Growth of ZnO nanoparticles prepared from cost effective laboratory grade ZnO powder and their application in UV photocatalytic dye decomposition

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Abstract

ZnO nanoparticles were prepared by mechanical grinding of laboratory grade ZnO powder. These nanoparticles were characterised by using X-ray diffraction analysis, transmission electron microscopy (TEM), photoluminescence and diffuse reflectance spectroscopy. From TEM study it reveals that the particles mostly show one dimensional morphology. The average length and diameter of these nanoparticles are 300 nm and 59.34 nm respectively. Studies on UV photocatalysis behaviour of these nanoparticles were done through their use in methylene blue dye decomposition. Particularly, the reaction kinetics and reaction rate are estimated by monitoring the dye decomposition activity with respect to UV exposure time. The kinetic is found to be pseudo-first order with the reaction rate constant (kinetic constant) 0.18 min^{-1} . In the comparative study it has been demonstrated that these ZnO nanoparticles can show three times higher dye degradation activity with respect to benchmark commercial nanoparticle P25. From the photocatalysis studies with scavengers like Isopropyl alcohol and ethylenediaminetetraacetate it is demonstrated that hole (h^+) and hydroxyl radical ($\cdot\text{OH}$) have a vital role in the dye decomposition activity. The used ZnO powders are of extremely low cost, so this material can be found to be a better choice for photocatalytic dye decomposition applications.

1 Introduction

Photocatalysis is a type of activity for the enhancement of chemical reaction in presence of light. It has been found to be very promising for applications like generation of green fuel (H_2) by splitting of water, sterilization of medical instruments by bactericidal effect, purification of water by decomposition of dye and other waste products of industries etc. There are two type of photocatalysis process viz homogeneous and heterogeneous process. The heterogeneous process is found to be much more efficient than the homogeneous photocatalytic process for the aforementioned applications. Zinc oxide (ZnO) is an II–VI compound semiconductor. It has very special properties like direct band gap (Eg $\sim 3.3 \text{ eV}$), large excitation binding energy ($\sim 60 \text{ meV}$ at room temperature) and good electrical conductivity.

Therefore nanoparticles of this material have been found to very promising for heterogeneous photocatalysis applications. The ZnO nanoparticles synthesized through various methods, such as solution combustion method [1], DC Thermal Plasma [2], Electrochemical [3], microwave-assisted ball milling [4], green synthesis [5], hydrothermal synthesis [6], precipitation [7], thermal decomposition [8] and sol–gel method [9] etc. have been used for this purpose. In order to have readymade availability materials in large amount, several investigations have also been made on use of commercial ZnO nanoparticles for photocatalysis reaction [10–21]. However, in all these works the ZnO nanoparticles used are generally of analytical or ACS reagent grades. The purity of these grades ZnO is extremely large and therefore these are quite expensive. In order to find cost effective alternative, in this work the dye decomposition activity was studied in the presence of UV exposure by using ZnO nanoparticles prepared from commercial laboratory grade ZnO powder through mechanical grinding. The reaction kinetics and reaction rate are estimated. The performance of these nanoparticles is compared with respect to benchmark commercial TiO_2 nanoparticles (Degussa P25). Scavengers based photocatalytic dye decomposition study is done to understand

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the mechanism of the reaction. Discussion is given on the advantage of this material for photocatalysis application.

2 Experimental details

2.1 Material preparation and characterization

The ZnO nanoparticles were prepared by grinding 10 gm of the laboratory grade ZnO powder (Product No.Q28975, Fisher Scientific, purity: 98%) for 2 h by taking 20 ml acetone as the wet medium. The structural and morphological properties of the grown nanoparticles were characterized by X-ray diffraction (XRD) analysis and high resolution transmission electron microscopy (HRTEM, JEOL-2010). The optical characterization of the nanoparticles was done by Photoluminescence (PL) study and diffused reflectance study. The PL study was done with the excitation wavelength of 325 nm. The diffused reflectance study was done by using an integrating sphere attached UV–Visible spectrophotometer (UV-2450, Shimadzu).

2.2 Photocatalysis study

Photocatalytic dye decomposition studies were carried out in an indigenously built UV reactor. It consists of UV light source (365 nm, 6 W) and a magnetic stirrer. Every time, for photocatalysis reaction 50 ml aqueous solution (2.5×10^{-5} molar conc.) of methylene blue (MB) dye was taken along with 0.05 gm of ZnO nanoparticles. Prior to the light exposure gentle stirring of the solution was done under dark condition for 30 min to ensure complete adsorption and desorption of MB dyes with the photocatalyst. After completion of this step, the sample was exposed to UV radiation. The distance between the solution surface and UV light source was 10 cm. After some duration of UV exposure, 2 ml of the decomposed solution was taken out from the beaker for absorbance measurement in UV visible spectrophotometer after separating the nanoparticles. Comparison with standard commercial TiO_2 nanoparticles (Degussa P25) is an excellent method to quantitatively evaluate photocatalytic activity of newly grown nanoparticles [22–26], we therefore also done this study by taking P25 (Sigma-Aldrich, TEM measured average size: 21 nm) as the reference material.

