Cobalt(II) and Zinc(II) Complexes of Hexamethylenetetramine as Single Source Precursors for their Metal Oxide Nanoparticles

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Abstract
Co3O4 and ZnO nanoparticles with different morphologies were synthesised by the thermal decomposition of single source precursors obtained from readily available and eco-friendly starting materials (hexamethylenetetramine and metal nitrates). The precursors, which were characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction and thermal gravimetric analysis, were calcined at 500°C for 2 h, and the oxide samples obtained were characterized by FTIR, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and nitrogen physisorption. XRD showed that the oxides obtained were crystalline and free of extraneous impurity phases. The morphology of the nanoparticles obtained changed from cube-like (Co3O4) to hexagonal-prism like morphology (ZnO), while the particle size increased from 19.6 to 64.5 nm, respectively. The method used simple and cheap precursors, which should make it suitable for large-scale synthesis.

Keywords: Cobalt oxide, Zinc oxide, Nanoparticle, Thermal decomposition, Hexamethylenetetramine, XRD

1. Introduction
Metal oxide nanoparticles constitute a class of functional materials on which much attention has been focused recently due to their morphology and size-dependent physical and chemical properties (Devan, Patil, Lin, & Ma, 2012; Niederberger, 2007).

The size reduction of these metal oxides, which leads to novel properties that are different from those of the individual atoms as well as their bulk counterparts, makes them potential materials for application in the fields of catalysis, electronics, storage devices, gas sensors and magnetic resonance imaging (de Rivas, López-Fonseca, Jiménez-González, & Gutiérrez-Ortiz, 2012; Devan et al., 2012; Gomez & Tigli, 2013; Kahn et al., 2009).

Among these metal oxide nanoparticles, nanoscale cobalt and zinc oxides have received much scientific attention because they have interesting size-dependent physico-chemical properties for material as well as industrial applications. Cobalt oxide, especially the cubic Co3O4 phase with a spinel structure (Fd3m), is a p-type semiconductor which has been employed in several technological applications in the field of heterogeneous catalysis, electronics, storage devices, gas sensors and magnetic resonance imaging (de Rivas et al., 2012), supercapacitors (Vijayakumar, Ponnalagi, Nagamuthu, & Muralidharan, 2013; H. Xu et al., 2014 ), anode materials in lithium ion rechargeable batteries (Huang et al., 2014; Rui et al., 2013), and magnetic materials (Moro, Yu Tang, Tuna, & Lester, 2013; Sharma & Jeevanandam, 2013).

ZnO is a thermally and chemically stable semiconducting material with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature. It has found application in the domains of gas sensors, catalysis and optical devices (Faisal, Khan, Rahman, Jamal, & Abdullah, 2012; Gomez & Tigli, 2013; Guo & Peng, 2015; Hirai & Asada, 2005; Karami, Eskandari, Khodabakhshi, Hoseini, & Hashemian, 2013; Pál et al., 2012; Xiong, Ma, Wang, & Xia, 2011). ZnO is also biocompatible, nontoxic, chemically stable, and electrochemically active; properties which have enabled its application in biosensing (Gomez & Tigli, 2013).
Various methods have been employed for the morphology-controlled synthesis of $\text{Co}_3\text{O}_4$ and $\text{ZnO}$ nanoparticles, which include microwave-assisted synthesis (Faisal et al., 2012; Vijayakumar et al., 2013), chemical precipitation (Greene, Yuhas, Law, Zitoun, & Yang, 2006; Romo et al., 2011; Rui et al., 2013), hydrothermal (Dakhlaoui, Jendoubi, Smiri, Kanaev, & Jouini, 2009; Lester et al., 2012; Moro et al., 2013; Pál et al., 2012; Rui et al., 2013), sonochemical (Banerjee, Chakrabarti, Maitra, & Dutta, 2012), solvothermal synthesis (Y. Xu, Wang, Sun, Zhang, & Gao, 2010), pulsed layer deposition (Warang et al., 2012), and biosynthesis (Fu & Fu, 2015). These varied methods have led to nanoparticles with diverse morphologies like nanocubes (Lester et al., 2012), nanorods (Fu & Fu, 2015; Romo et al., 2011), nanospheres (Dakhlaoui et al., 2009; Darezereshki, Alizadeh, Bakhtiari, Schaffe, & Ranjbar, 2011; Hirai & Asada, 2005), nanowires (Greene et al., 2006), nanoflowers (Pál et al., 2012), and nanotubes (Li, Dou, & Bao, 2012).

