Synthesis and Characterization of ZnO Nanoflowers as an Efficient Solar Photocatalyst

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Abstract. Present study reports the synthesis and characterization of ZnO nano flower through microwave assisted method as a low-cost efficient solar photocatalyst. The prepared ZnOphotocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV-Vis diffuse reflectance (UV-vis DRS) and photoluminescence (PL) spectroscopy. XRD spectra confirm the wurtzite structure with an average crystallite size of 36.39 nm.The FESEM results reveals the formation of ZnOnanoflowers with each petal having the single rod shape with 70-90 nm diameters and 1.2 μm length. The photocatalytic activity of the ZnO nano flower was evaluated using Methylene Blue (MB) as probe pollutant under solar irradiation. ZnO nano flower exhibits superior photoctalaytic performance than commercial Degussa P25in terms of rate constants. The improved photocatalytic activity of the ZnOnanoflower may be attributed to theeffective photon absorption due to flower like structure and reduced charge carrier recombination.

Keywords: Zinc Oxide, Microwave, Solar Energy, Photocatalyst

INTRODUCTION

Zinc oxide has attracted much attention due to its novel performances, such as photocatalyst, solar cell, gas sensor [1] etc. Various nanostructures of ZnO such as nano rods, nano flower, nanoparticles, and hollow spheres have been reported [2]. These structures showed superior photocatalytic activity for the degradation of dyes. Zinc oxide, is one of the most active oxide photocatalyst due to its low cost, non-toxicity and good chemical stability etc. [3-4]. Furthermore, ZnO has a band-gap of 3.37 eV and displays significant optical properties under UV absorption [5]. To improve the photocatalytic performance of ZnO, many research investigations has been carried out to tune and optimize their morphology. In recent years, ZnO nano materials have been synthesized by several techniques such as solvothermal process, sol-gel, hydrothermal etc. [6]. These methods require high temperature and sophisticated set up for the synthesis of ZnO nanostructures. Hence a simple and inexpensive synthesis process is required. Sa Liang et al., reported the synthesis of controlled ZnO structure with flower-like and rod-like morphologies via a microwave- assisted method with better gas sensing property [7]. Conventional synthesis deals with the transfer of heatto the material through convection, conduction and radiation, which cause the temperature gradient between surface and that of the bulk material. Microwaveassisted synthesis, however, offers a fast procedure for the synthesis of nanomaterials with uniform temperature from surface and bulk [8].Hence this microwave assisted method offers several advantages like simple reaction process, forming a chemically homogeneous composition, inexpensive, low energy loss, high-production efficiency, high purity and nontoxic products with good morphology.

Considering the above this work, reports the synthesis of ZnO nano flowers through microwave-assisted technique and evaluation of their photocatalytic performance under solar irradiation.

EXPERIMENTAL

The chemicals used for the synthesis of ZnO nano flowers were zinc acetate dihydrate [Zn(CH3COO)2.2H2O] and potassium hydroxide (KOH) purchased from Merck (India). All the reagents were of analytical grade and Millipore distilled water was used throughout the experiments.

ZnO nano photocatalyst was synthesized using a simple microwave assisted chemical process. Initially zinc acetate dihydrate [Zn(CH3COO)2.2H2O] and potassium hydroxide (KOH) were taken in 1:15 molar ratio and dissolved in 100 ml of deionized water in a round-bottom flask under constant stirring. Then the resultant solution was microwaved at 360Watt and 180oC for 15 min in a domestic microwave oven. The resulting white precipitates was separated by filtration and washed several times with deionized water and ethanol to remove the impurities. The filtered precipitate has been dried at 80 °C for 24 h. Finally the resultant sample werecalcined at 400^{o}C. Hereafter the sample is referred as ZnO-400.

CHARACTERIZATION

The X-ray diffraction (XRD) patterns of the samples were recorded using a diffractometer (Proto Model: AXRD Benchtop, Canada). Field Emission Scanning Electron Microscopy (FESEM) images were taken using Nova Nano FE-SEM 450 (FEI) operated at 1 kV (TLD-SE) & 1 nm at 15 kV (TLD-SE). The spectral response of the sample was evaluated using a UV- NIR spectrometer with diffuse reflectance attachment (Shimadzu| Model:UV 3600 plus| Origin:Japan). The photoluminescence measurements were carried out using a spectrophotometer (Fluromax4, Horibe, USA) for the identification of trap levels.

