PREPARATION AND CHARACTERIZATION OF Ga-DOPED ZnO PHOTOCATALYSTS

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Introduction

Zinc oxide (ZnO) is a unique semiconductor with wide band-gap (3.17 eV in the wurtzite crystalline phase). ZnO has been extensively applied in optoelectronic devices, sensor, energy materials and many other important areas [1-6]. ZnO is another most investigated photocatalyst in addition to titanium dioxide [7]. ZnO shows high reactivity and chemical stability under ultraviolet (UV) light (wavelength (λ) < 387 nm) [8]. In order to enhance the photo and electronic performances of ZnO, various metals or metal oxides are normally doped into ZnO [3,6]. Recently, gallium (Ga) as a dopant has received a great attention [9-14]. The bond length of Ga-O is 1.92 nm, close to that of Zn-O (1.97 nm), while the radius of Zn^{2+} (0.074 nm) is just a little larger than that of Ga^{3+} (0.062 nm). Therefore the use of Ga as the dopant will have very limited effect on the lattice of ZnO. Ga has been proposed to be the best dopant for ZnO [14]. However, most reported works on Ga doped ZnO were for ZnO thin films or ZnO nano wires. Few works can be found in the literature with Ga doped ZnO powders or particles [12-14]. In many cases (e.g., with photocatalytic applications), Ga doped ZnO powders or particles are normally requested. In this work, we attempted to dope Ga into ZnO powders to prepare Ga-doped ZnO nanoparticles. The photocatalytic degradation of methyl orange (MO) under solar irradiation was chosen as the test reaction for the obtained Ga-doped ZnO catalysts.

Experimental

To prepare Ga-doped ZnO catalysts, a aqueous solution of Na_2CO_3 (1 mol/L) was added as droplet into a 500 mL $Zn(NO_3)_2$ aqueous solution (1 mol/L) until the pH reaches 7.5. After aging at room temperature for 2 hrs, the precipitate was washed and filtrated with distilled water, followed by drying at 110 °C overnight. Then the obtained powder was impregnated with an aqueous solution of gallium nitrate (Alfa Aesar Co., USA) for 12 hrs. After drying at 110 °C for another 12 hrs, the obtained sample was decomposed by dielectric-barrier discharge (DBD) plasma for 60 min. The DBD plasma decomposition is an alternative way to the thermal calcination. The details about the DBD plasma catalyst preparation have been previously described [15,16].

The catalysts with different Zn/Ga molar ratios (27:1 and 49:1) were referred as ZnO-Ga-27:1 and ZnO-Ga-49:1. For the purpose of comparison, no doped ZnO photocatalyst was also prepared, which was referred as ZnO.

The photocatalytic degradation of methyl orange (MO) in water solution under solar irradiation was employed to test the above-obtained photocatalysts. To do so, 0.05 g catalyst powder was added into 50 mL aqueous solution of MO (3×10^{-5} mol/L). The reaction was then initiated under solar irradiation with constant stirring at 35 °C for 2 hrs (from 11 AM to 1 PM). At given intervals, samples were taken from the suspension for further analyses of the variation of MO concentration with time.

The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Perkin-Elmer PHI-1600 spectrometer with Mg Kα (1253.6 eV) radiation. The binding energy was calibrated by the C1s peak (284.6 eV) from the surface adventitious carbon.

The X-ray diffraction (XRD) characterization was conducted on a Rigaku D/MAX-2500V/PC system using Cu Kα radiation (λ = 0.154056 nm) at 40 kV and 200 mA. The phase identification was made by comparison with the Joint Committee on Powder Diffraction Standards (JCPDSs).

The field emission scanning electron microscope (FE-SEM) images were recorded on a JEOL JSM-6700F system.

The surface areas were measured with N_2 sorption analysis. N_2 adsorption-desorption isotherms were measured at -196 °C on an AUTOSORB-1-C analyzer by Quantachrome. Before the measurements, the samples were outgassed at 200 °C for 4 hrs. The Brumauer-Emmett-Teller (BET) method was employed to calculate the specific surface areas.

UV-visible (UV-Vis) spectra were recorded using a DU-8B UV-Vis spectrophotometer (Backman Co., USA). The pure powdered $BaSO_4$ was used as the reference sample for the analyses of MO in the solution.

Results and Discussion

Table 1 shows the specific surface area, particle size and Ga surface compositions of the Ga doped ZnO catalysts. From Table 1, the increasing doping amount of Ga leads to an increase in the specific surface area. The specific surface area of the un-doped ZnO is 17.2 m^2/g, while it becomes 27.9 m^2/g with ZnO-Ga-27:1. The particle size reduces with the increasing doping amount of Ga. The particle size of the un- doped ZnO is 31.2 nm but it changes to 27.9 nm with ZnO-Ga-27:1. The increase in the surface area is obviously resulted from the decreasing particle size.

