



Microwave assisted facile synthesis of 3D flower-like ZnO nanostructures for enhanced photocatalytic degradation/removal of Eosin Y from water

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Received 27 October 2020; accepted 22 February 2021

Three-dimensional ZnO nanoflower has been synthesized via microwave irradiation technique using glycine as complexing/capping agent for the first time. TEM, SAED, XRD, FTIR, UV and PL spectra have been recorded to characterize the synthesized ZnO nanostructures. The TEM image indicates the formation of 3D flower-like ZnO nanostructures having diameter ~ 0.74 - $1.60 \mu\text{m}$. The spacing between adjacent lattice fringes obtained from the HRTEM image is 0.145 nm which indicated the presence of (103) lattice plane of ZnO. The synthesized ZnO nanoflower show excellent luminescence properties. The photocatalytic properties of synthesized ZnO nanoflower is depicted by the degradation of Eosin Y dye under solar irradiation. It is found that 98.9% of Eosin Y dye is degraded within 50 min under solar irradiation. Henceforth, ZnO nanoflower acts as an effective photocatalyst for the degradation of Eosin Y dye.

Keywords: 3DZnO nanoflower, Eosin Y, FTIR, Microwave, Luminescence, X-ray technique

ZnO is a II-VI semiconductor having a wide band gap energy of 3.37eV^1 and has gained a lot of interest due to its promising applications in catalysis, sensors, antibacterial treatment, photocatalysis, etc.²⁻⁸ The non-toxicity, stability, environmentally friendly nature, and optical transparency of ZnO nanostructures in visible region make it one of the most promising materials in several areas. ZnO nanostructures were synthesized by numerous synthetic tools such as chemical precipitation, sol-gel, hydrothermal, microwave assisted method, etc.⁸⁻¹⁰. This article reported the synthesis of ZnO nanoparticles by microwave irradiation technique. Microwave irradiation method is a simple and environmentally benign technique which has various advantages over conventional heating such as short reaction time, high reaction rate, energy saving and provides uniform heating.

In this communication, ZnO flower-like nanostructures were fabricated via microwave irradiation technique using the amino acid glycine, which act as a good complexing and capping agent. It was evident from the literature that size, morphology and properties of nanoparticles were modified due to the presence of amino acids. Microwave assisted synthesis of ZnO nanoflower (ZnO NF) using glycine has not been reported in the literature.

Dyes constitute a major class of organic compound having huge applications in our daily life. Most of the

dyes are toxic and carcinogenic in nature. However, dyes find practical applications in textile industries, dyeing, printing, cosmetics etc. The effluents coming out from these industries contaminate water system thereby causing water pollution. For the treatment of such polluted water, metal oxide nanostructures were employed as photocatalyst. Herein, we reported for the first time the degradation of Eosin Y dye under solar irradiation using 3D ZnO NF as photocatalyst. Moreover, sunlight is the most abundantly available natural source of energy which can be easily utilized and the use of inexpensive and inexhaustible solar irradiation makes the degradation process economically more feasible.

Experimental Section

All the reagents, zinc nitrate hexahydrate NaOH, glycine and Eosin Y were of analytical grade (Merck, Darmstadt, Germany).

A solution of $0.01 \text{ M Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 20 mL was mixed with 20 mL of an aqueous solution of glycine, 0.01 molL^{-1} , and 20 mL of an aqueous solution of 0.01 molL^{-1} NaOH was added under vigorous stirring. The reaction mixture was then kept in a microwave oven and was irradiated with thirty 10s shots. This led to the formation of white precipitate which was centrifuged and washed three times with distilled water. The white product obtained was dried at 120°C and collected for characterization.

ZnO nanostructures were characterized by powder X-ray diffraction (XRD) (X'Pert PRO, Philips) with CuK_α radiation wavelength of 1.5418\AA . Size, morphology and diffracted ring pattern were investigated by transmission electron microscopy (TEM) (JEM-2100, Jeol). Infrared spectra (Hyperion 3000, Bruker) and absorption spectrum (100 BIO UV-Vis, Cary) were recorded. Photoluminescence measurements were carried out using a spectrofluorometer (LS 45, Perkin-Elmer).

The photocatalytic activity of ZnO NF was investigated by the degradation of Eosin Y (EY) dye under direct sunlight. To evaluate the photocatalytic activity, 10 mg of ZnO photocatalyst was dispersed in 200 mL of 10^{-4}M aqueous solution of EY by sonication. The solution was then kept in dark for 30 min to obtain the adsorption/desorption equilibrium. Afterwards, the reaction mixture was exposed to sunlight irradiation. The experiments were carried out on a sunny day at Silchar city between 10 a.m. – 3 p.m. (outside temperature $35\text{--}40^\circ\text{C}$). At a regular interval of time, 4 mL of the dye suspension was withdrawn and centrifuged immediately. The progress of the reaction was monitored by recording UV-visible spectroscopy at regular interval of time.

