Synthesis of transition metal oxide nanoparticles by homogeneous chemical precipitation route

5.1. Introduction

Precipitation from aqueous solution in the presence of urea has been described as an effective method to obtain metal oxide nanoparticles [264]. Precipitation of soluble metal salts by alkaline solution is commonly used for making oxide hydroxide of trivalent (Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$) or tetravalent (Ti$^{4+}$) metal ions [265, 266]. Sodium hydroxide or ammonium hydroxide is often used as precipitating agent. The production of metal oxide nanoparticles from the starting water soluble salts via homogeneous precipitation with urea has been demonstrated as a promising approach to successful preparation of powders with controlled particle size and shape [267, 268]. In contrast to heterogeneous precipitation with alkali or ammonia, during the homogeneous chemical precipitation the precipitating agent is slowly formed in the reaction mixture. The slow course of the reaction allows ripening of particles during precipitation resulting in better control of crystallinity, shape and size of the particles. The decomposition of urea (H$_2$NCONH$_2$) in aqueous solution is accompanied by slow and controlled supply of ammonia (NH$_3$) and carbon dioxide (CO$_2$) into solution. The smooth pH increase obtained by the degradation of urea in synchrony with the active release of OH$^-$ and CO$_3^{2-}$ ions, usually leads to the precipitation of metal hydrous oxide particles of controlled morphology. In this chapter
we report synthesis of nickel oxide and zinc oxide nanoparticles by homogeneous chemical precipitation route in the presence of urea as precipitating agent.

A part of the work described in this chapter has been published in


5.2. Synthesis of nickel oxide nanoparticles by homogeneous chemical precipitation

5.2.1. Synthesis

In a typical synthesis procedure, two separate solutions of nickel acetate, \( \text{Ni(CH}_3\text{COO)}_2.4\text{H}_2\text{O} \) and urea were made in deionized water maintaining molar ratio at 1:4. Then the two solutions were mixed in a beaker and stirred magnetically 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 1.5 h in an oil bath. Upon completion of the reaction, a green precursor product was obtained. The product 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, a metal hydroxide precursor, \( \alpha\text{-Ni(OH)}_2 \), was dried at 100°C for 1 h, and calcined in a muffle furnace at 400°C for 1 h to obtain black NiO nanoparticle powder.

5.2.2. Results and discussion

5.2.2.1. Powder X-ray diffraction study

The powder XRD pattern of as grown precursor powder is shown in Fig.99. The XRD pattern matched well with \( \alpha\text{-Ni(OH)}_2 \) (JCPDS File no: 38-0715) with an interplanar distance of \( \sim7.4 \ \text{Å} \), calculated using (003) reflections. \( \alpha\text{-Ni(OH)}_2 \) is a layered hydroxyl deficient compound with anions in the interlamellar space for compensating charge [269-
Heating at 85°C is known to afford nickel basic carbonate [118]. The turbostratic nature of the phases were indicated by the asymmetric nature of the (101) reflection peak in the XRD profile. The average crystallite size of the precursor calculated by the Debye-Scherrer formula, using a Gaussian fit was found to be 10.7 nm.

Fig. 99. XRD pattern of α-Ni(OH)₂.

The XRD pattern of the calcined α-Ni(OH)₂ powder (Fig. 100) showed peaks that can be well indexed to the cubic structure of NiO (JCPDS File no: 73-1523). No characteristic peaks of any impurity were observed. The diffraction peaks are all quite broad indicating the nanocrystalline nature of the material. The average crystallite size of NiO calculated by the Debye-Scherrer formula, using a Gaussian fit was found to be 4.9 nm.

Fig. 100. XRD pattern of NiO nanoparticles.
5.2.2.2. Transmission electron microscopy

The TEM image (Fig.101) for the nanocrystalline NiO depict spherical morphology of the synthesized material. The particles were well dispersed with weak agglomeration and have sizes in the range of 5-9 nm.

