipitation method using solvent solutions, such as benzene and toluene saturated with C₆₀ powder and isopropyl alcohol. The NiS₂ nanoparticles were synthesized by a reaction of NiCl₂·H₂O and Na₂S₂O₃·5H₂O in deionized water under microwave irradiation. The C₆₀ nanowhiskers/NiS₂ nanocomposites were calcined in an electric furnace at 700 °C for 2 h. The C₆₀ nanowhiskers/NiS₂ nanocomposites were characterized by X-ray diffraction and UV-visible spectrophotometry. The C₆₀ nanowhiskers/NiS₂ nanocomposites were evaluated as a photocatalyst by UV-visible spectrophotometry in the degradation of organic dyes, such as methylene blue and brilliant green, under ultraviolet light at 365 nm.

Keywords: [C₆₀]Fullerene nanowhiskers, NiS₂ nanoparticles, Methylene blue, Brilliant green, Photocatalytic degradation.

INTRODUCTION

[C₆₀]Fullerene has attracted considerable research interest owing to its large potential applications in semiconductors¹. The growth of C₆₀ crystals is dependent on the temperature and organic solvents used²⁻⁴. Recently, Miyazawa *et al.*⁵⁻⁸ reported another type of C₆₀ crystal with a hair needle-like morphology called C₆₀ nanowhiskers, which was obtained using a liquid-liquid interfacial precipitation method from a saturated toluene or benzene solution of [C₆₀]fullerene and isopropyl alcohol. Crystalline whiskers have also been grown from C₆₀ solutions in pentane, *n*-hexane and dichloromethane⁹. Typical C₆₀ nanowhiskers are hexagonal and hair needle-like crystals with diameters ranging from 0.5 to 100 μm. The synthesized single C₆₀ nanowhisker crystals were less than 1 μm in diameter and more than 100 μm in length^{2-7,9}.

Transition metal semiconductors have attracted considerable attention owing to their attractive properties, such as magnetic and catalytic effect^{10,11}. Transition metal sulfides, such as ZnS, SnS, CuS, CuS₂, FeS₂, CoS₂ and NiS₂, have been studied extensively¹². Nickel disulphide has two main phases, a triclinic phase¹³ and a cubic pyrite phase¹⁴. Cubic pyrite NiS₂ nanoparticles have interesting electrical, optical and magnetic properties¹⁵⁻¹⁷. Nickel disulphide has been synthesized using a range of methods. Chen *et al.*¹⁸ obtained NiS₂ nanoparticles from a reaction of NiCl₂·6H₂O and Na₂S₂O₃·5H₂O under hydrothermal conditions at 140-150 °C for 12 h. Qian *et al.*¹⁹ prepared NiS₂ nanoparticles from a reaction of NiSO₄·6H₂O

and Na₂S₃ in an ethylenediamine solvent at 130 °C for 8-12 h. Microwave irradiation has also been used in the synthesis of a range of nanomaterials including metals, metal oxides, chalcogenides and semiconductors with a controlled shape and size without the need for high temperatures or high pressures²⁰⁻²⁸.

EXPERIMENTAL

NiCl₂·6H₂O was purchased from Daejung Chemicals and Metals. Na₂S₂O₃·5H₂O was purchased from Shinyo Pure Chemicals. The organic dyes, such as methylene blue (MB) and brilliant green (BG) were purchased from Sigma-Aldrich. Ethanol, isopropyl alcohol (IPA) and tetrahydrofuran (THF) were obtained from Samchun Chemicals. C₆₀ was supplied by Tokyo Chemical Industry Co., Ltd.

An electric furnace (Ajeon Heating Industry Co., Ltd.) was used to heat the sample. A UV lamp (8 W, 365 nm, 77202 Marne La Valee-Cedex1 France) was used as the ultraviolet light irradiation source.

