

Enhanced Zeta Potential of Polyol Method Synthesized PVP-capped Sb_2S_3 Nanoparticles

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Abstract. Analysis of Rietveld refinement of XRD data confirms single phase orthorhombic crystal structure of pure and polyvinyl pyrrolidone (PVP)-capped Sb_2S_3 nanoparticles (NPs) synthesized successfully at 190 °C by facile polyol method. Raman modes further confirm their stoichiometric formation. Ratio of Sb to S was found to be a little deviated from 2:3 corresponding to Sb_2S_3 due to volatile nature of S. A striking effect on the surface charge of Sb_2S_3 NPs with and without PVP as surfactant was found in zeta potential (ξ) data collected using deionized water (DIW) for pH values in the range of 3 to 10.5. This reveals that an early constant ξ of -51.64 mV is found in pH = 6.5 to 8.5 for the PVP-capped Sb_2S_3 NPs indicating their high stability in DIW compared to that of unstable nature (ξ = -23.45 mV or less) for pure Sb_2S_3 NPs. The isoelectric point is found at pH = 4.2 for PVP-capped Sb_2S_3 , not for pure sample. This information is likely to be useful for many applications like in cosmetics, for waste water treatment, ceramics, pharmaceuticals and in medicine.

INTRODUCTION

Nowadays, transition metal chalcogenide nanomaterials (NPs) have emerged for applications in electronic, optical and semi-conductor devices [1]. Among these, Sb_2S_3 metal chalcogenide as a V-VI group semi-conductor with an orthorhombic crystal structure having a Pnma space group attracts a special attention because of its direct bandgap in the range of 1.65-2.5 eV. Sb_2S_3 is very well-known for its high thermoelectric power, broad spectral range response and good photovoltaic properties having wide range of applications as target for microwave devices and in solar energy conversion.

For the synthesis of Sb_2S_3 NPs, various techniques have been reported recently including vacuum evaporation, thermal decomposition, sol-gel method and hydrothermal method [2]. However, their high temperature requirements limit these techniques. Therefore, a polyol method, is one of the preferred options which is a facile, cost-effective method with high yield to prepare PVP-capped and uncapped Sb_2S_3 NPs. In addition, less toxic materials are highly desirable to control environmental issues. In this, Sb_2S_3 is an abundant material and more environmentally acceptable compared to other related compounds. In the present work, we capped the Sb_2S_3 NPs using PVP. PVP is a non-toxic and non-ionic polymer with C=O, C-N and CH₂ as functional groups and is used as a good stabilizer that prevents the aggregation of NPs [3]. PVP as a stabilizer and capping agent affects the surface charge of prepared NPs, which can be studied using zeta potential (ξ), which is very well known to study stability of particles in a dispersion medium.

In the present work, we report the successful growth of PVP-capped and pure Sb_2S_3 NPs using polyol method and study of their stability using dynamic light scattering (DLS) technique and ξ measurements in DIW at pH values in the range of 3 to 10.5. A significant effect on the surface charge of Sb_2S_3 NPs with PVP as surfactant was found from DLS and ξ studies. These results can be useful for many applications like pharmaceuticals, ceramics, for waste water treatment, in medicine and cosmetics [4].

EXPERIMENTAL TECHNIQUES

(a) Synthesis

All the reagents were used as-received with no further purification. In a typical synthesis of Sb_2S_3 , 4 mmol SbCl_3 (99%, Alfaesar) and 6 mmol thiourea (TU, 99% Merck) as Sb and S sources, respectively, were dissolved in 40ml diethyleneglycol (DEG, >98.5%) using (a) with polyvinylpyrrolidone (PVP) as non-ionic surfactant and (b) without PVP. In each case, the respective mixtures were stirred for 15 min under argon atmosphere to avoid oxygen. The solution was then heated in three-neck round-bottom flask at 190-195°C for 2 hours with continuous flow of argon gas at the rate of 5°C/min (a bubble formation on outlet confirms the passage of argon gas). This resulted in the formation of black coloured precipitate (ppt) NPs. The solution was kept to cool down to room temperature. Then, the product was centrifuged at 12000 rpm for 12 min to separate out the ppt from the supernatant. The ppt was then washed with ethanol by 5 min sonication. This was again centrifuged at 12000 rpm for 10 min from which the NPs were recovered and sonicated for 5 min in fresh ethanol. This process was repeated three times. After this, the ppt was allowed to settle down for two hours and then ethanol was decanted. Finally, both Sb_2S_3 samples with and without PVP obtained were vacuum-dried at 70°C for 1 hour. The resultant dark grey powder obtained in each case was used for the characterizations.

