Homogeneous Chemical Precipitation Route to ZnO Nanosphericals

Chira R Bhattacharjee¹, Debraj Dhar Purkayastha¹, Sumit Bhattacharjee¹ and Abhijit Nath²
¹Department of Chemistry, Assam University Silchar, Silchar -788011, India
²Department of Chemistry, S.S College, Hailakandi -788151, India
Correspondence; ¹email: crbhattacharjee@rediffmail.com

Abstract

Synthesis of spherical zinc oxide nanoparticles were successfully achieved by thermal annealing of hydrozincite (Zn₅(CO₃)₂(OH)₆) powder at 300°C in air for 1h. Zinc acetate dihydrate, Zn(CH₃COO)₂.2H₂O was used as precursor with urea (NH₂CONH₂) in 1:4 molar ratio for the synthesis of hydrozincite by homogeneous chemical precipitation method under reflux for 1.5h at 115°C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) has been used to study the morphological features of the ZnO nanoparticles. X-ray powder diffraction (XRD) along with SEM and TEM indicated the sizes of as prepared ZnO nanoparticles to be 20-30 nm. Room temperature photoluminescence (PL) spectrum showed a strong band at 384 nm at 325nm excitation arising from recombination of free excitons indicating synthesized particles to be perfectly crystalline having low density of deep-level defects. A standard peak of zinc oxide was observed at 496 cm⁻¹ from FT-IR spectroscopy.

Key words: Hydrozincite, Zinc oxide, Nanoparticles, Photoluminescence.

Introduction

Metal oxides play a very significant role in material science (Noguera, 1996; Kung, 1989; Henrich and Cox, 1994) for instance fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion and as catalyst (Ertl et al., 1997). Metal oxides have also been employed as sorbents for environmental pollutants (Shelef et al., 2002; Stirling, 2000). In the domain of nanotechnology, oxide nanoparticles can exhibit unique chemical properties owing to their limited size and high density of corner or edge surface sites. A number of physical and chemical preparative methods for accessing nanostructured oxides are on records (Edelstein and Cammarrata, 1991; Khaleel el al., 2001). Among the metal oxides, nano ZnO exhibits wide band gap (~3.4eV) and large exciton binding energy (60meV) and thus is considered most promising candidate for nano-optoelectronics, sensors, transistors, nanoelectronics and UV-detection (Chen et al., 1998; Jin et al., 2000; Chung et al., 2000).

Synthesis of dimensionally controlled particles in large quantities and study of their properties to explore newer applications is a favourite pastime for researchers in nanomaterials (Xia et al., 2003). ZnO nanoparticles are widely researched upon (Wong et al., 1998; Hu et al., 2003; Hung and Whang, 2005) owing to their potential application in pigments, cosmetics, varistors, solar energy conversion, photocatalysis, light emitting materials (Gattorno et al., 2003), transparent UV protection films (Meulenkemp, 1998). Physical methods developed for synthesis of ZnO nanoparticles often require special equipments or operational control (Yang et al., 2003; Wu and Xie, 2004; Gao and Wang, 2004). Moderate reaction conditions and convenient synthetic manipulation have rendered chemical methods an attractive option for accessing ZnO nanoparticles. Traditional chemical routes that are frequently used in recent years include sol-gel approach (Spanhel and Anderson, 1991), chemical precipitation (Wang and Muhammed, 1999) and colloidal synthesis.
Surfactants or polymer based preparative method for ZnO nanomaterials (Guo et al., 2000) are also quite popular to avoid agglomeration and achieve better control of ZnO nanoparticles. Removal of surfactants or polymers, however, poses serious limitations to such methods. Hence, delicate and precise control of experimental factors for the synthesis of nanoparticles with desired morphologies is a cherished goal for future device applications (Kim et al., 2003). Homogeneous chemical precipitation method is often considered economically viable for preparation of monodisperse metal oxide particles of different shapes and sizes. The method also provides better control of chemical and morphological characteristics. Accordingly, in this paper we report the synthesis and characterization of spherical ZnO nanoparticles by homogeneous chemical precipitation route in presence of urea as precipitating agent.

Experimental

In a typical synthesis procedure, two separate solutions of zinc acetate dihydrate, Zn(CH$_3$COO)$_2$.2H$_2$O and urea were made in deionized water maintaining molar ratio at 1:4. The two solutions were mixed in a beaker and magnetically stirred at room temperature until a homogeneous solution was obtained. The resultant solution was then transferred into a round bottomed flask, sealed and heated at a temperature of 115°C for 1.5h in an oil bath. Upon completion of the reaction, a white precursor product obtained was centrifuged at 10,000 rpm for 5 min and washed with deionized water till it was neutral, to remove any possible absorbed ions and chemicals to reduce agglomeration. The resulting precipitate, hydrozincite precursor, (Zn$_5$(CO$_3$)$_2$(OH)$_6$), was dried at 100°C for 1h, and calcined in a muffle furnace at 300°C for 1h to obtain ZnO nanoparticle powder.

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (λ=1.5418Å) with a scan speed 2θ/min. Photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301 PC spectrofluorophotometer at room temperature. FT-IR spectra were recorded using a FT-IR spectrometer on KBr pellets. Scanning electron microscopy images were obtained on a Jeol JSM-6360 scanning electron microscope (SEM) with an accelerating voltage of 20kV. Transmission electron microscopy images were obtained on a Jeol, 9JSM-100CX transmission electron microscope (TEM) with an accelerating voltage of 100kV. The sample powders were dispersed in ethanol, under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air.

Results and Discussions

XRD study

Powder X-ray diffraction pattern of as grown precursor powder is shown in Fig.1. The indexed peaks in the diffractogram closely matched with those of the hydrozincite(JCPDS File no.19-1458). The X-ray diffraction pattern of ZnO nanoparticles (Fig.2) recorded for annealed hydrozincite powder shows peaks that are well indexed to the hexagonal phase of ZnO (JCPDS File no. 36-1451). The obtained ZnO nanosphericals are of wurtzite structure. Peaks characteristic of any impurity were absent. The mean particle size of ZnO nanoparticles has been calculated by Debye-Scherrer formula d= 0.9λ/âCosè, where â is the full width at half maximum in radians, è is the position of the maximum of diffraction peak and λ is the X-ray wavelength (1.5418Å for Cu-Kα). The mean particle size of ZnO nanoparticles are determined to be 29 nm.

PL study

Fig.3 shows the room temperature PL spectrum of ZnO nanoparticles. The UV-emission band at 382 nm is attributed to a near-band-edge transition of ZnO, namely the recombination of free excitons. Occurrence of only one UV peak in the spectrum suggested that the as-synthesized sample has low density of deep-level defects such as Zn and O vacancies that often arises due to so-called green emission band around 510 nm.

FT-IR study

The composition of the synthesized powder was analysed by FT-IR spectroscopy acquired in the
range 400-4000 cm\(^{-1}\) at room temperature. The FT-IR spectrum of hydrozincite, Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\) powder contains the diagnostic features of carbonate group. The peaks at 1465 cm\(^{-1}\) and 1392 cm\(^{-1}\) are assigned to C-O stretching modes of carbonate group (Music et al., 2007). The band at 3455 cm\(^{-1}\) is attributed to O-H vibrational mode of adsorbed moisture. The two oxygen atoms of the carbonate are bonded to an octahedral and tetrahedral zinc atom, whereas the third oxygen is hydrogen bonded to three OH groups (Ghose, 1964). The carbonato groups in hydrozincite Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\) is shown to possess three types of interaction in chemical bonding.

FT-IR spectrum of ZnO nanoparticles exhibits a rather broad and moderately strong band at 495 cm\(^{-1}\), owing to Zn-O vibrational mode. The band at 3445 cm\(^{-1}\) corresponds to O-H mode of adsorbed moisture in the annealed sample. The stretching C-O vibration is observed at 1530 cm\(^{-1}\). The bands at 1625 and 2363 cm\(^{-1}\) are due to C=O and CO\(_2\) groups.

\[
\begin{align*}
(NH_2)_2CO + H_2O & \rightarrow 2NH_3 + CO_2 \quad (1) \\
CO_2 + H_2O & \rightarrow 2H^+ + CO_3^{2-} \quad (2) \\
NH_3 + H_2O & \rightarrow NH_4^+ + OH^- \quad (3) \\
5Zn^{2+} + 2CO_3^{2-} + 6OH^- & \rightarrow Zn_5(CO_3)\_2(OH)\_6 \quad (4) \\
Zn\_5(CO_3)\_2(OH)\_6 & \xrightarrow{300^\circ C} 5ZnO + 2CO_2 \uparrow + 3H_2O \quad (5)
\end{align*}
\]

Urea decomposes at the experimental temperature to NH\(_3\) and CO\(_2\) (Eq. (1)) which in turn combine with water to produce carbonate (CO\(_3^{2-}\)) and hydroxide (OH\(^-\)) ions (Eq. (2) and (3)). The free CO\(_3^{2-}\) ion then combines with Zn\(^{2+}\) ion under basic condition forming hydrozincite, Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\) (Eq. (4)). The hydrozincite on annealing at 300\(^\circ\)C leads to ZnO nanoparticles (Eq. (5)).

Wang et al. (2006) synthesized ZnO nanoparticles via nanowhisker precursor adopting a solvothermal route at 180\(^\circ\)C for 24h starting with zinc acetate dihydrate and urea. The as grown particles were polydisperse having size 50-200nm. In another report by Wahab et al., 2008 synthesis of ZnO nanoparticles of 20-30 nm size were accomplished by annealing hydrozincite powder at 300\(^\circ\)C. The hydrozincite was synthesized by sol-gel method with refluxing time of 6h at 70\(^\circ\)C from zinc acetate dihydrate and urea in 1:7 molar ratio. Annealing at higher temperature 500-900\(^\circ\)C has been shown to produce agglomerated ZnO nanoparticles of increased size upto 300nm. Hydrozincite precursor synthesized in the present work by homogeneous chemical precipitation method requires refluxing time of 1.5h at 115\(^\circ\)C. The precursor when subsequently annealed at 300\(^\circ\)C led to the formation of ZnO nanoparticles of size 20-30 nm. The molar ratio of zinc acetate and urea used was 1:4. Though the reaction temperature is somewhat higher, the reaction time is drastically reduced from 6h as reported by Wahab et al., 2008 to 1.5h.

**Conclusion**

Zinc oxide nanoparticles were successfully synthesized from hydrozincite precursor obtained by homogeneous chemical precipitation followed...
by annealing at 300°C. The XRD analysis, SEM and TEM images reveal that the synthesized particles are nearly spherical in shape with size 20-30 nm. FT-IR study shows a strong band at 495 cm\(^{-1}\), characteristics of Zn-O vibrational mode.

**Acknowledgements**

Authors are thankful to SAIF NEHU, Shillong for providing some instrumental facilities. DDP thanks UGC for RFSMS grant.

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**Figure 1:** XRD pattern of hydrozincite, Zn\(_5\)(CO\(_3\)\(_2\))(OH\(_6\)) powder

**Figure 2:** XRD pattern of ZnO nanoparticles
Fig.3 Room temperature PL spectrum of ZnO nanoparticles

Figure 4: SEM image of ZnO nanoparticles

Figure 5: TEM image of ZnO nanoparticles

Homogeneous Chemical Precipitation......
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References


Ghose, S. (1964), *The crystal structure of hydrozincite, Zn_{6} (CO_{3})_{6} (OH)_{6}*, *Acta Cryst.*, 17, 1051-1057.


Surfactant-assisted low-temperature thermal decomposition route to spherical NiO nanoparticles

Chira R. Bhattacharjee a, Debraj Dhar Purkayastha a & Jitu Ranjan Chetia b

a Department of Chemistry, Assam University, Silchar 788 011, Assam, India
b Department of Chemistry, Dibrugarh University, Dibrugarh 786 004, Assam, India

Available online: 06 Dec 2011

To cite this article: Chira R. Bhattacharjee, Debraj Dhar Purkayastha & Jitu Ranjan Chetia (2011): Surfactant-assisted low-temperature thermal decomposition route to spherical NiO nanoparticles, Journal of Coordination Chemistry, 64:24, 4434-4442

To link to this article: http://dx.doi.org/10.1080/00958972.2011.640396

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Surfactant-assisted low-temperature thermal decomposition route to spherical NiO nanoparticles

CHIRA R. BHATTACHARJEE*†, DEBRAJ DHAR PURKAYASTHA† and JITU RANJAN CHETIA‡
†Department of Chemistry, Assam University, Silchar 788 011, Assam, India
‡Department of Chemistry, Dibrugarh University, Dibrugarh 786 004, Assam, India

(Received 1 September 2011; in final form 4 November 2011)

Thermal decomposition has been employed to access spherical nickel oxide (NiO) nanoparticles from a new precursor, nickel-salicylate, \([\text{Ni(C}_7\text{H}_5\text{O}_3\text{)}_2\text{(H}_2\text{O})_4]\). Surfactants, triphenylphosphine \((\text{C}_6\text{H}_5\text{)}_3\text{P})\), and oleylamine \((\text{C}_{18}\text{H}_{35}\text{NH}_2)\) were added to control the particle size. The products were characterized by X-ray diffraction, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy, and thermogravimetric analysis. TEM images showed particles nearly spherical having sizes 5–15 nm. The magnetism of NiO nanoparticles was studied with a vibrating sample magnetometer. Due to smaller particle size and increased surface uncompensated spins, a superparamagnetic behavior is observed. The synthetic process is simple and affords high-purity material at a relatively lower calcination temperature.

