Enhanced photocatalytic properties of quantum-sized ZnO induced by La\(^{3+}\)-Nd\(^{3+}\) co-doping

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Abstract. Nanoparticles of ZnO doped with La\(^{3+}\), Nd\(^{3+}\), co-doped with La\(^{3+}\) and Nd\(^{3+}\) were prepared using the sol-gel method. The samples were characterized by means of X-ray diffraction (XRD), UV-Vis spectroscopy (UV). The photocatalytic reactivities were evaluated by photodegradation of unsymmetrical dimethylhydrazine solution. Nanocrystalline ZnO co-doped with La\(^{3+}\) and Nd\(^{3+}\) at optimal concentration (2 at.\% La\(^{3+}\) and 1.5 at.\% Nd\(^{3+}\)) shows a better synergistic effect, which significantly increases the photodegradation activity of nano-ZnO. The factors influencing photoreactivity of co-doped nanocrystalline ZnO have been discussed.

1. Introduction

Nanoparticles zinc oxide and doped zinc oxide have been used as effective, inexpensive, nontoxic semiconductor for the degradation of a wide range of organic chemicals\(^{[1-5]}\). The present work focuses on the use of ZnO and solar radiation for effective elimination of organic chemicals at ambient temperature\(^{[6-7]}\). However, ZnO has some drawbacks including the fast recombination rate of photogenerated electron-hole pair and a low quantum yield in the photocatalytic reactions in aqueous solutions, which obstruct commercialization of the photocatalytic degradation process\(^{[10]}\). Therefore, various methods have been developed to reduce the e\(^{-}\)/h\(^{+}\) recombination rate of ZnO in the photocatalytic processes. The challenge of this work is how to obtain different types of oxygen defects in ZnO nanocrystals\(^{[9]}\). One of the interesting approaches is to dope the transition, alkaline and rare earth metal atoms in semiconductors\(^{[9]}\). It has been known that the advantage of the doping of the metal ions in semiconductor particles is the temporary trapping of the photogenerated charge carriers by the dopant and the inhibition of their recombination during migration from inside of the material to the surface or the enhanced association of the functionalized organic pollutants to the doping ion surface sites. The efficiency of photocatalytic reactions is limited by the high recombination rate of photoinduced electron-hole pairs formed in photocatalytic processes and by the absorption capability for visible light of photocatalysts\(^{[10, 11]}\). Ping Yang et al\(^{[10]}\) found that TiO\(_{2}\) co-doped with Fe\(^{3+}\) and Eu\(^{3+}\) ions could lead to superior photocatalysis. A pronounced synergistic effect in catalytic activity was noted. The facts indicate that introducing two or more proper metals into nanocrystalline semiconductor particles will improve the photocatalytic effect.

We believe that co-doping rare earth metal ions onto the nanocrystalline ZnO may achieve the same effect as co-deposited onto TiO\(_{2}\). To the best of our knowledge, there are few studies carried out on ZnO semiconductor particles co-doped with two kinds of rare earth metal ions for photo-oxidative degradation of toxic compounds. Here, in order to research the photocatalytic property of
nanocrystalline ZnO co-doped with La$^{3+}$ and Nd$^{3+}$ metal ions, the samples synthesized by sol-gel technique was prepared, its characterizations were described in detail, and its photocatalytic property was investigated with unsymmetrical dimethylhydrazine solution as the model.

2. Experimental

2.1 Photocatalyst Determination

The crystalline structure was investigated by XRD on x’Pert. Pro. MPD X-ray diffractmeter with Ni filtered Cu K$_\alpha$ radiation of 0.1542 nm at the scan rate of 0.05$^\circ$/s. The UV of ZnO were carried out on HITACHI U-3310 UV-Vis spectrophotometer. All the chemicals and solvent used in present study were of AR grade. Anhydrous ethanol were refluxed over magnesium strips and then distilled.

