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Size-controlled synthesis and photocatalytic degradation properties of nano-sized ZnO nanorods

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ABSTRACT

ZnO nanorods with various ratios of length to diameter have been synthesized by combining the facile sol-gel process with hydrothermal methods. The obtained ZnO nanorods have been investigated by using electron microscopy, X-ray diffraction, electronic absorption and photoluminescence spectroscopy. The results show that the spectral properties of the ZnO nanorods can be adjusted by controlling the concentration of reactant during hydrothermal process. The photodegradation of methylene blue in the presence of ZnO has also been investigated detailedly. It is found that the ZnO nanorods prepared in 12.0 mM reactant condition exhibit the highest activity which is six times as large as the ZnO seeds, and that the activity of the optimum ZnO can reach above 80% after repeated uses of 5 times.

1. Introduction

Recently, photodegradation of organic contamination in the presence of photocatalyst (semiconductor particles) has stimulated much interest because this procedure can destroy the pollutants completely and has a broad optional semiconductor compound [1]. As a kind of semiconductors, ZnO can be used as photocatalyst to destroy the organic pollutants in water or air because its large band gap can offer the high driving force for the reduction and oxidation processes. In some cases, ZnO may exhibit a better efficiency than TiO_2 in photo-catalytic degradation for some dyes [2].

It has been proven that the activity of the semiconductors is strongly influenced by the crystal structure, particle size, band gap and so on [3]. Recently, more interest has been stimulated to study the relationship between the crystal surfaces of metal and their physical/chemical properties because of their important applications in catalytic reactions [4]. Among various physical/chemical properties, photocatalytic reaction occurs at the crystal surface [5], so the efficiency of photocatalysis should strongly depend on the surface structure.

The synthesis of ZnO with various morphologies, sizes, dimensionalities and properties depends strongly on the method and conditions of preparation. Up to now, many methods including hydrothermal, chemical vapor deposition, micro-emulsion and so-gel process are developed to control the morphologies and properties of ZnO in photocatalysis [6,7]. Usually, one-dimensional nanostructure can facilitate efficient carrier transport in comparison with zero-dimensional nanostructure due to decreased grain boundaries, surface defects and disorders [8]. ZnO nanorods can be conveniently prepared through hydrothermal method in the presence of some regulative reagent. In this paper, ZnO nanorods with various ratios of length to diameter (RLD) have been synthesized by changing the reagent concentration under ambient condition. Meanwhile, the photocatalytic activities of the ZnO nanorods have also been investigated.

2. Experimental procedure

The chemicals were analytical grade and obtained from Beijing Chemical Reagent Corp. ZnO nanorods were synthesized by two procedures. Firstly, the ZnO nanoparticles used as seeds were prepared by sol–gel method and conserved at 4 °C after being ultrasonic-treated for 15 min [9]. Secondly, ZnO seeds solution (10.0 mL) was directly dropped into 200 mL aqueous solution containing equal molar $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine (HMT) and heated at 90 °C for 3 h. The precipitate was then collected by filtering the mixture through the micro-porous filter membrane and washed by deionized water and ethanol thoroughly, then dried at 60 °C in a vacuum oven for 12 h. The ZnO samples prepared in the solution containing 1.0, 12.0 and 15.0 mM $Zn(NO_3)_2 \cdot 6H_2O$ and HMT were denoted as ZnO-1, ZnO-12 and ZnO-15, respectively.

The morphologies of the obtained ZnO nanorods were observed by using the scanning (SEM, JEOL-JSM-6701 F) and transmission electron microscope (TEM, JEOL-2010). The XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer (Cu *Ka*). The UV–visible spectra and the concentration of MB during the process of degradation were measured on a Varian 50 Bio UV–visible spectrophotometer, and

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the photoluminescence (PL) of ZnO were carried on a Hitachi F-2500 spectrofluorometer.

