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#### Research paper

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# Significantly enhanced photocatalytic performance of mesoporous C@ZnO hollow nanospheres via suppressing charge recombination

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Abstract: Mesoporous C@ZnO hollow nanospheres were prepared by carbon sphere template. The influence of defects and surface state on photocatalytic performance was studied. The photocatalytic activity of C@ZnO nanospheres without treatment is the worst, that of the sample via pickling and annealing is secondary, and the pickling sample is the best. The improved performance can be attributed to the reduction of defects, which suppress the charge recombination. This work helps us better understand the important effects of defects on photocatalytic properties, and provides us with a feasible way to improve the UV photocatalytic activity of ZnO and other metal oxide.

Keywords:ZnO; Hollow spheres; Templates; Defects; Photocatalys; Nanocomposites.

#### **1. Introduction**

With rapid development of urbanization and industrialization, a tremendous series of environmental pollution problems have been brought out. A great deal of attention has been thus paid to convert contaminants into non-toxic, harmless, and /or useful products [1]. As a sustainable advanced oxidation technology, semiconductor photocatalysis has been explored to oxidize or reduce environmental pollution [2-6].

ZnO has been proved as one of the most potential photocatalysts for water purification [2]. However, photocatalysts need to have higher activities to be economically competitive as a practical water treatment technology. This can be quantum efficiency. The recombination achieved by enhancing the and separation/migration processes of photo-generated carriers are crucial factors to improve the quantum efficiency [7]. Charge recombination reduces the number of electron-hole pairs by emitting light or generating phonons, which is ineffective for the quantum efficiency [7]. Efficient carrier separation avoids any interior/surface charge recombination and improves photocatalytic performance. To improve the quantum efficiency and photocatalytic performance, it is therefore important to enhance the charge separation and/or to suppress the charge recombination. During the past decades, many methods (e.g., noble metal loading [8], heterostructure [9], plasmonic structures [10], Graphenic carbon coatings [5], etc.) have been developed to improve the carrier transfer as well as their separation. To date, little effort has been made to improve the quantum efficiency by suppressing the charge recombination. Metal oxide semiconductor (MOS) nanostructures involve large specific surface area,

surface area and surface energy, which lead to more surface defects. The defects are recombination centers of photogenerated carriers [11], which reduce of quantum efficiency and photocatalytic activity.

In this paper, we show that mesoporous C@ZnO hollow spheres are prepared by a template technology, and that quantum efficiency and photocatalytic activity could be controlled by reducing defects. Furthermore, significantly enhanced photocatalytic performance via suppressing charge recombination was explored.

#### 2. Experimetal section

#### 2.1 Synthesis of mesoporous C@ZnO hollow spheres

The preparation of mesoporous C@ZnO hollow spheres was carried out according to the method reported in [12, 13], using carbon spheres as the template zinc acetate as the main raw material. Firstly, the carbon spheres were prepared from glucose solution (65 mL, 0.55 mol/L) under hydrothermal conditions at 180 °C for 9 h. Secondly, the suspension (0.171mol/L Zn(AC)<sub>2</sub>·2H<sub>2</sub>O, 0.30 g carbon spheres and 60 mL ethanol solution) ultrasound for 30 minutes. After magnetically stirred for 12 h at room temperature, the mixture was washed with ethanol there times and dried at 80 °C for 4 h. The final products were calcined in air at 550 °C for 4 h to form C@ZnO hollow structure, which were named S0. S0 powder was immersed in a 0.1 mol/L hydrochloric acid solution under ultrasonication for 3 minutes, subsequently washed and dried, which is designated as S1. S1 was annealed at 250 °C for 1 hour and the resulting sample was designated as S2.

2.2 Photocatalytic activity

The photocatalytic activities were studied by using Rhodamine B (RhB) as a contrast pollutant [8, 9]. The suspension consists of 50 mg of the photocatalyst and 50 mL of the RhB aqueous solution (10 mg/L), which were stirred in the dark for 30 min. Subsequently, the room-temperature photocatalytic performance was tested under a high-pressure mercury lamp (CHF-XM-300W).

