One pot synthesis of ZnO hexagonal bugle beads in a closed polypropylene vessel: a simple hydrothermal way of synthesizing nanocrystalline ZnO photocatalyst for waste water treatments

Khurshaid Ahmad Malik¹, Radha Tomar¹, Javied Hamid Malik¹ and M Burhanuz Zaman²

¹ School of Studies in Chemistry, Jiwaji University, Gwalior—474011, India
² School of Studies in Physics, Jiwaji University, Gwalior—474011, India

E-mail: bhatburhan91@gmail.com

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Abstract
Here, we report a novel and eco-friendly synthesis of zinc oxide (ZnO) hexagonal bugle beads in a closed polypropylene vessel. To the best of our knowledge, we are the first to report synthesis of ZnO nanostructures in a closed polypropylene vessel (a simple hydrothermal reactor). Structural, morphological, compositional and optical properties of the nanostructures were studied. X-ray diffraction (XRD) results demonstrate that ZnO nanocrystals grow in a single crystalline hexagonal phase. Scanning electron microscopy (SEM) reveal formation of nano-dimensional hexagonal bugle beads (base diameter ∼70 nm). The ZnO nanostructures were used to carry photocatalytic degradation of methylene blue (MB) dye. The beads show high photocatalytic performance against MB dye and degraded 89% of the dye in 120 min of UV light irradiation. The reusability test of zinc oxide bugle beads determine high stability of the photocatalyst.

Introduction
Present overpopulated and industrialized world is facing severe problems related to the energy crises and environmental pollution. Industrial boost and modern life style of people has greatly affected the environment by degrading the quality of basic resources like water, air and soil. Introduction of effluents from agriculture, textile and chemical industries have posed a serious threat to water resources that has caused severe shortage of drinking water worldwide. To neutralize the negative impacts of these wastes, catalyst technology was introduced and has been playing front role for degradation of such pollutants.

Wide band gap metal oxides semiconductors are the photocatalysts of high priority [1–5]. Zinc oxide (ZnO) is a wide band gap (3.3 eV) transition metal oxide like TiO₂ possessing exceptional optoelectronic properties and is an attractive multifunctional material [4–9]. ZnO as a photocatalyst has been used for carbon dioxide conversion to methanol, degradation of organic and inorganic pollutants and also in hydrogen generation. Its versatility in morphology and synthesis by low cost, low temperature approaches had make ZnO a material of intensive research.

We here report a novel and facile hydrothermal synthesis of ZnO nanostructures using a polypropylene closed vessel as a reactor. We aimed to synthesize ZnO nanostructures with large surface area exhibiting numerous catalytically active edge surfaces.

Experimental details
The precursor sources and reagents chosen for the synthesis were all of analytical reagent (AR) grade. We here have employed a simple one pot synthesis procedure to prepare nanocrystalline ZnO hexagonal bugle beads. The synthesis was carried out in a closed polypropylene bottle which served as a hydrothermal reactor. An aqueous solution of zinc acetate (0.1 M) was made by dissolving 4.38 g of zinc acetate dihydrate in 200 ml of
distilled water. 0.2 M NaOH solution (100 ml) was added to it while stirring. After few minutes of magnetic stirring, a white colored turbid solution was formed. This solution was then transferred to the polypropylene bottle, placed in a hot air oven maintained at a temperature of 70 °C for 6 h. After the fulfillment of reaction conditions, the oven was switched off and the bottle was cooled naturally at room temperature. Upper liquid of the bottle was decanted and settled white particles were collected. The particles thus collected were washed, dried and ground as described in our earlier reports [10–12]. The white powder thus obtained was captioned as sample A. Few more samples were synthesized at a reaction temperature of 90 °C, keeping rest of the parameters unaltered and were captioned as sample B.

The samples thus synthesized were studied for their structural, morphological, compositional, optical and photocatalytic properties using x-ray diffraction (XRD) technique (Rikagu MiniFlex-600), SEM (Philips, Model-Quanta 200 FEG) and UV-Visible spectroscopy (UV-2450 Shimadzu), respectively.

