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# Size controlled synthesis of silver sulfide nanostructures by multi-solvent thermal decomposition method

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ABSTRACT

Size and morphology controlled silver sulfide ($Ag_2S$) nanoparticles were synthesized using single (oleylamine) and mixed (octadecene and dodecanethiol) solvents by thermal decomposition method. Structural and morphological properties of $Ag_2S$ nanostructures were analyzed by X-ray diffraction method and transmission electron microscope. Comparatively higher crystalline $Ag_2S$ nanoparticles were synthesized in single solvent than mixed solvent, however, larger size of the particles ( & $2gt;10 nm) synthesized in single solvent became fluorescence inactive. The controlled size of 3–5 nm in diameter was achieved irrespective of increasing temperature till 225 °C by mixed solvent synthesis and the photoluminescence showed the emission in the second near infrared region (NIR II).

## 1. Introduction

In the past decades size controlled luminescent nanostructures have much attention towards biological imaging aimed for achieving higher resolution for better diagnostics [1–3]. Florescent imaging, magnetic resonance imaging (MRI), radio labelled and thermionic agents have been used as diagnostic tools in medical field [4–6]. Luminescent materials in near infrared emission under lower excitation have been developed in recent decades, including inorganic luminescent materials such as metal chalcogenide nanostructures, carbon dots, quantum dots, and semiconducting materials. Recent research has been undergoing in having more emission in the near infrared (NIR (700–2500 nm)) region [7,8]. Nanostructures with high fluorescent efficacy, high quantum yield and size dependent emission are the current research trend in NIR II window (1000–1400 nm) emission [9–11]. Nanostructures of PbS, PbSe, PbTe, InP and CdHgTe were well investigated but they have toxic elements [12–15]. Some plasmonic quantum dots are also applied for the fluorescent imaging with external selective modification using bio compatible polymers like lipids [16].

Recent advances in imaging field include both upconversion and down conversion imaging and other imaging agents such as magnetic and positron emission tomography (PET) [17,18]. NIR II imaging provides nontoxic, deep penetrating, minimal tissue scattered images that can reduce noise in tissue imaging [11]. Silver sulfide ($Ag_2S$) has more attention due to their size confined effect, direct band gap and the property of tunable NIR emission with size variants [19]. $Ag_2S$ quantum dots exhibit the high quantum yield and biocompatible with NIR emission for tissue labelling, tracking and therapy along with MRI and PET [20]. Tang et al. reported tunable emission of $Ag_2S$ from visible to extended NIR by changing the external coating of the molecules. Zhang et al. reported red shift in wavelength of the $Ag_2S$ QDs with increment in size [21,22]. Bulk bandgap of $Ag_2S$ made this material as a NIR probe. There are a few reports on $Ag_2S$ nanostructure with good biocompatible and homogeneously dispersed metal chalcogenide nanoparticles, however they were inefficient in controlling shape and size at higher temperature ranges above 200 °C. Good crystalline nature and faster synthesis were provided by only in higher temperature (≥200 °C) [23–25].

The temperature independent synthesis of size controlled $Ag_2S$ is required for thermodynamically stable and tunable emission property. In this study single source thermal decomposition method with multi-solvent (octadecene and dodecanethiol) technique was applied for $Ag_2S$ nanostructure synthesis and compared with single solvent (oleylamine) synthesized $Ag_2S$. This study demonstrated the effect of multi solvent method for temperature independent size controlled synthesis of $Ag_2S$

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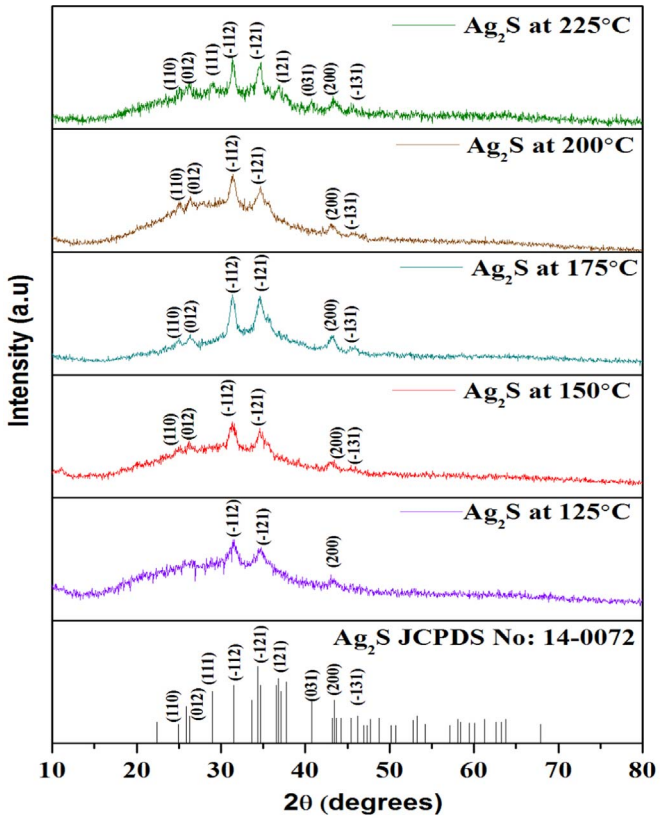


**Fig. 1.** XRD patterns of the standard cards of $Ag_2S$ and synthesized $Ag_2S$ using oleylamine at different temperatures.

with tunable NIR II emission.

## 2. Experimental procedure

Silver diethyldithiocarbamate (Ag DDTC) and dodecanethiol were purchased from Sigma Aldrich Company, USA. Cyclohexane, acetone, oleylamine (technical grade, 70%), and octadecene were purchased from Wako Pure Chemical Industries Ltd., Japan. All chemicals were used as without further purification.

