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The effect of temperature on the growth of Ag_2O nanoparticles and thin films from bis(2-hydroxy-1-naphthaldehydato)silver(I) complex by the thermal decomposition of spin–coated films

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ABSTRACT

Bis(2-hydroxy-1-naphthaldehydato)silver(I) complex (Ag-HNA) was prepared through the reaction of the ligand and silver nitrate. Silver oxide nanoparticles were synthesized *via* thermal decomposition at different temperatures by calcinating Ag complex inside a ceramic boat. The same metal precursor was used to prepare Ag_2O thin films at different temperatures by spin coating onto a glass substrate. The prepared silver complex was characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis, nuclear magnetic resonance (NMR) and thermogravimetric (TGA) analysis. The effects of decomposition temperatures (150, 200, 250 and 300 °C) and of the annealing temperatures for the films at 200, 250, 300 and 350 °C were studied. The surface morphologies, structural and optical properties of the nanoparticles and films were investigated. The results shows that the temperature plays a significant role in controlling nature of the nanoparticles and thin films. The X-Ray diffraction patterns of Ag_2O nanoparticles and the prepared thin films prepared revealed the face-centred cubic structures.

1. Introduction

Metal coordination compounds are widely used as precursors to produce nanosized materials. These substances represent a significant interaction between synthetic chemistry and materials [1–4]. Nanoscale materials have been intensively studied during the last few years due to their unusual properties and possible applications in therapeutic domain such as drug delivery systems. Nanomaterials can exhibit physical and chemical behaviour that are diverse from their bulk materials [5]. Metal oxide nanomaterials together with their synthetic approaches have been widely investigated. Recently, silver based nanomaterials, have been widely documented as antimicrobial agents [6–8]. Silver oxide nanoparticles and thin films can be applied as sensors [9], catalysts [10], photovoltaic cells [11], and fuel cells [12]. These materials can also be used as important components in optical memories [13], and plasmon photonic devices [14].

Silver oxide is a p-type semiconductor material with a band gap ranging between 1.2 and 3.4 eV [14,15]. Several forms are known including: Ag_2O, AgO, Ag_3O_4, Ag_4O_3, Ag_2O_3 and Ag_4O_4 [16]. Ag_2O and AgO have been reported to be the most stable of these oxides [17]. The morphology, stability, size, and properties of nanoparticles is dependent on the synthetic methods used [18]. Numerous methods have been reported for synthesizing these nanoparticles including chemical reduction using a variation of organic and inorganic reducing agents [19,20], electrochemical techniques [21,22], and physicochemical reduction [23]. Numerous techniques have also been used to prepare Ag_2O thin films. These methods include r. f. sputtering [24], electron beam evaporation [25] chemical bath deposition [26] etc.

The synthesis of silver oxide nanoparticles *via* a simple chemical procedure using silver nitrate in the presence of polyethylene glycol (PEG) as reducing agent was reported by Yong and co-workers [27]. Nwanya et al. reported the study based on the structural and optical properties of chemical bath deposited silver oxide thin films from different deposition times and temperature using pure $AgNO_3$ as silver source. From the observation of the morphologic features obtained from SEM, they showed that the Ag_2O structures changes with the change in deposition time. The band gap, film thickness, and refractive index were increasing as the deposition time increased while the crystal

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size decreased [26]. Recently, Hosseinpour-Mashkani and Ramezani reported the preparation of silver (I) salicylate precursor for the synthesis of Ag and Ag_2O nanoparticles by thermal decomposition. The p-XRD patterns of the nanoparticles showed pure cubic Ag and hexagonal Ag_2O at 400 °C [28]. Kim and co-workers reported that silver oxide films can also act as a cover layer in magneto-optical disk to improve the magneto optical signal [29].

Among numerous techniques developed for the synthesis of silver oxide nanomaterials, thermal decomposition techniques can be regarded as the alternative technique since it is fast, clean and potentially more economical methods to produce stable monodispersed products [30]. The present method has many advantages since it is an economical technique which is solvent and surfactant free. The ligand 2-hydroxy-1-naphthaldehyde is cheap and it has been widely used in biological synthesis to establish free amino acid groups in polymers. Its metal complexes are easily prepared and which can be used to prepare metal oxides nanoparticles with low cost [31]. Silver compounds have been utilized in the past to treat burns, wounds and infections [32] and the nanomaterial based on silver have been used as antimicrobial agents [33]. Thus, the silver oxide nanoparticles synthesized from *bis*(2-hydroxy-1-naphthaldehydato)silver(I) complex can serve in biological processes compared to the other silver precursors.

The synthesis of silver oxide nanoparticles by the thermal decomposition of *bis*(2-hydroxy-1-naphthaldehydato)silver(I) as a new precursor is reported. The silver complex was also used as single source precursors to prepare Ag_2O thin films at different annealing temperatures on the glass substrate by spin coating method. The prepared Ag_2O materials were characterized by several instruments such as Ultraviolet–Visible (UV–Vis) spectroscopy, photoluminescence (PL), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM), and atomic force microscopy (AFM).

2. Experimental

2.1. Materials and reagents

Silver nitrate, 2-hydroxo-1-naphthaldehyde, ethanol, tetrahydrofuran (THF), and toluene were reagents purchased from Sigma-Aldrich and were all used without further purification.

