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以陶瓷球为载体的铁掺杂氧化锌纳米棒光催化降解甲醛气体

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摘要:采用简单的湿化学法在陶瓷球上制备了纯氧化锌和铁掺杂的氧化锌纳米棒。利用 X 射线衍射仪(XRD)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和紫外可见分光光度计(UV-Vis)对样品的结构、形貌和光学性能进行了表征和分析。研究了纯氧化锌及铁掺杂的氧化锌在紫外光照射下对甲醛气体的降解效率。结果表明与纯氧化锌相比,铁掺杂的催化剂表现出更优越的光催化活性。当 Fe 的掺杂量为 4%时,催化剂对甲醛的降解效率最高。催化剂具有良好的稳定性,可以重复利用,循环使用 10 次之后,催化效率仍可达到 85%。

关键词:氧化锌纳米棒;铁掺杂;甲醛;光催化
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Photocatalytic Degradation of Gaseous Formaldehyde by Fe-Doped ZnO Nanorods Grown on Ceramic Spheres

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Abstract: Zinc oxide (ZnO) and Fe doped ZnO nanorods were fabricated on ceramic balls by a simple low cost wet-chemical route. The as-prepared samples were characterized by XRD, SEM, TEM and UV-Vis spectroscopy. Photocatalytic activities of pure ZnO and Fe doped ZnO nanorods were investigated for degradation of formaldehyde gas under UV irradiation. The results show that doped catalyst exhibits superior photocatalytic performance than that of pure ZnO nanorods and 4% Fe doping catalyst displays the optimal photoactivity. The catalyst has good stability and is easy to be recoverd. The catalytic efficiency still maintains 85% after 10 cycls.

Key words: ZnO nanorods; Fe doping; formaldehyde; photocatalysis

Formaldehyde is one of major pollutants indoors which brings serious threat to human health and life[1-2]. Photocatalysis has been considered as a promising method to remove formaldehyde[3-4]. Although TiO_2 is the most commonly studied photocatalyst for the decontamination of formaldehyde[5-8], as a semiconductor material, zinc oxide (ZnO) may be an alternative because that its band gap energy (3.37 eV) is similar to that of TiO_2 (3.2 eV) and has relatively lower production cost[9]. Moreover, ZnO has been reported to be more photoactive than TiO_2 due to its higher efficiency of generation and separation of photoinduced electrons and holes[10-14].

ZnO nanorods have been attracting a great deal of research interest owing to their promising applications in photocatalysis, gas sensor etc[15-18]. ZnO nanorods arrays grown on the sphere substrate combine properties of 3D (three-dimensional) and 1D

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(one-dimensional) materials, which make it emerged as a more practical alternative than traditional ZnO powders and simple ZnO films due to the higher specific surface and recyclability.

To date, ZnO photocatalytic performance study has mainly concentrated on water pollutant system. But ZnO is unstable in basic or acid aqueous solution and so the application is limited. In this work, we adopted a low cost approach to fabricate ZnO nanorods array on the surface of ceramic balls for removal of gaseous formaldehyde. In order to further improve ZnO phototocatlytic activity, transition metal Fe ion was doped. The as-prepared samples could decompose formaldehyde effectively. To the best of our knowledge, the work has little been reported.

1 Experimental

1.1 Materials

Zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$), ferric nitrate hydrate ($Fe(NO_3)_3 \cdot 9H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$, HMTA) and formaldehyde solution (37wt%~40wt%) are analytic grade reagents and were used without further purification. Ceramic spheres used as substrate are about 1 mm in diameter.

1.2 Sample preparation

1.2.1 Preparation of ZnO nanorods on ceramic balls

High-density urchin-like ZnO nanorods film was grown on ceramic spheres by a low temperature wet chemical route similar to the reference report[19]. The preparation process was as follows. Firstly, the ceramic balls were cleaned by water and ethanol successively by ultrasonic method to remove impurities on the surface of balls. Secondly the seed layer was formed by immersing the ceramic spheres into an aqueous solution of 0.05 $mol \cdot L^{-1}$ $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA at room temperature for 2 min and then annealing at 350 ℃ for 30 min. Thirdly the ceramic balls covered with seed layer were immersed in an aqueous solution of 0.02 $mol \cdot L^{-1}$ $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA at 95 ℃ for 4 h. Finally the substrate of balls was washed with deionized water three times and dried at 60 ℃ for 12 h, subsequently the samples were calcined at 450 ℃ for 1 h in air and cooled to room temperature and ZnO nanorods grown on ceramic balls were obtained.

