

# Preparation of Mesoporous InVO<sub>4</sub> Photocatalyst and Its Photocatalytic Performance for Water Splitting

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**Abstract:** The mesoporous photocatalyst InVO<sub>4</sub> was synthesized by the template-directing self-assembling method. The synthesized InVO<sub>4</sub> was characterized by means of X-ray diffraction, transmission electron microscopy, N<sub>2</sub> adsorption, and ultraviolet-visible spectroscopy. The results showed that the crystal structure of InVO<sub>4</sub> could be controlled by changing the calcination temperature. Compared with the anatase TiO<sub>2</sub> and conventional InVO<sub>4</sub>, the mesoporous InVO<sub>4</sub> was more responsive toward visible light. The evolution rate of H<sub>2</sub> from water over the mesoporous InVO<sub>4</sub> achieved 1836 μmol/(g·h) under UV light irradiation, which was much higher than the anatase TiO<sub>2</sub> and conventional InVO<sub>4</sub>.

**Key Words:** mesoporous material; indium vanadate; photocatalyst; hydrogen; visible light; water splitting

Photocatalytic production of hydrogen from water over semiconductor materials is of great interest from both theoretical and practical points of view due to its possible application for converting solar energies into chemical ones. Materials with a wide bandgap, such as metal-doped TiO<sub>2</sub> [1], BiVO<sub>4</sub> [2], La/NaTaO<sub>3</sub> [3], In<sub>1-x</sub>Ni<sub>x</sub>TaO<sub>4</sub> ( $x = 0-0.2$ ) [4], and LaMnO<sub>3</sub>/CdS [5], have been reported to be active in the splitting of water into its components H<sub>2</sub> and O<sub>2</sub>. Most of these photocatalysts, however, can only respond to the ultraviolet (UV) light. Recently, Ye et al. [6] reported a novel kind of photocatalytic material, InMO<sub>4</sub> (M = V, Nb, Ta), which can catalyze water to H<sub>2</sub> under visible light irradiation. These catalysts were prepared via a route of high-temperature pyrolysis, resulting in a rather low surface area (< 0.5 m<sup>2</sup>/g). The template-based hydrothermal method has been proved to be successful in preparing high-surface-area mesoporous materials. It was reported that TiO<sub>2</sub> with high surface area possessed much higher photocatalytic activity than those with low surface area [7,8]. Recently, we have made an attempt to prepare mesoporous InMO<sub>4</sub> (M = V, Nb, Ta) by means of the template-directing self-assembling method. In this paper, we re-

port the preparation, characterization, and photocatalytic properties of mesoporous InVO<sub>4</sub> (meso-InVO<sub>4</sub>). This new catalyst showed obvious absorption in the visible light region (up to 800 nm), and a high evolution rate of H<sub>2</sub> from water could be achieved under UV irradiation.

Meso-InVO<sub>4</sub> was prepared by using cetyltrimethylammonium bromide (CTAB) as the structure-directing agent. The typical synthesis procedure is as follows. The stoichiometric amounts of In(NO<sub>3</sub>)<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub> were dissolved in deionized water at 25°C to form the precursor solution. CTAB (the mole ratio of CTAB/precursor was 0.5) was also dissolved in deionized water, the above precursor solution was slowly added under vigorous stirring, and then ammonia was added dropwise until the pH value reached 9–10, resulting in a yellow precipitate. The thick yellow solid was filtered, washed with deionized water, and dried at 100°C for 4 h. The obtained powder was then transferred into an autoclave filled with 30 ml absolute ethanol for crystallization at 180°C for 24 h, and then it was extracted with absolute ethanol for 24 h. Finally, the powder was calcined in an oven at 600–900°C for 6 h to remove the template. Photocatalytic reactions were carried out