PHOTOCATALYTIC DEGRADATION EXPERIMENTS

The photocatalytic activity of ZnO-400 was investigated under solar irradiation (550 Watt/m^2) using methylene blue (MB) as probe pollutant in batch reactor. The catalytic material loading of the experiment was kept at 0.5 g/l and the average reactor temperature was maintained at 28^{o}C. The experiments were carried out under solar irradiation for 60 minutes by the simultaneous exposure of the catalysts in 0.01 molar concentration (60ml) under stirred condition. To ensure adsorption-desorption equilibrium each of the solutions were kept in dark for 2 hrs. The samples were taken from the reactor after every 15 min of exposure using a micropipette. The spectral responses of the centrifuged samples were checked at the wavelength of 664 nm (corresponding to absorption maxima of MB) using UV-Visible spectrophotometer (Thermo scientific, India).

RESULT AND DISCUSSION

The X-ray diffraction patterns of the sample was recorded using a diffractometer in the 2θ range of 20˚ to 80˚.Figure.1(a) shows the X-ray diffraction spectra of prepared sample calcined at 400 ˚C. The crystallographic phase of the sample was identified with the help of JCPDS database.All the broad peak positions at respective 2θ angles and the corresponding Miller indexed diffraction planes are found to be in the standard Bragg positions of hexagonal wurtzite phase which are in are in good agreement with JCPDS data (JCPDS No. 36-1541).

Table 1: Physicochemical Characteristics of the Sample.

Samples	**Crystallite Size (nm)**		**Strain**	**Specific surface area (m^2/gm)**	**Bandgap (eV)**
	(WH)	**(Scherrer)**			
ZnO-400	78.12	36.39	0.054	29.39	3.3

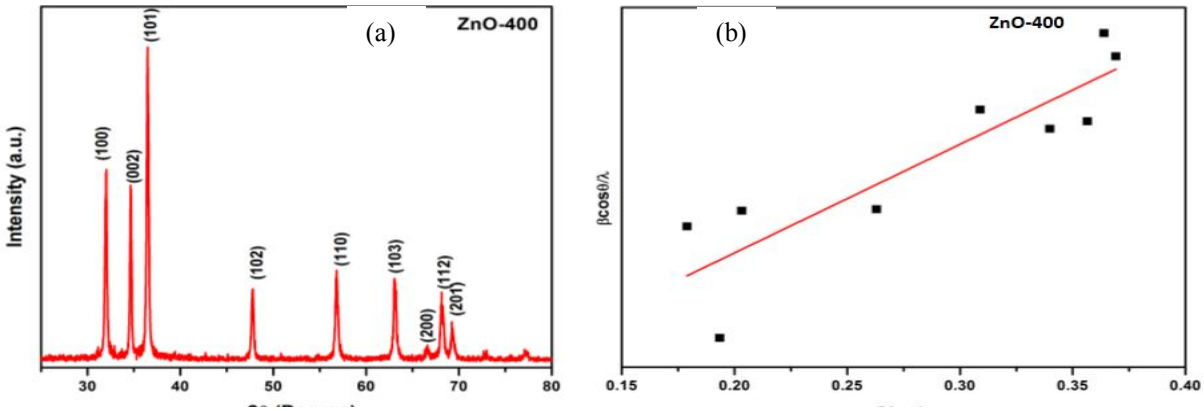

FIGURE 1. XRD spectra (a) and W-H plot (b) of ZnO-400.

The crystallite size of the sample was calculated using both Scherrer's formula and using (Williamson-Hall) W–H method [9-10]. Using W-H method, the strain and crystallite size of the sample was calculated as shown in Figure 1(b) and the values are depicted in table 1. It has been found that crystallite size obtained using Scherrer is different from that of W-H plot, depending on the nature of the strain (positive/negative). Positive strain increases the crystallite size which is shown in table 1 [10].

