Research Article

Synthesis of Novel ZnO Having Cauliflower Morphology for Photocatalytic Degradation Study

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ZnO nanowire morphology has been widely studied due to its unique material properties and excellent performance in electronics, optics, and photonics. Recently, photocatalytic applications of ZnO nanowire are creating an increasing interest in the environmental applications. This paper presents a low-cost and ecofriendly synthesis of ZnO with cauliflower morphology and its effectiveness in photocatalysis.

1. Introduction

Organic dyes are very important and widely used in different industries such as textile, rubber, and plastic and hence one of the largest group of pollutants released into wastewaters [1]. They have caused several environmental contaminations, affecting human survival and developments. Degradation and removal of them are a great challenge for protecting the environment. However, the routine techniques for treating organic dyes are usually ineffective and costly to remove pollutants from water [2]. Nanomaterials have attracted high interest due to their noticeable performance in electronics, optics, and photonics. One-dimensional (1D) nanostructures such as nanowire, nanorods, nanofibers, nanobelts, and nanotubes have been of intense interest in both academic research and industrial applications. They also play an important role as interconnectors and functional units in the fabrication of electronics, optoelectronics, electrochemical, and electromechanical nanodevices [3]. For their application in solar energy conversion and environmental purification, among various semiconductor photocatalysts, TiO 2 is much known for its strong oxidizing power and nontoxicity. But the major limitation in semiconductor photocatalysis is the relatively low value of the overall quantum efficiency, because of the high recombination rate of photo-induced electron-hole pairs at or near its surface.

ZnO is a semiconductor material with direct wide band gap energy (3.37 eV) and a large exciton binding energy (60 meV) at room temperature. ZnO is currently attracting worldwide intense interests because of its importance in fundamental studies and its numerous applications especially as optoelectronic materials [4, 5], UV lasers [6], Light-emitting diodes [7], solar cells [8], nanogenerators [9], gas sensors [10], photodetectors [11], and photocatalyst [12].

Photocatalysis is the promising process for environmental protection because of being able to oxidize low concentrations of organic pollutants into benign products [13–15]. Figure 1 shows mechanism of photocatalytic process. There are number of semiconductors that could be used as photocatalyst, such as TiO 2, ZnO, and WO 3. Although TiO 2 is the most widely investigated photocatalyst, ZnO has also been considered as suitable alternative of TiO 2 because of its comparability with TiO 2 band gap energy and its relatively lower cost of production [16–18]. Moreover, ZnO has been reported to be more photoactive than TiO 2 [19–22] due to its higher efficiency of generation and separation of photoinduced electrons and holes [16, 23, 24] to interactive bacteria, viruses, and for the degradation of environmental pollutants.

In this paper, the synthesis of low-cost and ecofriendly ZnO, an emphasis on cauliflower morphology of ZnO, is used...
in photocatalysis. We have presented the characterization of ZnO cauliflower and compare its properties with other semiconductors like ZnO nanowire and TiO₂.

2. Experimental Data

2.1. Synthesis of ZnO Nanoparticle. Sol-gel process has many advantages when compared to vapor phase and hydrothermal processes, because of its low cost, low temperature, scalability, and ease of handling. Generally, sol-gel reaction occurs at relatively low temperature (<200°C); therefore, to save energy sol-gel elemental reaction was used for the preparation of nanocauliflower ZnO particle. The ZnO crystalline powder was prepared by the following process with the use of zinc acetate as metal precursor and starch as stabilizer. Zinc acetate with purity (99%) and starch having purity (99%) were purchased from Merck India and used without further purification. Ammonia was purchased from S.D. Fine chem. Ltd. with purity (27%). The aqueous solution (0.1 mol/L) of zinc acetate dihydrate was prepared with deionized water, and 4% starch was added as stabilizer. The pure ammonia was slowly added into zinc acetate solution at room temperature under stirring rate of 4000 rpm, which resulted in the formation of a white suspension. Then, it refluxed for half an hour at 100°C. The suspension was then separated with a centrifuge 5000 rpm and washed properly with plenty of distilled water and was washed with absolute alcohol at last to remove the unreacted chemicals.

