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SOLVOTHERMAL SYNTHESIS OF UNDOPED AND Ni-DOPED FeS_2 NANOPARTICLES AND ITS COMPOSITE WITH REDUCED GRAPHENE OXIDE FOR PHOTOCATALYSIS APPLICATION

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ABSTRACT

The undoped and Ni-doped FeS_2 nanoparticles (NPs) with doping concentration of 4.0 wt.% are successfully synthesized by a facile solvothermal method. The undoped and Ni-doped FeS_2 NPs have a single-crystalline structure of pyrite phase. The photocatalytic activity of the films of undoped and Ni-doped FeS_2 NPs and its composite with reduced graphene oxide (rGO) fabricated by spray pyrolysis method is investigated and evaluated. The smaller size of the NPs is achieved by Ni doping, which seems to be main reason for the improved photocatalytic activity of Ni-doped FeS_2 NPs. In addition, the FeS_2 NPs and rGO composite shows higher the UV and visible light photocatalytic activity compared with both undoped and Ni-doped FeS_2 NPs. The obtained result indicates that the FeS_2 NPs and rGO composite can act as an efficient heterogeneous photocatalyst for degradation of organic contaminant and water treatment.

Keywords: Metamaterials, Visible light, Perfect absorption, Absorber.

INTRODUCTION

Metal sulfides have attracted considerable interest due to their promising properties for electronic, optical and optoelectronic applications [1]. Among them, iron disulfide (FeS_2) is abundant, nontoxic and low-cost material with small band gaps (0.95 eV) and high absorption coefficients, which make its suitable for photovoltaic, lithium ion batteries, hydrogen evolution, photocatalytic degradation of several organic pollutants [2,3]. Up to now, FeS_2 nanoparticles (NPs) have been prepared by several methods, such as hot injection, hydrothermal and solvothermal methods. However, the large scale synthesis of high-dispersive FeS_2 NPs is still challenge for improving their unique properties. Recently, doping with metal ions such as Ni and Co ions is an efficient way to improve the photocatalytic performance of the photocatalysts [4]. Furthermore, the combination of FeS_2 and rGO has been demonstrated to effectively improve the photocatalytic activities in these composite systems [5]. However, most of studies about photocatalytic activity of NPs and NPs and GO composite were implemented in a liquid solution so that it is difficult to get the photocatalyst recovery process and collect them after use [6].

In this paper, we report the synthesis of undoped and Ni-doped FeS_2 NPs by a facile solvothermal method. The undoped and Ni-doped FeS_2 NPs have a single-crystalline structure of pyrite phase. The photocatalytic activity of undoped and Ni-doped FeS_2 NP and its composite with reduced graphene oxide (rGO) films fabricated by spray pyrolysis method was investigated and evaluated.

EXPERIMENTAL

Synthesis and characterization of Undoped and Ni-doped FeS_2 NPs

The undoped and Ni doped FeS_2 nanoparticles (NPs) were synthesized via a solvothermal method. In a typical synthesis, 7.5 mL of oleylamine was added into a 50 mL teflon-lined stainless steel autoclave containing 0.25 mmol of iron (II) acetylacetonate, 0.25 mmol of 1,2 hexadecandiol, 1.5 mmol of sulfur flakes and 0.0125 mmol of nickel (II) chloride hexahydrate. The reaction mixture was sonicated for an hour to ensure homogenous mixing. The reaction temperature was fixed at 190ºC and reaction time was 20 h. The autoclave was then cooled to room temperature naturally and the

precipitate collected via centrifugation. After reaction period, the FeS_2 NPs samples were removed and washed with methanol and toluene, then dried in air before collection for further characterization.

The structure of the FeS_2 and Ni doped FeS_2 NPs were analyzed by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer using Cu Kα radiation with a 0.154 nm wavelength and raman spectra using a LabRAM HR800 (Horiba) with a 632.8 nm excitation laser at a resolution of 1.0 cm^{-1}. The surface morphology was studied in a scanning electron microscope (SEM, JEOL JCM-6000Plus). The optical absorption spectra were obtained from an ultraviolet visible spectroscopy (Agilent, 8453). The Ni doping concentration was determined to be 4 wt.% as analyzed by an inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer ELAN 9000).

Synthesis and characterization of GO

GO was synthesized from graphite flakes using the modified Hummers method. The detail synthesis and characterization were carried out as described in our previous study. The GO dispersion was suspended in DI water with concentration of 2 mg/ml.