The photodegradation of MB was carried out as follows: the mixture of MB (20.0 mg/L, 50.0 mL) and ZnO (30 mg) was exposed to the light produced by a 200 W Xe lamp positioned 36 cm away from the vessel after the mixture was stirring for 30 min under dark to get the absorption–desorption equilibrium. The concentration of MB was determined by using electron absorption spectra at given time intervals after the ZnO was centrifuged. The temperature was kept at about 25 °C and the pH value of the dispersion was about 6.5. The controlled experiments such as irradiating without photocatalyst or non-irradiating in the presence of photocatalyst were also carried out with the similar procedures. The durability test of the ZnO rods was performed by using the same procedure as above and the ZnO underwent five consecutive cycles, each lasting for 40 min. After each cycle, the catalyst was centrifuged and washed thoroughly with water, and then added to fresh MB solution.

3. Results and discussion

The typical micrographs of ZnO with various RLD are shown in Fig. 1. It is clear that the RLD of the ZnO increases with the increment of the reagent concentration. For example, the ZnO-1 sample exhibits rice-like morphology and a smaller RLD is estimated to be about 1.9 (Fig. 1A). However, the average diameter of ZnO-12 is about 13 nm and the length about 45 nm, so the RLD is calculated to be about 3.5 (Fig. 1B). When the concentration of the reactant is increased to 15 mM further, the length of ZnO rod reaches to about 51 nm although the diameter attains about 12 nm, then RLD is calculated to be about 4.2 (Fig. 1C). From the XRD patterns shown in Fig. 1D, it is found that all the samples present the typical character of wurtzite structure according to the standardized JCPDS (36–1451) card. The ZnO particles (seeds) (Fig. 1D-a) show broader and lower diffraction peaks, which indicate that the size of ZnO particles is smaller and exhibits poorer crystallization than that of other samples prepared by combining seeds with hydrothermal method. The width of the peak corresponding to (002) plane is narrower than that of (100) and (101), which indicates that the crystal is growing along the <0001> direction. Furthermore, the diffraction intensity ratios of (002) polar plane to (100) nonpolar plane ($I(002)/I(100)$) are calculated to be about 1.03, 1.37 and 1.64 for ZnO-1, ZnO-12 and ZnO-15, which indicates that the fraction of polar planes is different [8].

From the curves of $(\alpha h\nu)^2$ versus $h\nu$ shown in Fig. 2A, it is found that the ZnO particles used as seeds exhibit a band gap energy of about 3.30 eV, and that the samples of ZnO-1 and ZnO-12 exhibit a gap energy of about 3.21 and 3.17 eV. However, the band gap of ZnO-15 is about 3.19 eV and becomes larger than that of ZnO-12. From the PL spectra recorded at room temperature shown in Fig. 2B, it can be seen that ZnO particles show three strong and wide PL peaks at 410, 468 and 525 nm although the band–band PL phenomenon cannot be found. The PL peak at 410 nm is attributed to band edge free excitons, while that at 468 nm is attributed to bound excitons [10], and that at 525 nm is resulted from the high-level surface defects which accounts for the increase of the green emission [11]. However, the ZnO nanorods prepared by hydrothermal method exhibit much weaker emission at longer wavelength (525 nm) than ZnO particles, which indicates that the surface defects have been eliminated during the hydrothermal process. Furthermore, it can be found that the peaks located at around 410 nm have also changed with the change of the concentration of the reactant, for example,

