Chapter 4

Synthesis and characterization of metal oxide and hydroxide nanoparticles
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The metal oxides are the most common, diverse and probably the richest class of materials in terms of physical, chemical and structural properties. Such properties include for instance, optical, optoelectronic, magnetic, electrical, thermal, mechanical, photoelectrochemical and catalytic ones. The diversity of such properties and applications originates from the more complex crystal and electronic structures of metal oxides compared with other classes of materials. The main reasons are related to their variety of oxidation states, coordination number, symmetry, ligand-field stabilization, density, stoichiometry, and acid–base properties, which yield fascinating compounds. As a result, numerous applications of metal oxides, such as ceramics, sensors, actuators, lasers, waveguides, infrared (IR) and solar absorbers, adsorbents, pigments, optical switches, refractors, electrochromics, catalysts, insulators, semiconductors, superconductors, supercapacitors, piezoelectrics, ferroelectrics, transducers, thermoelectrics, fuel cells, alkaline and lithium batteries, and solar cells have been developed [1-6].

In the emerging field of nanotechnology, a goal is to make nanostructures or nano arrays with special properties with respect to those of bulk or single-particle species. Oxides can be prepared in the form of single crystals or polycrystalline or amorphous samples.
For studies where surface atomic arrangements need to be known, single crystal samples are used from which well-ordered crystallographic surface planes can be prepared. For most practical purposes where a large specific surface area is essential, polycrystalline or amorphous samples are desirable. Experience has shown that in general, low temperature processes are necessary to obtain oxides of large surface areas or small particle sizes [7-11].

The phase of nanoparticle depends on the methods used in its preparation. Some preparation methods produce amorphous materials, whereas other methods produce nanocrystalline materials. Increasing the stability and enhancing the dispersion of a narrow size range of the nanoparticles are primary goals in various synthetic methods. There have been several articles that summarize recent advances in the preparation methods and characterization techniques of oxide nanoparticles. As nanoparticles are usually sensitive to air and water, creative and skillful synthetic procedures are needed to make them in pure form. In the present work, synthesis and characterization of nanostructured metal oxides and hydroxides has been described. All the metal oxide nanoparticles were synthesized by the same method as described in the Chapter 3.

4.1 Characterization of zinc oxide and zinc hydroxide nanoparticles

Figure 4.1 shows a typical XRD spectrum of ZnO and Zn(OH)₂ nanoparticles prepared by the precipitation method. The XRD pattern of ZnO shows six major diffraction peaks at 2θ value of 31.9°, 34.6°, 36.4°, 47.7°, 56.7° and 63.0° which can be assigned for (100), (002), (101), (102), (110) and (103) planes respectively. This data reveal that ZnO has a crystalline hexagonal wurtzite structure (JCPDS: 75-0576). The XRD pattern of Zn(OH)₂ nanoparticles display the reflection lines corresponding
to tetragonal Zn(OH)$_2$ according to the standard JCPDS: 38-0356. The peaks at 2θ values of 12.1°, 24.7°, 34.8°, 41.3°, 51.1°, 58.2° and 72.7° can be indexed to the lattice planes of (101), (202), (312), (224), (316), (503) and (612) respectively.

Figure 4.1: XRD patterns of (a) ZnO and (b) Zn(OH)$_2$ nanoparticles.

Figure 4.2A shows the XRD patterns of Zn(OH)$_2$ particles prepared from different concentration of ZnSO$_4$ solution (0.025, 0.5, 0.1 and 0.2 M). Thus prepared Zn(OH)$_2$ particles were calcined for 2h at 400°C and so obtained ZnO particles were subjected to XRD studies and the corresponding patterns are presented in Figure 4.2B. The average crystallite size (D) of ZnO nanoparticles deduced from the broadening of major peaks were in the range 22-40 nm, and that of Zn(OH)$_2$ nanoparticles were in the range 20-32 nm. The results show that, with increase in the concentration of metal ions in the reaction mixture, the density of metal hydroxide formation increases, which is a favorable condition for the crystal growth. Hence, the average particle size of ZnO nanoparticles increases with increase in the metal ion concentration.
Figure 4.2: XRD patterns of (A) Zn(OH)$_2$ and (B) ZnO nanoparticles prepared at different concentration of ZnSO$_4$: (a) 0.025M, (b) 0.05M, (c) 0.1M and (d) 0.2M.

