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Article

Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ photocatalysts with enhanced activity under visible-light irradiation

Xiaopeng Han^a, Jianan Lü^a, Li Tian^a, Lingru Kong^a, Xuemei Lu^a, Yong Mei^a, Jiwei Wang^{a,b,#}, Xiaoxing Fan^{a,b,*}

^a School of Physics, Liaoning University, Shenyang 110036, Liaoning, China

^b Liaoning Key Laboratory of Semiconductor Light Emitting and Photocatalytic Materials, Liaoning University, Shenyang 110036, Liaoning, China

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ABSTRACT

Mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ photocatalysts were synthesized by the evaporation-induced self-assembly (EISA) method. Ag was deposited on the surface of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ by a facile photoreduction process. The as-prepared samples were characterized by TG-DSC, XRD, N_2 adsorption, HR-TEM and UV-Vis spectroscopy. The results revealed that mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ has a large specific surface area and uniform pore size distribution both before and after Ag deposition. The photodegradation of 2-propanol and acetaldehyde gas under visible-light ($\lambda > 420 \text{ nm}$) irradiation was employed to evaluate the photocatalytic activities of the samples. The results showed that the photocatalytic activity of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ is greatly improved by the Ag co-catalyst. These mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ exhibit photocatalytic activities as much as 41 times higher when compared with the $\text{Pb}_3\text{Nb}_2\text{O}_8$ prepared by the solid state reaction method. The content of loaded Ag ranged from 0.5% to 5% (Ag_2SO_4). The optimal loading was determined to be 1% corresponding the highest photocatalytic activity. These results clearly indicate that the activity of $\text{Pb}_3\text{Nb}_2\text{O}_8$ can be improved to obtain an outstanding performance for the photodegradation of organic pollutants.

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1. Introduction

Much attention has been paid to metal-oxide photocatalysts owing to their potential applications to the degradation of environmental pollutants using solar energy [1–3]. To date, research in photocatalysis has mostly focused on TiO_2 -based photocatalysts, which are only active in the UV range. In view of a better use of indoor light, it is therefore desirable to develop new highly active photocatalysts that can work efficiently under visible-light irradiation [4–6]. Although nonmetal-doped or dye-sensitized and transition metal-doped TiO_2 enable the use

of visible light [7–11], the design and development of undoped metal oxide photocatalysts working under visible light illumination are always the focus of attention for many researchers based on two facts: stable and efficient dyes are rare, and a dopant usually will act as a recombination center for the photogenerated electrons and holes [12–16].

Many multiple-metal oxides display promising functionality for a visible-light photocatalytic application. However, their activities are still low owing to their small specific surface area as a result of their preparation by a solid state reaction at high temperature. As is well known, a photocatalytic reaction is car-

* Corresponding author. Tel: +86-24-62202306; Fax: +86-24-62202309; E-mail: xxfan@lnu.edu.cn

Corresponding author. Tel: +86-24-62202306; Fax: +86-24-62202309; E-mail: jiweiwang6688@yahoo.com

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ried out on the surface of the photocatalyst. Hence, a larger specific surface area will enable more reaction sites, which will favor a high activity. Therefore, increasing the specific surface area of a photocatalyst is an efficient way to enhance its photocatalytic activity [17]. Since a mesoporous structure can provide a large surface area, many mesoporous materials have thus been used in the photocatalytic application for enhancing the activity [18,19]. For instance, owing to the large specific surface area, mesoporous TiO_2 possesses better photocatalytic properties than P25 in the gas and liquid phase reactions [20,21].

