Structural and optical properties of Ag\textsubscript{2}S nanotubes prepared by laser ablation in liquid

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Abstract: Synthesis of Ag\textsubscript{2}S nanotubes (NTs) by laser ablation of silver target in Thiourea (Tu) aqueous solution without using catalyst was demonstrated. The structure, morphology, size and elemental composition of Ag\textsubscript{2}S NTs were investigated. X-ray diffraction (XRD) results show that the Ag\textsubscript{2}S NTs are crystalline with monoclinic phase. The optical energy gap of Ag\textsubscript{2}S NTs is around 1.6 eV at fluence 4.7 Jcm\textsuperscript{-2}. Transmission electron microscope TEM investigation reveals the formation of NTs Ag\textsubscript{2}S morphologies with the diameter of 26-30 nm and lengths of 200-400 nm. Raman spectra of Ag\textsubscript{2}S nanorods show the presence of active Raman peaks indexed to A\textsubscript{g} modes and the stretching bending Ag-S bonds and 2LO mode of Ag\textsubscript{2}S.

Keywords: Silver sulfide nanotubes; Laser ablation; Thiourea; Laser fluence

1. Introduction:

In recent years, the synthesis of nanometer-sized semiconductors has attracted great interest due to their shape- and size-dependent physical and chemical properties [1-4]. As one of the most important semiconductors, Ag\textsubscript{2}S is a favorable prospective photoelectric and thermoelectric material with potential application in optical and electronic devices such as photoconductive cells, infrared detectors, photoconductors and magnetic field sensors, etc. [5-6] Various techniques for the synthesized of Ag\textsubscript{2}S nanostructures and their formation mechanism have been studied [7-11]. For example, Zhao et al. prepared rod-like Ag\textsubscript{2}S nanocrystals by using sodium thiosulfate Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} as a sulfur source via gamma-ray irradiation of aqueous solutions at room temperature [12]. Recently, the research of one-dimensional (1D) nanomaterials, including nanorods, nanobelts, nanotubes and nanowires, is the most active area due to their potential application in nanodevices. A number of methods have been developed to fabricate and assemble 1D nanostructure such as organometallic precursor, sacrificial template, gamma-ray irradiation, solvo-thermal, sonochemistry and microwave irradiation method [13-14]. This
paper focuses on the preparation and characterization $\text{Ag}_2\text{S}$ nanotubes by using laser ablation in pure thiourea (Tu) aqueous solution without catalyst.

2. Experimental work

Colloidal $\text{Ag}_2\text{S}$ nanotubes were prepared by laser ablation of high purity Ag target (99.9\%) in 0.3M thiourea (Tu) aqueous solution. The Tu represents a source of sulfur. The laser used was for this purpose was second harmonic Q-switched Nd:YAG laser operating at $\lambda=532$ nm, 7ns pulse width and 2Hz repetition frequency. High purity silver pellet with thickness of 10mm and diameter of 20mm was located in the bottom of glass vessel filed with Tu aqueous solution and the height of solution was 2mm above target. The laser was focused on the Ag pellet by using positive lens of 10cm focal length. The laser fluence for ablation was $4.7\ Jcm^{-2}/pulse$ and the ablation time was set 15min for each sample. Figure 1 shows the experimental schematic diagram of pulsed laser ablation in liquid PLAL system used in this work.

![Experimental set-up of PLAL system](image)

2.1 Characterization

The optical absorption of colloidal $\text{Ag}_2\text{S}$ nanotubes was measured by using UV–Vis double beam spectrophotometer (Lambda 750, Perkin Elmer). To study the structural properties of $\text{Ag}_2\text{S}$ nanotubes, x-ray diffractometer (XRD-6000, Shimadzu) was employed. Raman spectroscopy of the $\text{Ag}_2\text{S}$ was performed using Raman spectrometer (Bruker Optics, Germany). The morphology and size of nanotubes were transmission electron
microscope TEM (EM208, Philips) with EDX analysis to determine the chemical composition of the product.

3. Results and discussion

The XRD patterns of Ag₂S nanotubes prepared at laser fluence of 4.7J cm⁻² is shown in Figure 2.

