Influence of Mg dopant on photocatalytic properties of Mg-doped ZnO nanoparticles prepared by sol–gel method

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Mg-doped ZnO nanoparticles with different Mg contents were synthesized by sol–gel method with subsequently calcination at 600°C for 2 h. The X-ray diffraction results revealed the presence of wurtzite pure ZnO with hexagonal structure in both the undoped and doped samples. The crystallite size of the nanoparticle samples was calculated by Scherrer formula, 92 nm for ZnO and 43 nm for 5 wt% Mg-doped ZnO. Raman spectra of pure and Mg-doped ZnO show peak at 437 cm⁻¹ assigned to ZnO non-polar optical phonon high E₂ mode. The size of Mg-doped ZnO characterized by transmission electron microscopy is much smaller than that of pure ZnO. The photocatalytic properties of ZnO and Mg-doped ZnO were investigated by monitoring the methylene blue degradation under UV radiation. For the present study, the 5 wt% Mg-doped ZnO shows the highest photocatalytic activity of 92% within 300 min.

Key-words : Mg-doped ZnO, Sol–gel synthesis, Photocatalysis

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1. Introduction

Zinc oxide, a highly degrading semiconductor with a wide band gap of 3.37 eV and high excitation binding energy (60 meV at 300 K),1,2 has emerged as one of the most promising oxide materials. It has a number of industrial applications in photocatalysis, photodetector, energy storage, chemical sensing, nonlinear optics, dilute magnetic semiconductor, ultra-violet/catalysis, photodetector, energy storage, chemical sensing, non-linear optics, dilute magnetic semiconductor, ultra-violet/linear optics, dilute magnetic semiconductor, ultra-violet/blue emission, including optical, electronic and acoustic devices.3–5 It has antibacterial property, and superior physical and chemical stability, including inexpensive, easy to be synthesized and non-toxic.1,6,7 ZnO has low potential photocatalytic property owing to the recombination of photogenerated e−/h+ carriers and low surface area.1 To improve its photocatalytic activity, Mg-doped ZnO has received considerable attention because Mg has similar ionic radius and can extend the absorption wavelength from UV-A (320–400 nm) to UV-B (280–320 nm) and UV-C (200–280 nm) regions.8,9

In the present study, Mg-doped ZnO with different Mg contents was prepared by sol–gel method and used as a photocatalyst for degradation of methylene blue (MB). The effect of Mg dopant on phase, morphology and photocatalytic activity of ZnO was investigated and discussed in this report.

2. Experiment

The typical synthetic procedure of pure and Mg-doped ZnO with different Mg contents is as follows. 100 ml of 0.05 M Zn(NO₃)₂·6H₂O and 100 ml of 0.05 M C₆H₈O₇ (citric acid) in ethanol solution were mixed and stirred by a magnetic stirrer at 100°C for 30 min. 100 ml 0.05 M Mg(NO₃)₂·6H₂O and low surface area was added to the precursor solutions. The mixtures were stirred for 1 h and kept at 80°C until homogenous gel formed. The gel was heated at 120°C in an electric oven and calcined (heating rate = 10°C/min) at 600°C for 2 h in air to form products which were collected for further characterization.

Photocatalytic activity was evaluated through the degradation of MB solutions. Three black light lamps with 18 W were used as UV sources. The total 0.2 g catalysts were added to 200 ml of 10⁻⁵ M MB solutions which were magnetically stirred to homogenize the solutions. For every 60 min specific time interval, ~5 ml solution was withdrawn from the tested solution and centrifuged. The absorbance intensity was measured by a UV–vis spectrophotometer at 664 nm, corresponding to peak absorption wavelength of MB. The degradation of MB was calculated using the equation as follows.

\[
\text{Decolorization efficiency (\%) } = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)
\]

where \(C_0\) is the initial concentration of MB and \(C_t\) is the concentration of MB after UV light irradiation within the elapsed time (t).

