

**ORIGINAL RESEARCH PAPER**

## Solvothermal Synthesis of Cobalt and Copper Sulfides Nanoparticles with High Light Absorptance for New Solar Selective Coatings

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**Abstract**

New selective coating materials are developed and used in advanced solar collector and absorber designs with improved efficiency. Cobalt and Copper sulfides nanoparticles are high interest for absorbers of solar thermal collectors due to their optical properties and high absorptance in the solar wavelength range (> 96%). In the present work, Cobalt and Copper sulfides nanoparticles were synthesized successfully via a surfactant-assisted solvothermal process. The structural, morphological and optical characteristics of as-synthesized materials were investigated by X-ray diffraction, field emission scanning electron microscopy and diffuse reflectance spectroscopy. Evaluation of the obtained results indicated that the as-synthesized nanoparticles had well-defined morphology with very fine particles and higher light absorption in UV/vis region not only than the common inorganic pigments but also than common carbon black. Copper sulfide exhibited integral solar absorptance value equal to 0.97 that is very ideal for solar thermal collectors and thermal selective coatings. They also had low thermal emittances equal to 0.14 and 0.27 for cobalt and copper sulfides respectively.

### 1. INTRODUCTION

Spectrally selective solar absorbers are used for efficient conversion of solar energy to heating energy, e.g. for domestic hot water. State-of-the-art absorbers have good durability and excellent optical properties: solar absorptance is close to unity and thermal emittance is close to zero [1].

Efficient photo-thermal conversion of solar energy requires spectrally selective surfaces with high solar absorptance  $a$  in the wavelength range of 0.3–2.5  $\mu\text{m}$  and low thermal emittance in the infrared region ( $\lambda \geq 2.5 \mu\text{m}$ ). To obtain this graded selective surface, various mechanisms such as cermet, absorber–reflector tandem,

multilayer interference stacks, etc. have been used [2]. The function of the absorber of a solar collector is to transform the incident solar irradiation into heat and to suppress heat losses due to thermal radiation. These requirements, maximum absorptance of the solar irradiation and minimum emittance in the thermal infrared are met by applying a spectrally selective coating onto the absorber substrate material (usually copper, aluminium or steel). For a long time, mainly thin black chromium layers (chromium particles embedded in a chromium oxide, electro-deposited on nickel-plated copper) or also nickel-pigmented alumina (on aluminium) have been used for this purpose. However, advanced coating processes such as physical or chemical vapour deposition (PVD or CVD) promise some advantages. These include the optical characteristics of the coatings, the constancy of product quality and an improvement of the ecological balance. Whether these expectations can be fulfilled, is still to be confirmed. The most important sales argument for solar absorber coatings, apart from the price, concerns their optical characteristics that is vital such as high solar absorptance and low thermal emittance [3]. An efficient conversion of incident solar radiation into useful heat is characterized by the capacity of the solar device to absorb solar radiation and minimize thermal back-radiation. Thus, high values of solar absorptance and low values of thermal emittance are required, these values are controlled by the solar absorber material used for the thermal solar collector [4]. Thin film solar cells that have both of the high solar absorptance and low thermal emittance are subject to intensive research because of their potential for large-scale application and low production costs. They combine the advantage of high performance

with low production cost and therefore short energy pay back times [5]. These coatings that is formulated with light absorber pigments are very suitable and economic for these applications. In the present work, firstly cobalt sulfide and copper sulfide nanoparticles were synthesized successfully and then evaluated as selective solar absorber materials.

## 2. Experimental procedure

### 2.1. Reagent and materials

Poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P123) was purchased from Sigma Aldrich and used as surfactant and the other chemicals were purchased from Merck co. Carbon black spherical powder with particle size distribution of 0.4-12 micron was purchased from local market and used as received.

### 2.2. Synthesis of $\text{Cu}_2\text{S}$ nanoparticles

$\text{CuCl}$  (6 mmol) and thioacetamide (10.5 mmol) were used as Cu and S sources, respectively. They were mixed with 0.47 g the Pluronic P123 surfactant and dissolved in 80 ml of 96% ethanol. The mixture of reactants was put into a Teflon-lined stainless steel autoclave of 200 ml capacity and maintained at 160 °C for 24 h without shaking or stirring during the heating period. After cooling to room temperature, a black precipitate was collected and washed with distilled water and ethanol to remove surfactant and organic impurities.

### 2.3. Synthesis of $\text{CoS}$ nanoparticles

Cobalt nitrate, hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), (5 mmol) and thioacetamide (10 mmol) were used as Co and S sources, respectively. They were mixed with 0.8 g the Pluronic P123 surfactant and dissolved in 80 ml of 96% ethanol. The mixture of reactants was put into a Teflon-

lined stainless steel autoclave of 200 ml capacity and maintained at 180 °C for 24 h without shaking or stirring during the heating period. After cooling to room temperature, a black precipitate was collected and washed several times with distilled water, ethanol and dichloromethane to remove surfactant and organic impurities.