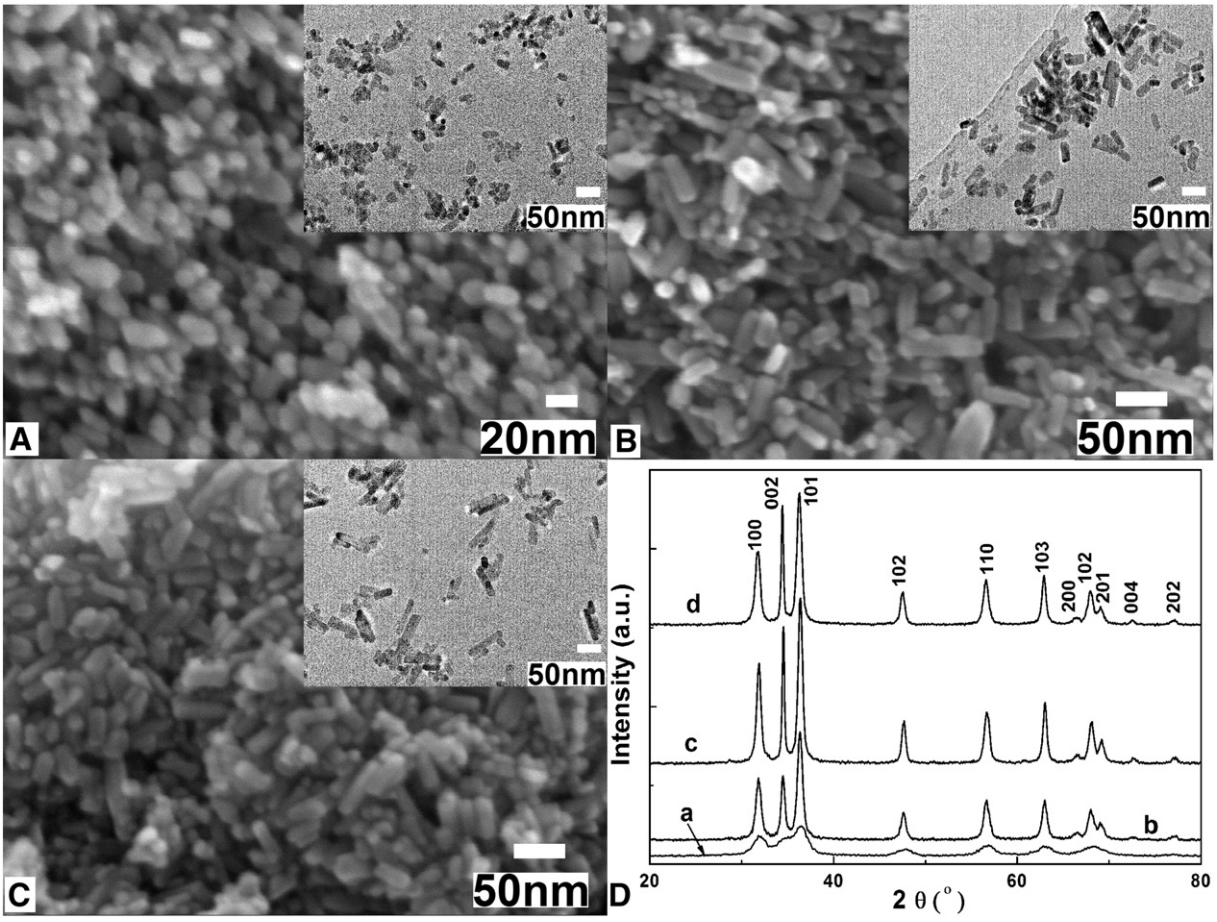

Fig. 1. The micrographs of the ZnO nanrods (A) ZnO-1, (B) ZnO-12, (C) ZnO-15 and the XRD patterns of the ZnO (D), a-ZnO particles, (b) ZnO-1, (c) ZnO-12 and (d) ZnO-15.