2.2 Sample preparation

The preparation procedure of ZnO nanoparticles was similar to a method described elsewhere$^{[12]}$, with some modifications. Lithium hydroxide monohydrate (0.29 g, 7 mmol) was dissolved in 50 ml of absolute ethanol at room temperature in an ultrasonic bath. Zinc acetate dihydrate (1.10 g, 5 mmol) was dissolved in 50 ml of refluxing ethanol. The stirred zinc acetate solutions were cooled to 50$^\circ$C and held isothermal while the lithium hydroxide monohydrate solution was added. The resulting mixtures were stirred for 40 minutes as ZnO sol, and then 200 ml of cold hexane was added to the ZnO sol and kept them at the temperature 4$^\circ$C for 24 h to prevent particles of ZnO growing rapidly. The white powder would be achieved by evaporated at room temperature. The powder was calcined for 2 h in muffle at 300$^\circ$C as the best calcined temperature$^{[12]}$. Doped and co-doped ZnO nanoparticles were synthesized using almost the same method. The appropriate amount of LaCl$_3$ and/or NdCl$_3$ was dissolved in 50 ml anhydrous ethanol which was added prior to the Zn(CH$_3$COO)$_2$·6H$_2$O The remaining procedures were the same as described above. For convenience, the samples were labeled as La(X) for La$^{3+}$doped ZnO, Nd(Y) for Nd$^{3+}$doped ZnO, and La(X)Nd(Y) for La$^{3+}$ and Nd$^{3+}$ co-doped ZnO, respectively, where X and Y refer to the nominal atomic concentration of La$^{3+}$ and Nd$^{3+}$, respectively, which is based upon the assumption of quantitative incorporation of the dopants.

2.3 Photocatalytic activity

Unsymmetrical dimethylhydrazine solution was chosen as the reaction to quantify the photocatalytic reactivity of each sample. The experiments were carried out with 100 ml reactive unsymmetrical dimethylhydrazine solution prepared with distilled water in 200 ml beakers. The beakers were put under the ultraviolet light maintaining the distance between the light source and the surface of the solution about 10 cm in the appropriate stirring. The known amount of ZnO was added to the solution. After a known period of time, the solution was centrifuged at 2000 rpm for 10 min and then filtered to remove the catalyst particles completely. Na$_3$[Fe(CN)$_6$]$_2$NH$_3$·3H$_2$O] (TPF) was obvious reagent of unsymmetrical dimethylhydrazine solution. The absorbency was measured with 722 UV-Vis spectrophotometer (λ$_{\text{max}}$ = 500 nm), and the degradation rate ($\eta$) was calculated according to the equation below:

$$\eta = \frac{(A_0 - A)}{A_0} \times 100\%$$

$A_0$ and A is the initial and absorbency of unsymmetrical dimethylhydrazine solution; A is the absorbency of unsymmetrical dimethylhydrazine solution after degradation.

3. Results and discussion

Figure 1 shows the XRD spectra. X-ray diffraction measurements show that all samples prepared have the wurtzite structure attached to hexagonal system according to the standardized JCPDS card. From the Figure 1 (b) we can see that the position of peak having a little remotion to the left. The particle characteristics and the average grain size calculated from the broadening of the XRD peak of wurtzite using Scherrer’s equation were listed in table 1. From table 1 we can see that co-doping makes the XRD peak getting wider compared with pure ZnO, the grain size is in the range from 10.69
to 32.55 nm. Compared with pure ZnO unit cell dimensions, the unit cell dimensions of doped sample changed: a getting longer and b getting shorter. But unit cell volume has little changed.

![Figure 1](image1.png)

**Figure 1.** X-ray diffraction patterns of Samples calcined at 300 °C. A: ZnO; B: Nd(2.5); C: La(2); D: La(1)Nd(2.5); E: La(2)Nd(2.5); F: La(2)Nd(1.5); G: La(3)Nd(2.5); H: La(2)Nd(3.5)

| sample | unit cell dimensin (nm) | grain size (nm) | unit cell volume (nm³) |
|--------|------------------------|----------------|-----------------------|
| A      | 3.2491 5.2350          | 10.69          | 143.57                |
| B      | 3.2545 5.2219          | 11.58          | 143.69                |
| C      | 3.2552 5.2122          | 25.27          | 143.49                |
| D      | 3.2497 5.2267          | 18.54          | 143.40                |
| E      | 3.2559 5.1990          | 22.79          | 143.19                |
| F      | 3.2594 5.2282          | 32.55          | 143.34                |
| G      | 3.2518 5.2095          | 21.30          | 143.11                |
| H      | 3.2663 5.1990          | 21.39          | 144.10                |

Table 1. The calculated unit cell parameter of Samples by XRD. A, B, C, D, E, F, G and H is the same sample as that in figure 1, respectively.

