

A Modern Hydrothermal Synthesis Method of Dendritic Silver Sulfide Nanostructures by Applying Novel Initiating Reagents and Verification of their Behavior in Solar Cells

Kouros Motevalli 1,*, Zahra yaghoubi 2

1- Applied Chemistry Department, South Tehran Branch, Islamic Azad University, Tehran, Iran

2- IT Department, South Tehran Branch, Islamic Azad University, Tehran, Iran

*Corresponding Author: kmotevalli451@gmail.com

ABSTRACT

In this research, the dendritic Silver sulfide nanostructures were successfully synthesized by a simple hydrothermal route. The effect of temperature, and reaction time, on the morphology and particle dimension was also investigated. Thus, the efficiency of synthesized Silver sulfide nanostructures in thin-film solar cells was evaluated. The results indicated very well that the particle dimension and morphology have effect on solar cells efficiency and dendritic Silver sulfide nano- structures have higher efficiency compared to spherical and rod-like Silver sulfide nanostructures. Moreover, depositing of dendritic Silver sulfide upon Silver sulfide nanoparticles led to obtaining 3.17% cell efficiency that in comparison with sole dendritic nanostructures and sole nanoparticles (1.81%), efficiency improvements of 48 and 85% were, respectively, obtained.

Keywords: synthesis, nanostructure, reagents , solar cells , hydrothermal , semiconductor

1. INTRODUCTION

Silver sulfide, a p-type semiconductor with a bulky bandgap of 1.24 eV which is in the best acceptable range for solar-energy conversion [1–4], can be used in solar cells [2–8], photocatalysts [9], catalysts [10], biosensors [11], nanoscale switches [12], and cold cathodes [13]. Hence, many studies have focused upon seeking an easy method for synthesis of Silver sulfide nanostructures such as nanoparticles [2, 14, 15], nanowires [16], nanorods [17], nanoplates, dendrites, and hollow microspheres. Different chemical methods such as solvothermal, hydrothermal [1], ultrasonic [6], microwave [4], and co-sedimentation [1] have been used to synthesize this substance. As seen these facts , dendrites, as a sort of fractal structure, which are generally created by hierarchical self-assembly under nonequilibrium conditions, have received intensive profit in recent years [2,3].

2. EXPERIMENTAL

Methods

All of the applied chemicals in this work were of analytical grade and used as-received without any further purification. Fourier transform infrared (FT-IR) spectra were recorded upon Magna-IR, spectrometer 550 Nicolet with 0.127 cm^{-1} resolution in KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. Photocurrent density–voltage (J–V) curve was measured using computerized digital multimeters (Ivium-n-Stat Multichannel potentiostat) and a variable load. A 400 W metal xenon power source (Luzchem) applied as assimilated sun light source, and its light intensity (or radiant power) was adjusted to simulated AM 1.8 radiation at 120 mW/cm^2 with a filter for this purpose.

Preparation of $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$

Firstly, 2 mmol of ethylenediamine (en) was added drop- wise to an AgCl solution (1 mmol in 50 ml of distilled water). Then, the mixture was stirred and heated at $65\text{ }^\circ\text{C}$ for 1 h. Finally, the obtained sediment was centri- fugged, washed with methanol and ether as the most effective solvents several times, and dried at $60\text{ }^\circ\text{C}$.

Synthesis of dendritic Silver sulfide nanostructures

In a typical experimental procedure, 2 mmol of $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ and 1 mmol of cysteine were mixed in 30 ml of distilled water and stirred for 15 minutes. The final solution was poured to the 200 ml Teflon-lined stainless steel autoclave maintained at $150\text{ }^\circ\text{C}$ for 15 h, and then, the autoclave was permitted to being cooled to room temperature virtually. The resulting black sediment was gathered and then washed with ethanol as suitable polar solvent and distilled water for several times and was dried at $74\text{ }^\circ\text{C}$ for 12 h (sample A2). The effects of temperature, time of reaction, and cysteine concentration were also investigated. Reaction cases are listed in Table 1.

