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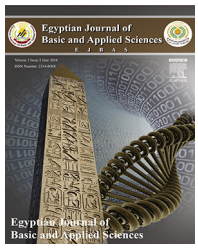

Full Length Article

A facile one-pot synthesis and characterization of Ag_2Se nanoparticles at low temperature

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ABSTRACT

A facile one-pot synthesis method has been developed successfully for the preparation of crystalline silver selenide (Ag_2Se) nanoparticles at low temperatures (5–7 °C) within few minutes. The method is based on the formation of phase separation and interface-reaction mechanism. During the synthesis, a microemulsion system (water/oleic acid/n-hexane) was used to make Ag_2Se nanoparticles. Selenium source (Sodium selenosulfate) used in this synthesis method was prepared by microwave heating due to the fact that the developed method of synthesis could eliminate toxic and expensive selenium sources. The prepared products (oleic acid coated Ag_2Se nanoparticles) were characterized by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), ultraviolet (UV)–visible analysis and photoluminescence (PL) analysis. The developed method became mild, fast, simple and environmentally benign, which would be helpful in scaling up production. Furthermore, the developed synthesis strategy could be used in making other nanoparticles for mass production through simple precipitation reactions.

1. Introduction

In past decades, silver selenide (Ag_2Se) has received great attention due to its special electronic and optical properties as well as potential applications [1–3]. Ag_2Se undergoes a polymorphic phase transition and has two stable solid phases. These are a low temperature orthorhombic phase (β-Ag_2Se) at 0 K, and a high temperature cubic phase (α-Ag_2Se) with a phase transition temperature from β to α-Ag_2Se taking place at about 135 °C or 409 K [2,4,5]. The low-temperature phase behaves as a semiconductor, while the high-temperature shows the properties of a metal. A low temperature phase (β-Ag_2Se) is a narrow band gap and n-type semiconductor with an energy gap of 0.07 eV at 0 K [5]. β-Ag_2Se is used as a photo sensitizer in photographic films or in thermo chromic materials and thermo electronic application due to its relatively high see back coefficient, low lattice thermal conductivity, and a high electrical conductivity [3,4,6–9]. The high-temperature phase (body-centered cubic), α-Ag_2Se, is a metallic compound with super ionic conductors that has been utilized as a solid electrolyte in photochargable secondary batteries and also used as an additive in highly conductive composite glasses for batteries, sensors, and displays [3,4,6–9].

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Recently, research reports indicated that a slight tuning of the stoichiometry to Ag_2Se could induce a remarkable magneto resistance, which is comparable to the giant magneto resistance perovskites [10–12]. Since nanoscale materials have some unique properties (that depend on the size and morphology of the particles) for a unique application [13,14], it would be a great challenge to fabricate Ag_2Se nanostructures having uniform size and morphology. A number of methods for the synthesis of Ag_2Se nanostructures have been explored [3,4,8,15,16]. All these routes to Ag_2Se nanostructures, however, did not satisfy the criteria that the method be simple and fast, i.e., Ag_2Se forms at low temperature in one step, and the prepared samples had nearly uniform morphology. Most of these Ag_2Se synthesis routes have also used expensive and toxic selenium sources.

In this report, we employed a single step (the one pot) synthesis strategy to prepare uniform-sized Ag_2Se nanoparticles at low temperature by reacting Ag^+ with $SeSO_3^{2-}$ under mild condition. In such synthesis approach, Na_2SeSO_3 was used as a selenium source since it could easily react with Ag^+ ions at room temperature without requiring the use of any other forms of energy [17]. Na_2SeSO_3 is much more active than Se powder, and is also less toxic, inexpensive and therefore safer to use than the Na_2Se or H_2Se [18]. Na_2SeSO_3 was prepared via microwave-enhanced method. A microwave-enhanced method, as opposed to conventional heating, has been proven to be an excellent technique for preparation of nanoparticles [18]. A few of the advantages of microwave-enhanced reactions include: simple to control the properties of the products, high yields of products, easy to control the temperature and pressure profile, the products have high purity levels, short reaction time, and environmental friendliness (e.g., improved safety, reproducibility, and selective heating, energy savings, etc.) [18]. A low-temperature microemulsion [19,20] environment was introduced to protect the prepared Ag_2Se nanoparticles from aggregation and to direct them into a relatively uniform size. The low temperature reaction conditions also helped the formation of nearly monodisperse Ag_2Se nanoparticles by slowing the growth speed and decreasing the surface atom activity.