These conventional methods, though successful, require specially designed and expensive equipment, extra purification steps, rigorous reaction conditions and/or relatively high temperatures. Some of the solution-based synthetic approaches employ surfactants and solvents which are toxic and not easily degraded in the environment. The synthesis of these nanomaterials with controlled size and shape is still a major challenge and large scale synthesis of phase pure $\text{Co}_3\text{O}_4$ and $\text{ZnO}$ nanoparticles at relatively low temperatures, using readily available, environmentally benign and cost-effective precursors is a synthetic challenge. Thus, the preparation of cobalt oxide and zinc oxide nanoparticles by thermal decomposition of cobalt and zinc complexes becomes increasingly important mainly due to its cost-effectiveness, careful choice of precursors and calcination conditions, high yields, easy control of synthesis conditions, particle size, crystal structure, and purity. For example, the synthesis of metal oxide nanoparticles by the thermal decomposition of organometallic compounds or metal complexes has been reported (Ahmad, Ganguly, Ahmed, Ganguli, & Alhartomy, 2011; Huang et al., 2014; Kahn et al., 2009; Palacios-Hernández et al., 2012; Sharma & Jeevanandam, 2013). Porous $\text{Co}_3\text{O}_4$ with different morphologies has been prepared by the thermal decomposition of cobalt carbonates (300 - 500°C for 2 – 3 h) and oxalate precursors (400 - 500°C for 6 h) (Che et al., 2013; de Rivas et al., 2012; Nassar & Ahmed, 2011). Rivas et al. obtained $\text{Co}_3\text{O}_4$ by the direct calcination of cobalt nitrate and cobalt oxalate nanorods at 500°C (de Rivas et al., 2012). $\text{Co}_3\text{O}_4$ nanoparticles were obtained by solid-state thermal decomposition of a Schiff base complex $[\text{Co(L)}_3]$ ($L = \text{N-salicylidin-2-chloroethylimine}$) at 450°C under air atmosphere for 3 h (Khalaji, Nikookar, Fejfarova, & Dusek, 2014). Hongwei and co-workers prepared $\text{Co}_3\text{O}_4$ microdiscs by a thermal decomposition of cobalt oxalate at 400°C, obtained by the solvothermal reaction of cobalt nitrate and ammonium oxalate in anhydrous alcohol (Che et al., 2013). $\text{Co}_3\text{O}_4$ nanoparticles were prepared via the decomposition of the pentammine(carbonato)cobalt(III) nitrate precursor complex $[\text{Co(NH}_3)_5\text{CO}_3]\text{NO}_3\cdot0.5\text{H}_2\text{O}$ at low temperature (175°C) (Farhadi & Safabakhsh, 2012). Palacios-Hernández et al. reported the synthesis of $\text{Cu}$ and $\text{Co}$ metal oxide nanoparticles by the thermal decomposition of the corresponding tartrate complexes ($[\text{M(C}_4\text{H}_4\text{O}_6\text{)}_n]\text{Cu}$, $\text{M} = \text{Cu}^{2+}$, $\text{Co}^{2+}$) at 500°C for 5 h (Palacios-Hernández et al., 2012). Aghababazadeh et al. prepared $\text{ZnO}$ nanoparticles by the thermal decomposition (170-380°C) of $\text{ZnCO}_3$ obtained by mechanochemical processing (Aghababazadeh, Mazinani, Mirhabibi, & Tamizifar, 2006). Hirai and co-workers obtained $\text{ZnO}$ nanoparticles by the calcination of $\text{Zn(OH)}_2$ nanoparticles, which were prepared in a polyethylene glycol mono-4-nonylphenyl ether (NP-5)/cyclohexane reverse micellar system and incorporated into polyurea via an in situ polymerization of hexamethylene diisocyanate (Hirai & Asada, 2005). Rajesh et al. prepared $\text{ZnO}$ nanoparticles by the mechanochemical synthesis of $\text{ZnC}_2\text{O}_4\cdot2\text{H}_2\text{O}$ nanoparticles followed by its thermal decomposition at 400°C (Rajesh, Vara Lakshmi, & Sunandana, 2012). Spherical $\text{ZnO}$ nanoparticles have also been prepared by the thermal decomposition of $\text{Zn}_2(\text{SO}_4)(\text{OH})_6\cdot0.5\text{H}_2\text{O}$ in air for 1 h at 825°C (Darezereshki et al., 2011).

