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Visible-light-driven Photocatalytic Activity of Mesoporous $AgInO_2$ Synthesized by Sol-gel Combined Ion Exchange

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Abstract: Design and fabrication of highly active photocatalysts under visible light irradiation are one of hotspots in the field of photocatalysis. In this paper, mesoporous $AgInO_2$ nanostructures have been synthesized through a combined sol-gel and ion exchange process. Thermogravimetric analysis-differential scanning calorimeter (TGA-DSC), X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), N_2 adsorption-desorption and ultraviolet-visible (UV-vis) analysis technologies were used to investigate the effects of preparation condition on the microstructure of the $AgInO_2$. The photocatalytic performances have been evaluated by degradation of the formaldehyde under visible light irradiation. The results demonstrate that the mesoporous $AgInO_2$ is a delafossite structure with the uniform size about 200~500 nm and nitrogen adsorption-desorption type IV isotherms, the absorption edge of $AgInO_2$ lies between 500nm and 600 nm in the visible light scope. As-synthesized $AgInO_2$ exhibits remarkably high photocatalytic activity of 93.97% in decomposing formaldehyde for 180 min. These results provide a basic experimental process for preparation novel photocatalyst of $AgInO_2$, which will possess a broad prospect in terms of the applications in improving indoor air quality.

Key words: $AgInO_2$; mesoporous; visible-light-driven; photocatalysis; sol-gel

Since the discovery of TiO_2 photocatalysis[1], metal oxide semiconducting nanostructures have been widely investigated as a typical photocatalyst for environment treatment and chemical energy conversion, such as water splitting, CO_2 reduction, thin film solar cell and contaminant degradation[2,3]. However, broader applications of pure TiO_2 are still limited due to its wide band gap and rapid recombination of photogenerated electron-hole pairs. Therefore, the effective utilization of solar energy to improve efficiency has become one of the most important goals in the field of photocatalysis.

Recently, the development in advanced photocatalyst focuses on novel and narrow band gap (NBP) semiconductor. Among them, Ag-based compounds or composites as one of alternative visible-light-driven candidates have aroused much interesting due to their strong visible light responsibility, e.g. AgX(Cl,Br,I), $AgPO_4$, Ag_2CrO_4, and $AgVO_3$ [4-6]. On the other hand, increasing surface area is another important strategy in (photo-) catalysis to improve activity. To obtain high surface areas, preparation strategies have been developed for oxide materials leading to nanoparticles or mesoporous (pores between 2 and 50 nm) materials mainly via sol-gel synthesis routes. To gain mesoporous materials with ordered pore geometry, template strategies have been developed in the last two decades [7]. However, to the best of our knowledge, there are few reports on mesoporous $AgInO_2$ nanostructures.

Herein, we design and synthesize a novel mesoporous $AgInO_2$ photocatalyst using a combined sol-gel and ion exchange method with commercial P-123 block copolymer as a soft-template. The effect of experimental process on microstructure and photocatalytic performance of mesoporous $AgInO_2$ has been investigated.

1 Experiment

All reagents were of analytical grade and used without further purification or treatment. Mesoporous $AgInO_2$ was synthesized by a sol-gel combined ion exchange method. Firstly, the precursor $NaInO_2$ was prepared via a sol-gel method. In a typical procedure, 0.013 mol $In(NO_3)_3\ 9H_2O$, 0.013 mol $CH_3COONa\ 3H_2O$ and 0.5 g P123 surfactants were dissolved in 60 ml ethylene glycol ($C_2H_6O_2$), where P123 block-copolymer

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was used as a soft-template. The mixed solution was magnetically stirred for 5 h at 60~70 ℃ to form yellow sol. The gel was further treated at 100 ℃ for 12 h, after being sintered at 650 ℃ for 4 h to obtain mesoporous $NaInO_2$ precursor. Secondly, $AgInO_2$ was synthesized though the ion exchange reaction. The powders of $NaInO_2$, $AgNO_3$, and KNO_3 were mixed with molar ratios of 1:1:1 and ground for 20 min[8]. Then the mixtures were heated to ion exchange at 250 ℃ for 12 h. The products were washed repeatedly with distilled water to remove $NaNO_3$, KNO_3, and excess $AgNO_3$. Finally, the mesoporous $AgInO_2$ were obtained after the samples were dried at 80 ℃ for 5~8 h.

