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Hydrothermal synthesis of novel Zn doped CuO nanoflowers as an efficient photodegradation material for textile dyes



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ABSTRACT

In this article, the investigations on the doping of cupric oxide (CuO) nanorods with Zn(II) ions and their photocatalytic properties have been reported. The Zn doped CuO nanoflowers were synthesized by hydrothermal method using three different concentrations of Zn (II) ions, without structure directing agent. The presence of Zn ions exhibits CuO growth with monoclinic structure which favors the formation of nanoflowers morphology. The crystalline structure, morphology and the optical properties of the obtained nanostructures were characterized using XRD, FESEM/EDX and UV-visible spectrometer. The photocatalytic performance of the prepared Zn-CuO nanoflowers was examined for the degradation of methylene blue (MB) and methylene violet (MV) under UV irradiation. 0.07 M Zn-CuO nanoflowers exhibited the highest degradation rate of 1.7175 h^{-1} for MB and 2.383 h^{-1} for MV.

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1. Introduction

Semiconductor-based photocatalytic degradation of organic pollutants has attracted great interest due to its unique features such as high specific surface area, chemical stability and electrochemical activity at nanoscale [1–2]. Among various semiconductor materials, copper based oxides such as cuprous oxide (Cu_2O), cupric oxide (CuO) and their composites (ZnO/CuO) [3] with unique properties are well known for their substantial applications in catalysis, sensors [4] and energy storage devices [5]. Cu_2O is widely employed in energy applications due to its high charge mobilities; whereas, research is going on to employ CuO p-type semiconductor with a band-gap E_g of 1.2 eV, due to its high carrier concentration. CuO is a very important photocatalyst, owing to its high photosensitivity, and physical and chemical stability which can degrade organic water pollutants [6–10]. So far, diverse CuO nanostructures such as nanowires, hollow spheres, dandelions and rods have been synthesized by complex or stringent reaction conditions [11–14]. However, the fast recombination rate of the photo-generated electron–hole pairs formed in the photocatalysis process limits the effective degradation. Therefore, CuO composites with other transition metal oxides (e.g. ZnO) were synthesized in order to reduce the recombination rate [15–16]. Also,

other transition metal oxide composites such as $\text{ZnO}-\text{TiO}_2$ were also used in order to suppress the recombination of charge carriers thereby leading to a remarkably enhanced photocatalytic activity [17]. However, synthesis of active photocatalysts with high specific surface area materials for the decomposition of various organic water pollutants is a challenging task for the materials scientist. In the present study, a simple and cost-effective hydrothermal method was used to synthesize novel flower-shaped Zn doped CuO nanostructures and its photocatalytic behavior at different concentrations of Zn(II) was studied.

2. Experimental

The CuO nanorods and Zn-CuO nanoflowers with 0.03 M, 0.05 M and 0.07 M of Zn were prepared by hydrothermal method. In a typical procedure, 0.3 M of copper nitrate was dissolved in 40 ml of distilled water under constant stirring. About 3 ml of ammonia and 3 M of sodium hydroxide was added to the above solution and was stirred for 30 min. This mixture was transferred to Teflon lined stainless steel autoclave which was then heated at 160 °C for 12 h in a hot-air oven. A black colored powder (CuO) was obtained after filtering, washing and drying the sample. The Zn-CuO nanoflowers were synthesized by the addition of zinc nitrate (0.03 M) to the above reaction product. The same procedure was repeated for various concentrations of zinc nitrate (0.05 M and 0.07 M). The crystal structures of the obtained