Keywords: Nanoparticles; NiO; Thermal decomposition; Superparamagnetic

1. Introduction

Science and technology of nanostructured metal oxides have captivated scientists during the last couple of decades. Particles of metal oxides from 1 to 100 nm can serve as good absorbents, carriers, and catalysts. Nickel oxide (NiO) is one of the most promising metal oxides for various applications. Besides fundamental research interests, nano-NiO, a p-type semiconductor, with a stable wide band gap (3.4–4.0 eV) [1] is used in alkaline batteries, gas sensors, electrochemical capacitors, smart windows, biomedicine, drug delivery, and magnetic bar codes [2–8]. The structural properties of nano metal oxides are intricately related to preparative techniques. Several methods such as thermal decomposition [9], electrodeposition [10], sputtering [11], homogeneous precipitation [12, 13], and sol–gel [14, 15] have been documented for the synthesis of nano-NiO. The preparation of well-crystallized oxide nanoparticles generally requires high-temperature treatment (typically above 1000°C), leading to irreversible growth and coalescence of starting particles [16]. Delicate control of synthetic conditions can afford ultra fine powders with narrow particle size distribution and enhanced material performance. Using different amines and surfactants, varying concentration, and

*Corresponding author. Email: crbhattacharjee@rediffmail.com
composition of solvents, Wu et al. [17] obtained nano-NiO particles possessing different morphologies, sizes, and shapes. Microemulsion route using cationic surfactant [18], chemical precipitation from nickel nitrate and urea [19] are also on record. Effects of anions such as nitrate, chloride, sulfate, or acetate on the sizes and morphology of nano-NiO and magnetism has been studied recently [20]. Li et al. [21] synthesized NiO nanoparticles using nickel nitrate and urea as starting materials and evaluated the catalytic properties of the material in pyrolyzing cellulose. Of all such methods, thermal decomposition method is a preferred process to access nano-NiO of different sizes and shapes, as it is simple, cost-effective, and affords high purity materials [22]. Although thermal decomposition of many metal salicylates [23] and nickel salicylate [23–25], in particular, has been investigated, no previous studies addressed the synthesis of metal oxide nanoparticles from such precursors. Addressing the challenge we intended to devise the synthesis of spherical NiO nanoparticles by thermal decomposition of nickel-salicylate complex, \([\text{Ni(C}_7\text{H}_3\text{O}_3\text{)}_2(\text{H}_2\text{O})_4]\), in the presence of surfactants triphenylphosphine (TPP) and oleylamine as stabilizers.

2. Experimental

2.1. Materials

The precursor \([\text{Ni(C}_7\text{H}_3\text{O}_3\text{)}_2(\text{H}_2\text{O})_4]\) was prepared according to the literature procedure [25] with little modification. Oleylamine, TPP, \(n\)-hexane, and ethanol were purchased from Aldrich and used as received.

2.2. Techniques

Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-K\(\alpha\) radiation \((\lambda = 1.5418 \text{ Å})\) with a scan speed 2\(^\circ\) min\(^{-1}\). FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrometer with KBr pellets. Elemental analyses (C, H, and N) were performed on a Heraeus Vario EL III Carlo Erba 1108 elemental analyzer. Nickel content was analyzed by atomic absorption spectroscopy (AAS) using Perkin Elmer ANA-Analyst 200 model equipment. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining a flow rate of 20 mL min\(^{-1}\) and a heating rate of 10\(^\circ\)C min\(^{-1}\) in air. Transmission electron microscopy (TEM) images were obtained on a Jeol, 9JSM-100CX TEM with an accelerating voltage of 100 kV. The sample powders were dispersed in \(n\)-hexane under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Magnetism of the material was studied using a Vibrating Sample Magnetometer (VSM, Lakeshore Model 7410) at 300 K.

2.3. Synthesis of \([\text{Ni(C}_7\text{H}_3\text{O}_3\text{)}_2(\text{H}_2\text{O})_4]\)

\(\text{NiCl}_2 \cdot 6\text{H}_2\text{O} (1.1885 \text{ g, 5 mmol})\) and salicylic acid \((1.3812 \text{ g, 10 mmol})\) were dissolved in distilled water separately and mixed in a conical flask and stirred for 1 h. The pH of the
resultant solution was maintained at ~8 by the addition of 5% aqueous KOH solution and further stirred for 2 h. The green precipitate thus obtained was filtered, washed, and dried. The product was characterized by FT-IR, elemental analyses, and TGA. Anal. Calcd for [Ni(C$_7$H$_5$O$_3$)$_2$(H$_2$O)$_4$] (%): C, 41.51; H, 4.45; Ni, 14.50. Found (%): C, 41.56; H, 4.49; Ni, 14.55. FT-IR ($v_{\text{max, cm}^{-1}}$, KBr): 3385 ($v_{\text{O-H}}$), 1600 ($\delta_{\text{HOH}}$), 1570 ($v_{\text{as(C-O)}}$), 1400 ($v_{\text{a(C-O)}}$), 1235 ($\delta_{\text{COH}}$).

2.4. Synthesis of NiO nanoparticles

[Ni(C$_7$H$_5$O$_3$)$_2$(H$_2$O)$_4$] (0.6 g) was taken in a round-bottomed flask and 5 mL of oleylamine was added to it and heated for 1 h at 140°C on an oil bath to get [Ni(C$_7$H$_5$O$_3$)$_2$(H$_2$O)$_2$(oleylamine)$_2$] complex. TPP (5 g) was then added to the resultant solution and temperature was raised to 240°C. The initial green color of the solution changed to black. The black solution thus obtained was aged at 240°C for 1 h and cooled to room temperature. The black solids were precipitated by adding excess ethanol to the reaction solution. The product is washed with ethanol several times. The solids could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene.

3. Results and discussion

The synthesis described herein is a modified version of the procedure developed by Hyeon and others for the synthesis of metal and oxide nanocrystals that utilizes thermal decomposition of transition metal complexes [22, 26]. In current synthesis (scheme 1), NiO nanoparticles were prepared by the thermal decomposition of a nickel-salicylate complex, [Ni(C$_7$H$_5$O$_3$)$_2$(H$_2$O)$_4$] as precursor in the presence of oleylamine and TPP. Oleylamine with its long hydrocarbon tail is considered to replace two non-hydrogen-bonded labile water molecules from the coordination sphere of nickel(II) forming [Ni(C$_7$H$_5$O$_3$)$_2$(H$_2$O)$_2$(oleylamine)$_2$] (scheme 1). A rather similar synthetic philosophy has recently been exploited for the preparation of nano-NiO from nickel oxalate complex, [Ni(C$_2$O$_4$)(H$_2$O)$_4$] [22]. Pertinent here is to mention that a calcination temperature lower than 240°C did not afford any NiO nanoparticles. In fact, the green reaction solution did not undergo any change until 240°C. Transformation to a blackish

![Scheme 1](image_url)
solution occurred only at 240°C while temperature above 240°C led to particles of bigger size. Further, under similar experimental conditions, when only oleylamine (no TPP) was used, highly agglomerated NiO particles were formed while with TPP alone (no oleylamine) no NiO could be obtained (table 1). Thus, it is evident that oleylamine and TPP together played a crucial role in the synthesis of low-dimensional NiO nanoparticles at a relatively low temperature. As the surface area of metal nanoparticles is related to their masses, they possess an excess surface free energy comparable to the lattice energy rendering the particles thermodynamically unstable. Protective or capping agents outweigh the attractive van der Waals forces by repulsive steric interaction. It is believed that the sterically demanding surfactant molecules aid in achieving greater interparticle separation [27].

The as-synthesized NiO nanoparticles were characterized by XRD, TEM, FT-IR, and VSM studies. The C, H, and N microanalysis as well as AAS analysis of the nickel content of the metal-salicylate precursor and the as-obtained NiO nanomaterial were carried out to confirm the compositions. Somewhat less nickel content is expected for NiO only and the occurrence of non-stoichiometric proportion of C, H, and N in the sample further affirms the presence of some surfactant molecules coating the nanoparticles. The TGA (figure 1) of the as-prepared precursor complex shows three distinct weight loss steps. The first step, in the temperature range 40–150°C, involves the loss of water yielding the anhydrous material. Such wide temperature range for loss of

<table>
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<tr>
<th>Sample</th>
<th>Surfactants</th>
<th>Calcination temperature (°C)</th>
<th>Time</th>
<th>Products (size)</th>
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<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>450</td>
<td>2 h</td>
<td>Bulk NiO</td>
</tr>
<tr>
<td>2</td>
<td>Oleylamine</td>
<td>240</td>
<td>2 h</td>
<td>Agglomerated NiO</td>
</tr>
<tr>
<td>3</td>
<td>TPP</td>
<td>240</td>
<td>2 h</td>
<td>No products</td>
</tr>
<tr>
<td>4</td>
<td>Oleylamine + TPP</td>
<td>240</td>
<td>2 h</td>
<td>NiO (5–15 nm)</td>
</tr>
</tbody>
</table>

Figure 1. TGA curve of [Ni(C₇H₅O₃)₂(H₂O)₄].
four water molecules alone clearly suggest that the four water molecules are not of the same type. A previous report [25] which dealt with structural characterization of nickel-salicylate complex shows that all four water molecules are coordinated, of which two are further H-bonded to each monodentate salicylate. In the present case the nickel-salicylate complex on being treated with oleylamine leads to the replacement of only two water molecules, presumably the non-H-bonded ones (scheme 1), further confirming the nature of water in the nickel-salicylate complex. The second step in the temperature range 150–340°C is due to the loss of one salicylate, and the third and final step in the temperature range 340–450°C is oxidation of this intermediate to the metal-oxide.

As evident from TGA analysis, the final weight loss step which corresponds to the loss of one salicylate leading to bulk NiO was found to occur at 450°C, however, use of capping ligands, oleylamine, and TPP lowered the decomposition temperature substantially, affording nano-NiO particles.

The proper selection of metal precursor and the method of synthesis is crucial to the preparation of nano metal oxides. Thermal treatment of different precursors can result in variation of particle sizes of nanocrystalline NiO depending on the temperature. For instance, surfactant-unassisted direct calcination of nickel dimethylglyoximate [28], nickel oxalate dihydrate [29], and nickel-o-phthalate [30] at different temperatures lead to NiO of different particle sizes. Calcination of nickel dimethylglyoximate at 500°C resulted in nanocrystalline NiO of mean particle size 35 nm, nickel oxalate dihydrate afforded NiO nanoparticles of mean size 30 nm at 450°C, while nickel-o-phthalate produced NiO of mean particle size 15 nm at 500°C. Not only the calcination temperatures are higher in these methods, but the sizes of the nanoparticles obtained are also larger. Nano-NiO of particle sizes <10 nm are difficult to obtain by these procedures. In this context a particle size of ~6 nm obtained for NiO at a relatively low temperature of 240°C is a redeeming feature of this work.

FT-IR spectroscopy was used to discern the nature of the surface-coordinating organic capping groups that facilitate dispersion of the nanoparticles in organic solvents. Figure 2 shows the FT-IR spectrum of NiO nanoparticles. The peak at

![FT-IR spectra](image_url)
490 cm\(^{-1}\) (curve b), attributable to Ni–O stretching vibration furnished clear evidence for the presence of crystalline NiO. A broad peak at \(\sim 3435\) cm\(^{-1}\) (curve b) indicates the presence of water. As the material was exposed to ambient conditions after calcination, some moisture was adsorbed on the external surface probably during spectrum recording. The H–O–H bending vibration appeared at \(\sim 1630\) cm\(^{-1}\) (curve b). The spectrum contains a number of weak peaks between 1000–1400 cm\(^{-1}\) and 2800–3000 cm\(^{-1}\) which arise due to symmetric and asymmetric stretching vibrations of –CH\(_2\), terminal –CH\(_3\) and =CH of oleylamine (C\(_{18}\)H\(_{35}\)NH\(_2\)). The material exhibited two weak stretching vibrations at \(\sim 2918\) and \(2845\) cm\(^{-1}\) assignable to C–H stretch of oleylamine carbon chain. Also, a broad band due to C–N the stretch of oleylamine was observed at \(\sim 1150\) cm\(^{-1}\) (curve b). These results indicate that some oleylamine molecules were adsorbed on the surface of NiO nanoparticles. The sharp peak at \(\sim 1435\) cm\(^{-1}\) (curve b) attributable to the phosphorus-phenyl stretching mode \(\nu(P-Ph)\) also suggested the occurrence of some TPP in the material.

At 240°C, most surfactant molecules (capping ligands) such as oleylamine and TPP were decomposed. The calcined NiO material was thoroughly washed with ethanol several times to remove any residual surfactant molecules and then subjected to elemental analysis (vide infra) to ascertain the extent of adsorbed surfactant molecules on the as-obtained material. Owing to the presence of the surfactant molecules, the NiO material can easily be dispersed in organic solvents such as \(n\)-hexane and toluene. Oleylamine serves as both solvent and capping agent for the nanoparticles. The long hydrocarbon chain of oleylamine exerts greater steric hindrance to control the size of metal nanoparticles. It is believed that oleylamine passivates the surface of grown nanoparticles, thus preventing agglomeration [27]. The stabilization of metal nanoparticles with TPP is also well documented in the literature [31, 32]. TPP, a high-boiling point surfactant with three phenyl rings impose greater steric hindrance slowing the rate of agglomeration of the nanoparticles during their growth, producing much smaller particles. Addition of TPP to \([\text{Ni(C}}_7\text{H}_5\text{O}_3\text{)}_2(\text{H}_2\text{O})_2(\text{oleylamine})_2\) (vide infra) resulted in much smaller particles with uniform size distribution.

### 3.1. Powder X-ray diffraction study

The X-ray powder diffraction pattern was recorded at room temperature for the identification of phases exhibited by the synthesized material. Figure 3 shows the XRD pattern of the synthesized material. The product is characterized as NiO (JCPDS file no: 73-1523). The diffraction peaks can be exactly indexed to a cubic structure of NiO with cell constant \(a = 4.197\) Å. No characteristic peaks of impurity were observed. The average particle size of NiO was estimated by Debye–Scherrer formula \((d = 0.9\lambda/\beta\cos\theta)\) to be 6.2 nm. The diffraction peaks are all quite broad, indicating the nanocrystalline nature of the material.

### 3.2. TEM

The morphology and particle size of the synthesized materials were determined by TEM. For preparation of the TEM sample, the powder was dispersed in \(n\)-hexane via ultrasonic equipment. The TEM image (figure 4) of NiO produced under the given experimental conditions exhibited nearly spherical morphology and is well dispersed.
with no agglomerations. The size of nanoparticles obtained from the XRD pattern are in close agreement with TEM studies which indicated the particle sizes to be 5–15 nm.

