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Microwave Assisted Synthesis of Zinc Oxide Nanoparticles

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Abstract: Zinc oxide nanorods have been synthesized through facile microwave assisted route using palmitic acid (PA) as a green stabilizer as well as bio-surfactant. The as-synthesized ZnO nanomaterials were characterized using X-ray diffraction (XRD), Scanning Electron microscope (SEM) and Micro-Raman spectroscopic techniques. The photocatalytic properties of synthesized ZnO nanorods were studied by the degradation of Alizarin Red S (ARS) dye.
Keywords: Zinc Oxide; Palmitic acid; Alizarin Red S dye; Photocatalyst.

1. Introduction

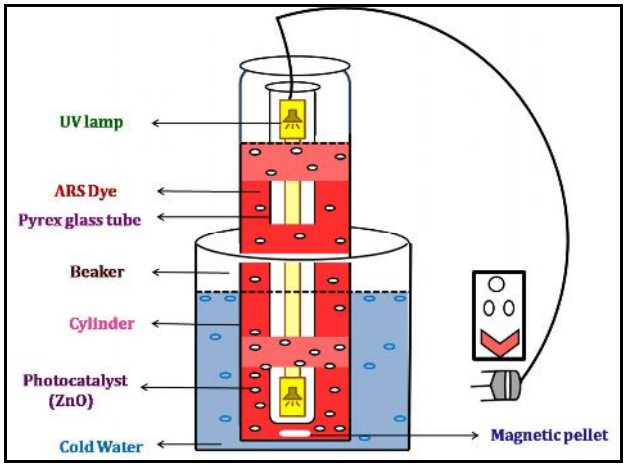
The industrial effluent water is discharged from various short scale and/or large scale industries such as chemical, pulp, dye, garments, plastic, paper, medical and biomedical industries. Industrial effluent water contains huge amount of organic dyes and the said industries generate enormous amount of dye waste. These dye effluents will pollute the environment and also affect the human being due to its mutagenic and carcinogenic properties, when disposed it without any prior treatment. There are several methods are already exist for wastewater treatment and one such technique is photocatalytic degradation[1-4]. Synthesis of appropriate nanostructured materials is an emerging research field and they have attracted much interest among the researchers especially in recent years due to their unique properties. Moreover, the nanomaterials are used in different areas such as chemistry, physics, nanotechnology, biotechnology, biomedical sciences etc.[5,6]. The nanomaterials are also used in various applications such as super capacitors, sensors, photocatalytic degradation and solar cells[7-12]. Among the semiconductor oxide nanomaterials, zinc oxide (ZnO) nanoparticles have attracted much interest on photocatalytic applications. ZnO materials are highly ionic; wide band gap and it has unique properties such as optoelectronic, ferromagnetic, piezoelectricity, catalysis, conductivity and sensing properties[13-15]. These properties are depends on the crystalline nature, surface change, size and shape of the ZnO nanomaterials. This Zinc oxide nanoparticles (NPs) also have a good biocompatibility, antibacterial and antifungal activity. Hence, we have synthesized ZnO nanomaterial using bio-surfactant such as palmitic acid (PA). In this work, we mingled nanotechnology with biological values to make healthy environment [16-21]. The palmitic acid is a bio-surfactant and it belongs to the category of fatty acids. Palmitic acid has low melting point (62.9° C) and boiling point (271-352° C) hence, it act as a catalyst throughout the reaction. The shape and size of the semiconductor materials are controlled using Palmitic acid as green stabilizer. To the best of our knowledge, the synthesis of ZnO nanoparticles using palmitic acid has never been reported previously by microwave method. The present work deals with the synthesis and characterization of ZnO nanorods by simple and economical microwave route. The photocatalytic activity of the synthesized zinc oxide powders was investigated by degrading the Alizarin Red S dye under UV light irradiation.

2. Experimental Methods

2.1. Materials and Methods

Zinc acetate dihydrate (ZnOAc. $2H_2O$), sodium hydroxide (NaOH), Palmitic acid were used as received. All the chemicals were purchased from Sigma–Aldrich. The ZnO nanopowder was synthesized by simple solution precipitation method. 0.1 M of zinc acetate dihydrate ($C_4H_6O_4Zn.2H_2O$) and 0.6 M of sodium hydroxide (NaOH) solutions were prepared separately using water. The NaOH solution was added slowly into a zinc acetate solution with constant stirring about an hour and the pH was maintained at 4–5. Then, the ethanolic solution of palmitic acid was added drop wise into the above mixer with vigorous stirring and eventually a nucleation formation occurred in a very short period. Finally, a white coloured precipitate was obtained. The presence of palmitic acid stimulates the reaction rate and it promotes the growth of ZnO crystallites. The resultant precipitate was washed and dried at 80°C for 2 hours. The final powder was placed on microwave oven and the microwave radiation (2.45 GHz) was introduced for 10 to 30 min. The microwave treated powder turned white into pale yellow colour.