The surfaces of the C₆₀ nanowhiskers/NiS₂ nanocomposites were observed by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an accelerating voltage of 0.5 to 15 kV. The morphology and crystallite size of the samples were examined by transmission electron microscopy (TEM, JEM-2010, JEOL Ltd.) at an acceleration voltage of 200 kV. The crystal structure of the nanomaterials was examined by X-ray diffraction (XRD, Bruker, D8 Advance) using CuK_α radiation and a secondary monochromator (V = 40 kV, A = 40 mA, Ni filter). Ultraviolet-visible spectrophotometer (Shimadzu, UV-

1601 PC) was used to characterize the nanomaterials and assess their photocatalytic activity. Microwave irradiation was performed by continuous heating at the maximum power in a domestic oven (2450 MHz, 700 W).

Synthesis of C₆₀ nanowhiskers: In a typical experiment, the C₆₀ nanowhiskers were synthesized using the liquid-liquid interfacial precipitation method. C₆₀ was dissolved in 5 mL of toluene to have a saturated state. Isopropyl alcohol was added to a C₆₀-saturated toluene solution to form a liquid-liquid interface between the C₆₀-saturated solution and isopropyl alcohol. The resulting mixture was left to stand at low temperature for a few days in a refrigerator to obtain the [C₆₀] fullerene nanowhiskers product.

Synthesis of NiS₂ nanoparticles: In a typical experiment, the NiS₂ nanoparticles were synthesized from NiCl₂·6H₂O (0.95 g, 4 mM NiCl₂) and Na₂S₂O₃·5H₂O (1.99 g, 8 mM Na₂S₂O₃) dissolved in 100 mL of deionized water. The mixture solution was stirred vigorously for 10 min. The beaker containing the mixture solution was reacted under microwave irradiation for 10 min. After the reaction was completed, the black precipitate was washed several times with ethanol and dried at room temperature.

Synthesis of C₆₀ nanowhiskers/NiS₂ nanocomposites: In a typical experiment, the prepared C₆₀ nanowhisker/NiS₂ nanocomposites were prepared from the C₆₀ nanowhiskers and NiS₂ nanoparticles at a mixing ratio of 1:1. The mixture was dissolved in 10 mL of THF with constant stirring to produce the C₆₀ nanowhiskers/NiS₂ nanocomposites. The mixture was then dried at room temperature. After drying, the hybrid nanocomposites were heated in an electric furnace at 700 °C for 2 h.

Photocatalytic degradation of organic dyes with hybrid nanocomposites: The photocatalytic activity of the C₆₀ nanowhiskers/NiS₂ nanocomposites was examined using methylene blue and brilliant green solutions. 5 mg of each nanomaterial which C₆₀ nanowhiskers/NiS₂ nanocomposites were dispersed in 10 mL of water containing 0.01 mM methylene blue or brilliant green. All mixture solutions were irradiated with ultraviolet light at 365 nm for 1 min. The methylene blue and brilliant green solutions degraded by each nanomaterial as a photocatalyst under ultraviolet light at 365 nm was observed by UV-visible spectrophotometry.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites. The C₆₀ nanowhiskers showed a rod needle-like morphology. The NiS₂ nanoparticles showed a cubic pyrite phase and agglomerated particles. The NiS₂ nanoparticles were located above the C₆₀ nanowhiskers which had a rod and needle type morphology in the C₆₀ nanowhiskers/NiS₂ nanocomposites.

Fig. 2 shows TEM images of (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites. The C₆₀ nanowhiskers were grown by the liquid-liquid interfacial precipitation method. The C₆₀ nanowhiskers had a rod needle-like type. The synthesized NiS₂ nanoparticles appeared to agglomerate. The synthesized NiS₂ nanoparticles had a cubic pyrite phase and a mean size of 70-100 nm. The C₆₀ nanowhiskers/NiS₂ nanocomposites showed