Structural features and phase composition of the samples were determined using Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation (λ=0.154 06 nm). Thermogravimetric analysis-differential scanning calorimeter (TGA-DSC) was employed on a Netzsch STA 409 PC/PG instrument from 50 ℃ to1000 ℃ with a heating rate of 5 ℃/min. The surface morphology of as-prepared samples were observed using a field emission scanning electron microscope (FESEM JEOL Model JSM-6360LV). The ultraviolet-visible (UV-vis) absorption spectra were acquired by UV-vis spectrometer (UV-2450, Shimadzu). The Brunauer-Emmett-teller (BET) specific surface area (S_{BET}) was determined by the AUTOSORB-IQ2-MP nitrogen adsorption apparatus (Quantachrome, USA).

The decomposition of formaldehyde was performed with visible light irradiation. In a typical process[9], 100 ml formaldehyde solution of concentration 10 mg/l was taken in the reactor along with 0.1 g catalyst, and the mixture was irradiated under a 300 W Xe arc lamp through a UV cutoff filter (380 nm<λ<750 nm). Before illumination the suspension was magnetically stirred in the dark for 30 min to reach an adsorption/desorption balance of formaldehyde on the catalyst surface. The formaldehyde concentration was measured with a UV-vis spectrophotometer, the maximum absorption peak of formaldehyde was at λ= 414 nm. The degrading rate D was calculated as follows:

$$D= (C_0-C_t)/C_0 \times 100\% \qquad (1)$$

where C_0 is the initial concentration of formaldehyde (mg/l) and C is formaldehyde concentration at special time point (mg/l).

2 Results and Discussion

2.1 Microstructure of the as-synthesized $AgInO_2$

The synthesis process involves two basic steps, the sol-gel method to prepare the precursor $NaInO_2$ and ion exchange reaction to prepare the mesoporous $AgInO_2$. To find the optimum temperature treatment for the template removal and the calcination of precursor $NaInO_2$, TGA-DSC analyses of the obtained gel were performed. As shown in Fig. 1, a small mass loss could be observed below 100 ℃ due to adsorbed water. Starting at around 100 ℃, a distinct mass loss of about 20% was observed up to 500 ℃. According to the recorded of DSC curves, there are two exothermic peaks are located at 142.3 and 214.6 ℃, which can be attributed to the decomposition of the ethylene glycol from the precursors inside the gel and the P-123 template. There is another distinct mass loss about 28% from 500 ℃ to 600 ℃ corresponding to DTA curves. Meanwhile, the exothermic peak at 541.4 ℃ is aroused from the formation of precursor $NaInO_2$.

Fig.2 shows the microstructures of the as-prepared precursor $NaInO_2$ and mesoporous $AgInO_2$. For the precursor $NaInO_2$, the typical XRD patterns reveal that all diffraction peaks can be well indexed to the JCPDS No.65-3663 standard data of $NaInO_2$. The precursor $NaInO_2$ shows irregular morphologies

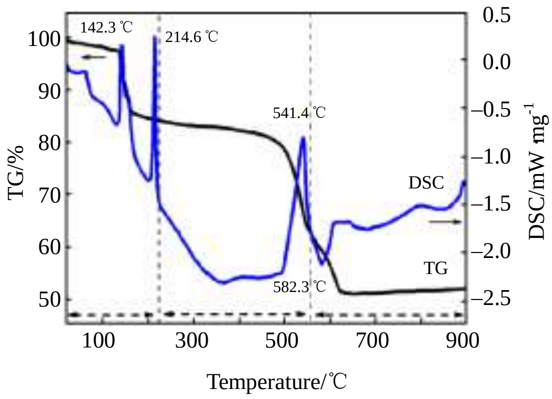

Fig.1 TDA-DSC curves from the gel to form the mesoporous $NaInO_2$ precursor

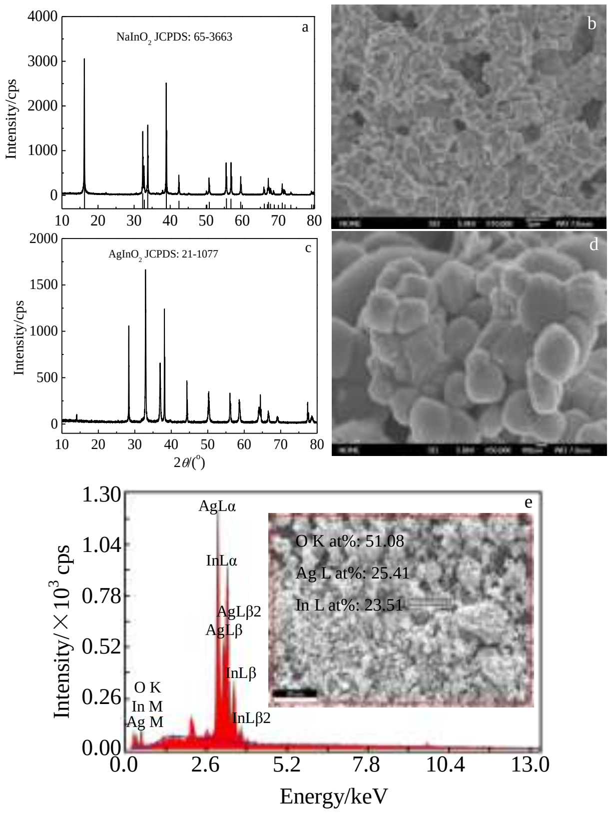

Fig.2 XRD patterns (a) and FESEM image (b) of the precursor $NaInO_2$; XRD patterns (c), FESEM image (d) and EDS spectra

