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Preparation of NiS_2 Nanoparticles under Microwave Irradiation and Catalytic Reduction of 4-Nitrophenol

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Nickel disulfide nanoparticles were synthesized from $NiCl_2{\cdot}6H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ under microwave irradiation. The nickel disulfide nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV-visible spectrophotometry. Nickel disulfide nanoparticles were used as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol. The resulting product was confirmed by UV-visible spectrophotometry.

Keywords: Nickel disulfide nanoparticles, Microwave irradiation, Catalyst, UV-visible spectrophotometer.

INTRODUCTION

Transition metal chalcogenide nanomaterials have attracted considerable attention because of their optical, magnetic and catalytic properties[1-3]. Transition metal disulfides, such as iron disulfide, copper disulfide and nickel disulfide, have been studied extensively[4]. These disulfides have attracted significant interest in a range of fields, such as hydrodesulfurization catalysts, photoactive materials, magnetic materials and solid-state lubricants[5,6]. In particular, NiS_2 has two main phases, a triclinic phase and cubic phase[7]. Cubic pyrite NiS_2 possesses significant electronic and magnetic characteristics[8]. Some methods for the synthesis of nanoscale nickel disulfide particles have been reported, such as chemical vapor deposition, solid-state reactions and wet chemical and thermal techniques[6,9-12]. The application of microwave irradiation in the synthesis of nanoparticles has been reported[13]. The microwave-assisted hydrothermal technique is one of the methods for nanoscale synthesis[14]. The microwave irradiation to hydrothermal reactions provides rapid, straightforward and inexpensive ways of obtaining the desired products from a given chemical reaction[4].

Aromatic amines are used widely as intermediates in industry for the synthesis of agrochemicals and dyes[15,16]. Aromatic amines are generally synthesized by the reduction of aromatic nitro compounds by catalytic hydrogenation and stoichiometric reduction[17,18]. Catalytic hydrogenation is a convenient method for reducing aromatic nitro compounds in high yield[19].

This paper reports the preparation of NiS_2 under microwave irradiation and the reduction of 4-nitrophenol in an aqueous solution with sodium borohydride in the presence of NiS_2 as a catalyst.

EXPERIMENTAL

$NiCl_2{\cdot}6H_2O$ was purchased from Daejung chemicals, $Na_2S_2O_3{\cdot}5H_2O$ was obtained from Shinyo pure chemicals. 4-Nitrophenol was supplied by Sigma-Aldrich. $NaBH_4$ and ethanol were acquired from Samchun Pure Chemical.

UV-visible spectroscopy of all the samples was performed using a UV-visible spectrophotometer (Shimazu, UV-1601 PC). The structure of the NiS_2 nanoparticles was characterized by X-ray diffraction (XRD, Bruker, D8 Advance). The morphology and size of the synthesized NiS_2 nanoparticles were investigated by transmission electron microscopy (TEM, JEOL Ltd, JEM-2010) at an acceleration voltage of 200 kV. The surface of the NiS_2 nanoparticles was examined by scanning electron microscopy (SEM, JEOL Ltd, JSM-6510) at an acceleration voltage of 0.5 to 30 kV. Microwave irradiation was performed with continuous heating at the maximum power using a domestic oven (2450 MHz, 700 W).

Preparation of NiS_2 nanoparticles under microwave irradiation: 0.9508 g of $NiCl_2{\cdot}6H_2O$ and 1.9854 g of $Na_2S_2O_3{\cdot}5H_2O$ were dissolved in 100 mL deionized water to prepare a solution containing 0.04 M $NiCl_2$ and 0.08 M $Na_2S_2O_3$. 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.

Catalytic efficiency of NiS_2 nanoparticles for the reduction of 4-nitrophenol: The catalytic efficiency of the NiS_2 nanoparticles for the reduction of 4-nitrophenol was analyzed. In a typical experiment, a solution containing 15 mg of $NaBH_4$ as a hydrogen source and 0.067 mM 4-nitrophenol was mixed with 2 mg of the NiS_2 nanoparticles. The UV-visible spectra of the mixture were recorded continuously after adding the NiS_2 nanoparticles. The product of 4-nitrophenol reduction to 4-aminophenol was confirmed by UV-visible spectrophotometry.

RESULTS AND DISCUSSION

Fig. 1 shows the optical properties of the synthesized NiS_2 nanoparticles dispersed in ethanol at λ_{max} = 264 nm.

