CHAPTER 4

RUTHENIUM DOPED ZnO: CHARACTERIZATION AND PHOTODEGRADATION OF DYE: CONGO RED

Zinc oxide semiconductor particle with large volume to surface area ratio, high ultraviolet light absorption and long life span features has been widely used as catalyst (Curridal et al 2003), gas sensor and UV absorber (Lin et al 1998) in cosmetics and anti-virus agent (Hu et al 2003). Over the years, many catalysts such as TiO$_2$, ZnO, WO$_3$ and SnO$_2$ have been tested for the photodegradation. Among them, TiO$_2$ and ZnO is largely used in waste water treatment, but its application is still limited because the activation requires ultraviolet irradiation. Also, the high recombination rate of the photo excited electron-hole pairs in the irradiated particles limits the overall efficiency. This problem can be overcome by changing the electronic structure of the catalyst by modifying its surface such as addition of metals, dopants, metal oxides or combinations with other semiconductors, thereby increasing the quantum yield and efficiency of the catalyst used in these reactions (Chen et al 2005).

Transition metal doping on semiconductors improves the trapping of electron and inhibits the electron-hole recombination. Ibhadon et al (2008) reported that Ru/CeO$_2$ catalysts have different behaviour in the catalytic wet air oxidation of acrylic, succinic acids depending on the support morphology and the metal/support contact. ZnO has emerged to be more efficient catalyst as far as the detoxification of water is concerned due to the production of
hydrogen peroxide with a high rate of total mineralization (Carraway et al 1994). ZnO has been proven to be an alternative to TiO$_2$ in the photodegradation of pesticide carbetamide and herbicide triclopyr (Percherancier et al 1995). Recently, Lizama et al (2002) and Daneshvar et al (2004) have reported that ZnO is a more efficient catalyst than TiO$_2$ in aqueous phase photodegradation of reactive blue 19 and acid red 14, respectively. ZnO can be synthesised by different approaches including sol-gel processing (Senthilkumaar et al 2008), homogeneous precipitation (Shishido et al 2007), mechanical milling (Damonte et al 2009), organometallic synthesis (Li et al 2008), microwave method (Cho et al, 2009) and spray pyrolysis (Gledhill et al 2009). In this chapter, we report the synthesis of pure ZnO and Ru doped ZnO by soft chemical route. The photocatalytic activity of Ru doped ZnO was tested using an azo dye, Congo red in an aqueous solution, as a model compound.

4.1 X-RAY DIFFRACTION STUDIES

The XRD patterns of pure ZnO and Ru$_x$Zn$_{1-x}$O ($x=0.002, 0.004, 0.006, 0.008, 0.01, 0.02, 0.03$) annealed at 500°C are shown in Figure 4.1. From the XRD pattern, there is no obvious change in the crystal structure up to the concentration 0.008. The slight peak shift was identified in the concentration of 0.01 and above. In order to understand the effects of doping pure ZnO and Ru$_{0.01}$Zn$_{0.99}$O (Ru:ZnO) were taken and subjected to study the effect the photocatalytic performance. The XRD pattern of pure ZnO and Ru doped ZnO were shown in Figure 4.2. The lattice parameters values for hexagonal system i.e. $a=b\neq c$, $a$ and $c$ values were calculated by using the following formulae, for (110) orientation $a = \lambda / \sqrt{3} \sin \theta$; For (002) orientation $c = \lambda / \sin \theta$. From XRD data, the lattice parameters of pure ZnO were found to be $a = 0.3245$ nm and $c = 0.5205$ nm, which are identical with the standard JCPDS card 89-1397, 36-1451 and are presented in Table 4.1. It’s observed
that there is a small shift of all diffraction peaks for Ru doped ZnO compared to pure ZnO. Also, we found that for Ru:ZnO samples, there is an increase of c-axis lattice value without any change in the crystal symmetry.

Figure 4.1 XRD pattern of pure and Ru doped ZnO nanostructures
It reveals from XRD data, the decrease in the value of FWHM indicates that larger Ru(III) ions occupy the Zn\(^{2+}\) site to form Ru:ZnO solid solution with wurtzite structure. It is seen from Table 4.1, the unit cell volume of Ru:ZnO slightly increased relatively to that of pure ZnO, suggesting that Ru doping in ZnO crystal structure. It is expected that Ru doping causes a lattice disorder in ZnO structure without affecting its wurtzite structure. The crystallite size of pure ZnO and Ru:ZnO were calculated by using Debye’s Scherrer Equation given below, \(
\text{Crystallite size} = \frac{0.9 \lambda}{\beta \cos \theta}
\) (Where, \(\lambda\) is the wave length; \(\beta\) is Full Width Half Maximum; \(\theta\) is the peak position) (Cullity 1978).