3.3. Room temperature magnetic study

The magnetization versus applied magnetic field (M–H) curve of NiO nanoparticles (figure 5) recorded at room temperature shows a hysteresis loop typical of superparamagnetic behavior. Bulk NiO is antiferromagnetic with a Neel temperature of 523 K [33]. Surface effects can dominate the net magnetic behavior for nano-NiO particles. Presence of a large fraction of atoms on the surface possessing uncompensated spins led to the net magnetization [34]. Greater surface spins with low coordination and broken exchange bonds enhance the net magnetization. The spherical nano-NiO prepared in this work possess smaller particle size (~6.2 nm). This increases the surface uncompensated spins, resulting in a superparamagnetic behavior (figure 5).
4. Conclusion

Spherical NiO nanoparticles of 5–15 nm have been synthesized via low-temperature thermal decomposition of a new precursor, [Ni(C\textsubscript{7}H\textsubscript{5}O\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{4}]. The role of surfactant stabilizers oleylamine and TPP was vital in controlling the growth of the particles and lowering the calcination temperature. The XRD pattern showed phase pure cubic NiO. The current method employed is an inexpensive reproducible process with potential for scale-up. The methodology can be readily extended for the synthesis of other nano metal oxides.

Acknowledgments

Authors are thankful to SAIF, NEHU, Shillong, and CIF, IIT, Guwahati, for providing instrumental facilities. D.D. Purkayastha thanks University Grants Commission, Government of India, for providing grants under Research Fellowship Scheme for Meritorious Students (RFSMS).

References

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Surfactant controlled low-temperature thermal decomposition route to zinc oxide nanorods from zinc(II) acetylacetonate monohydrate

Debraj Dhar Purkayastha, Bedabrat Sarma, Chira R. Bhattacharjee
Department of Chemistry, Assam University, Silchar 788011, Assam, India

Low temperature thermal decomposition of zinc(II) acetylacetonate monohydrate gave zinc oxide nanorods. Powder XRD showed hexagonal wurtzite structure of ZnO having average diameter about 24 nm. TEM images revealed the material to be of rod shape having diameter 30 nm and length 200 nm. ZnO showed band gap luminescence at 356 nm, excitonic emission at 382 nm and defect related blue bands. The synthesis is simple and can act as a paradigm for obtaining various metal oxide nanomaterials.
Surfactant controlled low-temperature thermal decomposition route to zinc oxide nanorods from zinc(II) acetylacetonate monohydrate

Debraj Dhar Purkayastha, Bedabrat Sarma, Chira R. Bhattacharjee*

Department of Chemistry, Assam University, Silchar 788011, Assam, India

A R T I C L E   I N F O

A B S T R A C T

Zinc oxide (ZnO) nanorods were synthesized via a low-temperature thermal decomposition of zinc(II) acetylacetonate monohydrate, \([Zn(C_5H_7O_2)\text{H}_2\text{O}]\). A relatively inexpensive surfactant, octadecylamine \((C_{18}H_{37}NH\_2)\) served both as a reaction solvent and a capping agent during the synthesis of ZnO nanorods. The synthesized nanorods were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR, UV-visible, and photoluminescence (PL) studies. The XRD spectrum furnished evidence for the hexagonal wurtzite structure of ZnO. TEM images revealed the material to be rod shaped having diameter 30 nm and length 200 nm. The HRTEM image showed that the lattice fringes between the two adjacent planes are 0.244 nm apart, which corresponds to the interplanar separation of the \((1 0 1)\) plane of hexagonal ZnO. The electron diffraction (ED) pattern confirmed the single crystalline nature of the nanorods. The PL spectrum showed two UV emissions at 356 nm \((\sim 3.48 \text{ eV})\) and 382 nm \((\sim 3.25 \text{ eV})\). ZnO nanorods also showed very weak blue bands at 445, 453 and 470 nm.

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1. Introduction

One-dimensional (1D) ZnO nanostructures such as nanowires, nanofibers, nanotubes, and nanorods have attracted enormous current interest owing to their wide applications in nanodevices such as light-emitting diodes [1,2], field-effect transistors [3,4], ultraviolet lasers [5,6], chemical sensors [7,8] and solar cells [9–10]. Various chemical synthetic routes like sol–gel [11], hydro-thermal [12,13], thermal decomposition [14], reverse microemulsion [15], etc. have been devised for the synthesis of ZnO nanorods. Amongst all, thermal decomposition has emerged as a quite popular synthetic option, as it is simple, of low-cost, and yields high purity materials. ZnO nanostructures exhibit luminescent properties in the near ultraviolet and visible regions. However, due to surface defects the emission properties of ZnO in the visible region usually depend on their synthesis method. Deep hole traps associated with the presence of oxygen vacancies can cause green emission above 500 nm [16]. Shorter wavelength emissions in the blue region are usually related to various defects such as interstitial zinc [17] or \(\text{OH}^\text{-}\) groups at the surface of the particles [18]. Zinc(II) acetylacetonate has been rather efficiently utilized by several researchers previously as a precursor for the synthesis of ZnO nanomaterials of various sizes and shapes. Thermal decomposition of zinc(II) acetylacetonate in oleylamine has been earlier shown to yield monodispersed ZnO nanoparticles [19]. ZnO nanoparticles of size 12–20 nm were previously accessed via thermal decomposition of zinc(II) acetylacetonate in the presence of surfactants oleylamine and triphenylphosphine [20]. Gross et al. developed a facile and reproducible route to nanostructured ZnO by controlling the hydrolysis and condensation of zinc(II) acetylacetonate in alkaline conditions [21]. Thermal decomposition of zinc(II) acetylacetonate monohydrate at and above 200 \(^\circ\)C afforded ZnO nanoparticles of size 20–40 nm [22]. Another strategy employed one-pot synthesis by refluxing an oversaturated solution of zinc(II) acetylacetonate monohydrate in 1-butanol, isobutanol or tert-butanol that yielded ZnO nanostructures of varying sizes and morphologies like nanorods, coral-like structures and nanospheres [23,24]. Though, ZnO nanomaterials of various morphologies were obtained earlier using zinc(II) acetylacetonate precursor under different reaction conditions there appears to be no report yet describing the synthesis of ZnO nanorods via thermal decomposition of zinc(II)acetylacetonate. As a part of our continued interest in accessing metal oxide nanomaterials from simpler metal precursors [25–27], we report herein the synthesis of ZnO nanorods via a low-temperature thermal decomposition of zinc(II)acetylacetonate monohydrate in the presence of a relatively inexpensive surfactant, octadecylamine \((C_{18}H_{37}NH\_2)\).
2. Experimental

2.1. Materials and physical measurements

All chemicals used were of analytical grade and used as received. The precursor zinc(II) acetylacetonate monohydrate \([\text{Zn(C}_5\text{H}_7\text{O}_2\text{)}_2]\cdot\text{H}_2\text{O}\) was prepared according to the literature procedure [28]. FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrometer and KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in air. X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (\(\lambda = 1.5418 \text{ Å}\)) at a scan speed of 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in n-hexane under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Absorption spectrum was taken with a Shimadzu 1601 PC UV-visible spectrophotometer. Photoluminescence (PL) spectrum was recorded on a Shimadzu RF-5301 PC spectrofluorophotometer.

2.2. Synthesis of ZnO nanorods

An amount of 0.6 g of \([\text{Zn(C}_5\text{H}_7\text{O}_2\text{)}_2]\cdot\text{H}_2\text{O}\) and 10 ml of octadecylamine were heated in a round bottomed flask for 1 h at 140 °C in an oil bath to get \([\text{Zn(C}_5\text{H}_7\text{O}_2\text{)}_2\text{octadecylamine}]_2\) complex. Thereafter the reaction temperature was raised to 200 °C. The light yellow solution gradually became hazy, indicating the formation of colloidal suspension. The solution was aged at 200 °C for 1 h and cooled to room temperature. The white product was precipitated by adding excess ethanol to the solution and washed with ethanol several times. The solid could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The current synthesis is a modified version of the procedure developed by Hyeon and others for metal and oxide nanocrystals that utilize thermal decomposition of transition metal complexes [20,29]. In the present synthesis (Scheme 1), zinc oxide nanorods were accessed by the thermal decomposition of zinc(II) acetylacetonate monohydrate, \([\text{Zn(C}_5\text{H}_7\text{O}_2\text{)}_2]\cdot\text{H}_2\text{O}\) precursor in the presence of surfactant octadecylamine. The decomposition temperature (200 °C) has been chosen based on the TGA behavior of \([\text{Zn(C}_5\text{H}_7\text{O}_2\text{)}_2]\cdot\text{H}_2\text{O}\) where the precursor compound degraded to ZnO. Octadecylamine served both as the reaction medium and the capping agent during the synthesis of nanorods. The synthesized nanorods were characterized by XRD, TEM, FT-IR, UV-visible, and PL studies. The TGA curve (Fig. 1) revealed that the precursor zinc(II) acetylacetonate monohydrate underwent decomposition in two steps. The first step is the dehydration, which commences at 70 °C and is completed at 100 °C accompanied by a weight loss of ~7.3%, due to the removal of one water molecule. A further weight loss of ~74.1% in the second step in the temperature range 115–195 °C furnished clear evidence for the loss of two acetylacetonate (acac) ligands, affording ZnO as end residue.

The FT-IR spectrum of zinc(II) acetylacetonate (Fig. 2(a)) showed a broad band centered at about 3180 cm\(^{-1}\) due to \(\nu(\text{O-H})\) of lattice water. The peaks at 2995 and 2920 cm\(^{-1}\) arose due to the C–H stretch. The FT-IR spectrum of ZnO nanorods (Fig. 2(b)) showed a broad band at around 430 cm\(^{-1}\) due to the stretching vibration of Zn-O bonds and the characteristic bands at 568 cm\(^{-1}\) and 640 cm\(^{-1}\) due to the bending vibration of Zn-O bonds.

![Fig. 1. TGA curve of zinc(II) acetylacetonate monohydrate.](image1.png)

![Fig. 2. FT-IR spectrum of (a) zinc(II) acetylacetonate monohydrate and (b) ZnO nanorods.](image2.png)

Scheme 1. Illustration of the formation of ZnO nanorods.

Please cite this article as: D.D. Purkayastha, et al., J. Lumin. (2014), http://dx.doi.org/10.1016/j.jlumin.2014.04.007
stretching vibration $\nu(C-H)$ of the methyl group. Coupling of the stretching vibrational modes of $C=O$ and $C=C$ groups was observed around, respectively, 1600 and 1515 cm$^{-1}$. The band at 420 cm$^{-1}$ can be assigned to the stretching vibrations of Zn–O. The FT-IR spectrum of the synthesized ZnO (Fig. 2(b)) showed a strong band at 488 cm$^{-1}$, characteristic of Zn–O stretching vibrational mode. Besides, $C-N$ stretching mode of octadecylamine was observed at 1120 cm$^{-1}$. A weak broad band (3100–3700 cm$^{-1}$) was observed due to N–H stretching; those at 2920 and 2845 cm$^{-1}$ were attributed to C–H stretching mode of octadecylamine; this clearly indicated that some octadecylamine molecules have been adsorbed on the surface of the synthesized ZnO nanorods.

The XRD spectrum (Fig. 3) of the synthesized material showed diffraction peaks, which can be well indexed to the hexagonal phase of ZnO. The obtained ZnO possesses the wurtzite structure. The relative intensities of the diffraction peaks matched well with the standard diffraction pattern of crystalline ZnO (space group P6$_3$mc, JCPDS File no. 89-1397). The sharp diffraction peaks also indicated high crystallinity of the material. The XRD spectrum also showed two extra peaks (asterisk marked), which are not characteristics of any other impurity phases. In fact these peaks correspond well with the peaks of octadecylamine reported in the literature [30]. It is pertinent to mention here that the calcined material was thoroughly washed with ethanol several times to remove the excess surfactant molecules. Thus, the extra peaks in the XRD spectrum may be attributed to the surfactant octadecylamine remaining at the surfaces of ZnO nanorods. The average diameter of the nanorods estimated by the Debye–Schererr formula using a Gaussian fit was around 24 nm.

The TEM image (Fig. 4) of the synthesized nanomaterials revealed them to be rod shaped, 200 nm long and possessing 30 nm diameter. The surfactant octadecylamine effectively controlled the size of the nanorods by limiting the growth at the nucleation stage. Since the surfaces of the nanorods were capped with the surfactant octadecylamine, these could be well dispersed in most hydrophobic solvents. The HRTEM image showed the lattice fringes between the two adjacent planes to be 0.244 nm apart, which corresponds to the interplanar separation of the (1 0 1) plane of hexagonal ZnO. This indicated that one of the growth planes of the nanorods is along the (1 0 1) plane. The ED pattern indicated single crystalline nature of the synthesized nanorods.

Earlier Klabunde and a coworker synthesized nanocrystalline ZnO utilizing organometallic compound diethylzinc (Zn(C$_2$H$_5$)$_2$) as precursor [31]. The synthesis involved transformation of Zn(C$_2$H$_5$)$_2$
into an alkoxide prior to hydrolysis and thermal treatment. Moreover, ZnO nanocrystallites were found to agglomerate into bigger spherical particles having a diameter of 260 nm. High-temperature thermal decomposition of Zn(C₂H₅)₂ in the presence of trioctylphosphine oxide (TOPO) and alkylamines is also known to afford ZnO nanocrystals [32]. Wachnicki et al. compared effectiveness of dimethylzinc (Zn(CH₃)₂) and diethylzinc (Zn(C₂H₅)₂) as precursors for monocristalline zinc oxide films grown by atomic layer deposition (ALD) [33]. Due to the pyrophoric nature of Zn(CH₃)₂ and Zn(C₂H₅)₂ precursors the reactions were often required to be performed under inert atmosphere. In contrast, air stable zinc(II) acetylacetonate monohydrate precursor utilized here can be easily accessed under mild reaction conditions. Moreover, it is a single source precursor, which provides both zinc and oxygen species via decomposition. Using a metal organic chemical vapor deposition (MOCVD) technique with diethylzinc (Zn(C₂H₅)₂) precursor, vertically aligned (c-axis oriented) ZnO nanorods were grown on sapphire (0 0 1) substrate [34]. A very high deposition temperature (> 600 °C) and inert condition were necessary to grow the nanorods. The nanorods were found to grow almost perpendicularly on the substrate and their lengths were about 3 µm. However, ZnO nanorods synthesized in the present study lacks vertical alignment and possess comparatively much smaller length than those obtained by the MOCVD technique [34]. The present synthesis is based on low decomposition temperature (~200 °C) and non-inert condition.

