

Effect of Different Surfactants on Thermoelectric Properties of CuS Nanoparticles

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Abstract. We report here the thermoelectric (TE) properties of CuS nanoparticles (NPs), synthesized by a facile polyol method using CTAB and PVP as surfactants. Systematic characterizations using powder XRD, Rietveld refinement of XRD and Raman spectroscopy confirm their single phase, hexagonal-closed structure with space group $P6_3/mmc$ and stoichiometric composition, respectively. The presence of surfactants during synthesis of CuS NPs seemingly prevents the volatility of S, making the capped samples a little S-rich and hence enhanced electrical conductivity and thermopower. Consequently, a significant improvement of more than 50% in thermoelectric power factor at 300 K is observed for CTAB and PVP capped CuS NPs as compared to pure one.

INTRODUCTION

Thermoelectric (TE) materials are the ones which can convert heat into electricity and vice versa. Hence they can be used for an alternative to the fossil fuel and meeting the ever increasing energy demand for the society. The efficiency of thermoelectric devices determined by the dimensionless figure of merit (ZT) which is expressed as, $ZT = S^2 \sigma T / \kappa$, where S , σ , κ and T represent Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. As S , σ and κ are inter-dependent, it is a difficult task to improve one parameter without compromising the other, and hence several techniques are used to increase ZT . Many of the recent advancements in enhancing the thermoelectric figure of merit (ZT) are linked to nanoscale phenomena found both in bulk samples containing nanoscale constituents and in nanoscale samples themselves. Also to improve TE power factor ($S^2 \sigma$), the concept of energy filtering of carriers (electron and hole) by introducing a barrier to restrict the charge carriers from entering the material is used.¹

Also, since mostly available TE materials with higher ZT contain toxic Pb, Se or Te, nanostructured transition metal sulphides are now emerging as a attractive class of materials for replacing toxic Te and Se-based materials. Copper sulphides are some of them, which found in different stoichiometric compositions such as Cu_2S , Cu_7S_4 , $Cu_{1.8}S$, CuS (covellite), and CuS_2 . Among these sulphides, CuS attracts special attentions because of its affordability, naturally abundant, low toxicity and metal-like behavior down to ~ 5 K. It is an indirect p-type semiconductor with energy band gap in the range 1.55 - 2.15 eV.² With this motivation, we investigated the effect of capping agent on thermoelectric properties of naturally abundant CuS NPs synthesized at low temperature (~ 160 °C).

2. EXPERIMENTAL SECTION

2.2 Method

In a typical synthesis of CuS NPs by modified polyol method, mixtures of 10 mmole of $Cu(NO_3)_2 \cdot 3H_2O$ (99% MERCK) and 25 mmole of thiourea (99% MERCK) along with 40 ml of ethylene glycol (EG) (99% MERCK) were taken in a three-necked round-bottom flask. Thiourea was taken in excess due to the volatile nature of sulphur.² These mixtures were heated at 160-165 °C for 12 hours with a continuous flow of argon gas that produced black

coloured precipitate (ppt). It was left for cooling down to room temperature for 2 hours. The product was directly centrifuged at 12,000 rpm for 12 min. The resulting supernatant was discarded and the black ppt was washed with ethanol using probe ultrasonication for 4 min. Ethanol was decanted after 1 hour when the NPs are completely settled down. These steps were repeated for another time to remove EG completely. Finally, the ppt was kept in a vacuum oven at 60 °C for 2 hours that gave the sample in powder form. Finally, around 97% yield was obtained and ~3% was lost while washing. Same process was repeated after adding the surfactants of 0.1 g each with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and thiourea along with the ethylene glycol. We have used polyvinyl pyrrolidone (PVP) (Sisco $\geq 94\%$) and cetyltrimethyl ammonium bromide (CTAB) (Sisco $\geq 98.5\%$) as surfactants. Samples were denoted as CSP, CSPV and CSCT, respectively.

2.2 Characterization techniques

Powder X-ray diffraction (XRD) for all CuS samples synthesized with different surfactants was performed using the Bruker D8 advance x-ray diffractometer with $\text{Cu K}\alpha$ radiation (1.54 Å) in the angle range from 5° to 80°. Raman spectra were recorded at room temperature using Jobin Yvon Horiba LABRAM-HR Visible instrument equipped with an Ar ion laser of wavelength 473 nm. Field emission scanning electron microscope (FESEM) using Carl Zeiss AURIGA FIBSEM in secondary emissions mode was used for determining the particle size distribution. Seebeck coefficient (S) and resistivity measurements of all samples in pellet forms, made in room temperature by cold pressing at an axial pressure of ~1 GPa for 1 minute, were performed in a specifically designed commercially available Dewar using differential direct current method in load based TEP setup and four-point probe method in a home-built setup in the temperature range of 5–300, respectively.³

3. RESULTS AND DISCUSSION

As-prepared blue-indigo-coloured CuS nanoparticles CSP, CSPV and CSCT are first characterized by XRD (Fig. 1 (a)). Diffraction peaks for these CuS samples are well-matched to those of hexagonal covellite CuS having space group $\text{P6}_3/\text{mmc}$. To further check the purity of phase, Rietveld refinement analysis was performed for powder XRD of CSP (Figure 1(b)) as an example using initial parameters from literature.⁴ Their refinement parameters are shown in Table 1. There is slight increase in the lattice parameters a and c in CSPV but decrease in CSCT compared to CSP suggesting that there is slight lattice disturbance on capping.

