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Facile Microwave Assisted Preparation of Hetero-Structured $CuCo_2S_4/CuCo_2O_4$ Nanoparticles Using Organic Agent of Thiourea †

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Abstract: Ultra-fast one-put microwave assisted strategy is introduced for the synthesis of hetero-structured $CuCo_2S_4/CuCo_2O_4$ nanoparticles into a domestic microwave oven with the power of 900 W for 20 min. Thiourea as an organic agent was used as a sulfur source and driving agent to lead the solvent free combustion reaction to obtain this earth-abundant and low-cost mixed chalcogenide/oxide product. The structural and morphological specifications were studied in details using powder x-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and energy dispersion of x-ray spectrometry (EDX). The employed strategy relatively clarifies a new facile, rapid and eco-friendly route to produce heterostructured nanocomposites for different functional purposes.

Keywords: microwave; nanoparticles; thiourea; chalcogenide

1. Introduction

Commonly, hetero-structured materials are defined as sandwich-like building blocks of two or more dissimilar layers with different features to create better functions than each components. One of the interesting heterostructures, is the growth of metal oxides in sulfide based materials such as chalcogenides. Carrollite compounds with itself layered structure and general formula of AB_2X_4, where X is sulfur (S) or selenium (Se), A is divalent (Fe, Ni, Co or Cu) and B is trivalent (Co, Ni), are promising candidates in the formation of the heterostructures materials. These materials attracted lots of attentions after their discovery by the Linnaeite group of the Swedish Carl Linnaeus in 1845, which caused more efforts in identification of more layered transition metal sulfides and also oxides. $CuCo_2S_4$ as a member of the carrollite compounds category is a notable material because of having the low-cost, nontoxic, abundant and available constituents [1,2]. On the other hand, metal oxide materials are widely available materials with crystalline structures and different applications in various fields e.g., electrical/optical industry, redox reactions, catalyst production, agricultural industry, drug delivery/medicine, etc. They have significant properties in terms of efficiency, reactivity, selectivity, and cycle repeatability so that their combination with other materials such as $CuCo_2S_4$ can be led to prepare new multifunctional materials.

Various chemical methods have been reported to synthesize variety of hetero-structured nanomaterials. The introduction of a simple, inexpensive, high efficiency and rapid technique is notable to reduce production costs [3–5]. Amongst different techniques such as sol-gel, hydrothermal/solvothermal, precipitation/calcination methods, microwave assisted method is considered as a facile and rapid strategy to produce nanomaterials. [2–8]. As a matter of fact, the synthesis of hetero-structured $CuCo_2S_4/CuCo_2O_4$ nanoparticles using ultra-fast solvent free microwave assisted procedure has not been yet reported. Thiourea was selected as a suitable sulfur source and also driving agent in process due to its availability, cheapness and ease of use.

2. Experimental

2.1. Materials and Method

All of chemicals were purchased from Merck Co. and used without further purification. Metal sources with stoichiometric ratio in the presence of thiourea were mixed to each other, put into a microwave oven and treated by microwave irradiation with a power of 900 W for 20 min. The obtained black powder was rinsed with distilled water and absolute ethanol for several times, dried at 70 °C and then, characterized.

2.2. Characterizations

X-ray diffraction (XRD) pattern was recorded by a DRON-8 powder diffractometer using Cu Kα radiation (λ = 1.54060 Å). Fourier transform infrared (FT-IR) spectrum was obtained by a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. Scanning electron microscopy (SEM) images and energy-dispersive X-ray were taken on a VEGA\\ TESCAN S360 with gold coating.

3. Result and Discussion

The observed strong peaks at around 500–700 cm^{-1} in the recorded FT-IR spectrum of the prepared product shown in Figure 1 can be related to the vibration frequencies of Co-O and Co-S and Cu-S bands of $CuCo_2S_4$/$CuCo_2O_4$ compound. The peaks at 3423 and 2360 cm^{-1} can be assigned to the vibrations of the adsorbed H_2O and CO_2 molecules.

