



Boosting photocatalytic water oxidation achieved by BiVO₄ coupled with iron-containing polyoxometalate: Analysis the true catalyst



Min Zheng^a, Xiaohu Cao^a, Yong Ding^{a,b,*}, Tian Tian^a, Junqi Lin^a

^a State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

ARTICLE INFO

Article history:

Received 5 March 2018

Revised 5 April 2018

Accepted 16 April 2018

Keywords:

BiVO₄

Polyoxometalate

Water oxidation

Visible light-harvesting material

Ultrathin nanofilm

ABSTRACT

In this work, BiVO₄ is selected as effective light-harvesting material to replace conventional unstable dye-sensitized photosensitizer ([Ru(bpy)₃]²⁺) that easily occurs photodecomposition during artificial photosynthetic system. The addition of an eleven iron-containing polyoxometalate (Fe₁₁POM) as efficient cocatalyst illustrates a dramatically improved photocatalytic water oxidation performance compared with that of pure BiVO₄. Through careful characterization and analysis of selected-area, highly selective in-situ photo-deposition of Fe₁₁POM into ultrathin nanofilm on the decisive 110 facet of BiVO₄ under ultrapure water is clearly observed, and an intimate connection between nanofilm and hole-rich 110 facet is obtained in favor of enhancing surface catalytic efficiency. The exquisite decoration of ultrathin nanofilm can be further clarified as FeO_x decomposed from Fe₁₁POM, which could effectively capture the photogenerated holes and suppress the recombination of electron-hole pairs for promoting water oxidation performance through fast interfacial hole transfer process.

© 2018 Elsevier Inc. All rights reserved.

1. Introduction

During the last several decades, sustainable and clean energies were needed urgently to replace conventional fossil resources [1]. Among those renewable and alternative energy sources (wind, solar, nuclear and biomass energy), solar energy has the most significant impact on economy and ecology in the long term by converting of solar light to useful chemical energy through water splitting, which possesses a better potential with environmental friendly and low-cost hydrogen fuel [2–4]. To solve the bottleneck problem among the overall water splitting, a vast majority of efforts have been conducted to develop effective water oxidation catalyst (WOC) to promote this sluggish kinetics of photocatalytic oxygen evolution reaction (OER) [5–7].

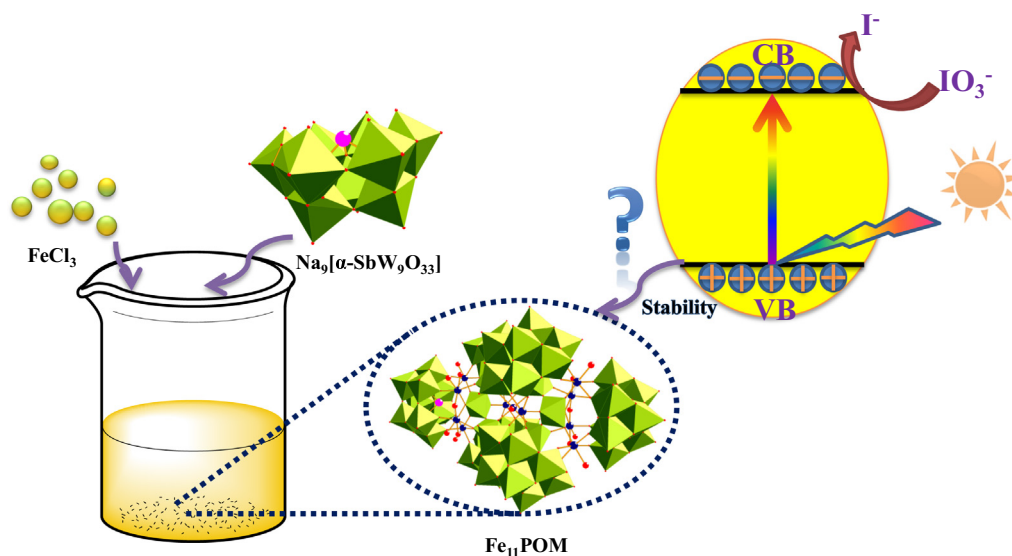
For the reported artificial photocatalytic system, the easy photolysis and poor stability of soluble photosensitizer ([Ru(bpy)₃]²⁺) would limit its potential application for OER [8–12]. Thus, developing highly stable and effective light-harvesting materials such as semiconductor micro/nanoparticles to replace conventional dye-

sensitized photosensitizer is very meaningful, in which inorganic metal oxides were selected as good candidates with high chemical stability for water oxidation due to their appealing band structure capable of the OER as well as wide spectral absorption to visible light [13–15]. Generally, extra cocatalysts containing noble metals are commonly used to improve the separation efficiency of photoinduced charge carriers and the surface catalytic efficiency, but the high value and scarcity restrict its wide application [16,17]. Thus, cocatalysts based on earth-abundant transition metal are desirable, among which heterogeneous catalysts containing metal oxides and homogeneous catalysts containing organic ligand complexes have been extensively investigated in water oxidation reaction [18–24]. However, molecular all-inorganic polyoxometalates (POMs) with excellent photoactivity [25–32] have never been reported as cocatalyst in photocatalytic semiconductor-based system. An eleven iron-containing polyoxometalate (Fe₁₁POM) performed fantastic photocatalytic water oxidation activity with a turn-over number (TON) of 1815 and a turn-over frequency (TOF) of 6.3 s⁻¹, which could be a potential cocatalyst candidate [33].

