Influence of Temperature and Concentration of Capping Molecule and *bis*(*N*-Cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) as Single Source Precursor for Synthesis of TOPO Capped Mn₃O₄ Nanoparticles

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In this study, the effect of temperature, amount of the precursor and the concentration of the stabilizer on the synthesis of manganese oxide nanoparticles using *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex has been investigated. The precursor was prepared from the chemical reaction of 2-hydroxy-1-naphthaldehyde, amine and manganese salt. The resulting precursor was thermally decomposed into tri-*n*-octylphosphine oxide (TOPO) to synthesize TOPO capped manganese oxide nanoparticles at the temperature ranging from 120 to 200 °C. Various instruments were used to characterize the prepared complex and manganese nanoparticles. The optical band gaps energies of the nanoparticles were decreasing from 1.48 to 1.35 eV when the decomposition temperature was increased.

Keywords: Manganese complex, Tri-*n*-octylphosphine oxide, Manganese oxide, Nanoparticles, Semiconductors.

INTRODUCTION

Metal complexes having nitrogen and phenolic oxygen donor atoms have been of great interest due to their potential application in nanotechnology, medicine and catalysis [1,2]. The metal complexes usually utilized to create prolonged network structures and to coordinate polymers with high structural strength and distinct topologies [3-6]. Transition metal complexes derived from Schiff bases such as salicylaldehyde and other primary amines are one of the most adaptable and most considered systems [7,8]. The study based on the synthesis of nanomaterials have gained interest across many different disciplines [9,10]. Semiconductor transition metals have studied due to their stimulating properties and applications compared to their bulk materials. Among semiconducting transition metal oxides, manganese oxides have attracted a broad significance. Its structures display oxygen vacancies that supply extra active sites for reduction and oxidation reaction intermediates, particularly those that contain oxygen. These properties are especially significant for catalytic applications such as water oxidation [11-13]. Manganese oxide can subsist in more than

five transferable transition states with several structural forms over extensive range of temperatures [14,15]. Mn₃O₄ is an important oxide due to its high theoretical lithium-storage capacity and ferromagnetic performance as related to other oxides [16,17]. Manganese oxide nanoparticles have been used in several fields such as electrochemical capacitors [18], immobilization of proteins [19], sensitive biosensors [20], lithium-ion batteries [21], removal of dyes [22], biomimetic catalysts [23], etc. Several methods have been used for the synthesis of Mn₃O₄ nanoparticles which include chemical bath deposition [24], hydrothermal [25], solvothermal [26], coprecipitation [27], microwave irradiation [28] and surfactant-assisted methods [29]. Among these methods, thermal decomposition technique has been used in the past since it is an innovative method to produce stable monodispersed nanoparticles [30].

Tai *et al.* [31] reported the preparation and spectroscopic properties of Mn(II), Co(II) and Cu(II) complexes with a novel Schiff base ligand derived from 2,2'-*bis*(*p*-methoxyphenylamine) and salicylaldehyde. Ozkaya *et al.* [32] reported a novel synthetic route to Mn₃O₄ nanoparticles and their magnetic evaluation using an oxidation-precipitation method. Their X-ray

diffraction (XRD) analysis confirmed the tetragonal hausmannite structure of Mn_3O_4 with different crystallite sizes. He and coworkers [33] synthesized polyetheramide templated mono-disperse Mn_3O_4 nanoparticles with controlled size and study based on their electrochemical properties through solvothermal method. They discovered that the higher concentration of polyetheramide block copolymers in the solution resulted in the formation of the smaller Mn_3O_4 particles.

Herein, we report the preparation of *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex for the synthesis of tri-*n*-octylphosphine oxide (TOPO) capped Mn_3O_4 nanoparticles by thermal decomposition method. The effect of temperature, concentration of the capping agent and concentration of the precursor were studied. To the best of our knowledge, synthesis of Mn_3O_4 nanoparticles using this particular complex has not been reported so far. The precursor was analyzed with FTIR, TGA and elemental analysis. The optical properties of the synthesized Mn_3O_4 nanoparticles were characterized with UV-visible and photoluminescence whereas the morphologies of the particles were measured with X-ray diffraction and TEM.

EXPERIMENTAL

2-Hydroxy-1-naphthaldehyde, manganese(II) acetate dihydrate, cyclohexamine and tri-*n*-octylphosphine oxide were purchased from Sigma-Aldrich. Methanol, ethanol, acetone and toluene were reagents purchased from Merck chemicals and used without further purification.

