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PHOTOCATALYTIC ACTIVITY OF Ce-DOPED ZnO NANOPARTICLES

FOTOKATALITIČNA AKTIVNOST S Ce DOPIRANIH ZnO NANODELCEV

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Semiconductor materials are often used as photocatalysts. In order to increase the photocatalytic ability, rare earths are usually added to change the properties of materials. In this paper, we report that Ce:ZnO nanoparticles were synthesized and their photocatalytic properties researched. Wastewater containing methyl blue was used as the object of investigation. Ce:ZnO samples were synthesized using a simple chemical method. Four samples were obtained: three containing Ce concentrations of (1, 2 and 3) % (*w*/%) and one of pure ZnO. Optical properties of the samples were investigated with UV-Vis. X-ray diffraction (XRD) and field-emission scanning electronic microscopy (FESEM) were employed to examine the chemical composition and microstructures. It was found that the size of ZnO crystallites is suppressed after Ce-doping. Further, the samples were used as efficient photocatalysts for a photocatalytic degradation of methyl blue. It was observed that Ce-doped ZnO nanoparticles exhibited excellent photocatalytic properties. The degradation ability increased with the increasing Ce concentration. For the sample of 3 % of mass fractions of Ce-doped ZnO, a complete photodegradation was observed after 60 min.

Keywords: Ce-doped ZnO, nanoparticles, photocatalyst, methyl blue, photodegradation

Polprevodniki se pogosto uporabljajo kot fotokatalizatorji. Povečanje katalitične sposobnosti dosežemo tako, da materialom dodamo elemente redkih zemelj in s tem spremenimo njihove lastnosti. V tem članku avtorji poročajo o sintezi nanodelcev ZnO z dodatkom cerija (Ce) in raziskavi njihovih fotokatalitičnih lastnosti. Kot predmet raziskovanja so izbrali odpadno vodo, ki je vsebovala metilensko modrilo. Vzorce Ce:ZnO so sintetizirali z enostavno kemijsko metodo. Izdelali so štiri vzorce; čisti ZnO, in tri vzorce, ki so vsebovali (1, 2, in 3) % masnih deležev Ce. Optične lastnosti vzorcev so določili s spektroskopijo, ki temelji na absorpciji ultravijolične in vidne svetlobe (UV-Vis). Za določitev kemijske sestave in mikrostrukture pa so uporabili rentgensko difrakcijo (XRD) in vrstično elektronsko mikroskopijo na emisijo polja (FESEM). Avtorji članka so ugotovili, da je rast ZnO kristalitov zavrta po dopiranju s Ce. Nadalje so vzorce učinkovito uporabili kot fotokatalizatorje za fotokatalitično degradacijo metilenskega modrila. Ugotovili so da imajo s cerijem dopirani nanodelci ZnO odlične fotokatalitične lastnosti. Stopnja degradacije se je povečevala s povečevanjem koncentracije Ce. Pri vzorcu nanodelcev ZnO s 3 mas. % dodatkom Ce je prišlo do popolne degradacije po 60 minutah.

Ključne besede: s Ce dopiran ZnO, nanodelci, fotokatalizator, metilensko modrilo, fotodegradacija

1 INTRODUCTION

Environmental pollution has become a world problem. At the international level, the governments and people pay more attention to our environment. With the development of science and technology, it became more important to protect our environment. Among environmental challenges, the most serious problems are the water and air pollution. With the development of modern agriculture and industry, more and more wastewater is poured into rivers, lakes and fields. The rivers are becoming so dirty that no living beings can live in it. The water is giving off a terrible smell, which is a threat to people's safety. Due to containing a large number of organic and inorganic compounds, wastewater has caused serious pollution in the world, especially in the developing countries. The pollution can harm crops, cause various diseases, such as digestive-system disease, respiratory disease, cardio-cerebrovascular disease, heavy-metal overdose, calculus, etc. Finding ways to protect our water from pollution has been one of the most difficult problems in the world. We must accept that, due to society development, we daily produce wastewater, polluting the waters. So, it is very important to control water pollution and purify wastewater.