The high costs, use of non-eco-friendly surfactants and solvents as well as the evolution of very toxic gaseous products during calcination, limits the use of some of these precursors. In continuation of our interest in the synthesis of phase pure metal oxide nanoparticles, we report herein a simple, environmentally benign and cost-effective method to synthesize $\text{Co}_3\text{O}_4$ and $\text{ZnO}$ nanoparticles by the thermal decomposition of their respective metal-hexamethylenetetramine (M-HMTA) complexes. Hexamethylenetetramine (HMTA) is a cheap, ecofriendly and readily available heterocyclic organic compound with a cage-like structure. It is highly soluble in water and polar organic solvents. Some metal complexes of HMTA had previously been used as precursors for metal dispersions (Afanasiev et al., 2008), metal carbides and nitrides (Chouzier, Afanasiev, Vrinat, Cseri, & Roy-Auberger, 2006; Chouzier, Vrinat, Cseri, Roy-Auberger, & Afanasiev, 2011), and oxide nanoparticles (Yufanyi, Tendo, Ondoh, & Mbadcam, 2014).
2. Method

2.1 Materials

Co(NO$_3$)$_2$.6H$_2$O, Zn(NO$_3$)$_2$.6H$_2$O, hexamethylenetetramine and ethanol were obtained from Sigma Aldrich. All the chemicals were of analytical grade and were used as obtained without further purification.

2.2 Synthesis of Metal(II) - HMTA Complex

The precursors were synthesized according to a procedure previously reported for a polymeric Co(HMTA)$_2$(NO$_3$)$_2$(H$_2$O)$_2$ complex, with slight modifications (Ndifon et al., 2009).

HMTA (4 mmol; 0.5608 g) was dissolved in 20 mL of ethanol/water mixture (6:1 v/v) by sonicating for 20 minutes, at room temperature. The solution was magnetically stirred while stoichiometric amounts of the metal nitrate (2 mmol) in 10 mL of ethanol was added drop wise to the HMTA solution and the mixture was stirred for two hours. The pink precipitate (Co-HMTA) and the white precipitate (Zn-HMTA) that were obtained were filtered, washed several times with 99% ethanol and dried in a desiccator over silica gel. Pink crystals (Co-HMTA) and colourless crystals (Zn-HMTA) suitable for single crystal XRD were obtained from the filtrates within two weeks.

2.3 Synthesis of Cobalt and Zinc Oxide Nanoparticles

The dry M-HMTA complex (0.5 g) was ground and placed in a ceramic crucible that had previously been washed, dried and weighed. The crucible was placed into a furnace and heated at a ramp rate of 5°C per minute until the desired temperature was reached (500°C) and calcined in the presence of air for two hours. The sample was allowed to cool slowly to room temperature. The obtained black powder (case of cobalt) and the white product (case of zinc) were weighed and could easily be re-dispersed in water and ethanol. The samples are referred to as Co$_3$O$_4$-500 and ZnO-500.