Up until now, silicon-based and single-metal oxide mesoporous materials have been obtained successfully by using a surfactant templating process, but an extension of the surfactant templating process to the formation of mesoporous multiple-metal oxides has been less studied, because their synthetic procedures are more complicated than those of conventional silicon-based and single-metal oxide mesoporous materials [22]. To date, the number of reported mesoporous multi-metal oxides is few, and of such, photoactive semiconductors are rare. Niobate is a popular photocatalyst which is mostly stable and has the ability to absorb visible light. Therefore, it would be of interest to construct the mesoporous structure of niobate to achieve a further improvement of the photocatalytic activity of semiconductors. Li et al. [23] reported a visible-light driven photocatalyst microcrystal $\text{Pb}_3\text{Nb}_2\text{O}_8$, which has activity in organic pollutant degradation. However, the photocatalytic activity is low because of the small specific surface area.

Herein, we report the synthetic procedure and photocatalytic activity of a mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ photocatalyst with a large specific surface area and crystalline pore walls. The specific surface area of the obtained sample was approximately 26.5 times larger than that of $\text{Pb}_3\text{Nb}_2\text{O}_8$ prepared by the conventional solid state reaction, and the photocatalytic activity of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was increased by 19.1 times. Moreover, Ag nanoparticles were used as a co-catalyst to further improve the photocatalytic activity of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$. The activity of Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was 2.17 times higher than that of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$. The content of Ag to mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was studied to determine the optimal loading conditions corresponding to the highest photocatalytic activity.

2. Experimental

2.1. Synthesis of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ and Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$

In a typical synthesis, PbO (0.03 mol) was dissolved in CH_3COOH (30 mL), and then a solution containing 0.04 mol $\text{Nb}(\text{OC}_2\text{H}_5)_5$ and EtOH (16 g) was added. F127 (8 g) was added to the solution with stirring until it was completely dissolved. The final solution was gelled at 40 °C in an oven for 1 d (static state). The as-prepared bulk sample was then calcined at 400, 500, and 600 °C for 90 min in air at a heating rate of 3 °C/min to form the mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ samples. The mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ samples were labeled as MPNO-400, MPNO-500, MPNO-600 for calcination at 400, 500 and 600 °C, respectively.

Determination of the optimal Ag-loading content was studied based on the photocatalytic performance of MPNO-500.

Ag-loaded MPNO-500 was obtained as follows. MPNO-500 (0.5 g) was added to a transparent solution formed by dissolving an appropriate amount of Ag_2SO_4 in a 200-mL beaker with distilled water (80 mL). The mass ratio of Ag_2SO_4 to MPNO-500 ranged from 0.5% to 5%. The obtained suspension was irradiated by a 300 W full arc xenon light with stirring. After 30 min irradiation, the suspension was centrifuged to remove the liquid phase, the obtained powder was then dried at 40 °C in an oven for 1 d and further heated at 300 °C for 30 min in a N_2 atmosphere. 1% Ag-loaded MPNO-400, MPNO-500 and MPNO-600 were obtained by the same process. The samples before annealing were labeled as MPNO-400/Ag, MPNO-500/Ag and MPNO-600/Ag, respectively, and after annealing, they were labeled as MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a, respectively. $\text{Pb}_3\text{Nb}_2\text{O}_8$ was also prepared by the solid state reaction method for comparison (labeled as PNO-SSR).

The solid-state reaction $\text{Pb}_3\text{Nb}_2\text{O}_8$ was synthesized as follows. Stoichiometric PbO and Nb_2O_5 were first mixed with ethanol and this combination was milled in an agate mortar for 30 min, after which time, the slurry was dried at 40 °C. The dried powders were then annealed at 600 °C for 6 h, cooled to room temperature and reground. The reground powders were finally sintered for 4 h at 850 °C.