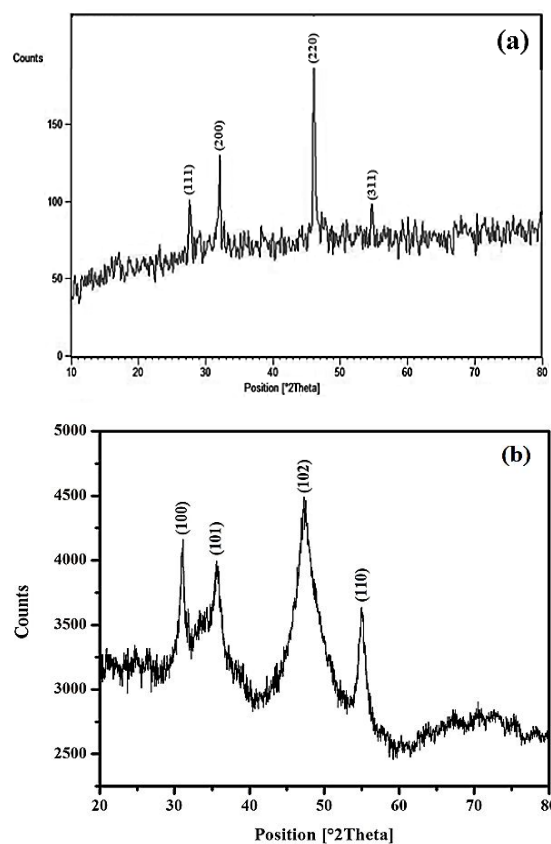
#### 2.4. Characterization

Crystal structures of as-prepared products were characterized by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu-K $\alpha$  radiation (40 kV, 40 mA and  $\lambda=0.1541$  nm). XRD patterns were recorded from 0° to 10° with a scanning step of 0.02°/s. Morphology and size of the samples were analyzed by Hitachi S-4160 Field Emission Scanning Electron Microscopy (FE-SEM) at an accelerating voltage of 15 kV. The diffuse reflectance spectra of as-prepared powders were measured by JASCO V-670 UV-Vis Spectrophotometer (in the range of 220-2200 nm). The thermal emittance of the samples was measured by Temp 2000 A infrared reflectometer (AZ Technology, USA) in the range of 3-30  $\mu$ m.

### 3. Results and discussion

The typical XRD patterns shown in Fig. 1 (a) and (b) revealed the phase and purity of the as-prepared Cu<sub>2</sub>S and CoS materials. For Cu<sub>2</sub>S sample, as shown in Fig. 1 (a), the observed peaks could be assigned to diffraction from the (111), (200), (220) and (311) faces. No other characteristic peaks from impurities, such as CuS, Cu<sub>1.96</sub>S, Cu<sub>1.8</sub>S, were detected, which revealed that the purity of the product was pretty high. Furthermore, the intensity and the sharp diffraction peaks suggested that the as-prepared product was well crystallized [6]. For CoS sample, as shown in Fig. 1 (b), all the diffraction

peaks can be indexed to a hexagonal phase of cobalt sulfide (CoS), matching well with its standard XRD pattern (JCPDS card No. 02-9305). No other impure diffraction peaks are detected, indicating that the as-synthesized product is high purity CoS [7].