Fabrication of thin-film solar cells (FTO/TiO₂/ Silver sulfide/Pt-FTO)

Electrophoresis deposition (EPD) was utilized to prepare TiO₂ films [3-11]. During EPD, the suitable FTO glass remained at a positive potential (anode), whereas a pure steel mesh was used as the counter (cathode) electrode. The linear distance between these two electrodes was about 6.5 cm. Power was supplied by a Megatek Programmable DC Power Supply (MP-3005D). The applied voltage was 13 V. The deposition cycle was repeated four times, each time 15 s, and the temperature of the electrolyte solution was kept constant at room temperature. The coated substrates were air dried. The apparent area of the film was $1.6 \times 1.4\text{ cm}^2$. The resulted layer was annealed under an air flow at $509\text{ }^\circ\text{C}$ for 30 minutes. Electrolyte solution consisted of 125 mg/l of I₂, 46 ml/l of acetone, and 25 ml/l of water in ethanol as a solvent.

Table 1. The reaction conditions for Silver sulfide nanostructures

Sample no.	Temperature (°C)	Time (h)	Ag source: cysteine ratio	Morphology
1	107	15	2:1	Dendritic
2	157	15	2:1	Dendritic
3	207	15	2:1	Nanorod
4	158	15	2:1	Dendritic
5	157	25	2:1	Dendritic
6	155	20	4:1	Nanoparticle/ dendritic
7	155	15	1:1	Nanosheet

substrate, a paste of Silver sulfide was initially prepared. The slurry was produced by mixing and grinding 1.1 g of the nanometer dimensioned Silver sulfide with ethanol and water in several steps. Afterwards, the ground slurry was sonicated with ultrasonic horn (Sonicator 3000; Bandeline, MS 72, Germany) and then mixed with terpineol and ethyl cellulose as binders. After removing the ethanol and water with a rotary evaporator, the final paste was prepared. The prepared Silver sulfide paste was coated on TiO₂ film by a Dr. Blade technique. After that the electrode was gradually heated under an air flow at 455 °C for 30 min. Counter electrode was made from deposition of a Pt solution on FTO glass. Afterwards, this electrode was placed over TiO₂/Silver sulfide electrode. Sealing was accomplished by pressing the two electrodes together on a double hot-plate at a temperature of about 115 °C. The redox electrolyte comprising of 0.07 M of LiI, 0.07 M of I₂, and 0.52 M of 4-tert-butyl- pyridine in acetonitrile as a solvent was introduced into the cell through one of the two small holes erected in the counter electrode. Finally, these two holes were sealed by a small square of sealing sheet and characterized by I–V test. The results are presented for different samples in Table 2. For fabrication of FTO/TiO₂/Silver sulfide-nanoparticle/dendritic Silver sulfide/Pt-FTO structure (cell C1), Silver sulfide nanoparticles prepared as mentioned in the literature [3] were used. Chemical bath deposition (CBD) method used for fabricating cell C1, FTO/TiO₂ prepared by EPD technique was immersed in suspension containing Silver sulfide nanoparticles for about 4 h.

Table 2. J–V characterization of samples A2, A3, A7, B1, and C1

Cell no.	Voc (V)	Jsc (mA/cm ²)	FF	η(%)
A2	0.64	5.91	0.59	2.16
A3	0.61	5.532	0.63	2.06
A7	0.52	4.46	0.47	1.07
B1	0.57	4.53	0.65	1.63
C1	0.66	7.04	0.67	3.03

3. RESULTS AND DISCUSSION

In this section, this fact should be mentioned that figure 3a, b indicate the FTIR spectra of $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ complex and dendritic Silver sulfide nanostructures (sample A2), respectively. In the case of $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ (Fig. 1a), two absorption bands located at 3370 and 3243 cm^{-1} are related to N–H stretching of primary amine ($-\text{NH}_2$) and two bands at 2950 and 2890 cm^{-1} correspond to $-\text{CH}_2$ asymmetric and symmetric stretching cases [20].