1.2.2 Preparation of Fe-doped ZnO nanorods on the surface of ceramic balls

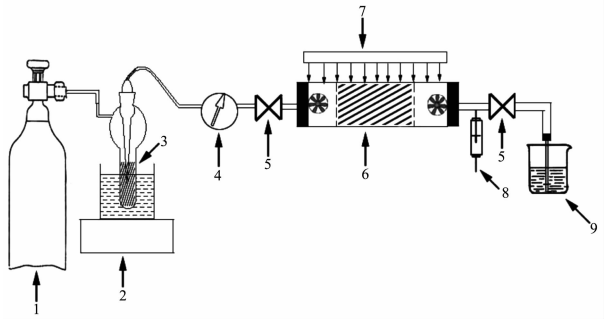
The procedure was the same as that of undoped catalysts described above except for the adding different amounts of $Fe(NO_3)_3 \cdot 9H_2O$ by controlling the molar ratio of Fe/Zn 3%, 4%, 5%, respectively in the second and the third steps.

1.3 Sample characterization

The as-prepared samples were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), X-ray diffraction (XRD, Rigaku DMAX-2500), transmission electron microscopy (TEM, JEOL JEM-2100) and ultraviolet-visible spectrophotometer (UV-Vis, TU-1901).

1.4 Photocatalytic degradation of gaseous formaldehyde

The photodegradation of gaseous formaldehyde experiment was carried out in a homemade gas-solid photocatalytic reactor. The test apparatus is shown in Fig.1, the reaction vessel is a quartz tube whose inner diameter was 34 mm and length was 39 cm. The ceramic balls being covered with ZnO nanorods were placed in the center of the tube and two 5 W electric fans were placed on both sides of tube. A 300 W UV light (365 nm) was put on the top of reactor as light source. In the reaction, the formaldehyde solution was heated to 80 ℃ and N_2 was acted as carrier gas. Firstly the formaldehyde gas was flowed through the test apparatus for 20 min to remove air. Secondly



1. N_2-carrier gas; 2. Heating units; 3. Formaldehyde solution (37%); 4. Gas flow meter; 5. Valve; 6. Reactor vessel; 7. UV lamp; 8. Sampler; 9. Exhaust gas treatment

Fig.1 Schematic diagram of photocatalytic reactor

when the formaldehyde concentration in the apparatus was constant, the reaction system valve was closed and the UV lamp was turned on. Thirdly, the gas after flowing through the catalysts was sampled using a gas-tight needle every 30 min. and the degradation experiment lasted for 3 hour. In the photocatalytic reaction, four comparative experiments were designed (a: light but no catalyst; b: catalyst but no light; c: light and ZnO catalyst; d: light and Fe-doped catalyst). The other experimental conditions were all the same. The concentration of formaldehyde gas in the reactor was measured by UV-Vis spectrometer by the acetylacetone method [20]. After the first round of the experiment, the ceramic balls loaded with ZnO nanorods were vacuum dried for 2 h and then were recycled for the next cycle of photodegradation of formaldehyde.

The degradation efficiency (D) was calculated according to the following equation.

$$D=\frac{C_0-C_t}{C_0}\times 100\%$$

C_0: The initial concentration of the formaldehyde before the light illumination

C_t: The concentration of the formaldehyde after light illuminating t

2 Results and discussion

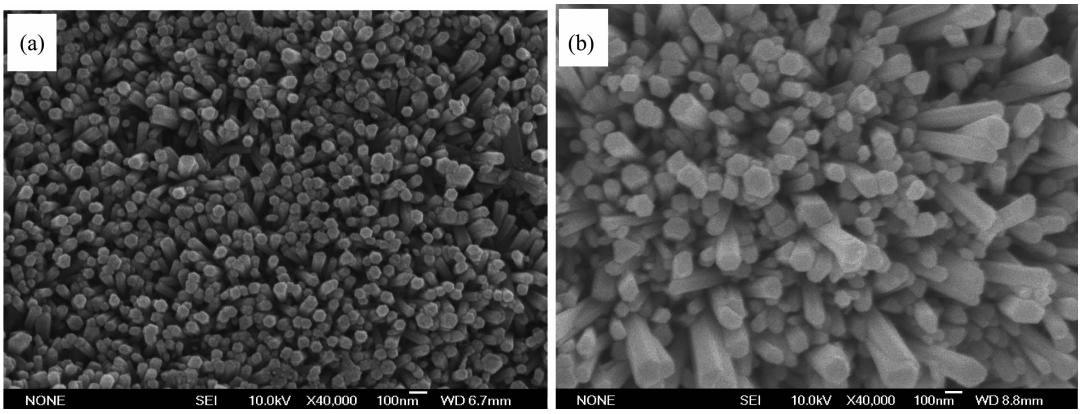
2.1 Characterization of ZnO nanorods array film on ceramic balls