Up to now, nano-semiconductor oxides such as TiO2 and ZnO have been given a lot of attention in the field of photocatalysis.[1–6] Their photocatalytic ability to degrade organic pollutants in water and air were widely studied. Both of them have many advantages such as a strong oxidation power, chemical inertness and stability against chemical corrosion and photocorrosion.[7–12]

For the past few years, ZnO has been a hot academic topic. Due to its excellent optical and electrical properties, large band gap (3.37 eV) and exciton energy (60 MeV), ZnO is expected to be important in applications such as sensing, light-emitting diodes, photocatalysts, solar cells and transparent conducting layers.[13–17] As we know, the photocatalytic efficiency is relative to the surface chemical reaction and electron-

hole recombination. If the course of electron-hole recombination is too fast, the surface chemical reaction will not occur. The photocatalytic efficiency will be low. So, finding a way to restrain electron-hole recombination is the key to increasing the photocatalytic efficiency.

In order to improve optical, electronic and magnetic properties, multiple elements are doped into ZnO to form a ternary or a multicomponent. After doping, the band gap, electron mobility and photocurrent response are greatly changed. To achieve these changes, the rare earth Ce doped into ZnO to get a $Ce_xZn_{1-x}O$ ternary is widely researched and used. When Ce-doped ZnO is used in a photocatalytic study, increasing the photocatalytic efficiency is a problem that must be solved urgently.[18,19]

In this paper, we report on our research work including the synthesis of pure and Ce-doped ZnO nanomaterials with different concentrations of Ce, and on a photocatalytic experiment. The photocatalytic-efficiency dependence on the Ce-concentration was studied.

2 EXPERIMENT

Ce-doped ZnO samples were synthesized using a simple chemical-precipitation method.[20] In brief, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and ammonium bicarbonate (NH_4HCO_3) were chosen as the starting material and cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) was used as the dopant source. Deionized water was used as the solvent. All the analytical-grade reagents were purchased from Sinopharm Chemical Regent Co., Ltd., without further purification. The synthesis method was as follows: first, $Zn(NO_3)_2{\cdot}6H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in deionized water with a molar ratio of Ce/(Ce+Zn) being x:1 (x = 0.00, 0.01, 0.02 and 0.03). Second, the amounts of the NH_4HCO_3 aqueous solution were transferred into the ZnO/Ce aqueous solution during constant stirring. Then, white precipitates were formed in the above mixture solution and washed with deionized water and alcohol for several times. After having been dried in an oven at 60 °C for several hours, the white precipitates were finally annealed under air atmosphere for 3 h at 450 °C.

An X-ray diffractometer (XRD, D/Max-2400) was used to analyze the crystal structures of synthesized nanoparticles. The morphology was investigated with a field scanning electron microscope (FSEM, S-4800). Optical properties of the samples were studied by measuring the transmittance in a range of 300–800 nm. The photocatalytic activity of the light-degraded methyl blue was investigated.

Experimental details of the photocatalysis are as follows: 100 mL of wastewater containing methyl blue was poured into a 200-mL breaker. The concentration of methyl blue was 40 mg/L. 10 mg of Ce-doped ZnO nanoparticles with different Ce molar ratios (Ce/(Ce+Zn) was x:1 (x=0.00, 0.01, 0.02 and 0.03)) were put into the wastewater solution. All the samples were dispersed under magnetic stirring for 10 min. A 15-watt UV lamp was used as the excitation light source, fixed 15 cm above the treated solution. The decay of methyl blue was monitored with UV-Vis absorbance measurements, made at intervals of 20 min. All of the experiments were carried out against a dark background and at room temperature.

The photocatalytic efficiency can be characterized with photodegradation percentage defined as #, where A_0 and A are the initial concentration and the concentration obtained over a period of time, respectively. According to the Beer Law, the concentration can be expressed with absorbance.