Preparation of *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex: The complex was produced using the reported procedure [34–36]. Briefly, an equimolar of cyclohexamine (10 mmol) was added into 2-hydroxy-1-naphthaldehyde (10 mmol) in methanol followed by the addition of manganese(II) acetate dihydrate (5 mmol) in methanol into a 100 mL two-necked flask. The mixture was refluxed at 50 °C for 3 h. The dark grey precipitate was filtered, washed three times with ethanol and dried in a desiccator. The product was obtained as a very dark brown solid, m.p. 173 °C, CHN analysis: Anal. % calcd. (found) for $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_2\text{Mn}$: C, 72.96 (71.29); H, 6.50 (6.40); N, 5.01 (5.08); O, 5.72 (6.72). FT-IR (KBr, ν_{max} , cm^{-1}): 1634 $\nu(\text{C}=\text{N})$, 1391 $\nu(\text{C}-\text{O})$, 615 $\nu(\text{Mn}-\text{O})$, 469 $\nu(\text{Mn}-\text{N})$.

Synthesis of Mn_3O_4 nanoparticles: Tri-*n*-octylphosphine oxide (5 g) was mixed with *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) precursor (0.5 g) in a two necked flask to synthesize manganese oxide nanoparticles. The mixture was refluxed and heated to 120, 160 or 200 °C under nitrogen environment. The temperature was maintained for 1 h. The mixture was then allowed to cool to a temperature of about 70 °C. An addition of methanol (30 mL) produced a reddish brown precipitate which was separated by centrifugation. The product was washed three times with methanol and re-dispersed in toluene for characterization. To study the effect of concentration of the complex and capping agent, the procedure was repeated with 10 g of TOPO and 1 g of complex instead of 5 g and 0.5 g at a constant temperature of 160 °C.

Physical measurements: The FTIR spectrum for complex was collected from a Bruker FT-IR tensor 27 spectropho-

meter in the range 4000 to 400 cm^{-1} . Elemental analysis of the manganese complexes was performed on a Perkin-Elmer automated model 2400 series II CHNS/O analyzer. TGA/DTG analysis was carried out using a Perkin-Elmer Pyris 6 TGA up to 900 °C in a closed perforated aluminium pan under inert environment to characterize the manganese complex at a 10 °C/min heating rate. A Perkin-Elmer Lambda 1050 UV/vis/NIR spectrometer was used to measure the optical absorption measurements of the manganese oxide nanoparticles. The quartz cuvettes (1 cm path length) was used to carry the solution into the instrument employing toluene as a solvent. The emission spectra were collected from a Perkin-Elmer LS 55 spectrofluorimeter to measure the photoluminescence of the nanoparticles. The quartz cuvette (1 cm path length) was also utilized to carry the solution using toluene as a solvent. Powder X-ray diffraction patterns were recorded at an angle of 2θ for 2° values over 10 to 90° using a Bruker AXS D8 diffractometer equipped with nickel filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV, 40 mA, at a normal room temperature. Transmission electron microscopy (TEM) was carried out using a JEOL 1010 TEM, with an accelerating voltage of 100 kV, Mega view III camera and Soft Imaging Systems TEM software on a lacey carbon copper grids which was previously prepared by placing 1 or 2 drop of manganese oxide nanoparticles in toluene on the grid.

RESULTS AND DISCUSSION

The chemical reaction between 2-hydroxy-1-naphthaldehyde, amine and manganese acetate in methanol at 50 °C produced *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex (Scheme-I). The precursor was then used to synthesize TOPO capped manganese oxide nanoparticles by thermal decomposition. The purity of the manganese complex was confirmed by elemental analysis, FTIR spectroscopy, melting point and TGA/DTA.

Scheme-I: Preparation of the *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex

Spectroscopic and thermal studies: The FTIR spectrum of *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex in Fig 1a revealed the characteristic -C-H peaks from the benzene ring located at 2935–2216 cm^{-1} along with the strong bands at 1634–1537 cm^{-1} that are ascribed to a stretching vibration of C=N groups of imine. The presence of a strong band was observed at 1391 cm^{-1} which is due to the

Fig. 1. FTIR spectra and TGA/DTA curves of *bis*(N-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex

phenolic C-O stretching. The stretching vibrations that confirm the attachment of nitrogen and oxygen to the metal ion were also detected. These stretching bands were located at 615 and 469 cm^{-1} which are ascribed to Mn-O and Mn-N bonds, which is also found is similar to reported results [32,37].