The surface morphology of the sample synthesized by microwave irradiation is analyzed using FESEM micrographs and shown in Figure 2. The sample showed flower-like structure with each petal having the single rod shape. Rod-like nanostructures exhibit uniform morphology with 70–100 nm diameter and a maximal length of 1.2μm.

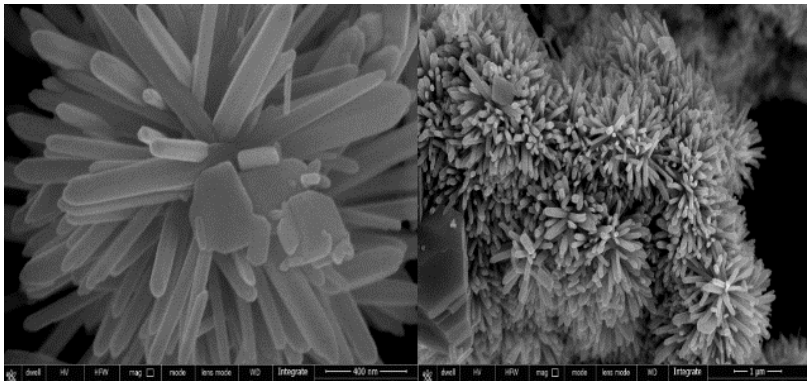

FIGURE 2. FESEM micrographs of as-synthesized ZnO-400

This can be attributed to the strong polarization effects of microwave and high selectivity. Through microwave irradiation, the ZnO particles are more easily formed and moreover, it plays a crucial role in making part of the ZnO particles to form the regular geometric shape [11].

The spectral response of the catalyst material was evaluated with UV-NIR spectra using UV-NIR spectrophotometer shown in Figure 3. The band gap of sample was calculated using modified Tauc's relation by plotting $[F(R)hu]^2$ vs. hυ as shown in Figure 3 and the values are depicted in Table 1 [12]. The samples showed an absorption edge around 390 nm which is in good agreement with the band gap of ZnO.

To identify the trap states of the sample the photoluminescence responses was studied using PL spectra at an excitation wavelength of 360nm. Figure 4 shows the PL spectrum of the synthesized nano flower consists of highintense peaks centered at ~382.48 nm and peaks at ~401 nm (NBE). The PL signal at ~400 nm is a typical ZnO UV emission wavelength. The PL spectrum also has two weak emission peaks at ~471 nm. The UV emission peak which is also known as near band emission (NBE) could be attributed to the recombination of free excitons through an exciton–exciton collision process. [11, 13].

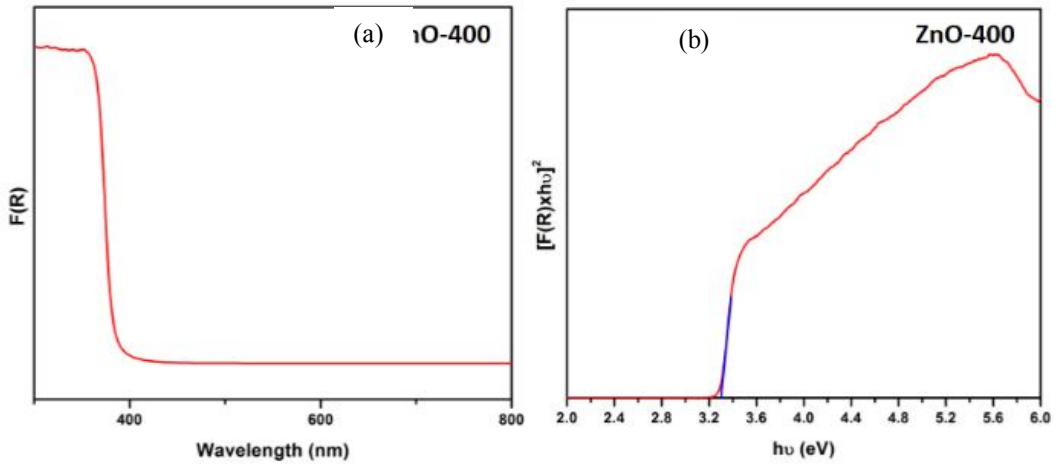

FIGURE 3. Diffuse reflectance spectra (a) and Taucs plot (b) of znO-400.