2.2. Structure characterization

Thermogravimetric-differential scanning calorimetry analysis (TG-DSC) measurements were performed on a NETZSCH STA 409 PG/PC analyzer. The detected range of temperatures was from room temperature to 900 °C at a heating rate of 10 °C/min in a flow of air. Wide-angle X-ray powder diffraction (XRD) measurements were performed on a Rigaku Ultima III X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Nitrogen adsorption-desorption isotherms were collected on a Micromeritics Tristar-3000 surface area and porosity analyzer at -196 °C after the samples had been degassed in a flow of N_2 at 150 °C for 5 h. The BET surface area was calculated from the linear part of the BET plot ($p/p_0 = 0.1\text{--}0.25$). The pore size distribution plots were obtained by using the Barret-Joyner-Halenda (BJH) model. Images from a high-resolution transmission electron microscope (HRTEM) were obtained by employing a TECNAI F20 high-resolution transmission electron microscope with a 200 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) data were obtained on a PHI 5000 Versa Probe using 200 W monochromated $\text{Al K}\alpha$ radiation. Binding energies were calibrated using adventitious carbon ($\text{C } 1s = 284.6 \text{ eV}$). The UV-Vis diffuse reflectance spectra were measured on a UV-Vis spectrometer (UV-2550, Shimadzu). The photoluminescence spectra (PL) of the samples were obtained using a fluorescence spectrometer (Hitachi F-4500) at 20 °C.

2.3. Investigations of photocatalytic properties

The photocatalytic activities of the calcined samples for the oxidation of acetaldehyde in air were performed at room tem-

perature. In a typical process, the powder sample (0.2 g) was put on a 4-cm² glass groove. The glass with the powder photocatalyst was then placed into a clean 300-mL gas-tight cylindrical reactor with a quartz window. Then, 10 μ L of 2-propanol or acetaldehyde (40% CH₃CHO aqueous solution) was injected into the reactor to generate a high concentration of 2-propanol (or acetaldehyde) gas. Prior to light irradiation, the reactor was left in the dark for at least 3 h until the adsorption-desorption equilibrium was finally established. A 300 W Xe lamp equipped with a $\lambda > 420$ nm cutoff filter was used as the light source for the visible-light photocatalytic reaction. After 60 min irradiation, the evolved acetone or remanent acetaldehyde was detected by gas chromatography with an FID detector (GC1690, JieDao Tech).

3. Results and discussion

3.1. TG-DSC analysis

The TG-DSC analysis was undertaken from 30 to 900 °C in air. As shown in Fig. 1, below 200 °C, the mass loss was a result of the volatile species (including water, CH₃COOH and ethanol). Between 200 and 350 °C, a rapid mass loss arose from the oxidation of the F127 template. As a result, a substantial exothermic peak was observed because the organic matter reacted with oxygen to generate heat. At temperatures from 350 to 420 °C, a slow mass loss occurred, possibly caused by the decomposition of Pb(CH₃COO)₂ along with removal of some residual organic matter, such as amorphous carbon or carboxylate species, and possibly also hydroxyl groups. At the same temperature, the Pb compound reacted with the Nb compound for the formation of crystalline Pb₃Nb₂O₈ in an exothermic reaction.

3.2. Phases and morphology

Fig. 2 displays the XRD patterns of the obtained mesoporous samples. MPNO-400 and MPNO-500 showed wide diffraction peaks, indicating that the samples were crystallized but with low crystallinity. The peaks of the crystalline samples can be indexed as Pb₃Nb₂O₈ (JPCDS, No. 30-0712). When increasing the calcination temperature to 600 °C, the width of these peaks

Fig. 1. TG-DSC curves of the as-synthesized mesoporous Pb₃Nb₂O₈ gel.

Fig. 2. XRD patterns of mesoporous Pb₃Nb₂O₈ calcined at different temperatures.

became narrow, indicating the high crystallization of the sample. The peaks of the crystalline sample correspond well to Pb_{2.31}Nb₂O_{7.31} (JPCDS, No. 72-1494). The phase change may arise from the evaporation of Pb and/or the occurrence of phase separation. The crystal sizes were 8.2, 10.0 and 16 nm for MPNO-400, MPNO-500 and MPNO-600, respectively. No Ag component diffraction peaks appeared from the XRD patterns of the Ag-loaded samples both before and after annealing treatment, meaning that the Ag may disperse uniformly and not form large Ag particles. The crystal sizes were 8.3, 10.1 and 24.9 nm for MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a, respectively. The increase in crystal size arose from the additional annealing during the process of Ag loading. PNO-SSR prepared by the solid-state reaction method showed a pure phase with high crystallinity.