Further, the effect of calcination temperature on phase structures of ZnO nanoparticles generated from 0.05 M ZnSO$_4$ solution was studied. Figure 4.3 shows that diffraction lines of ZnO nanoparticles calcined at 200°C are broader and peaks were correspond to both zinc hydroxide and zinc oxide. On increasing the calcination temperature to 400°C, the characteristic ZnO peaks become sharper and more crystalline. A significant change in diffraction peaks is observed at a calcination temperature of 800°C. These results show that the broadening of diffraction lines
decreases with increasing the calcination temperature. The average crystallite sizes increased from 21 to 62 nm indicated that an increase in calcination temperature, resulted in migration of grain boundaries causing the coalescence of small grains and formation of large grains of ZnO nanoparticles, leading to sharper diffraction peaks.

![XRD patterns of ZnO nanoparticles subjected to calcination at different temperatures](image)

Figure 4.3: XRD patterns of ZnO nanoparticles subjected to calcination at different temperatures: (a) 200°C (b) 400°C (c) 600°C and (d) 800°C for 2 h.

The presence of additives are expected to influence the particle size and shape, hence the ZnO nanoparticles were prepared in presence of cetyltrimethylammonium bromide (CTAB) and poly vinyl alcohol (PVA). Thus obtained hydroxides were calcined at 400°C in a muffle furnace and subjected to XRD analysis. Figure 4.4 shows powder XRD patterns and the texture co-efficients of ZnO nanoparticles obtained in presence of CTAB and PVA. The preferred orientation (texture co-efficient) of ZnO nanoparticles was estimated from the X-ray data according to the Muresan method. Figure 4.4B shows that the majority of the crystallites are oriented parallel to the (100), (002) and (101) planes in case of ZnO prepared in presence of CTAB. The orientation of ZnO crystallites generated in presence of PVA was in (101), (102) and (112) planes.
Figure 4.4: (A) XRD patterns and (B) Texture coefficient of ZnO nanoparticles generated from 0.05 M ZnSO$_4$ in presence of: (a) CTAB and (b) PVA, calcined at 400°C for 2 h.

Figure 4.5 shows the SEM images of ZnO nanoparticles obtained in presence of CTAB and PVA. The spindle-like ZnO nanoparticles were generated in presence of both the addition agents. It can be seen from the SEM images the particles grown in presence of PVA were marginally larger than in presence of CTAB. The particle size of ZnO nanoparticles obtained in presence of CTAB and PVA was calculated by Scherrer equation and found to be 24 and 30 nm respectively.

Figure 4.5: SEM images of ZnO nanoparticles prepared in presence of: (a) CTAB and (b) PVA.
The ZnO nanoparticles synthesized in presence of CTAB and calcined at 400°C was subjected to EDX analysis. Only zinc and oxygen signals have been detected in the EDX spectrum of ZnO nanoparticles (Figure 4.6), suggesting that the nanoparticles are indeed made up of Zn and O only. There were no evidences for the presence of any other impurities.

![EDX spectrum of ZnO nanoparticles prepared from 0.05M ZnSO₄ solution in presence of CTAB calcined at 400°C.](image)

**Figure 4.6:** EDX spectrum of ZnO nanoparticles prepared from 0.05M ZnSO₄ solution in presence of CTAB calcined at 400°C.

Further the same sample ZnO nanoparticle was subjected to FT-IR studies (Figure 4.7). The peak observed at 3400 cm⁻¹ can be assigned to the -OH stretching vibration of surface hydroxyl groups [12]. The peaks observed at 715, 825 and 1045 cm⁻¹ is assigned to the internal vibration of the ZnO matrices [13]. The peaks present in the FTIR spectrum confirms the formation of ZnO particles and is in agreement with X-ray diffraction data.
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1.05

T—'—I—•—I—•—r

4000 3500 3000 2500 2000 1500 1000 500

Wavenumbers (cm⁻¹)

Figure 4.7: FT-IR spectrum of ZnO nanoparticles prepared from 0.05M ZnSO₄ solution in presence of CTAB, calcined at 400°C.