2.4 Characterisation

Elemental analysis (C, H, N) of the precursor was carried out on a Flash 2000 Thermo Scientific analyser while the FT-IR spectra were recorded from 4000 to 400 cm$^{-1}$ on a PerkinElmer Spectrum Two universal attenuated total reflectance Fourier transform infrared (UATR-FT-IR) spectrometer.

Single crystal X-ray data were collected using a graphite monochromatic Mo-K$_\alpha$ radiation ($\lambda$=1.54178 Å) from a Bruker APEX diffractometer. The structures were solved by direct methods and refined by full-matrix least squares on F$^2$ (Sheldrick, 1997a, 1997b). The non-hydrogen atoms were refined anisotropically. H atoms were included in calculated positions with C-H lengths of 0.95(CH), assigned isotopic thermal parameters and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package (Bruker, 2001).

Thermogravimetric measurements were obtained using a Pyris 6 PerkinElmer TGA 4000 thermal analyser. The TGA analyses were conducted between 30 and 900°C under nitrogen atmosphere at a flow rate of 20 mL/min and a temperature ramp of 10°C/min. The XRD diffractogram were recorded on a Bruker D8 Advance X-ray diffractometer using a Cu K$_\alpha$ radiation source ($\lambda$ = 0.15406 nm, 40 kV and 40 mA). Scans were taken over the 20 range from 10$^\circ$ to 100$^\circ$ in steps of 0.01$^\circ$ at room temperature in open quartz sample holders. The phases were identified with the help of the Bruker DIFFRACplus evaluation software in combination with the ICDD powder diffraction data base (International Centre for Diffraction Data). FESEM images and energy dispersive X-ray (EDX) spectra were obtained on a JEOL JSM-7600F field-emission scanning electron microscope (FESEM), with a lens diameter of 800 mm$^2$ (Oxford Instruments Ltd, UK) coupled to a silicon drift energy-dispersive X-ray detector. Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100F microscope using a maximum acceleration voltage of 200 kV from the field emission gun. The particle size distributions were determined from the TEM images using the ImageJ software. N$_2$-physisorption experiments for the determination of the total surface area and the average pore diameter were conducted on a Micromeritics ASAP 2020 instrument. Prior to the measurement, the samples were degassed at 200°C for 6 h.

3. Results and Discussion

By careful choice of the precursor, coupled with a rational control of temperature and other conditions, nano-sized cobalt and zinc oxides were obtained by thermal decomposition of their corresponding hexamethylenetetramine (HMTA) complexes. These complexes were prepared in a single step, in high yield at room temperature.

The elemental analytical data of the precursors (Table 1) correspond closely to the empirical formulae CoC$_{12}$H$_{28}$N$_{10}$O$_8$ and ZnC$_{12}$H$_{44}$N$_{10}$O$_{16}$ which matches the structural formulae [Co(HMTA)$_2$(H$_2$O)$_2$(NO$_3$)$_2$] and [Zn(H$_2$O)$_6$](HMTA)$_2$(NO$_3$)$_2$·4H$_2$O, respectively, for cobalt and zinc.
Table 1. Elemental analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Yield (%)</th>
<th>Colour</th>
<th>Elemental Analysis: % Found (% Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(HMTA)$_2$(H$_2$O)$_2$(NO$_3$)$_2$]</td>
<td>85</td>
<td>Pink crystals</td>
<td>%C: 28.73 (28.86) %H: 5.82 (5.65) %N: 27.56 (28.05)</td>
</tr>
<tr>
<td><a href="HMTA">Zn(H$_2$O)$_6$</a>$_2$(NO$_3$)$_2$·4H$_2$O</td>
<td>78</td>
<td>Colourless crystals</td>
<td>%C: 22.21 (22.18) %H: 6.74 (6.82) %N: 21.23 (21.55)</td>
</tr>
</tbody>
</table>

3.1 X-ray Crystal Structure

The crystal structures of the precursors Co-HMTA and Zn-HMTA were found to be the same as those of the complexes [Co(HMTA)$_2$(H$_2$O)$_2$(NO$_3$)$_2$] (Ndifon et al., 2009) and [Zn(H$_2$O)$_6$](HMTA)$_2$(NO$_3$)$_2$·4H$_2$O (Singh et al., 2008) respectively, found in literature.

