Chapter VI

Micro Particles of ZnO

Results and Discussion
Shape selected nano and micro particles are becoming centre of attraction for many researchers as they are considered to be potential candidates for many applications [VI.1 - VI.3]. As discussed in the Chapter I, section I.6, zinc oxide can be synthesized in variety of shapes like spheres, hollow spheres, rods, tetrapods, ribbons, wires, discs, rings, pins etc [VI.4 – VI.6]. Interest in growing microparticles of ZnO in the spherical shape has been increased in recent years due to their interesting properties like photonic band gap and low lasing threshold [VI.7, VI.8].

In this chapter results of the zinc oxide micro spheres synthesized using a chemical route will be discussed. While obtaining the spheres we observed some novel morphologies which will also be discussed in details here. ZnO micro-phcres were characterized using UV-Vis absorption spectroscopy, X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy to study their structural, chemical, optical properties and their morphology.

VI.1: Zinc oxide microspheres synthesis

Procedure for the synthesis of zinc oxide micro spheres has been discussed in details in chapter II, section II.2. In this procedure spheres have been synthesized by chemical route in autoclave. The procedure gives spheres with uniform size and novel morphology with a cavity in each sphere. But before adopting this method we tried the synthesis with a similar way as reported by Seeling et al. [VI.7] with some modifications in it. The procedure was simple and it include following steps. First 0.03 M zinc acetate \([\text{Zn(CH}_3\text{COO)}_2]\) was dissolved in the mixture of di-ethylene glycol and water (140 ml + 10 ml respectively). The solution was then stirred at room temperature for 30 minutes and then heated at ~ 120 °C for 3 hours. A white precipitate was formed which was washed with ethanol and dried in air.

We observed that water is taking an important part in formation of ZnO spheres. Earlier we tried the synthesis without water and found that no precipitate was formed even at 160 °C. As can be seen from Table VI.1 addition of water not only ensures the formation of ZnO but it reduces the desired reaction temperature. We
carried out some systematic experiments to set the parameters like amount of water, reaction temperature and time of reaction to obtain uniform ZnO spheres. Results are depicted in Table VI.1.

Table VI.1: Parameters for the synthesis of ZnO spheres

<table>
<thead>
<tr>
<th>Water content (ml)</th>
<th>Temperature at which ZnO formation occurs (°C)</th>
<th>Morphology observed in SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ml</td>
<td>90 °C</td>
<td>Particles of irregular shapes and sizes.</td>
</tr>
<tr>
<td>10 ml</td>
<td>105 °C</td>
<td>Spherical particles in the size range of 250 nm to 300 nm with some polydispersity.</td>
</tr>
<tr>
<td>5 ml</td>
<td>120 °C</td>
<td>Polydisersed spheres in the size range of 150 to 350 nm.</td>
</tr>
<tr>
<td>1 ml</td>
<td>145 °C</td>
<td>Polydisersed spheres. The solution became yellow.</td>
</tr>
<tr>
<td>0 ml</td>
<td>Solution was heated till 160 °C as reported in [VI.7]</td>
<td>No precipitate was formed and the solution turned yellow.</td>
</tr>
</tbody>
</table>

From the Table VI.1 it is clear that for the formation of ZnO addition of water is important. It increases the rate of reaction by suppling more OH ions to the reaction with which oxidation of zinc salt is taking place quite easily as compared to that in bare di-ethylene glycol.

The possible reaction for the formation of zinc oxide can be described as follows

\[
Zn(CH_3COO)_2 + 2H_2O \rightarrow Zn(OH)_2 + 2(CH_3COOH)
\]

\[
Zn(OH)_2 \rightarrow ZnO + H_2O
\]

Figure VI.1(a) gives the scanning electron microscopy image of sample synthesized by using a method described by Seeling et al [VI.7] along with the size distribution given in the Figure VI.1(b).
Fig. VI.1: Scanning electron micrograph and particle size distribution for the ZnO micro spheres synthesized as described in section VI.1.

As can be seen from the figure, the particles are spherical in shape with the average size of ~ 0.28 μm. But the particles seen in the image are not uniform in size and shape. They have a rough surface. A plot of particle size against the number of particles (VI.1(b)) shows that particles are polydispersed.
This forced us to change the synthesis method and adopt a new one which is discussed in chapter II, section II.2 in details.

With procedure described in II.2, samples with two different heating rates were obtained to see the effect of rate of heating on the morphology of the spheres. Table VI.2 gives the details about the synthesis and observed morphology of the respective product which will be discussed in following sections.

As will be discussed later a cavity in the nanometer range could be seen in each sphere synthesized with this method. To understand the growth mechanism of spheres with cavity we have performed some systematic experiments in which part of the sample was removed from the reaction at different time intervals. The details are given in Table VI.2.

