Study of Catalytic Capacity of ZnO Nano Particles by Blue Methylen

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ZnO nanostructures were prepared by hydrothermal method starting from Zn(CH₃COO)₂, citric acid and NaOH. SEM images indicated that the samples have a spherical shape consisting of small wires with a diameter of about 50 nm. It is seen that the samples have large surface areas and will be attractive for applications like catalyst, catalyst sensors and solar cells. In this report, photocatalytic capacity of ZnO nanoparticles was investigated by time-dependent absorption spectra of 10 mg/L blue methylen solution. The results show that catalysis was almost complete after 120 minutes. The effects of pH value on the morphology and photoluminescence properties of the samples have also been investigated.

Keywords: Hydrothermal; Photocatalysis; ZnO

I. INTRODUCTION

Recently, a lot of studies have been concentrated on the degradation of toxic organic compounds in waste water via photocatalysis of various semiconductors [1–3]. Till now, many kinds of semiconductors have been studied as photocatalysts including TiO₂, ZnO, CdS, WO₃, SnO₂ and so on [3]. ZnO is the most widely used effective photocatalyst for its high efficiency, photochemical stability, non-toxic nature, larger band gap and low cost. Since the photocatalytic reaction occurs at surfaces, a semiconductor with high porosity and nanosized features will increase the decomposition rate because of the increased surface area [3]. Therefore, the synthesis of nanostructures ZnO, which is stable and possesses a higher surface-to-volume ratio, is still one of the most important tasks for its environmental remediation applications.

In this paper, we report a simple route of synthesizing higher surface-to-volume ratio ZnO nano material by hydrothermal method. Citric acid is chosen as the structure-directing agent because it strongly adsorbs metal cation and significantly alters the surface properties. Photocatalytic capacity of ZnO nanoparticles was investigated by absorption spectra vs times. The results show that catalysis was almost complete after 120 minutes.

II. EXPERIMENTAL

The hydrothermal process was carried out with following steps. 1g Zn(CH₃COO)₂ was put into 120 ml water under stirring. After stirring for 10 min, 1 g citric acid (CA) was added into the above solution. When the CA was dissolved, NaOH 2M solution (with 23, 25 and 27 ml for changing pH value) was introduced into the aqueous solution, resulting in a white aqueous solution. The solution was transferred into Teflon lined stainless steel autoclave, which was sealed and maintained at 180, 200 and 220°C for 20 h. After the reaction completed, the resulted white solid products were centrifugalized, washed with distilled water to remove the ions possibly remaining in final products, and finally dried at 100°C in air.

The crystal structures of the samples were characterized by a Brucker D5005 X-ray diffractometer using CuKα radiation (λ =1.54 Å). The morphology was characterized by scanning electronic microscopy (SEM) JEOL 5410 LV. For photocatalytic measurement, 50 mg of catalytic sample was suspended in 50 mL of standard methylene blue (C₁₆H₁₈N₃SCl, MB) aqueous solution (10 mg/L), then UV light illumination was conducted after the suspension was strongly magnetically stirred for 0.5h. UV irradiation was carried out using a 25 W Hg lamp. The absorption spectra were collected by UV-VIS 2450 PC spectrometer.

III. RESULTS AND DISCUSSION

Figure 1 shows a typical XRD pattern of hydrothermally synthesized ZnO. The detectable peaks in this pattern can be assigned...
to the hexagonal wurtzite structure. The sharp peaks imply a well-crystallized ZnO material and no new phase appeared.

The effects of the annealing temperature and the pH value on the morphology and the photoluminescent (PL) properties of the samples have been investigated. Figure 2 shows the morphology of the samples which were annealed at the same temperature (220°C), but the $V_{NaOH}$ (the pH value) was varied at 23, 25 and 27 ml respectively. When $V_{NaOH}$=23 ml (Fig. 2(a)) the SEM images consisted of smaller spherical particles. It is observed that the sample with $V_{NaOH}$=25 or 27 ml (Figs. 2(b) and 2(c)) has the most uniform spherical particles. However the experimental results show that white precipitate exhibits tendency to dissolve, so the ZnO particles were not obtained when $V_{NaOH}$ is over 27 ml (not show here). The effect of pH on morphology of the samples was also studied by keeping all other experimental conditions constant and changing the annealed temperature at 180, 200 and 220°C (Fig. 3). The SEM images of the samples with the annealed temperatures at 200 and 220°C (Figs. 3(b) and 3(c)) are better than that at 180°C.

All SEM images indicated that the samples have a spherical shape consisting of small wires with a diameter of about 50 nm (Fig. 4). The circle shape and nanosized (small wires) structure made the samples have higher surface-to-volume ratio. Since the photocatalytic reaction occurs at surfaces, the material with the increased surface area will increase the catalysis rate. The small wires with a diameter of about 50 nm that should allow electrons and holes easily to access to the surface and possess high conductivity for the flow of water. On the other hand, nanoscale slits, which are between nanowires, aid material accessible to the reactant molecules. So, ZnO nanocrystals structures have significantly photocatalytic activity. Furthermore, this structure of ZnO architectures might be found to have potential applications in many other fields such as: chemical sensor, solar cells, optoelectronic devices, etc [4].

