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Preparation of $Cu_4SnS_4/CuCo_2S_4$ Nanoparticles Using Combustion Reaction Accelerated by Organic Driving Agents under Microwave Irradiation †

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Abstract: Copper based sulfide-rich nanomaterials have recently attracted attentions in various applications due to inexpensive, abundance and non-toxicity of their constituent elements. Cu_4SnS_4 and $CuCo_2S_4$ as the members of this family have exhibited good capability with a stable manner in solar cells, energy storage electrodes, batteries, etc. In this work, through a facile and rapid combustion reaction accelerated by microwave irradiation, $Cu_4SnS_4/CuCo_2S_4$ nanoparticles was prepared. Thiourea was used as a sulphur source and also organic driving agent. The features of the synthesized product were studied using fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion of x-ray spectrometry (EDX) techniques. The FT-IR and XRD results showed the formation of a multi-components structure containing orthorhombic crystalline phase of Cu_4SnS_4 alongside carrollite $CuCo_2S_4$ phase.

Keywords: nanoparticles; combustion; multi-components structure; microwave

1. Introduction

In recent years, copper-based sulfide rich nanomaterials have attracted lots of attentions because of having abundant, low-cost, easily available and non-toxic constituents compared to cadmium and lead-based compounds [1]. Usually, sulfide-rich materials have higher activity and conductivity as well as lower electronegativity and band gap than metal oxides. These compounds have significant features such as layered structures and suitable band gaps for light absorption, which bring up their ability as semiconductor materials in various applications [2].

Copper-based ternary sulfides such as Cu_4SnS_4 and $CuCo_2S_4$ as the members of this large family have been studied in variety of photovoltaic, energy storage, solar cells, catalytic, etc. applications [3–5]. The synthesis of hetero-structured building blocks consisting of these compounds to improve multifunctional features and reach highly efficient products is notable. Amongst different reported synthesis methods such as solvothermal/hydrothermal, hot-injection, sol gel, etc., microwave assisted technique can be introduced as a simple and rapid method to prepare nanomaterials [6–8]. As a matter of fact, the synthesis of $Cu_4SnS_4/CuCo_2S_4$ heterostructure nanoparticles using solvent free microwave assisted procedure has not been yet reported.

2. Experimental Section

2.1. Materials

All initial reactants were provided from valid Co. and used without further purification.

2.2. Synthesis Method

The proper stoichiometrical amounts of metal sources in the presence of thiourea as a sulphur source and driving agent were mixed to each other, put into a microwave oven and treated microwave irradiation with a power of 900 W for 20 min. the resulting black powder was washed, dried overnight and then, characterized by FT-IR, XRD and SEM analyses.

2.3. 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. Results and Discussion

Figure 1 indicates the FT-IR spectrum of the prepared sample. The observed strong peaks at 522, 569 and 664 cm^{-1} can be assigned to vibration frequencies of the Co-O, Sn-S, CoS and Cu-S bands from the prepared heterostructure molecule [9,10]. The peaks at 2361 and 3403 cm^{-1} can be related to the vibrational frequencies of the H-O and C-O-C functional groups from the adsorbed H_2O and CO_2 molecules on the product surface.