3 RESULTS AND DISCUSSION

The absorption spectra of a sample were measured at room temperature in the range of 300–800 nm. The result is shown in **Figure 1**. The sample exhibited high transmittance in the visible regions. With the increasing Ce concentration, the absorption edge of the sample moved slightly to the lower-energy direction. However, as the Ce concentration changed only slightly, the valence band of the sample could not be changed too much. For our samples, the experimentally measured valence-band gap is about 3.36 eV. The result is similar to the report of Varughese et al.[21]

The XRD patters of the samples are shown in **Figure 2**. It was found that all the diffraction peaks of ZnO

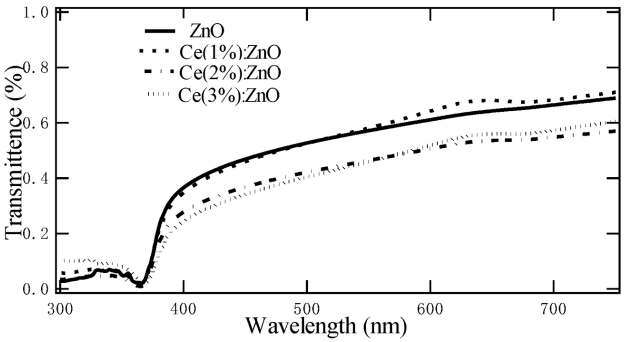

Figure 1: Transmittance spectra of the Ce:ZnO nanoparticles

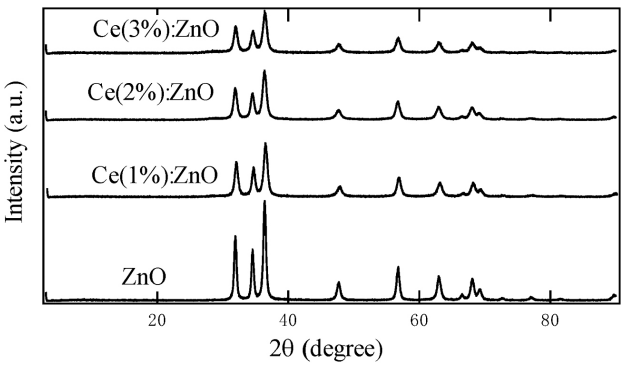

Figure 2: XRD patterns of the Ce:Zno nanoparticles with Ce concentrations of (0, 1, 2 and 3) %

and Ce:ZnO can be indexed as a hexagonal wurtzite structure, without the characteristic peaks for the other impurities.

The intensity of diffraction peaks decreases with the increasing concentration of Ce. The half-width of a peak becomes wider when the concentration of Ce increases. Besides, the positions of the corresponding diffraction peaks of Ce-doped ZnO shift slightly toward the lower angle.

This phenomenon can be explained as follows: due to the fact that Ce^{4+} (0.092 nm) and Ce^{3+} (0.103 nm) are a bit larger than Zn^{2+} (0.074 nm), this shift of diffraction peaks indicates that the Ce ions were incorporated into the ZnO lattice, substituting the Zn ion sites. The information about the lattice constants of pure and Ce-doped ZnO obtained from the XRD data can be calculated using the Scherrer formula, $D = 0.89\lambda/(\beta \cdot \cos\theta)$, where $\lambda = 0.154056$ nm at the Cu $K_{\alpha 1}$ radiation, β is the half-width of the diffraction peak and θ is the Bragg angle.

In our case, the crystallite size is estimated to be about 35–50 nm. It is found that the crystallite size decreases with the increasing Ce concentration. This can be explained as follows: In the course of the crystallite growth, the particle size is dependent on the particle boundary motion. When increasing the Ce concentration, the lattice agglomerates and the distortion caused by the addition of Ce decreases the particle mobility and, therefore, inhibits the growth of the ZnO crystallites.

The morphology of pure and Ce-doped ZnO was observed with FSEM. The images of pure and Ce-doped ZnO are shown in **Figure 3**. The usual nanoparticles with a diameter of about 35–50 nm (**Figure 3**) were observed, which accords with the results calculated from the XRD data.

It was found that the size of nanoparticles decreases with the increasing Ce concentration.