4.2 Characterization of nickel oxide and hydroxide nanoparticles

![X-ray diffractograms](image)

Figure 4.8: X-ray diffractograms of: (a) NiO and (b) Ni(OH)₂ nanoparticles.

The samples of NiO and Ni(OH)₂ nanoparticles obtained by precipitation method were characterized by X-ray diffraction analysis (Figure 4.8). For the sample of NiO (curve a), peaks were identical to those of NiO-cubic (JCPDS: 78-0423) with
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respect to position and relative intensity. The peaks observed at 2θ values of 36.8°, 43.6°, 62.2°, 75.01° and 78.98° corresponds to the reflections from (111), (200), (220), (311) and (222) crystal planes respectively. These results show that the particles were composed of pure nickel oxide. The Ni(OH)₂ peaks were observed at 19.4°, 33.4°, 38.7°, 51.2°, 59.6° and 72.5° corresponding to the reflection from (001), (100), (011), (012), (003) and (201) planes (JCPDS:74-2075).

The concentration of the metal ion influences the particle size. Hence, nickel hydroxide and nickel oxide nanoparticles were prepared by varying the concentration of NiSO₄ in order to know the effect of concentration of metal ions on particle size of nanoparticles. The X-ray diffraction studies show that the average particle size of NiO and Ni(OH)₂ nanoparticles calculated from scherrer equation were in the range 20-34 nm and 18-29 nm respectively (Figure 4.9). These results show that, the average particle size of NiO nanoparticles increases with increase in the metal ion concentration.

![XRD patterns](image)

**Figure 4.9:** XRD patterns of (A) Ni(OH)₂ and (B) NiO nanoparticles prepared at different concentration of NiSO₄: (a) 0.025 M (b) 0.05 M (c) 0.1 M and (d) 0.2 M.
The NiO nanoparticles obtained from 0.05 M NiSO$_4$ were calcined at different temperature. With increase in the calcination temperature from 200°C to 800°C, the diffraction peaks become more intense and sharper, which results in the larger grain sized particles. As the calcination temperature increases the average crystal size increased from 20 to 41 nm (Figure 4.10). The XRD pattern for the NiO sample calcined at 400 and 600°C exhibited broader peaks while for that calcined at 800°C demonstrated high intense and a quite sharper peak. Therefore, it can be concluded that the particles become well ordered after calcinations at higher temperatures. An increase in the calcination temperature brings about the corresponding increase in crystallite sizes of NiO nanoparticles leading to sharper diffraction peaks.

![Figure 4.10: XRD patterns of NiO nanoparticles obtained from 0.05M NiSO$_4$ solution and calcined at different temperatures: (a) 200°C (b) 400°C (c) 600°C and (d) 800°C for 2 h.](image)

Figure 4.11A shows XRD patterns of NiO nanoparticles obtained in presence of PVA and CTAB and the Figure 4.11B shows the corresponding texture coefficients calculated by Muresan method for NiO nanoparticles synthesized in presence of CTAB and PVA.
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Figure 4.11: (A) XRD patterns and (B) Texture coefficient of NiO nanoparticles generated from 0.05 M NiSO₄ in presence of: (a) CTAB and (b) PVA, calcined at 600°C for 2 h.

It can be seen that the majority of NiO crystallites are oriented parallel to (111), (200) and (220) planes. It is clear that the presence of additives does not alter the preferential orientation of crystals of NiO nanoparticles to a greater extent. From the result it can be concluded that the growth of NiO nanoparticles was not influenced much by the presence of CTAB or PVA. The crystal planes of NiO were arranged in the same direction in presence of CTAB and also in presence of PVA. The particle size calculated for NiO nanoparticles obtained in presence of CTAB and PVA were found to be 25 and 32 nm respectively.

The NiO nanoparticles synthesized in presence of additives were subjected to surface morphology analysis. From the Figure 4.12 it can be noticed that NiO nanoparticles were in the nanometer range and porous in nature. NiO nanoparticles generated in presence of CTAB have got much smaller size compared to the NiO generated in presence of PVA.
Figure 4.12: SEM images of NiO nanoparticles prepared in presence of: (a) CTAB and (b) PVA.