The structure, morphology, elemental composition, and optical properties of the prepared Ag_2Se nanoparticles were characterized by XRD, TEM, EDX, and UV–vis and Fluorescence spectrophotometer respectively. The developed synthesis method used very simple reagents such as oleic acid, $AgNO_3$ and Na_2SeSO_3 as precursors; was fast, easy/simple, mild, environmentally benign and of low temperature, which would be useful for large scale production and could be applied for the synthesis of other similar nanostructure materials.

2. Experimental section

2.1. Chemicals

Selenium powder (Se, 99.70%, <325 mesh), sodium sulfite (Na_2SO_3, >95%), and n-hexane (>99%) were bought from Acros; ethanol (>99%) and oleic acid (65–88%) were brought from Aldrich; Sliver nitrate ($AgNO_3$, >99%) and sodium hydroxide (NaOH, >95%) were bought from Shimakyus Pure Chemicals. The chemicals were used without further purification. The microwave system was employed for the synthesis of sodium selenosulfate (Na_2SeSO_3).

2.2. Synthesis of sodium selenosulfate (Na_2SeSO_3)

It was prepared in the laboratory using microwave-enhanced methods. The advantages of microwave heating over the conventional heating are explained above. Microwave (MW) synthesis was done by using a single-mode CEM Discover System operating at 300 W and 2.45 GHz. The reaction mixture was rapidly cooled with high-pressure air following termination of the reaction. Na_2SeSO_3 was prepared from sodium sulfite and selenium powder by microwave heating in aqueous solution for 30 min at 100 °C. For a typical preparation, selenium powder (0.4 g) and Na_2SO_3 (0.76 g) were dissolved in distilled water (50 mL); then, they were transferred to the microwave system. The following chemical reaction describes the formation of Na_2SeSO_3 under microwave system for 30 min reaction time at 100 °C.

$$Na_2SO_3 + Se \xrightarrow{MW(100^\circ C \text{ and } 30\ min)} Na_2SeSO_3$$

Sodium selenosulfate (Na_2SeSO_3) was considered to be a greener selenium precursor than organic-based Se sources such as trioctylphosphine/Se or trioctylphosphine oxide/Se or others [18].

2.3. Synthesis of Ag_2Se nanoparticles

The synthesis of Ag_2Se nanoparticles was done in three steps. First step, NaOH (0.12 g) and oleic acid (2 mL) were dissolved in the mixture of deionized water (15 mL), C_2H_5OH (15 mL), and n-hexane (1.5 mL) to form a transparent microemulsion. Second, AgNO3 (0.23 g) dissolved in deionized water (5 mL) was added to the solution (transparent microemulsion) under vigorous stirring, forming a white Ag^+ containing emulsion quickly. Third and the last step, after the emulsion had been maintained in the temperature range of 5–7 °C in the water bath, Na_2SeSO_3 solution (5 mL) was injected into it. The prepared solution changed its color from transparent to black in a few seconds, and stirring continued for up to 10 min.

After the reaction, n-hexane (20 mL) was added to destroy the microemulsion and extract the oleic acid-coated Ag_2Se nanoparticles into the oil phase, which was centrifuged to give Ag_2Se nanoparticles by adding C_2H_5OH. Then, the samples were washed more than three times by dissolving n-hexane coupled with precipitation from ethanol to remove oleic acid residues on the particle surface. Finally, the as prepared Ag_2Se nanoparticles were dispersed in n-hexane for storage. The following chemical reaction describes the formation of Ag_2Se nanoparticles with simple precipitation reactions.

$$Na_2SeSO_3 + 2AgNO_3 + H_2O \rightarrow Ag_2Se(s) + 2NaNO_3 + H_2SO_4$$

2.4. Characterization

Photoabsorption and photoluminescence measurements were performed by using a Jasco 560 UV/Vis Spectrophotometer and a Hitachi F-7000 Fluorescence spectrophotometer, respectively.