The degradation efficiency could be expressed as  $\eta = (C_0 - C_t)/C_0 \times 100\%$ , where  $C_0$  is the initial concentration of RhB and  $C_t$  is the concentration after t minutes of light exposure. In order to quantify the degradation rate, we use the pseudo first-order kinetic equation  $\ln(C_0/C_t) = Kt$  (K is the kinetic rate constant, t is the irradiation time) [9, 14].

#### 3. Results and discusstion

Figure 1 shows X-ray diffraction patterns. All diffraction peaks could be indexed as the wurtzite ZnO, and no impurity phase is found. The diffraction intensity of S1 is sharper than that of S0, which can be attributed to the reduction of surface defects by an acid cleaning process. Then the neat lattice structure increases, the X-rays scattering reduces, and the diffraction intensity increases. After annealing, the diffraction intensity decreases, indicating the surface atoms reconstruct, and that the neat and clear surface structure were disrupted. TEM and SEM images of S0 (as shown in inset of Figure 1) indicate a mesoporous spherical shell structure, which is assembled by nanoparticles.

The surface composition and chemical state of nanospheres were analyzed by X-ray photoelectron spectroscopy (XPS) (Figure 2). The characteristic peaks of Zn, O

and C can be observed in Figure 2a. The C element comes from carbon sphere templates, which is not completely removed by calcination and proved by previous work [13].

Figure 2b-c shows the high resolution XPS spectra of the Zn 2p and C 1s. Figure 2b shows the binding energy of the Zn 2p of the samples is slightly different, which may be corresponding to the difference of surface defects and states. For Zn  $2p_{1/2}$ , the binding energy of S0, S1 and S2 is respectively 1045.1, 1044.8 and 1045.1 eV [8,15]. For Zn  $2p_{3/2}$ , the binding energy is respectively 1022.0, 1021.8 and 1022.0 eV [8,15]. The spin splitting Zn 2p energy was 23.0 eV, indicating that the chemical valence of Zn is Zn<sup>2+</sup> [16]. Figure 2c shows the C 1s spectrum of S1. The typical C 1s peak can be fitted by two approximate Gauss distributions, and the binding energy of 284.8 and 288.5eV is assigned to C-C and C=O respectively [17, 18].

Figure 3 shows high resolution XPS spectra of O 1s, which can be fitted by two symmetrical Gauss function curves, centered at ~530.2 and ~531.6 eV, respectively. The peak at 530.2 eV corresponds to the crystal lattice oxygen ions ( $O_{latt}$ ) in the form of ZnO, which is relatively stable. The peak at 531.6 eV correlates with the adsorbed oxygen ions ( $O_x^-$ ) caused by oxygen vacancy ( $V_0$ ), oxygen interstitial ( $O_i$ ), and oxygen antisite ( $O_{Zn}$ ) in the ZnO matrix [19], which is related to the surface defects. For S0, S1, and S2, the area ratios of  $O_x^-$  and  $O_{latt}$  are respectively calculated to be 0.871, 0.755, and 1.222, which means difference of the surface defects and state. Compared with S0, the surface defects of S1 reduce and those of S2 increase, which is consisted with the results of XRD.

UV–vis spectra of RhB on samples after 30 min dark adsorption/desorption and t minutes of light exposure (as described earlier) are shown in Figure 4a-c. The spectral intensity in the UV-Vis is proportional to the concentration of Rhodamine B. The intensity decreases with time, reflecting the decrease of RhB concentration with time. Figure 4d shows the degradation efficiency of S1, S2 and S0 decrease in sequence. The degradation efficiency of S1 and S2 can reach 97.16% and 96.06% in 30 minutes, which is significantly higher than S0. Figure 4e shows the K of S0, S1 and S2 are 0.0978, 0.117 and 0.106 min<sup>-1</sup>, respectively. The results indicate the processing technology would enhance the photocatalytic activity of nanospheres by changing surface state and defects.