The UV-visible spectrum (Fig. 5) shows a strong absorption at around 375 nm (band gap = 3.31 eV), which corresponds to the bulk value of the band gap of ZnO. No blueshift was observed in the spectrum of ZnO nanorods, which indicated the nanorods to be too large to show any quantum confinement related effects. The strong excitonic absorption observed is possibly due to the effective surface passivation of ZnO by the surfactant octadecylamine and the more efficient dispersion of the nanorods. As a result, light scattering is reduced, causing the long wavelength tail to extend up to 800 nm. A similar absorption feature was observed earlier for the oleic acid passivated ZnO nanotetrapods [35]. The PL spectrum (Fig. 6) of ZnO nanorods excited at 320 nm showed two UV emissions at 356 nm (~3.48 eV) and 382 nm (~3.25 eV). The emission peak at 356 nm may be attributed to the band gap luminescence as it is blueshifted compared to the optical absorption. The near-band edge (NBE) emission peak at 382 nm is assigned to the recombination of free excitons [36]. In addition to the UV emissions, a broad shoulder in the range 400–425 nm and very weak defect-related blue emissions at 445, 453 and 470 nm were also observed. The blue bands were also reported earlier in ZnO nanostructures [37–40] and are believed to be associated with various intrinsic or extrinsic lattice defects. Due to the effective surface passivation by the surfactant octadecylamine, ZnO nanorods showed very weak defect-related visible blue emissions and were less intense compared to the UV emissions [41–43]. ZnO nanorods grown on Al₂O₃ (0 0 1) substrate by the MOCVD technique with Zn(C₂H₅)₂ showed NBE emission as well as quite high defect-related visible emissions [44]. In contrast, the PL spectrum of ZnO nanorods synthesized in the present study showed considerably quenched defect-related visible emissions, which indicated high optical quality of the nanorods. This inference was further corroborated by the XRD and TEM observations. Very recently, improvement of the optical and structural properties of ZnO nanorods grown by ALD on the seed ZnO nanorods has been observed [45]. A high-temperature annealing is also utilized to improve the optical and structural properties of ZnO nanorods [46,47]. ZnO nanorods accessed in the present study without any additional surface treatment or high-temperature processing exhibited good optical and structural quality.

4. Conclusion

A low-temperature thermal decomposition of zinc(II) acetylacetonate monohydrate in the presence of an inexpensive surfactant octadecylamine successfully resulted in ZnO nanorods. Though, zinc (II) acetylacetonate has been exploited earlier as precursor for accessing ZnO nanomaterials, the formation of nanorods as reported herein appears to be the first of its kind. The synthetic strategy adopted is simple and should serve as a paradigm to access other metal oxide nanomaterials of specific size and morphology.

Acknowledgment

Authors are thankful to SAIF, NEHU, Shillong, for providing TEM facility. DDP thanks University Grants Commission, Government of India, for Research Fellowship Scheme for Meritorious Students (RFSMS). We are thankful to DBT e-Library Consortium (DeLCON) of Bioinformatics Centre, Assam University, Silchar.

References


Please cite this article as: D.D. Purkayastha, et al., J. Lumin. (2014), http://dx.doi.org/10.1016/j.jlumin.2014.04.007
Surfactant mediated low temperature thermal decomposition route to zinc oxide nanocrystals

Chira R. Bhattacharjee *, Debraj Dhar Purkayastha, Nirmalendu Das

Department of Chemistry, Assam University, Silchar 788011, India

A R T I C L E   I N F O

Keywords: Nanocrystalline materials Semiconductors Luminescence X-ray techniques

A B S T R A C T

Zinc oxide nanocrystals were synthesized via thermal decomposition of a new precursor zinc malonate, [ZnCH_2C_2O_4]_2H_2O in the presence of surfactant stabilizers oleylamine (C_18H_35NH_2) and triphenylphosphine ((C_6H_5)_3P). The nanocrystals were characterized by X-ray diffraction, transmission electron microscopy, FT-IR and UV–visible spectroscopy. XRD pattern showed a hexagonal wurtzite structure of ZnO having average crystallite size of about 22 nm. The TEM image showed the nanocrystallites constituting the flower-like pattern to be of 25–55 nm sizes. The band gap luminescence was observed at 354 nm (≈2.75 eV) alongwith defect related blue emission at 450 nm (≈2.75 eV).

1. Introduction

Semiconductor nanocrystals have engrossed much interest due to their basic importance in bridging the gap between bulk matter and molecular species [12]. Technologically, materials with unusual electrical and optical properties may be produced based on semiconductor nanocrystals [3]. Zinc oxide, a wide band gap semiconductor with high exciton binding energy of 60 meV possesses stable wurtzite structure. An array of high-technology applications ranging from surface acoustic wave filters [4], photonic materials [5], light emitting diodes [6], photodetectors [7], varistors [10], gas sensors [11] and solar cells [12], are based on ZnO nanomaterials. However, due to surface defects the emission properties of ZnO nanoparticles in the visible region usually depend on their synthetic method. Deep hole traps associated with the presence of oxygen vacancies can cause green emission above 500 nm [13]. Shorter wavelength emissions in the blue region are usually related to various defects such as interstitial zinc [14] or OH− groups at the surface of the particles [15]. Kahn et al. [16] described a possible hole trapping effect by the amine groups on the surface of the ZnO particles as the origin of blue emission. Several methods for the synthesis of ZnO nanomaterials have been devised such as solvo/hydrothermal reactions [17,18], sol–gel process [19], microwave synthesis [20], precipitation [21], solution–combustion [22], thermal decomposition [23], etc. In particular, thermal decomposition is simple, low cost and readily affords high purity products. Hence, it serves as a viable route for industrial applications. Exploiting novel inorganic compounds open up newer avenues and enable one to control the nanocrystal size, shape, and size distribution. We report herein surfactant mediated synthesis of ZnO nanostructures by thermal decomposition of a new precursor, zinc malonate.

2. Experimental

**Materials and physical measurements:** All chemicals used were of analytical grade and used as received. Zinc malonate, [ZnCH_2C_2O_4]_2H_2O was prepared according to the literature procedure [24]. FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrometer on KBr pellets. Elemental analysis was performed on a Heraeus Vario EL III Carlo Erba 110B elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in air. X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) with a scan speed 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in n-hexane under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Electronic spectrum was taken on a Shimadzu 1601 PC UV–visible spectrophotometer. Photoluminescence spectrum was recorded on a Shimadzu RF-5301 PC spectrophotoluminescence.

**Synthesis of zinc oxide nanocrystals:** 0.6 g of [ZnCH_2C_2O_4]_2H_2O was taken in a round bottom flask and 5 mL of oleylamine was added to it and heated for 1 h at 140 °C on an oil bath. After that 5 g of triphenylphosphine was added to the mixture and temperature was increased to 240 °C. The light yellow solution gradually becomes hazy, indicating generation of colloidal...
particles. The solution was aged at 240 °C for 1 h and cooled to room temperature. The white products were precipitated by adding excess ethanol to the solution. The products were washed with ethanol several times. These products could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The present synthesis is a modified version of the procedure developed by Hyeon and others for metal and oxide nanocrystals that utilizes thermal decomposition of transition metal complexes [23,25]. The synthetic pathway is shown in Scheme 1. In the current synthesis, zinc oxide nanocrystals were prepared by the thermal decomposition of zinc malonate, [ZnCH$_2$C$_2$O$_4$]·2H$_2$O as precursor in the presence of surfactants oleylamine and triphenylphosphine. The as-synthesized nanocrystals were characterized by XRD, TEM, FT-IR, and UV–visible studies. In order to ascertain the precursor composition, elemental analysis was performed. The TGA curve (Fig. S1 in ESI) revealed that zinc malonate undergoes decomposition in two steps. The first step is the dehydration, which commences at 130 °C and completes at 192 °C as indicated by a weight loss of 17% due to the removal of two water molecules. The anhydrous zinc malonate remains stable up to 258 °C and thereafter undergoes a rapid decomposition releasing various gaseous products such as C$_2$H$_4$, CO and CO$_2$ with an overall weight loss of 60% till 500 °C forming ZnO. The chemical reaction involved in the decomposition process is as follows:

\[
\text{ZnCH}_2\text{C}_2\text{O}_4 \cdot \text{2H}_2\text{O} \xrightarrow{130–192 \degree \text{C}} \text{ZnCH}_2\text{C}_2\text{O}_4 \\
\]

\[
\text{ZnCH}_2\text{C}_2\text{O}_4 \xrightarrow{258–500 \degree \text{C}} \text{ZnO(s)} + \frac{1}{2}\text{C}_2\text{H}_4(g) + \text{CO(g)} + \text{CO}_2(g) \\
\]

The X-ray powder diffraction pattern (Fig. 1) was recorded for the identification of phases exhibited by the synthesized material. The diffraction peaks can be well indexed to the hexagonal phase of ZnO (space group P6$_3$/mc, JCPDS File no. 89-0510). The obtained ZnO are of wurtzite structure. The characteristic peaks of any impurity were absent. The average crystallite size estimated by the Debye–Scherrer formula, using a Gaussian fit, was found to be 22 nm.

The TEM image (Fig. 2) of ZnO nanomaterial showed flower-like pattern. Crystallites constituting those flowers have sizes 25–55 nm. However, the higher crystallite size obtained from TEM as compared to XRD may be attributed to agglomeration. The XRD and TEM data can be reconciled by the fact that smaller primary crystallites have a large surface free energy and would, therefore, tend to agglomerate faster and grow into larger ones. The HRTEM image of a nanocrystallite showed the lattice fringes between the two adjacent planes to be 0.26 nm apart, which is equal to the interplanar separation of (002) plane of the standard ZnO. Electron diffraction (ED) pattern revealed single crystalline nature.

The symmetric and asymmetric vibrational modes of –N–H were observed around 3489 and 3297 cm$^{-1}$ respectively. A number of weak peaks between 1000–1400 cm$^{-1}$ and 2800–3000 cm$^{-1}$ occurred due to the symmetric and asymmetric stretching vibrations of –CH$_2$ terminal –CH$_3$ and –CH of oleylamine. Two weak bands at ~2925 and 2853 cm$^{-1}$ were assigned to C–H stretching mode of oleylamine carbon chain. Also, a characteristic band due to the C–N stretching mode of oleylamine was observed at ~1182 cm$^{-1}$. These results indicate that some oleylamine molecules were adsorbed on the surface of the zinc oxide nanocrystals. The spectrum shows a strong band at 499 cm$^{-1}$, characteristics of Zn–O stretching vibrational mode. The sharp peak at ~1434 cm$^{-1}$ attributable to the phosphorus–phenyl stretching mode, ν(P–Ph) also suggested occurrence of some triphenylphosphine molecules in the material. TPP was widely used in the synthesis of phosphate-stabilized metal nanoparticles [23,26]. It is appropriate to mention herein that at the experimental temperature of 240 °C, most of the surfactant molecules (capping ligands) were decomposed. The calcined material was washed with ethanol several times to remove any residual surfactant molecules. However, peaks due to oleylamine and TPP arose from coated surface of zinc oxide nanocrystals. Owing to the presence of the surfactant molecules the zinc oxide nanocrystals thus obtained can easily be dispersed in organic solvents such as n-hexane and toluene. Oleylamine served both as solvent and capping agent for the nanocrystals. The long hydrocarbon chain of oleylamine exerts greater steric hindrance to control the size of zinc oxide nanocrystals.

FT-IR spectrum (Fig. S2 in ESI) was recorded to discern the nature of the surface-coordinating organic capping groups that facilitate dispersion of the nanocrystals in organic solvents. The asymmetric and symmetric vibrational modes of –N–H were observed around 3489 and 3297 cm$^{-1}$ respectively. A number of weak peaks between 1000–1400 cm$^{-1}$ and 2800–3000 cm$^{-1}$ occurred due to the symmetric and asymmetric stretching vibrations of –CH$_2$ terminal –CH$_3$ and –CH of oleylamine. Two weak bands at ~2925 and 2853 cm$^{-1}$ were assigned to C–H stretching mode of oleylamine carbon chain. Also, a characteristic band due to the C–N stretching mode of oleylamine was observed at ~1182 cm$^{-1}$. These results indicate that some oleylamine molecules were adsorbed on the surface of the zinc oxide nanocrystals. The spectrum shows a strong band at 499 cm$^{-1}$, characteristics of Zn–O stretching vibrational mode. The sharp peak at ~1434 cm$^{-1}$ attributable to the phosphorus–phenyl stretching mode, ν(P–Ph) also suggested occurrence of some triphenylphosphine molecules in the material. TPP was widely used in the synthesis of phosphate-stabilized metal nanoparticles [23,26]. It is appropriate to mention herein that at the experimental temperature of 240 °C, most of the surfactant molecules (capping ligands) were decomposed. The calcined material was washed with ethanol several times to remove any residual surfactant molecules. However, peaks due to oleylamine and TPP arose from coated surface of zinc oxide nanocrystals. Owing to the presence of the surfactant molecules the zinc oxide nanocrystals thus obtained can easily be dispersed in organic solvents such as n-hexane and toluene. Oleylamine served both as solvent and capping agent for the nanocrystals. The long hydrocarbon chain of oleylamine exerts greater steric hindrance to control the size of zinc oxide nanocrystals.
The UV–visible spectrum (Fig. S3 in ESI) of the material showed a strong absorption characteristic of nano-ZnO displaying a band gap around 367 nm (~3.38 eV). Light-emitting nanostructures based on semiconducting materials are currently of considerable significance owing to unique optoelectronic properties. ZnO, a wide band-gap II–VI semiconductor (band gap = 3.37 eV, 298 K), exhibits significant quantum confinement effect when its size reaches the Bohr radius. The photoluminescence spectrum (Fig. 3) of ZnO nanocrystals showed two emissions at 354 nm (~3.50 eV) and at 450 nm (~2.75 eV).