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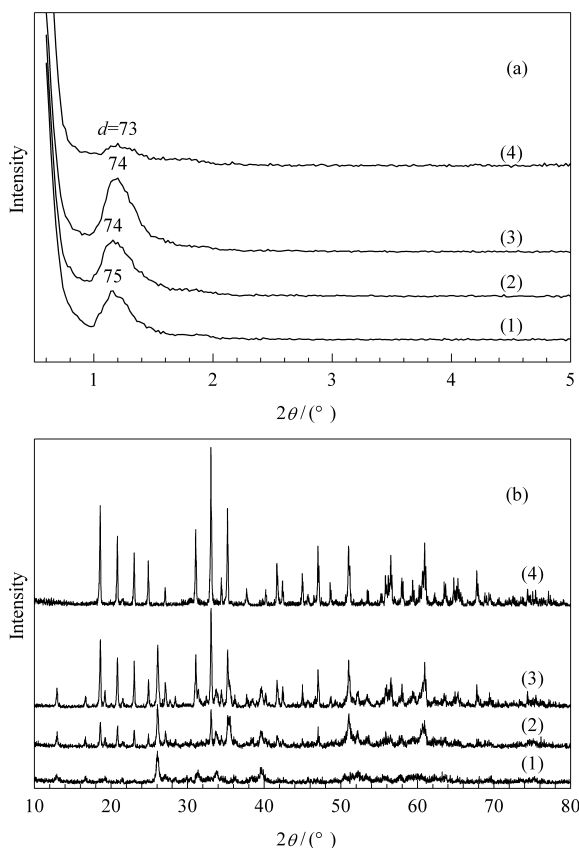
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in a closed gas circulation system, and an inner irradiation reaction quartz cell was used. The system was cooled by water circulation to room temperature during the experiments. The experiments were carried out in a 270 ml vessel filled with methanol solution, and the catalyst loading was 0.5 g. A 300 W Xe arc lamp was employed to generate light (no cut-off filter was used). Prior to illumination, the suspension was stirred for 1 h. Before starting the photocatalytic reaction, a flow (400 ml/min) of argon was passed through the system for 30 min to remove the dissolved oxygen in the solution.

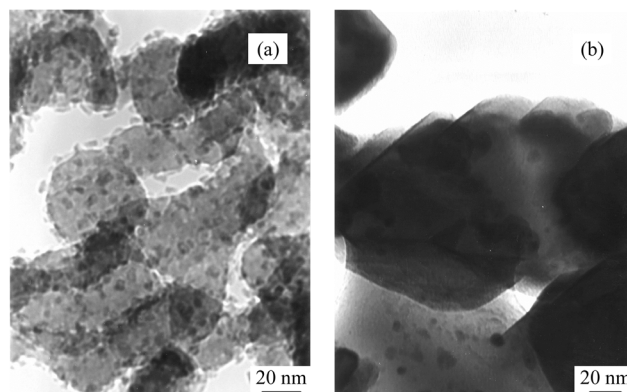
Fig. 1 shows the X-ray diffraction (XRD) patterns of  $\text{InVO}_4$  samples calcined at different temperatures. A strong diffraction peak at  $2\theta = 1.2^\circ$  in the small-angle region for each sample was observed in Fig. 1(a), which indicates the presence of mesoporous structure. With the increase of calcination temperature, the  $d$ -spacing of the layers decreased slightly from 75 to 73 nm, indicating that a higher temperature brought about a negative effect on the stability of the material as thicker pore walls can improve the thermal and hydrothermal stability of the mesopore framework [9]. From the wide-angle diffraction patterns as shown in Fig. 1(b), it can be seen that the meso- $\text{InVO}_4$  calcined at different temperatures possessed different crystal structures. Monoclinic  $\text{InVO}_4$  was obtained at low temperature ( $< 700^\circ\text{C}$ ), and the lattice parameters were  $a$