The crystallite sizes were estimated using FWHM values and are found to be 25.01 - 27.81 nm for ZnO and Ru:ZnO, respectively. The incorporation of Ru ion in ZnO structure does not assure that Ru\(^{2+}\) substituted for Zn\(^{2+}\) ions of ZnO lattice forming wurtzite Ru:ZnO solid solution. Most of the added Ru ions go into interstitial position of ZnO crystal lattice.

Figure 4.2  XRD pattern of a) pure ZnO and b) Ru:ZnO
(Bruce 1982). It is also expected that part of Ru ion did not enter inside crystal structure of ZnO and thus crystallized alone, forming RuO$_2$ nano grains. It is being evident from the peak observed at $2\theta = 28^\circ$ in XRD pattern of Ru:ZnO (Figure 4.1, marked as *). Further, it is identical with the tetragonal RuO$_2$ standard JCPDS card 88-0286. Ru ions entered into crystal lattice of ZnO and may replace Zn$^{2+}$ ions, leaving to the formation of more Zn vacancy ($V''_{Zn}$) defects along with some oxygen vacancy ($V''_{o}$) (Equations 4.1 and 4.2).

Neutral = $V''_{Zn} + V''_{o}$

$$2\text{Ru}^{III} \rightarrow \text{ZnO} \quad \text{Ru}''_{Zn} + \text{RuO}_2 + 2V''_{Zn} + O_o$$

**Table 4.1 XRD and EDS data for pure ZnO and Ru:ZnO**

<table>
<thead>
<tr>
<th>Samples</th>
<th>FWHM for 101, 100 and 002 planes</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameters (for hexagonal, $a = b \neq c$)</th>
<th>Volume of the unit cell ($\text{Å}^3$)</th>
<th>Composition by EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.3492, 0.3456 &amp; 0.3237</td>
<td>25.01</td>
<td>$a = 3.2450, c = 5.2057$</td>
<td>47.47</td>
<td>65.27 34.73 --</td>
</tr>
<tr>
<td>Ru:ZnO</td>
<td>0.3142, 0.3081 &amp; 0.2803</td>
<td>27.81</td>
<td>$a = 3.2452, c = 5.2414$</td>
<td>47.80</td>
<td>44.68 54.40 0.92</td>
</tr>
</tbody>
</table>

Due to annealing during crystal growth a loss of oxygen from the lattice can leads to oxygen vacancy (Moos & Hardtl 1996) (Equation 4.3).

$$O_o \rightarrow V''_{o} + \frac{1}{2} O_2 + 2e$$

Several researchers have shown that intrinsic defects in ZnO is due to oxygen vacancy (Banerjee et al 2008) and can cause highly self compensation through acceptor doping (Wan et al 2008); we believe that
similar type of reaction exist in Ru doped ZnO samples. A decrease in the FWHM intensity value was observed for Ru: ZnO compared to pure ZnO, indicating the increase in the crystallinity and crystal size. Hei et al (2008), also reported the similar observation in their Ru addition (0.5 – 3.0 wt%) on Al- doped ZnO thin films prepared by magnetron sputtering method. As seen from Figure 4.1 and Table 4.1, Ru: ZnO tends to grow along the c-axis of (101) plane, where sp³ hybridized orbits were present. It is been realized that the structure slightly changed with doping of Ru ions leading to change in the Zn/ZnO ion ratio in the lattice.

4.2 HRSEM AND HRTEM ALONG WITH EDS

High-resolution Scanning Electron Microscopic (HRSEM) images of pure ZnO and Ru: ZnO samples are presented in Fig. 4.3 (a, b). It is clearly seen that the grains are homogenously packed with sphere like morphology for pure ZnO and are less ordered in Ru:ZnO sample, suggesting the incorporation of Ru ions in the crystal lattice. Further, there was no separate grain boundary characteristics were observed. This is further comparable with the FWHM values from the XRD data presented in the Table 4.1. Furthermore the incorporation of Ru ions in the ZnO crystal lattice is analyzed using energy dispersive spectroscopy (EDS) in the selected area of the HRSEM images for pure ZnO and Ru doped ZnO, respectively and the results are given in Table 4.1. The Table 4.1 confirms the concentration of Ru metal ion (0.92 atomic %) corresponding to the calculated solution concentration in the preparation for 1.0 mol %.