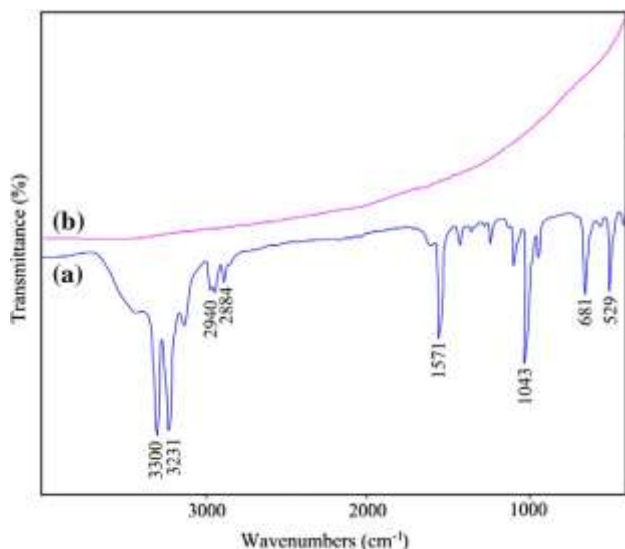


Fig. 1. FT-IR spectra of a $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ and b dendritic Silver sulfide nanostructure (sample A2)

The absorption band at 1580 cm^{-1} is dedicated for N–H bending of $-\text{NH}_2$, the band at 1051 cm^{-1} is related to C–N stretching state, and the bands at 688 and 531 cm^{-1} correspond to Ag–N and Ag–O stretching vibrations [18,19]. The FTIR results indicate that the $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ complex was well formed. Figure 1b represents FTIR spectrum of synthesized dendritic Silver sulfide nanostructures. Since the curve in this condition has no absorption peaks, pure Silver sulfide nanostructures were synthesized without any organic impurities. The effect of temperature, reaction time, and the ratio of reactants on the morphology and particle dimension were examined by different experiments and the obtained products were verified using SEM images. For verifying temperature effect on morphology, three experiments were conducted at 110 °C (sample A1), 160 °C (sample A2), and 210 °C (sample A3) and their SEM images are verified in Fig. 2a–c. As being indicated, at 110 °C for 15 h, the nanoparticles were self-assembled to form dendritic-like structures (Fig. 2a). By increasing temperature from 110 °C (sample A1) to 160 °C (sample A2), the particles were smaller and well-ordered and uniform dendritic nanostructures were produced (Fig. 2b). At higher temperatures in hydrothermal reaction, the nucleation rate is faster than growth rate and so smaller particles will be formed. When the temperature was increased to 210 °C (sample A3), morphology was changed and rod-like nanostructures with average diameter of 20–40 nm and average length of 100–300 nm were prepared (Fig. 2c). As can

be observed in Fig. 3a, reaction time of 10 h (sample A5) is not sufficient for simple synthesis of dendritic nanostructures. For instance A5, dendritic structures have been created, but due to high growth opportunities, their dimension is great. Therefore, reaction time of 15 h is optimum time for preparation of appropriate dendritic Silver sulfide nanostructures at 150 °C (sample A2). Figure 2 is relevant to the effect of $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}/\text{Cysteine}$ mole ratio, and for this purpose, the ratio of 4:1 and 1:1 (in addition to the 2:1) was selected (samples A6 and A7, respectively). As is obvious, in both cases, the morphology has altered and spherical nanoparticles and nanosheets, respectively, have been synthesized.