Table VI.2: Details of the samples prepared to study the growth process of ZnO microspheres with cavity.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature [°C]</th>
<th>Reaction time</th>
<th>Heating rate [°C/min]</th>
<th>Size [μm]</th>
<th>Cavity (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>160</td>
<td>4 hrs</td>
<td>~10</td>
<td>5.0 ± 1.0</td>
<td>~750</td>
</tr>
<tr>
<td>B1</td>
<td>160</td>
<td>3 hrs</td>
<td>~4</td>
<td>1.5 ± 0.5</td>
<td>-</td>
</tr>
<tr>
<td>B2</td>
<td>160</td>
<td>3hrs 50 min</td>
<td>~4</td>
<td>0.85 ± 0.05</td>
<td>-</td>
</tr>
<tr>
<td>B3</td>
<td>160</td>
<td>4 hrs</td>
<td>~4</td>
<td>0.95 ± 0.05</td>
<td>~200</td>
</tr>
</tbody>
</table>

Depending on the rate of heating there are two main sets of the sample A, (with ~10 °C/min heating rate) and B (with ~4 °C/min heating rate). Set B is again subdivided into three samples depending on three different time intervals at which samples are removed from the reaction, B1 (180 min), B2 (210 min.) and B3 (240 min.).

VI.2: Scanning electron microscopy analysis

To study the morphology of the samples electron microscopy was used. Samples were prepared by putting a drop of well dispersed sample in ethanol on the
silicon substrate and drying it in air. The film was coated with thin layer of Pt to get rid of charging.

Figure VI.2 shows the scanning electron microscopy images of a sample from the set A as explained in Table VI.2.

Fig. VI.2: Scanning electron microscopy images of ZnO micro spheres synthesized as described in section II.2. (a) shows as synthesized sample, (b) after filtering the same sample by a filter paper and (c) is a magnified image of a single ZnO sphere.
Figure VI.2(a) is an overview image of the as synthesized sample. Zinc oxide spheres can be seen having diameter of ~ 5 \( \mu \text{m} \). The most interesting thing in this sample is that every sphere is having a cavity in it. Image (b) is taken for the same sample after filtering it to remove particles with irregular shapes. In the image spheres with uniform size could be seen. Surface of the sphere is smooth and uniform. Magnified view of a single sphere is shown in Figure VI.2 (c). It can be noticed from an image, spheres are made up of small particles of ZnO. These are the basic building blocks of the bigger particles.

Similar experiments were carried out on the samples in set B described earlier. The sample shows similar spheres with cavities but of smaller dimension of the order of ~ 1 \( \mu \text{m} \). The cavity seen in this sample is ~ 200 nm wide.

To understand the mechanism of sphere formation and mainly to get an idea how cavity might have been formed, experiments were carried out. As explained above samples B1, B2 and B3 were removed from the reacting solution after 180 minutes, 210 minutes, and 240 minutes respectively.

Figure VI.3 (a-c) shows the scanning electron microscopy images of the samples B1, B2 and B3 respectively.
Fig. VI.3: Scanning electron microscopy images of ZnO micro spheres from the set B. Figures (a), (b) and (c) show the images for samples B1, B2 and B3 respectively.

Figure VI.3 (a) shows SEM image of sample B1. The figure shows that ZnO spheres coming together to form a bigger sphere. Some of the agglomerating spheres are indicated by arrows in the Figure (a). In image (b) an interesting thing was
seen. It shows that there is a small sphere at the surface of the bigger sphere which looks like it is coming out of the bigger sphere. In image (c) a sphere with central cavity could be seen.

Depending on these observations we have proposed a model for the growth of the ZnO microspheres with central cavity in it. The model is depicted pictorially in Figure VI.4. From SEM analysis the observed growth steps in the formation of ZnO spheres with cavity are as follows.

In the first step smaller ZnO spheres are formed which act as building blocks for bigger spheres. Formation of bigger spheres starts after heating the reactants in autoclave for not less than 2 hours. As the growth precedes these individual spheres start coming together, as shown in the Figure VI.4, step 2 and also in the SEM, Figure VI.3 (a). The bunch of the spheres thus formed starts becoming more compact and mass from each individual sphere starts mixing (Figure VI.4, Step 3). At the step 4 one of the ZnO sphere, which is located in centre, starts coming out. This is observed in the SEM, see Fig. VI.3 (b), which was recorded for the sample B2. As the synthesis goes further, after 4 hours of heating in autoclave, the sphere at the centre comes completely out and falls apart (Figure VI.4, step 5).

![Possible growth model for the formation of zinc oxide microspheres with central cavity.](image-url)
This may be happening because mass from all individual agglomerating spheres starts coming together to form a single sphere with slightly smaller diameter. It may push the sphere in the center, which might be loosely bound to other spheres away from them.