Thermal decomposition profile and purity of manganese complex was investigated using the thermogravimetric analysis (TGA). Fig. 1b shows TGA and DTG curves of the manganese complex. The TGA analysis which is supported by the DTG graph on the dotted lines displayed two decomposition stages at 134 to 239 $^{\circ}\text{C}$ and 318 to 347 $^{\circ}\text{C}$ with the weight losses of 53 and 11 %. The first decomposition stage can be ascribed to the loss of ligand moiety with its oxidative degradation to nitrogen-metal-oxide and the second decomposition may be due to the loss of metal nitrogen.

Synthesis of MnO-TOPO capped nanoparticles: Manganese oxide nanoparticles were synthesized from the decomposition *bis*(N-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex in TOPO at 120, 160 and 200 $^{\circ}\text{C}$ to study the effect of temperature. The effect of concentration of the capping molecule and the complex were also investigated. The

synthesized manganese nanoparticles were analyzed with UV-visible, photoluminescence, XRD and TEM.

Effect of temperature on the formation of Mn_3O_4 -TOPO capped nanoparticles: Fig. 2a shows the UV-visible absorption spectra of Mn_3O_4 that were synthesized at 120, 160 and 200 $^{\circ}\text{C}$ were recorded in the range 250-800 nm. The spectra show flat absorption maximum at 371, 377 and 379 nm which was increased as the temperature was increased. Fig. 2b displays the vacancy energy level plots of $(\alpha h\nu)^2$ as a function of $h\nu$.

The Mn_3O_4 nanoparticles synthesized at different temperatures has energy band gap of 1.48, 1.37 and 1.35 eV. Emission spectra of Mn_3O_4 nanoparticles with an excitation wavelength 350 nm at room temperature are shown in Fig. 2c. The spectra of the synthesized nanoparticles shows two strong and wide emission peaks around 408-409 and 433-434 nm. The emission spectrum of Mn_3O_4 nanoparticles synthesized at higher temperature exhibit a strong intensified third peak at 456 nm.

The XRD patterns of synthesized nanoparticles are shown in Fig. 3. The pattern of nanoparticles that were prepared at a lower temperature [Fig. 3(i)] revealed a mixture of tetragonal

Fig. 2. Absorption (a), tauc plot (b) and emission (c) spectra of Mn_3O_4 -TOPO capped nanoparticles prepared at (i) 120 $^{\circ}\text{C}$, (ii) 160 $^{\circ}\text{C}$ and (iii) 200 $^{\circ}\text{C}$

phase intrinsic hausmannite Mn_3O_4 (JCPDS: No. 24-0734), with major thirteen peaks that exactly fit the (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224) and (400) together with monoclinic birnessite MnO_2 (JCPDS: No. 80-1098) with four peaks that correspond to (001), (002), (111) and (020) miller indices. The manganese oxide nanoparticles that were prepared at higher temperatures of 160 and 200 °C [Fig. 3(ii) and (iii)] showed a single phase of tetragonal intrinsic hausmannite Mn_3O_4 (JCPDS: No. 24-0734) which is an indication of the formation of the well crystallized and highly purified particles. Similar results were reported by Xiao *et al.* [38].

Fig. 3. XRD patterns of Mn_3O_4 -TOPO capped nanoparticles prepared at (i) 120 °C, (ii) 160 °C and (iii) 200 °C

TEM analysis of nanoparticles (Fig. 4) were carried out to reveal the particle sizes and micrographs of the particles. All the samples that were prepared at different temperatures showed spherical particles. The average particle sizes for the manganese oxide nanoparticles synthesized at 120, 160 and 200 °C were found to be 3.52 ± 0.343 , 6.03 ± 0.900 and 7.11 ± 0.755 nm.

Effect of concentrations of capping molecule during the synthesis of Mn_3O_4 -TOPO capped nanoparticles: The absorption spectra of Mn_3O_4 nanoparticles synthesized from different amounts of capping agent at a temperature of 160 °C are shown in Fig. 5a. The absorption bands for the particles prepared at 5 and 10 g of TOPO while keeping the amount of the complex constant were observed at 360 (3.44 eV) and 358 (3.46 eV) nm. The results revealed that when the concentration of stabilizer is increased, the absorption peak becomes red shifted towards the higher wavelength.