$= 1.0271 \text{ nm}$ ,  $b = 0.9403 \text{ nm}$ ,  $c = 0.7038 \text{ nm}$ , and  $\beta = 105.08^\circ$ . Orthorhombic  $\text{InVO}_4$  was obtained at high temperature ( $> 700^\circ\text{C}$ ), and the lattice parameters were  $a = 0.5765 \text{ nm}$ ,  $b = 0.8542 \text{ nm}$ ,  $c = 0.6592 \text{ nm}$ , and  $\beta = 90.0^\circ$ . When the sample was calcined at  $600^\circ\text{C}$  and  $900^\circ\text{C}$ , pure monoclinic and orthorhombic meso- $\text{InVO}_4$  was obtained, respectively. The sample calcined at  $700^\circ\text{C}$  had a mixed crystal structure (the molar ratio of monoclinic  $\text{InVO}_4$  to orthorhombic  $\text{InVO}_4$  was about 1/1). More orthorhombic  $\text{InVO}_4$  was found in the sample calcined at  $800^\circ\text{C}$ . The nitrogen adsorption–desorption results showed that the meso- $\text{InVO}_4$  calcined at  $600^\circ\text{C}$  possessed a surface area of about  $31.8 \text{ m}^2/\text{g}$ , which is much larger than that (ca.  $0.5 \text{ m}^2/\text{g}$ ) reported by Ye et al. [6]. The surface area decreased with the rise in calcination temperature. The sample calcined at  $700^\circ\text{C}$  had a surface area of  $16.8 \text{ m}^2/\text{g}$ , and when the calcination temperature rose to  $900^\circ\text{C}$ , the surface area dropped to  $9.3 \text{ m}^2/\text{g}$ . It can be concluded that increasing the calcination temperature undermines the mesostructure.

Transmission electron microscopy (TEM) is a powerful tool to visualize different pore orderings [10]. Fig. 2 presents the TEM images of meso- $\text{InVO}_4$  calcined at different temperatures. It can be seen from Fig. 2(a) that the sample calcined at  $600^\circ\text{C}$  displayed the patterns characteristic of the disordered mesostructure, and the corresponding average particle size was 30–40 nm. This result is similar to that of mesoporous  $\text{TiO}_2$  reported by Wang et al. [11]. It is also observed that the sample calcined at  $700^\circ\text{C}$  had stepped surface near the edges of the particles (Fig. 2(b)). This unique stepped structure on the surface may contribute to the creation of highly photo-active sites, and a similar viewpoint has been proposed by Kudo et al. [3], who believed that a multi-electron transfer reaction of water deoxidization to form  $\text{H}_2$  seems to proceed more favorably on the steps than on the flat surface due to a geometric effect. The scanning electron microscopic photographs (not shown here) revealed that when the calcination temperature was raised to  $900^\circ\text{C}$ , small nanoparticles agglomerated to larger particles, causing the surface area to decrease abruptly.

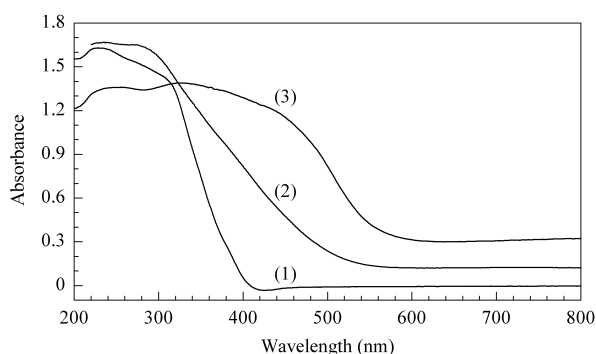


**Fig. 1** XRD patterns of mesoporous  $\text{InVO}_4$  samples calcined at  $600^\circ\text{C}$  (1),  $700^\circ\text{C}$  (2),  $800^\circ\text{C}$  (3), and  $900^\circ\text{C}$  (4) (There exist traces of  $\text{In}_2\text{O}_3$  impurity in the samples.)