2.2. Photocatalytic Activity of ZnO Nanocauliflower. Photocatalytic activities of nano-ZnO sample were evaluated by photocatalytic degradation of MB under UV lamp (Philips 18W) using as a light source. A beaker of 100 mL was used as reaction vessel, and the distance from the lamp to the solution was 12.5 cm. The experiments were performed at room temperature as follows: 0.1 g of photocatalyst was added into 100 mL MB solution of 2 ppm (2 mg/Liter), and the pH of the initial solution was about 7. Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to ensure the adsorption/desorption equilibrium between the photocatalyst powders and the solution. At given time intervals of 10 minute, 4 mL of suspensions were sampled and centrifuged to remove the photocatalyst powders. Evaluation of photocatalytic activities of photocatalyst was conducted.

Figure 1: A schematic of the principle of photocatalysis from [25].

Figure 2: X-ray diffraction of cauliflower ZnO nanocauliflowers.
by recording the variations of absorption band maximum through a UV-Visible spectrophotometer (Shimadzu UV-1800). MB concentration was analyzed by recording the variations of the absorption band maximum (663 nm).

3. Result and Discussion

3.1. XRD. The X-ray diffraction analysis of prepared ZnO nanocauliflowers was carried to identify the product (Figure 2). All diffraction peaks are indexed with the corresponding planes of ZnO. The XRD spectra showing the highest intense peak at 36.16, 31.73, and 34.40 which are the crystal plane of ZnO. The low intensity peaks at 47.46, 56.47, and 62.83 which match well with the JCPDS File no. 00-036-1451. No other diffraction peaks arising from metallic Zn or Zn(OH)$_2$ are present in the XRD pattern, which indicates the high phase purity of the synthesized sample. The crystal size of products calculated by Scherrer formula was $50 \pm 100$ nm.

3.2. Morphology. Texture, thickness, and crystal size of ZnO also affect the quality of ZnO [26–29]. Wu et al. [27] studied the effect of seed layer characteristics on the synthesis of ZnO nanowire. The effect of the starch on the morphology of products has been reported in the literature [28]. Figure 3 shows the role of starch in the preparation of ZnO. So, a control experiment without the addition of starch was done here, and the SEM images of the products are exhibited in Figure 4(a). It shows cauliflower like morphology. This may attribute to the larger surface-to-volume ratio of ZnO cauliflowers than that of rocks, which helps to increase the photocatalytic reactions sites and promote the electron-hole separation. Additionally, the PL results indicate that ZnO nanocauliflowers have fewer defects compared with ZnO nanorods. Defects may serve as recombination centers for photoexcited electron-hole pairs during photocatalysis; therefore, the decrease of defects implied the decrease of photocatalytic activity. From the TEM (Figure 5) image, it is confirmed that the particle size between 50 and 100 nm agrees well with XRD analysis. TEM images confirmed the connectivity between cauliflowers which is observed in SEM images. The SEM and TEM images of ZnO show that the growth of particle is very well organized. Nuclei formation and growth of the particle simultaneously occur, and hence it is appears like cauliflower. Starch is biological molecule having symmetric orientation and may not allow the growth of the particles in random manner. This is may be advantages to use of the biological molecule as a stabilizer of nanoparticle having a specific orientation as well as beautiful morphological nature having tailored properties of specific application [28].

3.3. FTIR. Figure 6 shows the FTIR of the ZnO nanoparticle prepared by the sol-gel method, in the range of 4000–600 cm$^{-1}$. A broad absorption band was observed at around 616, 716, and 2913 cm$^{-1}$; it clearly represented bonding between Zn–O and C–H. There were several small absorption bands at 921, 1024, 1062, and 3316 cm$^{-1}$ that are likely related to CO$_2$ (C–O) and H$_2$O (O–H) absorbed from the atmosphere (air), and these absorption bands can be neglected. The FTIR results show the high purity of the obtained ZnO nanoparticle.
3.4. Optical Properties. The room temperature UV absorption spectra of ZnO nanoparticle are shown in Figure 7. The spectrum reveals a characteristic absorption peak of ZnO at wavelength of 378 nm which can be assigned to the intrinsic band gap absorption of ZnO due to the electron transitions from the valence band to the conduction band ($\text{O}_2^p \rightarrow \text{Zn}_{3d}$). In addition, this sharp peak shows that the particles are in nanosize, and the particle size distribution is narrow. It is clearly shown that the maximum peak in the absorbance spectrum does not correspond to the true optical band gap of the ZnO nanoparticle. A common way to obtain the band gap from absorbance spectra is to get the first derivative of the absorbance with respect to wavelength and find the maximum in the derivative spectrum at the lower energy sides. It indicates a band gap of 3.26 eV. for the nanocauliflower ZnO particle. The good absorption of the ZnO nanoparticle in the UV region proves the applicability of this product in photocatalytic applications.