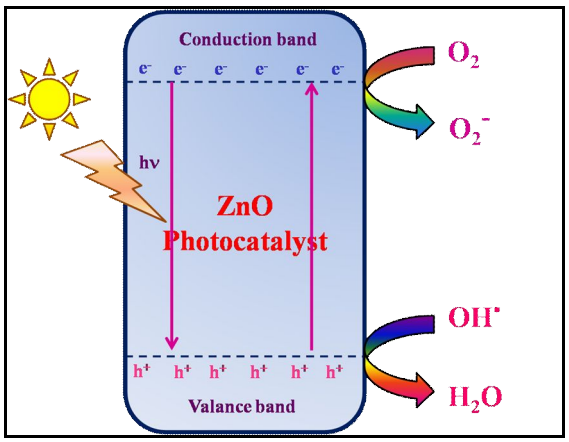
2.2. Photoreactor Setup



Scheme 1: Schematic diagram of Photo-reactor Setup

The synthesized zinc oxide powder was used as a photocatalyst for the degradation of ARS dye under UV light illumination. The schematic diagram for photoreactor setup is shown in scheme 1. Photoreactor consists of the following parts, which are UV-light lamp (6 W UV lamps), Pyrex glass tube (inner tube), 1000 ml beaker, magnetic stirrer and clamp. The UV lamp is situated inside the inner tube and the magnetic stirrer is placed under the beaker. The magnetic stirrer is used for the circulation of dye (800 rpm) with photocatalyst. Pyrex glass was selected for inner tube based on its excellent transmittance of UV light. The reactor contains 10 ppm ARS dye and photocatalyst. 1000 ml Beaker contains cold water to control the temperature.

2.3. Photocatalytic Study



Scheme 2: Photocatalytic reaction mechanism – A schematic representation

The photocatalytic activity of the ZnO powder was investigated by the degradation of Alizarin red S dye under UV light. 0.1 g of ZnO was dispersed in 10 ppm Alizarin red S dye (ARS) solution. ARS dye with photocatalyst (reaction mixture) was stirred in a cylinder at room temperature. The UV light source is also used. The photocatalytic reaction mechanism is shown in scheme 2.

2.4. Characterization

The prepared ZnO powder was characterized by using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Micro-Raman spectroscopic techniques. The dye degradation was measured by UV-vis spectra. The structural property of ZnO was studied by XRD using Cu-Kα (λ = 0.154 nm) radiation source (X' pert Pro PAN alytical) over a 2θ scan range of 10–80°. Morphological features of the samples were examined by Scanning Electron Microscope (SEM; JEOL JCM-6000, 15 KV). Micro-Raman studies were done using STR Raman spectroscopy. The ARS dye degradation was measured by UV–vis spectrophotometer (SHIMADZU UV-1800) in the wavelength range of 200–1100 nm.

3. Result and Discussion

3.1. X-Ray Diffraction Analysis

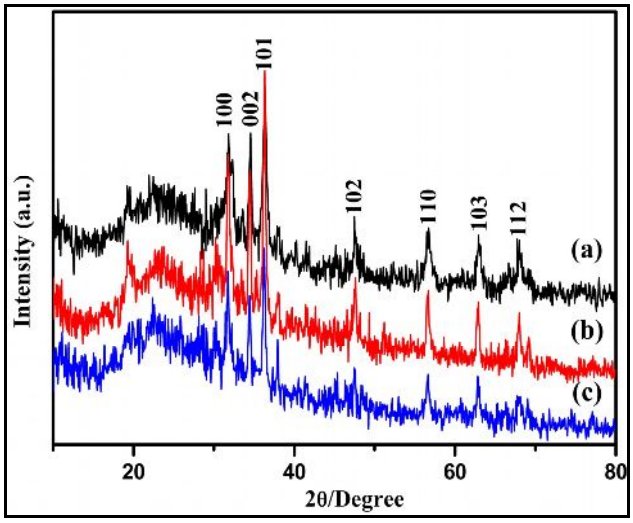


Figure 1: XRD patterns of ZnO nanomaterials prepared by microwave irradiation of (a) 10, (b) 20, and (c) 30 min, respectively.