(b) Characterization

To confirm the phase purity of the samples prepared, they were characterized by XRD using the Bruker D8 advanced x-ray diffractometer with high intensity Cu K- α radiation (1.54 Å), scanning rate of 0.02°/s in the 2 θ range of 10-70°. Raman spectroscopic measurements were performed at 300 K using a micro-Raman spectrometer (JobinYvon Horiba LABRAM HR-800) equipped with a He-Ne laser in a backscattering configuration of wavelength 633 nm. For both the samples, data were recorded for fixed 100 s, to avoid random intensity variation and exciting source (633 nm). EDAX measurement was done on pure sample using Model JEOL JSM 5600 scanning electron microscope equipped with it. Particle size and ξ measurements using a DLS-based Zeta/nanoparticle analyzer (NanoPlus-3) were performed at 300 K with detection angle of 15° after thorough sonication for 5 min of the NPs dispersed in DIW.

RESULTS AND DISCUSSION

XRD patterns of obtained pure and PVP-capped Sb_2S_3 NPs prepared are shown in Fig. 1. All the diffraction peaks are well-matched with the orthorhombic crystal structure of stibnite Sb_2S_3 phase with its reported lattice parameters $a = 11.23\text{Å}$, $b = 3.841\text{Å}$ and $c = 11.31\text{Å}$ (JCPDS-42-1393) [4]. No impurity peaks were found, which confirms the single phase nature of the samples prepared. Structural Rietveld refinement data further confirms the orthorhombic stibnite Sb_2S_3 phase purity (Table 1).

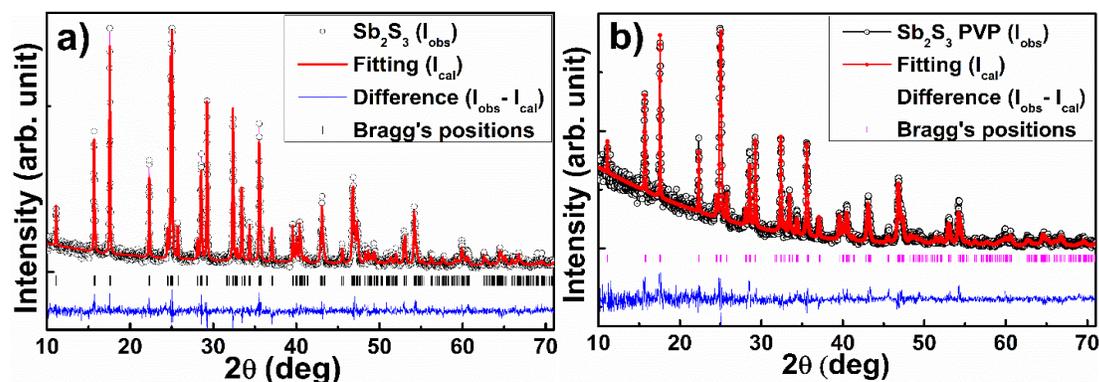


Fig. 1. Powder XRD patterns of (a) pure Sb_2S_3 NPs and (b) PVP-capped Sb_2S_3 NPs along with the respective Rietveld refinement fitted, difference curves and Bragg reflection positions.

Table 1. Crystallographic information obtained after Rietveld refinement for PVP-capped Sb_2S_3 along with that of pure one (the standard errors are in parentheses)

Parameters	For Sb_2S_3	For PVP-capped Sb_2S_3
a (Å) & c (Å)	11.310(9) & 11.229(4)	11.300(7) & 11.221(6)
b (Å)	3.837(5)	3.837(3)
Volume (Å ³) & Mass density (g/cm ³)	487.45(4) & 4.557	486.597(8) & 4.785
Bragg R-factor and R _f factor	8.84 and 6.86	12.9 and 8.10

The average crystallite diameter (D) of the obtained products was estimated from Debye–Scherrer equation. The values of D of the pure and PVP-capped Sb_2S_3 NPs were about 98 nm and 40 nm, respectively with an error of ± 1 nm. This clearly indicates that introduction of PVP reduces the average crystallite size of the synthesized Sb_2S_3 NPs compared to pure one.