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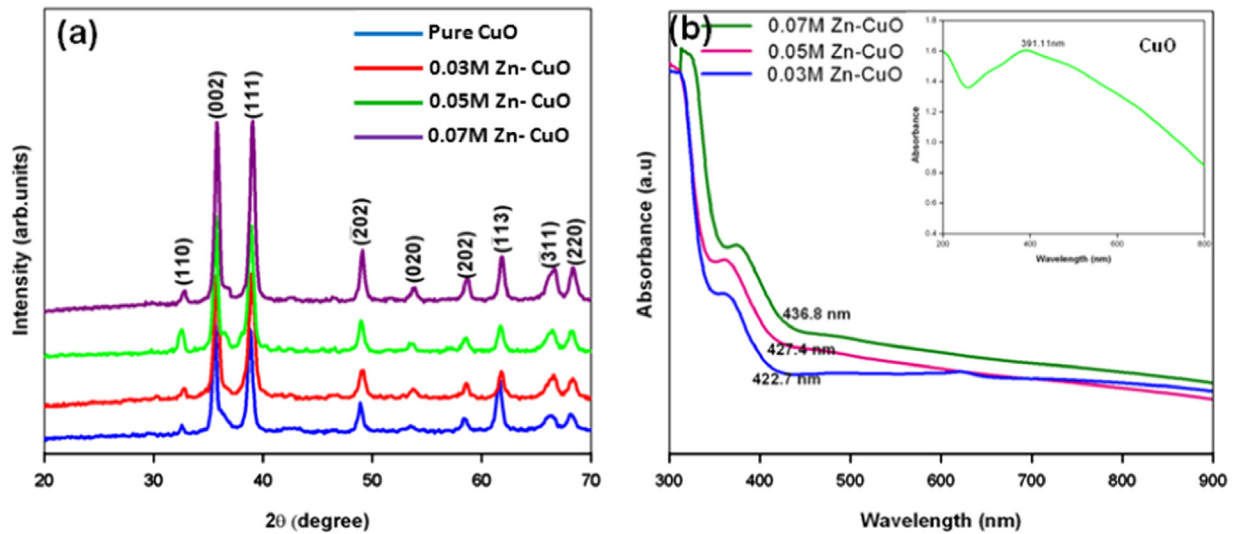


Fig. 1. a) XRD pattern of pure and Zn-CuO nanostructures and b) Absorption spectra of Zn-CuO nanostructures; the inset shows the absorption spectrum of pure CuO.

Table 1

Comparison of average crystalline sizes of pure CuO and Zn doped CuO obtained by Scherrer formula and Williamson-Hall plot (W-H plot)

Samples	Scherrer formula (nm)	W-H plot (nm)
CuO	21.70	21.93
0.03 M Zn-CuO	22.83	22.16
0.05 M Zn-CuO	24.39	25.21
0.07 M Zn-CuO	26.64	26.37

