



# Leaf-like ZnO nanostructure and its excellent photocatalytic activity



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## ABSTRACT

In this study, uniformly distributed leaf-like ZnO nanostructure on glass substrates had been prepared by a simple two-step method. The structural properties were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic activity of the leaf-like ZnO nanostructure had been investigated through the degradation of Rhodamine B under UV illumination and using a ZnO thin film and ZnO nanorods as the references. The results show that the photocatalytic activity of leaf-like ZnO nanostructure is higher than that of the ZnO thin film or ZnO nanorods. This is mainly because the leaf-like ZnO nanostructure has a larger surface area than ZnO thin films or ZnO nanorods. What is more, the leaf-like ZnO nanostructure is very firm on the substrate and its photocatalytic activity can be recycled and is stable.

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## 1. Introduction

In recent years, with the rapid development of industry, the pollution of air and water is gradually exacerbated in some areas especially in some developing countries. Therefore, exploring some new techniques to control pollution becomes an important research subject at present. The photocatalytic technique is widely considered as a promising new environmental protection technique which could be used to control water pollution and prepare clean energy H<sub>2</sub> in the near future. For the photocatalytic technique, the most important factor is the photocatalyst. Due to inexpensive raw materials, low production cost and abundant nanostructures, the semiconductor photocatalysts have attracted much attention. The most common semiconductor photocatalysts include TiO<sub>2</sub>, SnO<sub>2</sub>, and ZnO etc. Because ZnO has a variety of nanostructures and possesses high photocatalytic activity [1], it has raised much research enthusiasm of lots of researchers. In the previous years, the photocatalytic properties of ZnO powders have been widely and deeply investigated [2,3]. However, ZnO powder is easy to aggregate and is hard to be retrieved in water, which is possible to result in the secondary pollution. Therefore, ZnO thin films or ZnO nanostructures grown on substrates are more preferable for photocatalytic applications. But the specific surface area

of ZnO thin films is smaller than that of ZnO powder, leading to the decline of photocatalytic activity. In order to increase the photocatalytic activity of ZnO thin films, one can fabricate ZnO thin films with nanostructured morphology such as porous morphology [4], ganglia-like morphology [5], sheet-like or leaf-like morphology [6] etc. to enhance the specific surface area. Compared with other surface morphologies, the leaf-like or sheet-like nanostructure makes ZnO thin films have a larger surface area and correspondingly a higher surface activity. The leaf-like or sheet-like ZnO nanostructures not only can be used as photocatalysts but also can be utilized in gas sensors [7]. Now, although some sheet-like or leaf-like ZnO nanostructures have been prepared and investigated [6–11], the adopted preparation methods are relatively complicated. Thus, it is still a challenge to fabricate uniform leaf-like or sheet-like ZnO nanostructures by a simple method.

In this study, we adopted a simple two-step method to obtain leaf-like ZnO nanostructure. This leaf-like ZnO nanostructure has a very thin thickness and a large specific surface area. To our knowledge, this peculiar ZnO nanostructure is not reported previously.

## 2. Experiments

First ZnO seed layers were prepared on glass substrates with dimensions of 20 mm × 15 mm by the sol–gel method. ZnO sol was prepared using zinc acetate, ethanol and monoethanolamine as the solute, solvent and stabilizer, respectively. The transparent sol was

