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Short Communication

Ionic liquid assisted sonochemical synthesis of NiS submicron particles

Salomé M. de la Parra-Arciniega [a], Nora A. García-Gómez [a], Domingo I. Garcia-Gutierrez [b,c], Pablo Salinas-Estevané [a], Eduardo M. Sánchez [a,*]

[a] Universidad Autónoma de Nuevo León, UANL, Facultad de Ciencias Químicas LabMat2: Almacenamiento y Conversión de Energía, Av. Universidad S/N Ciudad Universitaria, San, Nicolás de los Garza, Nuevo León, C.P. 66451, México

[b] Universidad Autónoma de Nuevo León, UANL, Facultad de Ingeniería Mecánica y Eléctrica, Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451, México

[c] Universidad Autónoma de Nuevo León, UANL, Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología, CIIDIT, PIIT, Av. Universidad S/N Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451, México

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ABSTRACT

A novel synthesis methodology is reported for the preparation of NiS submicron particles in a green solvent 1-butyl-3methylimidazolium tetrafluoroborate ($BMImBF_4$) ionic liquid (IL), using ultrasonic sonochemical technique. Structural, morphological and optical properties of nickel sulfide powders were obtained by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and diffuse reflectance spectroscopy (DRS). Composition was corroborated by energy dispersive X-ray spectroscopy (EDXS), both in the SEM and in the TEM. Regular shape particles were obtained under high-intensity ultrasonic irradiation for 105 min from the reaction between nickel nitrate and thioacetamide in ethanol/$BMImBF_4$ (80:20), respectively. After vacuum annealing treatment at 180 °C overnight, spherical crystalline NiS particles were observed. The powders showed a band gap of 0.74 eV.

1. Introduction

Nickel sulfide has a number of applications such as IR detectors, solar storage, hydrosulfurization catalysis, as a potential cathode material for the rechargeable lithium battery, as a catalyst in the degradation of organic dyes, and in magnetic devices. The nickel sulfide system is very fascinating not only because of its numerous phases and stoichiometry, such as α-$Ni_{3+x}S_2$, β-Ni_3S_2, Ni_3S_4, NiS_2, α-NiS (rhombohedral, millerite), β-NiS (hexagonal, NiAs-type), Ni_9S_8, and Ni_7S_6 [1–3]; but also due to different synthesis methods such as sonochemical method [1], thermolysis [4,5], microemulsion system [6], metathetical reaction [7], γ-irradiation method [8], hydrothermal [9], microwave radiation [10] and colloidal chemical method [11]. Besides these, the nickel sulfide nanomaterials has been focused on a micro/submicrometer scale with novel and complicated morphologies, such as NiS spheres [1,6], hollow spheres [8,12], nanorods [13], flowerlike architectures [14,15] and wires [4]. Ni_3S_4 was obtained in different morphologies (wires, rods, spheres, and triangulars) [4].

Among the synthesis methods used for preparing nickel sulfide is the sonochemical method, which is attractive due to its simplicity. The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth and implosive collapse of bubbles in a

* Corresponding author.
E-mail address: eduardo.sanchezcv@uanl.edu.mx (E.M. Sánchez).

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liquid. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. The temperature is estimated to be 5000 K, the pressure reaches more than 1800 kPa and the cooling rate is more than 10^{10} K/s when the bubbles explode [16]. Ionic liquids (ILs) have successfully been employed in the preparation of inorganic materials. They often act as solvents, reactants or morphology templates, which enable the synthesis of inorganic materials with novel morphologies or improved properties. The physical and chemical effects of cavitation are highly dependent on the contents of the collapsing bubbles. Low vapor pressure hydrocarbon solvents have generally been employed to enhance the choice of solvent during the reactions and the maximization of the temperatures and pressures reached within cavitating bubbbles. Since ionic liquids have essentially no vapor pressure, they should be ideal as solvents for sonochemical reactions [17]. So far, only a handful of studies have reported on the fabrications of nano- or micro-scaled materials including particles of metal oxide and sulfide [18,19]. Others have used binary mixtures of ILs with water and/or ethanol for the preparation of materials [20–23]. In the present study, we employed the sonochemical method to prepare nickel sulfide using the IL 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) and absolute ethanol as solvents.