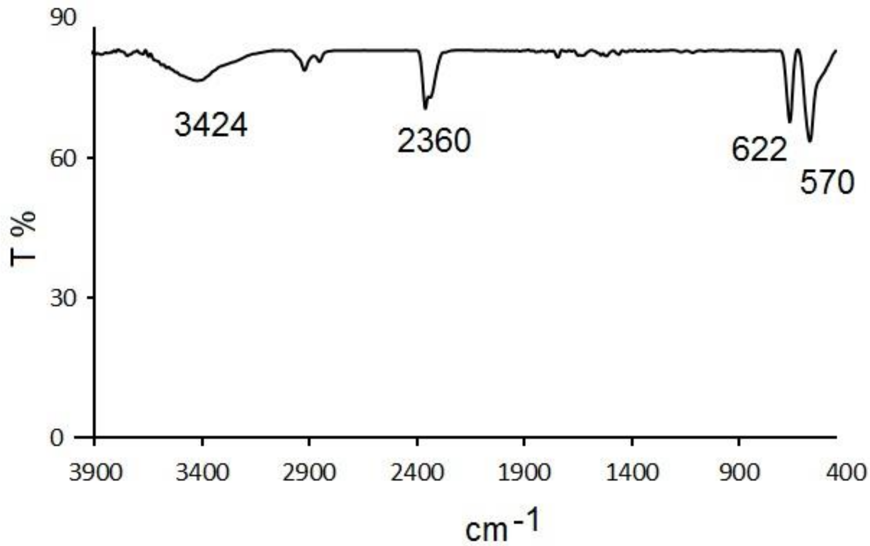

Figure 1. FT-IR spectrum of the synthesized nanoparticles.

Figure 2 exhibits XRD pattern of the prepared product. The appeared peaks at 16.8°, 31.19°, 35.50°, 38.76°, 41.58°, 47.17°, 50.23°, 54.91°, 59.24°, 62.21°, 64.02°, 65.13°, 68.70°, 71.13°, 75.10° and 77.45° which are in a good agreement with 111, 220, 311, 222, 004, 331, 422, 333, 440, 531, 620, 533, 622, 444, 711, 642 and 731 planes confirm the formation of cubic carrollite phase of $CuCo_2S_4$ (JCPDS card No. 75-1570). The diffraction lines at 2 Theta position of 31.36°, 36.95°, 38.94°, 45.06°, 56.02°, 59.60°, 65.70°, 69.00°, 77.55° in a close accordance with 220, 311, 222, 400, 422, 511, 440, 531 and 533 are related to cubic planes $CuCo_2O_4$ (JCPDS card No. 1-1155), which has been formed alongside carrollite phase [6].

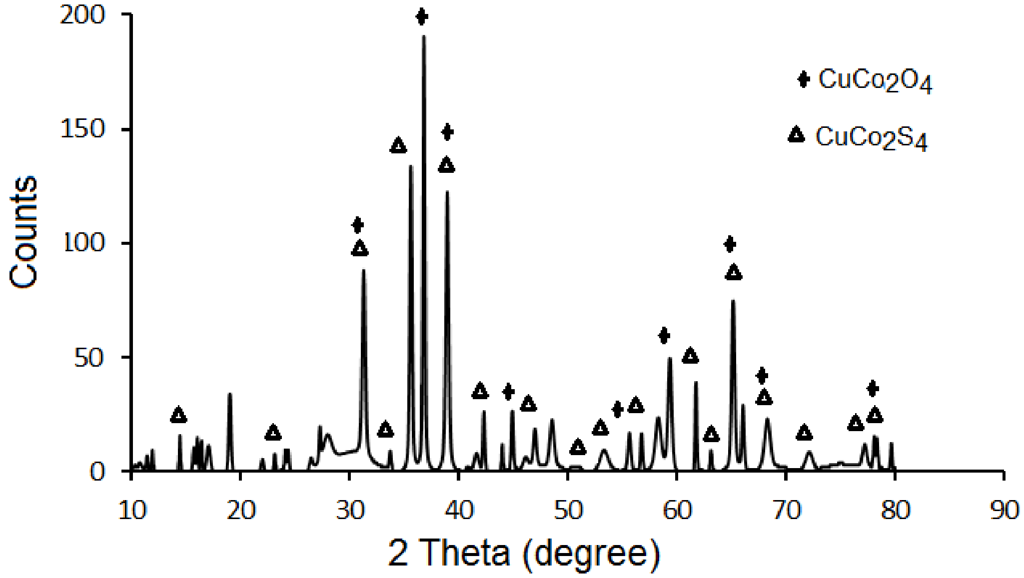

Figure 2. XRD pattern of the prepared $CuCo_2S_4/CuCo_2O_4$ nanoparticles.