For comparison, all the aforementioned characterizations as well as photocatalytic study were done with the ungrinded ZnO powder.

2.3 In situ active species determination

In photocatalysis various processes like photoexcitation, charge separation, migration and surface oxidation–reduction reaction occurs [27]. For a better understanding of

photocatalysis reaction it is better to determine which type of active species is responsible for the degradation of organic dyes. There are several active radical species such as hole (h^+), hydroxyl radical ($\cdot\text{OH}$), superoxide anion radical (O_2^-) and electron (e^-) responsible for this process. To know more details about this, photocatalysis studies were conducted in the presence of scavengers like isopropyl alcohol (IPA) and ethylenediaminetetraacetate (EDTA). By following the procedure given by Liu et al. [28], the quantity of EDTA was taken to be 0.015 gm and 0.013 ml of IPA per 50 ml of MB dye solution.

3 Results and discussion

3.1 Structural analysis

The XRD pattern of the grown ZnO nanoparticles is shown in Fig. 1. From this it is observed that the material has Hexagonal/Wurtzite structure with space group P6₃mc (JCPDS No.-00-036-1451) [29]. The lattice parameters are found to be $a = 3.25 \text{ \AA}$, $b = 3.25 \text{ \AA}$, $c = 0.520 \text{ \AA}$. The diffraction pattern at angle $2\theta = 31.7^\circ$, 34.4° , 36.2° , 47.5° , 56.6° , 62.8° , 66.3° , 67.9° , 69.1° are corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes respectively. In ungrinded ZnO powder the same XRD peaks (Fig. 2) are also observed indicating that there is no change of crystal structure in grinding process.

3.2 Morphological study

TEM images of ZnO nanoparticles were shown in Fig. 3. From TEM image (Fig. 3a) it reveals that the particles

Fig. 1 XRD pattern of ZnO nanoparticles

Fig. 2 XRD pattern of ZnO powder before grinding

mostly show one dimensional morphology. The average length and diameter of these nanoparticles are 300 nm and 59.34 nm respectively. The SAED pattern (Fig. 3b) consists of 8 concentric rings corresponded to (100), (002), (101), (102), (110), (103), (200), (112) & this result is consistent with the XRD analysis. Figure 3c presents the high resolution (HRTEM) image of ZnO nanoparticles. The interplanar distance $d = 2.4$ Å corresponding to (101) crystal plane. From the TEM image of the ungrinded ZnO powder, (Fig. 4) the average length and diameter of the particles are found to be 365 nm and 102 nm respectively. This indicates that, the grinding process helps in reduction of both average length and diameter of the particles.

3.3 Diffuse reflectance study

Diffuse reflectance spectra of ZnO nanoparticles and ungrinded ZnO powders are shown in Fig. 5. This figure indicates that the band edge absorbance behaviour for both of this materials is same i.e. grinding has no significant effect in optical behaviour of the material. The drastic reduction of diffuse reflectance around 380 nm for both of the materials corresponds to the band edge absorption of the ZnO.

3.4 Photoluminescence study

The PL spectra of ZnO nanoparticles and grinded ZnO powder are shown in Fig. 6. The PL peak at around 400 nm is due to the excitonic band edge emission. Apart from this we got a weak peak in the visible range having centre at 532 nm that is related to the defect level [30]. The similar PL spectra

Fig. 3 a TEM image b SAED pattern c HRTEM images of ZnO nanoparticles

for both of these materials further confirm the fact, that there is no significant change of optical behaviour of the material in the grinding process. This result is almost consistent with the result obtained in the diffuse reflectance study.

Fig. 4 TEM image of ungrinded ZnO powder

Fig. 5 UV-Visible diffuse reflectance spectra of ZnO nanoparticles and ungrinded ZnO powder

3.5 Photocatalytic dye decomposition activity

3.5.1 Evaluation of photocatalytic activity, its comparison with ungrinded ZnO powder and standard commercial material P25

Figure 7a shows image of dye solutions after photocatalytic activity for duration of 0, 4, 8, 12, 16 min. The absorption spectra of these dye solutions around the wavelength 664 nm (highest peak) have been shown in Fig. 7b. From these figures it can be found that the dye got completely decomposed

Fig. 6 PL spectra of ZnO nanoparticles and ungrinded ZnO powder

Fig. 7 a Image of MB dye solutions after various time interval of UV photocatalysis with ZnO nanoparticles, b and their absorption spectra

by 16 min of UV photocatalysis in presence of the ZnO nanoparticles. There was no MB dye degradation occurs in the absence of ZnO nanoparticle under UV irradiation.

