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Synthesis of Copper Sulfide Nanoparticles by Pulsed Plasma in Liquid Method

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Abstract—Copper sulfide nanoparticles (CuS) were successfully synthesized by the pulsed plasma in liquid method, using two copper rod electrodes submerged in molten sulfur. Low electrical energy and no high temperature were applied for synthesis. Obtained CuS nanoparticles were then analyzed by means of X-ray diffraction, Low and High Resolution Transmission Electron Microscopy, Electron Diffraction, X-ray Photoelectron, Raman Spectroscopies and Field Emission Scanning Electron Microscopy. XRD analysis revealed peaks for CuS with hexagonal phase composition. TEM and HRTEM studies showed that sizes of CuS nanoparticles ranged between 10-60 nm, with the average size of about 20 nm. Copper sulfide nanoparticles have short nanorod-like structure. Raman spectroscopy found peak for CuS at 474.2cm^{-1}of Raman region.

***Keywords*—**Copper sulfide, Nanoparticles, Pulsed plasma, Synthesis.

I. Introduction

SEMICONDUCTOR transition-metal compounds have been of much interest because of their excellent properties and potential applications [1]. Among these transition-metal compounds, copper sulfide CuS is widely used as a thermoelectric cooling materials [2], optical filers [3], optical recording materials [4], solar cells [5], [6], nanoscale switches [7], and superionic materials [8]. In the nature copper sulfide can occur in a wide range of stoichiometric compounds, such as copper-rich and copper-poor copper sulfides. The stoichiometric composition of copper sulfide varies from Cu_2S (chalcocite), CuS_2 (copper sulphide), CuS (copper monosulphide), $Cu_{1.96}$ S (djurleite), $Cu_{1.94}$ S (djurleite), $Cu_{1.8}$ S (digenite), and Cu_7 S_4 (anilite) [9], [10]. Traditionally, copper sulfide was synthesized by a solid-state reaction of elements [11], solid-state metathesis [12], and self-propagating high-temperature synthesis [13]. Recently, CuS with different morphologies, including nanoparticles [14], [15], nanorods [16]-[21], millimeter-scale tubes [22]-[24], nanowires [25]-[27], nanodisks [28] and flower-like structures [29] have been synthesized.

Copper monosulfide is also known as a rare mineral covellite.

Nowadays a lot of advanced nanomaterials have been discovered and synthesized by scientists. It is very interesting to synthesize, analyze and study the morphology, structure and applications of the copper sulfide nanoparticles. Advantage of copper sulfide nanoparticles synthesis is that, initial materials and chemicals for synthesis are cheaper and obtainable.

We have applied the pulsed plasma in liquid method for synthesis of copper sulfide nanoparticles. This method can be considered as cheaper and easy way to synthesize the copper sulfide nanoparticles. Because there is no necessity of using the high energy, high temperature, pressure, vacuum and cooling system during synthesis procedure.

II. Experimental Procedure

In this section, low temperature, catalyst-and template-free, simple synthesis for copper sulfide CuS nanoparticles by pulsed plasma submerged in molten sulfur is described. Experimental setup for copper sulfide nanoparticles synthesis given in the Fig. 1, it consists of power source and glove box, containing the Pyrex beaker with sulfur, which needs to be heated (120°C) in order to be in a liquid state. Two copper electrodes were submerged in the molten sulfur, and connected to a power source. After the sulfur powder was melted, another 150g of sulfur was added and heated to 140°C to melt, and was kept at this temperature by a temperature controller throughout the experiment. Copper rod electrodes with diameter of 5mm and 150mm in length were purchased from Rare Metallic, (purity of 99.98%). Sulfur powder was purchased from Kanto Chemicals, (purity of 99.9%). Electrical voltage of 180V, current of 3A, and frequency of 60Hz were applied for the synthesis. Single pulse duration was equal to 10 microseconds (μs). Nitrogen gas (N_2) was blown into the glow box, in order to keep the oxygen content below 5 % for safety purpose.