The obtained nanomaterials were further characterized by transmission electron microscopy (TEM). TEM was used to investigate the microstructure of pure and Ru doped ZnO.
Figure 4.3 HRSEM micrographs of a) pure ZnO and b) Ru:ZnO

Figure 4.4 (c,d) shows typical TEM images of the pure and Ru doped ZnO samples conforming that the as-synthesised samples are in the nano form and the sphere like morphology was observed. Inset of Figure 4.4 (c,d) shows the corresponding selected area diffraction pattern (SAED) of pure and Ru doped
ZnO. It clearly shows that the samples are in the same wurtzite structure. It reveals from the TEM analysis, the average particle size of the pure and Ru doped ZnO nano spheres are about in the range of 10-50 nm it is consistent with the XRD results.

Figure 4.4 HRTEM images of c) pure ZnO and  d) Ru:ZnO (inset: corresponding SAED pattern)
4.3 UV-VIS ABSORPTION SPECTROSCOPY

The UV-Vis. absorption spectra of as-synthesized samples are shown in Figure 4.5. Both the ZnO and Ru:ZnO spectra revealed a characteristic absorption peak of ZnO. It is obvious from the Figure 4.5, the absorption peak is red shifted on 1 mol% Ru doping. The peak in the absorption spectra does not correspond to the true optical band gap of ZnO which is about 3.27eV at room temperature. It is interesting to note that the absorption increases as the photon energy decreases and at energies higher than the absorption band edge it decreases. Studenikin et al. (1998) observed similar phenomena on the optical property of ZnO films grown by spray pyrolysis and reported it is a common absorptive characteristic for semiconductors. Also, this behaviour is due to scattering phenomenon in colloidal samples. The obtained absorption spectra have two components, one being the dispersed light due to scattering countered as observed light by the spectrophotometer and optical absorption due to the electronic transitions in the sample. The increase in absorption at lower photon energy side is due to electronic transitions in semiconductor materials.

Instead, it may be due to the result of scattering from the surface containing Ru metal ion in ZnO, suggesting the incorporation of Ru ion in ZnO lattice. It is also interesting that the absorption maximum increased due to surface plasmon resonance from the Ru particle indicating the presence of Ru metal clusters which is in good agreement with the XRD, HRSEM, HRTEM and EDS results.
Figure 4.5 Photon energy spectrum of a) ZnO and b) Ru:ZnO

Further, the absorption results were also consistence with the visible powder color shift from light gray to dark purple. It is worth to notice that the absorption at visible wavelength of Ru:ZnO showed constant absorption due to equal sized metal clusters formed on the surface of ZnO. This corresponds to the excitation of electrons from the valance band of ZnO to the unoccupied level of metal cluster (Sakthivel et al 2004). Several researchers have also reported the red shift in optical absorption studies on Ru doped titania (Houskova et al 2009), Ru doped titania nanotubes (Khan et al 2009).
4.4 PHOTODEGRADATION OF AZO DYE

Congo red (CR) was selected as a representative azo dye to evaluate the photocatalytic performance of Ru doped ZnO. Figure 4.6 (a, b) illustrates the time-dependent absorption spectra of CR aqueous solution during UV irradiation in presence of pure ZnO and Ru:ZnO, respectively. The blank experiment shows that the concentration of CR changes negligibly after irradiation, suggesting that the photo induced self-sensitized photolysis can be neglected in comparison with the photo catalysis performed in presence of catalysts. It is noteworthy that the percent removal of the dye in aqueous solution depends strongly on the initial concentration of CR as shown in Figure 4.7 (a,b).