The NiO nanoparticles obtained in presence of CTAB and calcined at 600°C were subjected to EDX studies. The Figure 4.13 shows the EDX spectrum of NiO nanoparticles, one can see from the figure that the synthesized NiO nanoparticles were composed of only Ni and O, no other signals for impurities were observed.

Figure 4.13: EDX spectrum of NiO nanoparticles prepared from 0.05M NiSO₄ solution in presence of CTAB calcined at 600°C.
The same sample of NiO nanoparticles was analyzed by FT-IR studies. NiO, generally give absorption bands below 1000 cm\(^{-1}\) arising from inter-atomic vibrations. Two peaks were observed at 425 and 480 cm\(^{-1}\) in the spectrum (Figure 4.14) and these peaks were undoubtedly assigned to Ni–O stretching frequencies [14]. The broad absorption at 3340 and 1640 cm\(^{-1}\) are assigned to the existence of water as the NiO particles have strong absorption ability for moisture [15].

![FT-IR spectrum of NiO nanoparticles prepared from 0.05M NiSO\(_4\) solution in presence of CTAB calcined at 600°C.](image)

**Figure 4.14:** FT-IR spectrum of NiO nanoparticles prepared from 0.05M NiSO\(_4\) solution in presence of CTAB calcined at 600°C.

### 4.3 Characterizations of copper oxide and hydroxide nanoparticles

The structural properties of the prepared copper oxide and copper hydroxide nanoparticles were investigated by XRD. Figure 4.15 shows the X-ray diffractograms of CuO and Cu(OH)\(_2\) nanoparticles. The crystalline phases of CuO were identified by JCPDS file. The XRD measurement shows the presence of single-phase, monoclinic CuO particles. The observed diffraction data are in good agreement with JCPDS card
no: 80-1917. The peaks observed at 2θ values of 31.9°, 35.5°, 38.7°, 48.3°, 53.3°, 58.1°, 61.4°, 65.7°, 67.0°, 72.7° and 75.1° correspond to the reflections from the (110), (002), (111), (202), (020), (202), (113), (022), (113), (311) and (004) crystal planes, respectively. The typical indexed powder XRD pattern of Cu(OH)$_2$ is given in Figure 4.15 curve-b. Diffraction peaks observed at 2θ values of 13.4°, 18.7°, 21.5°, 27.0°, 30.8°, 33.4°, 35.5° and 41° corresponds to the reflections from (101), (102), (110), (202), (211), (005), (114) and (214) crystallographic planes. The observed XRD pattern of Cu(OH)$_2$ is consistent in terms of diffraction angle with the values in the JCPDS card No 36-0545.

![Figure 4.15: XRD patterns of: (a) CuO nanoparticles obtained from the 0.05M CuSO$_4$ solution and calcined at 600°C for 2 h and (b) Cu(OH)$_2$ nanoparticles.](image)

The copper hydroxide nanoparticles were prepared at different concentrations of CuSO$_4$. Thus obtained precipitate was filtered, dried at 100°C in hot air oven and characterized by powder XRD (Figure 4.16A). Further these hydroxides were calcined at 600°C and subjected to XRD analysis [Figure 4.16B]. The average particle
size calculated from the peak broadening were in the range 26-44 nm for CuO and 17-29 nm for Cu(OH)$_2$ nanoparticles.

Figure 4.16: XRD patterns of (A) Cu(OH)$_2$ and (B) CuO obtained from the different concentration of CuSO$_4$: (a) 0.025 M (b) 0.05 M (c) 0.1 M and (d) 0.2 M.

The X-ray diffraction patterns of Cu(OH)$_2$ calcined at 200 to 800°C for 2h are presented in Figure 4.17. These diffractograms revealed that the experimental method used for the synthesis of CuO gave pure and uniform sized crystals with monoclinic phase structure. The diffractograms of CuO calcined at 200°C exhibits broader peaks than those of the samples calcined at 400 and 600°C, indicating that at low temperature, the average particle size of CuO is small. Calculations based on Scherrer’s equation show that the average particle size for the samples calcined at 200°C is 20 nm and those calcined at 800°C is 68 nm. Thus it can be concluded that the smaller particles can be obtained at lower calcination temperature. But at the low calcination temperature the presence of precursor was observed. Hence the optimum temperature selected for this study was 600°C, at which the orderly arranged crystals with an average particle size of 30 nm have been obtained.
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Figure 4.17: XRD patterns of CuO nanoparticles obtained from 0.05 M CuSO₄ solution and calcined at different temperatures: (a) 200°C (b) 400°C (c) 600°C (d) 800°C for 2 h.