Room temperature PL spectra of ZnO nanopowders prepared at different pH values and annealed at different temperatures are shown in Figs. 5 and 6. The exciting
wavelength was 335 nm. It is seen that all spectra consist of two main emission bands: an UV emission band at 390 nm and a strong visible band at 600 nm. The UV band is attributed to an exciton emission [5]. The 600 nm band is an emission from deep level defect associated with oxygen vacancies in ZnO lattices [5].

Figure 5 shows that when the $V_{\text{NaOH}}$ increases to 27 ml, the spectra have two extra weak peaks at 418 nm and 442 nm. It may be due to the excess OH- from NaOH [6]. Figure 6 shows the PL spectra of ZnO ($V_{\text{NaOH}}=25$ ml) which were synthesized at different annealing temperatures (180, 200 and 220°C). When the sample was annealed at 180°C, the reaction was not completed, so the hydroxyl (OH-) was excessive and the peaks at 418 nm and 442 nm exist.

From the above SEM images and PL results we can say that the best ZnO nanoparticles were obtained when $V_{\text{NaOH}} = 25$ ml, annealing temperatures are over 180°C.

In this paper, catalytic capacity of nano ZnO particles was investigated. The photocatalytic reactions are carried out in the presence of ZnO particles ($V_{\text{NaOH}}=25$ ml, annealed temperature at 200°C) after UV light illumination. During the photocatalytic process, the intense blue color of the MB solution gradually faded with increasingly longer exposure times. At last, The MB solution was almost colorless and simultaneously the initial white ZnO nanoparticles became blue particles (Fig.7). It is possible the ZnO particles adsorbed a part of MB.

Time-dependent absorption spectra of MB solution in presence of ZnO catalyst were analyzed in order to investigate photocatalytic activity of ZnO (Fig. 8). At the first 20 minutes, The absorption peaks (at 663 nm) corresponding to the MB molecules diminish quickly as the exposure time increases. So, the MB solution quickly faded. After about 120 minutes, the absorption peaks almost disappeared. But, it was not completely lost (MB solution was not completed colorless). It is due to two mechanisms in the MB solution: photocatalytic and adsorption

FIG. 5: PL spectra of ZnO nanopowders prepared at different pH values ($V_{\text{NaOH}}$=23, 25 and 27 ml).

FIG. 6: PL spectra of ZnO nanopowders prepared at different temperature (180, 200, and 220°C).

FIG. 7: Blue methylen solution (a) before and after (b) in the presence of nano ZnO particles

FIG. 8: Time-dependent absorption spectra of MB solution in presence of ZnO catalyst.
blue methylen on the surface ZnO particles. When blue methylen covered on the surface of ZnO particles, the capacity of catalytic of ZnO particles was disappeared (after about 120 minutes in our case).

The photodegradation mechanism of methylene blue (MB) on the ZnO network might be as follows [7]:

The absorption of efficient photons \((hw > E_g = 3.37 \text{ eV})\) by ZnO, and the \(e^-/h^+\) pairs were form:

\[
\text{ZnO} + h\nu \rightarrow e^- + h^+ \tag{1}
\]

Reactions of \(e^-\) and \(h^+\) with \(O_2\) and \(H_2O\) form other active species such as \(\text{OH}^*\):

\[
\text{H}_2\text{O} + h^+ \rightarrow \text{OH}^* + \text{H}^+ \tag{2}
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- \tag{3}
\]

\[
\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- \tag{4}
\]

\[
2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{5}
\]

\[
\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{OH}^* + \text{O}_2 + \text{OH}^- \tag{6}
\]

The reactions (1) to (7) can be explained as follows. When electrons and holes were created by the UV radiation, the hole initiates an oxidative reaction while the electron initiates a reductive reaction if the recombination does not occur. The highly reactive hydroxyl radicals (\(\text{OH}^*\)) is formed by hole reacting with water, as shown in (2). From reaction (3) to (6), oxygen acts as an electron acceptor by forming a super-oxide radical anion (\(\text{O}_2^-\)), then the suspension of super-oxide radical anions act as oxidizing agents or as an additional source to form hydroxyl radicals (\(\text{OH}^*\)). Finally, highly reactive hydroxyl radicals (\(\text{OH}^*\)) react with the methylene blue (\(\text{MB}^+\)), which make the blue solution colorless, as shown in (7).

\[
\text{OH}^* + \text{MB}^+ \rightarrow \text{Colorless} \tag{7}
\]

IV. CONCLUSION

ZnO nanopowders have been successfully prepared by the hydrothermal method. All samples have wurtzite structure of ZnO material and have the circle shape consisting of small wires with the diameter of about 50 nm. All the PL spectra consist of two emission bands: the UV emission band at 390 nm and the strong visible band at 600 nm. The peaks at 412 nm and 442 nm exist when the samples were annealed below 200°C or from \(V_{\text{NaOH}}=27\) ml. But these conditions (pH value and annealed temperature) do not much affect on the morphology. The photocatalytic capacity of the ZnO nanoparticles was investigated by the time-dependent absorption spectra of blue methylen solution in the presence of ZnO particles. The results show that the catalysis was almost complete after 120 minutes.

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