2. Experimental

2.1. Materials

The precursors used for preparing nickel sulfide were Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and thioacetamide (TAA, CH_3CSNH_2). 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) and absolute ethanol were used as solvents.

2.2. Preparation

During the early stages of the work, the solvent was added in a 20-mL vial that consisted of different ratios and ranges of IL/ethanol, the absence of IL or ethanol; in a solvent (mL)/Ni (mmol) ratio of 2 or 4 (samples A–D, Table 1). With the purpose of investigating the effect of

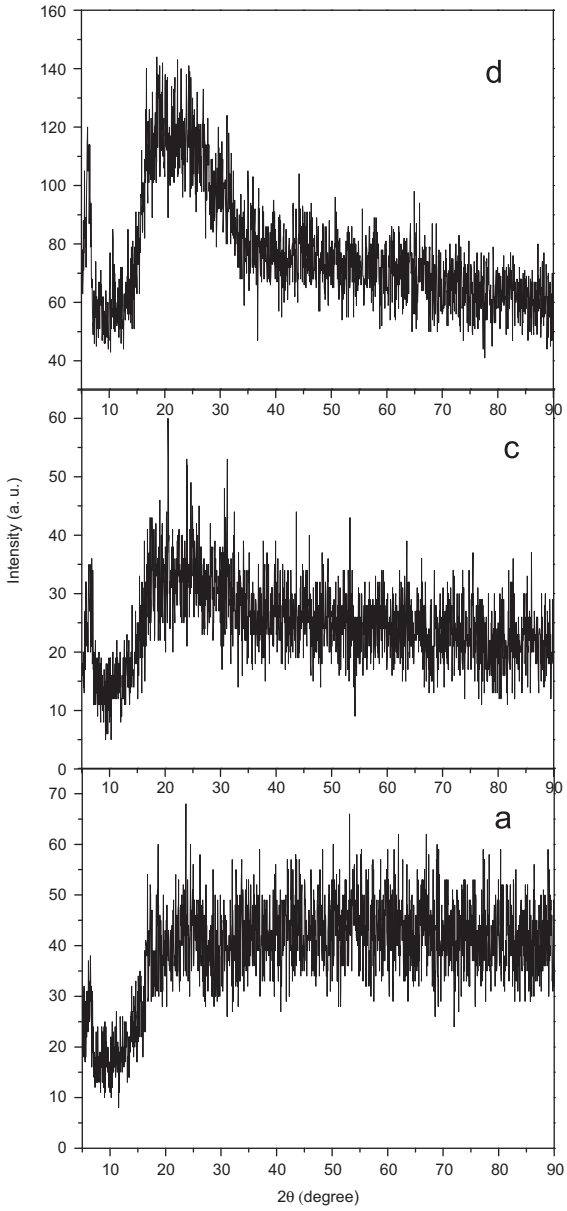

Fig. 1. Powder X-ray diffraction patterns of samples A, C and D, prepared according to Table 1.

Table 1
Synthesis conditions.

Sample	$Ni(NO_3)_2 \cdot 6H_2O$ mmol	C_2H_5NS mmol	S/Ni	Solvent/Ni mL/mmol	$[BMIm][BF_4]$ mL	EtOH mL	Ultrasound min
A	2	2.1	1.05	2	0	4	30
B	2	2.1	1.05	2	2	2	30
C	1	1.05	1.05	2	4	0	30
D	2	2.1	1.05	4	4	4	30
E	4	4.2	1.05	2	0	8	60
F	4	4.2	1.05	2	0.8 (10%)	7.2	60
G	4	4.2	1.05	2	1.6 (20%)	6.4	60
H	8	8.4	1.05	0.5	0.8 (20%)	3.2	105
I	8	8.4	1.05	0.5	0	4	105

Each solution was irradiated at 20% output power (100 W) in air.