Results and Discussion

The FTIR spectrum of ZnO NF was depicted in Figure 1(a). The peak arising at 552 cm^{-1} represented

the characteristic stretching vibration of Zn-O bond¹¹. Therefore, the FTIR spectrum showed the formation of ZnO. The bands at 3418 cm^{-1} , 2924 cm^{-1} , 2853 cm^{-1} and 1629 cm^{-1} were attributed to the characteristic O-H, C-H asymmetric and symmetric stretch of $>\text{CH}_2$ group and C=O stretching mode respectively, present in the amino acid namely, glycine, which indicated the binding of amino acids tightly on the surface of ZnO nanoparticles. Therefore, the FTIR spectrum depicted the adsorption of amino acid, namely glutamic acid, on the surface of ZnO and predicted the role of amino acid as capping agent in the synthesis of ZnO NF.

The crystal structure, purity and the crystalline nature of the synthesized ZnONF was elucidated using XRD pattern (Fig. 1b). The diffraction peaks were well indexed to the hexagonal wurtzite structure of ZnO and were in good agreement with the JCPDS card no. 65-3411. Meanwhile, no peaks for the precursor molecules or intermediates were observed which implied the complete conversion of precursor molecules into final products. The XRD pattern also depicted the highly crystalline nature of ZnONF.

Absorption and photoluminescence spectra were recorded in order to study the optical properties of the synthesized ZnO NF. Figure 1(c) represented the UV-visible spectra of the synthesized ZnO NF. The absorption spectra showed broad band around 380 nm which corresponded to the characteristic absorption

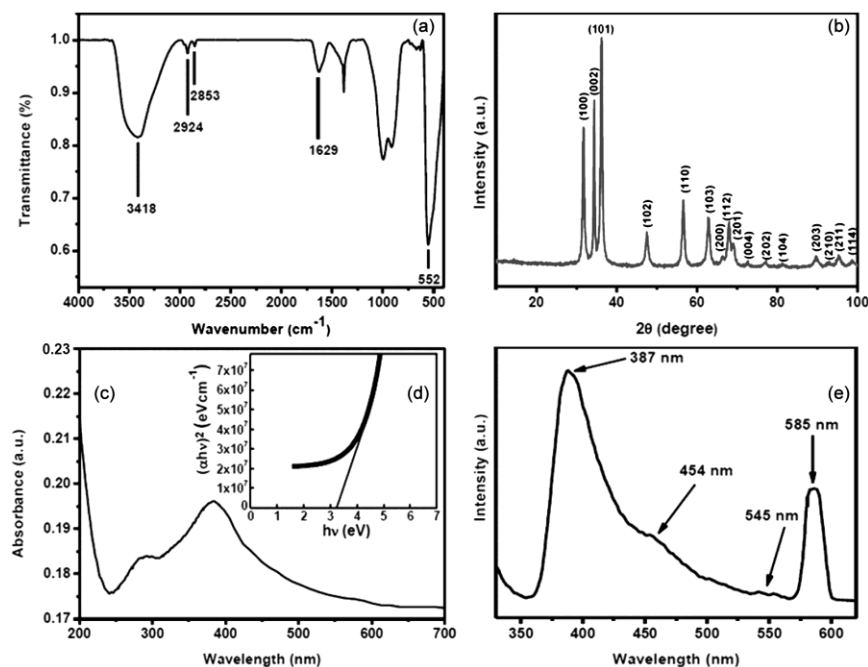


Fig. 1 — (a) FT-IR spectrum of ZnONF; (b) XRD pattern of ZnONF; (c) Absorption spectrum of ZnONF; (d) Plot of $(\alpha hv)^2$ versus photon energy ($h\nu$) and (e) PL spectrum of ZnONF

band for hexagonal pure ZnO nanoparticles¹². Therefore, the absorption spectra confirmed the formation of ZnO nanostructures. The band gap energy of synthesized ZnONF was calculated using Tauc plot by plotting $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$) and extrapolating the linear portion of the curve to zero absorption coefficient¹⁰. Figure 1(d) represented the graphical plot of $(\alpha h\nu)^2$ versus incident photon energy ($h\nu$) for the synthesized ZnONF and from the graphical plot band gap energy was calculated and found to be 3.25 eV. Hence, a clear blue shift in the band gap energy was observed with a decrease in particle dimension which is attributed to the quantum effect observed in semiconductor metal oxide nanoparticles.

Figure 1(e) represented the PL spectra of synthesized ZnONF. The ZnONF showed a broad UV emission band around 387 nm at $\lambda_{ex}=300$ nm. A high intensity yellow emission band around 585 nm along with low intensified blue and green emission bands around 454 and 545 nm, respectively was also observed in the PL spectra of ZnO NF¹⁰. Hence, aminoacid mediated synthesis of ZnO nanostructures showed excellent unusual luminescence properties and this property may arise due to the presence of aminoacids on the surface of ZnONF as capping agent.