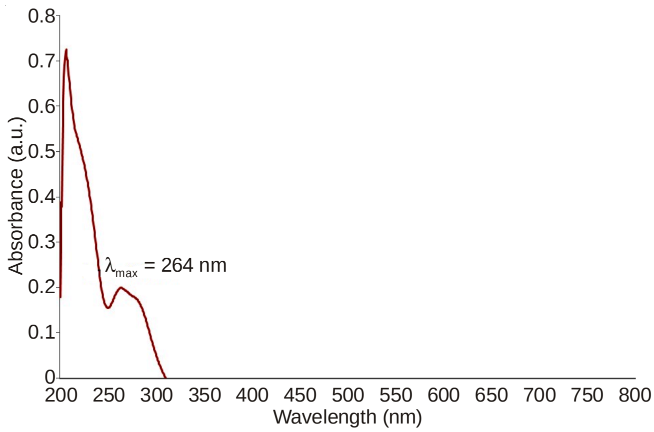

Fig. 1. UV-visible spectrum of the synthesized NiS_2 nanoparticles

The crystal structure of the synthesized NiS_2 nanoparticles was examined by XRD with CuK_α radiation. Fig. 2 shows XRD patterns of the synthesized NiS_2 nanoparticles. The characteristic peaks of the synthesized NiS_2 nanoparticles were observed at 27.35°, 31.68°, 35.28°, 38.59°, 45.42°, 53.38°, 56.43°, 59.43° 61.89° and 72.92° 2θ, which were assigned to the (111), (200), (210), (211), (220), (311), (222), (023), (321) and (331) plane indices.

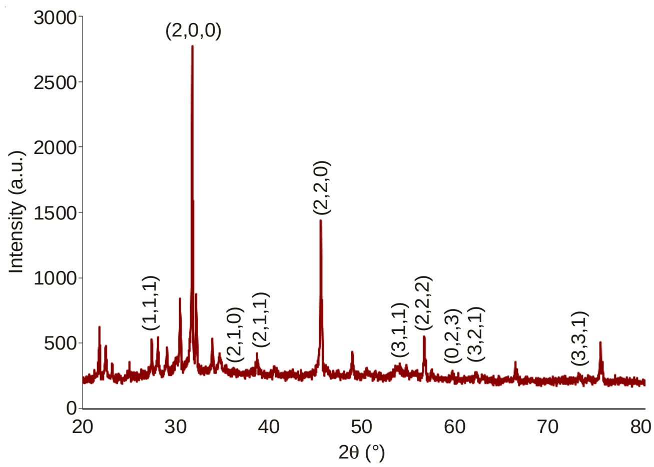

Fig. 2. XRD pattern of the synthesized NiS_2 nanoparticles

Fig. 3 shows TEM images of the synthesized NiS_2 nanoparticles. The synthesized NiS_2 nanoparticles appeared to agglomerate. The synthesized NiS_2 nanoparticles had a quasi-spherical shape. The mean size of the synthesized NiS_2 nanoparticles was 70 nm.

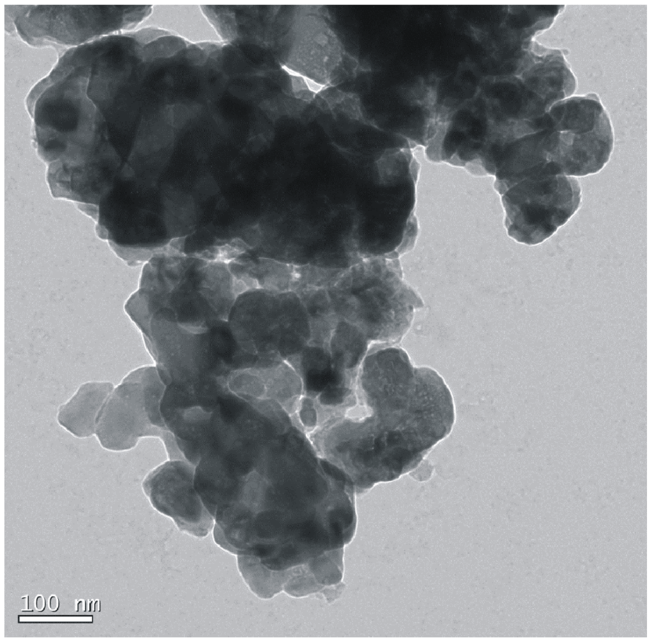

Fig. 3. TEM image of the synthesized NiS_2 nanoparticles

Fig. 4 shows SEM images of the synthesized NiS_2 nanoparticles. SEM images of the synthesized NiS_2 nanoparticles showed a triangle shape and a finely agglomerated phase.