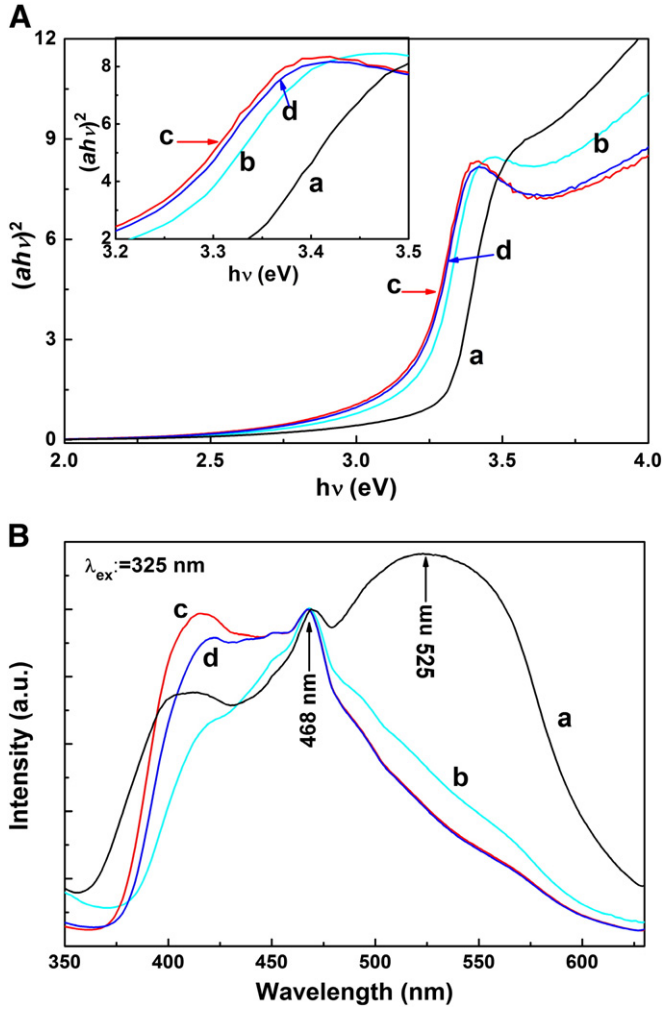

Fig. 2. The plots of $(ahv)^2$ versus hv (A) and the PL spectra (B) of ZnO, a-d are corresponding to the ZnO nanoparticles, ZnO-1, ZnO-12 and ZnO-15.

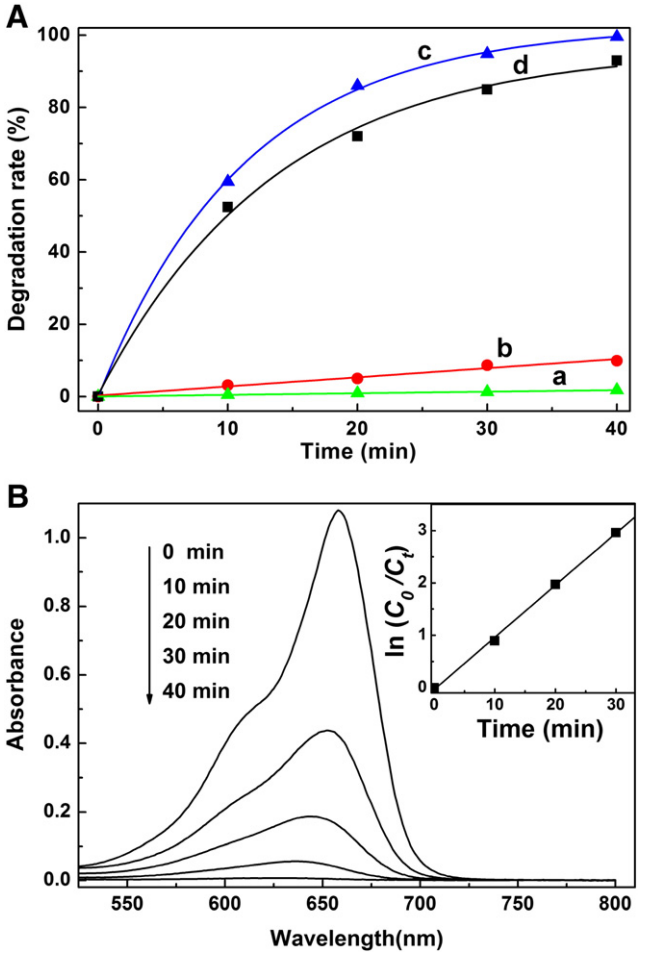

Fig. 3. (A) The photodegradation of MB in dark with (a) and under light without (b) or under light with (c) ZnO-12, with P25 (d), (B) the electron adsorption spectra of MB during the photodegradation with ZnO-12 (inserted: the relationship between $\ln(c_0/c)$ and time).

the peak located at 410 nm has the weakest relative intensity in ZnO-1 and the strongest relative intensity in ZnO-12. These phenomena may be resulted from the quality of the crystalline of the sample which will be influenced by the crystal rate during thermal process adjusted by the concentration of the reactant [8,11].