Figure 2 shows the UV-Vis absorption spectra of colloidal solutions of pure, doped, and co-doped ZnO. The onset of the absorption spectrum of the ZnO colloid appears at about 360 nm. The absorption profile of doped ZnO appears a blue-shift about 10 nm. The absorption profile of co-doped ZnO shows the same blue-shift. The threshold value of semiconductor photoabsorption $\lambda_g$ has a relation with the band gap $E_g$, the relation formula is $E_g (eV) = 1240/\lambda_g (nm)$. From the Fig.2 we can see that a smaller $\lambda_g$ lead to a wider band gap, and this makes photogenerated holes have a stronger reductive electric potential which may result in the increasing of photocatalysis of semiconductor.

![Figure 2](image2.png)

**Figure 2.** UV-Vis spectra of samples

![Figure 3](image3.png)

**Figure 3.** Degradation rate of UDMH using different La,Nd-doped ZnO samples. A, B, C, D, E, F, G and H is the same sample as that in figure 1, respectively.
The photoreactivities of pure ZnO, Nd(Y), La(X), and La(X)Nd(Y) samples are presented in Figure 3. Curve B (Nd(2.5)) and curve C (La(2)) are the best degradation effect for mono-doped ZnO. Curve F (sample La(2)Nd(1.5)) is the best degradation effect for co-doped ZnO. The degradation effect of samples La(1)Nd(2.5) (curve D) and La(2)Nd(2.5) (curve E) is better than mono-doped ZnO. The degradation effect of samples La(3)Nd(2.5) (curve G) and La(2)Nd(3.5) (curve H) are worse than mono-doped ZnO. So ZnO co-doped with La\textsuperscript{3+} and Nd\textsuperscript{3+} ions could lead to superior photocatalysis. Using the sample La(2), Nd(2.5), La(2)Nd(1.5), the degradation rate of unsymmetrical dimethylhydrazine could reach 83\%, 91\%, 97\% respectively by catalyst of 0.1 g/L in 100 min at room temperature.

The effect may be explained by the cooperative operation of the two dopants in trapping charge carriers and mediating interfacial charge transfer process. Co-dopant of La\textsuperscript{3+} and Nd\textsuperscript{3+} could effectively inhibit the recombination of the photoinduced electrons and holes. We also notice that the proportion of dopants beyond the optimal proportion would lead to the decreasing of photodegradation efficiency which coincides with the situation of doping La\textsuperscript{3+} or Nd\textsuperscript{3+} alone such as sample La(2.5)Nd(2.5), its grain size is smaller than ZnO, but photodegradation rate do not increase than ZnO without dopant.

Nanocrystalline ZnO co-doped with La\textsuperscript{3+} and Nd\textsuperscript{3+} at optimal concentration (2 at.\% La\textsuperscript{3+} and 3 at.\% Nd\textsuperscript{3+}) shows a better synergistic effect, which significantly increases the photodegradation activity of pure ZnO. The separation of the charge carriers is attributed to such trappings. The co-doped ZnO photocatalysts with appropriate content of La\textsuperscript{3+} and Nd\textsuperscript{3+} possessed abundant electron traps so as to be favorable for the separation of the photoinduced electron-hole pairs, which could greatly enhance the activity of the photocatalysts. The efficiency of photocatalytic reactions is limited by the high recombination rate of photoinduced electron-hole pairs formed in photocatalytic processes and by the absorption capability for visible light of photocatalysts.

4. Conclusion

We prepared quantum-sized ZnO of doped with La\textsuperscript{3+} or Nd\textsuperscript{3+} and co-doped with La\textsuperscript{3+} and Nd\textsuperscript{3+} using sol-gel method. An investigation on the photodegradation of unsymmetrical dimethylhydrazine solution has been revealed that the photocatalytic reactivity of optimal co-doped ZnO was significantly increased as compared with ones over nanoparticles of ZnO no doped or monodoped with La\textsuperscript{3+} or Nd\textsuperscript{3+} alone. The photodegradation rate of unsymmetrical dimethylhydrazine solution reaches 97\% by catalysis of 0.1g/L La\textsuperscript{3+}-Nd\textsuperscript{3+} co-doped ZnO at room temperature in 100 minutes. The synergistic effect of two dopants leads to significant enhancement of photodegradation. It can be expected that photocatalytic activity can be further improved by choosing proper dopants.

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