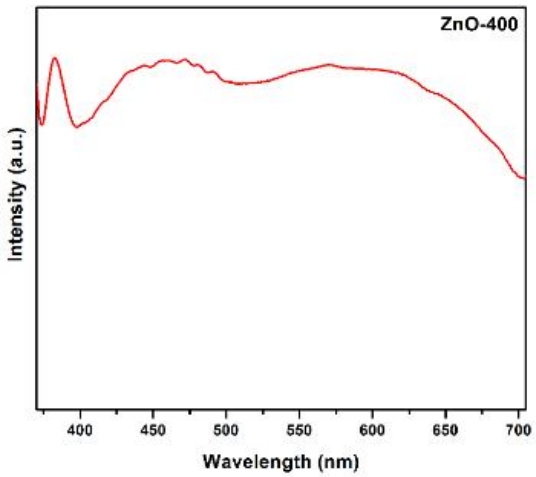

FIGURE 4. Photoluminescence spectra of ZnO-400.

The photocatalytic performance of the sample was evaluated using Methylene Blue (MB) as probe pollutant under solar irradiation. The degradation spectra of the sample with respect to time are shown in Figure 5 (a & b). The degradation rate constant of the sample was calculated by plotting time and $-\ln(C/C_0)$. ZnO-400 photocatalyst showed 10 times superior photocatalytic performance than that of Degussa P25 and other reported photocatalyst [14], which may be attributed to the effective photon absorption and charge carrier separation due to the presence of nano flowers. Compared with Degussa P25 [14], the solar photocatalytic activity of ZnO-400 has improved significantly, suggesting that the effect of good morphology of the product on photocatalytic activities cannot be ignored. The apparent reaction rate constant of ZnO-400 is 0.0626 min^{-1}.

CONCLUSION

In summary, we have demonstrated a simple microwave assisted route to obtain ZnO nano flower as a highly efficient photocatalyst. XRD spectra reveal the wurtzite structure of the ZnO with no impurity phases. It has been found that flower-like ZnO exhibits 10 times superior photocatalytic performance under solar irradiation compared to commercial Degussa P25 and ZnO powder. PL study confirms the efficient suppression of recombination of photogenerated electrons and holes, which plays a vital role in enhancement of photocatalytic performance.

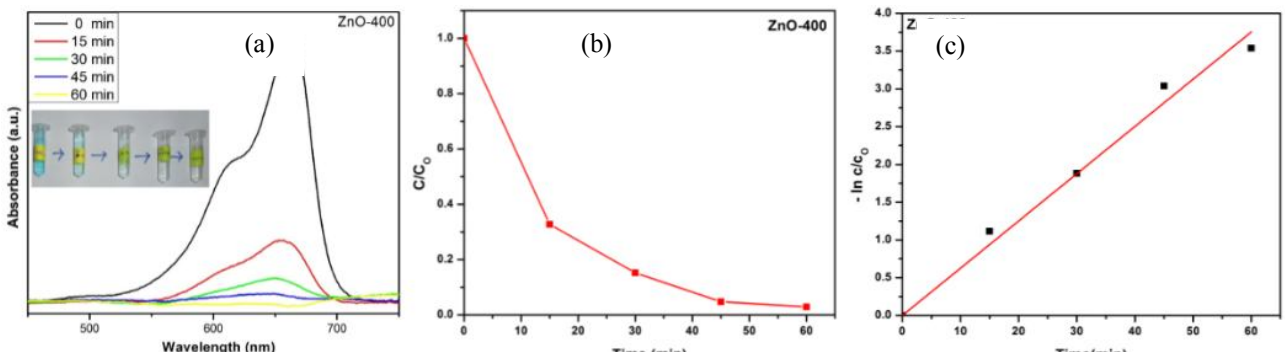

FIGURE 5.UV-vis absorption spectra of MB at different time in the presence of ZnO-400 (a) MB degradation spectra (b) and rate constant calculation spectra (c) of the sample.

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