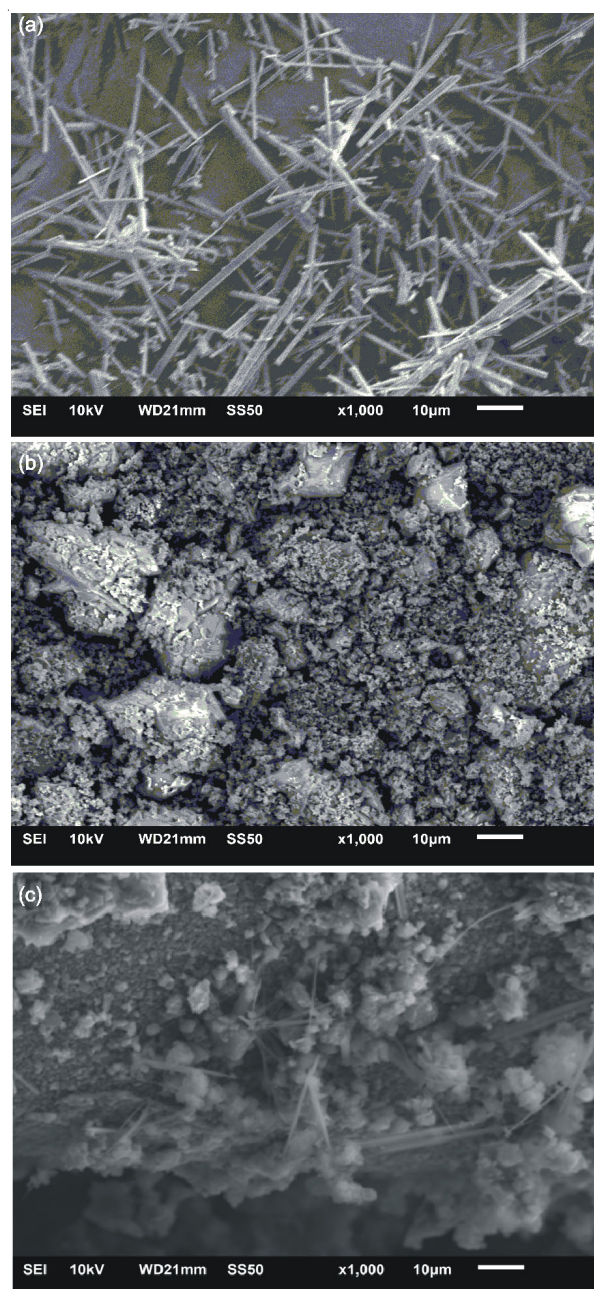


Fig. 1. SEM images of (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites

an agglomerate state and NiS₂ nanoparticles were on the C₆₀ nanowhiskers.

Fig. 3 shows XRD patterns of (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites. The C₆₀ nanowhiskers/NiS₂ nanocomposites observed at 27.13, 31, 43, 35.25, 38.75, 45.04, 53.38, 55.96, 58.46, 60.89 and 72.36° 2θ due to NiS₂ nanoparticles and 10.73, 17.57, 20.64, 27.96, 30.69 and 32.60° 2θ due to C₆₀ nanowhiskers. The XRD peaks at 27.13, 31.43, 35.25, 38.75, 45.04, 53.38, 55.96, 58.46, 60.89 and 72.36° 2θ were assigned to the (111), (200), (210), (211), (220), (311), (222), (302), (321) and (331) planes of NiS₂ nanoparticles. The XRD peaks at 10.73, 17.57, 20.64, 27.96, 30.69 and 32.60° 2θ were assigned to the (111), (220), (311), (420), (422), (333) planes of C₆₀ nanowhiskers.

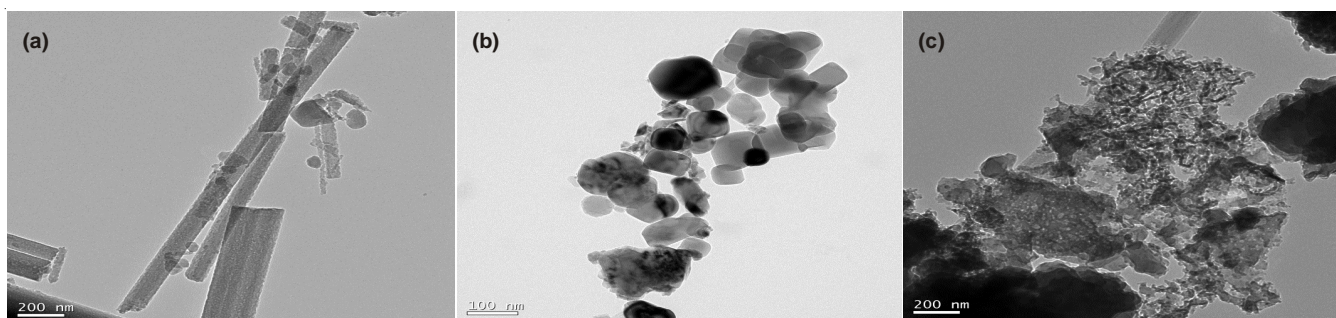


Fig. 2. TEM images of the (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites

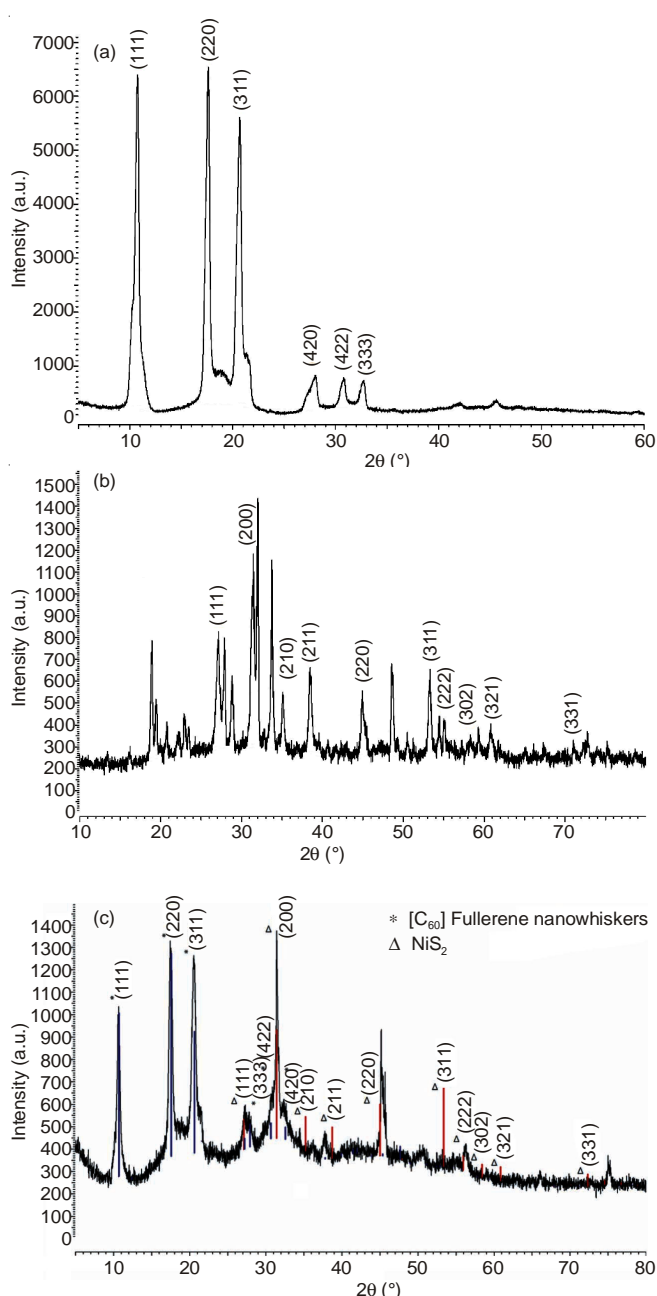


Fig. 3. XRD patterns of the (a) synthesized C₆₀ nanowhiskers, (b) synthesized NiS₂ nanoparticles and (c) C₆₀ nanowhiskers/NiS₂ nanocomposites

Fig. 4 shows the UV-visible spectra of (a) the synthesized C₆₀ nanowhiskers, the degraded (b) methylene blue and (c) brilliant green solution with of C₆₀ nanowhiskers/NiS₂ nano-