3.2 FTIR Analyses of the Precursor Complexes

The relevant infrared bands of HMTA and the precursor complexes are listed in Table 2, while the FTIR spectra of the precursor complexes and the corresponding oxides are shown in Figure 1. The broad bands at 3400 - 3501 cm$^{-1}$ in the spectra of M-HMTA are attributed to ν(OH) of coordinated water, while that at 3383 cm$^{-1}$ is assigned to ν(OH) of lattice water (Hee Ng, Guan Teoh, Moris, & Yang Yap, 2004). The band at 1235 cm$^{-1}$, assigned to the ν(CH$_2$) rocking vibration of the free HMTA ligand is observed at 1238 cm$^{-1}$ in the Zn-HMTA complex, while it is split into 1240 and 1227 cm$^{-1}$ in the Co-HMTA precursor suggesting that HMTA is coordinated to the cobalt ion (Ndifon et al., 2009). Strong prominent peaks at 812 and 1000 cm$^{-1}$ due to the C-N stretching vibration of HMTA are shifted to 818-819 cm$^{-1}$ and 1002 cm$^{-1}$, respectively in the Co-HMTA and Zn-HMTA precursor complexes (Jensen, 2002). The weak band observed at 1780 cm$^{-1}$ shows the coordination of a monodentate nitrate ion, Co-NO$_3$ (Ndifon et al., 2009). The coordination of water molecules is also indicated by the IR bands in the region 400–600 cm$^{-1}$, assigned to M-H$_2$O (Ndifon et al., 2009).

Table 2. Relevant FTIR bands of HMTA and the M-HMTA precursor complexes

<table>
<thead>
<tr>
<th>HMTA</th>
<th>[Co(HMTA)$_2$(NO$_3$)$_2$(H$_2$O)$_2$]</th>
<th><a href="HMTA">Zn(H$_2$O)$_6$</a>$_2$(NO$_3$)$_2$·4H$_2$O</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>3501</td>
<td>3480</td>
<td>ν(OH) (coordinated water)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3383</td>
<td>ν(OH) (lattice water)</td>
</tr>
<tr>
<td>2955</td>
<td>-</td>
<td>2970</td>
<td>ν(CH$_2$)</td>
</tr>
<tr>
<td>-</td>
<td>1780</td>
<td>-</td>
<td>Co-NO$_3$</td>
</tr>
<tr>
<td>-</td>
<td>1675</td>
<td>1674</td>
<td>HOH bend (lattice water)</td>
</tr>
<tr>
<td>1457</td>
<td>1475</td>
<td>1463</td>
<td>ν(CH$_2$) scissor (HMTA)</td>
</tr>
<tr>
<td>1370</td>
<td>1349</td>
<td>1343</td>
<td>ν(CH$_2$) wag (HMTA)</td>
</tr>
<tr>
<td>1236</td>
<td>1240</td>
<td>1238</td>
<td>ν(CH$_2$) rock (HMTA)</td>
</tr>
<tr>
<td>1227</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>1002</td>
<td>1002</td>
<td>ν(CN) stretch (HMTA)</td>
</tr>
<tr>
<td>811</td>
<td>819</td>
<td>818</td>
<td>ν(CN) stretch (HMTA)</td>
</tr>
<tr>
<td>670</td>
<td>682</td>
<td>687</td>
<td>N-C-N bend (HMTA)</td>
</tr>
<tr>
<td>-</td>
<td>504</td>
<td>505</td>
<td>M-O stretch</td>
</tr>
</tbody>
</table>