The emission spectra of nanoparticles synthesized at different concentration of TOPO are represented in Fig. 5b. The emission peaks were broad which indicate polydispersity of the particles. The emission maxima of manganese oxide nanoparticles were red shifted from their respective absorption bands and observed at 408 and 433 nm for the particles prepared with 5 g while the nanoparticles synthesized at 10 g of TOPO showed the emission peaks at 409 and 434 nm.

The manganese oxide nanoparticles that were prepared at different concentrations of TOPO (Fig. 6a) showed a single phase of tetragonal intrinsic hausmannite Mn_3O_4 (JCPDS: No. 24-0734) with peaks at (101), (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224) and (400) correspon-

Fig. 4. TEM images of Mn_3O_4 -TOPO capped nanoparticles prepared at (i) 120 °C, (ii) 160 °C and (iii) 200 °C

Fig. 5. Absorption (a) and emission (b) spectra (a) of Mn_3O_4 nanoparticles capped with (i) 5 g and (ii) 10 g of TOPO at 160 °C

Fig. 6. XRD patterns (a) and TEM images (b) of Mn_3O_4 nanoparticles capped with (i) 5 g and (ii) 10 g of TOPO at 160 °C

ding to 18.43°, 29.23°, 31.42°, 32.67°, 36.43°, 37.68°, 43.95°, 51.31°, 54.13°, 55.38°, 58.67°, 60.23°, 64.78°. The TEM micrograms of synthesized nanoparticles in Fig. 6b revealed spherical particles which were increasing as the concentration of TOPO was increased. The average particle sizes were found to be 6.03 ± 0.900 and 6.19 ± 1.321 nm.

Effect of concentrations of the precursor during the synthesis of Mn_3O_4 -TOPO capped nanoparticles: The effect of the amount of manganese complex was also investigated by decomposing 0.5 or 1 g of *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese (II) complex into 5 g of TOPO at 160 °C. The absorption spectra of Mn_3O_4 nanoparticles synthesized from different concentrations of the complex are displayed in Fig. 7a. The absorption peaks becomes blue shifted towards the lower wavelength when the amount of precursor was increased. The absorption band were observed at 377 nm (3.29 eV) and 371 nm (3.34 eV) for the nanoparticles synthesized with 0.5 and 1 g of the complex.

The emission spectra of Mn_3O_4 nanoparticles that were synthesized from different concentrations of the complex are displayed in Fig. 7b. The emission maxima of Mn_3O_4 nanoparticles at an excitation wavelength of 350 nm were red shifted from their respective absorption bands. The emission peaks were located at 408 and 433 nm for nanoparticles synthesized with 0.5 g of complex while the particles prepared with 1 g of precursor showed their emission maxima at 407 and 432 nm.

Fig. 8a shows XRD diffraction pattern of manganese oxide nanoparticles that were prepared at different concentrations of the complex. All the patterns showed the peaks that were indexed to tetragonal intrinsic hausmannite Mn_3O_4 (JCPDS: No. 24-0734) at (101), (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224) and (400) miller indices. The peaks were very wide, which is an indication of the presence of smaller particles. The TEM images of synthesized Mn_3O_4 nanoparticles in Fig. 8b displayed spherical particles which were decreasing as the concentration of the precursor was

Fig. 7. Absorption (a) and emission (b) spectra of Mn_3O_4 -TOPO capped nanoparticles prepared with (i) 0.5 g and (ii) 1 g of the precursor at 160°C

Fig. 8. XRD patterns (a) and TEM images (b) of Mn_3O_4 -TOPO capped nanoparticles prepared with 0.5 g (i) and 1 g (ii) of the precursor at 160°C

increased. The average particle sizes were found to be 6.03 ± 0.900 and 6.02 ± 0.831 nm.

Conclusion

The preparation of *bis*(*N*-cyclohexyl-2-hydroxy-1-naphthaldehydato)manganese(II) complex and the synthesis of mono-disperse Mn_3O_4 nanoparticles through thermal decomposition method has been accomplished. The optical properties of the synthesized particles showed that the temperature of the synthesis, concentration of stabilizer and precursor has a special role on the preparation of Mn_3O_4 nanoparticles. X-ray diffraction patterns of the nanoparticles synthesized at higher temperatures displayed tetragonal intrinsic hausmannite Mn_3O_4 phase. TEM of all the synthesized nanoparticles at different temperatures showed spherical shaped particles that were increased in sizes at the higher concentration of capping molecule and decreased in sizes, when the amount of precursor was increased.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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