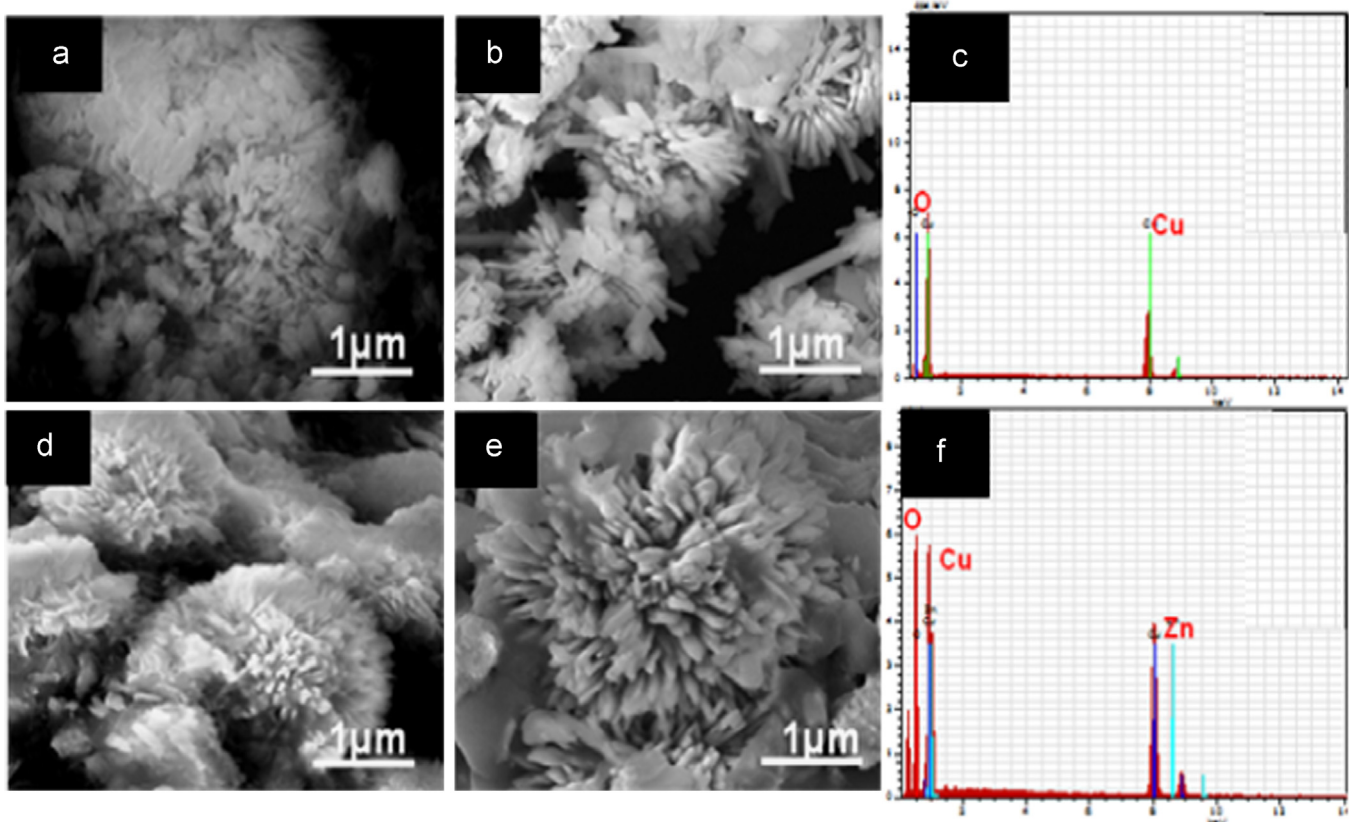


Fig. 2. FESEM images of (a) pure CuO, (b) 0.03 M Zn-CuO, (d) 0.05 M Zn-CuO, (e) 0.07 M Zn-CuO and (c and f) EDS spectra of pure and Zn-CuO nanostructures.