Fig. 3 shows the N₂ adsorption-desorption isotherms and the pore size distributions of mesoporous samples. All the isotherms present stepwise adsorption and desorption and are type IV with a clear characteristic hysteresis loop of the mesoporous materials. As listed in Table 1, the BET specific surface areas were 69, 47, 19, 56, 41 and 19 m²/g for MPNO-400, MPNO-500, MPNO-600, MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a, respectively. These values are significantly higher than that of the reference sample of PNO-SSR prepared by a high-temperature ceramic method (2.6 m²/g). The BET specific surface area decrease with the increase in the calcination temperature is caused by the grain growth. High temperature leads to the large grain growth, which can be observed from the XRD data. The crystallization as well as the grain growth leads to the collapse of the pore wall and decrease in porosity. In addition, it can be found that the sample with small specific surface area exhibits a larger pore diameter and a wider pore size distribution. This phenomenon was caused by two small size pores merging into a large size pore during the mesoporous structure collapse. After Ag loading treatment with

Fig. 3. N₂ absorption-desorption isotherms of the samples. The insets are the corresponding BJH pore size distribution.

300 °C annealing, the hysteresis loop of MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a still existed, indicating the mesoporous structures were preserved. MPNO-400/Ag-a and MPNO-500/Ag-a showed narrow pore size distributions, which were the same as those of MPNO-400 and MPNO-500, respectively. This implies that the pores were open and no excessive Ag particles agglomerated in the pores to change the pore size distribution. MPNO-600/Ag-a shows that the random pore size distribution may be caused by the small surface area of MPNO-600 that cannot provide enough surface for the Ag particles, leading to the agglomeration of Ag particles at the

surface or in the pores and disorder in the uniform mesoporous structure. The atomic ratios of all elements are listed in Table 1, according to the XPS data. The ratio of Pb/Nb for all samples was close to 1.5, which is consistent with the ratio of Pb/Nb in the precursor. A large ratio of Ag/Nb can be detected, indicating the Ag particle mainly locates on the surface of the mesoporous structure.

To directly confirm the existence of the mesostructure, transmission electron microscopy (TEM) was performed. In the TEM images (Fig. 4), a wormhole-like mesostructure without long-range order was observed in MPNO-400 and MPNO-500.

Table 1

The BET specific surface area, pore volume and atomic ratio for the samples.

Sample	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Atomic ratio from XPS (Pb:Nb:O:Ag)
PNO-SSR	2.6	—	1.55:1:6.81:—
MPNO-400	69	0.1749	1.52:1:7.68:—
MPNO-500	47	0.2041	1.57:1:7.27:—
MPNO-600	19	0.1681	1.58:1:7.44:—
MPNO-400/Ag-a	56	0.236	1.56:1:7.37:0.24
MPNO-500/Ag-a	41	0.184	1.58:1:7.16:0.25
MPNO-600/Ag-a	19	0.125	1.55:1:7.75:0.13

Fig. 4. TEM and HRTEM images of mesoporous MPNO-400 (a, b), MPNO-500 (c, d) and MPNO-500/Ag-a (e, f).