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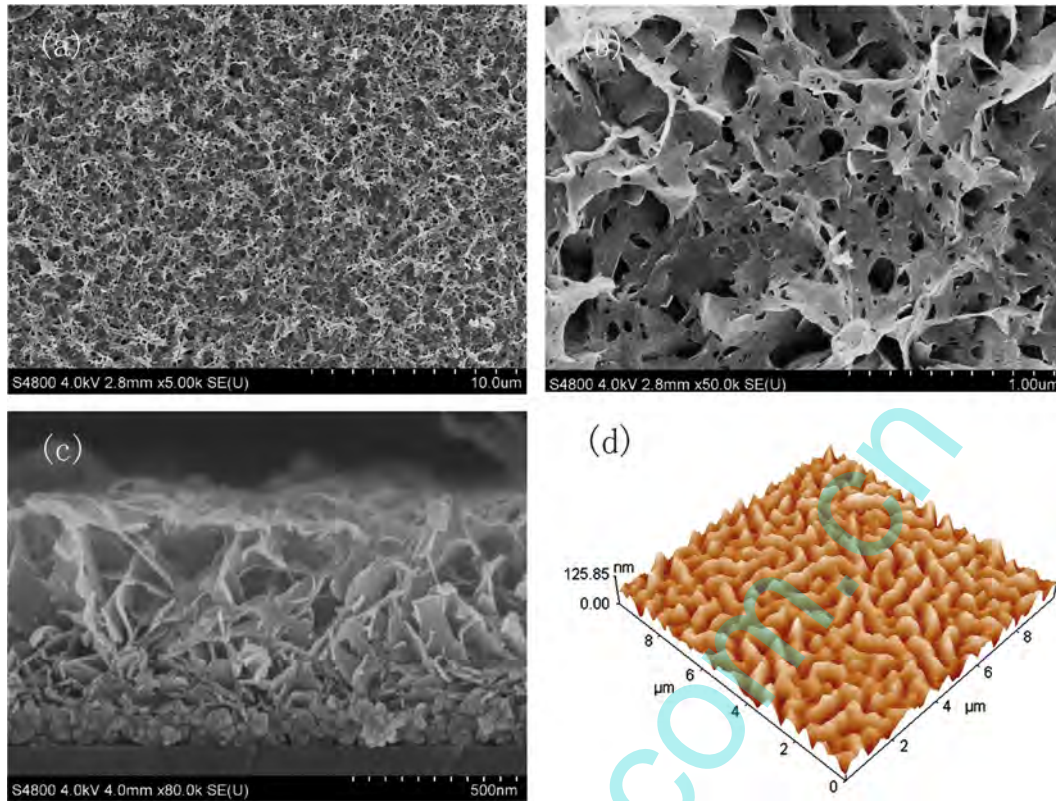


Fig. 1. Morphology images of the ZnO nanostructure (a), (b), (c) and ZnO seed layer (d).

aged at room temperature for 24 h and then ZnO seed layers were deposited by spin-coating this sol on glass substrates. The spin-coating process was repeated several times in order to make ZnO layers reach a desired thickness. At last, the ZnO seed layers were annealed at 450 °C in air for 40 min. Then, the glass substrate with ZnO seed layers was put into a 50 ml Teflon-lined stainless steel autoclave which contained a growth solution for the hydrothermal growth of leaf-like ZnO nanostructures. The growth solution was composed of  $\text{Zn}(\text{NO}_3)_2$  and hexamethylenetetramine (HMT) and the  $\text{Zn}^{2+}$  concentration in this solution is 0.02 mol/L. The growth temperature is 70 °C and the growth time is 3 h. In order to compare the photocatalytic activity of the leaf-like ZnO nanostructures with others, a ZnO thin film was also prepared by the sol-gel method under the same preparation conditions as mentioned above. In addition, ZnO nanorods were also obtained by the hydrothermal growth on a glass substrate with ZnO layers deposited by electron beam evaporation. For the growth of ZnO nanorods, the  $\text{Zn}^{2+}$  concentration in the growth solution is 0.05 mol/L; the growth temperature is 90 °C and the growth time is 3 h.

The crystal phase and crystalline orientation of the samples was analyzed by an X-ray diffractometer (Bruker D8). The surface morphology and cross-section morphology were observed by a scanning electron microscope (S4800). The surface morphology of the ZnO seed layer was measured by an atomic force microscope (CSPM4000). The photocatalytic activity of ZnO materials was studied using Rhodamine B as the degradation target. The concentration of the Rhodamine B was  $1 \times 10^{-5}$  mol/L. An Hg lamp of 175 W was utilized as the light source.