3. Results and discussion

X-ray diffraction (XRD) patterns of the as-prepared samples are showed in Fig. 1. The XRD pattern of pure ZnO shows peaks at 2θ of 31.63, 34.36, 36.12, 47.46, 56.55, 62.84, 66.36, 67.88 and 69.01° corresponding to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of wurtzite ZnO (JCPDS No. 05-066410). The pattern shows strong and sharp peaks which confirm the high crystalline wurtzite ZnO sample with hexagonal structure. XRD patterns of 1, 3 and 5 wt% Mg-doped ZnO show similar diffraction peaks to those of pure ZnO, confirming that there were no second phase (such as MgO) formation in the present study. The XRD pattern of 5 wt% Mg doped ZnO shows peaks at 2θ of 31.66, 34.44, 36.21, 47.47, 56.57, 62.84, 66.40, 67.97 and 69.08° corresponding to the (100), (002), (101), (102), (110), (103), (200) and (201) planes of wurtzite ZnO. Moreover, the XRD peaks of Mg-doped ZnO [Fig. 1(b)] shifted

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to a slightly higher angle as compared to those of the undoped ZnO because the ionic radius of Mg$^{2+}$ (0.57 Å) is less than the ionic radius of Zn$^{2+}$ (0.74 Å). The crystallite size of the Mg doped ZnO nanoparticles was calculated by the X-ray line broadening method using the Scherrer equation:

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta},$$

(2)

where $D$ is the crystallite size, $\lambda$ is the wavelength of Cu-K$_{\alpha}$ radiation (1.5406 Å), $K$ is the shape factor (0.9), $\beta_{hkl}$ is the full width at half maximum and $\theta$ is the diffraction angle. The average crystallite size is 92 nm for ZnO and 43 nm for 5 wt% Mg-doped ZnO.

Figure 2 shows Raman spectra of the pure and Mg-doped ZnO. The peak at 437 cm$^{-1}$ is assigned to ZnO non-polar optical phonon high E$_2$ mode whereas the peak of 378 cm$^{-1}$ in both ZnO and Mg-doped ZnO corresponds to the A$_{1(LO)}$ [4,7,13]. Two Raman peaks at about 439 and 333 cm$^{-1}$ correspond to the E$_{2H}$ and E$_{2H}$–E$_{2L}$ modes [4,7,13]. That at 583 cm$^{-1}$ is assigned to E$_{1(LO)}$ mode which is related to defects such as oxygen vacancies, zinc interstitials, free carriers, etc. [4,7]. Raman measurement shows that both undoped and Mg-doped ZnO are good crystal with hexagonal wurtzite structure, and that Mg dopant did not change the structure of ZnO.

Transmission electron microscopic (TEM) images and selected area electron diffraction (SAED) patterns of undoped and Mg-doped ZnO nanocrystalline samples were shown in Figure 3. Both the ZnO and Mg-doped ZnO samples were composed of nanoparticles. Their size is uniform distribution with average size of 95, 86, 53 and 24 nm for 0, 1, 3 and 5 wt% Mg-doped ZnO, respectively. These results indicate that the particle size decreased gradually with increasing of Mg content in good agreement with the particle size calculated using the XRD patterns. Their SAED patterns show a number of bright spots arranged in concentric rings confirmed the products as polycrystals. They correspond to the (100), (002), (101), (102), (110), (112) and (201) planes of the JCPDS standard [10]. The BET surface areas for ZnO, 1 wt% Mg-doped ZnO, 3 wt% Mg-doped ZnO and 5 wt% Mg-doped ZnO were calculated to be 11.91, 15.96, 18.42 and 23.63 m$^2$·g$^{-1}$, respectively. 5 wt% Mg-doped ZnO has the largest specific surface area.

The UV–vis absorption spectra of ZnO and 5 wt% Mg-doped ZnO are shown in Figure 4. The band edge of 5 wt% Mg-doped ZnO shifts to shorter wavelength region comparing to that of ZnO. The energy gap ($E_g$) values of ZnO and 5 wt% Mg-doped ZnO were calculated from the absorption edge of UV–vis absorption spectra. They are 2.91 eV for the undoped ZnO and 3.13 eV for 5 wt% Mg-doped ZnO, confirming that Mg ions had incorporated into the ZnO lattice. It can be seen that the Mg doped ZnO shows a high absorption in UV–vis region which influence the photocatalytic activity higher than ZnO.