The morphology and the microstructure of ZnO NF were analyzed using TEM and HRTEM images. The TEM image (Fig. 2a) displayed the formation of three-dimensional flower-like ZnO nanostructures with diameter of $\sim 0.74 - 1.60 \mu\text{m}$. The flower-like structure arises due to the self-orientation of closely arranged multiple petals. The spacing between adjacent lattice fringes obtained from the HRTEM image was 0.145 nm which reflected the presence of (103) lattice planes of ZnO (Fig. 2b). The SAED pattern (Fig. 2c) revealed the d-spacings of 0.28 nm, 0.145 nm and 0.098 nm corresponding to (100), (103) and (212) lattice planes, respectively of standard ZnO crystal (JCPDS 65-3411). The SAED pattern indicated the hexagonal phase of ZnONF which was in concordance with the XRD pattern of ZnO.

The photocatalytic activity of the synthesized 3D ZnONF was evaluated by monitoring the changes in the absorption spectra of EY solution during its photo degradation process. The characteristic absorption band of EY observed at 517 nm decreases gradually during the course of degradation of EY dye under solar irradiation and the color of the solution also fades away with the increase in irradiation time within 50 min (Figure 3a). The degradation reaction followed pseudo first order kinetics.

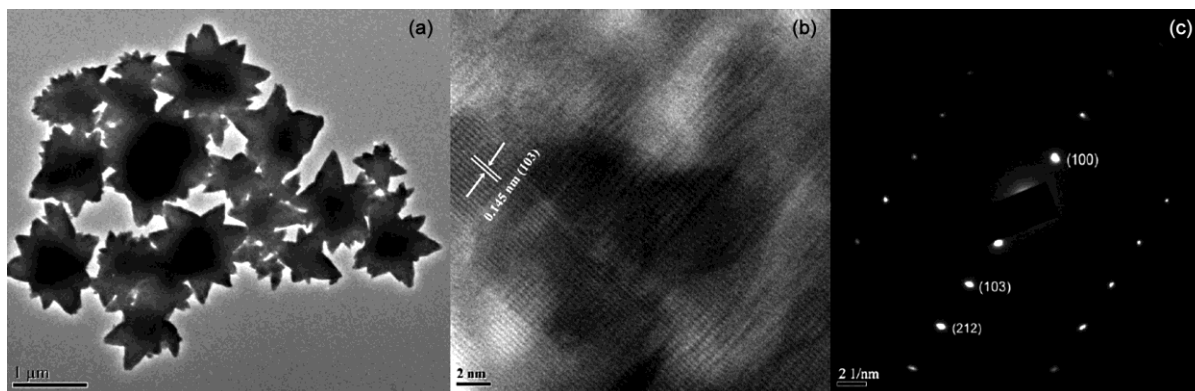


Fig. 2 — (a) TEM microphotograph of ZnONF; (b) HRTEM image of ZnONF and (c) SAED pattern of ZnONF

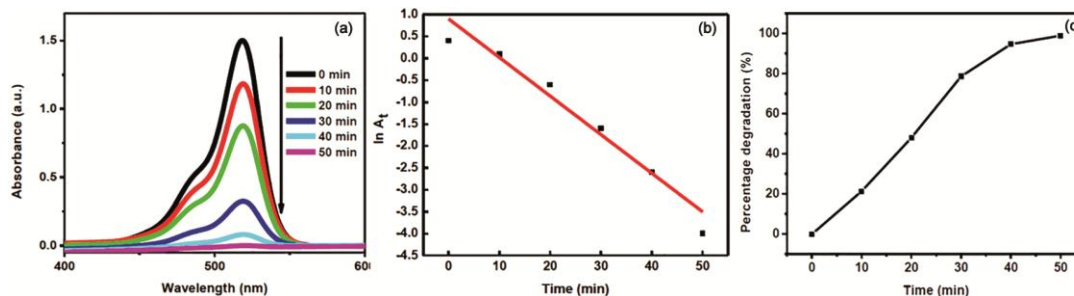


Fig. 3 — (a) Photodegradation of Eosin Y (EY) dye by solar irradiation using synthesized ZnONF as photocatalyst; (b) Plot of $\ln A_t$ versus irradiation time for photodegradation of EY dye using ZnONF and (c) Percentage efficiency of photodegradation of EY dye with time

Therefore, the rate constant for the degradation of EY was obtained from the linear plot of $\ln A_t$ versus irradiation time (Figure 3b). The slope of the linear plot represents the rate constant (k) for the degradation of EY dye and was found to be 0.088 min^{-1} . Figure 3(c) graphically represents the percentage efficiency of photodegradation of EY dye with time and it is observed that 98.9% of EY degraded within 50 min under solar irradiation. Hence, ZnO NF acts as an effective photocatalyst for the degradation of EY dye.

Conclusion

A facile microwave assisted route has been developed for the synthesis of 3D ZnO NF using glycine as complexing and capping agent. The ZnO NF having an average diameter of $\sim 0.74\text{-}1.60 \mu\text{m}$ possesses hexagonal crystal structure and is well crystalline in nature. ZnONF showed unusual luminescence properties wherein, high intensity UV and yellow emission bands are observed along with negligible blue and green emission bands.

The synthesized ZnO NF also acts as an efficient photocatalyst in the degradation of Eosin Y dye within 50 min by solar radiation for the first time.

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