### 3. Results and discussion

Fig. 1(a) displays the low-resolution surface morphology image of the ZnO nanostructure from which we can see that the ZnO

nanostructure is very uniform in a large area but the real morphology cannot be clearly recognized. Fig. 1(b) and (c) exhibit high-resolution surface and cross-section morphology images of the ZnO nanostructure from which it can be clearly seen that the ZnO nanostructure presents a leaf-like morphology and these nanoleaves are not completely upright. The top of the ZnO nanostructure is bent and parallel to the substrate surface while the bottom and the central part are upright or aslant standing. These nanoleaves overlap each other. There are many irregular pores on the nanoleaves. Since the nanoleaves are not completely upright, their length cannot be accurately measured. From Fig. 1(c), it can be roughly estimated that the length of the nanoleaves is  $\sim 600$  nm and the thickness is about 5–10 nm. Also, it can be seen that the thickness is very uniform for all the nanoleaves. These nanoleaves are rooted in the ZnO seed layers, which makes the nanoleaves very firm on the substrates. This ZnO nanostructure with a peculiar three-dimensional morphology is not reported before.

As we know, the morphology features of ZnO nanostructures are very sensitive to the growth conditions. As for the hydrothermal method, the growth conditions like growth temperature, the nature of growth solution, the  $\text{Zn}^{2+}$  concentration in growth solution, growth time and the morphology of ZnO seed layers all have a great effect on the morphology and physical properties of ZnO nanostructures. For example, Wang et al. [6] found that the nature of the growth solution played a great role for controlling the morphology of ZnO nanostructures. Tian et al. [1] found that the  $\text{Zn}^{2+}$  concentration and growth time had a great influence on the morphology of ZnO nanostructures. Here, it is found that the leaf-like ZnO nanostructure can be obtained only under some specific conditions which have been mentioned in the experiment section. There are three main factors which are growth temperature, the  $\text{Zn}^{2+}$  concentration and surface morphology of the ZnO seed layer. The low growth temperature and low  $\text{Zn}^{2+}$

concentration can slow down the growth speed of ZnO and the induction of ZnO seed layer maybe plays a decisive role for forming leaf-like nanostructure. Fig. 1(d) shows the three-dimensional surface morphology of the ZnO seed layer measured by AFM. It presents many nanoridge and nanovalley-like structures; a nanovalley lies between two adjacent nanoridges. In fact, the similar surface morphology of ZnO thin films has been reported [5,12]. We think that the nanovalley should play an important role for forming the leaf-like nanostructure. It is well known that ZnO is apt to grow selectively. That is to say, ZnO will choose some “hot spots” on the patterned substrates or ZnO seed layers to nucleate and grow [13]. For our seed layers, the nanovalleys could be the “hot spots” for ZnO nucleation. With

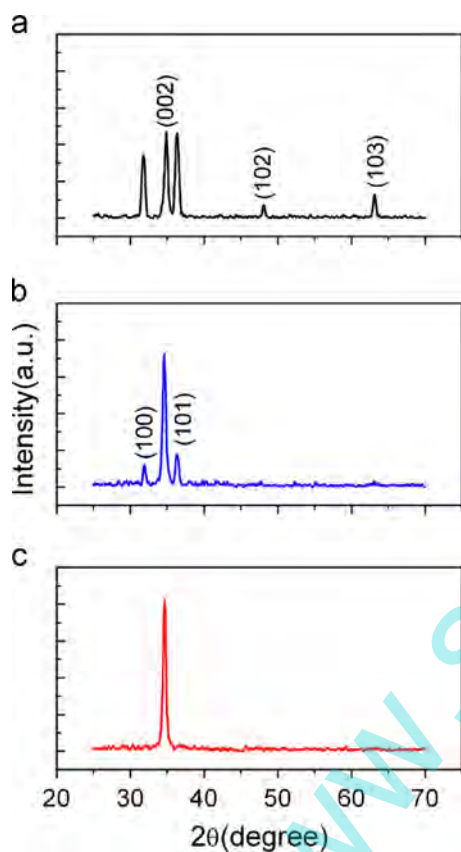


Fig. 2. XRD patterns of the leaf-like ZnO nanostructure (a), ZnO thin film (b) and ZnO nanorods (c).

the common role of low growth temperature and low  $\text{Zn}^{2+}$  concentration, leaf-like ZnO nanostructure is formed eventually.

Fig. 2 shows the XRD patterns of leaf-like ZnO nanostructure (a), ZnO thin film (b) and ZnO nanorods (c). All the diffraction peaks in the patterns belong to the wurtzite phase ZnO, indicating all the samples have a wurtzite structure. However, by comparing the patterns, it can be noticed that the leaf-like ZnO nanostructure has no preferred orientation while the ZnO thin film and ZnO nanorods are all preferentially oriented along the *c*-axis direction.