Preparation of FeS_2 NPs, Ni-doped FeS_2 NPs and FeS_2 NPs and rGO composite films

The films were deposited by spray pyrolysis method onto a 2×2 cm^2 glass substrate using an airbush system with the nozzle diameter of 0.2 mm. The inlet pressure is fixed at 3 bar. The distance between the tip of the nozzle and the substrate is kept at 8 cm. The volume of spray solution is 2 ml. The solution of GO, rGO, FeS_2 NPs, and FeS_2 NPs and rGO composite are used to fabrication of the films shown in Figs. 1(a)-(d). The final FeS_2 NPs and FeS_2 NPs and rGO composite (FeS_2 NPs/rGO) films were obtained after spray deposition, which are shown in Figs.1 (e) and (f), respectively.

For the growth of undoped and Ni-doped FeS_2 NPs films: The initial undoped and Ni-FeS_2 NPs solutions (20 mg/ml) were created by diluted undoped and Ni-FeS_2 NPs in cyclohexane. The growth temperature is fixed at 100 °C.

For the growth of the FeS_2 NPs and rGO composite film: The GO dispersion (2 mg/ml) was vigorously mixed with hydrazine monohydrate with a volume ratio of 1:2 for 5 min and then diluted 10 times with DI water/ethanol/hydrazine monohydrate with a volume ratio of 1:1:2. Sonication was then applied by a sonication bath for one minute in order to obtain stable and homogenous GO-hydrazine dispersion. Finally, the FeS_2 NPs (20 mg/ml) and GO-hydrazine (0.2 mg/ml) solution with a volume ratio of 1:1 was sonicated for 5 min to ensure homogenous mixing. The growth temperature is fixed at 200 °C in oder to obtain the rGO [26].

Photocatalytic activity

Photocatalytic activity was studied by measuring the decomposition of methylene blue (MB) in aqueous solution using UV-VIS spectroscopy. In each experiment, the sample was added into 10 mL of MB aqueous solution with concentration of 10^{-5}M. The white light of a tungsten light bulb (100 W) and UV light of 365 nm (6 W) were used as visible light and UV irradiation sources, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows SEM image of the undoped and Ni-doped FeS_2 NP samples. All the samples exhibit uniform morphology and particle size distribution. The smaller NPs are obtained in the NP sample with Ni doping. The size of undoped and Ni-doped FeS_2 NPs is ~ 100-150 nm and 80-120 nm, respectively.

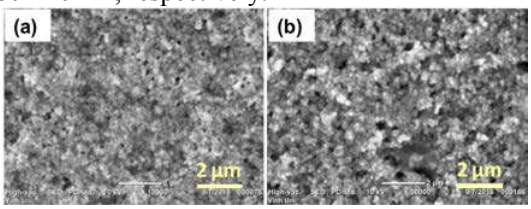

Figure 1. SEM images of the undoped and Ni-doped FeS_2 NPs.

The crystal phases of the undoped and Ni-doped FeS_2 NP samples were investigated using XRD. Fig. 2 shows XRD patterns of these samples. Both undoped and Ni doped FeS_2 NP samples show a similar XRD pattern. The discernible peaks can be indexed as pyrite FeS_2 (JCPDS No. 01-079-0617). No additional peaks corresponding to secondary phases such as metallic nickel and nickel oxide, marcasite, pyrrhotite, troilite or greigite phases are observed. This may either indicates that the concentration of secondary phases formed in the samples is too low to detect by XRD measurement or Ni ions are doped into pyrite FeS_2 matrix. Furthermore, the formation of

a lowered intensity and wider peaks in Ni-doped FeS_2 NP samples corresponds to the decrease the NP size after Ni doping as observed in SEM image (Fig. 1).

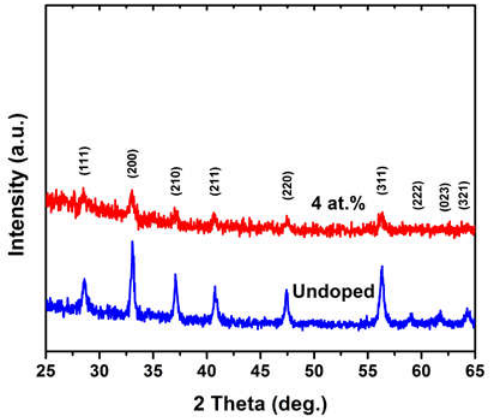

Figure 2. SEM images of the undoped and Ni-doped FeS2 NPs.