3.5. PL Spectrum. Optical properties of functional nanomaterials are of importance considering further applications in nanoelectronic devices. Therefore, the optical properties of the prepared ZnO nanocauliflower were further investigated by PL spectroscopy. Figure 8 shows a typical room temperature photoluminescence (PL) spectrum of ZnO nanorods and nanocauliflower with excitation wavelength 325 nm at room temperature. The spectrum exhibits two bands including a strong ultraviolet emission at 378 nm (or 3.26 eV) and a weak spectral band in visible region. The UV emission
was contributed to the near band-edge emission of the wide band gap of ZnO. Visible emission is due to the presence of various defects such as oxygen vacancies.

4. Photocatalytic Degradation of Methylene Blue

The various organic pollutants that have been tested and removed under UV light illumination include methylene blue, monocrotophos, and diphenylamine. ZnO nanowires used as photocatalysts have been recently reported by many research groups [30–33]. Sugunan et al. [30] described a continuous flow water purification system by the fabrication of ZnO nanowires. Baruah et al. [34] reported a fast crystallization ZnO nanorods synthesis method to increase the surface defect of the ZnO nanowires, an increase in the surface defects and vacancies are capable of exhibiting visible light photocatalysis even without doping with transition metal [34]. In this paper, photocatalytic activity testing was carried out in UV light and was degraded 2 ppm of methylene blue solution.

The control analyses show that the degradation of MB is negligible in the absence of ZnO catalysts. The degradations of the MB in the presence of ZnO nanorods (Figure 9(a)) and ZnO nanocauliflowers (Figure 9(b)) were measured by UV irradiation ($\lambda_{\text{max}} = 365$ nm) at room temperature at various times. The result indicates that the ZnO cauliflowers show higher photoactivity after 120 minutes (Figure 9(c)). We also tested the photocatalytic activity for ZnO nanocauliflowers, ZnO nanowires, and TiO$_2$. Figure 10 revealed that ZnO nanocauliflowers accelerate the photocatalytic degradation process as compared to ZnO nanowires and TiO$_2$ nanoparticles. It is due to surface properties, such as surface defects and oxygen vacancies of photocatalysts, that play a significant role in the photocatalytic activity and also morphology of ZnO that affects the photocatalytic activity, SEM images for prepared ZnO showed cauliflower-like structure which may absorb more light because of surface modification as compared to nanowires and enhance the photocatalytic activity.

To further investigate the mechanism, we studied the photocatalytic reaction dynamics. It has been well established that heterogeneous photocatalysis by semiconductors follows the Langmuir-Hinshelwood (LH) dynamic model:

$$\frac{1}{R} = \frac{1}{kK} \times \frac{1}{C} + \frac{1}{k'},$$

(1)

where $R$ is the reaction rate, $k$ is the reaction rate constant, $K$ is the adsorption equilibrium constant, and $C_0$ is the initial dye concentration. When $C_0$ is small, the reaction follows first-order kinetics with a rate equation in the form

$$-\ln \frac{C}{C_0} = kKt = k't,$$

(2)

where $C$ is the dye concentration at time $t$ and $k'$ is the apparent first-order rate constant.

5. Conclusion

This paper provides an overview of the synthesis, characterizations, and application of ZnO nanocauliflowers. The sol-gel method is simple, low cost, and efficient, and it has received an increase attention. Through changing the morphologies, starch play an important role in the growth
of ZnO nanocauliflowers. Due to the unique properties of material, ZnO nanocauliflowers are attractive for the number of potential application such as photocatalysis, solar cell, sensor, and generators. Among the application of the ZnO nanocauliflowers, photocatalysis is used for environmental protection. Based on this paper, ZnO nanocauliflowers promise to be one of the most important materials in photocatalytic as well as other application.
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