Table 1. Specific surface area, partlce size and Ga surface composition of ZnO-Ga-27:1 and ZnO-Ga-49:1 and ZnO samples

sample	$S_{BET}/m^2\,g^{-1}$ 1)	particle size/nm 2)	Ga surface composition /atom % 3)
ZnO	17.2	31.2	0.0
ZnO-Ga-49:1	18.3	29.7	0.7
ZnO-Ga-27:1	22.7	27.9	1.7

1) BET surface area was calculated from the linear part of the BET plots
2) particle size was calculated using Scherrer formula
3) surface composition was obtained from XPS analysis

XPS analysis shows a significant effect of Ga doping on the Ga surface composition. With the increasing Ga doping, the Ga surface composition has a very slow increase. This means that Ga would be included in the lattice of ZnO. This will be confirmed by the XRD results, as shown in Figure 1. The XRD patterns suggest the formation of ZnO with the Wurtzite structure. No other structures can be identified. Especially, no diffraction peaks can be assigned to Ga related crystallite. We can conclude that Ga has been successfully doped into the ZnO completely.

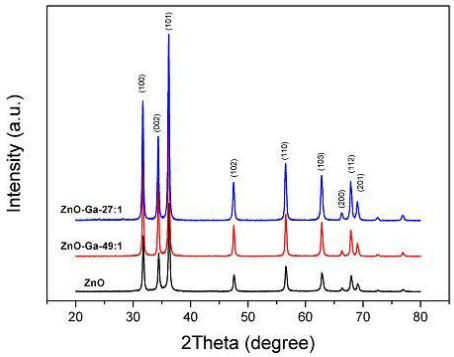

Figure 1. XRD patterns

Figure 2 compares the FE-SEM images of ZnO, ZnO-Ga-27:1 and ZnO-Ga-49:1. By comparing the morphology of nanoparticles, one can also observe that Ga has a special influence on the formation of nanoparticles. With the increasing doping amount of Ga, the mean size of nanoparticles decreases and the nanoparticles tend to form as nano wires. As a result, the mean size decreases as follows ZnO-Ga-27:1 > ZnO-Ga-49:1 > ZnO, consistent with the XRD results.

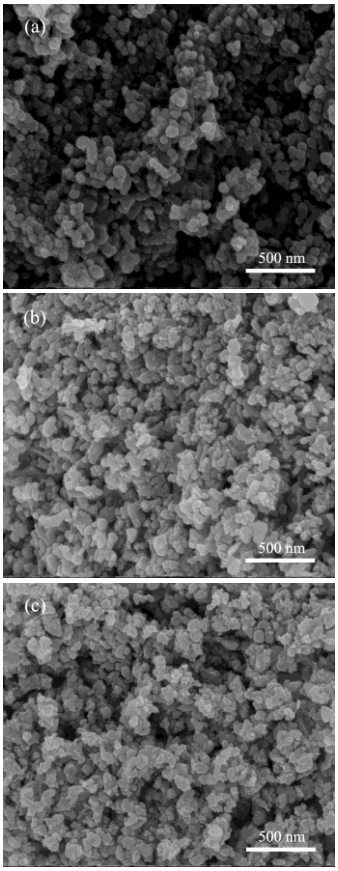

Figure 2. SEM images (a)ZnO; (b)ZnO-Ga-49:1 (c) ZnO-Ga-27:1

Figure 3 shows the degradation rates of MO over all the prepared photocatalysts. Compared to the pure ZnO, all the Ga doped catalysts exhibit the significantly enhanced activity under the solar irradiation. The catalytic activity increases with the Ga doping amount. This confirms that the Ga doped ZnO is a good photocatalyst that can be applied directly under the solar irradiation.

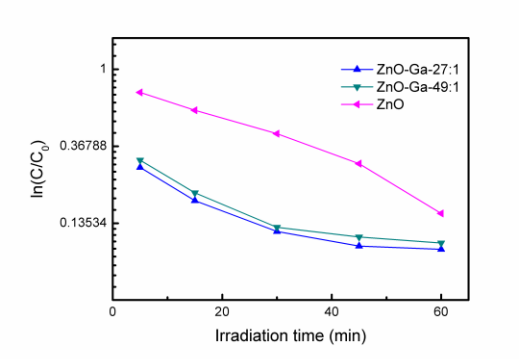

Figure 3. The photocatalytic activity

From the UV-Vis diffuse reflectance spectra, the band gap absorption edge of ZnO is 392 nm, corresponding to the band gap energy of 3.17 eV. The absorption edge shifts to longer wavelengths as Ga doping amount increases. Then the band gap absorption edge of ZnO-Ga-49:1 and ZnO-Ga-27:1 is 415 and 428 nm, respectively, which correspond to the band gap energy of 2.99 and 2.90 eV.

The experimental results for the band gap energy of ZnO are in good agreement with the reported value of 3.17 eV [18]. For the sample ZnO-Ga-27:1, the band gap energy value is 2.90 eV, which is significantly less than that for ZnO (3.17 eV). As mentioned above, ZnO is a wide band gap material. After doping Ga into ZnO, the band gap of the sample reduces. This induces an enhanced photocatalytic activity.

Conclusions

We confirm in this work that Ga doped ZnO nanoparticle can be a good photocatalyst. The Ga doping reduces the band gap of ZnO from 3.17 eV (pure ZnO) to 2.90 eV (ZnO-Ga-27:1). The Ga doping not only increases the specific surface area but also reduces the band gap of the photocatalyst. The Ga doped ZnO catalyst has shown a higher activity in the degradation of MO under the solar irradiation compared to pure ZnO powders. The Ga doped ZnO nanoparticle is also promising for many other applications that will be reported in the future.

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