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Synthesis of Zno Microspheres Via P-123 Assisted Precipitation Route and Its Photodegradation Ability

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ABSTRACT

Flower like ZnO microspheres were synthesised by a conventional precipitation route using Pluronic P-123 triblock copolymer as the template. X-ray diffraction analysis (XRD) confirmed the hexagonal wurtzite crystalline structure of ZnO with the mean crystalline size of 37 nm. Fourier transform infrared spectrum (FT-IR) showed the existance of Zn-O stretching vibration, indicating the formation of ZnO with surface adsorbed water molecules. Field emission scanning electron microscopy (FESEM) images presented the microsphere like morphology of ZnO crystals with special aggregation of cubic units, after calcination. Photocatalytic activity of ZnO microflowers was investigated for methylene blue degradation. ZnO microflowers enhanced the degradation of methylene blue under UV-light irradiation. Effect of initial dye concentration and catalyst dosage were varied to get better degradation results.

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INTRODUCTION

Nanomaterials have been extensively used in many applications because of their exceptional properties, altered from that of the bulk form. ZnO is one of the most widely used n-type semiconductor with a wide band gap of 3.37 eV and a binding energy of 60 meV. It has caught the attention of researchers based on its excellent optical and electrical properties. ZnO finds application in the field of photonics, electronics and heterogeneous catalysis and it is also used in the assembly of solar cells, gas sensors, light emitting diodes etc. (Chen, K.J., 2009; Wang, Z.S., 2001). Different methods such as precipitation, sol gel, hydrothermal, pulse laser deposition, chemical vapor deposition, microwave synthesis, sonochemical and ultrasonic route etc. have been established for the synthesis of ZnO nanoparticles (Paul, G.K., 2003; Zareie, M., 2013). Out of these, precipitation route provides the uniform distribution of particles in nanorange (Hong, R.Y., 2009). In addition to this, precipitation is one of the most active techniques reported so far for the synthesis of ZnO, since it offers a modest method to switch the several characters of ZnO nanostructures (Amornpitoksuk, P., 2012).

Many synthesis reports based on the precipitation route uses sodium hydroxide and ammonium or sodium carbonate as the precipitants, which further require a calcination step to synthesize pure ZnO from the intermediate precursor (Pudukudy, M. and Z. Yaakob, 2013). ZnO nanostructures with characteristic morphology were obtained by those techniques. For the first time, Kumar *et al*. (2011) synthesized ZnO nanopowders by precipitation method using ammonium hydroxide as the precipitating agent at room temperature. In this article, Pluronic P-123 triblock copolymer aided precipitation method was employed to synthesize ZnO microspheres with attracted morphology. The material was characterized for its phase, structure and morphology identification. Photocatalytic activity of the prepared sample was investigated for dye degradation under UV-light irradiation.

Experimental Procedure:

In a 1 L beaker, 3 g of Plutonic P-123 triblock copolymer was dissolved in 500 ml of distilled water with proper stirring and 18.2 g zinc nitrate hexahydrate was added into it and stirred for 10 minutes. After that slight excess of NH_4OH solution was added drop wise with stirring so that the pH of the solution becomes 12-14. The precipitated solution was then boiled for 30 minutes and allowed to cool at room temperature very slowly. The obtained precipitates were filtered, washed with distilled water and dried at 100°C for 12 hours. The dried powder is then calcined at 400°C to obtain ZnO microcrystals. The prepared ZnO material was characterised for

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its phase, structure and morphology identification. FT-IR spectrum of the sample was recorded in a thermoscientific NICOLET 6700 apparatus in the 400-4000 cm^{-1} region. XRD analysis was performed using a Bruker D8 Focus powder diffractometer with Cu Kα radiation at a wavelength of 0.15406 nm. FESEM study for the morphology determination was done in a Zeiss SUPRA 55 scanning electron microscope with an operating voltage of 10 kV. Methylene blue dye was selected to monitor the photodegradation capacity of ZnO microspheres. In the typical experiment, weighed amount of ZnO (0.05g except for the catalyst dosage study) was suspended in 50 ml of dye solution and the reaction mixture was kept in dark for the establishment of adsorption desorption equilibrium, for 15 minutes with continuous air bubbling. After that the dispersed solution was irradiated under UV light in a photoreactor, with the continuous air bubbling. After 10 minutes duration of time interval, the solution was centrifuged and its absorbance was measured for the calculation of efficiency of photodegradation, using UV-vis spectrophotometer. Efficiency = $((A_0-A)/A_0)*100$, where A_0 and A represents the absorbance of the dye solution before and after the reaction.