**Results and discussion**

Phase and crystallinity of the as-prepared samples was determined by the XRD technique. Figures 1(a) and 1(b) shows the XRD patterns of samples A and B respectively. The diffraction peaks obtained are exactly of hexagonal wurtzite ZnO (JCPDS 65–3411) [13]. Absence of extraneous peaks and presence of high intense sharp peaks indicate formation of single phase crystalline ZnO. Sample B grown at higher reaction temperature possess higher intensity peaks than sample A revealing its better crystallinity. The lattice parameters were calculated using the relation:

\[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \]

Lattice parameters calculated are \( a = b = 3.2 \) Å and \( c = 5.18 \) Å which are very close to the reported values for hexagonal ZnO [4]. The single crystalline domain size of samples A and B calculated from the FWHM of (101) peaks using Scherrer formula are 70 nm and 75 nm respectively. Difference in the crystallite size is ascribed to the enhanced growth at higher temperatures. Williamson Hall (WH) plots were drawn (see figures 1(c) and
(d)) to find the presence and nature of strain in the samples. Positive slope of WH plots confirm the presence of lateral strain in the samples[10].

Crystalline behaviour of the synthesized samples was also determined by the selected area electron diffraction (SAED). The SAED patterns of samples A and B are shown in figure 2 and the patterns comprise of concentric bright rings. This indicates the synthesized samples are polycrystalline in nature. d-spacing calculated from the SAED patterns of these samples exactly matches with those obtained from the XRD patterns and hence are in good agreement with each other.

SEM micrographs of samples A and B are shown in figures 3(a) and 3(b) respectively. Hexagonal based bugle bead shaped nanostructures (∼70 nm) are clearly visible in the micrographs. However, formation of the bugle beads is not complete in the case of sample A. Sample B grown at 90 °C comprise these structures throughout, and confirms that this temperature is ideal for the formation of hexagonal bugle beads under the subjected circumstances. Growth in both the samples is anisotropic and this anisotropy is ascribed to the nature of the reaction medium (distilled water) used for the synthesis. During the hydrothermal synthesis, autogeneous pressure developed inside the polypropylene vessel decreases the viscosity of water and facilitates the motion of the ions in the medium. This results in higher reaction rates and favors anisotropic growth thereby leading to such morphology of particles. Moreover growth is preferred along certain facets because of the fact that such facets are energetically favorable.

Figures 3(c) and (d) represents the EDS spectrum of samples A and B respectively. Pie charts in insets of 3(c) and 3(d) show atomic percentages of comprising elements in the material. The comprising elements i.e., Zn and O are in stoichiometry having atomic ratio nearly 1:1. Sample B has a better stoichiometry.

Optical properties of the nanostructures were determined by observing the optical absorbance spectra (see figure 4(a)) of samples A and B. From the absorbance spectra, it is clearly visible that both the samples are transparent to the visible light and at a wavelength of 365 nm there occur a sharp rise in absorbance. This wavelength corresponds to the band edge of the material. Direct energy band gap of ZnO samples was determined using the following relation:

\[
(\alpha h\nu) = A(h\nu - E_g)^{1/2}
\]

Or,

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]

This is a straight line equation and the intercept made by the extrapolated part of the linear portion of the graph \((\alpha h\nu)^2\) Vs \(h\nu\) on hv axis shown in figure 4(b) corresponds to the band gap value. The band gap values are around 3.4 eV that is very close to the earlier reported band gap value of ZnO [4].