The absorbance changes of methyl blue with the UV irradiation time are shown in **Figure 4**.

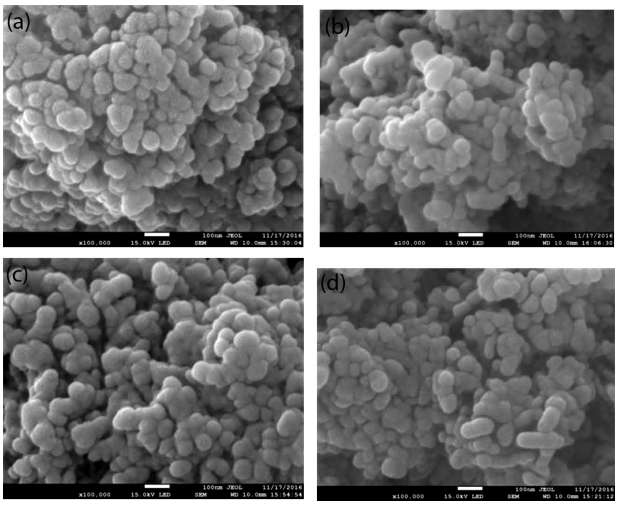

Figure 3: FSEM images of Ce-doped ZnO, Ce concentrations of: a) 0 %, b) 1 %, c) 2 % and d) 3 %

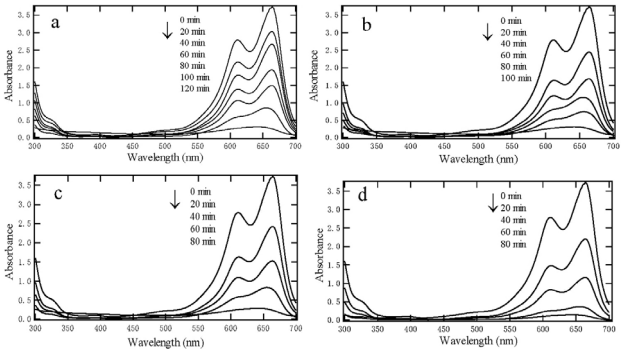

Figure 4: Absorbance changes of methyl blue with UV irradiation time for: a) pure ZnO, b) 1 % Ce, c) 2 % Ce and d) 3 % Ce:ZnO nanoparticles as the photocatalysts

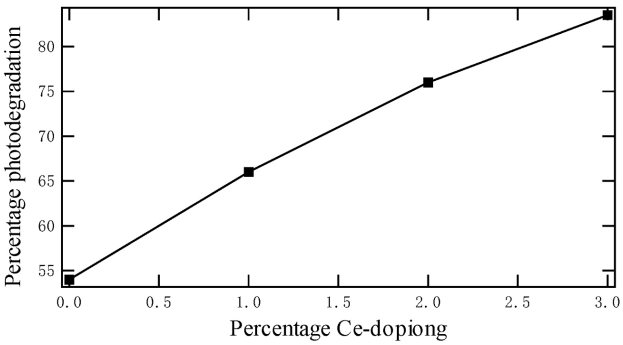

Figure 5: Percentage of photodegradation vs Ce-doping after 60 min of UV irradiation

The absorption band at a wavelength of about 650 nm decreases with the increasing irradiation time for all the Ce-doped ZnO photocatalysts. After about 80 min of UV irradiation, a complete photodegradation is observed for the Ce (3 %) doped ZnO sample. After 60 min of UV irradiation, the percentage of the photodegradation of methyl blue was measured for the four samples. The result is shown in **Figure 5**. It is very clear that the photocatalytic effect increases with the increasing Ce concentration.

Using the 650-nm absorption intensity related to the concentration of methylene blue, variations A_0 and A versus the irradiation time are shown in **Figure 6**.