RESULTS AND DISCUSSION

Figure 1(a) represents the FT-IR spectrum of the synthesised ZnO sample. The well intense narrow band centered at 470 cm^{-1} indicated the formation of ZnO. It is attributed to the stretching vibration of zinc-oxygen bond in transmission mode. The broad bands in the spectrum at ~1500 and ~3500 cm^{-1} were attributed to the bending and stretching vibration of O-H bond arose due to the adsorbed water molecules. Negligible amounts of organic impurities were present in the sample as shown in Figure 1(a), which is due to the template used in the synthesis.

Figure 1(b) represents the XRD pattern of the ZnO powder. All indexed peaks at the 2θ values 31.68°, 34.48°, 36.38°, 44.78°, 56.68°C and 62.76°, with the corresponding (h k l) planes i.e. (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) were directly indexed to the hexagonal wurtzite crystalline structure of ZnO (JCPDS - 00-36-1451). Lattice parameters of the hexagonal ZnO was found to be a = 0.3251 nm and c = 0.5207 nm. No other peaks of impure phase were detected in the plot, which confirms the phase purity of the ZnO. The average crystalline size calculated using the Scherrer's equation was found to be ~37 nm.

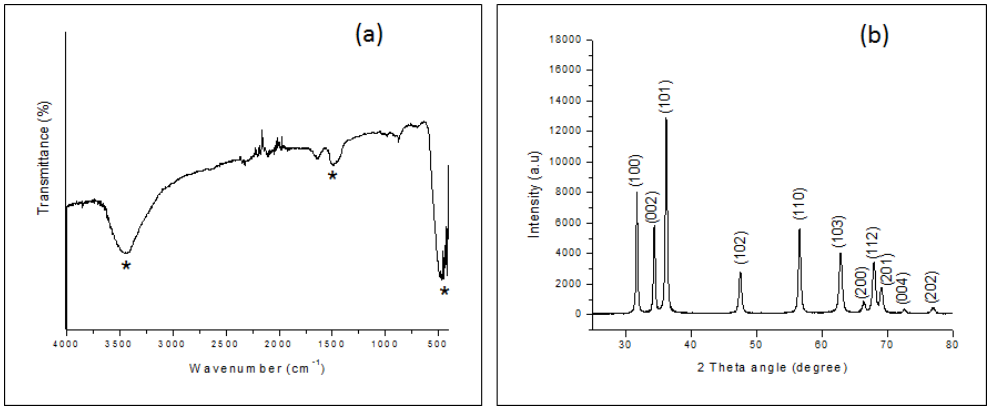

Fig. 1: (a) FTIR spectrum; (b) XRD pattern of the ZnO

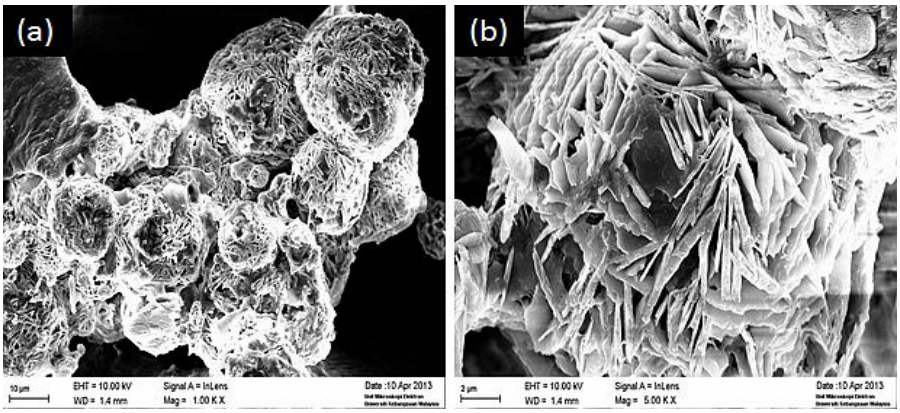

Fig. 2: FESEM image of precipitated sample dried at 100°C.

Figure 2(a) represents the FESEM image of the precipitated sample dried at 100°C. It shows the sphere like structures with the bulk porosity and the size of such spheres are in micro range. High magnification image in Figure 2(b) show that the microspheres were composed of several vertically aligned flake/plate like units with fine edges. The sharp edged plate like structures was aggregated in such way to form the microspheres. This may be due to the effect of Pluronic P-123 used in the synthesis. Figure 3 shows the FESEM images of the calcined ZnO sample. Flower like microspheres were observed in Figure 3(a) and which are formed by the agglomeration of several cubic units as shown in Figure 3(b).