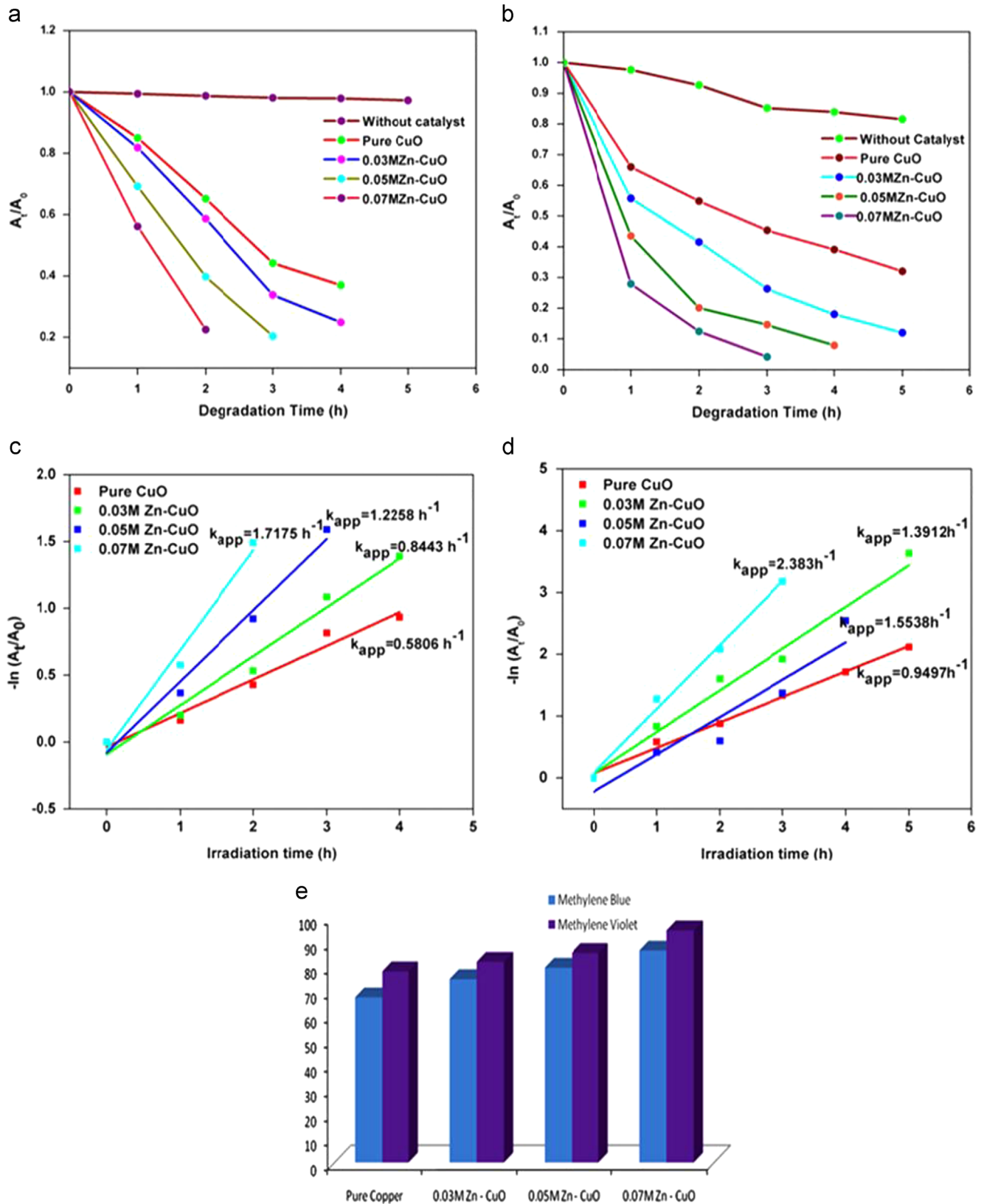


Fig. 3. Effect of different catalysts on the photodegradation of a) methylene blue, b) methylene violet, degradation rate for, c) methylene blue, d) methylene violet and e) the comparison of degradation efficiency of different photocatalysts.

products were characterized by studying the X-ray diffraction pattern (PANalytical X'pert Pro with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$)). The morphology and elemental composition of the samples were analyzed using a field

emission scanning electron microscope (FEI QUANTA-250). Absorption spectra (JASCO V-650 Spectrophotometer) were used to analyze the optical properties of the prepared nanostructures.

3. Results and discussion

Fig. 1a shows the XRD patterns of CuO and Zn doped CuO nanoflowers. All the samples are highly crystallized as indicated by the sharp diffraction peaks. The diffraction peaks along the (1 1 0), (0 0 2), (1 1 1), (2 0 2), (1 1 3) and (2 2 0) planes confirm the monoclinic structure of CuO and are well matched with the standard data (JCPDS- Card #05-0661). Also no diffraction peak of ZnO appears in the XRD pattern. Cu²⁺ ions in the lattice structure were replaced by Zn²⁺ ions since there was not much difference in the ionic radius of Cu²⁺ (0.73 Å) and Zn²⁺ (0.74 Å). The average grain sizes estimated from Scherrer formula ($D = 0.89\lambda/\beta\cos\theta$) and W-H plot (Fig. S1) are shown in Table 1. From Fig. 1a it is observed that the peak intensity of Zn doped CuO is higher when compared to undoped CuO.

The optical properties of nanostructures strongly depend on the absorbance of the material related to the transition of charges from the valence band to the conduction band [18]. Fig. 1b shows the UV–vis spectrum of Zn doped CuO and the inset of Fig. 1b shows the absorption spectra of pure CuO. It can be observed that pure CuO shows strong absorption in the UV-region at the wavelength of 391 nm and this absorption varies from 422–436 nm for various concentrations of Zn with CuO.