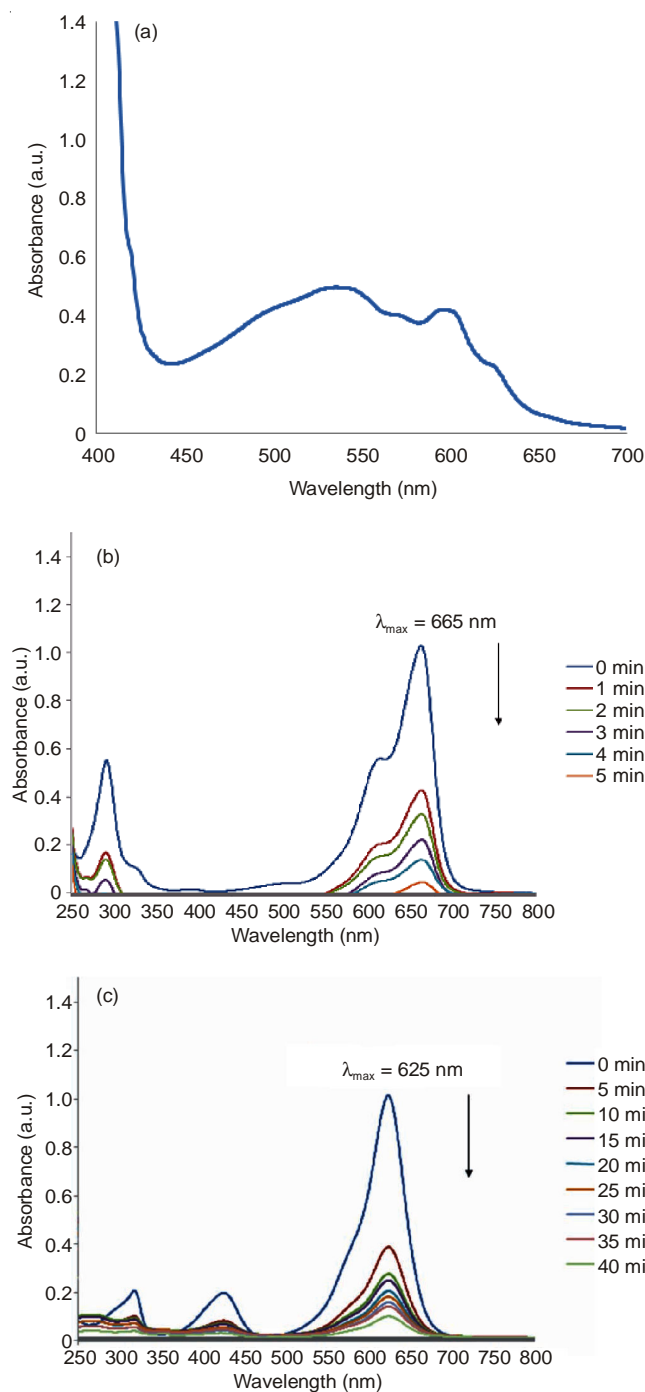


Fig. 4. UV-visible spectra of (a) the synthesized C₆₀ nanowhiskers, the degradation of (b) methylene blue and (c) brilliant green solution with of C₆₀ nanowhiskers/NiS₂ nanocomposites

composites under ultraviolet irradiation at 365 nm. As a result, C₆₀ nanowhiskers/NiS₂ nanocomposites were more effective in the degradation of the methylene blue solution than the brilliant green solution.

Conclusion

C₆₀ nanowhiskers were synthesized using the liquid-liquid interfacial precipitation method. Microwave irradiation was one of the methods to synthesize NiS₂ nanoparticles. The C₆₀ nanowhiskers/NiS₂ nanocomposites were prepared by heat treatment in an electric furnace at 700 °C under an argon atmosphere for 2 h. The C₆₀ nanowhiskers/NiS₂ nanocomposites were used as a photocatalyst for the degradation of a methylene blue and brilliant green solution under ultraviolet irradiation at 365 nm. C₆₀ nanowhiskers/NiS₂ nanocomposites formed a rod and needle-like morphology after heating at 700 °C. The C₆₀ nanowhiskers/NiS₂ nanocomposites were more efficient in the degradation of methylene blue solution than brilliant green solution under ultraviolet irradiation at 365 nm.

ACKNOWLEDGEMENTS

This study was supported by Sahmyook University funding in Korea.

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