Figure 8a indicates the quantitative degradation of MB dye with respect to the UV exposure time (graphical representation of C/C_0 vs. time). Here C_0 is the initial

Fig. 8 **a** Normalized MB dye concentration at different interval of photocatalytic reaction in presence of ZnO nanoparticles, ungrinded ZnO powder and P25 **b** the corresponding $\ln(C_0/C)$ versus time graphs (scatter points : experimental data and solid lines : their linear fits)

concentration of MB dye and C is the concentration of MB dye after a certain time of UV irradiation. As can be seen from Fig. 8a after 16 min of UV irradiation the degradation efficiency $[(C_0 - C)/C_0 \times 100]$ is found to be 96%. In case of Degussa P25 and ungrinded ZnO it took 60 min and 32 min respectively for similar amount of dye decomposition. So from this experiment, it is found that the ZnO nanoparticles prepared from laboratory grade powder is superior UV photocatalyst than both the ungrinded ZnO powder and P25.

The $\ln(C_0/C)$ versus irradiation time graph is shown in Fig. 8b. Here scattered points and solid line represent the experimental data and their linear fit. This graph indicates that the dye decomposition follows the pseudo-fast-order reaction kinetics. The reaction rate constant of ZnO nanoparticle, ungrinded ZnO powder and P25 are estimated to be 0.18 min^{-1} , 0.11 min^{-1} and 0.06 min^{-1} respectively

Fig. 9 Photocatalytic decomposition of MB dye solution by ZnO nanoparticles in absence and presence of scavengers

from the slop of their linear fit lines. From the ratio of this rate constant, it is found that ZnO nanoparticles can exhibit almost double UV photocatalytic activity than the ungrinded powder due to reduction of the average size. The ratio of the reaction rate constants further indicates that the grown ZnO nanoparticles can show 3 times higher UV photocatalytic activity than the standard commercial TiO_2 nanoparticle Degussa P25.

3.5.2 Active species responsible for photocatalytic activity

Figure 9 shows the UV photocatalytic degradation of MB dye solution in the presence and absence of scavengers. When EDTA was added in to the solution, the photocatalytic dye degradation of MB solution after 16 min was 15.40% whereas with the addition of IPA, the degradation was 24.28%. Without any scavenger these degradation was 96%. Generally IPA and EDTA can act as scavengers for hydroxyl radical species ($\cdot\text{OH}$) and holes (h^+) respectively [28].

As, in the presence of these scavengers the dye degradation decreased drastically, it is clear that that h^+ and $\cdot\text{OH}$ takes a crucial role in the decomposition of MB dye.

Based on this scavenger based study the dye degradation mechanism of MB dye with the presence of ZnO nanoparticles under UV exposure can be explained through the following equations [31]:

When UV light falls on the catalyst surface then the electron transfer from valence band to the conduction band. This facilitates photo generation of electron (e^-) and holes (h^+) in the conduction band and valence band respectively (Eq. 1).

The holes could either directly oxidize adsorbed dyes or react with H_2O to generate hydroxyl radicals ($\cdot\text{OH}$) (Eq. 2). The electrons in the conduction band react with dissolved oxygen species to form superoxide radical (O_2^-) (Eq. 3). These $\cdot\text{OH}$ and O_2^- enhance the decomposition process of the dye molecule in to smaller molecules (Eq. 4).

3.5.3 Comparison of the performance with previously reported result on ZnO nanostructures

It is to be mentioned here that the highest value of photocatalytic reaction rate that has been reported with ZnO nanostructures is 2.7 times than that of P25 [26]. So the ZnO nanoparticles reported in this work show the highest photocatalytic activity. The one dimensional structures of our ZnO nanoparticles may attribute to this higher photocatalytic activity, as such structures not only offer large surface area but good charge transport properties.

3.6 Cost aspect of the used ZnO powder

The cost of the used laboratory grade ZnO powder was very less (\$10 for 500 gm). This cost is much lower than the analytical or ACS grade ZnO powder. So the nanoparticles reported by us are very cost effective.

4 Conclusion

In summery the laboratory grade nanoparticles were prepared through the mechanical grinding laboratory grade ZnO powder. For structural analysis, morphology and band edge determination of the nanoparticles different studies like XRD, TEM and diffuse reflectance spectroscopy were done. From XRD result it is found that the material contains Hexagonal/wurzite structure. From TEM analysis it is found that the particles mostly show one dimensional morphology. The average length and diameter of these particles are 300 nm and 59.34 nm respectively. In the diffuse reflectance study the band edge of the nanoparticles is found to be 380 nm. The photocatalytic dye decomposition study was done by using MB dye in the UV light exposure. The reaction kinetics and rate constant are studied by varying the UV exposure time. Performance of ZnO powder is compared with the performance of standard commercial P25 nanoparticles. From this comparison, it is found that the reaction rate constant of our ZnO nanoparticles and P25 are 0.18 min^{-1} and 0.06 min^{-1} respectively. From the ratio of these rate constants it is found that ZnO nanoparticles exhibited three times more UV photocatalytic activity than that of P25. From the photocatalysis studies with scavengers like IPA and EDTA we demonstrated that h^+ and $\cdot\text{OH}$ plays an important role in the photocatalytic dye degradation. The

ZnO powder used by us is extremely low cost, so this material can be a suitable choice for photocatalytic dye decomposition applications.

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