The UV emission may be attributed to band gap luminescence as it is blue shifted compared to the optical absorption. The visible blue emission in the present case is associated with the presence of surface defects on the nanocrystals. As the surface of the ZnO nanocrystals were capped with oleylamine a possible hole trapping effect of amine group is attributed for the blue emission [16]. Based on Brus model [27] the effective band gap was found to be 3.37 eV.

4. Conclusion

Photoluminescent zinc oxide nanocrystals have been successfully synthesized via low temperature thermal decomposition of a new precursor zinc malonate, \([\text{ZnCH}_2\text{C}_2\text{O}_4] \cdot 2\text{H}_2\text{O}\) in the presence of surfactant stabilizers oleylamine and triphenylphosphine. The synthetic strategy adopted is simple and anticipated to serve as a paradigm to access different metal oxide nanomaterials.

Acknowledgments

Authors thank SAIF, NEHU, Shillong for instrumental facilities. DDP thanks University Grants Commission, Government of India for grants under Research Fellowship Scheme for Meritorious Students (RFSMS).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012.07.049.
References

Surfactant-controlled low-temperature thermal decomposition route to monodispersed phase pure tricobalt tetraoxide nanoparticles

Chira R. Bhattacharjee*, Debraj Dhar Purkayastha, Nirmalendu Das

Department of Chemistry, Assam University, Silchar 788011, India

A R T I C L E   I N F O

Article history:
Received 23 July 2012
Accepted 8 September 2012
Available online 15 September 2012

Keywords:
Nanoparticles
Electron microscopy
FT-IR
Raman
X-ray techniques

A B S T R A C T

A low-temperature synthesis of tricobalt tetraoxide, Co$_3$O$_4$ nanoparticles was accomplished via thermal decomposition of a new precursor cobalt malonate, [CoCH$_2$C$_2$O$_4$]. $\cdot$ $\text{H}_2\text{O}$ in presence of surfactant stabilizers oleylamine (C$_{18}$H$_{35}$NH$_2$) and triphenylphosphine ((C$_6$H$_5$)$_3$P). The synthesized nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR and Raman spectroscopy. Powder XRD pattern furnished evidence for a face-centered cubic structure of Co$_3$O$_4$ with average crystallite size of about 10 nm. TEM studies revealed Co$_3$O$_4$ nanoparticles to be monodispersed, mostly cubic having sizes 4–12 nm. Electron diffraction pattern indicates polycrystalline nature of the synthesized material. Raman spectrum showed four characteristic peaks of Co$_3$O$_4$ which further affirmed the phasic purity of the material.

1. Introduction

In recent years, cobalt oxides (CoO and Co$_3$O$_4$) nanomaterials have enjoyed pervasive attention due to their attractive multifunctional properties of technological interest. Devising synthetic strategies and optimizing reaction conditions for accessing high purity nanomaterials with specific features for developing new generation nanodevices with improved performances is a recurring theme of current research [1–7]. Particularly, tricobalt tetraoxide (Co$_3$O$_4$) nanomaterials are being extensively studied for their application in heterogeneous catalysis, lithium ion rechargeable batteries, solid-state sensors, electrochemical devices, field-emission materials, magnetic materials and so on [8–13]. Various strategies have been devised for the synthesis of Co$_3$O$_4$ nanomaterials. Feng et al. proposed a nitrate salt mediated route to synthesize Co$_3$O$_4$ nanocubes, and further achieved the size control of these nanocubes by varying reaction temperature and time [14,15]. Triangular, bullet-like and rod-like Co$_3$O$_4$ nanostructures have been prepared via the pyrolysis of metal fatty acid salts in a hydrocarbon solvent at above 320 °C [16]. Surfactants such as sodium dodecyl sulfate have been used as a capping agent to obtain 25 nm Co$_3$O$_4$ nanocubes by oxidizing freshly-reduced cobalt nanoparticles in the reaction system [17]. Co$_3$O$_4$ nanocrystals with different morphologies including spheres, cubes, and rhombohedra were accessed by employing differently charged surfactants and solvents in the solvothermal system [18].

Zhang et al. reported cetyltrimethylammonium bromide assisted synthesis of quasi-spherical cobalt oxide nanospheres of diameter 15–25 nm [19]. Despite such progress in synthetic methodologies, conventional synthetic methods often require some specially fabricated instruments, stringent conditions, and/or relatively high temperature. Large-scale production of phase pure Co$_3$O$_4$ nanomaterials at a relatively low temperature are thus a much sought after synthetic goal. The preparation of cobalt nanostructures by thermal decomposition of cobalt complexes becomes increasingly important mainly due to easy control of process conditions, particle size, crystal structure, and purity [20,21]. For instance, cobalt carbonyl [Co$_2$(CO)$_6$] has often been used to produce nanoparticles [22,23]. However, high cost and toxicity of cobalt carbonyl serve as a deterrent. As a sequel to our interest in accessing nanomaterials from simpler metal complexes, we report herein synthesis of phase pure monodispersed Co$_3$O$_4$ nanoparticles by thermal decomposition of a new precursor, cobalt malonate in presence of surfactant stabilizers oleylamine and triphenylphosphine.

2. Experimental

Materials and physical measurements: All chemicals used were of analytical grade and used as received. Cobalt malonate, [CoCH$_2$C$_2$O$_4$]. $\cdot$ $\text{H}_2\text{O}$ was prepared according to the literature procedure [24]. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrometer on KBr pellets. Elemental analysis was performed on a Heraeus Vario El III Carlo Erba 1108 elemental analyzer. Thermogravimetric analysis (TGA) was performed on a
Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in nitrogen atmosphere. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) with a scan speed of 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM2100 equipment. The sample powders were dispersed in n-hexane under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. The Raman spectrum was recorded on a RENISHAW RM1000B LRM using a 514.5 nm Ar+ laser as source.

Synthesis of Co₃O₄ nanoparticles: A quantity of 0.6 g of [CoCH₂C₂O₄·2H₂O] was taken in a round bottomed flask and 5 mL of oleylamine was added to it and heated for 1 h at 140 °C on an oil bath. A quantity of 5 g of triphenylphosphine was then added to the mixture and temperature increased to 240 °C. The purple color of the solution changed to black. The solution was aged at 240 °C for 1 h and cooled to room temperature. The black products were precipitated by adding ethanol and washed with ethanol several times. These products could be easily re-dispersed in nonpolar solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The synthesis described herein is a modified version of the procedure developed by Hyeon and others for metal and oxide nanoparticles that utilizes thermal decomposition of metal complexes [20,21,25]. In the present synthesis, Co₃O₄ nanoparticles were prepared by the thermal decomposition of cobalt malonate, [CoCH₂C₂O₄·2H₂O] as precursor in the presence of surfactant stabilizers oleylamine and triphenylphosphine. The as-obtained nanoparticles were characterized by XRD, TEM, FT-IR, and Raman studies. In order to confirm the precursor composition, elemental analysis was performed. The TGA (Fig. S1 in ESI) studies carried out under N₂ atmosphere revealed that cobalt malonate undergoes decomposition in four steps. The first one is the dehydration step which commences at 130 °C and completes at 230 °C corresponds to weight loss of 18.07% due to the removal of two water molecules. The second and third steps (280–390 °C) together accounts for 39.01% weight loss representing the decompositions of different reaction intermediates. The fourth and the final step (390–460 °C) corresponding to weight loss of 10.62% brings the total weight loss, after complete decomposition, to 67.7% of the original sample weight suggesting the formation of CoO. The major chemical reactions involved in the TGA are as follows:

\[
\text{CoCH}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{130-230°C} \text{COCH}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \quad (i)
\]
\[
\text{CoCH}_2\text{C}_2\text{O}_4 \xrightarrow{280-460°C} \text{CoO(s)} + 1/2\text{C}_2\text{H}_6(g) + \text{CO}_2(g) \quad (ii)
\]

The powder XRD pattern (Fig. 1) shows the material to be face-centered cubic Co₃O₄ (space group Fd3m, JCPDS File No. 78-1969). The diffraction peaks are clearly broad indicating reduced crystallite size. The average crystallite size obtained by Debye–Scherrer formula, using a Gaussian fit was found to be about 10 nm.

The TEM image (Fig. 2) of Co₃O₄ nanoparticles showed that the particles were monodispersed and mostly cubic in shape having sizes in the range 4–12 nm. The HRTEM image showed the lattice fringes between the two adjacent planes are 0.24 nm apart, which corresponds to the interplanar separation of the (3 1 1) plane of fcc Co₃O₄. Electron diffraction (ED) pattern showed polycrystalline nature of the material.

FT-IR spectrum was recorded for the obtained nanoparticles to discern the nature of the surface-coordinating organic capping groups that facilitate dispersion of the nanoparticles in organic solvents. FT-IR spectrum (Fig. S2 in ESI) shows bands attributable to the asymmetric and symmetric vibrational modes of –N–H around 3502 and 3283 cm⁻¹, respectively. The spectrum contains a number of weak peaks between 1000–1400 cm⁻¹ and 2800–3000 cm⁻¹ which appear due to the symmetric and asymmetric stretching vibrations of –CH₂, terminal –CH₃ and –CH of oleylamine (C₁₈H₃₅NH₂). The material exhibited two weak stretching vibrations at ~2925 and 2853 cm⁻¹ assignable to C–H stretching mode of oleylamine carbon chain. These results indicate that some oleylamine molecules were adsorbed on the surface of the Co₃O₄ nanoparticles. The sharp peak at ~1434 cm⁻¹ attributable to the phosphorus–phenyl stretching mode, v(P–Ph) also suggested occurrence of some triphenylphosphine (TPP) molecules in the material. Both oleylamine and triphenylphosphine thus played a crucial role in controlling the size and growth of the nanoparticles. The stabilization of metal nanoparticles with triphenylphosphine (TPP) is well documented in literature [20–23]. The spectrum also contains two strong
absorptions at ~698 and 579 cm\(^{-1}\) attesting the spinel structure of Co\(_3\)O\(_4\). The peak at 698 cm\(^{-1}\) arose due to the stretching vibration of Co(II)–O for Co\(^{2+}\) in tetrahedral environment while the peak at 579 cm\(^{-1}\) has been attributed to the stretching vibration of Co(III)–O for Co\(^{3+}\) in octahedral environment [26]. The Raman spectrum (Fig. 3) showed prominent peaks which correspond to \(E_g\) (482 cm\(^{-1}\)), \(F_{2g}\) (521 and 619 cm\(^{-1}\)), \(A_{1g}\) (690 cm\(^{-1}\)) modes of the crystalline phase of Co\(_3\)O\(_4\) and were consistent with the previous investigations [27,28]. Raman measurement further supported the XRD and HRTEM observations.

Choice of appropriate metal precursor and reaction condition is crucial to the synthesis of nano-metal oxides. Recently syntheses of nano-cobalt and cobalt oxide of particle size 15–35 nm were reported by thermal decomposition of cobalt–salicylaldehyde and cobalt–2-hydroxyacetophenone complexes [20,21]. In these studies, inert reaction condition was maintained to get metallic cobalt first and their successive aerial oxidation to cobalt oxide. In the present case Co\(_3\)O\(_4\) of particle size 4–12 nm was synthesized via direct thermal decomposition of cobalt malonate without any need for metallic cobalt formation or inert gas protection.

4. Conclusion

Monodispersed phase pure tricobalt tetraoxide nanoparticles of size 4–12 nm have been successfully synthesized by a low temperature thermal decomposition of a new precursor, [CoCH\(_2\)C\(_2\)O\(_4\)]\(_2\)H\(_2\)O in presence of surfactants oleylamine and triphenylphosphine. The current method is inexpensive, reproducible and may be employed for the large-scale synthesis of the cobalt oxide nanoparticles. The methodology can serve as a paradigm for accessing different metal oxide nanomaterials.

Acknowledgements

The authors are thankful to SAIF, NEHU, Shillong for providing instrumental facilities. DDP thanks University Grants Commission,
Government of India for providing grants under Research Fellowship Scheme for Meritorious Students (RFSMS). Prof. T. Pal, IIT, Kharagpur is thanked for help with the Raman spectral data.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012.09.031.

References

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Surfactant-mediated low-temperature synthesis of phase pure multiply twinned copper nanoparticles under non-inert condition via thermal decomposition of copper malonate

Chira R. Bhattacharjee*, Debraj Dhar Purkayastha, Nirmalendu Das

Department of Chemistry, Assam University, Silchar 788011, India

Abstract

Multiply twinned phase pure copper nanoparticles were successfully synthesized without any inert gas protection via a low-temperature thermal decomposition of a new precursor copper malonate, \([\text{CuCH}_2\text{C}_2\text{O}_4]/\text{C}_1\text{2H}_2\text{O}\) in the presence of surfactant stabilizers oleylamine \((\text{C}_{18}\text{H}_{35}\text{NH}_2)\) and triphenylphosphine \((\text{C}_6\text{H}_5)\text{3P}\). The synthesized nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR and UV–vis spectroscopy. Freshly prepared copper nanoparticles showed surface plasmon resonance (SPR) around 574 nm. TEM studies revealed a five-fold multiply twinned morphology of decahedral shape for the copper nanoparticles. Powder XRD pattern furnished evidence for a face-centered cubic crystal structure of pure metallic copper having an average crystallite size of about 35 nm.