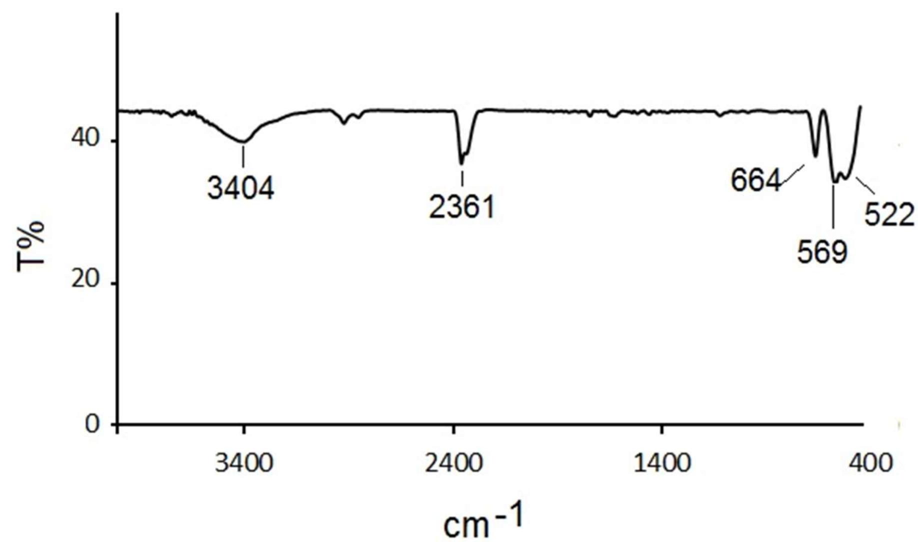

Figure 1. FT-IR spectrum of the synthesized $Cu_4SnS_4/CuCo_2S_4$.

The recorded XRD pattern of $Cu_4SnS_4/CuCo_2S_4$ nanoparticles is shown in Figure 2. Based on this pattern, the appeared diffractions peaks are related to the formation of orthorhombic phase of Cu_4SnS_4 structure (JCPDS card No. 27-0196). In addition, the diffraction peaks at 26.59°, 31.26°, 32.70°, 38.88°, 44.88°, 48.84°, 51.89°, 54.73°, 58.29°, 61.74°, 64.79°, 66.11°, 68.14°, 71.39°, 75.36° and 78.91° in a close accordance with 220, 311,222, 400, 331, 422, 333,440, 531, 620, 533, 622,444, 711, 642 and 731 crystal planes are attributed to the cubic phase of carrollite $CuCo_2S_4$ structure (JCPDS card No. 75-1570). The slight shift at the 2 theta positions can be a result of being sandwich and crystallization of the carrollite $CuCo_2S_4$ phase between the Cu_4SnS_4 layers.

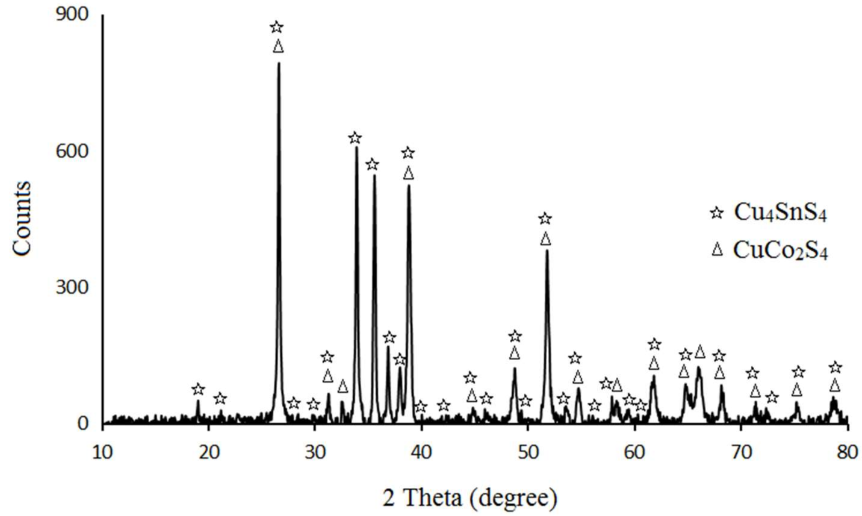

Figure 2. XRD pattern of the prepared $Cu_4SnS_4/CuCo_2S_4$ nanoparticles.

The elemental EDS analysis (Figure 3) revealed the presence of Cu, Sn, Co and S elements confirming the mentioned structural data of FT-IR and XRD analyses.

