



Synthesis of Cu₂S Ultrasmall Nanoparticles in Zeolite 4A Nanoreactor

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Abstract

In this work, Cu₂S ultrasmall nanoparticles were synthesized in a zeolite 4A nanoreactor (ZA) by the ion exchange method, which consisted of two steps: (1) the ion exchange of Na⁺, located in ZA, for Cu⁺ and Cu²⁺, and (2), formation of Cu₂S nanoparticles, using Na₂S by metathesis reaction (double displacement reaction). The molecular structure of ZA was verified by FT-IR and XRD and the formation of Cu₂S nanoparticles in the ZA matrix by DSC, UV–Vis, Raman, TEM, and HRTEM characterizations. The results showed a non-modified molecular structure of the Z4 by synthesis of Cu₂S nanoparticles with a size distribution of 4–8 nm.

Keywords Cu₂S nanoparticles · Zeolite 4A · Nanoreactor · Copper sulfide · Chalcocite

Introduction

Nanoreactors are small-sized chemical reactors where chemical reactions can be controlled and carried out [1]. And they have the ability to create a unique chemical environment that is different from the surrounding space as it can isolate the compounds from the outside mass and affect the reaction inside the nanoreactor [2]. Zeolite nanoreactor is used to promote uniform nanoparticle formation and inhibit the sintering of active nanoparticles [3].

Zeolites have attracted the attention of scientists since they were discovered in nature, because of their excellent physicochemical properties, especially in catalysis and adsorption-separation [4]. The zeolites are hydrated crystalline aluminosilicates with a uniform microporous structure formed by cages and channels with a molecular dimension of 2.5–12 Å in size, making them suitable to accommodate sub-nanometer particles and clusters. In addition, their high

surface area and excellent ion-exchange properties make interesting functional materials [5, 6]. Zeolite A has a cavity with a minimum free diameter of 1.14 nm, which may allow the growth of larger nanoparticles in it [7]. On the other hand, the use of different acidic or alkaline substances may cause mesoporous of size 5–50 nm. [8, 9]. Recently, zeolites have been used as hosts or templates to synthesize new nanomaterials, which have a great interest because of their unique and promising properties. In this route, Ag, Pd, and Cu-based nanoparticles and clusters have been synthesized within the zeolite pores, resulting in confined [10, 11], encapsulated [12], or just supported nanoparticles [13]. The nanoparticles inside the zeolites can have different types of applications [14–16]. In the case of nanoparticles of copper sulfide, could be an electrocatalyst application [17].

The semiconductors nanoparticles are one of the most exciting materials in recent years, and it is considered for the future due to their advanced and novel ways of applications [18]. Some semiconductors have been hosted in zeolites, such as nanoparticles of nickel sulfide (NiS), and cobalt sulfide (CoS) with sizes 6–10 nm, in mordenite zeolite [19, 20]. In addition, nanocluster of gallium sulfide (Ga₂S₃) in zeolite Y [21], cadmium sulfide (CdS) in A4 and MCM [22, 23], ETS [24] and Y [25] are also reported. Considering the chalcogenides, the copper sulfide compounds have been attractive and are receiving substantial attention for many applications because there are not toxic and have excellent photo and physicochemical properties [26].

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The understanding of Copper sulfide properties and their many possible stoichiometries (Cu_{2-x}S) and crystal phases such as chalcocite (Cu_2S , monoclinic/hexagonal), djurite ($\text{Cu}_{1.95}\text{S}$, monoclinic), digenite ($\text{Cu}_{1.8}\text{S}$, cubic), anilite ($\text{Cu}_{1.75}\text{S}$, orthorhombic), and covellite (CuS , hexagonal) are still lacking [27, 28]. Covellite and chalcocite synthesized as nanostructures are the most studied copper sulfides due to their absorption bandgap in the near-infrared region [29, 30]. They have been reported in zeolites; for instance, CuS nanoparticles of 125 nm average size with spherical morphology in zeolitic imidazole framework-8 were encapsulated without affecting its crystal structure [31].