Photocatalytic activity of the undoped NPs, Ni-doped FeS_2 NPs, and FeS_2 NPs and rGO composite samples were evaluated by measuring the decomposition of methylene blue in an aqueous solution. Fig. 3 shows the changes of MB concentration as a function of irradiation time under both UV and visible light. As seen in Fig. 3a, the undoped NPs decompose methylene blue effectively through photocatalytic reaction under visible light irradiation due to its narrow bandgap energy. Compared with the undoped NPs, the Ni-doped FeS_2 NP sample shows much higher photocatalytic activity (Fig. 3a). The Ni doping can be decreased the NP size, resulting in the increase of its specific surface area and improve the visible light photocatalysis. Furthermore, due to the doped of metal ions such as Ni^{2+}, the defects ware created in FeS_2 matrix that leading to the increase of electron and hole generation. The visible photocatalytic activity is further enhanced by using the FeS_2 NPs and rGO composite. It was reported the composite of FeS_2 NPs and GO composite can improve the visible light photocatalysis compared to pure synthetic FeS_2 NPs. It can be ascribed to the unique properties of GO or rGO such as larger surface area, full surface accessibility, and fast charge transport and the synergistic effects between both components of GO or rGO and NPs. Under UV irradiation, the NPs and rGO composite sample also show much stronger photocatalytic activity than the undoped and Ni-doped FeS_2 NP samples (Fig. 3b).

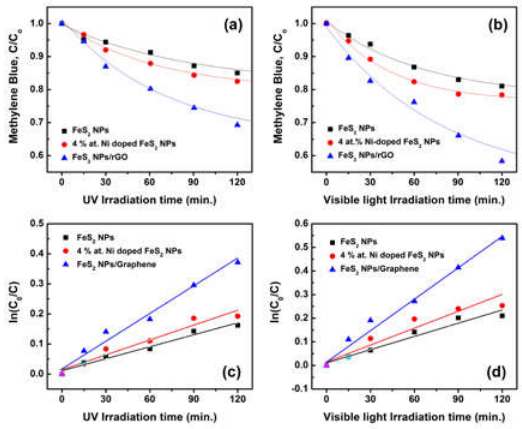

Figure 3. Photocatalytic properties of the undoped NPs sample (solid squares), Ni-doped FeS2 NPs sample (solid circles) and the FeS2 NPs and rGO composite under (a) visible light and (b) UV irradiation. The linearized kinetic plots for the degradation o

Moreover, the MB photodegradation clearly obeyed the first-order reaction kinetics. The linearized kinetic plots for the degradation of MB with the presence of the undoped NPs, Ni-doped FeS_2 NPs, and FeS_2 NPs and rGO composite samples under UV and visible light irradiation are shown in Fig. 3 (c) and (d). The apparent rate constants of visible light and UV photocatalytic degradation of MB with the presence of the undoped FeS_2 NPs sample were $1.33\times10^{-3}min^{-1}$ and $1.87\times10^{-3}min^{-1}$, respectively. They increased markedly to $1.65\times10^{-3}min^{-1}$ and $2.17\times10^{-3}min^{-1}$ for Ni-doped FeS_2 NPs sample and $2.95\times10^{-3}min^{-1}$ and $4.3\times10^{-3}min^{-1}$ for the FeS_2 NPs and rGO composite sample, respectively.

CONCLUSION

A facile solvothermal approach was developed to synthesis the undoped and Ni-doped FeS_2 NPs with doping concentration of 4.0 wt.%. The undoped and Ni-doped FeS_2 NPs have a single-crystalline structure of pyrite phase. The photocatalytic activity of the films of the undoped and Ni-doped FeS_2 NPs and FeS_2 NPs and rGO composite fabricated by spray pyrolysis method was investigated. The smaller size of the NPs was achieved by Ni-doping, which seems to be main reason for the improved photocatalytic activity of Ni-doped FeS_2 NPs. Furthermore, the composite of FeS_2 NPs and rGO exhibited higher the UV and visible light photocatalytic compared with both undoped and

Ni-doped FeS_2 NPs. The obtained result revealed that the FeS_2 NPs and rGO composite is a promising candidate for degradation of organic contaminant and water treatment.

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