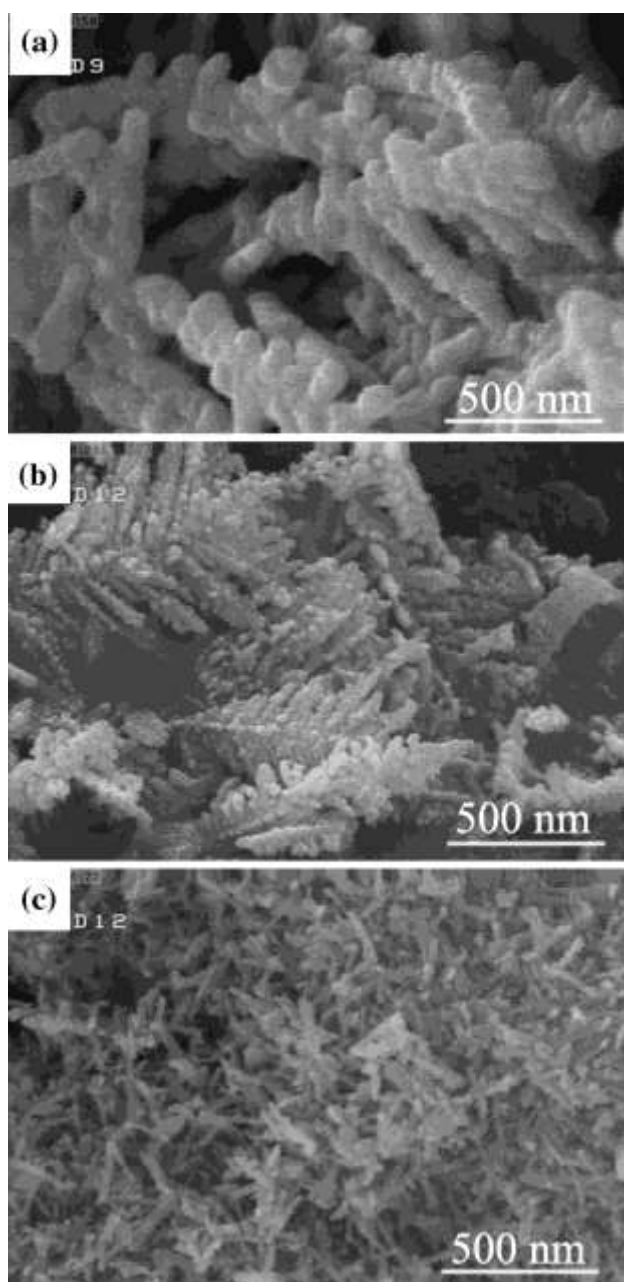


Fig. 2. SEM images of the synthesized Silver sulfide for 15 h at different temperatures a 110 °C (sample A1), b 160 °C (sample A2), and c 110 °C (sample A3)

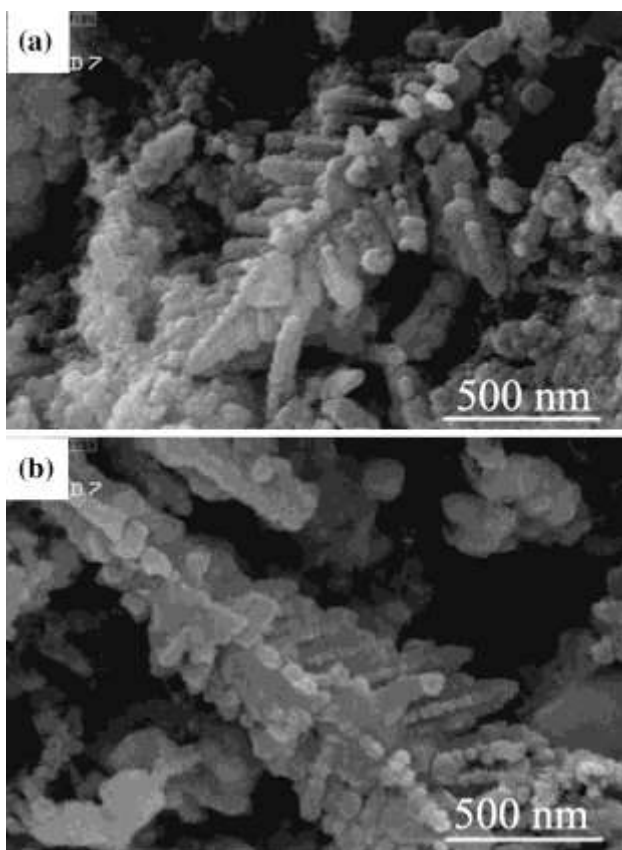


Fig. 3. SEM images of the synthesized Silver sulfide for different times a 10 h (sample A4) and b 20 h (sample A5)

