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Catalytic effects of $[\text{Ag}(\text{H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^{3-}$ on a TiO_2 anode for water oxidation

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

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

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ABSTRACT

A $[\text{H}_3\text{Ag}^{\text{I}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}/\text{TiO}_2/\text{ITO}$ electrode was fabricated by immobilizing a molecular polyoxometalate-based water oxidation catalyst, $[\text{H}_3\text{Ag}^{\text{I}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$ (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 $\text{AgPW}_{11}/\text{TiO}_2/\text{ITO}$ electrode gave currents respectively 10 and 2.5 times as high as those of the TiO_2/ITO and $\text{AgNO}_3/\text{TiO}_2/\text{ITO}$ 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 $\text{AgPW}_{11}/\text{TiO}_2/\text{ITO}$ electrode. Under illumination, the photocurrent was not obviously enhanced although the total anode current increased. The $\text{AgPW}_{11}/\text{TiO}_2/\text{ITO}$ 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 $[\text{H}_2\text{Ag}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$ might have occurred and the resulting $[\text{H}_3\text{Ag}^{\text{III}}\text{OPW}_{11}\text{O}_{39}]^{3-}$ oxidized water to O_2 .

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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 $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ and $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-B-PW}_9\text{O}_{34})_2]^{10-}$, 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 $[\text{Ru}_4(\text{H}_2\text{O})_4(\mu\text{-O})_4(\mu\text{-OH})_2(\gamma\text{-SiW}_{10}\text{O}_{36})_2]^{10-}$ @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

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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 $\eta = 0.60 \text{ V}$). Hill *et al.* [26] immobilized $[\text{Ru}^{\text{IV}}_4\text{O}_5(\text{OH})(\text{H}_2\text{O})_4(\gamma\text{-PW}_{10}\text{O}_{36})_2]^{9-}$ and $[\{\text{Ru}^{\text{IV}}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\gamma\text{-SiW}_{10}\text{O}_{34})_2]^{10-}$ 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, $[\text{H}_3\text{Ag}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$, and proposed its mechanism of chemical water oxidation in the presence of $\text{S}_2\text{O}_8^{2-}$ [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 $[\text{Ag}(\text{H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^{3-}$ 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. $\text{K}_3[\text{Ag}(\text{H}_3\text{PW}_{11}\text{O}_{39})]\cdot 12\text{H}_2\text{O}$ (AgPW_{11}) and $\text{K}_4[\text{H}_3\text{PW}_{11}\text{O}_{39}]\cdot 14\text{H}_2\text{O}$ (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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) 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.

$\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode: The TiO_2/ITO electrode was dipped into 20 mL of $\text{K}_3[\text{H}_3\text{AgPW}_{11}\text{O}_{39}]\cdot 12\text{H}_2\text{O}$ solution (2.00 mmol L^{-1}) overnight, followed by washing with 5 mL deionized water three times followed by drying in air.

$\text{AgNO}_3\text{-TiO}_2/\text{ITO}$ and $\text{PW}_{11}\text{-TiO}_2/\text{ITO}$ 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 $0.05 \text{ }\mu\text{m}$ 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} $\text{NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4$ electrolyte, having a pH in the range of 5.3–6.7, at different scan rates in the range of $100\text{--}900 \text{ mV s}^{-1}$ 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 $0.01\text{--}1\times 10^5 \text{ Hz}$. 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 $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ 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 $2\theta = 26.5^\circ, 33.7^\circ, 37.9^\circ, 51.7^\circ, 61.8^\circ$, and 65.9° . Both TiO_2/ITO and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrodes showed characteristic peaks from anatase at 2θ of $25.2^\circ, 48.0^\circ$, and 54.4° and characteristic peaks from rutile at 2θ of $27.3^\circ, 36.0^\circ$. 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 $\text{AgPW}_{11}\text{-TiO}_2$ films on the ITO substrate. As shown in Fig. 2, both the TiO_2 and $\text{AgPW}_{11}\text{-TiO}_2$ films showed typical granular patterns and no cracks. The film thickness was estimated to be approximately $7 \text{ }\mu\text{m}$ (Fig. 1(b)). The pure TiO_2 film consisted of particles with size in the range of $10\text{--}40 \text{ nm}$ (Fig. 2(a)); however, the average particle size was slightly larger ($15\text{--}60 \text{ nm}$) 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 $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ 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 $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ 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 $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ 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 $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode were small and

Fig. 1. (a) XRD patterns of ITO, TiO_2/ITO and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrodes. (b) Cross-sectional SEM image of TiO_2/ITO film layer.