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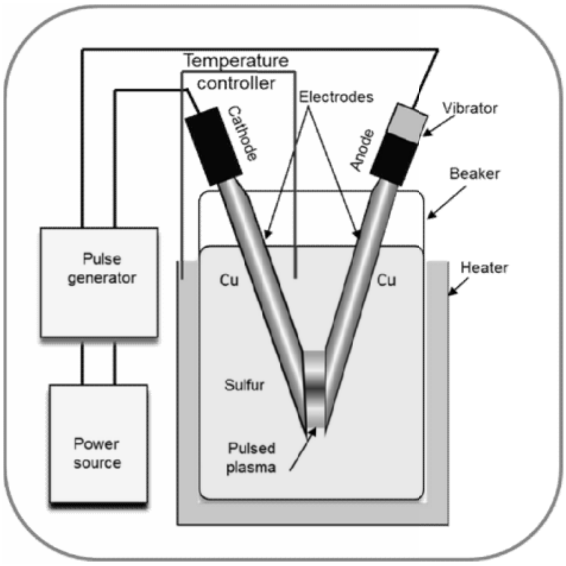

Fig. 1 Schematics of the experimental setup for synthesis of CuS nanoparticles by pulsed plasma in liquid method

III. Results

Fig. 2 shows the (a) FE-SEM, (b) TEM, (c) HRTEM, and (d) Fast Fourier Transform (FFT) images of CuS nanoparticles synthesized by pulsed plasma in liquid method. Hexagonal crystal structure is clearly seen from the FE-SEM and HRTEM images. HRTEM studies revealed short nanorod-like CuS particles. And also, FFT digital diffractogram taken from the Fig. 2 (c), shows lattice spacings of the copper sulfide nanoparticles correspond to the (100) and (110) *d* spacings, respectively of hexagonal copper sulfide.

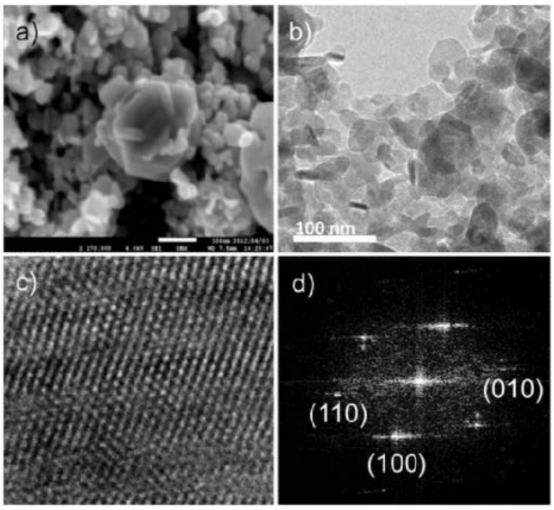

Fig. 2 (a) FE-SEM, (b) Low resolution TEM, (c) High resolution TEM, and (d) FFT images of CuS nanoparticles synthesized by pulsed plasma in liquid method

In order to better investigate the crystallographic structure of the copper sulfide nanoparticles synthesized by pulsed plasma in liquid, X-ray diffraction pattern was taken and analyzed. Fig. 3 displays peaks for copper sulfide nanoparticles, and inset is a model of hexagonal CuS.

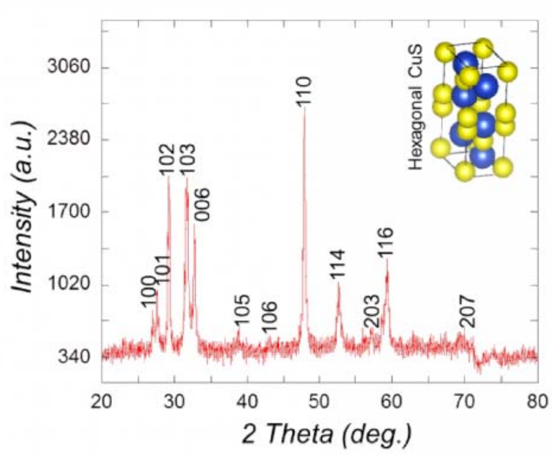

Fig. 3 XRD pattern for CuS nanoparticles, inset is a model of hexagonal CuS nanoparticles

Raman spectroscopy was applied to analyze crystalline quality, surface condition and homogeneity of copper sulfide nanoparticles prepared by pulsed plasma in liquid. Crystalline sample can exhibit sharp Raman peaks. However, if sample is amorphous or polycrystalline, it will have broad Raman peaks. Copper sulfide nanoparticles synthesized by pulsed plasma in liquid consists of a hexagonal crystal structure with a space group P63/mmc and a primitive unit cell contain twelve atoms, six for Cu and six for S. Raman spectra presented in the Fig. 4 shows slightly board peak for CuS nanoparticles at 474.2cm^{-1}, characterizing the S-S stretching mode of S_2 ions at 4e sites [29, 30].