Only was found one work of Cu_2S nanoparticles of 32 nm on size average synthesized in RWY zeolite by the ion exchange method, which resulted in complex with multiples steps, and it did not allow the Cs^+ ions to be exchanged completely, furthermore, the structure of the zeolite can be destroyed for higher concentrations the Cu^{2+} solution [17]. In this work, we report the synthesis of Cu_2S ultrasmall nanoparticles in zeolite A4 nanoreactor by ion-exchange, performing a simple two-step process as an alternative to contribute to the continuous development of accessible and green strategies to synthesize copper sulfides nanostructures in zeolites. With this procedure and using zeolite as a nanoreactor, the nanoparticles obtained were four times smaller and more uniform in size than those reported in the literature. The Cu_2S nanoparticles were successfully synthesized in ZA and have been characterized by DRX, FTIR, UV-Vis, DSC, Raman, and TEM. The particle size, less than 10 nm, and the Cu_2S structures were identified by indexing the crystal plane by HR-TEM, which is the most used for the identification of nanoparticles [15, 23, 32–34].

Materials and Methods

Materials

Synthetic zeolite 4A (ZA, Sigma-Aldrich), cupric sulfate ($\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$, 99.5%, Faga Lab), Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98%, Faga Lab), deionized water, Faga Lab.

Method

The experimental method used, applied in previous work [35], consists of two steps, as follows.

Step 1: Cu Ion Exchange in ZA (ZACu)

First, 10 g of ZA was dissolved in 50 ml of deionized water for 12 h for its hydration. At the same time, a solution of 150 ml of CuSO_4 (0.1 M) was prepared. Next, the CuSO_4 solution and the hydrated ZA were heated to a temperature of 50 °C, and keeping the temperature conditions, the CuSO_4 solution was added to the hydrated ZA, applying magnetic stirring for 50 min to mix. ZACu was obtained, as a fine blue powder, which was recovered by filtration and a triple wash with deionized water to remove the remaining ions. Subsequently, it was dried at room temperature (35 °C in summer).

Step 2: Nanoparticles of Copper Sulfides in ZA ($\text{ZACu}_2\text{S}_{0.1}$)

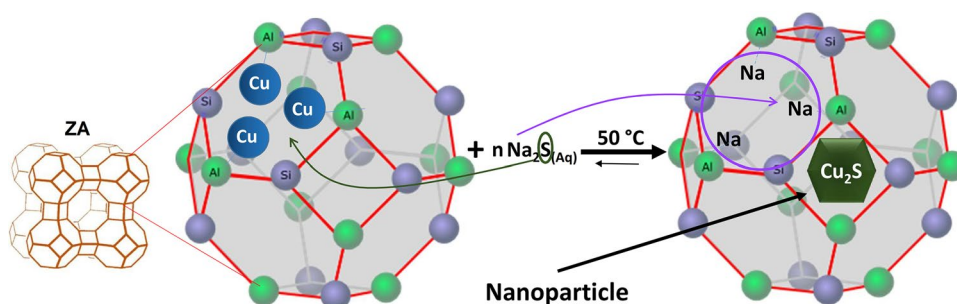
First, 5 g of ZACu (obtained in step 1) was dissolved in 50 ml of deionized water for 12 h for its hydration. At the same time, a solution of 150 ml of Na_2S (0.1 M) was prepared. Subsequently, the same procedure is performed as Step 1, $\text{ZACu}_2\text{S}_{0.1}$ was obtained, as a fine green powder.

Figure 1 shows a proposed reaction mechanism for the formation of Cu_2S nanoparticles (the structure selected is named *sodalite* and could be used as a representative). Once the copper is inside ZA (step 1) the Na_2S solution is added (step 2), occurring a metathesis reaction at 50 °C. The S^{2-} ions travel through the zeolite cavities to reach and react with the copper ions of ZA, to form Cu_2S nanoparticles, in the zeolite nanoreactor. While the Na^+ ions recover their initial position in ZA and this one recovers its original structure.