The SEM images of pure and Fe-doped ZnO nanorods are shown in Fig.2. The diameter of undoped ZnO nanorods is about 70 nm with a hexagonal structure and most of the rods are vertically deposited on the substrate. Compared with pure ZnO, the average diameter of doped ZnO is larger than that of pure ZnO nanorods, the result is consistent with the reference report[9] and the reason is due to the difference of ZnO seed layer. The doped ZnO contains iron ion and has larger grain size[21].

Fig.3 shows the high-resolution TEM image of ZnO nanorods grown the ceramic balls. TEM results show that the ZnO nanorods are single crystalline with growth direction along [001]. The interplanar spacing is 0.52 nm, which matches well with the [001] planes of wurtzite ZnO, showing that the nanorods grow along the [001] direction.

Fig.4 shows the XRD patterns of ZnO nanorods on ceramic balls. XRD results show that the deposited ZnO nanorods are hexagonal wurtzite structure and the diffraction peaks are in agreement with PDF card 36-1451. Fe doped samples do not exhibit the obvious peak position difference with pure ZnO and the intensity of peak weakens. The result indicates that the Fe doping into the lattice of ZnO inhibits the crystallization of samples. From the Fig.4b, we also see that weak Fe_2O_3 diffraction peak appears at $2\theta=33.1°$, which suggests the doping Fe^{3+} partly transforms into Fe_2O_3 in ZnO nanorods.

The absorbance spectra of undoped and Fe doping ZnO nanorods are shown in Fig.5. A significant absorbance increase in the visible light region is observed for the Fe doped ZnO.



(a) Pure ZnO nanorods; (b) 4% Fe doped ZnO nanorods

Fig.2　SEM images of ZnO nanorods

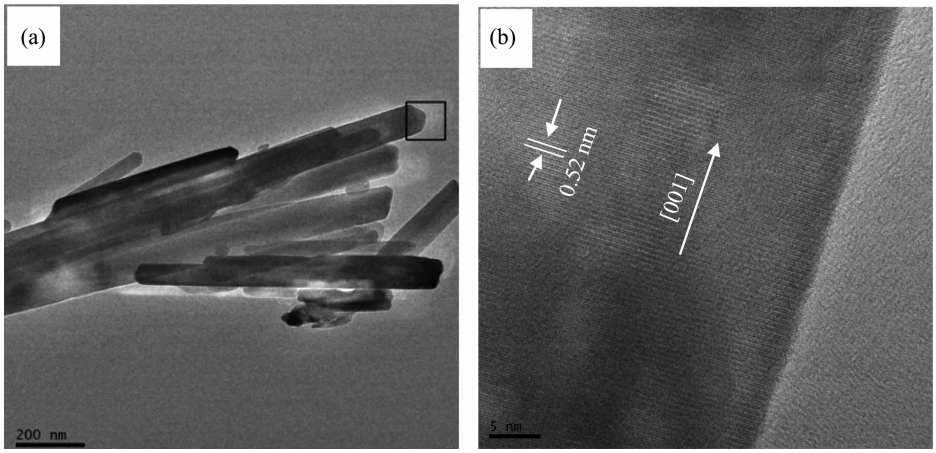
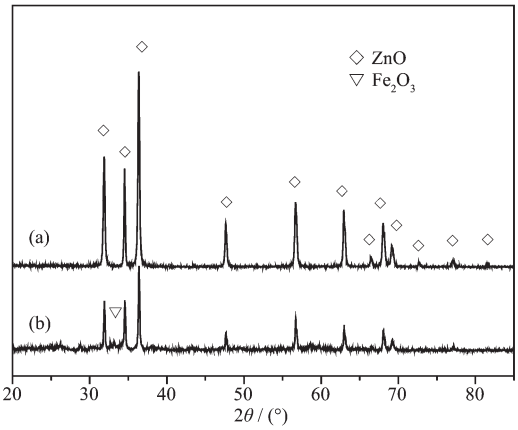
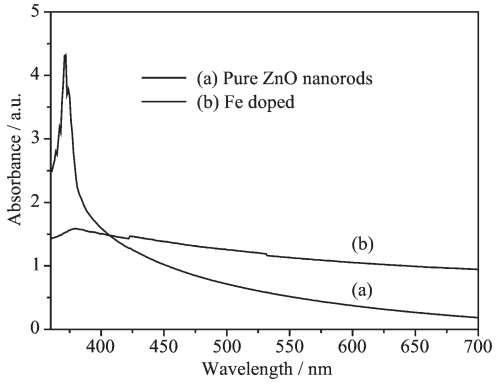


