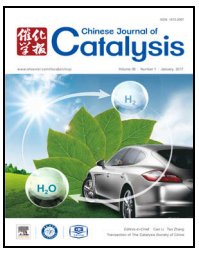
Chinese Journal of Catalysis 38 (2017) 83–91

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc



Article

# Ag-loaded mesoporous $Pb_3Nb_2O_8$ 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*

ARTICLE INFO

*Article history:*
Received 29 August 2016
Accepted 15 October 2016
Published 5 January 2017

*Keywords:*
Mesopore
$Pb_3Nb_2O_8$
Photocatalysis
Ag loading
Gas-phase degradation

ABSTRACT

Mesoporous $Pb_3Nb_2O_8$ photocatalysts were synthesized by the evaporation-induced self-assembly (EISA) method. Ag was deposited on the surface of mesoporous $Pb_3Nb_2O_8$ 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 $Pb_3Nb_2O_8$ 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 nm) irradiation was employed to evaluate the photocatalytic activities of the samples. The results showed that the photocatalytic activity of mesoporous $Pb_3Nb_2O_8$ is greatly improved by the Ag co-catalyst. These mesoporous $Pb_3Nb_2O_8$ exhibit photocatalytic activities as much as 41 times higher when compared with the $Pb_3Nb_2O_8$ 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 $Pb_3Nb_2O_8$ can be improved to obtain an outstanding performance for the photodegradation of organic pollutants.



## 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
This work was supported by the National Natural Science Foundation of China (11274150, 11574124), the Education Minister of Liaoning Province (JG2016ZD0015), and the Open Research Fund of Jiangsu Provincial Key Laboratory for Nanotechnology Nanjing University.
DOI: 10.1016/S1872-2067(16)62575-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 1, January 2017

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 $Pb_3Nb_2O_8$, 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 $Pb_3Nb_2O_8$ 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 $Pb_3Nb_2O_8$ prepared by the conventional solid state reaction, and the photocatalytic activity of mesoporous $Pb_3Nb_2O_8$ was increased by 19.1 times. Moreover, Ag nanoparticles were used as a co-catalyst to further improve the photocatalytic activity of mesoporous $Pb_3Nb_2O_8$. The activity of Ag-loaded mesoporous $Pb_3Nb_2O_8$ was 2.17 times higher than that of mesoporous $Pb_3Nb_2O_8$. The content of Ag to mesoporous $Pb_3Nb_2O_8$ was studied to determine the optimal loading conditions corresponding to the highest photocatalytic activity.

## 2. Experimental

### 2.1. Synthesis of mesoporous $Pb_3Nb_2O_8$ and Ag-loaded mesoporous $Pb_3Nb_2O_8$

In a typical synthesis, PbO (0.03 mol) was dissolved in $CH_3COOH$ (30 mL), and then a solution containing 0.04 mol $Nb(OC_2H_5)_5$ 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 $Pb_3Nb_2O_8$ samples. The mesoporous $Pb_3Nb_2O_8$ 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 photocalytic performance of MPNO-500.

Ag-loaded MPNO-500 was obtained as follows. MPNO-500 (0.5 g) was added to a transparant 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 irradated by a 300 W full arc xenon light with stirring. After 30 min irradation, 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. $Pb_3Nb_2O_8$ was also prepared by the solid state reaction method for comparison (labeled as PNO-SSR).

The solid-state reaction $Pb_3Nb_2O_8$ 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 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 ($p/p_0$ = 0.1–0.25). 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 Al $K_\alpha$ radiation. Binding energies were calibrated using adventitious carbon (C 1*s*) = 284.6 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-