Characterizations

The microstructural, morphology, size, and chemical composition of nanoparticles were analyzed by high-resolution transmission electron microscopy (HRTEM) in a JEOL JEM-2200FS + Cs equipped with a spherical aberration corrector in the condenser lens and operated at an accelerating

Fig. 1 Proposed reaction mechanism for Cu_2S nanoparticle formation



voltage of 200 kV. To analyze the zeolite samples by XRD, the PHI5100 BRUKER AXS D8 ADVANCE diffractometer was used. The characteristic molecular bonds of the zeolite were identified using the FT-IR spectrometer Bruker-Alpha tensor spectrophotometer. To evaluate its thermal properties, differential scanning calorimetry (DSC) SDT Q6000 was used. Absorption wavelengths of Cu₂S nanoparticles were obtained with the Perkin Elmer Lambda 19 UV–vis (powder) spectrophotometer. The vibrational energy of Cu₂S bonds was determined using a Raman spectrophotometer LABram HR Evolution, Horiba (with AFM, AIST-NT coupled).

Results and Discussion

FT-IR Analysis

Figure 2 shows the FT-IR spectra of ZA and ZACu₂S0.1, where peaks at 557, 667, 1000, 1657, and 3437 cm⁻¹ are observed, which are characteristic of ZA [36]. Only the characteristic peaks of ZA are observed. There is no presence of Cu–O vibrations, or Copper sulfate, which have been reported as impurities in the synthesis of Cu–S nanostructures [37]. The FT-IR studies demonstrate that the molecular structure is not affected in this work that used the two steps ion-exchange method [17], and it is the first evidence of ZA, are hosting nanoparticles [38–40].

X-Ray Diffraction (XRD)

Figure 3 shows X-ray diffraction of (a) ZA and (b) ZACu₂S0.1. In (a) the Miller indices characteristic of ZA are observed in 2 theta range 5–37 degrees, presenting a cubic structure, lattice $a = 2.461$ nm, and space group Fm-3c (226) indexed by JCP2 01–073–2340. In (b) the same characteristic peaks of ZA are observed, with a slight decrease in relative peak intensity, mainly in Miller's index (220), which may be associated with the presence of Cu₂S in ZA. In addition, no

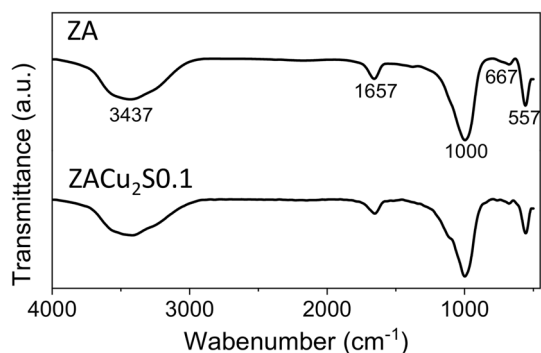


Fig. 2 FT-IR spectrum of ZA and ZACu₂S 0.1

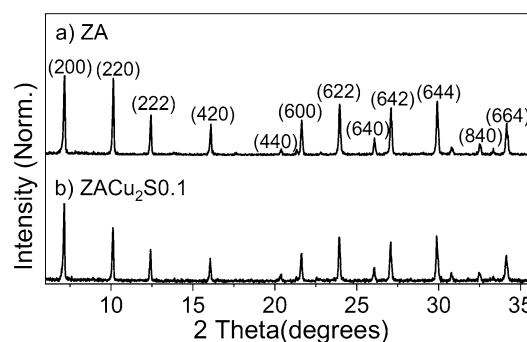


Fig. 3 X-ray diffraction of ZA and ZACu₂S0.1

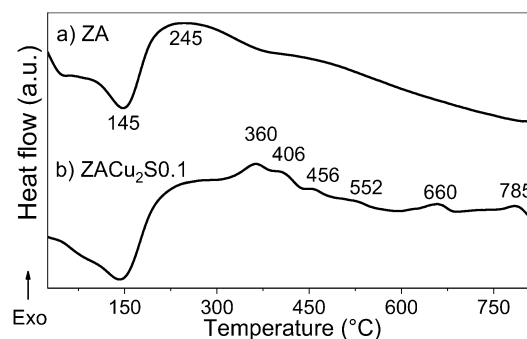


Fig. 4 DSC of a ZA and b ZACu₂S0.1

evidence of peaks associated with Cu₂S is observed, which may indicate that they do not satisfy the diffraction criteria [41] it is verified that the crystalline structure of ZA remains unchanged.