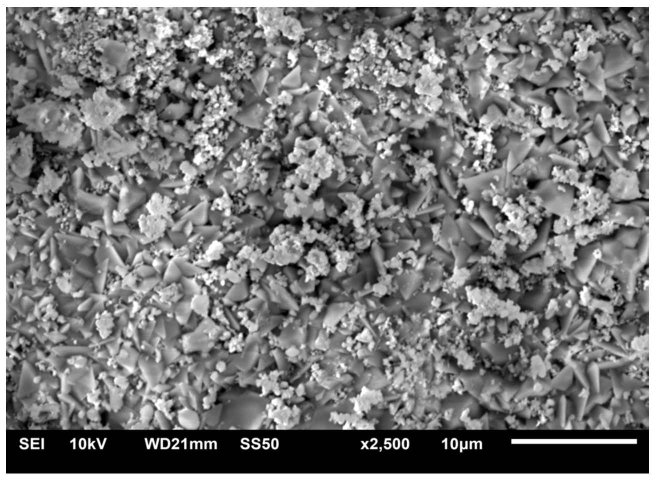

Fig. 4. SEM image of the synthesized NiS_2 nanoparticles

Fig. 5 showed UV-visible spectra of the reduction of (a) 4-nitrophenol to (b) 4-aminophenol with 15 mg $NaBH_4$ by 2 mg of NiS_2 nanoparticles as a catalyst for 5 min; the interval between each peak was 1 min. The absorbance of the peak at 400 nm due to the 4-nitrophenolate ion decreased gradually with time due to the reduction of 4-nitrophenol. The absorbance of the peak at 300 nm due to 4-aminophenol increased gradually with time. This reduction was highlighted by the disappearance of the peak at 400 nm with the accompanied appearance of a new peak at 300 nm. The color of the solution changed from yellow to colorless. Therefore, NiS_2 nanoparticles could be used as an effective catalyst to reduce 4-nitrophenol to 4-aminophenol with $NaBH_4$.

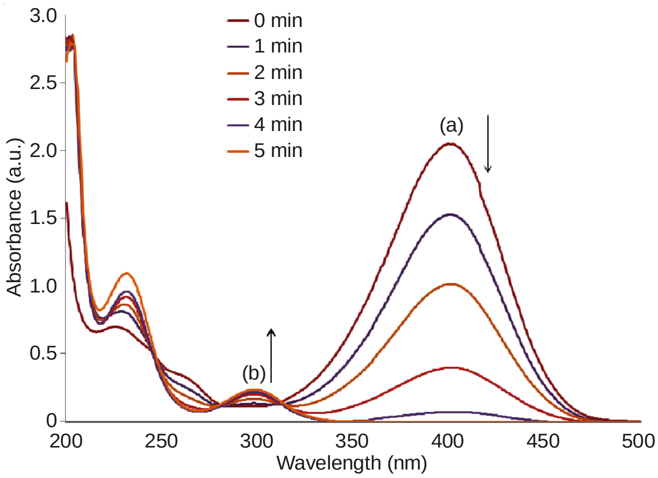

Fig. 5. UV-visible spectra of the reduction of (a) 4-nitrophenol to (b) 4-aminophenol with 15 mg of $NaBH_4$ and 2 mg of NiS_2 nanoparticles as a catalyst for 5 min; the interval between each peak is 1 min

Conclusion

Microwave irradiation was used to synthesize NiS_2 nanoparticles. The resulting NiS_2 nanoparticles showed a quasi-spherical shape with a mean size of 70 nm. The NiS_2 nanoparticles showed a maximum absorption wavelength of 264 nm. The characteristic peaks of the NiS_2 nanoparticles were observed at 27.35°, 31.68°, 35.28°, 38.59°, 45.42°, 53.38°, 56.43°, 59.43° 61.89° and 72.92° 2θ. UV-visible spectroscopy confirmed the reduction of 4-nitrophenol by a decrease in the peak at 400 nm with the concomitant appearance of a new peak at 300 nm due to 4-aminophenol. Overall, NiS_2 nanoparticles are effective as a catalyst for the reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$.

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