3.3 Thermogravimetric Analysis

The TG curves of the precursor complexes are presented in Figure 2 and summarised in Table 3. The curves indicate that both complexes decompose in more than one step to give the metal oxides. The thermal decomposition of these precursors is accompanied by the evolution of a mixture of gases.
Figure 1. FTIR spectra of HMTA, the precursor complexes and the oxide nanoparticles

Table 3. Thermal decomposition data for the precursor complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Step</th>
<th>Temperature range (ºC)</th>
<th>% Mass Loss</th>
<th>Obs.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(HMTA)_2(NO_3)_2(H_2O)_2]</td>
<td>I</td>
<td>135 - 198</td>
<td>8.5</td>
<td>10.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>200 - 315</td>
<td>53.6</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>320 - 540</td>
<td>13.6</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td><a href="HMTA">Zn(H_2O)_6</a>_2(NO_3)_2·4H_2O</td>
<td>I</td>
<td>40 - 100</td>
<td>14.8</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>105 - 153</td>
<td>4.71</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>160 - 420</td>
<td>42.4</td>
<td>43.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>420 - 740</td>
<td>23.4</td>
<td>27.4</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. TG curves of the precursor complexes
For the Co-HMTA, the mass loss of 8.5% in the temperature region from 135 - 198ºC is most probably due to the loss of two coordinated water molecules (10.02%). The major mass loss of 53.6% takes place in the range 200 - 315ºC, and is attributed to the complete decomposition of HMTA (56%) in the form of various gases (Afanasiev et al., 2008). In the range 320 – 540ºC we have another distinctive decomposition step with a mass loss of 13.6% which can be assigned to the decomposition of the nitrate. A stable mass is reached at 540ºC. The calcination temperature was chosen as 500°C from the derivative TG plot.

Considering the decomposition of the Zn-HMTA complex, the mass loss of 14.8% in the temperature region from 50 – 102ºC is attributed to the loss of five water molecules (13.8%). The next decomposition step in the range 105 – 155ºC with mass loss of 4.71% is probably due to the loss of two coordinated water molecules (5.5%). In the temperature range 155 – 380ºC which, from the derivative TG plots, consists of several overlapping decomposition steps, there is a major mass loss of 42.4% which can be assigned to the decomposition of two HMTA molecules (43.1%) (Afanasiev et al., 2008; Hee Ng et al., 2004). The decomposition step in the range 400 – 740ºC involves a mass loss of 23.4% which can be assigned to the decomposition of the two nitrates and two water molecules (calc. 27.4%). A residual mass of 14.6% is observed at 740ºC which is probably due to zinc metal (10.1%).

The last decomposition step for Zn-HMTA is probably accompanied by the reduction of ZnO to zinc by carbon from 570°C. From the Ellingham diagram, carbon will reduce zinc oxide above 950°C for CO/CO2 ratio of 1. In an oxygen deficient atmosphere, the ratio will probably decrease pushing the reduction temperature to the observed lower value.

The calcination temperature was chosen as 500ºC from the derivative TG plot which indicates that 600°C is the optimum temperature. The decomposition pattern of the Zn-HMTA complex is slightly different from that reported in the literature, where the complex decomposes in two major steps in the temperature ranges 65 – 100ºC and 600 – 645ºC (Singh et al., 2008).

3.4 Structural Characterisation of the Oxide Nanoparticles

The FTIR spectra of the oxides are shown in Figure 1. The spectra show bands in the 500 - 650 cm⁻¹ region which are attributed to the stretching vibration of the M-O bond. The bands at 547 and 645 cm⁻¹ for cobalt oxide, suggest the formation of spinel Co₃O₄ that is (Co²⁺)(Co³⁺)(O²⁻), (Makhlof, Abu-Zied, & Mansoure, 2013; Nguimezong et al., 2014). These bands have been attributed to the (Co²⁺)-O-(Co³⁺) and to (Co³⁺)-O-(Co³⁺) vibrations, respectively (Makhlof et al., 2013; Nguimezong et al., 2014).