Formation of orthorhombic stibnite phase was further confirmed from Raman data (Fig. 2. (a)) for both samples. Fig. 2 (b) shows the lorentzian fitting of Raman spectra for pure sample. Raman spectra depicted by the six peaks viz, one strong peak at 280.4 cm^{-1} , three moderate peaks at 189.8 , 237.7 and 306.6 cm^{-1} and two weak peaks at 113.1 and 156.7 cm^{-1} confirm the formation of stibnite phase of Sb_2S_3 in both the samples in line with those reported earlier [4, 5]. Fig. 2 (c) shows the EDAX spectrum of the pure Sb_2S_3 NPs, which confirms the sample is composed of only Sb and S elements with atomic ratio of nearly 47:53 showing slight deviation from 2:3 ratios and hence deficiency of S, which is expected due to its volatile nature. No traces of other elements are observed.

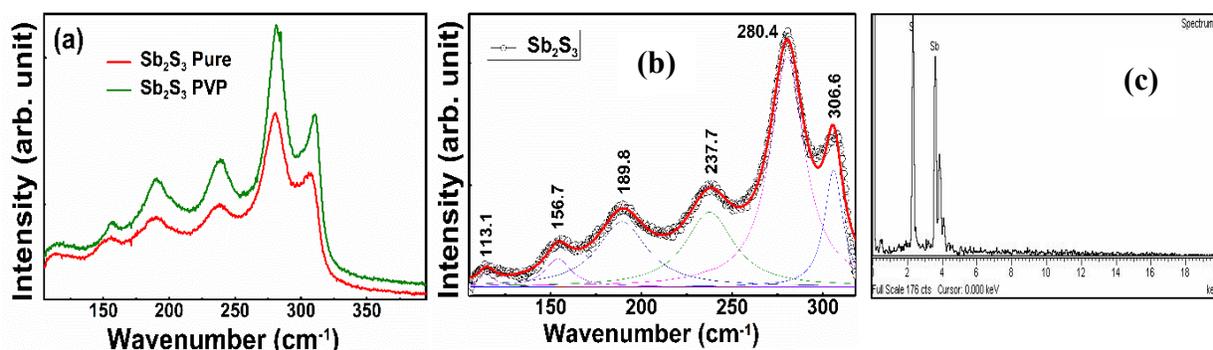


Fig. 2. (a) Room temperature Raman spectra of pure and PVP-capped Sb_2S_3 NPs, (b) Multi-peak lorentzian raman fitting of pure Sb_2S_3 NPs. and (c) EDAX spectrum of pure Sb_2S_3 NPs.

We studied the effects of the particle size and PVP as capping agent on the zeta potential (ζ) and hydrodynamic diameter (HD) in DIW. Fig. 3 shows the intensity distribution of HD of both the samples for first and second run at pH 7.

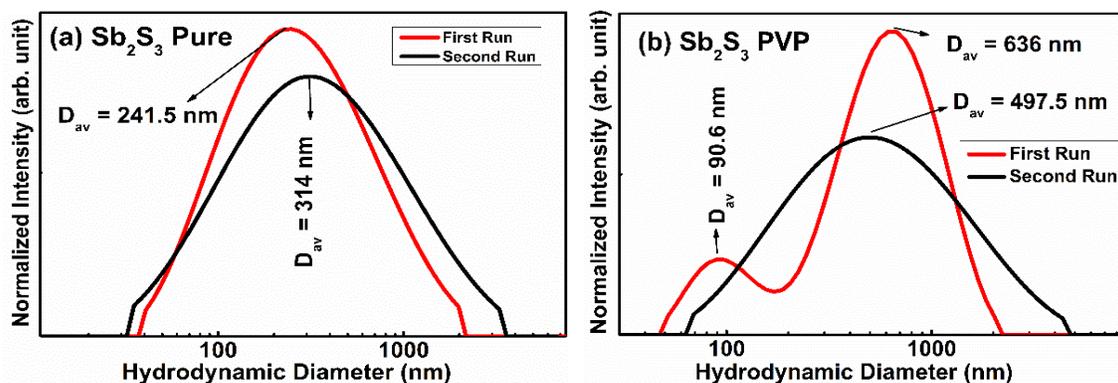


Fig. 3. Intensity distribution curve of HD of (a) pure Sb_2S_3 NPs and (b) PVP-capped Sb_2S_3 NPs; for first run and second run at pH 7.

The HD distribution curves shows a single peak, which may be attributed to the monodispersed nature of the particles.