From the data of controlled experiments shown in Fig. 3A-a and b, it is found that the degradation of the MB is about 9.4% under light irradiation without ZnO, and about 4.8% in the presence of ZnO under the dark condition. However, the degradation of MB in the presence of ZnO-12 under light reaches 100% at 40th min which is larger than that of P25 (85%). This result demonstrates that the degradation of the MB may be catalyzed by ZnO-12 dramatically. Fig. 3B shows the typical absorption spectra of the MB during the process of photodegradation, it is clear that the absorbance of the MB decreases dramatically with the increment of the irradiation time. It is well accepted that the photocatalytic degradation of the organic pollutants follows the pseudo first-order kinetic and the kinetics equation of the first-order reaction can be described as [12]:

$$\ln\frac{C_0}{C_t} = Kt \tag{1}$$

where C_0 is the initial concentration of MB, t the reaction time and C_t the concentration of MB at reaction time t. It is found that the photodegradation of MB in the presence of ZnO obeys the first-order equation.

The relationship between the apparent reactive constants (K_{app}) for the degradation of MB in the presence of ZnO prepared from various reactants is show in Fig. 4A. It can be seen that ZnO-12 exhibits the largest K_{app} of about 0.099 min^{-1} which is about five times greater than that of ZnO particles (0.017 min^{-1}) and obviously larger than that of commercial P25 (0.065 min^{-1}). The recycled property of the ZnO-12 is also measured by keeping the condition of photocatalytic degradation invariable. From the results shown in Fig. 4B, it is found that the degradation rate of MB is above 80% after the catalyst has been used 5 times repeatedly (40 min each time), indicating that it can be reused.

4. Conclusions

ZnO nanorods with various RLD have been synthesized by combining the seeds with hydrothermal method. The structure of the ZnO may be adjusted by the concentration of the growing solution. The optimum ZnO nanorods exhibit the highest kinetic which is about 6 times as large as that of nano-sized ZnO particles.

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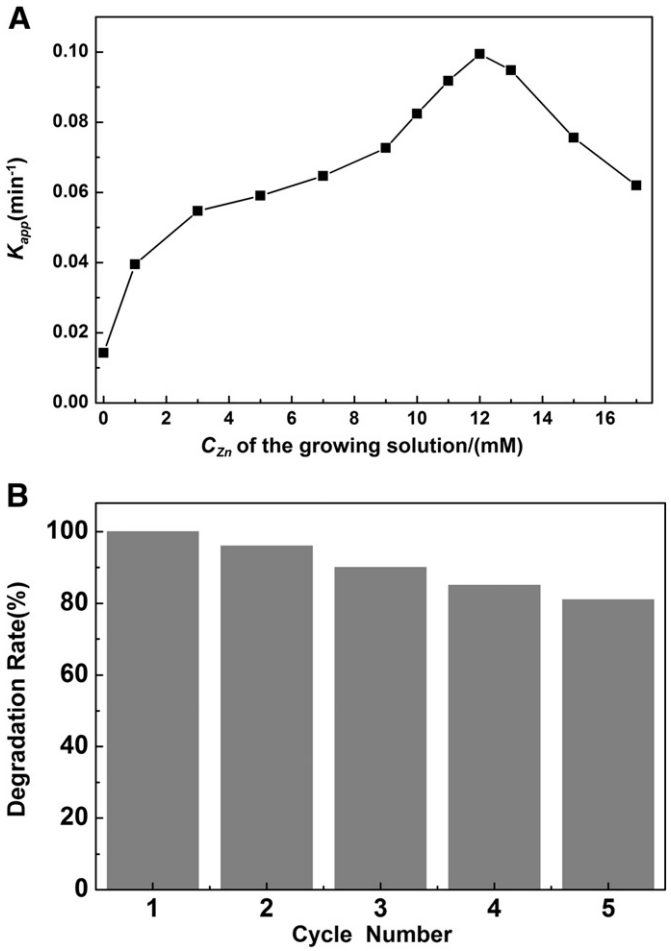

Fig. 4. The plot of K_{app} versus ZnO nanorads prepared from different concentrations of reactant (A) and the influence of using times on activity of ZnO-12 (B).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matlet.2011.12.047.

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