Chinese Journal of Catalysis 39 (2018) 534–541

available at www.sciencedirect.com

ScienceDirect

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

Article (Special Issue of Photocatalysis for Solar Fuels)

Catalytic effects of $[Ag(H_2O)(H_3PW_{11}O_{39})]^{3-}$ on a TiO_2 anode for water oxidation

Jiansheng Li, Lei Wang, Wansheng You *, Meiying Liu#, Lancui Zhang, Xiaojing Sang

Institute of Chemistry for Functionalized Materials, Liaoning Normal University, Dalian 116029, Liaoning, China

ARTICLE INFO

Article history:
Received 30 September 2017
Accepted 9 November 2017
Published 5 March 2018

Keywords:
Water oxidation
Electrocatalysis
Photoelectrochemistry
TiO_2
Polyoxometalate
Ag^+ complex

ABSTRACT

A $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$-$TiO_2$/ITO electrode was fabricated by immobilizing a molecular polyoxometalate-based water oxidation catalyst, $[H_3Ag^{I}(H_2O)PW_{11}O_{39}]^{3-}$ ($AgPW_{11}$), on a TiO_2 electrode. The resulting electrode was characterized by X-ray powder diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy. Linear sweep voltammetry, chronoamperometry, and electrochemical impedance measurements were performed in aqueous Na_2SO_4 solution (0.1 mol L^{-1}). We found that a higher applied voltage led to better catalytic performance by $AgPW_{11}$. The $AgPW_{11}$-TiO_2/ITO electrode gave currents respectively 10 and 2.5 times as high as those of the TiO_2/ITO and $AgNO_3$-TiO_2/ITO electrodes at an applied voltage of 1.5 V *vs* Ag/AgCl. This result was attributed to the lower charge transfer resistance at the electrode-electrolyte interface for the $AgPW_{11}$-TiO_2/ITO electrode. Under illumination, the photocurrent was not obviously enhanced although the total anode current increased. The $AgPW_{11}$-TiO_2/ITO electrode was relatively stable. Cyclic voltammetry of $AgPW_{11}$ was performed in phosphate buffer solution (0.1 mol L^{-1}). We found that oxidation of $AgPW_{11}$ was a quasi-reversible process related to one-electron and one-proton transfer. We deduced that disproportionation of the oxidized $[H_2Ag^{II}(H_2O)PW_{11}O_{39}]^{3-}$ might have occurred and the resulting $[H_3Ag^{III}OPW_{11}O_{39}]^{3-}$ oxidized water to O_2.

1. Introduction

Efficient oxidation of water to O_2 is key to the production of H_2 fuel and for the reduction of CO_2 by electrolysis, photocatalysis, photoelectrocatalysis, and other approaches. Therefore, considerable attention has been paid to developing viable water oxidation catalysts (WOCs) [1–6]. Polyoxometalates have been selected as carbon-free inorganic ligands for the construction of these catalysts because of their high stability towards oxidative degradation and capacity to transfer electrons and protons [7]. As a class of homogenous molecular WOCs, a series of ruthenium- [8–14] and cobalt- [15–21] polyoxometalate complexes, including $[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ and $[Co_4(H_2O)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]^{10-}$, have been intensively studied. These investigations have demonstrated the promise of polyoxometalates for multi-electron-transfer catalysis.

Recently, immobilization of molecular polyoxometalate-based WOCs for the development of electrodes and photoelectrodes has drawn interest. We found that the high reactivity of molecular WOCs was retained when supported on various materials [22–24]. Bonchio *et al.* [25] deposited $[Ru_4(H_2O)_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$@multi-walled carbon nanotubes (MWCNTs) on an ITO substrate to obtain an

* Corresponding author. Tel/Fax: +86-411-82159378; E-mail: wsyou@lnnu.edu.cn
# Corresponding author. Tel/Fax: +86-411-82159256; E-mail: myliu312@yahoo.com
This work was supported by the National Natural Science Foundation of China (21573099, 21601077, 21573100).
DOI: 10.1016/S1872-2067(17)62973-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 3, March 2018

oxygen-evolving electrode that produced an over-potential (η) as low as 0.35 V and TOFs approaching those of the cluster in homogeneous solution (306 h^{-1} at η = 0.60 V). Hill *et al*. [26] immobilized $[Ru^{IV}_4O_5(OH)(H_2O)_4(\gamma\text{-}PW_{10}O_{36})_2]^{9-}$ and $[\{Ru^{IV}_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{34})_2]^{10-}$ on TiO_2/FTO electrodes via the a silanization-cationization process, which resulted in a continuously enhanced photocurrent or catalytic water oxidation activity.

In 2015, we reported a new WOC, Ag^+-based polyoxometalate complex, $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, and proposed its mechanism of chemical water oxidation in the presence of $S_2O_8^{2-}$ [27]. Herein, this Ag^+-polyoxometalate complex was further immobilized on a nanocrystalline TiO_2 electrode owing to its sufficient stability and notable catalytic ability when combined with photosensitizers. Moreover, the electrocatalytic and photoelectrocatalytic effects of $[Ag(H_2O)(H_3PW_{11}O_{39})]^{3-}$ on a TiO_2 anode for water oxidation were investigated and the electrocatalytic mechanism is proposed.