1. Introduction

In recent years, copper nanoparticles have attracted enormous attention due to their excellent catalytic, optical and conducting properties [1–3]. Compared to other noble metals, copper possesses high electrical conductivity and is substantially cheaper. However, metallic copper is extremely susceptible to oxidation [4]. Anchoring suitable surfactant at the outer surface can offer protection from surface oxidation and also control the nucleation of particles by serving as a particle growth terminator. Copper nanoparticles have been synthesized via various routes such as the microemulsion technique [5], thermal decomposition [6], chemical reduction [7], polyol method [8], etc. As compared to conventional methods, the thermal decomposition method is much faster, cleaner and economical. Devising strategic synthetic protocol for preparing copper nanoparticles with controllable size and shape is anticipated to extend the application areas and also augment fundamental research in the field. Recently chemical synthesis of metallic copper and copper oxide nanoparticles via thermal decomposition of copper complexes was described [6,9]. However, the difficulty of copper reduction under mild reaction conditions or the easy oxidation of copper nanoparticles in air under ambient conditions in sharp contrast to noble metals like Au and Ag poses great challenges to afford pure metallic copper devoid of any oxide impurities. In order to protect copper nanoparticles against oxidation during preparation and storage, the reactions are often performed in non-aqueous media, at low precursor concentration, and in an inert atmosphere [10]. Very recently, we reported low-temperature surfactant-assisted synthesis of ZnO and Co\(_3\)O\(_4\) nanomaterials via thermal decomposition of zinc and cobalt malonates [11,12]. Besides nanoparticle size and composition, particle shape also plays a crucial role in achieving different applications. Multiply twinned particles (MTPs) are the naturally abundant seed morphology and this twin defect is often attributed to their higher reactivity trend [13,14]. Though leaving aside oxalates, thermal decomposition of various other metal dicarboxylates (malonates/succinates) were studied earlier [15–17], but till date there has not been any report on the preparation of metal nanoparticles from such precursors. Accordingly, we report herein the synthesis of multiply twinned, phase pure copper nanoparticles capped with surfactants oleylamine and triphenylphosphine (TPP) by thermal decomposition of a new precursor, copper malonate.

2. Experimental

Materials and physical measurements: All chemicals were of analytical grade and used without further purification. Oleylamine, TPP, n-hexane and ethanol were purchased from Aldrich. The precursor copper malonate, \([\text{CuCH}_2\text{C}_2\text{O}_4]/\text{C}_1\text{2H}_2\text{O}\) was prepared according to the literature procedure [16]. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrometer on KBr pellets. Elemental analyses were performed on a Heraeus Vario EL III.
undergoes rapid oxidative pyrolysis till a weight loss of 64.5% at 10 °C/min in air. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS DB-Advance powder X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) with a scan speed 2°/min. Transmission electron microscopy (TEM) images were obtained on a Jeol JEM2100 transmission electron microscope with an accelerating voltage of 200 kV. The sample powders were dispersed in n-hexane, under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Electronic spectrum was taken on a Shimadzu 1601 PC UV–vis scanning spectrophotometer.

Synthesis of copper nanoparticles: 0.6 g of [CuCH$_2$C$_2$O$_4$]–2H$_2$O was taken in a round bottomed flask and 5 ml of oleylamine was added to it and heated for 1 h at 140 °C on an oil bath to get [CuCH$_2$C$_2$O$_4$]–oleylamine complex. Triphenylphosphine (5 g) was then added to the resultant solution and temperature was raised to 240 °C. The green solution changed to red, indicating the formation of metallic copper. The reddish solution was aged at 240 °C for 1 h and cooled to room temperature. The reddish products were precipitated by adding excess ethanol to the solution. The products were washed with ethanol several times. These products could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The principle of synthesis is based on a modified procedure developed by Hyeon and others for the synthesis of metal and oxide nanocrystals [6,9,18]. In the current synthesis (Scheme 1), copper nanoparticles were prepared by the thermal decomposition of copper malonate, [CuCH$_2$C$_2$O$_4$]–2H$_2$O as precursor in the presence of surfactants oleylamine and triphenylphosphine. The as-synthesized nanoparticles were characterized by XRD, TEM, FT-IR, and UV–vis studies. In order to ascertain the precursor composition, elemental analysis was performed. The thermal decomposition behavior of the neat precursor (Fig. S1 in ESI) revealed that copper malonate undergoes decomposition in two steps. The first step is dehydration which commences at 100 °C and is completed at 150 °C as indicated by a weight loss of 16%. The anhydrous compound remains stable up to 225 °C and then undergoes rapid oxidative pyrolysis till a weight loss of 64.5% at 250 °C suggesting the formation of Cu$_2$O. However, Cu$_2$O formed underwent oxidation up to 315 °C accompanied by an increase of weight approximately 4% suggesting the formation of CuO. However, use of surfactant molecules like oleylamine and TPP as capping ligands lowered the decomposition temperature of copper malonate to 240 °C yielding copper nanoparticles.

The powder XRD pattern (Fig. 1) shows the material to be face-centered cubic Cu (space group Fm3m, JCPDS File no.89-2838). No peak attributable to possible impurities such as Cu$_2$O/CuO were observed indicating the formation of phase pure metallic Cu. The average crystallite size estimated using the Debye–Scherer formula was found to be about 35 nm.

The TEM images (Fig. 2) show typically multiply twinned copper nanoparticles. A multiply twinned boundary at the center of copper nanoparticles can be clearly observed from different angles; the lattice plane is separated by a twin boundary indicated as a line on the image. Formation of multiply twinned copper nanoparticles has been documented earlier [19,20]. Initially, copper ions (Cu$^{2+}$) are reduced to metallic copper (Cu$^0$), which assemble together to form nuclei. At this point the available thermal energy causes the structure of the nuclei—a miniscule cluster of few metal atoms to fluctuate, allowing defects to form or be removed depending upon their energetic favorability [21]. It has been argued that most copper nuclei incorporate twin boundary defects because such defects enable a lower surface energy [22]. As the nuclei grow into a seed, changes in the defect structure become too costly relative to the available thermal energy which confines the particles to a fixed morphology. This process results in a Boltzmann-like distribution of multiply twinned, singly twinned, and single-crystal seeds, with the five-fold twinned decahedron being the lowest in free energy thus constituting the most dominant morphology [23]. In summary, the growth of a copper nanocrystal during the synthesis involves three distinct stages: nucleation (reduction of metal ions to zerovalent atoms), seeding (evolution from nuclei to seeds), and growth (evolution from seeds to nanocrystals) [19]. Bigger particle sizes obtained from TEM (40–120 nm) as compared to the average crystallite size from XRD is attributed to the polycrystalline nature of the nanoparticles. From HRTEM image (Fig. 2(c)) two types of lattice fringes were observed having interplanar distance of 0.18 nm and 0.21 nm which correspond to (200) and (111) planes of fcc-copper, respectively. The electron diffraction (ED) pattern (Fig. 2(d)) indicated the polycrystalline nature of the nanoparticles.

FT-IR spectrum (Fig. S2 in ESI) shows bands attributed to the asymmetric and symmetric vibrational modes of −N−H around 3489 and 3257 cm$^{-1}$, respectively. The peaks between 1000–1400 cm$^{-1}$ and 2800–3000 cm$^{-1}$ arose due to the symmetric and asymmetric vibrations of O−H stretch

![Scheme 1. Illustration of the formation of copper nanoparticles.](image-url)
stretching vibrations of –CH$_2$, terminal –CH$_3$ and =CH of oleylamine. The C–H and C–N stretching mode of oleylamine appeared at $\nu$2919, 2853 and 1182 cm$^{-1}$. The phosphorus–phenyl stretching mode, $\nu$(P–Ph) of TPP was observed around 1434 cm$^{-1}$. TPP was widely used in the synthesis of phosphine-stabilized metal nanoparticles [6,9,24]. The oleylamine and TPP served as the capping ligands that controlled growth.

Copper nanoparticles generally show SPR around 600 nm [25]. The UV–vis spectrum (Fig. 3) of freshly synthesized copper nanoparticles showed SPR around 574 nm. This blue shift matches with observations reported earlier [6]. Owing to the presence of the surfactants, the copper nanoparticles thus obtained can easily be dispersed in n-hexane (inset of Fig. 3) forming a red color. It is noteworthy that during the copper nanoparticle synthesis, no inert conditions were required to be maintained. The surfactant oleylamine is believed to inhibit oxygen diffusion to the nanoparticle surface thus preventing oxidation and resulting in metallic copper instead of copper oxide. However, as evident from the TGA profile, thermal decomposition of copper malonate without surfactants ultimately yields CuO.

4. Conclusion

Multiply twinned phase pure copper nanoparticles have been successfully synthesized via low-temperature thermal decomposition of copper malonate, [CuCH$_2$C$_2$O$_4$]$\cdot$2H$_2$O. Oleylamine, herein, plays a two-fold role—as reaction medium and stabilizer, which prevents oxidation of copper nanoparticles. The current method employed is an inexpensive reproducible process for the synthesis of multiply twinned copper nanoparticles.

Acknowledgments

Authors are thankful to SAIF, NEHU, Shillong for providing instrumental facilities. DDP thanks University Grants Commission,
Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2012.12.047.

References


Government of India for Research Fellowship Scheme for Meritorious Students (RFSMS).
Surfactant-assisted low-temperature synthesis of monodispersed phase pure cubic CoO solid nanoparallelepipeds via thermal decomposition of cobalt(II) acetylacetonate

Debraj Dhar Purkayastha, Bedabrata Sarma, Chira R. Bhattacharjee*

Department of Chemistry, Assam University, Silchar 788011, Assam, India

A R T I C L E  I N F O

Article history:
Received 30 March 2013
Accepted 25 May 2013
Available online 31 May 2013

Keywords:
Nanoparticles
Electron microscopy
FT-IR
XRD

A B S T R A C T

Cubic CoO solid nanoparallelepipeds have been successfully synthesized via a low-temperature thermal decomposition of cobalt(II) acetylacetonate in the presence of a relatively inexpensive surfactant octadecylamine (C_{18}H_{37}NH_{2}). Synthesis of cubic CoO nanoparallelepipeds via thermal decomposition of cobalt(II) acetylacetonate has also been reported [12]. In contrast, reaction of cobalt(III) acetylacetonate with different amines have been strategically utilized for selective preparation of hexagonal and cubic CoO nanoparticles [13,14]. Very recently, we have reported surfactant-assisted low-temperature thermal decomposition of cobalt malonate to afford tricobalt tetroxide nanoparticles [15]. As a sequel to our continued effort in devising convenient synthetic approaches for nanomaterials using simpler metal precursors we report herein the synthesis of cubic CoO solid nanoparallelepipeds via a low-temperature thermal decomposition of cobalt(II) acetylacetonate in the presence of a relatively inexpensive surfactant, octadecylamine (C_{18}H_{37}NH_{2}). Synthesis of cubic CoO nanoparallelepipeds via thermal decomposition of cobalt(II) acetylacetonate do not appear to have been accomplished earlier.

1. Introduction

Cobalt monoxide (CoO) nanoparticles have long been utilized as catalyst in organic reactions, gas sensors, anode material in lithium-ion battery, and magnetic data storage devices [1—5]. It is well known that CoO typically crystallizes into two stable structures viz. hexagonal wurtzite phase (space group: P63mc) with tetrahedral Co^{2+} and cubic rock salt phase (space group: Fm3m) with octahedral Co^{2+} ions. Out of these two, the cubic CoO structure is thermodynamically stable, but the hexagonal structure is relatively unstable and can easily change into cubic structure by application of heat and pressure [6,7]. In recent years, copious synthetic methods for the cubic and hexagonal CoO phase have been reported. For example, synthesis of cubic CoO nanocrystals with tetrahedral shapes via oxidation of Co(OH)_{3} in toluene in the presence of sodium bis(2-ethylhexyl) sulfosuccinate at 130 °C has been documented [8]. Cubic CoO nanoparticles of sizes 4.5—18 nm was accessed by thermal decomposition of cobalt(II) cupferronate in decaline under solvothermal conditions [9]. A series of cubic CoO nanocrystals of various morphologies and sizes via thermal decomposition of cobalt(II) oleate complex at 280—320 °C have been synthesized [10]. As a case in point, pencil-shaped hexagonal CoO nanorods have also been accessed by the thermal decomposition of cobalt(II) oleate complex [11].

2. Experimental

2.1. Materials and physical measurements

All chemicals used were of analytical grade and used as received. The precursor cobalt(II) acetylacetonate, [Co(C_{5}H_{7}O_{2})_{2}(H_{2}O)] was prepared according to the literature procedure [16]. FT-IR spectra were recorded on a Shimadzu Varian 4300 spectrometer on KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in nitrogen atmosphere. X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation.
(λ = 1.5418 Å) with a scan speed 2 °/min. Transmission electron microscopy (TEM) images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in n-hexane under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Energy dispersive X-ray (EDX) pattern was recorded on a JEOL, JED2300 equipment.

2.2. Synthesis of CoO solid nanoparallelepipeds

An amount of 0.6 g of \([\text{Co} (\text{C}_5\text{H}_7\text{O}_2)_2 (\text{H}_2\text{O})_2]\) and 10 ml of octadecylamine was heated in a round bottomed flask for 1 h at 140 °C on an oil bath to form \([\text{Co} (\text{C}_5\text{H}_7\text{O}_2)_2 (\text{octadecylamine})_2]\) complex. On further heating to 240 °C the initial pink color of the solution turned brown. The solution was aged at 240 °C for 1 h and cooled to room temperature. A brown product was precipitated by adding excess ethanol to the solution. The product was washed with ethanol several times and could be easily re-dispersed in nonpolar organic solvents like n-hexane or toluene (Scheme 1).

3. Results and discussion

The synthesis described herein is a modified version of the procedure developed by Park and others for metal and oxide nanomaterials that employs thermal decomposition of transition metal complexes [17–19]. In the current synthesis (Scheme 1), CoO solid nanoparallelepipeds were synthesized by the thermal decomposition of cobalt(II) acetylacetonate, \([\text{Co} (\text{C}_5\text{H}_7\text{O}_2)_2 \text{H}_2\text{O})_2]\) precursor in the presence of surfactant octadecylamine. Octadecylamine served both as reaction media and capping agent. It effectively controlled the size of the nanoparallelepipeds by limiting the growth at the stage of nucleation. Since the surfaces of the nanoparallelepipeds were capped with octadecylamine, these could be well dispersed in most hydrophobic solvents. Recently, octadecylamine was utilized effectively as reaction solvent, reducing and capping agent during the synthesis of various nanocrystals including metals, mixed metal oxides, metal/metal oxide heterostructures, intermetallics, and alloys [20]. The synthesized nanoparallelepipeds were characterized by XRD, TEM, FT-IR, and EDX studies. The TGA curve revealed that cobalt(II) acetylacetonate undergoes decomposition in three steps. The first is the dehydration step which commences at 70 °C and completes at 105 °C accompanied by a weight loss of 13.9%, due to the loss of two water molecules. The second and third steps (120–425 °C) together account for weight loss of 76.2%, corresponding to the removal of two acetylacetonate molecules leading to the formation of CoO. About 15% of the sample escaped without pyrolysis. The presence of CoO as residue has been confirmed by powder XRD. However, the long hydrocarbon chain of surfactant octadecylamine exerted greater steric hindrance that lowered the decomposition temperature of cobalt(II) acetylacetonate precursor substantially to 240 °C affording CoO nanomaterials. Moreover, no inert condition was maintained during the synthesis. The surfactant octadecylamine formed a protective coating around the synthesized CoO nanoparticles which prevented any further oxidation.