The elemental EDX analysis shown in Figure 3 revealed the presence of Cu, Co and S elements confirming the mentioned XRD data of the formation of layered building blocks of $CuCo_2S_4/CuCo_2O_4$.

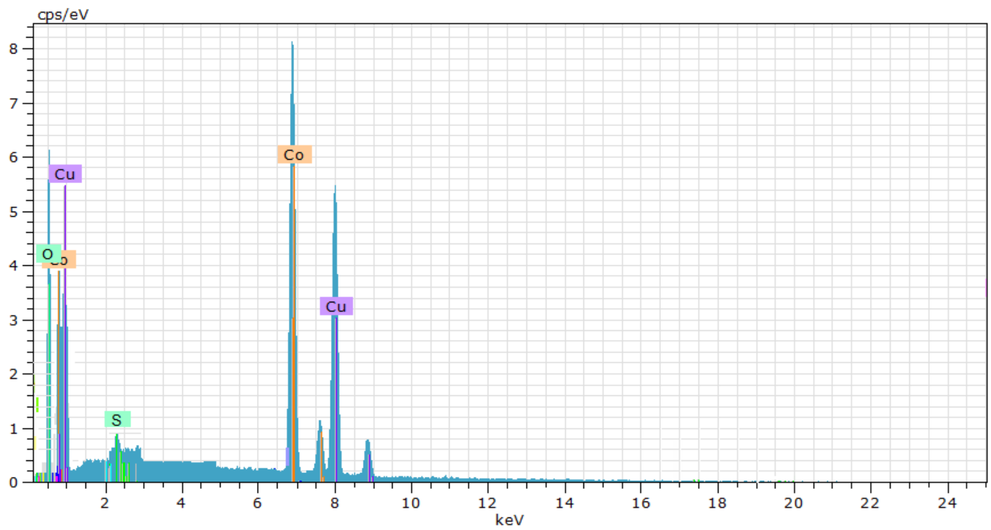

Figure 3. EDX analysis of the prepared product.

SEM images (Figure 4) recorded of the resulting product depict a spherical particulate morphology with the average particle size of about 40 nm. It is observed that these fine nanoparticles have been gathered together and formed a bundle-like texture consisting of particles. It can provide a large surface with more available active sites and efficiently contacts for various targets [7].

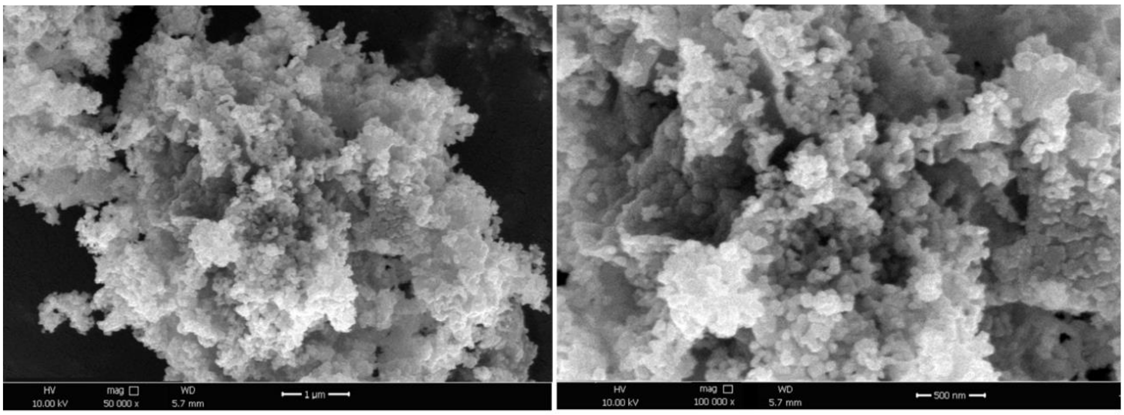

Figure 4. SEM images of resulting $CuCo_2S_4/CuCo_2O_4$ heterostructure.

4. Conclusions

In a summary, the hetero-structured $CuCo_2S_4/CuCo_2O_4$ nanoparticles were successfully synthesized by a rapid one-put microwave assisted strategy. This in situ treatment easily produces a suitable medium for the formation of heterostructure nanomaterial with a layered architecture. In fact, the microwave irradiation in presence of proper chemicals creates efficient interactions between reactants in solid state to reach this target. In addition, this procedure is carried out in a solid state without using any organic solvent, which can nominate it as an environment friendly method to prepare various nanomaterials.

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