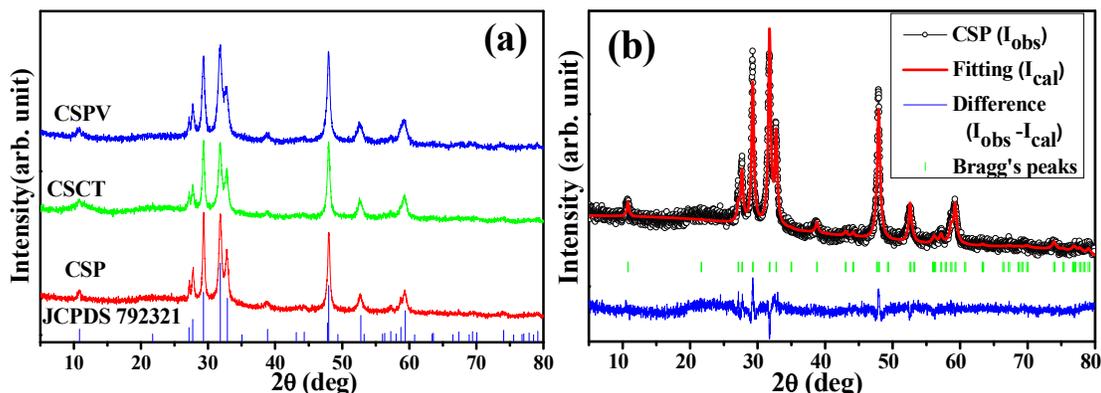
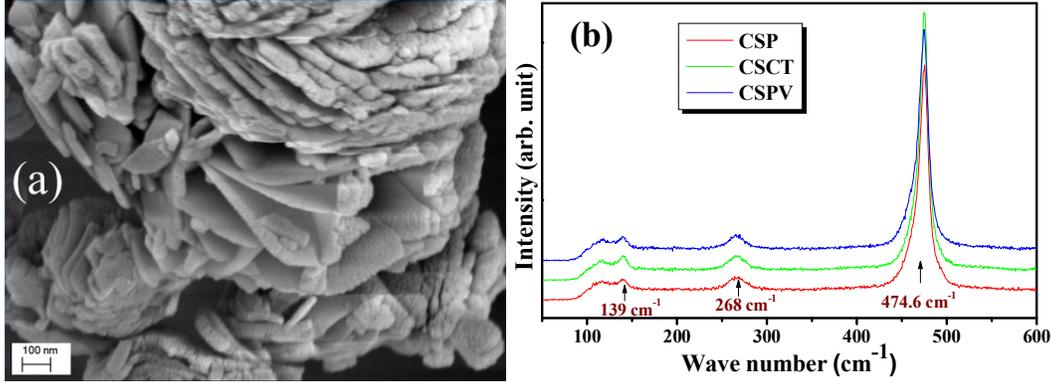


FIGURE 1 (a) Powder XRD of CSP, CSCT and CSPV, and (b) a representative Rietveld refinement of powder XRD of CSP.

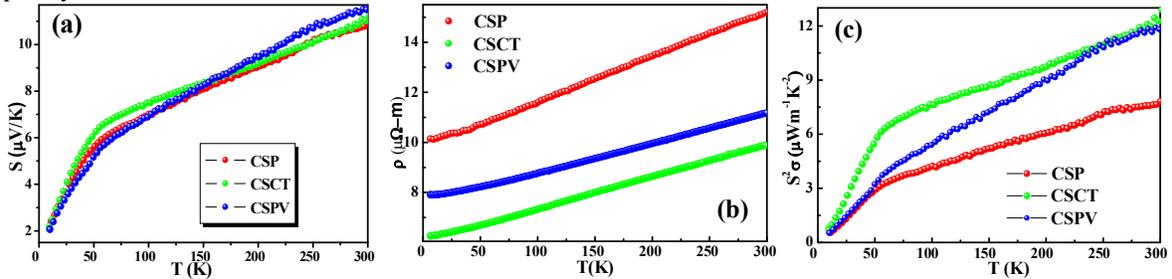
The average crystalline size was estimated using Debye-Scherrer equation $D = \frac{k\lambda}{\beta \cos\theta}$, where D is the crystallite size, λ is the wavelength of x-ray source used in XRD (0.154 nm), k is the geometrical factor which is considered to be 0.90 in the case of spherical crystals, θ is the Bragg angle taken in radians, and β is the full width at half maximum (FWHM) in radians. Using the FWHM of the diffraction peak associated with (102) crystalline plane, the average crystallite diameters were estimated to be 22.3 nm, 20.4 nm and 17.1 nm for CSP, CSCT and CSPV, respectively.