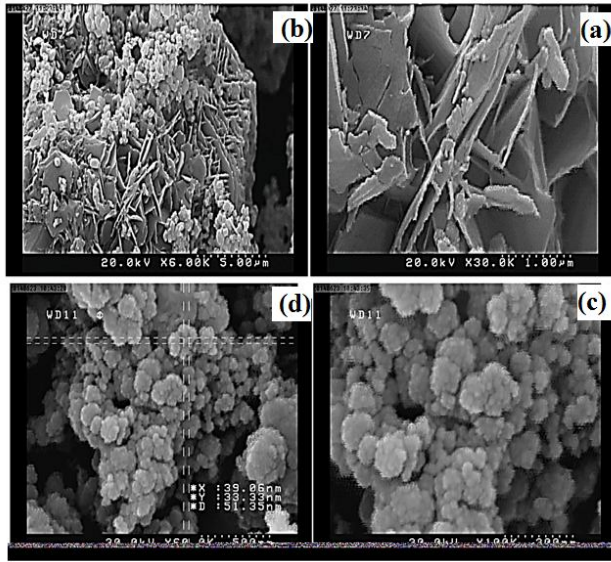


**Fig. 1.** XRD pattern of the as-synthesized materials: (a) copper sulfide and (b) cobalt sulfide.

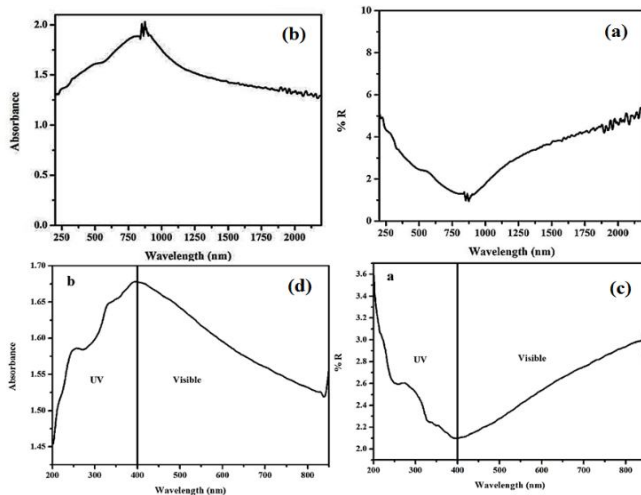
Field emission scanning electron microscopy (FESEM) observations with low and high magnification of Cu<sub>2</sub>S and CoS samples have shown in Fig. 2 (a,b) and (c,d), respectively that show the obtained products have collective-like morphology. These nano powders are 10-20 nm in mean diameter.

The diffuse reflectance and UV/vis absorbance spectra of as-synthesized nanomaterials are indicated in Fig. 3 (a,b) and (c,d) for copper and

cobalt sulfides, respectively. As seen in these figures, their reflectance was very low and their absorption was so high. These nanoparticles have very high absorption in the whole wavelength range compared with the other shapes of materials that used in selective coatings [8.9].

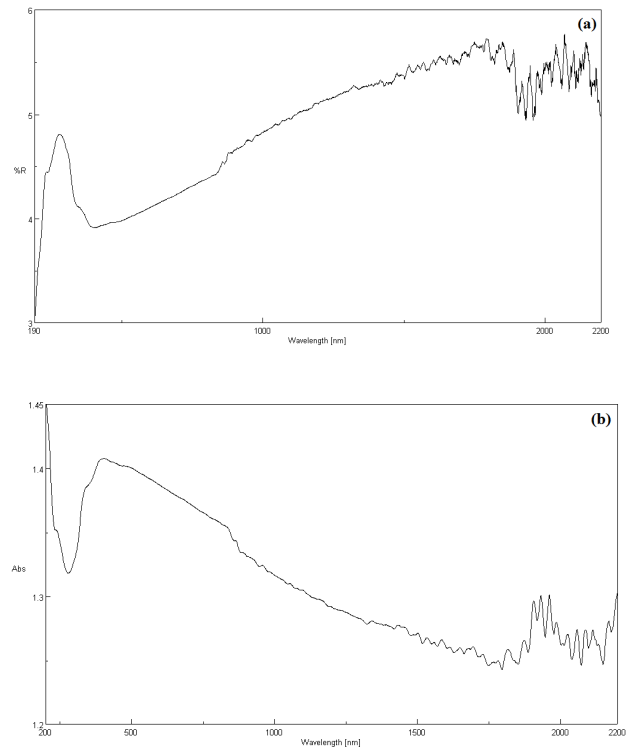


**Fig. 2.** SEM micrographs in low and high magnifications of the as-synthesized materials: (a,b) copper sulfide and (c,d) cobalt sulfide.



**Fig. 3.** (a,c) Diffuse reflectance spectra and (b,d) UV/vis absorbance spectra of the as-synthesized materials: copper sulfide and cobalt sulfide respectively.

The carbon black diffuse reflectance and UV/vis absorbance spectra also is presented in Fig. 4 for comparison. As seen in this figure, the reflectance of carbon black was so high in comparison with as-synthesized sulfide materials and this mater indicates that these materials are so efficient than carbon black. Evaluation of optical absorption of these synthesized materials indicate that they are more suitable and efficient for selective solar absorbers and thermal selective coatings than another coatings that used currently [10-12].



**Fig. 4.** (a) Diffuse reflectance and (b) UV/vis absorbance spectra of the carbon black.

Thermal emittances of copper and cobalt sulfides were equal to 0.27 and 0.14, respectively that is low and suitable for selective coatings. In the some selective solar coatings, low emittance flakes must be included in the paint to reduction of thermal emittance in the far infrared region [13] while we

do not need to this flakes with copper and cobalt sulfide nanoparticles.

#### 4. Conclusion

In the present work, copper and cobalt sulfides nanoparticles were synthesized successfully and their reflectance and absorptance investigated. The obtained results indicated that UV/vis absorptance of these structures were so high and they almost absorb the whole wavelength range. Because the multiple light reflection through the porous skeleton, UV/vis absorption was increased while their thermal emittance were low. This feature is very important and considerable for thermal selective coatings and solar thermal collectors to absorb all of the wavelengths. Therefore, as-synthesized nanoparticles are excellent selection for new selective coatings.

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