Fig. 3(a) gives the absorption spectra of Rhodamine B solution through different degradation time using the leaf-like ZnO nanostructure as a catalyst. Obviously, the Rhodamine B concentration in aqueous solution gradually decreases with the increase of degradation time. In fact, the Rhodamine B can be slightly decomposed under a UV irradiation, but the decomposition rate is very low. Fig. 3(b) gives the degradation rate of Rhodamine B under UV irradiation for 2 h without ZnO catalyst (A), with ZnO thin film (B), ZnO nanorods (C) and ZnO nanoleaves (D). The degradation rate is calculated by the following formula:

$$\eta = \frac{A_0 - A}{A_0} \times 100\%$$

where  $A_0$  is the initial absorbance of Rhodamine B solution after the absorption equilibrium without UV irradiation,  $A$  is the absorbance of Rhodamine B solution measured after photocatalytic degradation for 2 h. Clearly, the leaf-like ZnO nanostructure shows a higher degradation rate than ZnO thin film and ZnO nanorods. This can be mainly attributed to the following two reasons: (1) compared with ZnO thin films and ZnO nanorods, the leaf-like ZnO nanostructure has a larger specific surface area; (2) the thickness of the nanoleaves is very thin, so photogenerated electrons and holes are easier to transfer to the surface and react with the organic substance. In order to examine the renewable behavior of the photocatalytic activity of leaf-like ZnO nanostructure, we have performed the photocatalytic degradation of Rhodamine B under identical conditions for 8 times. After each test, the ZnO sample will be withdrawn from the Rhodamine B solution and rinsed by deionized water and then dried by an infrared lamp for 15 min. The results show that no distinct decrease of degradation rate for Rhodamine B is observed. This means the leaf-like ZnO nanostructure has a good recycling property for the photocatalytic application.

#### 4. Conclusion

In this work, the uniform leaf-like ZnO nanostructure was prepared by a simple route. This leaf-like ZnO nanostructure

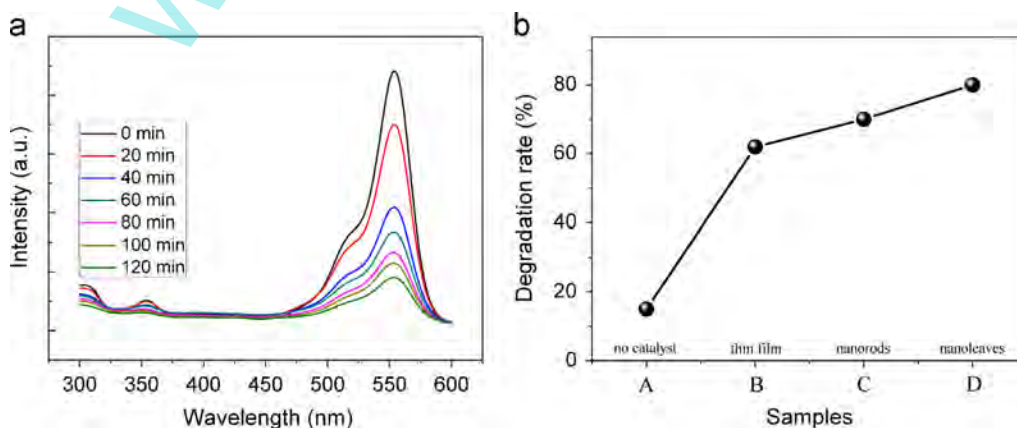


Fig. 3. Absorption spectra of Rhodamine B solution as a function of photocatalytic degradation time (a) and degradation rate of different ZnO materials (b).

shows a higher photocatalytic activity than ZnO thin films and ZnO nanorods, which could be used to clean the contaminated water in future. However, the growth of the leaf-like ZnO nanostructure is affected by many factors such as growth temperature,  $Zn^{2+}$  concentration and surface morphology of ZnO seed layers. Which factor plays the most important role for forming leaf-like ZnO nanostructure still needs more investigation. Furthermore, since the leaf-like ZnO nanostructure has a large surface area and exhibits a high photocatalytic activity, it should also possess a good gas-sensing property.

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