The FT-IR spectrum of cobalt(II) acetylacetonate (Fig. 1(a)) showed a broad band centered at about 3422 cm\(^{-1}\) due to \(\nu(\text{O–H})\) of coordinated water. The peaks at 2987 and 2937 cm\(^{-1}\) arose due to the C–H stretching vibration \(\nu(\text{C–H})\) of the methyl group. Coupling of the stretching vibrational modes of \(\text{C=C}\) and \(\text{C=N}\) groups was observed around 1613 and 1518 cm\(^{-1}\). Band at 574 cm\(^{-1}\) can be assigned to the stretching vibrations of Co–O. The FT-IR spectrum of the synthesized CoO (Fig. 1(b)) showed a strong band at 607 cm\(^{-1}\), characteristics of Co–O stretching vibrational mode. Besides, C–N stretching mode of octadecylamine was observed at 1123 cm\(^{-1}\). A weak broad band (3100–3700 cm\(^{-1}\)) was observed due to the N–H stretching, those at 2919 and 2853 cm\(^{-1}\) attributable to the C–H stretching mode of octadecylamine, clearly indicated some octadecylamine molecules being adsorbed on the surface of the synthesized CoO nanoparallelepipeds. It is pertinent to mention here that at the experimental temperature of 240 °C, most of the surfactant molecules (octadecylamine) were decomposed. The calcined material was thoroughly washed with ethanol several times to remove any residual surfactant molecules. However, FT-IR signatures for octadecylamine arose from coated surfaces of CoO nanoparallelepipeds.

The XRD pattern (Fig. 2) of the synthesized material showed diffraction peaks which can be well indexed to the face-centered cubic structure of CoO (space group Fm3m, JCPDS File No. 75-0533). No peak attributable to impurities were observed. The average crystallite size of CoO estimated by the Debye–Scherrer formula, using a Gaussian fit was about 20 nm.
The TEM image (Fig. 3) of the synthesized CoO nanoparticles showed that the particles were monodispersed with no agglomerations. The particles possess parallelepiped shape and have sizes in the range of 10—20 nm. The HRTEM image showed the lattice fringes between the two adjacent planes to be 0.21 nm apart which corresponds to the interplanar separation of the (200) plane of face-centered cubic CoO. Polycrystallinity of the material was confirmed from the electron diffraction (ED) pattern. The EDX pattern recorded on the synthesized material indicated the presence of C, Co and O atoms which proved formation of octadecylamine capped CoO. The EDX measurement thus augmented the results obtained from XRD and HRTEM.

Phase selective preparation of hexagonal and cubic CoO nanoparticles via thermal decomposition of cobalt(II) acetylacetonate in the presence of surfactant oleylamine under an inert atmosphere has been documented recently [21]. Green hexagonal CoO nanoparticles were obtained at a reaction temperature of 200 °C. Addition of water and maintaining the reaction temperature at 250 °C alters the reaction pathway selectively generating brown cubic CoO nanoparticles. In the current synthesis no green product could be isolated at a reaction temperature of 200 °C rather thermodynamically more stable brown cubic CoO nanoparallelepips could be accessed only at a reaction temperature of 240 °C without any requirement of water addition or inert gas protection.

4. Conclusion

Synthesis of monodispersed phase pure cubic CoO nanoparticles with solid parallelepiped morphology of size 10—20 nm have been accomplished by a low-temperature thermal decomposition of cobalt (II) acetylacetonate in the presence of a relatively inexpensive surfactant octadecylamine. The surfactant octadecylamine played dual role as reaction media and capping agent in the synthesis. The synthetic strategy adopted herein is simple and should be readily extendable to access other metal oxide nanomaterials.
Acknowledgment

Authors thank SAIF, NEHU, Shillong for TEM facilities. DDP thanks University Grants Commission, Government of India for Research Fellowship Scheme for Meritorious Students (RFMS). We are thankful to DBT e-Library Consortium (DeLCON) of Bioinformatics Center, Assam University, Silchar.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2013.05.122.

References

Synthesis and antioxidant activity of cupric oxide nanoparticles accessed via low-temperature solid state thermal decomposition of bis(dimethylglyoximato)copper(II) complex

Debraj Dhar Purkayastha, Nirmalendu Das, Chira R. Bhattacharjee*

Department of Chemistry, Assam University, Silchar 788011, India

Abstract

Cupric oxide (CuO) nanoparticles have been successfully synthesized via low-temperature thermal decomposition of bis(dimethylglyoximato)copper(II) complex. The synthesized nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS) and Raman spectroscopy. The powder XRD pattern furnished evidence for a monoclinic structure of CuO with average crystallite size 28.9 nm. The TEM image showed aggregation of some quasi-spherical nanoparticles. The Raman spectrum showed three characteristic modes of CuO which further affirmed the phasic purity of the obtained material. The CuO nanoparticles studied in an in vitro system using the modified diphenylpicrylhydrazyl (DPPH) method exhibited pronounced antioxidant activity.

1. Introduction

Current interests in transition metal oxide nanomaterials have been spurred by their unique properties and various potential applications. As a case in point, cupric oxide (CuO) nanoparticles have shown potential to replace noble metal catalysts for carbon monoxide oxidation [1] and often found use as antimicrobial agents [2], semiconductors [3], heat transfer fluids in machine tools [4], intrauterine contraceptive devices [5] etc. Besides, CuO nanomaterials may be quite useful as highly proficient biosensors owing to their high surface area, suitable electrochemical activity, and electron transfer capability [6]. CuO nanoparticles have been efficiently utilized as peroxidase mimics for detection of hydrogen peroxide and glucose [7]. Antioxidant properties of copper, nickel and iron oxide nanoparticles were studied rather recently [8–11]. Synthesis of CuO nanomaterials by different methods such as sonochemical [12], electrochemical [13], sol–gel [14], thermal decomposition [15] etc. are on record. However, devising polymer- or surfactant-free mild and simple strategies for accessing metal/metal oxide nanomaterials is crucial to the development of newer methods. Earlier, a low-temperature hydrothermal method based on in situ solution phase formation of copper dimethylglyoximate complex has been employed to access CuO microcrystals [16]. We report herein a low-temperature solid state thermal decomposition of bis(dimethylglyoximato) copper(II) complex as an access to cupric oxide nanoparticles and their antioxidant activity. In the current synthesis, the complex bis(dimethylglyoximato)copper(II) served as an ideal precursor due to its relatively high volatility and conveniently low decomposition temperature.

2. Experimental

Materials and physical measurements: All chemicals used were of analytical grade and used as received. The precursor bis(dimethylglyoximato)copper(II), [CuC₈H₁₄N₄O₄] was prepared according to the literature procedure [17] with little modification. FT-IR spectrum was recorded on a Shimadzu Varian 4300 spectrometer on KBr pellets. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min in air. Powder X-ray diffraction measurement was done on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) with a scan speed of 2°/min. Transmission electron microscopy images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in ethanol under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. The particle size distribution was determined by dynamic light scattering technique using a Delsa Nano S, Beckman Coulter, USA. Raman spectrum was recorded on a RENISHAW RM1000B LRM using

*Corresponding author. Tel.: +91 3842 270848; fax: +91 3842 270342.
E-mail address: crbhattacharjee@redifmail.com (C.R. Bhattacharjee).

http://dx.doi.org/10.1016/j.matlet.2014.02.097
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a 514.5 nm Ar⁺ laser excitation source. Shimadzu 1601 PC UV-visible spectrophotometer was used to determine the variation in DPPH concentration at 517 nm.

**Synthesis of CuO nanoparticles:** An amount of 0.995 g (5 mM) of Cu(CH₃COO)₂·H₂O and 1.16 g (10 mM) of dimethylglyoxime (DMG) was dissolved in ethanol separately. Then the metal solution was added dropwise to the DMG solution and stirred for 2 h. The brown product thus obtained was filtered, washed with ethanol several times and dried. The synthesized bis(dimethylglyoximato)copper(II) complex is then calcined in a muffle furnace at 220 °C for 2 h to yield black CuO nanoparticles (Scheme 1).

**Assessment of antioxidant activity:** The antioxidant activity of the CuO nanoparticles was assessed using a modified DPPH method [18]. At first 100 mg of the powdered CuO nanoparticles was taken in a test tube and to it 3 mL, 100 μM methanolic solution of DPPH was added. To enhance the surface reaction between the nanoparticles and the DPPH reagent, the mixture was further sonicated and kept in the dark. After centrifugation at 10,000 rpm the supernatant was collected and absorbance was measured at 517 nm. A DPPH control was also measured as reference. The aforementioned procedure was followed to examine the time dependent DPPH scavenging at an interval of 5, 15, 30, 45 and 60 min. The percentage scavenging was calculated using the formula

\[
\text{DPPH scavenging} (%) = \left( \frac{A_r - A_t}{A_r} \right) \times 100
\]

where \(A_r\) and \(A_t\) are absorbances of the control DPPH and DPPH with the CuO nanoparticles at 517 nm, respectively. For evaluating SC50 (the amount of samples required to scavenge 50% of DPPH) a similar procedure is adopted with 10, 20, 30, 50, 70, and 100 mg of the CuO nanoparticles and absorbances were recorded after 30 min.

3. Results and discussion

The synthesized bis(dimethylglyoximato)copper(II) complex is characterized by TGA and FT-IR. The nanoparticles were characterized by powder XRD, TEM, DLS, and Raman studies. The antioxidant activity of the CuO nanoparticles was studied in an *in vitro* system, using modified DPPH method as reported by Serpen et al. [18] for insoluble solid materials. The TGA curve of the complex (Fig. 1(a)) showed a single step decomposition pathway. The weight loss in the temperature range 210–215 °C occurred due to the removal of two dimethylglyoximinate molecules and the subsequent formation of CuO. About 15% of the sample escaped without pyrolysis. The reaction was violent and difficult to recognize. The presence of CuO nanoparticles has been confirmed by powder XRD study. The FT-IR spectrum of bis(dimethylglyoximato)copper(II) complex (Fig. 1(b)) with a square-planar structure showed characteristic bands in the range 1600–450 cm⁻¹ [19]. The band at 3323 cm⁻¹ is probably due to an intramolecular hydrogen bond of the type H–O···H. Oximes normally show an absorption band in the region 1700–1600 cm⁻¹ due to C=O stretching vibrations. This band is, however, shifted to lower frequency (1540 cm⁻¹) in the spectrum of bis(dimethylglyoximato)copper(II) complex.

The powder XRD pattern (Fig. 1(c)) of the synthesized material showed diffraction peaks which can be indexed to the typical monoclinic structure of CuO (space group C2/c, JCPDS File no. 89-5896), and no extra peaks of other phases were observed. The average crystallite size estimated by the Debye–Scherrer formula, \(d = \frac{0.9\lambda}{\beta\cos\theta}\) using a Gaussian fit was found to be 28.9 nm.

The TEM image (Fig. 2(a)) showed some quasi-spherical nanoparticles aggregated together. The HRTEM image (Fig. 2(c)) showed the lattice fringes between the two adjacent planes are 0.253 nm apart, which is equal to the inter-planar separation of the (002) plane of the standard CuO. The electron diffraction (ED) pattern (Fig. 2(d)) showed the polycrystalline nature of the nanoparticles.

The average particle size obtained from DLS study (Fig. S1 in ESI) was found to be 79.2 nm. The Raman spectrum (Fig. 1(d)) exhibited prominent peaks which correspond to \(A_g(295\ \text{cm}^{-1})\) and \(B_g(343\ \text{and} \ 629\ \text{cm}^{-1})\) modes of the crystalline phase of CuO and were consistent with the previous investigations [20,21]. The Raman spectral data further augmented the results obtained from XRD and HRTEM.

The control DPPH does not show any change of absorbance with time. However, DPPH with CuO nanoparticles showed a steady decrease of absorbance at 517 nm (Fig. 3(a)). The DPPH scavenging percentage can be calculated from the decrease of absorbance at 517 nm, which corresponds to the quantity of DPPH in the methanolic solution. It is clear from Fig. 3(a) that after 30 min and 60 min more than 50% and 80% of the DPPH got scavenged for 100 mg of the CuO nanoparticles. The SC50 value was ascertained graphically (Fig. 3(b)) and was found to be 46.91 mg. The observed antioxidant activity is attributed to the neutralization of free-radical character of DPPH by the transfer of an electron [9,22].

Recently, antioxidant activity of CuO nanoparticles obtained via thermal decomposition of Cu₄(SO₄)(OH)₆ precursor was studied [8]. High decomposition temperature (600 °C) for synthesis and relatively larger amount of sample requirement for DPPH scavenging were some of the inherent limitation of this process. In contrast, the present synthesis involves much lower decomposition temperature (220 °C) and the DPPH scavenging (%) of CuO nanoparticles thus obtained compare well with the reported value [8]. The reported SC50 values of sonicated iron and nickel oxide nanomaterials are 52.88 mg and 7.49 mg, respectively [10]. Thus SC50 value of iron oxide is higher and that of nickel oxide is quite lower than the presently synthesized CuO nanoparticles. Barring these few reports including the present one there appears to be virtually no other documented work that deals with the antioxidant activity of metal...
Fig. 1. (a) TGA curve (b) FT-IR spectrum of bis(dimethylglyoximato)copper(II) complex (c) XRD pattern and (d) Raman spectrum of CuO nanoparticles.