Differential Scanning Calorimetry (DSC)

Figure 4 shows the DSC of (a) ZA and (b) ZACu₂S0.1. Endothermic and exothermic signals are observed at 145 °C and 245 °C characteristics of the loss of physically and chemically housed water of ZA [42–46]. In sample (b), exothermic signals in the 360–785 °C range are observed, attributed to deformation transitions of Cu₂S, which have been reported for the formation of Cu_{2-x}S nanoparticles under other synthesis methods [47, 48], demonstrating the presence of nanoparticles on the ZA matrix.

UV-Vis Spectroscopy

Figure 5 shows the optical absorption spectrum (300 to 850 nm) of (a) ZA and (b) ZACu₂S0.1. In (a), the spectrum is transparent with a high bandgap, by that there is no absorbance band [49]. On the other hand, in (b), shows a broad absorption band characteristic of Cu_{2-x}S, and most of the time, a blue-shifted peak was reported when the size

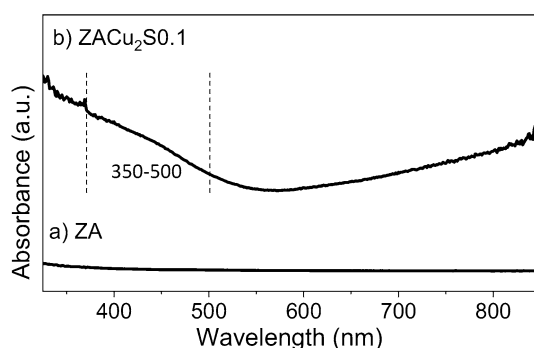


Fig. 5 UV-vis of ZA and $\text{ZACu}_2\text{S}_{0.1}$

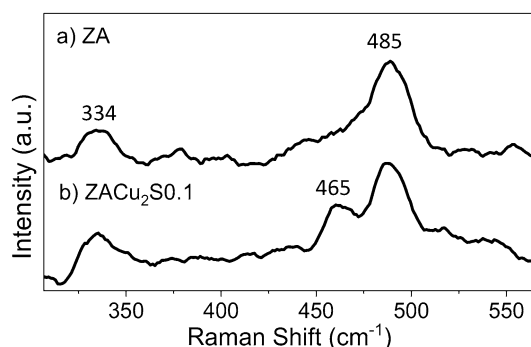


Fig. 6 Raman shift of ZA and $\text{ZACu}_2\text{S}_{0.1}$

quantization effect is produced in the range of 5–20 nm [50]. In this case, the broadband indicates the formation of small nanoparticles [51], and the energy bandgap of 2.1 eV was calculated, characteristic of Cu_2S nanostructures [52–54]. It since is ≥ 1.2 eV for bulk copper sulphides [27, 28].

Raman Spectroscopy

Figure 6 shows the Raman spectrum of (a) ZA and (b) $\text{ZACu}_2\text{S}_{0.1}$ in (a) Peaks at 334 and 485 cm^{-1} are observed, characteristic of ZA [55]. In (b) The peak at 465 cm^{-1} can be attributed to the Cu_2S formation, also the signal at 485 cm^{-1} has been reported for copper sulfides [56–58]. However, in this case, the zeolite peak is more intense and the interference with the Cu_2S peak can be observed.

TEM Analysis

Figure 7 shows a TEM micrograph of $\text{ZACu}_2\text{S}_{0.1}$ which was taken in STEM mode. In this figure, a total of 170 nanoparticles were measured, with diameters in the range of 4–8 nm, with homogeneous size distribution and uniformly dispersed in the zeolite matrix.