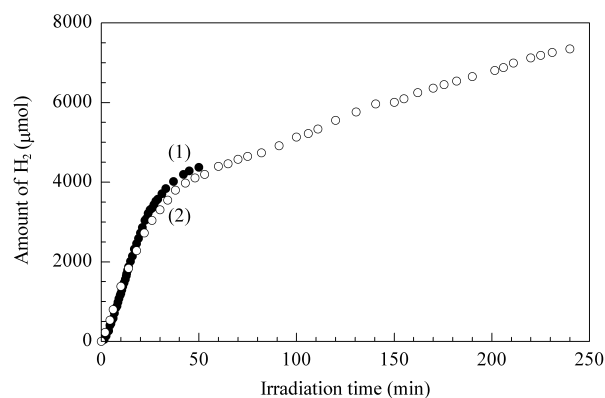
**Fig. 2** TEM images of mesoporous  $\text{InVO}_4$  samples calcined at  $600^\circ\text{C}$  (a) and  $700^\circ\text{C}$  (b)

Fig. 3 shows the UV-Vis diffuse reflectance spectra of different samples. It can be seen that the orthorhombic  $\text{InVO}_4$  calcined at  $900^\circ\text{C}$  exhibited more absorbance than the monoclinic  $\text{InVO}_4$  calcined at  $600^\circ\text{C}$  in the visible light region. The photon absorption edge of meso- $\text{InVO}_4$  extended to 800 nm, which is much higher than that of the well-known P25 (about 400 nm). According to the literature [12], 0.1 wt%  $\text{Pt/InVO}_4$  showed an obvious absorption up to 600 nm, and its bandgap was estimated to be 2.0 eV. The bandgap of our meso- $\text{InVO}_4$  was estimated to be 1.8 eV based on the diffuse reflectance spectra shown in Fig. 3, which is narrower than the 0.1 wt%  $\text{Pt/InVO}_4$  catalyst [12].



**Fig. 3** UV-Vis diffuse reflectance spectra of  $\text{TiO}_2$  (1), mesoporous  $\text{InVO}_4$  calcined at  $600^\circ\text{C}$  (2) and  $900^\circ\text{C}$  (3)

Fig. 4 displays the photocatalytic performance of meso- $\text{InVO}_4$  under UV light irradiation. The sample calcined at  $700^\circ\text{C}$  was selected for the activity evaluation because it had unique stepped surfaces, relatively high surface area, and orthorhombic  $\text{InVO}_4$  structure with good visible-light absorbance.  $\text{H}_2$  was evolved at a high rate within the first 40 min in the first run, but after that the  $\text{H}_2$  evolution rate decreased. Such a phenomenon might be due to a drop in methanol concentration. To verify it, we turned off the lamp and added 15 ml of methanol to the system. The results showed that the  $\text{H}_2$  evolution rate in the second run was almost restored to the level in the first run, indicating that no deactivation occurred on the catalyst. Therefore, the drop in the  $\text{H}_2$  evolution rate is mainly due to the decrease in methanol concentration in the reaction system. The average  $\text{H}_2$  evolution rate was estimated to be  $1836 \mu\text{mol}/(\text{g}\cdot\text{h})$  after 4 h of reaction, which is much higher than that of the nonporous  $\text{NiO}_x/\text{InVO}_4$  catalyst ( $12 \mu\text{mol}/(\text{g}\cdot\text{h})$ ) [12]. The XRD patterns (not shown here) also confirmed that there was no significant difference between the diffraction patterns of meso- $\text{InVO}_4$  before and after the photocatalytic reaction, suggesting that no observable structural changes in the catalyst occurred.



**Fig. 4** Photocatalytic performance of mesoporous  $\text{InVO}_4$  calcined at  $700^\circ\text{C}$  for water decomposition to produce hydrogen under UV light irradiation

- (1) The first run with 50 ml  $\text{CH}_3\text{OH}$  + 220 ml pure  $\text{H}_2\text{O}$ ;  
(2) The second run, the system was laid aside in the darkness for 24 h after the first run and then additional 15 ml  $\text{CH}_3\text{OH}$  was added

In summary, the meso- $\text{InVO}_4$  photocatalyst was synthesized via the template-directing self-assembling procedure. Monoclinic- and orthorhombic-phase  $\text{InVO}_4$  could be selectively obtained by controlling their calcination temperatures. The meso- $\text{InVO}_4$  photocatalyst calcined at  $700^\circ\text{C}$  gave a hydrogen evolution rate of  $1836 \mu\text{mol}/(\text{g}\cdot\text{h})$  under UV light irradiation.

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