The cobalt oxide and zinc oxide nanoparticles were obtained by thermal decomposition of their respective M-HMTA precursors at 500 ºC. The XRD patterns of Co₃O₄ and ZnO (Figure 3) indicate that pure and crystalline metal oxide phases are formed in both cases. The samples have well defined diffraction patterns. The peaks for Co₃O₄ correspond to the (111), (220), (311), (222), (400), (511) and (440) crystals planes and match the spinel structure of cubic Co₃O₄ JCPDS card no 43-1003 (space group: Fd3m) (Lester et al., 2012). The peaks for ZnO correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes and match the wurtzite structure of hexagonal ZnO JCPDS card no. 36-1451 (Zhang, Ram, Stefanakos, & Goswami, 2012). The average crystallite sizes determined by the Debye-Scherrer equation (Klug & (Eds.), 1974) from the peak-width at half-height of the (311) peak for Co₃O₄ and the (101) peaks for ZnO, were found to be 23 and 32.5 nm for Co₃O₄-500 and ZnO-500, respectively.

The morphologies and other structural features of the precursor complexes, Co₃O₄-500 and ZnO-500 samples were determined by FESEM, TEM and SAED. The FESEM images (Figure 4) show that the precursor complexes Co-HMTA (Figure 4a) and Zn-HMTA (Figure 4b) have spike-like and bar-like morphologies, respectively, while Co₃O₄-500 (Figure 4c) is highly porous and foam-like. The ZnO-500 particles (Figure 4d) exhibit a rod-like shape. The formation of highly porous foam can be attributed to the large amounts of gases evolved when HMTA and nitrates decompose (Afanasiev et al., 2008).

The corresponding TEM images (Figure 5) confirm cube-like (Co₃O₄) and hexagonal-prism like (ZnO) morphologies, with average particle sizes of 19.6 and 64.5 nm, respectively. The average particle diameter was determined after a log normal fitting of the data obtained from the TEM images. The SAED images (Figure 5) show patterns corresponding to the polycrystalline nature of the Co₃O₄ and ZnO formed.
Figure 3. XRD patterns of Co$_3$O$_4$-500, ZnO-400 and ZnO-500 obtained by thermal decomposition

Figure 4. FESEM images of (a) Co-HMTA precursor; (b) Zn-HMTA precursor; (c) Co$_3$O$_4$-500 and (d) ZnO-500
The particle size distributions and average particle sizes for Co$_3$O$_4$-500 and ZnO-500 nanoparticles are shown in Figure 6. From this histogram it is observed that the particle sizes for Co$_3$O$_4$-500 and ZnO-500 vary from 15 – 25 nm and 45 – 85 nm, respectively. The average particle sizes from TEM are consistent with values obtained by XRD.
For comparison, the precursors, decomposition time and temperatures used to obtain Co$_3$O$_4$-500 and ZnO-500 nanoparticles by thermal decomposition, with various morphologies and sizes, found in the literature are listed in Table 4. The results show that cube-like (Co$_3$O$_4$-500) and hexagonal-like (ZnO-500) nanoparticles with average particle sizes of 19.6 and 64.5 nm, respectively obtained from the M-HMTA precursors of this study compares favorably with those obtained from other starting materials. It can also be observed from Table 4 that our starting materials are the simplest, most readily available, and very cost-effective.