The efficiencies of photocatalytic activities of Mg-doped ZnO with different Mg contents were evaluated by monitoring the decomposition of methylene blue (MB) under UV light as shown in Figure 5(a). The plot shows that ZnO nanoparticles have the lowest photocatalytic activity which indicates the efficiency of migration of photo-generated charges to active sites inside. For the Mg-doped ZnO, the photocatalytic activity gradually increases with increasing the concentration of Mg dopant owing to
increase the UV absorbance of ZnO nanoparticles and lower efficient migration of photo-generated charges to active sites in the Mg-doped ZnO nanoparticles. They should be noted that TiO\textsubscript{2}-P25 was found to photocatalytically degrade of 40.5\% MB within 240 min which has lower photocatalytic activity than 5 wt\% Mg-doped ZnO. In addition, the surface area of nanoparticles gradually increases with increasing concentration of Mg dopant. Thus the surface area plays more important role than UV absorbance for enhancing photocatalytic activity. The photocatalytic efficiencies of MB degradation by 0, 1, 3 and 5 wt\% Mg-doped ZnO are 76, 83, 89 and 92\%, respectively. In this study, 5 wt\% Mg-doped ZnO has the highest photocatalytic activity because the 5 wt\% Mg-doped ZnO has the highest BET surface area (23.63 m\textsuperscript{2}·g\textsuperscript{-1}).

The photocatalytic degradation was investigated by first-order kinetics, called the Langmuir–Hinshelwood (L–H), below

\[
\ln(C_0/C_t) = kt,
\]

where \(C_0/C_t\) is the ratio of dye concentration at adsorption–desorption equilibrium of those at different time intervals \((t)\) and \(k\) is the apparent first-order rate constant \((\text{min}^{-1})\).\cite{1,6,7,9} Figure 5(b) shows the plot of \(\ln(C_0/C_t)\) versus time. The reaction rate constants for the photocatalytic degradation of MB by pure ZnO and Mg-doped ZnO containing 1, 3 and 5 wt\% were 4.28 × 10\textsuperscript{-3}, 6.67 × 10\textsuperscript{-3}, 7.52 × 10\textsuperscript{-3} and 8.83 × 10\textsuperscript{-3} min\textsuperscript{-1}, respectively. The excellent UV light photocatalytic activity of the as-prepared Mg-doped ZnO nanoparticles is attributed to the excellent crystalline degree, unique morphology, high surface area and inhibition of recombination of photogenerated electrons and holes.

The photocatalysis of Mg-doped ZnO can be explained as follows. When the photocatalyst absorbs photons under UV radiation, electrons in the valence band (VB) can be excited to the conduction band (CB) with leaving holes behind. The e\textsuperscript{−}−h\textsuperscript{+} pairs react with \(\text{O}_2\) and \(\text{H}_2\text{O}\) on the surface of the nanoparticles to form superoxide \(\text{O}_2\textsuperscript{2−}\) and hydroxyl \(\text{OH}\) radicals. The \(\text{O}_2\textsuperscript{2−}\) and \(\text{OH}\) radicals as strong oxidants can oxidize the MB into the final products \((\text{CO}_2\) and \(\text{H}_2\text{O})\). Upon doping with Mg, the photocatalytic activity of MB was increased. The 3s electrons in the conduction band may provide a favorable channel for the photoinduced charge carrier migration and reduce the electro-hole recombination rate.\cite{12}

\[\text{4. Conclusions}\]

In conclusion, ZnO and Mg-doped ZnO nanoparticles were synthesized by sol–gel method using citric acid as a chelating agent. XRD patterns and TEM images show that the products are very good crystalline nanoparticles with less than 100 nm. The photocatalytic properties of ZnO and Mg-doped ZnO were investigated by monitoring MB degradation under UV light irradiation. In this study, 5 wt\% Mg-doped ZnO shows the highest photocatalytic activity under UV radiation, 92\% within 300 min. Thus Mg-doped ZnO is a promising candidate for photocatalysis in the future.

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