2. Experimental

2.1. Materials and characterization

All chemicals were commercially available and used without further purification. $K_3[Ag(H_3PW_{11}O_{39})]\cdot 12H_2O$ ($AgPW_{11}$) and $K_4[H_3PW_{11}O_{39}]\cdot 14H_2O$ (PW_{11}) were synthesized according to reported methods [27,28]. The TiO_2 powder was commercial P25. The TiO_2 paste was prepared according to a previous report [29]. X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance diffractometer with the use of Cu K_α radiation (λ = 1.5418 Å) in the 2θ range of 5°–60° with a step size of 0.02°. Scanning electron microscope (SEM) images and energy dispersive X-ray (EDX) analytical data were obtained on a scanning electron microscope (ZXM6360-LV) with an EDX detector.

2.2. Fabrication of the electrodes

TiO_2/ITO electrodes: a piece of ITO conductive glass was successively ultrasonically cleaned with detergent, isopropanol, ethanol and deionized water for 20 min each, and finally dried in air. The clean ITO substrate was then coated with TiO_2 pasted by a screen-printing [30] technique to obtain a film with an area of 0.36 cm^2. The screen-printing process was repeated three times. Finally, a TiO_2/ITO electrode was obtained by annealing the TiO_2-coated ITO at 450 °C for 1 h.

$AgPW_{11}$-TiO_2/ITO electrode: The TiO_2/ITO electrode was dipped into 20 mL of $K_3[H_3AgPW_{11}O_{39}]\cdot 12H_2O$ solution (2.00 mmol L^{-1}) overnight, followed by washing with 5 mL deionized water three times followed by drying in air.

$AgNO_3$-TiO_2/ITO and PW_{11}-TiO_2/ITO electrodes were fabricated by the same process except that $AgNO_3$ or PW_{11} replaced the $AgPW_{11}$.

2.3. Electrochemical measurements

All electrochemical experiments were performed on a CHI600B electrochemical workstation (Shanghai Chenhua Instrument Corp., China) with a three-electrode system. A Pt wire and Ag/AgCl (3.00 mol L^{-1} KCl) were used as the counter and reference electrodes, respectively. The working electrodes included a glassy carbon electrode, a TiO_2/ITO electrode and modified TiO_2/ITO electrodes. The glassy carbon electrode was polished for 60 s with 0.05 μm alumina particles and sonicated twice for 30 s in reagent grade water prior to use. Cyclic voltammograms (CVs) were collected in 0.10 mol L^{-1} NaH_2PO_4-Na_2HPO_4 electrolyte, having a pH in the range of 5.3–6.7, at different scan rates in the range of 100–900 mV s^{-1} and at 1.0 or 0.1 mA V^{-1} sensitivity. Other electrochemical measurements were performed in 0.10 mol L^{-1} Na_2SO_4 electrolyte. Electrochemical impedance spectra (EIS) were measured at a bias voltage of −0.3 V with an alternating current (ac) bias signal of 5 mV in the frequency range of 0.01–1×10^5 Hz. The photo-electrochemistry was measured under simulated AM 1.5 G illumination (1 sun, 100 mW cm^{-2}) from a 300 W Xe arc lamp without a filter.

3. Results and discussion

3.1. Characterization of $AgPW_{11}$-TiO_2/ITO electrodes

The TiO_2 powder used to fabricate the electrodes was commercial P25. XRD patterns of the electrodes are shown in Fig. 1(a). The ITO conductive glass showed strong diffraction peaks at 2θ = 26.5°, 33.7°, 37.9°, 51.7°, 61.8°, and 65.9°. Both TiO_2/ITO and $AgPW_{11}$-TiO_2/ITO electrodes showed characteristic peaks from anatase at 2θ of 25.2°, 48.0°, and 54.4° and characteristic peaks from rutile at 2θ of 27.3°, 36.0°. No diffraction peaks were observed for $AgPW_{11}$, likely because of the small amount present on the TiO_2 surface [31].

SEM imaging was conducted to provide detailed information about the surface morphology and homogeneity of the TiO_2 and $AgPW_{11}$-TiO_2 films on the ITO substrate. As shown in Fig. 2, both the TiO_2 and $AgPW_{11}$-TiO_2 films showed typical granular patterns and no cracks. The film thickness was estimated to be approximately 7 μm (Fig. 1(b)). The pure TiO_2 film consisted of particles with size in the range of 10–40 nm (Fig. 2(a)); however, the average particle size was slightly larger (15–60 nm) for the $AgPW_{11}$-decorated TiO_2 film (Fig. 2(b)), which could be attributed to the introduction of $AgPW_{11}$. The EDX spectra indicated the existence of Ag, P, and W on the $AgPW_{11}$-TiO_2/ITO electrode (Fig. S1). This result confirms that $AgPW_{11}$ was present on the TiO_2 surface.

3.2. Electrocatalysis of $AgPW_{11}$ in TiO_2/ITO electrode

The behaviors of the TiO_2/ITO and $AgPW_{11}$-TiO_2/ITO electrodes in the electrocatalytic oxidation of water were studied in Na_2SO_4 solution (0.1 mol L^{-1}). Fig. 3 shows the results of linear sweep voltammetry of the TiO_2/ITO electrode and $AgPW_{11}$-TiO_2/ITO electrode. When the applied voltage was less than 1.3 V *vs.* Ag/AgCl, the anode currents of both the TiO_2/ITO electrode and $AgPW_{11}$-TiO_2/ITO electrode were small and