Some distinctive features between the two samples can be assessed. In the pure one, only single peak is seen in both the runs, indicating that particles agglomerated are of one average size. In the case of PVP-capped sample, one main peak at 636 nm associated with smaller one at 90.6 nm in the first run is seen in contrast to a single stabilized peak at 497.5 nm. The former features could be due to the presence of two drastically different sets of particle sizes. They become only one peak in the second run with medium size and may indicate that the smaller particles in PVP-coated Sb_2S_3 NPs quickly get agglomerated in the second run until they attain an average particle size of 497.5 nm as a consequence of the competition of repulsive forces of hydrophobic $-\text{CH}_2$ group and the strongly attractive forces of the hydrophilic pyrrolidone groups in DIW since the highly polar amide groups within the pyrrolidone rings attract and non-polar alkyl groups repel water molecules to form micelles [3]. In the process, re-arrangement of agglomeration of smaller particles of 90.6 nm and de-agglomeration of larger particles of 636 nm suggestively took place to finally form an average particles size of 497.5 nm. Reduced HD in the second run is anomalous with other NPs wherein, it is generally enhanced as in Fig. 3 (a) or ref. [6], indicating significant role of PVP. As a result, pure Sb_2S_3 NPs have less HD in comparison with PVP-capped Sb_2S_3 , just in contrast to those found from crystallite size of XRD.

Representing the overall charge that the particle acquires in a particular medium, their zeta potential (ξ) measurements were performed in DIW in the pH 3 to 10.5 range using auto titration, and two independent solutions. Fig. 4 shows the effect of different pH values on ξ of pure and PVP-capped Sb_2S_3 . The iso-electronic point, the point at which the system is highly unstable and has maximum agglomeration of particles [4], was found at pH = 4.2 for PVP-capped, not found for pure Sb_2S_3 NPs. Since prevention of agglomeration requires a colloidal system with a zeta potential (ξ) $> \pm 30$ mV, PVP-capped Sb_2S_3 NPs is indicative of unstable nature for pH = 4.2 to 5.8 range as $\xi < \pm 30$ mV. Above this, particles are considered to be stable, especially beyond pH = 6.5, wherein $\xi \sim -51.64$ mV that maintains nearly constant up to pH = 8.5 compared to the unstable maximum ξ of -23.45 mV at pH = 8.19 for pure sample.

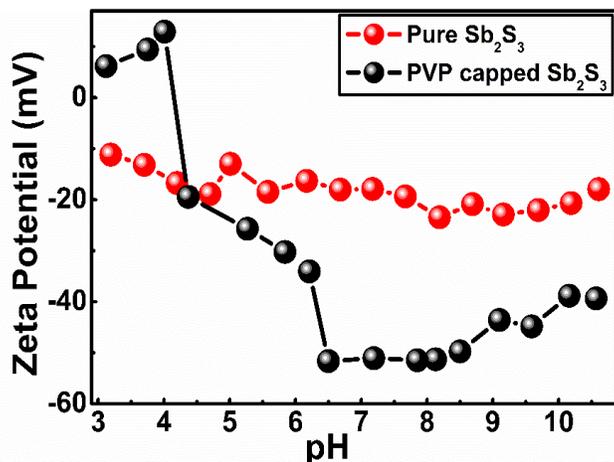


Fig. 4. Effect of pH on zeta potential of pure and PVP-capped Sb_2S_3 nanoparticles

Although PVP is non-ionic surfactant, the high negative ξ clearly indicates the formation of negative double layer on the surface of the PVP-capped Sb_2S_3 NPs and high stability in DIW compared to pure Sb_2S_3 NPs. This is attributed to the fact that the steric hindrance arisen from its long hydrophobic carbon chains of PVP on the surface of Sb_2S_3 prevents further agglomeration with best equilibrium dispersion in and around neutral pH in DIW (Fig. 4).

CONCLUSIONS

PVP-capped Sb_2S_3 NPs have been successfully synthesized by the facile polyol method at ~ 190 °C. XRD and Rietveld refinement data confirms the single phase orthorhombic crystal structure of both the samples with no impurity peaks. Raman modes further confirms their stoichiometric formation. EDAX spectrum confirms the elemental composition of Sb and S without any traces of other elements in pure sample. HD for pure Sb_2S_3 (314 nm) is less than that of PVP-capped Sb_2S_3 (497.5 nm). With isoelectronic point for PVP-capped Sb_2S_3 NPs at pH = 4.2, its zeta potential data reveal its highly stable value of -51.64 mV setting in at pH = 6.5 extending nearly this value

up to pH = 8.5 compared to that smaller ξ and hence low stability of pure sample. This information is expected to be useful for many applications like in cosmetics, for waste water treatment, ceramics, pharmaceuticals and in medicine.

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