In contrast with MPNO-500, MPNO-400 showed a higher porosity wall. This phenomenon arose from the growth of grains, which led to the increase in the thickness of the pore wall as well as low porosity. From the high resolution TEM images, $\text{Pb}_3\text{Nb}_2\text{O}_8$ nanocrystals were clearly observed, which connected with each other to form the crystalline framework walls of the mesopore. The lattice plane spacing of MPNO-400 and MPNO-500 was 0.295 and 0.307 nm, respectively. Both can be indexed to the (202) diffraction plane of crystalline $\text{Pb}_3\text{Nb}_2\text{O}_8$ ($d_{202} = 0.29$). Fig. 4(e) and (f) shows the TEM and HRTEM photographs of Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$. It can be seen that the mesoporous structure was preserved well after Ag loading. From the high resolution image, the lattice plane spacing ($d = 0.235 \text{ nm}$) should be indexed to the (111) diffraction

Fig. 5. Ag 3d spectra of MPNO-500/Ag-a.

plane of metal Ag. The average size of Ag particles was less than 10 nm, and no large Ag particles were formed. To further confirm the valence state of Ag, high resolution XPS spectra of Ag 3d were obtained and are displayed in Fig. 5. Two individual peaks located at 367.9 and 373.4 eV, which could be assigned to $\text{Ag } 3d_{5/2}$ and $\text{Ag } 3d_{3/2}$, suggest the presence of metal Ag. Based on the XPS and the HRTEM results demonstrated above, we can conclude that the loaded Ag should be metal Ag.

3.3. Optical properties

Fig. 6 shows the UV-Vis absorption spectra of the obtained samples. All the samples exhibited an obvious absorption in the visible-light range ($\lambda > 400 \text{ nm}$). The absorption edges of MPNO-600, MPNO-500 and MPNO-400 were tailed from approximately 530 to 550 nm. However, the absorption edge of PNO-SSR tailed to 600 nm. Compared with $\text{Pb}_3\text{Nb}_2\text{O}_8$ synthesized by a solid-state reaction, the mesoporous samples exhibited an obvious blue shift owing to the quantum confinement effect. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. The quantum confinement effect makes the energy levels discrete and ultimately the band gap energy increases, which leads to a blue shift of absorption edge [24–26]. The pore walls of the mesoporous structure are usually constructed by nanocrystals, because the larger sized crystals will lead to the collapse of the mesoporous structure and decrease in the specific surface area. Therefore, owing to the small grain size, the absorption edge of the mesoporous materials exhibited a blue shift compared with that of the sample prepared by the solid state reaction. As for a comparison of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ annealed at different temperatures, their different crystallinity and amorphous matter effects on the band gap should be considered. Usually, the amorphous effect leads to band tails extending to the gap, which may exceed the quantum confinement effect and decrease the band gap. Therefore, even with the nano-size of MPNO-500, MPNO-400 is smaller than that of MPNO-600, so the quantum confinement effect is precluded owing to their low crystallinity. The conduction band should be composed of the empty Nb 4d orbitals and the valence band should be composed of hybridized O 2p and Pb 6s orbitals. The level of the valence band in-

Fig. 6. UV-Vis absorption spectra (a), the transformed Kubelka-Munk function versus the energy of light absorbed (b) of PNO-SSR, MPNO-400, MPNO-500 and MPNO-600 and UV-Vis absorption spectra (c) of MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a.

creases slightly with an increasing content of PbO in these compounds [23]. After calcination at 600 °C, part of the $\text{Pb}_3\text{Nb}_2\text{O}_8$ transferred to $\text{Pb}_{2.31}\text{Nb}_{2.07}\text{O}_{7.31}$, which may arise from the evaporation of Pb elements at the high calcination temperature. The band gap energy (E_g) can be estimated from the intercept of the tangents to the plots of $(\alpha h\nu)^{1/2}$ versus photon energy, as shown in Fig. 6(b). The band gaps optically obtained were approximately 2.83, 2.95, 3.00 and 3.22 eV for the samples of PNO-SSR, MPNO-500, MPNO-400 and MPNO-600, respectively. Fig. 6(c) show the UV-Vis absorption spectra of the Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$. It can be clearly seen that the Ag-loaded samples show an obvious absorption band between 450 and 700 nm, which could be attributed to the surface plasmon absorption of the Ag nanoparticles.