At the beginning of this process the loosely bound sphere gets pushed from all the sides and comes out of the bunch. This creates a cavity in the sphere. see Figure VI.3 (b) and Figure VI.4 step 6. Further heating in the autoclave makes the sphere with cavity slightly bigger and more uniform.

VI.3: Structural analysis

X-ray diffraction experiment was performed on the samples of ZnO microspheres. Figure VI.5 shows a spectrum for sample from set A. All the samples discussed above show same results as shown in the Figure VI.5.

![X-ray diffraction pattern](image)

**Fig. VI.5:** X-ray diffraction pattern for the ZnO micro spheres sample from the set A
From the comparison of the d values calculated from the diffraction peaks with standard JCPDS data [JCPDS data card no: 5 - 0664] it is clear that the synthesized samples are of crystalline zinc oxide with hexagonal wurtzite structure.

**VI.4: X-ray photoelectron spectroscopy analysis**

Purity of the samples was checked using x-ray photoelectron spectroscopy. Figure VI. 6 shows the XPS spectra for sample A. Figure (a) gives the survey scan recorded for the sample in the powder form. As can be seen from the figure core level photoemission peaks due to zinc, oxygen and carbon only could be seen. Thus the purity of the sample was confirmed. Positions for all the peaks are corrected with respect to that of carbon 1s photoemission peak at 285.0 ±0.2 eV as an internal reference and gold 4f at 84.0 ± 0.2 eV as an external reference.
Fig. VI.6: X-ray photoelectron spectroscopy of sample from set A. Spectrum (a) shows the survey scan, (b) depicts the detail scan for Zn 2p core level and (c) shows that for oxygen 1s region.
Figure VI.6 (b) gives the detailed scan for the Zn 2p region. Zn 2p_{3/2} peak appears at 1021.9 eV and that for 2p_{1/2} appears at 1044.9 with spin orbit splitting of 23.0 eV confirming that the sample is in the form of zinc oxide [VI.9]. The peak is symmetric indicating that no other species like unreacted zinc acetate or metallic zinc present, which would have given a shoulder at ~ 1021.1 eV [VI.9].

Core level photo emission peak for the oxygen 1s region is given in Figure VI.6 (c). The peak is not symmetric means along with O^2-, oxygen is present in another form in the sample. To find out the existing species deconvolution of the O 1s peak was done using XPS PEAK 41 software.

The peak is fitted with two components. The component appearing at binding energy of 531.4 eV denoted as O_1 is due to the oxygen co-ordinated with zinc in ZnO and that appearing at 533.2 eV was assigned to the oxygen in the form of hydroxide [VI.10]. This is possible in case of zinc oxide as it is known that hydroxide is always present on the surface of zinc oxide, which in fact is responsible for the well known green luminescence observed in case of ZnO [VI.11].

Along with zinc and oxygen some amount of carbon was found in the sample. Presence of carbon might be due to sample handling and some carbon migrated from filaments in the vacuum system.

Concentration of the elements detected in the sample was calculated from the area under the curve and atomic sensitivity factor for the particular element [VI.9]. Calculations shows that 33.4% zinc, 47.8% oxygen and 18.8% carbon is present in the sample. Excess oxygen than zinc can be attributed to the presence of hydroxide on the surface of the particles.

VI.5: **UV-Vis absorption spectroscopy**

Optical absorption study on the zinc oxide microspheres with central cavity was performed using UV-Vis absorption spectrometer. Results for the samples B1, B2, B3 and a sample where growth of spheres was not observed are shown in the figure VI.7.
As can be seen from the figure, absorption spectra for the samples B1, B2, B3 with increasing reaction time develop a broad band peak from 375 nm to 550 nm. This kind of band is unusual.

Fig. VI.7: UV-Vis absorption spectra for samples B1, B2, B3 and a sample where sphere formation could not be seen given for comparison.

Usually for a bulk ZnO or thin films of ZnO a sharp absorption peak appears at 375 nm corresponding to the bulk band gap of 3.3 eV. For sample with no spheres a single absorption peak could be seen at ~ 374 nm which is typically observed in case of bulk ZnO. The reason why this kind of strange phenomena in the optical absorption data could be observed only in case of samples in which sphere formation has taken place is still unknown.
Conclusions

Zinc oxide spheres in the sub micron to micrometer range have been synthesized using a chemical route at high temperature. A novel morphology was observed in which each sphere is having a cavity few nanometers wide. A systematic study has been performed to find out the origin of the cavity. Scanning electron microscopy analysis reveals that the cavity is formed due to the particular growth mode of the spheres. A model has been proposed for the growth of spheres with cavity.

XRD, XPS analysis shows that sample is of wurtzite ZnO and pure without any contamination respectively. Optical absorption data for the spheres shows strange behavior, origin of which could not be understood yet.
References