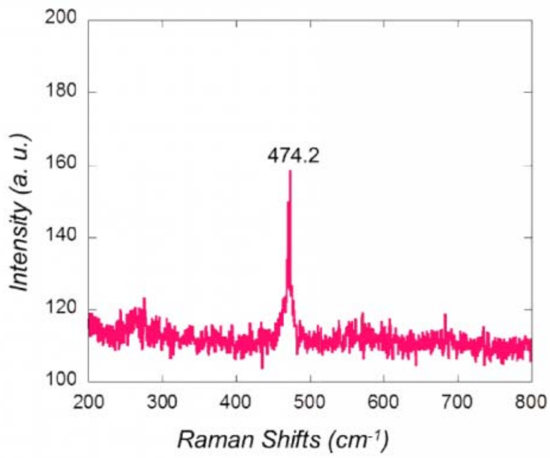

Fig. 4 Raman shift for CuS nanoparticles characterizing the S-S stretching mode of S_2 ions at 4e sites

Energy dispersive X-ray spectrum (EDX) taken during the HRTEM observations showed the elemental composition of sample to be Cu – 54.62 wt%, S – 27.19 wt%, and C – 4.68 wt%. Presence of carbon may be caused by sample holder grid, which is made of copper and coated by carbon. Weight % of the copper from grid was subtracted from the total wt% of Cu taken by EDX analysis. According to this data, stoichiometric formula of compound was calculated as copper monosulfide (CuS), and this is in a good agreement with XRD analysis data. The EDX chart for copper sulfide nanoparticles synthesized by pulsed plasma in liquid method is given in the Fig. 5.

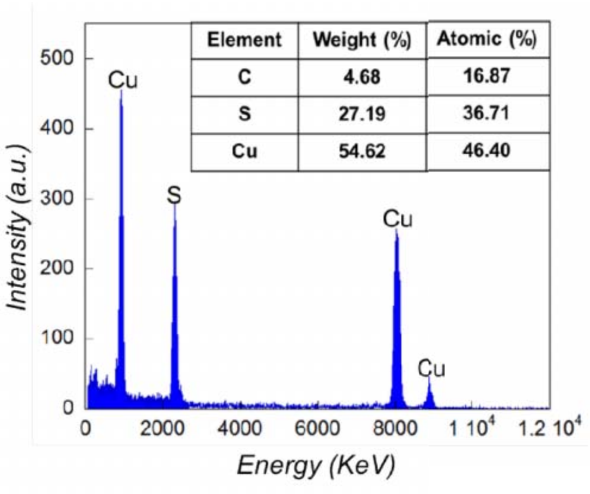

Fig. 5 EDX chart showing the elemental composition of CuS nanoparticles synthesized by pulsed plasma

X-ray Photoelectron Spectroscopy (XPS) given in the Fig. 6, used to determine the atomic states of the compositional elements in the CuS sample prepared by pulsed plasma in liquid method. Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks were detected at 952.30 and 932.4eV, characterizing copper element in the CuS. The S 2p peak observed at 162.29eV corresponds to sulfur in the copper sulfide nanoparticles [31].

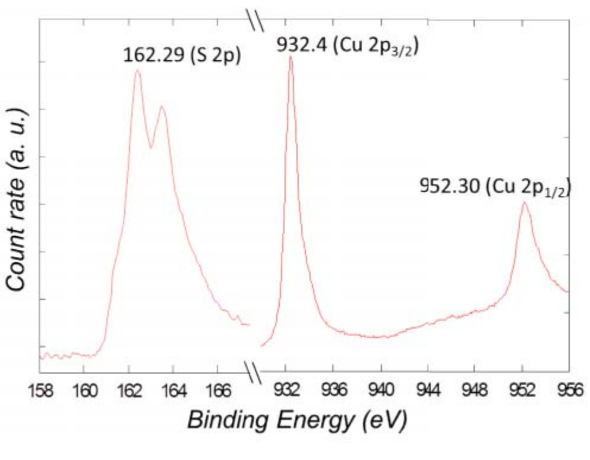

Fig. 6 XPS peaks for CuS nanoparticles synthesized by pulsed plasma

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