Figure 8 shows the analysis of a TEM micrograph enlargement of $\text{ZACu}_2\text{S}_{0.1}$, which is presented in three

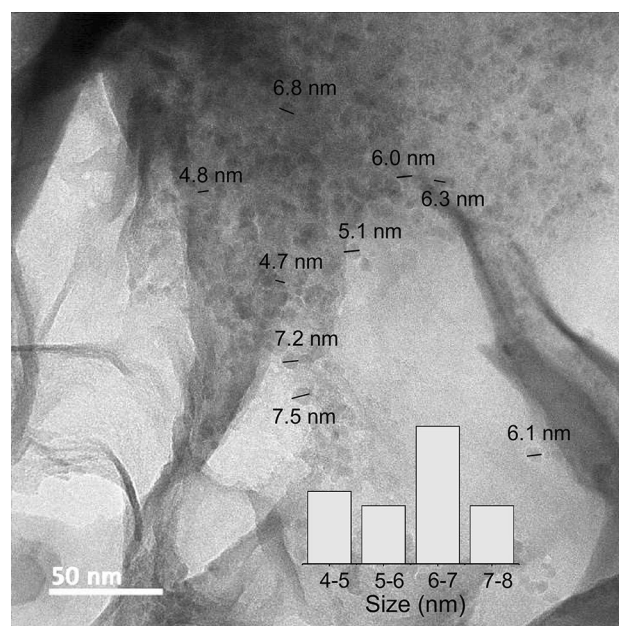


Fig. 7 TEM image taken in STEM mode of $\text{ZACu}_2\text{S}_{0.1}$

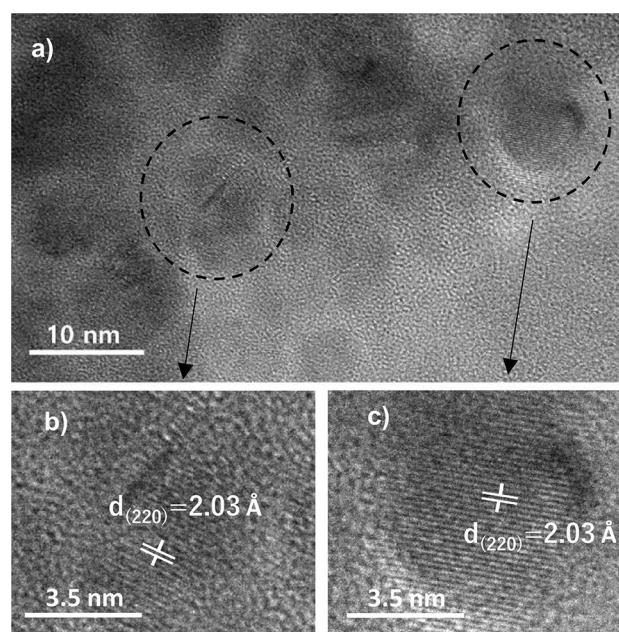


Fig. 8 **a** TEM Image of $\text{ZACu}_2\text{S}_{0.1}$ taken in HRTEM mode; **b** and **c** are a zoom image of the square red region in **a**

parts (a–c). In (a) a micrograph taken in HRTEM mode is shown, where two nanoparticles with a size around 7 nm and semi-spherical shape are observed and were indicated with a dotted black circle. In (b) and (c) shows an enlargement of (a) in the regions dotted, where the crystalline planes with an interplanar distance of $d = 2.03$ Å is observed, corresponding to the Miller crystallographic plane (2 2 0) of Cu_2S

nanoparticles with cubic phase and *Fm-3 m* space group indexed with the JCP card number 00-012-0175.

Conclusions

The synthesis of Cu₂S ultrasmall nanoparticles in zeolite 4A nanoreactor was successfully achieved by the ion-exchange method in a two steps procedure without compromising the zeolite structure. Obtaining uniform nanoparticles with a size of 4–8 nm, homogeneously dispersed in zeolite nanoreactor and with a cubic phase.

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Declarations

Conflict of Interest The authors have no relevant financial or non-financial interests to disclose. The authors have no conflicts of interest to declare that are relevant to the content of this article.

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