The phase, structure, crystalline nature and purity of the synthesized zinc oxide powder were determined from XRD analysis [22-24]. Fig. 1 shows a typical XRD pattern of the prepared ZnO nanomaterials. The appeared diffraction peaks are indexed to the ZnO and it matches very well with JCPDS Card No. 897102. There was no impurity peaks detected in the XRD, indicating that the prepared ZnO powders are pure. The XRD peaks are observed corresponds to the directions of (101), (002) and (100), respectively. XRD shows the prepared samples have hexagonal wurtzite structure and good crystalline nature. The average crystallite size of prepared metal oxide nanomaterials was calculated using Debye Sherrer's formula.

$$D = 0.89\lambda / \beta \cos\theta$$

Where, D is the average crystallite size, λ (=0.15405 nm) is the Cu Kα wavelength, β is the full width at half maximum (FWHM) and θ represents Bragg angle. From Fig.1, the peak (a), (b) and (c) shows the average crystallite size range of about 43.97, 21.85 and 25.29 nm, respectively.

3.2. Scanning Electron Microscopic Observations

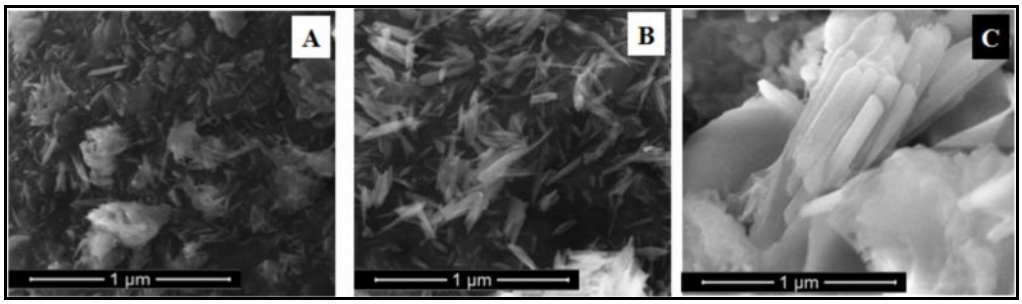


Figure 2: SEM images of zinc oxide particles prepared by microwave irradiation of (a) 10, (b) 20 and (c) 30 min, respectively.

Figure 2 shows the typical SEM micrographs of as-prepared ZnO nanomaterials. The formation of zinc oxide particles by microwave irradiation was confirmed by XRD pattern. SEM pictures of the samples heated at 10 min, 20 min and 30 min are shown in Fig. 2 (a), (b) and (c), respectively. The SEM images of the prepared samples confirm the formation of rod shaped zinc oxide morphology.

3.3. Raman Spectroscopic Analysis

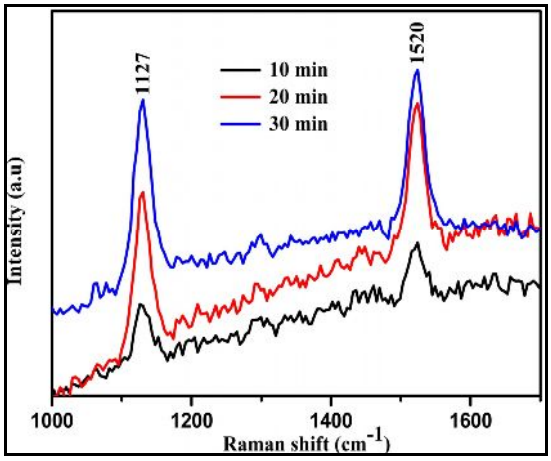


Figure 3: Raman spectra of ZnO nanorod shaped particles prepared by microwave irradiation of (a) 10, (b) 20 and (c) 30 min, respectively

4. Photocatalytic Degradation of Alizarin Red S Dye

The Raman spectra of ZnO nanorods prepared by microwave irradiation are shown in Fig. 3. Raman scattering is a powerful technique to examine the defects, structure and crystallization in the ZnO nanostructured materials. Fig. 3 shows the appearance of Raman shift at 1127 and 1520 cm^{-1}. The Raman shift observed at 1127 cm^{-1} is corresponding to the second order vibration mode. The peaks at 1127 cm^{-1} corresponds to the B_1 mode and 1520 cm^{-1} corresponds to H_g (8) mode [25].

The photocatalytic degradation of ARS dye was carried out using 0.1 g of ZnO photocatalyst under UV light irradiation. The colour removal efficiency of ARS dye by synthesized ZnO nanorods is shown in Fig.6a. The photocatalytic degradation efficiency of 74.55%, 35.79% and 50.34% was obtained using ZnO samples a, b and c (microwave irradiated at 10 min, 20 min and 30 min), respectively. The higher decolourization efficiency of 74.55% was achieved by 0.1 g of 10 min irradiated photocatalyst, owing to the existence of best active site for attacking of molecule by rapid development of hydroxyl radicals. Further, the investigation on the effect of photocatalyst dose on photodecomposition was also studied and it was found that the increase of photocatalyst dose decreases the colour removal efficiency of ARS dye. This may be due to the formation of turbidity in the ARS dye solution and the diffusion of UV light may be delayed by the increase in scattering effect by low UV

light penetration [26-33]. The kinetics study was performed for the photocatalytic degradation of ARS dye and it follows first-order kinetics (Fig. 6b).