In order to further confirm that the change of photocatalytic performance mainly comes from the change of surface state and defect rather than the change of specific surface area and mesoporous size distribution. Nitrogen adsorption–desorption isotherm measurements were utilized to investigate sample structure, surface area and pore size distribution. The isotherm of the samples exhibits a hysteresis loop, associated with the filling up and emptying of mesopores by capillary condensation (Figure 5). This phenomenon clearly indicates that the samples exhibit a large structural porosity. The BET surface area of S0, S1 and S2 was calculated as 147.3, 162.9 and 156.5 m<sup>2</sup> g<sup>-1</sup>, respectively. Using the BJH method, the desorption branch of the nitrogen isotherm indicates that the pore size distribution of S0, S1 and S2 is respectively 1.6–32.5 nm, 0.9-42.3 nm and 1.1-38.9 nm (Table 1). Comparing S0, S1 and S2, the specific area and the average mesopores size of the mesoporous spheres

first increase then decrease, which further confirms that acid washing and subsequent annealing change the microstructure and surface state. The large surface area also provides numerous active sites for surface contact reactions. The large mesopores size of the samples are advantageous for molecular adsorption–desorption and diffusion. The large surface area and mesopores size result in the excellent photocatalytic performance. However, a small change in the surface area and mesopores size does not bring significant changes in photocatalytic performance.

Sample	surface area	pore size distribution	average pore size
number	(cm3/g)	(nm)	(nm)
SO	147.3	1.6-32.5	16.5
<b>S</b> 1	162.9	0.9-42.3	19.8
S2	156.5	1.1-38.9	17.8

Table 1 the surface area and pore size distribution by BET analysis

In order to further investigate the relationship between the defects and photocatalytic performance, we focused on the key processes affecting the quantum efficiency and photocatalytic reaction: charge recombination. Surface and interior defects are recombination centers of photogenerated carriers, which reduce of quantum efficiency. Compared with S1, S0 and S2 have more surface defects, as is proved by XPS results. Thus, the photocatalytic performance of S1 is better than that of S0 and S2 by suppressing charge recombination. Compared with S0, S2 has more surface defects. However, annealing would reduce the internal defects of S2. The sum defects of S2 are less than S0. Thus, photocatalytic performance of S2 is significantly better than that of S0.

#### 4. Conclusions

Mesoporous C@ZnO hollow nanospheres were synthesized by carbon sphere templates. The sample without treatmeat has the poor photocatalytic performance, while the pickling sample and the sample via pickling and annealing have excellent performance. Pickling or annealing would reduce surface or internal crystal defects that are recombination centers of photogenerated carriers, which is an effective method to improve the photocatalytic performance by suppressing charge recombination.

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Figure 1 X-ray diffraction patterns of the samples, insets a and b show the TEM and SEM images of S0.



Figure 3 High resolution spectra of the O 1s spectra of SO (a), S1(b) and S2 (c).



Figure 4 UV–vis spectra changes of RhB of S0 (a), S1(b) and S2 (c), photocatalytic degradation efficiencies of samples (d), Kinetics curves of samples (e).



Figure 5 Nitrogen adsorption–desorption isotherm and pore size distribution (inset) of S0 (a), S1(b) and S2 (c).



### **Graphical Abstract**

(a) X-ray diffraction patterns of samples, TEM (a) and SEM (b) pictures inserted, (b) photocatalytic kinetic curve of mesoporous C@ZnO hollow nanospheres via surface treatment process

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## Highlights

Mesoporous C@ZnO hollow nanospheres were prepared by carbon sphere template.

Enhanced photocatalytic performance can be realized by suppressing charge recombination.

Pickling process reduces surface defects and improves photocatalytic performance.

Annealing reduces internal defects and improves photocatalytic performance.

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