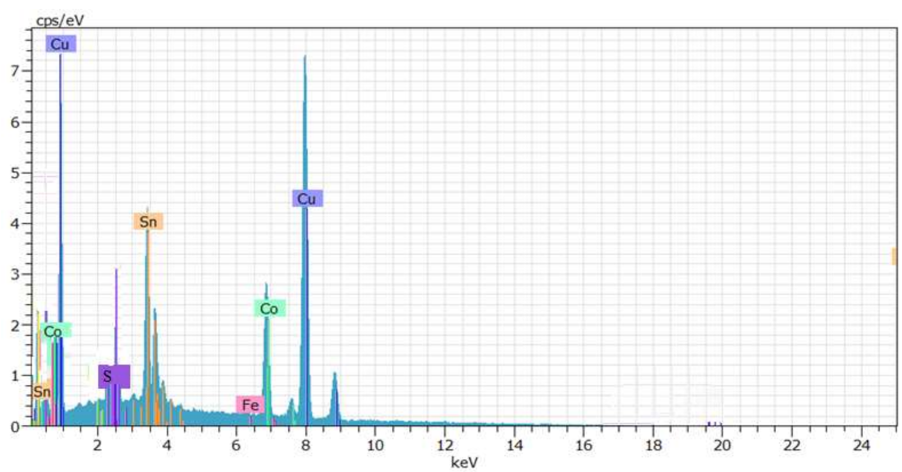

Figure 3. EDS analysis of the resulting product.

The recorded SEM images of the prepared product depicted aggregations of crystalline flake-like morphology with an average thickness of 40 nm and width size of 210 nm. This morphology can be originated from the role of thiourea as a driving agent alongside being sulfide source. Some particulate morphology with an average particle size of 60 nm are also observed.

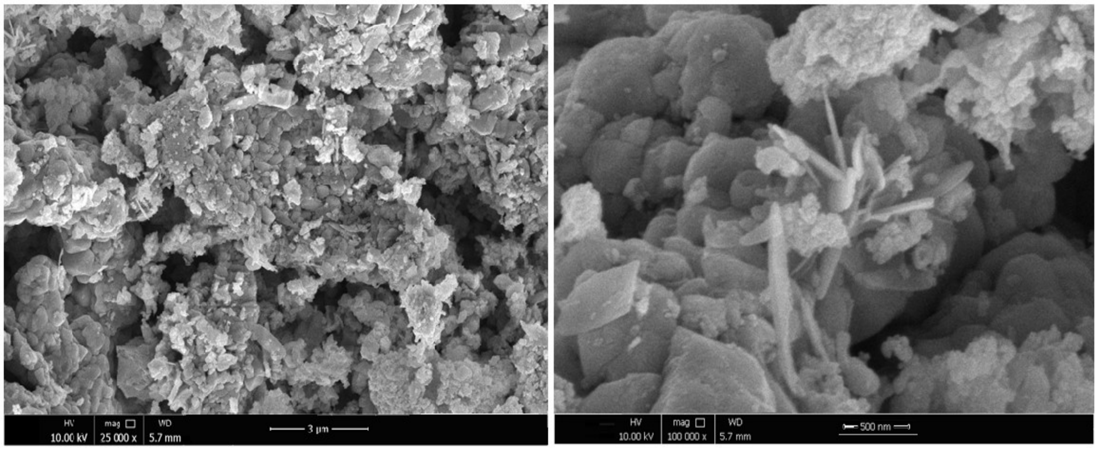

Figure 4. SEM images of the synthesized $Cu_4SnS_4/CuCo_2S_4$.

4. Conclusions

$Cu_4SnS_4/CuCo_2S_4$ nanoparticles was well synthesized by microwave assisted method. Amongst various chemical methods, the advantages of this synthesis technique includes simplicity, high speed, low energy consumption and solvent-free reaction. As an effort to decrease the growth time, microwave heating treatment can be introduced as a capable technique to produce nanomaterials in the short reaction time compared to the conventional procedures with a long reaction time.

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