![TEM image of NiO nanoparticles.](image1)

**Fig.101. TEM image of NiO nanoparticles.**

5.2.2.3. FT-IR study of NiO nanoparticles

The FT-IR spectrum of NiO nanoparticles (Fig.102) exhibited a band at 473 cm\(^{-1}\), which corresponds to Ni-O stretching vibrational mode. The band at 3429 cm\(^{-1}\) and that at 1384 cm\(^{-1}\) have originated from the calcined powder which tends to physically absorb water and carbonate.

![FT-IR spectrum of NiO nanoparticles.](image2)

**Fig.102. FT-IR spectrum of NiO nanoparticles.**
5.2.2.4. Photoluminescence study of NiO nanoparticles

**Fig.103** shows the room temperature PL spectrum of NiO nanoparticles excited at 300 nm. The UV-emission band at 337 nm is attributed to recombination of electrons in conduction band and holes in the valence band. The spectrum also showed a visible emission at 423 nm due to defects-related to deep level emission such as oxygen vacancies and Ni-interstitials.

![Photoluminescence spectrum of NiO nanoparticles](image)

**Fig.103. Photoluminescence spectrum of NiO nanoparticles.**

The possible steps for formation process of the nanoparticles may be illustrated as follows:

\[
\begin{align*}
(NH_2)_2CO + H_2O &\rightarrow 2NH_3 + CO_2 & (1) \\
CO_2 + H_2O &\rightarrow 2H^+ + CO_3^{2-} & (2) \\
NH_3 + H_2O &\rightarrow NH_4^+ + OH^- & (3) \\
Ni^{2+} + 2OH^- &\rightarrow \alpha-Ni(OH)_2 & (4) \\
\alpha-Ni(OH)_2 &\rightarrow 400^\circ C \rightarrow NiO + H_2O & (5)
\end{align*}
\]
Urea decomposes at the experimental temperature to \( \text{NH}_3 \) and \( \text{CO}_2 \) (Eq. (1)) which in turn combines with water to produce carbonate (\( \text{CO}_3^{2-} \)) and hydroxide (\( \text{OH}^- \)) ions (Eq. (2) and (3)). The free \( \text{OH}^- \) ion then combines with \( \text{Ni}^{2+} \) ion forming \( \alpha-\text{Ni(OH)}_2 \) (Eq. (4)). The \( \alpha-\text{Ni(OH)}_2 \) on calcination at 400°C leads to NiO nanoparticles (Eq. (5)).

The proper selection of metal precursor and the method of synthesis is a key feature in the preparation of nano metal oxides. Thermal treatment of the precursor at various temperatures can result in variation of particle sizes of nanocrystalline NiO. For example, calcination of nickel dimethylglyoximate [273], nickel oxalate dihydrate [274], nickel-o-phthalate [275] at different temperatures can result in variation of particle sizes of NiO. Calcination of nickel dimethylglyoximate at 500°C results in nanocrystalline NiO of mean particle size 35.3 nm, nickel oxalate dihydrate results in NiO nanoparticles of mean size 30 nm (calcination temperature: 450°C), while nickel-o-phthalate results in NiO of mean particle size 15 nm (calcination temperature: 500°C). However, nanocrystalline NiO of particle sizes < 10 nm are difficult to achieve by these methods. In this context, low particle size (5-9 nm) obtained for NiO is a redeeming feature of the present synthesis.

5.3. Synthesis of zinc oxide nanoparticles by homogeneous chemical precipitation

5.3.1. Synthesis

In a typical synthesis procedure, two separate solutions of zinc acetate dihydrate, \( \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \) 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 1.5 h 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, \((\text{Zn}_5\text{(CO}_3\text{)}_2\text{(OH)}_6)\), was dried at 100°C for 1 h, and calcined in a muffle furnace at 300°C for 1 h to obtain ZnO nanoparticles.

5.3.2. Results and discussion

5.3.2.1. Powder X-ray diffraction study

The powder XRD pattern of as grown precursor powder is shown in Fig.104. The indexed peaks in the diffractogram closely matched with those of the hydrozincite (JCPDS File no.19-1458).