From the Figure 2, we found there are several XRD peaks at 2θ = 23.16°, 25.4°, 28.34°, 31.3°, 32.54°, 35.42°, 36.26, 38.82°, 43.8°, 51.54° and 64.32° corresponding to (-101), (-111), (111), (-112), (120), (022), (121), (-103), (023), (-221) and (-134) planes. All these peaks are belonged to crystalline Ag₂S nanotubes with cubic phase according to (JCPDS Card # 652356) [15]. These XRD peaks indicate formation Ag₂S NTs with highly crystalline and pure Ag₂S. The average crystallite size D along of Ag₂S nanotubes along (-101) plane was calculated from XRD peak broadening using Debye–Scherrer equation:

\[ D_{ave} = \frac{0.9 \lambda}{\beta \cos \theta} \]  \hspace{1cm} (1)
Where the $\beta$ is the full width at the half maximum in units of radians and $\lambda$ is the X-Ray wavelength of CuK$\alpha$ source (0.1549nm). According the XRD analysis of Ag$\textsubscript{2}$S nanotubes, the average diameter of Ag$\textsubscript{2}$S nanotubes was 43 nm.

Figure 3 (a) shows the TEM image of Ag$\textsubscript{2}$S nanotubes which confirms the formation of monodisperse nanotube adhered with some of nanoparticles. The diameter of nanotubes was around 75nm and about 2$\mu$m in length. The nanoparticles adhered to nanotubes are spherical with average diameter of 85nm. As shown; the nanotubes are distributed over the glass substrate with high density. EDX data shows the presence of two peaks related to S and Ag with small-off stoichiometry Ag$\textsubscript{2}$S NTs as shown in Figure 4[16-17].

![ TEM image of Ag$\textsubscript{2}$S nanotubes ](image)

Figure 3. a) the TEM images with b) EDX of Ag$\textsubscript{2}$S nanotubes at laser fluence 4.7 J cm$^{-2}$

According to EDX analysis as shown in Figure (3 b), the content of Ag and sulfur in Ag$\textsubscript{2}$S NTs formation is about 0.39 and 55.71 wt.%, respectively. These results reveal that the content of sulfur is higher than Ag due to the stoichiometry of Ag$\textsubscript{2}$S at high laser laser fluence [18].
Figure (4 a), shows the UV-Vis absorption of colloidal Ag₂S NTs prepared at laser fluence 4.7 J/cm². It is obviously reveal that the optical absorption peak appear at about 315 nm due to the absorption edge of the Ag₂S. Besides, the optical energy gap of Ag₂S NRs was calculated using Tauc plot and the extrapolation of the linear part of the curve as shown in Figure (4 b) is about 1.6 eV. The energy gap of Ag₂S NTs was larger than bulk Ag₂S (1.5eV) at room temperature due to quantum size effect.

Figure 4: a) Optical absorption of Ag₂S NTs prepared at laser fluence 4.7 J/cm² and b) (αhν)^2 versus photo energy plot
Figure 5: Raman spectra of Ag$_2$S NTs prepared in Tu solution laser fluence 4.7 J/cm$^2$

Figure 5 displays Raman spectrum of Ag$_2$S NTs. Raman peaks are noticed at 67 cm$^{-1}$ and 100 cm$^{-1}$ which can assigned to A$_g$ modes and the stretching bending Ag-S bonds. The peak at 475 cm$^{-1}$ is related to second order overtone 2LO mode of Ag$_2$S NRs. The peaks positions at 738, 1093 and 1385 cm$^{-1}$ are related to the optical transitions connected with Ag vacancies state [19].

4. Conclusion
In this study, we report on the preparation and characterization of Ag$_2$S nanotubes by laser ablation in liquid. XRD reveals the formation of crystalline cubic Ag$_2$S. SEM investigation confirms the formation of nanotubes with some of spherical nanoparticles. The optical energy gap of Ag2S NTs was 1.6eV at room temperature. Raman spectrum confirms the presence of Ag modes and the stretching bending Ag-S bonds and 2LO mode of Ag$_2$S.

5. References
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