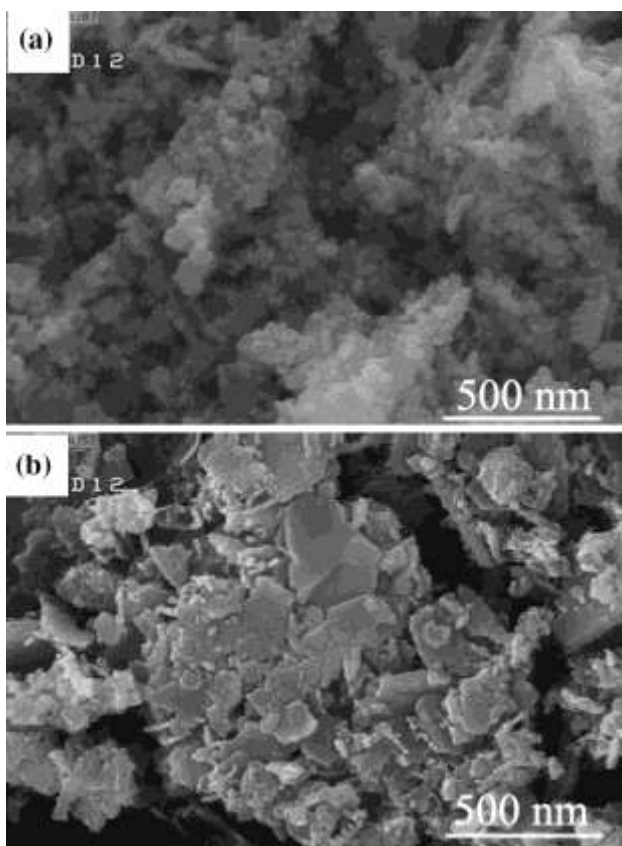


Fig. 4. SEM images of the synthesized Silver sulfide with different Ag⁺/Cysteine mole

ratios a 4:1 (sample A6) and b 1:1 (sample A7)

Before the hydrothermal process, the production rate of sulfide from cysteine is very low and the formation of $(\text{Ag}(\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH})_2)_k/2$ complex is so limited. In Fig3, we can observe the SEM images of the synthesized Silver sulfide for different times. a 10 h (sample A4) and b 20 h (sample A5). In Fig4 we can observe the SEM images of the synthesized Silver sulfide with different Ag^+ / Cysteine mole ratios a 4:1 (sample A6) and b 1:1 (sample A7). In comparison with similar works presented for Silver sulfide preparation [1–10], we prepared dendritic Silver sulfide nano-structures using new starting reagents and without using surfactants by a simple route which can be more capable in solar cells. Moreover, effect of morphology on solar cell efficiency was investigated, and using modern and suitable approach in cell preparation, important improvement in cell was obtained.

4. CONCLUSIONS

As summarized phrases, dendritic-like, rod-like, and sheet-like Silver sulfide nanostructures were synthesized by a facile hydrothermal method using new starting reagents including $[\text{Ag}(\text{en})_2(\text{H}_2\text{O})_2]\text{Cl}$ and cysteine. In accordance with our knowledge, this is the first The characterization of the synthesized Silver sulfide nano-structures was carried out using SEM and FT-IR. Afterwards, the conduct of obtained nanostructures in solar cells was verified. Our results displayed that morphology and dimension have remarkable effect on efficiency of cells and prepared dendritic Silver sulfide nanostructures have the highest efficiency. Moreover, being sedimented of dendritic nanostructures upon nanoparticles created a 91% improvement in solar cell efficiency (from 1.66 to 3.15%) [21].

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