Table 1 Obtained parameters from Rietveld refinement with errors of the samples.

| Parameters | CSP | CSCT | CSPV |
|-----------------------------|------------|------------|------------|
| a & b (Å) | 3.794(1) | 3.792(1) | 3.795(1) |
| c (Å) | 16.407(3) | 16.394(2) | 16.426(3) |
| V(Å ³) | 204.541(5) | 204.147(6) | 204.878(4) |
| ρ (g/cm ³) | 4.657 | 4.666 | 4.650 |
| χ^2 value | 1.71 | 1.59 | 1.59 |

**FIGURE 2** (a) FESEM of CSP nanoparticles and (b) Raman spectra of CuS synthesized with different capping agent.

FESEM image of CSP NPs is shown in Figure 2 (a). The particles look like somewhat disk-like shape, which has breadth of different sizes, with an average size of 30 nm. Raman spectroscopy was performed on the NPs of CuS to characterize the atomic vibrations. An intense peak was observed at 474.6 cm^{-1} (Figure 2 (b)) corresponding to S-S stretching vibrational mode of A_{1g} symmetry of sulfur (S2) atoms at 4e sites⁴, as 2/3 of sulfur atoms form covalent S-S bonds in covellite structure of CuS. Also two less intense peaks were observed at 268 cm^{-1} (for Cu-S vibrational mode) and 139 cm^{-1} are also observed, consistent with earlier reports.^{2,5} Other peaks observed towards lower frequency are well accordance with theoretical calculation available in literature.²

**FIGURE 3** Temperature dependence of (a) Seebeck coefficient S , (b) electrical resistivity ρ , and (c) thermoelectric power factor ($S^2\sigma$) of compacted CSP, CSPV and CSCT nanoparticles.

CuS is p-type semiconductor and shows metallic behavior down to 5 K due to holes in the valence band arising from the S 3p orbitals.⁶ The temperature dependence of Seebeck coefficient for all samples (Figure 3 (a)) shows positive values confirming the majority charge carriers as holes in whole 5-300 K range. A slope change is observed near 55 K that may be related to second order structural transition reported in literatures.² Seebeck coefficient of CSP, CSCT and CSPV at around 300 K are somewhat metallic with its values at $10.90 \text{ } \mu\text{V/K}$, $11.06 \text{ } \mu\text{V/K}$ and $11.52 \text{ } \mu\text{V/K}$, respectively. Metallic behavior for all the three samples is also seen from the ρ curves (Figure 3 (b)) such that the metallicity is slightly improved in CSPV and further in CSCT. This increase can be understood in terms of volatile nature of S. Usually, S come out from reaction in the form of H_2S or SO_2 . Due to this we added an excess amount of S-source during sample synthesis. On other hand in presence of complex structures of CTAB and PVP as surfactants, S appears to be not able to easily come out. Thus, S content has been apparently increased in capped samples as compared to CSP NPs, which causes enhancement in its conductivity because metallic conduction comes from partially filled 3p orbital of S.²

The effect of increased Seebeck coefficient and decreased resistivity is attributed to energy filtering effect, caused by combine effect of interface and adsorbed surfactant at surface of NPs, and can be seen from thermoelectric power factor (Figure 3 (c)), which have been increased significantly for the surfactant capped CuS. For CSP at 300K, TE power factor is $7.75 \mu\text{Wm}^{-1}\text{K}^{-2}$, which for CSPV and CSCT are $11.81 \mu\text{Wm}^{-1}\text{K}^{-2}$ and $12.26 \mu\text{Wm}^{-1}\text{K}^{-2}$, an increase of $\sim 52\%$ and $\sim 58\%$, which are reasonably significant.

CONCLUSIONS

Pure and capped with PVP and CTAB surfactants of CuS samples were successfully prepared using a facile polyol method at low reaction temperature and less quantity of S-source. XRD and Raman data prove the formation of well-crystalline and stoichiometric covellite CuS NPs with hexagonal symmetry. The positive thermopower data confirms that the majority charge carriers are holes. Their electrical resistivity and thermopower data are indicative of metallic and anomalous nature. Therefore, we have observed more than 50% enhancement in the thermoelectric power factor for the surfactant capped CuS NPs as compared to pure CuS. These results may be further used for improving TE power factor ($S^2\sigma$) and figure of merit (ZT) at room temperature for this naturally abundant mineral.

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