Fig. 2. (a) TEM image (b and c) HRTEM images and (d) ED pattern of CuO nanoparticles.
oxide nanoparticles. Pertinent here is to mention that though copper is an essential biological element, CuO nanoparticles are known to induce hepatotoxicity and nephrotoxicity in rats and human laryngeal epithelial cells [5].

4. Conclusion

Cupric oxide nanoparticles were accessed via thermal decomposition of a new precursor bis(dimethylglyoximato)copper(II) complex. The synthetic methodology adopted is simple and afforded high purity material at a relatively lower decomposition temperature. The nanomaterial thus obtained has been demonstrated to be a potent antioxidant.

Acknowledgment

Authors are thankful to SAIF, NEHU, Shillong for providing TEM facility. DDP thanks the University Grants Commission, Government of India for Research Fellowship Scheme for Meritorious Students (RFSMS). Prof. T. Pal, IIT, Kharagpur is thanked for help with the Raman spectral data. We are thankful to DBT e-Library Consortium (DeLCON) of Bioinformatics Centre, Assam University.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.02.097.

References

Surfactant-free thermal decomposition route to phase pure tricobalt tetraoxide nanoparticles from cobalt(II)-tartrate complex

Chira R. Bhattacharjee · Debraj Dhar Purkayastha · Nirmalendu Das

Received: 31 October 2012 / Accepted: 3 December 2012 / Published online: 12 December 2012 © Springer Science+Business Media New York 2012

Abstract Tricobalt tetraoxide nanoparticles have been successfully synthesized following a ‘bottom-up’ approach by surfactant-free thermal decomposition of cobalt(II)-tartrate complex obtained by a modified sol–gel route. The synthesized complex was characterized by Fourier transform infrared (FT-IR) spectroscopy, elemental and thermogravimetric-differential thermal analysis (TG–DTA). The nanoparticles were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman studies. The powder XRD pattern furnished evidence for a face-centered cubic structure of Co₃O₄. With the rise in calcination temperature from 400 through 500 to 600 °C, the average crystallite sizes of Co₃O₄ were found to increase from 28 through 36 to 46 nm. The TEM image revealed a faceted morphology of the as-synthesized Co₃O₄ nanoparticles. The high-resolution TEM image indicated the interplanar separation to be 0.28 nm which corresponds to the (220) plane in face-centered cubic Co₃O₄. The electron diffraction (ED) pattern showed single-crystalline nature of the synthesized nanoparticles. Raman spectrum showed four characteristic peaks of Co₃O₄ which further confirmed the phasic purity of the material.

Keywords Nanoparticles · Cobalt oxides · Chemical synthesis · Electron microscopy · X-ray diffraction

1 Introduction

Nanostructured cobalt oxides (CoO and Co₃O₄) have attracted great interest in both fundamental as well as applied research domains owing to their interesting physical and chemical properties and also promising applications in nanodevices [1–5]. Tricobalt tetraoxide (Co₃O₄) nanomaterials, in particular, are being intensely investigated for their applications in heterogeneous catalysis [6], sensors [7], anode materials in lithium ion rechargeable batteries [8], energy storage [9], magnetic materials [10], and so on. Different synthesis techniques such as sol–gel, polyol, solvo-thermal/hydrothermal, thermal decomposition etc. have been employed for the preparation of Co₃O₄ nanomaterials [11–15]. Thermal decomposition technique, among others, is considered a promising ‘bottom-up’ process as it is simple, cost-effective and affords high purity materials. High boiling point surfactants/solvents such as octadecylamine, oleic acid, oleylamine, 1,2-hexadecane diol among several others used for preventing agglomeration of nanoparticles in such method complicate the synthetic process affecting the purity of the final product. Additional purification steps to remove residual surfactant molecules from the nanoparticle surface are quite cumbersome [16–18]. Cobalt carbonyl, Co₂(CO)₈, has often been used as precursor to obtain nanoparticles [19, 20]. High cost and toxicity of cobalt carbonyl, however, posed limitations to such synthetic protocol. Only very recently we reported surfactant-controlled low temperature synthesis of monodispersed phase pure Co₃O₄ nanomaterials [21]. Conventionally, the sol–gel method synthesizes the precursor through hydrolysis of organic alkoxide to form sol and gelation [22]. Modified sol–gel method, however, relies on the formation of a dispersive gel precursor through the coordination of a monodentate ligand with the metal ion [23]. Finally, the nanoparticles are accessed by removing the
carbon based organic ligands via thermal decomposition. In “solvothermal” protocol differently charged surfactants and solvents are employed for accessing Co$_3$O$_4$ nanomaterials of varying sizes and morphologies [24]. One major disadvantage in such method is that the surfactant or solvent molecules caps the surface of the nanomaterials and obtaining pure products becomes extremely difficult. Surface-adsorbed surfactants not only inhibit catalytic and sensing applications or other surface related phenomena of nanoparticles but also add to the toxicity of such materials. Devising surfactant-free synthetic routes for obtaining pure nanoparticles therefore currently constitute a much sought after goal. Prompted by this, we report herein a surfactant-free synthesis of phase pure Co$_3$O$_4$ nanoparticles by thermal decomposition of cobalt(II)-tartrate complex obtained by a modified sol–gel route.

2 Experimental

2.1 Materials and physical measurements

All chemicals used were of analytical grade and used as received. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrometer on KBr pellets. Elemental analyses were performed on a Heraeus Vario EL III Carlo Erba 1108 elemental analyzer. Cobalt content was analyzed by AAS technique using a Perkin Elmer ANA-Analyst 200 model equipment. Thermogravimetric-differential thermal analysis (TG–DTA) was performed in air on a Perkin Elmer Pyris Diamond thermal analyzer maintaining flow rate of 20 mL/min and heating rate of 10 °C/min. Powder X-ray diffraction (XRD) measurements were carried out on a Bruker AXS D8-Advance powder X-ray diffractometer with Cu-K$_\alpha$ radiation (\(\lambda = 1.5418\) Å) with a scan speed of 2°/min. Transmission electron microscopy (TEM) images were obtained on a JEOL, JEM2100 equipment. The sample powders were dispersed in ethanol under sonication and TEM grids were prepared using a few drops of the dispersion followed by drying in air. Raman spectrum was recorded on a RENISHAW RM1000B LRM using a 514.5 nm Ar$^+$ laser excitation source.

2.2 Synthesis of Co$_3$O$_4$ nanoparticles

1.46 g (5 mM) of Co(NO$_3$)$_2$·6H$_2$O and 0.75 g (5 mM) of tartaric acid were dissolved in a minimum volume of distilled water separately and mixed together. The mixed solution was then stirred and maintained at \(\sim 70^\circ\)C till a pink colored viscous residue obtained. The residue was kept at 120 °C for 4 h and thoroughly ground. The as-obtained gel precursor was then calcined in a muffle furnace for 2 h at 400, 500 and 600 °C separately when a black powdered solid was obtained in each case. The synthetic procedure is illustrated in Scheme 1.

3 Results and discussion

Following an elicit reaction strategy (Scheme 1), a cobalt-tartrate (1:1) sol formed initially at 70 °C is converted into a dry gel at 120 °C and ground before calcining at and beyond 400 °C. As the composition of the precursor complex is [Co(C$_4$H$_4$O$_6$)]·0.5 H$_2$O, the optimum ratio of reactants (Co$^{2+}$:tartaric acid) needed for the gel formation is 1:1. We, however, checked conducting the reaction using 1:2 ratio as well and noted that though the gel formation took place at enhanced metal:tartrate ratio, its TG–DTA profile indicated presence of metal-free excess tartaric acid and nanoparticles accessed from this precursor also revealed faceted morphology but no discernible size variation was noticed either in XRD or TEM studies. The tartrate ligand prevented any close contact of individual particles due to its steric effects thus reducing agglomeration substantially without the need for any high boiling surfactants/solvents. A low calcination

![Scheme 1](https://example.com/scheme1.png)

Scheme 1 Illustration of the formation of Co$_3$O$_4$ nanoparticles
temperature favored reduced size Co$_3$O$_4$ nanoparticles. The synthesized Co(II)-tartrate complex, [Co(C$_4$H$_4$O$_6$)]0.5 H$_2$O was characterized by FT-IR, elemental, AAS, and TG–DTA studies. The FT-IR spectrum of d-tartaric acid showed a sharp peak at 1,750 cm$^{-1}$ due to free carboxyl groups [25, 26]. Both the carboxylic acid are alike. The spectrum of Co(II)-tartrate (Fig. S1 in ESI), showed a single sharp peak at 1,613 cm$^{-1}$. The shift of this peak to lower wave numbers attest the occurrence of the coordinated carboxylate group [26, 27]. A rather sharp peak indicates that both the coordinated carboxylate groups are equivalent. The spectrum of d-tartaric acid also showed an absorption around 1,130 cm$^{-1}$ corresponding to a secondary alcohol group, C–O stretching [26]. This band is shifted to lower wave numbers with a split (1,069 and 1,116 cm$^{-1}$) in the spectrum of Co(II)-tartrate complex. A third diagnostic peak is found at 1,460 cm$^{-1}$ (O–H bending) in the spectrum of tartaric acid which does not undergo significant change in the spectrum of Co(II)-tartrate complex. This indicates that both the alcoholic hydroxyl groups remained intact without any loss of protons.

Anal. Calc: for [Co(C$_4$H$_4$O$_6$)]0.5 H$_2$O (%): C, 22.22; H, 2.31; Co, 27.31. Found: C, 22.51; H, 2.69; Co, 26.96.

The TG–DTA of the complex (Fig. 1) carried out in air exhibited a two step decomposition pathway. The first step is the endothermic process which commences at 40 $^\circ$C and completes at 170 $^\circ$C due to dehydration as indicated by a weight loss of 4.6 % (loss of 0.5 H$_2$O). The second step in the temperature range 170–345 $^\circ$C accompanied by a weight loss of 63.3 %, corresponding to the broad exothermic peak between 265 and 345 $^\circ$C is due to the continuous oxidation of organic substance and the formation of Co$_3$O$_4$. This accounts for the choice of ~400 $^\circ$C as the optimum decomposition temperature for accessing the Co$_3$O$_4$ nanomaterial.

The powder X-ray diffraction pattern (Fig. 2) of the Co$_3$O$_4$ nanomaterials revealed that the sample have face-centered cubic structure (space group Fd3 m, lattice constant a = 8.154 Å, JCPDS File No. 80-1544). Absence of any peak due to impurity indicated high purity of the final product. The average crystallite sizes were estimated using the Debye–Scherrer formula, $D = \frac{0.9}{\beta \cos \theta} \frac{\lambda}{b}$ where $\lambda$, $\beta$ and $\theta$ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle respectively. With the rise of calcination temperature from 400 through 500 to 600 $^\circ$C, the average crystallite sizes of the Co$_3$O$_4$ also increased from 28 through 36 to 46 nm, respectively. At higher calcination temperature, no new phases were found but the intensity of the diffraction peaks increased implying higher crystallinity of the as prepared Co$_3$O$_4$ nanoparticles with increasing temperature. The diffraction peaks also got gradually narrower with the rise in calcination temperature which may be correlated with increased crystallite size.

The TEM image of Co$_3$O$_4$ nanoparticles accessed at different decomposition temperatures all exhibited a faceted morphology. The representative TEM image of Co$_3$O$_4$ nanoparticles synthesized at 400 $^\circ$C is shown in Fig. 3a. The high-resolution TEM (HRTEM) image (Fig. 3b) revealed highly crystalline nature of the nanoparticles. The clear lattice fringes and about 0.28 nm spacing of the two adjacent planes is concordant with the interplanar separation of the (220) plane in face-centered cubic Co$_3$O$_4$. The electron diffraction (ED) pattern (Fig. 3c) indicates that Co$_3$O$_4$ nanoparticles are single-crystalline in nature.

Raman spectrum (Fig. 4) of the crystalline phase of Co$_3$O$_4$ synthesized at 400 $^\circ$C showed prominent peaks which correspond to Eg (484 cm$^{-1}$), F$_{2g}$ (517 and 622 cm$^{-1}$), and A$_{1g}$ (685 cm$^{-1}$) modes and were consistent with the previous
findings [28, 29]. Raman measurements further augmented the XRD and HRTEM observations.

It is important here to mention that though the thermal decomposition of M-L compounds (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and L = tartrate) were studied earlier [30, 31], barring a very current report on surfactant-free synthesis of Co$_3$O$_4$ and CuO nanoparticles from corresponding metal-tartrate complexes [32] synthesis of nanoparticles from such precursor is scarce. The synthesized Co$_3$O$_4$ nanoparticles were of average size $\sim$ 300 nm. The precursor in this case accessed from water metathesis reaction has been characterized to be a polymeric species with two water molecules of crystallization while the precursor complex, in the present work, obtained as a dispersive gel by a modified sol–gel technique is a monomer with only half a molecule of lattice water. The marked difference in elemental analyses and TGA trace of the metal-tartrate complex [32] vis-a-vis that in the present work has also been noticed. The average size of as-synthesized Co$_3$O$_4$ nanoparticles obtained in the present work are $<$50 nm as against $\sim$ 300 nm in the previous work at similar calcination temperature [32]. Thus more than the calcination temperature, precise composition and formation of a dispersive gel precursor is believed to be crucial in controlling the particle size of the nanomaterials. That an initial crystalline ordering of the chosen precursor indeed exert a strong influence on the nanocrystallite size of the end product has been stressed by others earlier [32–34].
4 Conclusion

Phase pure tricobalt tetraoxide nanoparticles of <50 nm size free of surface-adsorbed surfactants have been successfully synthesized by thermal decomposition of Co(II)-tartrate complex via a modified sol–gel approach. The average crystallite sizes of Co$_3$O$_4$ were found to increase with the rise in calcination temperature. The current synthetic strategy employed is an inexpensive reproducible process for large-scale production of phase pure surfactant-free Co$_3$O$_4$ nanoparticles. The methodology is anticipated to be readily extendable for the synthesis of other metal oxide nanomaterials.

Acknowledgments Authors are thankful to SAIF, NEHU, Shillong for providing TEM facility. DDP thanks University Grants Commission, Government of India, for grants under Research Fellowship Scheme for Meritorious Students (RFSMS). Prof. T. Pal, IIT, Kharagpur is thanked for help with the Raman spectral data.

References