Figure 2. SAED patterns of samples (a) A and (b) B.
Photocatalytic degradation of methylene blue

To demonstrate photocatalytic capability of the ZnO nanostructures, photocatalytic degradation of MB dye solution was performed under UV-visible light source (150-W Xe lamp) in a self made photo-reactor as described in our earlier work [10–12]. Two aqueous solutions of MB dye (30 ppm) were made; one without ZnO catalyst and another with the catalyst (sample B). The solution with sample B was stirred under dark for two hours in order to get adsorption desorption equilibrium. Both the solutions were then exposed to UV-visible light and after every 20 min sample aliquots were observed for absorbance using a UV-Visible spectrophotometer. Figure 4(c) shows the time dependent absorbance spectra of sample B treated MB dye solution. It is seen that all the dye bands present in visible (664 nm) as well as in the ultra violet regions (246 nm and 292 nm) show a regular fall in the absorbance with the illumination. As the illumination duration was prolonged, the amount of absorbance showed a regular decaying trend. This decay in the absorbance upon UV-visible light illumination indicates fall in the dye concentration within the solution and hence its degradation. Disappearance of the dye band only in the visible region represents discoloration of the dye solution (the band represents chromophoric group of Methylene blue). However, disappearance of the dye bands in the ultra violet region indicates cleavage of the aromatic rings (Auxochrome groups). Diminishing of all the bands represents the degradation. Thus, the discoloration we obtained upon UV-visible light illumination is because of photodegradation. Percentage degradation of the dye in the solution was calculated using the following relation:

\[ \text{Percentage degradation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]

where, \( C_0 \) is the initial absorption without illumination and \( C_t \) is the absorbance after time ‘t’. It was found that ZnO (sample B) degraded 89% of the dye in 120 min of light illumination. High surface area together with presence of photocatalytically active edge surfaces of the crystalline hexagonal bugle beads are believed to be responsible for such a high photocatalytic activity.

The generation of electron hole pairs upon absorption of light photons by the catalyst is believed to be responsible for the production of highly active free radicals that mineralizes the dye during photocatalytic reactions. Upon illumination with photons of energy greater or equal to the energy band gap of the photocatalyst, photons get absorbed by the catalyst generating electrons-holes pairs. Water molecules adsorbed over the dispersed catalyst surfaces consume these generated charged species and form more active free radicals. Hydroxyl groups of water molecules take up the valance holes and form hydroxyl free radicals. Simultaneously,
the conduction electrons convert the molecular oxygen into superoxides which are believed to form peroxides and finally hydroxyl free radicals. The hydroxyl free radicals are highly oxidizing species and are believed to mineralize most of the pollutants.

From the concentration curves (see figure 4(d)) it is observed that with the catalyst the dye concentration falls very fast in comparison to the blank (without ZnO) solution. The concentration curves clearly determined the catalytic behavior of ZnO.

Stability of ZnO photocatalyst

To commercialize a photocatalyst, stability is an important criterion. We determined the stability of ZnO bugle beads by repeatedly using the nanostructures for three successively degradation cycles of MB. Figures 5(a)–(c) shows the absorbance spectra of sample B treated MB solution for three successive cycles. While using the catalyst for three successively degradation cycles, the degradation percentage falls from 89% to 83% (negligible fall) depicted from the bar diagram shown in figure 5(d). This confirms the stability and reusability of ZnO nanostructures.

Conclusions

In summary, single phase crystalline hexagonal wurtzite ZnO nanostructures were synthesized in a polypropylene vessel serving as a hydrothermal reactor. Influence of reaction temperature was studied and it was concluded that higher reaction temperature enhance crystallinity. Morphological studies showed hexagonal based bugle bead shaped nanostructures with base dimensions ∼70 nm. The material was found to be ultra-violet active with a band gap of 3.4 eV. ZnO bugle bead nanostructures showed enhanced photocatalytic activity against MB dye degrading 89% of the dye in 120 min of UV-visible light illumination. Reuse experiment determined that the nanostructures are very much stable during the photocatalytic reactions. Thus, ZnO bugle
bead nanostructures proved to be promising and feasible photocatalysts for carrying photodegradation of methylene blue dye.

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ORCID iDs

M Burhanuz Zaman https://orcid.org/0000-0003-0691-6338

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Figure 5. (a)–(c) Time dependent absorption spectra of MB dye solution containing sample B catalyst under UV-visible light illumination and (d) degradation efficiencies for three successive cycles.

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