The kinetics equation can be expressed as follows:

$$ln\ C_0/C_t = kt$$

where, Ct is the concentration of the ARS dye solution at t time, C_0 is the initial concentration of the ARS dye solution and k is the rate constant.

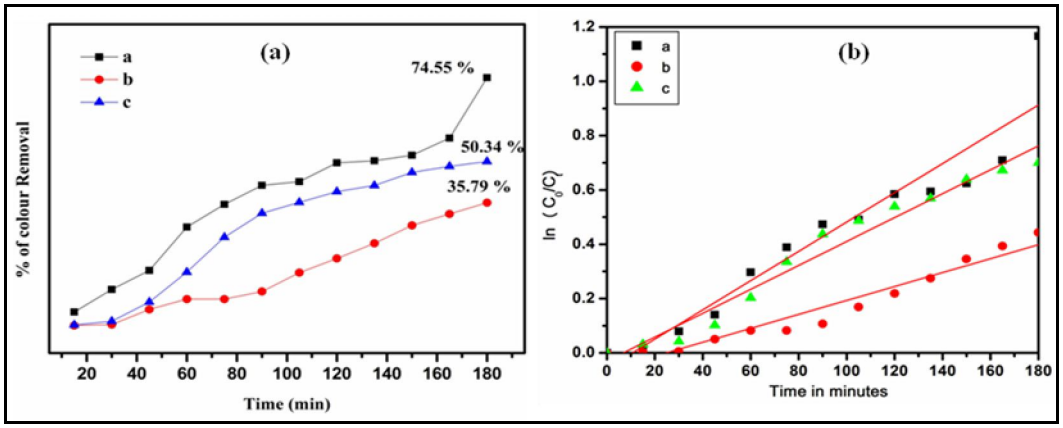


Figure 4: (a) Comparison of dye degradation efficiency in presence of zinc oxide particles prepared by microwave irradiation of (a) 10 (b) 20 and (c) 30 min, respectively under UV light irradiation. (b) The plot of ln(*Co*/*Ct*) Vs irradiation time for photocatalytic degradation of ARS dye using zinc oxide particles prepared by the microwave irradiation of (a) 10, (b) 20 and (c) 30 min, respectively, under UV light irradiation.

The kinetic rate constant value of ARS dye in presence of ZnO samples (samples prepared by microwave irradiation of 10, 20 and 30 min) were calculated and the values are 0.00648, 0.002461 and 0.00389 min^{-1}, respectively. The higher rate constant was observed for the ZnO samples prepared by microwave irradiation of 10 min. It further confirms that the sample (a) has good photocatalytic activity. Figure 7 shows the UV-vis spectra of degraded ARS dye using ZnO photocatalyst within 180 min under UV light.

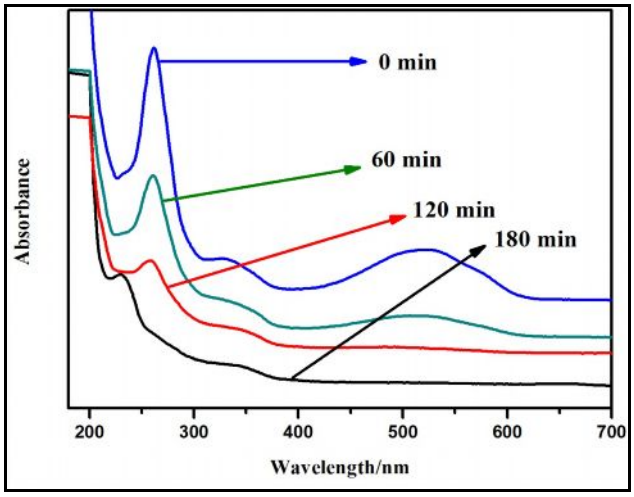


Figure 5: UV-vis spectra of degraded ARS dye solutions

The typical band of the ARS dye exhibited maximum absorption peak at 260, 330 and 480 nm wavelength. The decrease in the absorption of ARS dye was found while increasing the light irradiation time. There is no any new band was observed in the UV-vis spectra of ARS dye, indicates the ARS was directly decomposed into harmless CO_2 and water [34-37].

5. Conclusions

In summary, we have developed nanorod shaped zinc oxide particles by microwave method. The structural characterization confirmed the formation of crystalline ZnO. SEM micrograph revealed the rod shape morphology of synthesized ZnO materials. The synthesized zinc oxide nanomaterials could decompose the ARS dye under UV light. The highest decomposition efficiency of 74.55% was achieved by ZnO which was prepared by 10 min microwave irradiation.

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