Table 4. Particle sizes (TEM) and morphologies of Co$_3$O$_4$-500 and ZnO-500 nanoparticles prepared by the thermal decomposition of various precursors at different calcination temperatures

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Calcination Time (h)</th>
<th>Calcination Temp. (°C)</th>
<th>Particle Size (TEM) (nm)</th>
<th>Morphology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO$_3$)$_2$$\cdot$6H$_2$O + (NH$_4$)$_2$CO$_3$</td>
<td>2 - 3</td>
<td>300 - 500</td>
<td>12 - 14</td>
<td>Pseudo-hexagonal</td>
<td>(de Rivas et al., 2012)</td>
</tr>
<tr>
<td>Co(acetate)$_3$ + oxalic acid</td>
<td>2 - 3</td>
<td>500</td>
<td>12 - 14</td>
<td>Pseudo-hexagonal</td>
<td>(de Rivas et al., 2012)</td>
</tr>
<tr>
<td>CoCl$_2$ or Co(NO$_3$)$_2$ or Co(acetate)$_3$ + urea + CTAB</td>
<td>6</td>
<td>400 - 500</td>
<td>30 - 39</td>
<td>Rounded and squared</td>
<td>(Nassar &amp; Ahmed, 2011)</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$ + (NH$_4$)$_2$OX</td>
<td>6</td>
<td>400</td>
<td>25</td>
<td>microdiscs</td>
<td>(Che et al., 2013)</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_2$CO$_3$]NO$_3$$\cdot$0.5H$_2$O</td>
<td>1</td>
<td>175 - 300</td>
<td>10</td>
<td>Quasi-spherical</td>
<td>(Farhadi &amp; Saffabakhsh, 2012)</td>
</tr>
<tr>
<td>Zn$_4$(SO$_4$)(OH)$_6$$\cdot$0.5H$_2$O</td>
<td>1</td>
<td>825</td>
<td>92</td>
<td>Spherical</td>
<td>(Darezereshki et al., 2011)</td>
</tr>
<tr>
<td><a href="HMTA">Zn(H$_2$O)$_6$</a>$_2$(NO$_3$)$_2$$\cdot$4H$_2$O</td>
<td>2</td>
<td>500</td>
<td>64.5</td>
<td>Hexagonal-like</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.5 Surface Area and Pore Size Analyses

The surface areas of Co$_3$O$_4$-500 and ZnO-500 were determined by N$_2$ physisorption. All isotherms (Figure 7) were typical of mesoporous solids (type IV), for which both the surface area and the pore size distribution can be determined (Greg & Sing, 1982). The hysteresis loops (according to the IUPAC classification) were of type H1, which are often obtained for agglomerates or compacts of spheroidal particles of fairly uniform size and array (Greg & Sing, 1982). The BET surface areas of the samples (according to Brunauer, Emmett and Teller) are 5.1 and 10.4 m$^2$/g, respectively. The corresponding Barrett-Joyner-Halenda (BJH) desorption pore sizes are 25 and 12 nm. Table 5 summarizes the results.

Figure 7. N$_2$ adsorption/desorption isotherms for the Co$_3$O$_4$-500 and ZnO-500 samples

Table 5. Surface area, average pore diameter (APD) and pore volume of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>BJH Desorption APD (nm)</th>
<th>Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_3$O$_4$-500</td>
<td>5.1</td>
<td>25</td>
<td>0.043</td>
</tr>
<tr>
<td>ZnO-500</td>
<td>10.4</td>
<td>12</td>
<td>0.035</td>
</tr>
</tbody>
</table>
4. Conclusion

Pure and crystalline Co₃O₄ and ZnO nanoparticles, with defined morphologies, have been obtained from their corresponding metal-HMTA complexes by thermal decomposition. While Co₃O₄ is foam-like, ZnO nanoparticles have a rod-like shape according to FESEM. The corresponding TEM images confirm cube-like (Co₃O₄) and hexagonal-prism like (ZnO) morphologies, with average particle sizes of 19.6 and 64.5 nm, respectively. All oxide particles were mesoporous with BET surface areas of 5.1 m²/g (Co₃O₄) and 10.4 m²/g (ZnO). This technique that makes use of simple and readily available precursors for metal oxide nanoparticle synthesis could be extended to the synthesis of other metal oxide nanoparticles.

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