![Fig.104. XRD pattern of hydrozincite, Zn5(CO3)2(OH)6.](image)

The XRD pattern of the calcined hydrozincite powder (Fig.105) showed peaks that are well indexed to the hexagonal phase of ZnO (JCPDS File no. 36-1451). The obtained ZnO are of wurtzite structure. Peaks characteristic of any impurity were absent. The average crystallite size of ZnO nanoparticles calculated by the Debye-Scherrer formula, using a Gaussian fit was found to be 29 nm.
5.3.2.2. Transmission electron microscopy

Fig. 106 (a and b) shows the low and high magnification TEM images of ZnO nanoparticles. The image revealed that particles were well dispersed with weak agglomeration. The particles were nearly spherical in shape and have sizes 20-30 nm.

Fig. 106. TEM images of ZnO nanoparticles.

5.3.2.3. FT-IR study of ZnO nanoparticles

FT-IR spectrum of ZnO nanoparticles (Fig. 107) exhibits a rather broad and moderately strong band at 496 cm⁻¹, owing to Zn-O stretching vibrational mode. The band at
3446 cm$^{-1}$ corresponds to O-H mode of adsorbed moisture in the calcined sample. The bands at 1625 and 2363 cm$^{-1}$ are due to C=O and CO$_2$ groups.

![FT-IR spectrum of ZnO nanoparticles.](image)

**Fig.107.** FT-IR spectrum of ZnO nanoparticles.

### 5.3.2.4. Photoluminescence study of ZnO nanoparticles

**Fig.108** shows the room temperature PL spectrum of ZnO nanoparticles excited at 325 nm. 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.

![Photoluminescence spectrum of ZnO nanoparticles.](image)

**Fig.108.** Photoluminescence spectrum of ZnO nanoparticles.
The possible steps for formation process of the nanoparticles may be illustrated as follows:

\[
\begin{align*}
\text{(NH}_2\text{)}_2\text{CO} + \text{H}_2\text{O} & \rightarrow 2\text{NH}_3 + \text{CO}_2 \quad \text{(1)} \\
\text{CO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{H}^- + \text{CO}_3^{2-} \quad \text{(2)} \\
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{(3)} \\
5\text{Zn}^{2+} + 2\text{CO}_3^{2-} + 6\text{OH}^- & \rightarrow \text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 \quad \text{(4)} \\
\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 & \xrightarrow{300^\circ\text{C}} 5\text{ZnO} + 2\text{CO}_2 \uparrow + 3\text{H}_2\text{O} \quad \text{(5)}
\end{align*}
\]

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

Wang et al. synthesized \( \text{ZnO} \) nanoparticles via nanowhisker precursor adopting a solvothermal route at \( 180^\circ\text{C} \) for 24 h starting with zinc acetate dihydrate and urea [276]. The as grown particles were polydisperse having size 50-200 nm. In another report by Wahab et al. synthesis of \( \text{ZnO} \) nanoparticles of 20-30 nm size were accomplished by annealing hydrozincite powder at \( 300^\circ\text{C} \) [277]. The hydrozincite was synthesized by sol-gel method with refluxing time of 6 h at \( 70^\circ\text{C} \) from zinc acetate dihydrate and urea in 1:7 molar ratio. Annealing at higher temperature 500-900°C has been shown to produce agglomerated \( \text{ZnO} \) nanoparticles of increased size up to 300 nm. Hydrozincite precursor synthesized in the present work by homogeneous chemical precipitation method requires refluxing time of 1.5 h at \( 115^\circ\text{C} \). The precursor when subsequently calcined at \( 300^\circ\text{C} \) led to the formation of \( \text{ZnO} \) 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 6 h as reported by Wahab et al. [277] to 1.5 h.

5.4. Conclusion

NiO and ZnO nanoparticles were successfully synthesized from their respective hydroxide ($\alpha$-Ni(OH)$_2$) and hydrozincite ($\text{Zn}_5(\text{CO}_3)_{2}(\text{OH})_6$) precursors obtained by homogeneous chemical precipitation followed by calcination. The synthetic strategy adopted herein is simple and should be readily extendable for the synthesis of other metal oxide nanomaterials.