Further the study on the effect of size controlling agents on crystallization of CuO nanoparticles has been undertaken. Figure 4.18 shows the X-ray diffractograms and texture coefficient of CuO nanoparticles obtained from precipitation method in presence of organic additives, CTAB and PVA.

Figure 4.18: (A) XRD patterns and (B) Texture coefficient of CuO nanoparticles generated from 0.05M CuSO₄ in presence of 0.05 wt% of: (a) CTAB and (b) Polyvinyl alcohol and calcined at 600°C 2 h.
The majority of crystal planes of CuO nanoparticles were oriented to (020), (202) and (113) planes in presence of PVA and to (202) and (020) planes in presence of CTAB. The average particle size calculated by Scherrer equation, in presence of CTAB and PVA were found to be 30 and 32 nm respectively.

The surface morphology of CuO nanoparticles obtained in presence of different additives can be seen from SEM images (Figure 4.19). From the Figure it can be seen that the synthesized CuO nanoparticles are porous in nature.

![SEM images of CuO nanoparticles prepared in presence of: (a) CTAB and (b) PVA.](image)

**Figure 4.19:** SEM images of CuO nanoparticles prepared in presence of: (a) CTAB and (b) PVA.

Figure 4.20 shows the EDX spectrum of CuO nanoparticles synthesized in presence of CTAB and calcined at 600°C. It was noticed that the obtained CuO nanoparticles were composed only of Cu and O elements. No peaks for any other impurities were detected.

Figure 4.21 shows the FT-IR spectrum of CuO nanoparticles synthesized in presence of CTAB and calcined at 600°C. The CuO generally gives absorption bands below 1000 cm\(^{-1}\) because of the inter-atomic vibrations. The symmetric absorption peak was observed at 1115 cm\(^{-1}\) and the appearance of two absorption peaks at 593
and 517 cm$^{-1}$ correspond to Cu-O bond vibrational frequencies of monoclinic phases present in CuO nanoparticles [16].

**Figure 4.20:** EDX spectrum of CuO nanoparticles prepared from 0.05M CuSO$_4$ solution in presence of CTAB, calcined at 600°C.

**Figure 4.21:** FT-IR spectrum of CuO nanoparticles prepared from 0.05M CuSO$_4$ solution in presence of CTAB, calcined at 600°C.
4.6 Conclusion

> Pure and crystalline metal hydroxides \([\text{Zn(OH)}_2, \text{Ni(OH)}_2 \text{and Cu(OH)}_2]\) and oxides \((\text{ZnO, NiO and CuO})\) were successfully synthesized by precipitation method using metal sulphates as precursor, \(\text{NaOH}\) as precipitator in presence of CTAB and PVA.

> The metal oxides synthesized by this method were of nano scale in range and have got high purity and homogeneity.

> The average particle size increases with increase in initial metal ion concentration and calcination temperature.

> Among the two additives used, CTAB had better control over the growth of nano metal oxide when compared to PVA.

> The X-ray diffraction patterns reflected the high purity and crystallinity of the synthesized metal oxides. The size and morphology of the metal oxides can be controlled with the addition of surfactants.

> The FT-IR spectrums of synthesized nano metal oxides are in agreement with reported literature.

The Tables 4.1 and 4.2 shows the effect of calcination temperature and metal ion concentration on size of different nanoparticles.

**Table 4.1:** Average particle size (nm) of oxide nanoparticles obtained at different calcination temperature.

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<th>800</th>
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<td>41</td>
</tr>
<tr>
<td>CuO</td>
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<td>30</td>
<td>68</td>
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</tbody>
</table>
Table 4.2: Particle size (nm) of oxide/hydroxide nanoparticles obtained at different concentrations of metal ions.

<table>
<thead>
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<th>Concentration of metal ions</th>
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<th>0.05 M</th>
<th>0.1 M</th>
<th>0.2 M</th>
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References:


