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Short communication

The formation of $(NH_4)_2V_6O_{16}$ phase in the synthesized $InVO_4$ for the hydrogen evolving applications

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ABSTRACT

By controlling the synthesized conditions such as the compositions, pH and hydrothermal temperature of the In (or NH_4)-V-O compounds, the structural information have been determined with the potential application in the hydrogen evolving efficiency. When the addition of ammonium ions to adjust the pH with the hydrothermal time of 4 h, there is a maximum hydrogen production of 140.8 μmol/g·cat. The maximum hydrogen production reaches at pH of 5. In addition, the $(NH_4)_2V_6O_{16}$ phase in the synthesized $InVO_4$ has been observed. This crystalline ammonia vanadium-based material is capable to perform the photocatalysis process in hydrogen evolving.

1. Introduction

Semiconductor photocatalysis has attractively been interested because of its special photocatalytic and electrochemical properties to split water into clean-energy hydrogen under solar energy [1–3]. Ye et al. have investigated the photocatalytic efficiency of InMO4 series ($M = V^{5+}$, Nb^{5+}, Ta^{5+}) under visible light irradiation [4]. The band gap of $InVO_4$ (1.9 eV) depicts much narrower than those of $InTaO_4$ (2.6 eV) and $InNbO_4$ (2.5 eV). This suggests that $InVO_4$ is possibly more efficient at photocatalytic production of H_2 from water under visible light irradiation. Also, Fei et al. [5] have discussed that the molar ratio with In/V and pH value synthesize a single phase of $InVO_4$, and $InVO_4$ has been found to be a new photocatalyst because the chemical stability and lower band gap of about 1.9 eV.

However, the previous studies commonly use the sodium hydroxide to adjust the pH and result in the formation of the $Na_2V_6O_{16}$. The formation of $Na_2V_6O_{16}$ prevents to form an active $InVO_4$ phase at higher pH value. From literatures survey, ammonium vanadium oxides possess the advantages of low cost, easy to synthesize and high-energy density, and thus have much interested for further investigations [6–11]. Various ammonium vanadium oxide nano-structures have been applied as lithium-ion battery cathode materials, such as $NH_4V_4O_{10}$ nano-belts [12,13], $(NH_4)_2V_6O_{16}$ nano-rods [14], $NH_4V_3O_8{\cdot}0.2H_2O$ flakes [15] and $NH_4V_3O_8$ nano-rods [16].

In addition, $(NH_4)_2V_6O_{16}$ is a member of the Hewettite ($M_2V_6O_{16}{\cdot}nH_2O$, M = monovalent element, and $MV_6O_{16}{\cdot}nH_2O$, M = divalent element) group [17], and is a typical layered structure which consists of V_3O_8 layers which composed of VO_6 and V_2O_8 units and interstitial hydrated $NH_4{}^{+}$ and found to be potential Li + lithium-ion battery materials. Nevertheless, ammonium vanadium oxide species have not been investigated in photocatalytic application. In our preliminary studies, it appears that ammonium vanadium oxide possesses the photocatalytic ability. Therefore, ammonia hydroxide has been used to replace sodium hydroxide to control the solution pH, and synthesized the $InVO_4$ crystalline phase by hydrothermal method. The formation of $(NH_4)_2V_6O_{16}$ and $InVO_4$ phase can be optimized by pH value and hydrothermal treatment time.

2. Experimental methods

2.1. Catalyst preparation

The $InVO_4$ powder were firstly prepared by hydrothermal process from $InCl_3$ (Indium(III) chloride, Sigma-Aldrich, 98%) and NH_4VO_3 (Ammonium metavanadate, Sigma-Aldrich, 99.99%) precursors. The $InCl_3$ and NH_4VO_3 was dissolved in 40 ml distilled water separately, and controlled at a specific In:V molar ratio of 1:2. The $InCl_{3(aq)}$ solution was then mixed with $NH_4VO_{3(aq)}$ drop wisely and adjust the pH value to 3, 5, 7, and 9 by adding proper amount of ammonium hydroxide. After continuous stirring for 1 h, the mixed solution was transferred into a Teflon-lined stainless steel autoclave. Hydrothermal treatment was set to 1, 4, 6, and 8 h under 200 °C. After completing the hydrothermal procedures, the powder was centrifuged, washed with distilled water and ethanol several times. The powder was dried under 60 °C in vacuum oven for 1 h. For $(NH_4)_2V_6O_{16}$, the previous procedures were repeated without the addition of $InCl_3$, the hydrothermal

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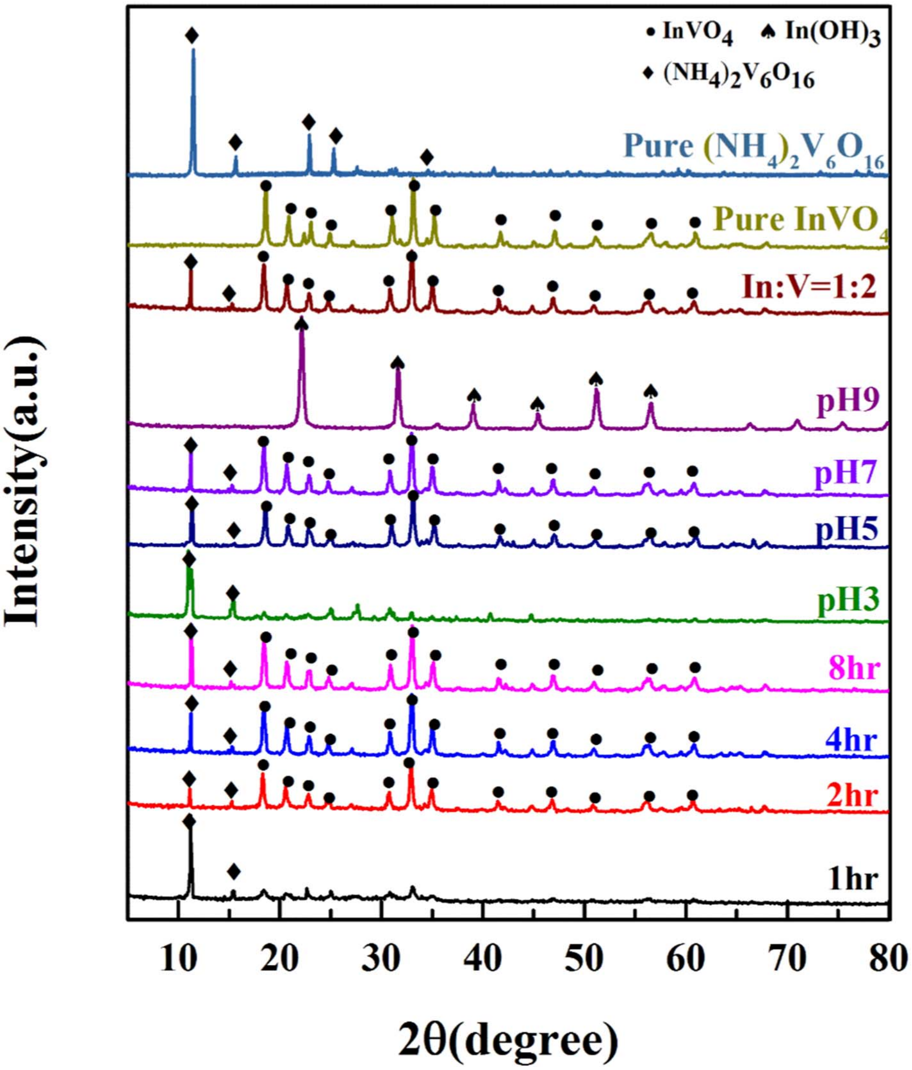

Fig. 1. XRD results of pure $(NH_4)_2V_6O_{16}$, pure $InVO_4$ and synthesized $InVO_4$ (In:V = 1:2) as a function of hydrothermal time and pH value.

conditions were controlled under pH = 5, hydrothermal temperature at 200 °C with 4 h reaction time to form the $(NH_4)_2V_6O_{16}$. For comparison, the previous procedures were repeated and used the sodium hydroxides to adjust pH value, the hydrothermal conditions were controlled under pH = 5, hydrothermal temperature at 200 °C with 4 h reaction time to form the $Na_2V_6O_{16}$ instead of $(NH_4)_2V_6O_{16}$ and $InVO_4$ crystalline phases.

2.2. Characterizations

The crystalline phase of $InVO_4$ with/without the presence of the $(NH4)_2V_6O_{16}$ crystalline phase was identified by X-ray diffraction (XRD, PANalytical X'Pert Pro MRD) with a CuKα irradiation (λ = 1.5406 Å). Fourier transform infrared (FT-IR) spectra were recorded on a Horiba FT-720 spectrophotometer using the standard KBr disc method. The absorbance of catalyst over the spectrum range of 420–800 nm was determined by UV–vis spectrophotometer (Shimadzu UV-3600). The micro-structural morphology was observed by using field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-7401F). The above characterization techniques were performed as a function of pH value and hydrothermal treatment time.

2.3. Photocatalytic activity

Photocatalytic reactions were carried out in a closed gas circulation system. A 0.15 g of powder sample was suspended in 300 ml distilled water contain 100 ml methanol within a quartz reactor. A 300 W Xe lamp was placed in center of reactor. The gases evolved were analyzed with a TCD equipped gas chromatograph (China chromatography, GC9800). The hydrogen product rate was quantified using the calibration curve.

3. Results and discussion

3.1. Crystalline phase of In (or NH_4)-V-O as a function of preparation conditions

The XRD patterns of pure $(NH_4)_2V_6O_{16}$, $InVO_4$, and synthesized In-V-O as a function of preparation conditions are shown in Fig. 1. All catalysts possesses a peak at 2θ = 33.052°, which is the characteristic peak of $InVO_4$, and 2θ = 11.323° is the characteristic of the (100) peak of the $(NH_4)_2V_6O_{16}$. It appears that the crystalline structure of the synthesized In-V-O catalyst with the In:V = 1:2 ratio is in good agreement with the orthorhombic $InVO_4$-III phase (JCPDS 48-0898) and $(NH_4)_2V_6O_{16}$ phase (JCPDS 79-2051).

The XRD patterns of the synthesized In-V-O catalyst as a function of hydrothermal treatment time are also shown in Fig. 1. The characteristic XRD peaks of $InVO_4$ are not well defined for only 1 h reaction time. It's insufficient to form $InVO_4$ phase, and the $(NH_4)_2V_6O_{16}$ phase is dominate in the crystalline structure according to XRD results. Upon increasing the treatment time from 2 to 8 h, the well-defined $InVO_4$