(e) of the mesoporous $AgInO_2$

with an average particle size of 200~500 nm in addition to a certain degree of agglomeration in Fig.2b. The major diffraction peaks at 14.0°, 28.3°, 32.9°, 36.9°, 50.3°, 56.1°, 58.6°, 64.0° and 66.6° are also observed in Fig.2c, which correspond to the JCPDS No.21-1077 standard data of $AgInO_2$ with delafossite phase and no impurity phase is found, indicating the obtained samples with single phase of $AgInO_2$. The samples consist mainly of irregular agglomerated particles with a diameter about 100~200 nm (Fig.2d). Benefiting from the low-temperature only 250 ℃ in the process of ion exchange reaction, it is difficult for $NaInO_2$ to grow further or decompose; on the other hand, KNO_3 is used to promote the reaction. As a result, the morphologies and crystallite sizes from the precursor $LiInO_2$ to mesoporous $AgInO_2$ have no obvious change before and after ion exchange reaction. EDS spectra of the mesoporous $AgInO_2$ are shown in Fig.2e. The sample contains indium, silver and oxygen elements, and the percent of elements atom are 25.41%, 23.52% and 51.08% for Ag, In and O, respectively. These results are further confirmed that $AgInO_2$ has been synthesized by the sol-gel method combined ion exchange reaction.

Brunauer-Emmett-Teller (BET) gas adsorptometry measurements were conducted to examine the porous nature of the samples. Fig.3 reveals the nitrogen adsorption/desorption isotherms and pore size distribution curves of the prepared mesoporous $AgInO_2$. According to IUPAC classification [10], the similar nitrogen adsorption-desorption isotherms of samples can be classified as a type IV isotherm, and hysteresis loop is type H_2, which is the characteristic of a typical mesoporous material. The sharp decline in the desorption curve and the hysteresis loop at high relative pressure are indicative of mesoporosity. During the process of adsorption, single molecular layer adsorption occurred at relatively low pressure and multimolecular layer adsorption occurred at higher pressure [11-15]. The calculated BET specific surface area and pore volume are 34.87 m^2/g and 0.094 cm^3/g, respectively. From Fig.3b, it can be seen that the average pore sizes of mesostructure $AgInO_2$ is about 8.91 nm. However, the shape of the curve indicates the absence of a broad pore size distribution, suggesting that there is no ordering of mesopores, in contrast to the results known for mesoporous silica materials prepared with P-123. In the latter case, a much narrower pore size distribution can be achieved.

Fig.4 displays the UV-vis absorption spectrum of $AgInO_2$, together with that of the precursor $NaInO_2$ for a comparison. It can be observed that the absorption onset of $NaInO_2$ is ~400 nm, which shows that $NaInO_2$ is active mainly in UV light region, whereas $AgInO_2$ shows obvious absorption in visible light region up to 535 nm. The UV-vis absorption spectra show that absorption edge for mesoporous $AgInO_2$ has a red shift compared with $NaInO_2$, which shifts towards visible light region. It will probably make a good foundation for the investigation of mesoporous $AgInO_2$ applied in improving indoor air quality fields.

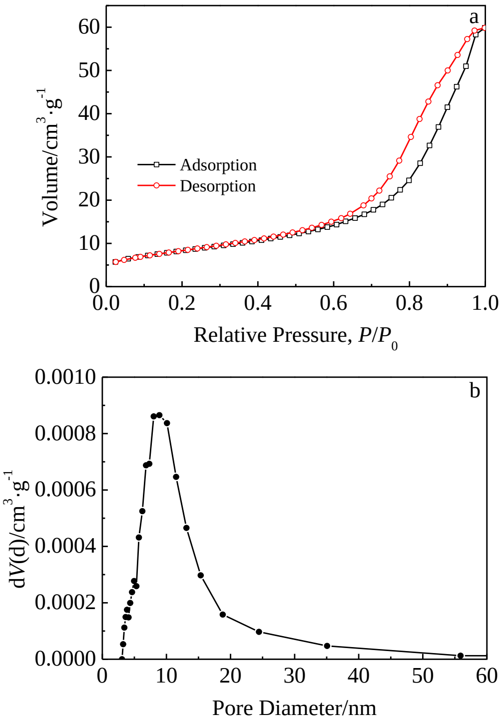

Fig.3 Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) curves of the prepared mesoporous $AgInO_2$