Doping of Zn into CuO leads to the formation of shallow levels inside the bandgap causing a red shift in the absorption spectra of Zn doped CuO compared to CuO [19]. The optical band gap energy (E_g) was calculated using the Eq. (1):

$$\alpha h\nu = K(h\nu - E_g)^{m/2} \quad (1)$$

where, α is the absorption coefficient, $h\nu$ is the energy of the photon, K is a constant, and E_g is the band gap of the material.

The band gaps of the three samples are obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ in the high absorption range followed by extrapolating the linear portion of the absorption edge to find the intercept with the X-axis as shown in Fig. S2. The bandgap of the pure CuO is found to be around 3.01 eV, whereas Zn-CuO of concentrations 0.03 M, 0.05 M and 0.07 M show band gaps of 2.83 eV, 2.65 eV and 2.49 eV respectively (Fig. S2). Fig. 2 shows the FESEM images of the CuO and various concentrations of Zn-CuO nanostructures. A rod like structure is formed in the absence of dopant (Zn) as shown in Fig. 2a. These nanorods lead to the aggregation of flower like structures when 0.03 M of Zn is doped with CuO (Fig. 2b). When the concentration of Zn is increased to 0.05 M a spherically aligned flower-like structure (Fig. 2d) is formed. Thereafter when the concentration of Zn is increased to 0.07 M, further nucleation and assembly process take place for the crystals to grow into carnation flower-like nanostructures (Fig. 2e). Therefore, it is proved that the higher concentration of Zn inhibits the specific growth planes of CuO nanorods and generates flower-like morphology. Fig. 2c shows the EDS spectra of pure CuO sample (which contains only the elements Cu and O) and Zn-CuO which confirms the presence of Zn with no other impurities (Fig. 2f).

The photocatalytic activity of Zn-CuO nanostructures was examined through the photodegradation of 15 mg/L organic dyes (MB and MV) in Zn-CuO (5 mg) aqueous suspensions under UV light irradiation. Absorption spectrum was obtained by the plot between absorbance and irradiation time and the efficiency of degradation was determined in terms of the change in intensity of absorption maximum of the dyes. As seen in Fig. 3(a and b) the organic dyes (MB and MV) do not decompose in the absence of photocatalysts. It can be observed that the maximum absorbance of MB and MV at 665 nm and 583 nm respectively, disappear almost completely after being irradiated for 3 h in the presence of 0.07 M Zn-CuO (Fig. S3). The efficiency of decolorization (η) was calculated using the formula (2):

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\%, \quad (2)$$

where A_0 is the maximum at $t=0$ and A_t is the absorption maximum after complete degradation. It can be seen from Fig. 3 that Zn-CuO shows relatively higher photocatalytic activity than pure CuO.

The plot between $-\ln(A_t/A_0)$ and time is linear and so this reaction obeys the pseudo-first order kinetics. The degradation rate was determined using the expression $k = 2.303 \times \text{slope}$ and Fig. 3(c and d) clearly proves that, the dyes such as MB and MV are degraded by 0.07 M Zn-CuO at a faster efficiency rate and the rate constants are 1.7175 h⁻¹ for MB and 2.383 h⁻¹ for MV. The excited electron from the conduction band of CuO is transferred to Zn which acts as the lower oxidation state and thus prevents electron-hole recombination. The degradation efficiency of Zn-CuO photocatalyst is compared with previous reports (Table S1.)

It is observed from Fig. 3e that the degradation efficiency increases with the increase of dopant concentration and it is suggested that a small amount of Zn reduces the electron-hole recombination efficiently, thereby enhancing the photocatalytic activity. In the present work, the nanoflower-like morphology allows more efficient transport of reactant molecules to get more active sites and hence enhances the efficiency of photocatalysis [20].

4. Conclusions

Zn doped CuO nanoflowers were synthesized by hydrothermal method and characterized by XRD, SEM and EDS. Synthesized Zn doped CuO nanoflowers exhibit significant enhancement in photocatalytic activity towards methylene blue and methylene violet dyes in compared to CuO nanorods. These results display an effective way to improve photocatalytic activity of semiconductors by doping with metals.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2015.01.026>.

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