3.4. Photocatalytic activities

The photocatalytic activities of the obtained mesoporous photocatalysts were evaluated by 2-propanol photodegradation in the gas phase under visible-light irradiation ($\lambda > 420$ nm). 2-Propanol photodegradation was first photo-oxidatively dehydrogenated to acetone and eventually photo-oxidized to CO_2 [1,23]. The self-oxidation of 2-propanol was negligible.

Fig. 7. Photocatalytic production of acetone from 2-propanol over different Ag content loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ samples.

2-Propanol photodegradation can serve as a good reaction model to evaluate the photocatalytic activities of semiconductors. Fig. 7 shows the evolution rate of acetone on MPNO-500 samples with different Ag-loaded content under visible-light irradiation ($\lambda > 420$ nm). The photocatalytic activity was 54.6, 67.5, 65.6, 58.8, and 56.8 ppm/min on MPNO-500 loaded with 0.5%, 1%, 2%, 3%, 4% and 5% Ag (count by Ag_2SO_4), respectively. It can be seen that a 1% Ag-loaded content is the optimal loading condition, which corresponds to the highest photocatalytic activity. The different activities can be explained by the improvement of the charge separation, which is highly dependent on the Ag-loaded content. When the Ag content was lower than 1%, the photocatalytic activity of mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was enhanced with an increase of the Ag content. However, when above 1%, the photocatalytic activity decreased with the increase of Ag content because more Ag deposits conversely behaved as recombinant centers, encouraging the recombination of charge carriers.

At the same 1% Ag content, the effect of the calcination temperature on the photocatalytic activity was studied. Fig. 8 shows that the Ag co-catalyst can enhance the photocatalytic activity. During a 1 h reaction, the evolution rate of acetone on

Fig. 8. Photocatalytic production of acetone from 2-propanol over PNO-SSR (a), MPNO-400/Ag-a (b), MPNO-400 (c), MPNO-500/Ag-a (d), MPNO-500/Ag (e), MPNO-500 (f), MPNO-600/Ag-a (g) and MPNO-600 (h). The Ag content was 1%.

MPNO-400, MPNO-500, MPNO-600 and PNO-SSR was 55.5, 28.2, 9.3, 2.9 ppm/min, respectively. The activity of MPNO-400 was 19.1 times higher than that of PNO-SSR. The enhancement of the photocatalytic activity can be attributed to the large specific surface area which provides more active sites for the catalysis reaction. Increasing the calcination temperature results in the decrease in activity. This decrease can be ascribed to the small specific surface area caused by the high calcined temperature providing less activity sites than a larger specific surface area. It should be noted that crystallinity is also an important factor for determining the photocatalytic activities of mesoporous materials, because a high calcination temperature can reduce the amorphous phase existing among grains. These amorphous materials usually lead to defect states in the band gap, and act as recombination centers of photogenerated e^- and h^+ [27]. High crystallinity is beneficial for the transport of e^- and h^+ to the surface, and will improve the photocatalytic activity. In our research, it can be found that the MPNO-600 sample, possessing a large specific surface area, showed a higher activity, which implies that the specific surface area plays an important role.

The activities of MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a were 120.7, 67.5 and 14.2 ppm/min, respectively. The photocatalytic activity was greatly improved, compared with mesoporous $Pb_3Nb_2O_8$ without loaded Ag, where the photocatalytic activity of MPNO-400/Ag-a was approximately 2.17 times higher than that of MPNO-400 and approximately 41.6 times higher than that of PNO-SSR. As is well known, the photocatalytic behavior is closely related to the efficiency of the photogenerated electron-hole separation and the diffusion from the inner regions to the surface of the grains. While the Ag-loaded mesoporous $Pb_3Nb_2O_8$ photocatalyst is being irradiated, CB-electrons of $Pb_3Nb_2O_8$ easily flow into the metal Ag through the Schottky barrier because the CB of $Pb_3Nb_2O_8$ is higher than that of the loaded metal Ag, which is consistent with the previous study on metal-loaded semiconductor photocatalysts [28–30]. The process of electron transfer is faster than the electron-hole recombination between the VB and CB of $Pb_3Nb_2O_8$, thus, plenty of CB electrons can be stored in the Ag component. Furthermore, the annealing treatment

Fig. 9. The room temperature photoluminescence (PL) spectra of MPNO-400 and MPNO-400/Ag-a ($\lambda_{\text{excitation}} = 310 \text{ nm}$).