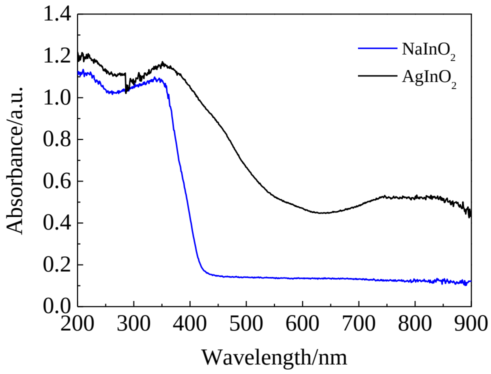

Fig.4 UV-vis absorption spectra of the precursor $NaInO_2$ and mesoporous $AgInO_2$

2.2 Photocatalytic performance of the as-prepared mesoporous $AgInO_2$

The photocatalytic activity of the as-prepared precursor $NaInO_2$ and mesoporous $AgInO_2$ was evaluated by the degradation of formaldehyde under visible light irradiations. The degradation rates of formaldehyde over different photocatalysts are discussed in Fig.5. Almost no change occurs in formaldehyde solution without catalyst under visible light, indicating direct photolysis of HCHO is negligible. When the $NaInO_2$ sample is employed as photocatalysts, about 36.44% formaldehyde molecules are decomposed within 180 min. It suggests that the obvious decrease of formaldehyde concentration in the presence of photocatalysts should be mainly attributed to the photocatalytic degradation under light irradiation. In the case of mesoporous $AgInO_2$ under the similar experimental conditions, the degradation rate is 93.97% and the photocatalytic activity is enhanced by 57.53% comparing to that of the $NaInO_2$ sample. This indicates that the photocatalytic activity of formaldehyde degradation is significantly enhanced for mesoporous $AgInO_2$ compared with that for the $NaInO_2$.

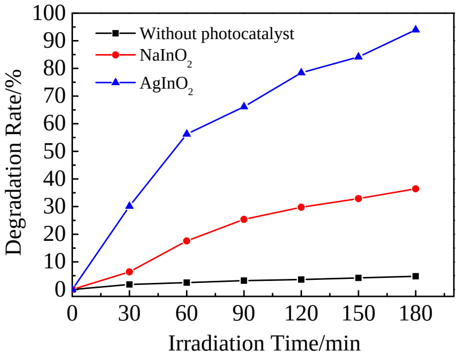

Fig.5 Photocatalytic activities for degradation formaldehyde of the precursor $NaInO_2$ and mesoporous $AgInO_2$

3 Conclusions

1) Mesoporous $AgInO_2$ nanostructures have been synthesized by a combined sol-gel and ion exchange method.

2) The as-synthesized $AgInO_2$ with a delafossite structure has uniform size about 200~500 nm and the isotherms are indentified as type IV, which shows obvious absorption in visible light region

3) The photocatalytic activity in decomposing formaldehyde reaches to 93.97% for 180 min under visible light irradiation, which is enhanced 57.53% compared with that of $NaInO_2$.

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溶胶凝胶-离子交换法制备具有可见光活性介孔 $AgInO_2$ 光催化剂

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摘　要：具有可见光响应高效光催化剂的设计和制备是环境与能源光催化研究领域的前沿和热点之一。本文采用溶胶凝胶-离子交换法制备 $AgInO_2$ 介孔纳米材料，利用热分析(TGA-DSC)、X 射线衍射(XRD)、场发射扫描电镜(FESEM)、N_2 吸附脱附以及紫外-可见吸收光谱等测试手段，研究了制备条件对 $AgInO_2$ 微观结构的影响因素，并以甲醛为目标降解物研究了 $AgInO_2$ 在可见光条件下光催化性能。结果表明：制备的介孔 $AgInO_2$ 具有铜铁矿结构的晶型，颗粒尺寸 200~500 nm，N_2 吸附脱附非等温曲线呈 IV 型，吸收边位于 500~600 nm 可见光范围内，在可见光照射 180 min 的条件下，介孔 $AgInO_2$ 对甲醛的光催化降解率达 93.97%。本研究为介孔 $AgInO_2$ 光催化剂在净化室内空气的广泛应用奠定了实验基础。

关键词：$AgInO_2$；光催化；介孔材料；可见光；溶胶-凝胶

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