The effective removal was achieved at lower concentration of dye. When the initial concentration increases, more and more dye molecules adsorbed on the surface of the catalyst thereby decreasing the number of active sites for the adsorption of hydroxyl ions. Consequently, the generation of hydroxyl radical will be reduced. It is expected that in more concentrated CR solution, there will more number of photons collide with each other before reaching the catalyst surface and consequently decrease the total number of available photon on the catalyst surface, leading to decrease the percent removal of the dye (Chakrabarti & Dutta 2004). Behnajady et al (2006) reported the same trend in the photo degradation of acid yellow 23 on ZnO catalyst. The change in the absorption of light during the photodegradation of CR dye in presence of pure ZnO and Ru:ZnO is shown in Figure 4.6 (a, b). The complete degradation was achieved after irradiation 160 min.
Figure 4.6 Change in absorption spectrum of CR (a = ZnO; b = Ru:ZnO), Conditions: [CR] = 2.15 x 10^{-5} mol/L; Weight of ZnO = Weight of Ru:ZnO = 0.066 g/L; Irradiation time: 60 min; pH = 6.5
Figure 4.7  Normalized absorption change in spectrum (a = ZnO; b = Ru:ZnO), Conditions: [CR] = 2.87 \times 10^{-5} \text{mol/L}; \text{Weight of ZnO} = \text{Weight of Ru:ZnO} = 0.066 \text{ g/L}; \text{Irradiation time: 60 min.; pH} = 6.5
It is observed from Figure 4.8, the mineralization degree was found to be 30% and 43% after irradiation for a period of 30 min., for pure ZnO and Ru:ZnO, respectively. The photocatalytic performance of Ru:ZnO is found to be more encouraging. The better activity of Ru:ZnO is due to better charge separation compared to pure ZnO. On the other hand, incorporation of Ru metal onto ZnO surface increases the rate of electron transfer to dissolved oxygen. It is also expected that Ru metal can acts as a recombination center, which is due to electrostatic attraction between negatively charged metal surface and the positively charged holes (Vamathevan et al, 2002). As a result of this, Ru metal can reduce electron-hole recombination and increase the photocatalytic activity. This observed phenomenon is supported from the results obtained in the analysis of UV-Vis spectroscopy as shown in Figure 4.4.

![Absorption Spectrum](image)

**Figure 4.8** Change in absorption spectrum of CR (a = ZnO; b = Ru:ZnO), Conditions: [CR] = 2.15 × 10^{-5} mol/L; Weight of ZnO = Weight of Ru:ZnO = 0.066 g/L; Irradiation time: 30 min; pH = 6.5
The incorporated Ru metal into the ZnO crystal lattice leads to change in the band gap energy from 3.27 eV (pure ZnO) to the visible light of 3.20 eV (Ru:ZnO). The ejected electrons from the valance band of pure ZnO captured by the Ru metal in the semiconductor surface having partially filled atomic orbitals placed in between the valance and conduction band. Since, the introduction of interband owing to Ru ions in the ZnO crystal lattice, accelerates the interfacial electron transfer process and there by changes the ZnO excitation energy. Also, the doped Ru ion modifies the surface properties of ZnO by changing the distribution of electrons and prevents the recombination of electron and hole. Also, holes generated at the valance band, forming hydroxyl radicals utilized effectively for the photo catalytic activity of Ru:ZnO (Tennakone & Bandara 2000). From the Literature survey, Surface area plays an important role in the absorption and catalytic activity. Adsorption and catalytic activity increases with increase in the surface area.

The effect of photocatalyst weight on the degradation of Congo red was studied in the range of 0.0 to 0.3 g/L. A significant increase was observed in the percent degradation of Congo red for both pure ZnO and Ru:ZnO (figure not given), with an increase in the catalyst weight from 0.0 to 0.267g/L for both pure ZnO and Ru:ZnO. Further increase in the catalyst weight resulted decrease in the percent removal. This is explained in terms of the availability of active sites on the catalyst surface and the penetration of UV light into the suspension. This observed phenomenon is due to screening effect of excess catalyst particle in the solution. A detailed account on this screening effect is explained in our earlier works (Senthilkumaar et al 2006 and Senthilkumaar & Porkodi 2005). The experimental data obtained are in good agreement with those reported earlier (Sauer et al 2002 and Hermann 1995). The relationship between initial rate of degradation of CR and weight of photocatalyst as given by the empirical equation $r_0 \alpha [\text{photocatalyst}]n [\text{Dye}]$
were, \( n \) is the exponent less than one for the dye studied in reactions at lower concentration of catalyst (Galindo et al 2001) (Figure 4.9).

**Figure 4.9** Charge separation of pure ZnO and Ru:ZnO