Fig. 10. Photocatalytic degradation of acetaldehyde over 1% Ag-loaded mesoporous $Pb_3Nb_2O_8$. (a) MPNO-400/Ag-a; (b) MPNO-500/Ag-a; (c) MPNO-600/Ag-a.

was also studied. Through a comparison of MPNO-500/Ag with MPNO-500/Ag-a, it can be shown that the annealing treatment can improve the photocatalytic activity. The increase mainly arises from the connection between the semiconductor photocatalyst and Ag co-catalyst being stronger than that before annealing, thus benefiting the charge transfer. Moreover, the PL spectrum was employed to analyze the effects of Ag as a co-catalyst on the photocatalytic performance. Fig. 9 shows that the PL emission spectra of the MPNO-400 and MPNO-400/Ag-a photocatalysts exhibited the main peaks at similar positions but with different intensities. The PL intensity of MPNO-400/Ag-a was lower than that of MPNO-400, which clearly indicates that the Ag co-catalyst decreased the recombination of photo-generated charge carriers, thus decreasing the fluorescence.

The photocatalytic degradation of acetaldehyde was carried out to prove that the Ag-loaded mesoporous $Pb_3Nb_2O_8$ is a general photocatalyst and is useful for use in the degradation of other kinds of gas pollutants. Fig. 10 shows that Ag-loaded mesoporous $Pb_3Nb_2O_8$ exhibits high activities under visible illumination. The photocatalytic activity of MPNO-400/Ag-a, MPNO-500/Ag-a and MPNO-600/Ag-a could reach 80.4%, 47.8% and 32.4%, respectively, after illumination for 1 h under visible light. The best activity was achieved on MPNO-400/Ag-a, with stepwise decreases for MPNO-500/Ag-a and MPNO-600/Ag-a, which is consistent with the results of the photocatalytic degradation of 2-propanol.

To examine the stability of the sample, the recyclability of the as-prepared catalyst was investigated in a four-run recycling test of catalytic 2-propanol degradation. The test was carried out over MPNO-400/Ag-a, which exhibited the best photocatalytic performance. Fig. 11 shows that no obvious decrease in the photocatalytic activity was observed after the four-run recycling test. This indicates that the Ag-loaded mesoporous $Pb_3Nb_2O_8$ photocatalysts have excellent photocatalytic stability.

4. Conclusions

We successfully synthesized mesoporous $Pb_3Nb_2O_8$ photo-

Fig. 11. Four-run recycling test of MPNO-400/Ag-a.

catalysts driven by visible light using the EISA method. Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was obtained by a photoreduction process. When the photocatalytic degradation of 2-propanol under visible-light irradiation ($\lambda > 420 \text{ nm}$) was compared with the bulk sample obtained by a solid state reaction, the mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ and Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ samples exhibited a 19.1 times and 41 times higher activity, respectively. The enhanced performance was mainly ascribed to both the high specific surface area, which contains more active sites for the reaction, and the Ag co-catalyst, for improving the separation of the photogenerated electrons and holes. The optimal Ag-loaded content for mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ was 1% to achieve the highest photocatalytic activity in our research. Based on this research, it is believed that $\text{Pb}_3\text{Nb}_2\text{O}_8$ is a promising material that possesses good potential for use in photocatalytic fields if some techniques, such as increasing the surface area and loading co-catalyst, are used to improve its photocatalytic activity.