2.2. Preparation of bis(2-hydroxy-1-naphthaldehydato)silver(I) complex [$AgC_{11}H_6O_2$]

The bis(2-hydroxy-1-naphthaldehydato)silver(I) complex was prepared by the procedure reported previously [34]. In a typical preparation, a 20 mL ethanolic solution of $AgNO_3$ (5 mmol) was added into a 20 mL ethanolic solution of 2-hydroxo-1-naphthaldehyde (HNA) (5 mmol) to form a homogeneous mixture. The solution was stirred and refluxed at 60 °C for an hour. The precipitate was then filtered and washed three times with ethanol. The dark brown product was dried in a vacuum oven at room temperature, weighed and characterized. Percentage yield: 74%. m.p. 91 − 100 °C. CHN analysis: Calc.: C, 47.35; H, 2.53; O, 11.47. Found: C, 50.36; H, 2.73; O, 11.50%. Significant IR bands: *ν(C=O): 1647 cm^{-1}, ν(Ag-O): 494 cm^{-1}. ^1H NMR δ (ppm): (400 MHz, DMSO-d_6, 295 K): δ = 10.82 (s, 1H, CH), 8.99 (m, 1H, CH), 8.21 (m, 1H, CH), 7.92 (m, 1H, CH), 7.61 (m, 1H, CH), 7.42 (m, 1H, CH), 7.30 (m, 1H, CH). ^{13}C NMR (400 MHz, DMSO-d_6, 296 K) δ (ppm): 192 (C=O), 165 (C-O), 138 (C-H), 133 (C-H), 130 (C-H), 129 (C-H), 128 (C-H), 127 (C-H), 125 (C-H), 122 (C-H), 111 (C-H).*

2.3. Synthesis of silver oxide (Ag_2O) nanoparticles

A sample of the dry silver precursor (0.3 g) was placed inside a small, clean and dried ceramic boat. The boat was then placed in the glass tube which was then transferred into the tube furnace under the fume hood. The sample was calcinated at a temperature of 150 °C under the nitrogen gas atmosphere for 1 h. The sample was allowed to cool down to room temperature in the furnace. The method was repeated at 200, 250, and 300 °C. The resulting silver oxide nanoparticles were dispersed in toluene for further analysis.

2.4. Deposition of silver oxide thin films by spin coating

Prior to the experiment, the glass substrate (a microscope slide) was first cut into pieces of 2 × 1.5 cm using a diamond glass cutter and ultrasonically cleaned with acetone for 1 h and then dried in an open air. Exactly, 0.15 g (0.33 mmol) of the silver precursor was dissolved in 20 mL of tetrahydrofuran (THF) in a small beaker. The precursor solution was then deposited on the glass substrate using the spin coater at 3000 rpm for 30 s. After the deposition, the film was dried for about 5 min at a temperature of 30 °C on a hotplate in order to evaporate the solvent and remove organic residuals. Finally, the substrate with the precursor film was then annealed at 200, 250, 300 or 350 °C for an hour in a tube furnace under nitrogen gas environment.

2.5. Characterization techniques

2.5.1. Fourier transform infrared (FTIR) spectroscopy (FTIR)

Infrared spectra for the silver complex were recorded in the range 400–4000 cm^{-1} using a Bruker FT-IR tensor 27 spectrophotometer.

2.5.2. Elemental analysis (EA)

Microanalysis was performed on a Perkin-Elmer automated model 2400 series II CHNS/O analyzer.

2.5.3. Thermogravimetric analysis (TGA)

TGA was carried out at a 10 °C/min heating rate using a Perkin-Elmer Pyris 6 TGA up to 700 °C in a closed perforated aluminium pan under N_2 gas to characterize the complex.

2.5.4. UV–Visible spectroscopy (UV/Vis)

Optical absorption measurements were carried A Perkin-Elmer Lambda 1050 UV/vis/NIR spectrometer was used to carry out UV–vis absorption measurements of the Ag_2O nanoparticles and thin films. The Ag_2O particles were dissolved in toluene, and solution was placed in a quarts cuvettes with 1 cm path length for analysis. The Ag_2O thin films were analysed as presented using a clean glass as a blank.

2.5.5. Photoluminescence (PL)

A Perkin-Elmer LS 55 spectrofluorometer was used to measure the photoluminescence of the Ag_2O nanoparticles and thin films. The same solution that was prepared for UV–vis analysis was also used to analyse the emission of the nanoparticle. All the analysis was carried out using the same excitation wavelength of 300 nm at room temperature.

2.5.6. X-ray diffraction (XRD)

Powder diffraction patterns were recorded in the high angle 2θ range (20–90°) using a Bruker AXS D8 diffractometer equipped with nickel filtered Cu-Ka radiation (l = 1.5418 Å) at 40 kV, 40 mA, room temperature. The scan speed and step sizes were 0.051 min^{-1} and 0.006571 respectively.

2.5.7. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was performed using a JEOL 1010 TEM, with accelerating voltage of 100 kV, Mega view III camera, and Soft Imaging Systems TEM software. High-resolution transmission electron microscopy (HRTEM) analyses were per-formed using a JEOL 2010 HRTEM with an accelerating voltage of 200 kV.

2.5.8. Scanning electron microscope (SEM)

SEM analysis was performed using a Philips XL-30 FEG scanning electron microscope, and EDXS was carried out using a DX4 detector.