$Ag_2S$ nanostructures were synthesized using different solvents such as oleylamine and octadecene + dodecanethiol mixture in single pot thermal decomposition method using Ag DDTC as a source. 1 mmol of Ag-DDTC was dissolved in 10 mL of oleylamine solvent at 80 °C and excess air present in the reaction vessel was removed under vacuum. After that, reaction was carried out at different temperature (125, 150, 175, 200, 225 °C) under nitrogen bubbling for 1 h. They were cooled to room temperature and washed thoroughly with acetone. Synthesized nanostructures were dispersed in cyclohexane for further analysis. Mixed solvent synthesis was performed using 7 mL of octadecene and 3 mL of dodecanethiol instead of oleylamine with same procedure as above.

Structural property of the particles was measured by X-ray diffraction method (XRD) using Rigaku (Japan) powder X-ray diffractometer with 0.04° $s^{-1}$ in the 2θ range of 10–80° (RINT-2200, Cu $K_\alpha$ radiation, λ=1.54178 Å). Transmission electron micrograph (TEM) and high resolution transmission electron micrograph (HRTEM) were carried out using JEOL TEM 2100 F microscope (Japan) with accelerating voltage 200 kV to analyze the morphologies. Photo luminescence (PL) spectra were measured in JASCO FB-8700 fluorescence spectrophotometer with excitation at 500 nm.

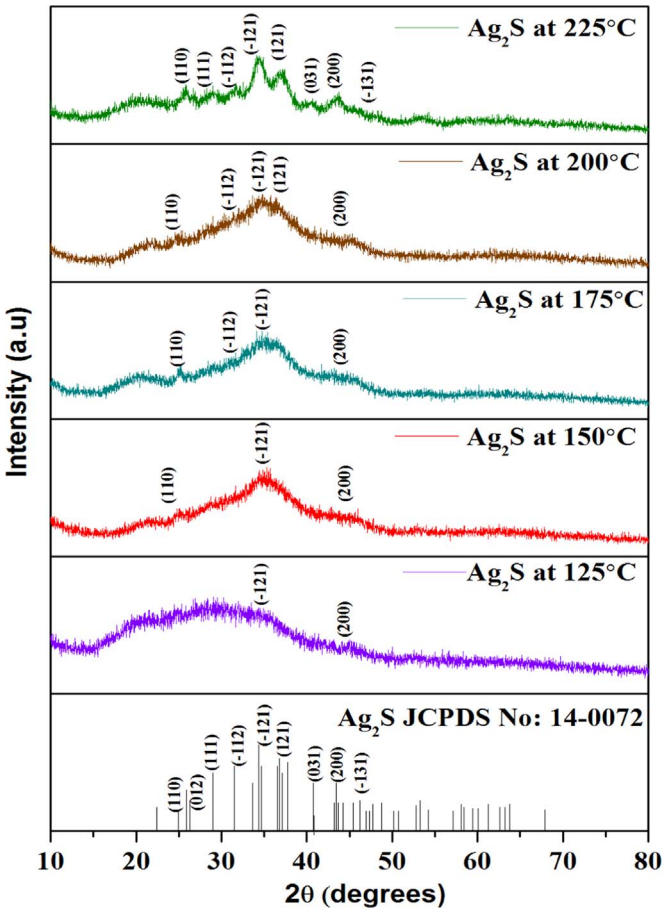


**Fig. 2.** XRD patterns of the standard cards of $Ag_2S$ and synthesized $Ag_2S$ using mixture of octadecene and dodecanethiol solvent at different temperatures.

## 3. Results and discussion

XRD patterns of synthesized $Ag_2S$ using oleylamine and octadecene- dodecanethiol mixture are shown in Figs. 1 and 2 with standard JCPDS files, respectively. Obtained XRD patterns of synthesized $Ag_2S$ nanoparticles were matched with the standard $Ag_2S$ (JCPDS No. 14–0072), which were monoclinic structure with $P21/n$ space group [22,26]. Fig. 1 indicates the XRD patterns of temperature dependent synthesis of $Ag_2S$ (125, 150, 175, 200, 225 °C) using oleylamine, which clearly depicted that crystallinity increased with increasing synthesis temperature. Sharp reflections arose in higher temperature because of the increase in the crystallinity. Fig. 2 shows XRD patterns of nanoparticles synthesized with octadecene and dodecanethiol mixed solvent, in which the particles were not improved much from 125 to 225 °C. It showed that the synthesis with multi solvent condition was entirely different from particles synthesized with oleylamine. However, multi-solvent showed slightly improved crystallinity with increasing synthesis temperature.

$Ag_2S$ crystal structure attains polymorphic modifications with temperatures, such as monoclinic phase α-$Ag_2S$ (acanthite) below ~173 °C, body centered cubic β-$Ag_2S$ (argentite) between 178 and 585 °C, and face centered cubic γ-$Ag_2S$ (stable face (above 585 °C)) [27,28]. Powder XRD of synthesized samples was measured at room temperature and all the samples showed monoclinic phase $Ag_2S$ (α-$Ag_2S$). Since $Ag_2S$ attains reversible polymorphic phase change, there was no trace identification of β-$Ag_2S$. High temperature synthesized $Ag_2S$ samples at 175, 200 and 225 °C remained in α-$Ag_2S$ phase at room temperature [29].

Fig. 3 shows TEM images and particles size distribution of $Ag_2S$ using single solvent method. Grown nanoparticles were monodispersed