Fig.3 (a) TEM image of ZnO nanorods, (b) HRTEM image of ZnO nanorods



(a) Pure ZnO nanorods; (b) 4% Fe doped ZnO nanorods

Fig.4 XRD patterns of ZnO nanorods



(a) Pure ZnO nanorods; (b) 4% Fe doped ZnO nanorods

Fig.5 UV-Vis absorption spectra of ZnO nanorods

2.2 Photocatalytic property of ZnO nanorods

The photocatalytic results are shown in Fig.6. Formaldehyde could not be removed under the absent of a catalyst or with no light illumination. Under UV light irradiation, ZnO nanorods film could effectively decompose formaldehyde and the degradation efficiency increases gradually with illumination time. The photocatalytic property of Fe doped catalyst is better than pure ZnO nanorod and after 3 h formaldehyde is almost completely degraded. The higher photocatalytic activity observed in the Fe doped ZnO sample could be due to the existence of more oxygen vacancies, which act as electron capture center and so promote electron hole pair separation. Moreover iron ion could also capture photogeneration electrons and reduce the probability of recombination of electrons and holes, which is beneficial to improve ZnO photocatalytic efficiency. From the figure, it could also be seen that the photocatalytic property improves with increasing the Fe doping amount and the optimal doping concentration is 4%. When the content of Fe is higher than 4%, the photocatalytic efficiency is decreased. The possible reason is that when the Fe content is lower than the optimal ratio, it acts as electron capture center, and the greater the content of Fe ions,

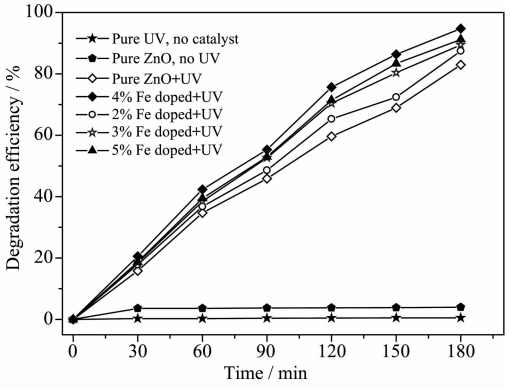


Fig.6 Degradation efficiency of formaldehyde under different reaction conditions

the higher the photogenerated carriers separation efficiency. But when the content of Fe is higher than its optimal ratio Fe would be carriers combination center thereby the photocatalytic activity decreases.

The ZnO nanorods catalysts deposited on the ceramic balls could be recycle after dry treatment. The recovery property of pure ZnO nanorods and Fe doped ZnO nanorods was evaluated. The experimental results are shown in Fig.7. From the figure, we could see that both samples′ photocatalytic activities reduce slowly with increase of recycle time and the recovery of the Fe doped ZnO nanorods is superior to pure ZnO nanorods. The degradation efficiency of pure ZnO nanorods is above 70% after ten cycles and Fe-doped ZnO nanorods exhibit superior performance with degradation efficiency of 85% after ten cycles.

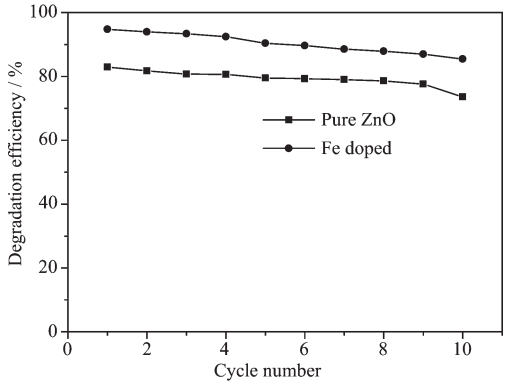


Fig.7　Effect of cycle times on the photocatalytic activity of samples

3　Conclusions

In summary, we have utilized a simple low temperature wet-chemical method to fabricate Fe doped and pure ZnO nanorod arrays on ceramic spheres. The as-prepared Fe doped ZnO nanorods achieve satisfactory formaldehyde removal efficiency and the photocatalytic performance is better than pure ZnO nanorods. The Fe optimal doping amount is 4mol% of ZnO. Furthermore the catalysts have good cycle stability remaining high photocatalytic activity after using 10 times.

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