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Graphical Abstract

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Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ photocatalysts with enhanced activity under visible-light irradiation

Xiaopeng Han, Jianan Lü, Li Tian, Lingru Kong, Xuemei Lu, Yong Mei, Jiwei Wang*, Xiaoxing Fan*
Liaoning University

Ag-loaded mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ photocatalysts are synthesized by Ag photodeposition on the as-obtained mesoporous $\text{Pb}_3\text{Nb}_2\text{O}_8$ by the evaporation-induced self-assembly (EISA) method. The photocatalysts show outstanding performance in the photodegradation of organic pollutants compared with $\text{Pb}_3\text{Nb}_2\text{O}_8$

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Ag担载介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 光催化剂的制备及其增强的可见光催化活性表征

韩晓鹏^a, 吕佳男^a, 田莉^a, 孔令茹^a, 卢雪梅^a, 梅勇^a, 王绩伟^{a,b,#}, 范晓星^{a,b,*}

^a辽宁大学物理学院, 辽宁沈阳110036

^b辽宁大学辽宁省半导体发光与光催化材料重点实验室, 辽宁沈阳110036

摘要: 光催化技术在环境净化方面, 尤其是降解有机污染物应用上表现出潜在价值。可见光响应型光催化剂具有优异的光吸收特性和高的光催化活性, 因而备受人们关注并被大量研究。 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 光催化剂由于其自身的稳定性以及对可见光响应的能力是一种潜在的高效光催化材料。但是, 有报道表明 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 光催化剂对可见光降解有机物活性较低, 这主要归因于它较小的比表面积以及较高的电子-空穴复合率。为了解决这个问题, 本文采用蒸发自组装技术制备了大比表面积的介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$, 采用光沉积方式在介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 上负载了均匀分散的纳米Ag颗粒, 并对不同焙烧温度、载Ag量以及进一步的热处理对光催化活性的影响作了深入研究。

XRD结果表明, 在400 °C和500 °C焙烧条件下获得的样品属于 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 相, 600 °C焙烧使得介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 发生相变。氮气吸附-脱附表征表明, 升高焙烧温度使样品比表面积从最大69 m²/g (400 °C)减小到19 m²/g (600 °C)。透射电子显微镜分析结果表明, 所获得样品具有蠕虫状介孔孔道结构, 并且Ag纳米颗粒均匀分散在介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 表面。紫外-可见吸收光谱表明, 介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 的吸收边拖尾到530–550 nm, 担载Ag之后光吸收发生显著变化, 光吸收拓展到700 nm。

光催化活性测试采用可见光催化氧化脱氢异丙醇气体至丙酮反应。结果表明, 在420 nm以上可见光照射下, 1 h内的光催化反应过程中, 采用高温固态反应制备的 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 上丙酮生成速率为2.9 ppm/min, 而介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 催化剂上最高可达55.5 ppm/min。介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 负载Ag之后, 400 °C焙烧的介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 光催化活性显著提高, 降解速率达120.7 ppm/min。

通过介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 和固相合成 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 的光催化活性对比发现, 大比表面积样品的光催化活性显著提高。这可归结为大的比表面积提供了大量的催化反应活性位点, 从而提高了光催化反应活性, 此外介孔材料的孔壁结构为纳米结构, 有利于光生电子-空穴传输到表面参加反应。担载Ag后介孔 $\text{Pb}_3\text{Nb}_2\text{O}_8$ 的光催化活性进一步提高, 主要是因为助催化剂Ag纳米颗粒促进了光生电子-空穴分离, 延长了载流子寿命, 从而提高了光催化活性。

关键词: 介孔; $\text{Pb}_3\text{Nb}_2\text{O}_8$; 光催化; 银担载; 气相降解

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*通讯联系人. 电话: (024)62202306; 传真: (024)62202309; 电子信箱: xxfan@lnu.edu.cn

#通讯联系人. 电话: (024)62202306; 传真: (024)62202309; 电子信箱: jiweiwang6688@yahoo.com

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