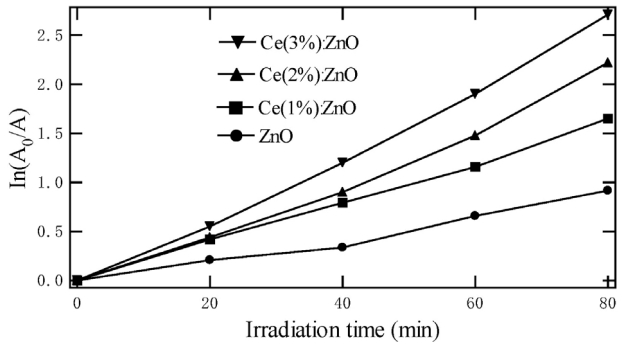

Figure 6: A0/A as a function of irradiation time for methyl blue photodegradation using Ce:ZnO as the photocatalyst

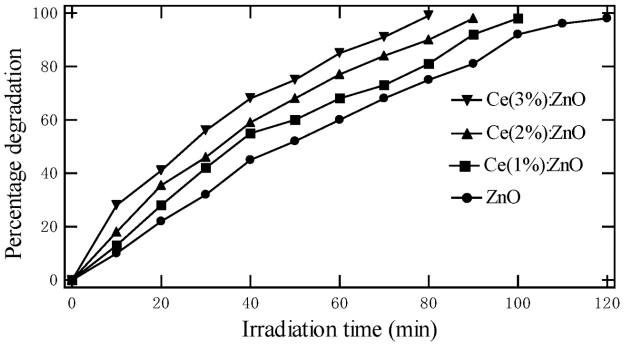

Figure 7: Percentage of photoabsorbance of methylene blue with Ce-doped ZnO samples vs UV irradiation time

The variation in the percentage of photodegradation of methyl blue with irradiation time was investigated and shown in **Figure 7**.

The experimental results show that the absorbance of methyl-blue solution decreases with the increasing UV irradiation time. It takes about 120 min for ZnO to become completely photodegraded. However, for the Ce-doped ZnO samples, the time of complete photodegradation reduces to 98 min (1 % Ce), 85 min (2 % Ce) and 75 min (3 % Ce).

The experiments prove that Ce-doped ZnO improves the photocatalytic ability. As we know, the mechanism of photocatalysis is based on the migration of electrons and holes to the surfaces of catalytic nanoparticles upon an UV irradiation and their subsequent participation in a redox reaction with the adsorbed methylene blue in the solution. The reason for enhanced photocatalysis can be explained as follows: Firstly, when the Ce^{4+} ions are doped into the ZnO lattice, the Zn site is replaced by Ce^{4+} to form electron-donor defects. In order to maintain electronic neutrality, Ce ions must release electrons into the conduction band, which increases the concentration of free electrons. Hence, the increased transport of electrons results in a higher response. Secondly, Ce^{4+} can also trap the conduction-band electrons to eliminate or reduce the probability of electron-hole recombination. Thirdly, the oxygen vacancy after doping Ce on photolytic surfaces can serve as a trap for the electrons from the conduction band. Fourthly, because Ce^{4+} ion radius is larger than that of Zn^{+}, the average crystalline of Ce-doped ZnO is smaller than that of pure ZnO. This makes the specific surface increase and provide for more active centers for oxygen molecules adsorbed on the surface, which increases the electron transport. All of these can efficiently enhance the transfer of photogenerated electrons to participate in the redox reaction, forming OH free radicals causing methylene-blue degradation.

4 CONCLUSION

Pure ZnO and various Ce:ZnO samples were prepared with a simple chemical-precipitation method. The results of XRD and FESEM clearly revealed the microstructures of the samples with a size of about 35–80 nm. Using methylene blue as the reactant, photocatalytic properties of ZnO and Ce-doped ZnO were investigated. The experimental results show that Ce-doped ZnO is more photocatalytically active than pure ZnO. The ability of photodegradation increases with the increasing Ce concentration. For pure ZnO and 3 % Ce-doped ZnO, a complete degradation was observed in 120 min and 75 min, respectively. Furthermore, this work implies that suitable Ce-doping can improve the photocatalytic ability of a ZnO NP-based photocatalyst. Moreover, more research will be carried out within our forthcoming work.

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