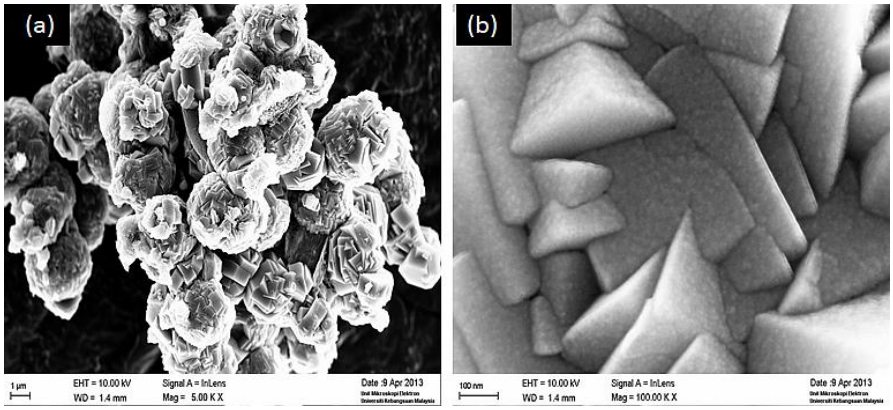

Fig. 3: FESEM images of ZnO.

To validate the impending environmental application of the ZnO microspheres, we investigated the photodegradation of dyes. Methylene blue was selected to monitor the degradation ability of ZnO under UV irradiation. Photodegradation effectiveness of the sample was shown in Figure 4(a). From the figure it is clear that the direct photolysis of MB was negligible under UV light irradiation, because only 1.5% self-degradation was noted within 70 minutes. The addition of ZnO increased the degradation rate drastically as shown in the degradation plot. For 5 mg/L dye concentration, within 40 minutes 100% degradation was observed. But with increase in the initial dye concentration, the percentage of degradation was decreased as we expected. Under UV illumination for 70 minutes, 83 and 61 % degradation was observed for 10 and 15 mg/L dye concentrations respectively.

Figure 4(b) shows the influence of catalyst dosage on the degradation rate of 10 mg/L dye concentration for 30 minutes. Several experiments were carried out to optimize the effect of catalyst dosage by varying the catalyst amount from 0.05 g to 0.25 g. From the figure, it is clear that the rate of photodegradation increased with increase in the amount of catalyst from 0.05 g to 0. 15 g, which is attributed to the increased number of photons absorbed on the catalyst, so that more active catalyst surfaces were available for the reaction. There is no effect was observed with further increment of the catalyst weight.

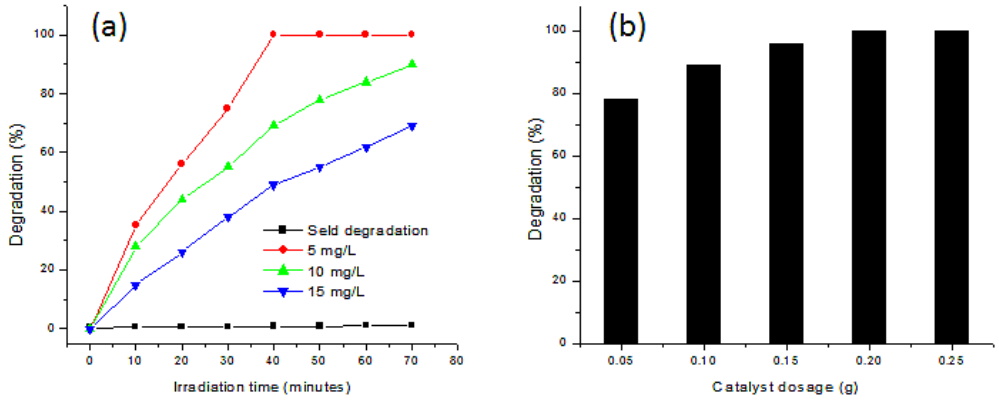

Fig. 4: (a) Photocatalytic degradation of MB with different dye concentrations; (b) Effect of catalyst dosage.

Conclusion:

Flower like ZnO microspheres were synthesised by conventional precipitation route using the Pluronic P-123 tri block copolymer as the template. FT-IR spectrum and XRD pattern confirmed the formation of

hexagonal wurtzite crystalline structure of ZnO with the average crystalline size of ~37 nm. High phase purity was observed by calcination of the precipitated sample. FESEM images confirmed that the ZnO microspheres were formed by the aggregation of cubic units. Photodegradation of methylene blue was carried out to confirm the permanent dye pollutant removal capacity of the as-synthesised ZnO sample. With increment in the dosage of ZnO photocatalyst, the degradation time was reduced as expected.

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