Herein, we construct a photocatalytic water oxidation system using molecular Fe₁₁POM as cocatalyst and stable BiVO₄ as visible light absorbing material for the first time (Scheme 1). The new designed photocatalytic device illustrates a dramatically improved water oxidation performance compared with that of pure BiVO₄.

* Corresponding author at: State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China.

E-mail address: dingyong1@lzu.edu.cn (Y. Ding).



Scheme 1. The synthetic process of Fe_{11}POM and designed device using molecular Fe_{11}POM as cocatalyst and BiVO_4 as light-harvesting material.

The accelerated charge separation efficiency and surface catalytic kinetics are confirmed by various kinds of technologies, like UV–vis diffuse reflectance spectra, transient absorption spectra, photoluminescence (PL) spectra and so on. Furthermore, since the stability of molecule catalyst exists a huge controversy, detailed investigations should be carried out to estimate whether the homogeneous molecular WOC of Fe_{11}POM is true cocatalyst during OER.

2. Experiment section

2.1. Preparation of $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$

The salt was prepared by the reaction of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (40 g, 121 mmol) in boiling water (80 mL) and dropwise adding of Sb_2O_3 (1.96 g, 6.72 mmol) dissolved in concentrated HCl (10 mL). The mixture was refluxed for 1 h and allowed to cool slowly. Colourless crystals of $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$ were formed after evaporation of one-third of the solution volume.

2.2. Synthesis of $\text{Na}_{27}[\text{Fe}_{11}(\text{H}_2\text{O})_{14}(\text{OH})_2(\text{W}_3\text{O}_{10})_2(\alpha\text{-SbW}_9\text{O}_{33})_6]$

1.16 g (7.2 mmol) of FeCl_3 was dissolved in 80 mL of H_2O , and then 9.45 g (3.3 mmol) of $\text{Na}_9[\alpha\text{-SbW}_9\text{O}_{33}]$ was added. The pH of the solution was adjusted to 3.0 by 4.0 M NaOH. Then, the solution was heated to 90 °C for 1 h and filtered after cooling to room temperature. Slow evaporation of the clear filtrate at room temperature led to yellow crystals which are suitable for X-ray diffraction within 8–9 days.

2.3. Synthesis of powder BiVO_4

The powder BiVO_4 sample was synthesized by a hydrothermal procedure. Typically, the precursors NH_4VO_3 (36 mmol) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (36 mmol) were dissolved in 300 mL of 2.0 M nitric acid solution, then the pH value of the solution was adjusted to 2.0 with ammonia solution under stirring until formation of the orange precipitate. After about 2 h aging, the orange precipitate at the bottom of the beaker was transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL and hydrothermally treated at 200 °C for 24 h. After the autoclave was cooled to room temperature, a vivid yellow powder was separated by filtration,

washed with de-ionized water for more than 3 times, and then dried at 60 °C in air for overnight.

2.4. Photocatalytic water oxidation

Typical photocatalytic water oxidation perform under our laboratory condition is shown below. Adding the optimal quantities of 80 μM Fe_{11}POM and 50.0 mg BiVO_4 to the ultrapure water (18.2 $\text{M}\Omega\text{ cm}$) containing 10.0 mM NaIO_3 . The mixed solution was agitated and deaerated by purging with Ar gas for 10 min in a flask (23.3 mL) sealed with a rubber septum (the volume of reaction solution was 10 mL) at the same time. The reaction was then started by irradiating the solution with a LED light source (50 mW/cm^2 under illumination at 460 nm) at ambient temperature. After exposure in the light corresponding to several times, 100 μL of Ar was injected into the flask and then the same volume of gas in the headspace of the flask was withdrawn using a SGE gas-tight syringe and analysed by gas chromatography (GC). The O_2 in the sampled gas was separated by passing through a 2 m \times 3 mm packed molecular sieves 5 Å column with an Ar carrier gas and quantified using a thermal conductivity detector (TCD) (Shimadzu GC-9A). A total produced O_2 of the quantity was calculated on the basis of the concentration of O_2 in the headspace gas. Contamination of the headspace with air was calibrated by measuring N_2 present in the headspace through measuring the N_2 peak in the GC traces. The pH of the solution was monitored using a METTLER TOLEDO FEP20 pH meter.

2.5. Materials and characterization

All the chemicals and salts used for synthesizing the catalysts were obtained from a chemical company and used without further purification. Ultrapure water (18.2 $\text{M}\Omega\text{ cm}$) for the preparation of solutions was attained from a Molecular Lab Water Purifier. Crystalline structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX 2400 diffractometer (Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) spectra were measured by ESCA-LAB250xi with X-ray monochromatisation. The binding energy of each element was corrected by C 1s peak (284.8 eV) from residual carbon. The surface morphologies of the samples were characterized by scanning electron microscope (SEM, S4800) and transmis-

Download English Version:

<https://daneshyari.com/en/article/6526625>

Download Persian Version:

<https://daneshyari.com/article/6526625>

[Daneshyari.com](https://daneshyari.com)