Fig. 2. SEM images of TiO_2/ITO (a) and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ (b) electrodes. Insets show particle size distributions.

showed no obviously differences. However, when the applied voltage was more than 1.3 V vs. Ag/AgCl the anode currents of the TiO_2/ITO electrode and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode increased gradually as the voltage increased. Moreover, the increase of the range of the latter was clearly greater than that of

Fig. 3. Linear sweep voltammetry curves of $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ and TiO_2/ITO electrodes in aqueous Na_2SO_4 solution (0.1 mol L^{-1}) under no illumination.

the former. In other words, a larger applied voltage led to a greater difference in their catalytic behaviors. At an applied voltage of 1.5 V vs. Ag/AgCl, the anode current density of the TiO_2/ITO electrode was less than 0.3 mA cm^{-2} ; however, that of the $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode reached 1.5 mA cm^{-2} . Thus, AgPW_{11} has a pronounced electrocatalytic effect on water oxidation at a TiO_2 anode, particularly at a higher applied voltage. To further verify the catalytic effect, the behaviors of TiO_2/ITO , $\text{PW}_{11}\text{-TiO}_2/\text{ITO}$, $\text{AgNO}_3\text{-TiO}_2/\text{ITO}$, and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrodes at bias voltages of 1.5 V vs. Ag/AgCl were studied by chronoamperometry. As shown in Fig. 4, their anode currents were stable in the range of 300 s, and their current densities were -0.1 , -0.2 , -0.4 , and -1.0 mA cm^{-2} , respectively. The current density of the $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode was 10 times as high as that of the TiO_2/ITO electrode and 2.5 times as high as that of $\text{AgNO}_3\text{-TiO}_2/\text{ITO}$ electrode.

Electrochemical impedance spectra of TiO_2/ITO , $\text{AgNO}_3\text{-TiO}_2/\text{ITO}$ and $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrodes were measured at a bias voltage of -0.3 V vs. Ag/AgCl (Fig. 5). The Nyquist curves of the three electrodes represent the charge transfer resistance (R_{ct}) at the electrode-electrolyte interface. A variety of impedance parameters can be obtained by fitting the Nyquist curve [32]. The R_{ct} values were 4774, 1257 and 840Ω , respectively. The $\text{AgPW}_{11}\text{-TiO}_2/\text{ITO}$ electrode showed the lowest R_{ct}

Fig. 4. Current density-time curves of AgPW₁₁-TiO₂/ITO, AgNO₃-TiO₂/ITO, PW₁₁-TiO₂/ITO and TiO₂/ITO electrodes in aqueous Na₂SO₄ solution (0.1 mol L⁻¹) under an applied potential of 1.5 V vs. Ag/AgCl.

Fig. 5. (a) Nyquist curves of the AgPW₁₁-TiO₂/ITO, AgNO₃-TiO₂/ITO and single TiO₂/ITO electrodes in Na₂SO₄ (0.1 mol L⁻¹) at -0.3 V vs. Ag/AgCl without irradiation. The frequency range was 0.01 to 10⁵ Hz, with the ac amplitude perturbed at 5 mV; (b) An equivalent circuit, which exhibited a two-time constant model, where: R_s is the series resistance, CPE represents the constant phase elements, the resistance related to the surface porosity is depicted by R_p , and the charge transfer resistance related to the electrode and electrolyte interface is R_{ct} .

value, which suggested that AgPW₁₁ had the capacity to transfer electrons at the electrode-electrolyte interface. This result explains the catalytic effect of the AgPW₁₁-TiO₂/ITO electrode for water oxidation. The R_{ct} value of the AgPW₁₁-TiO₂/ITO electrode was lower than that of AgNO₃-TiO₂/ITO, which suggests that the PW₁₁ ligand plays an important role in transferring electrons and proton in the water oxidation process.

3.3. Photo-electrocatalysis of AgPW₁₁ on TiO₂/ITO electrode

Photo-electrocatalysis with the TiO₂/ITO and

AgPW₁₁-TiO₂/ITO electrodes was performed in 0.1 mol L⁻¹ Na₂SO₄ solution under simulated AM 1.5 illumination (100 mW cm⁻²). The *I*-*V* curves of AgPW₁₁-TiO₂/ITO and TiO₂/ITO electrodes under light irradiation are shown in Fig. S2. The current densities of both electrodes increased upon irradiation. Thus, light has a certain role in the process. Furthermore, AgPW₁₁-TiO₂/ITO showed a higher current density than that of TiO₂/ITO under illumination. Fig. 6 shows current density-time curves measured at different bias voltages for the TiO₂/ITO electrode and the AgPW₁₁-TiO₂/ITO electrode. As shown in Fig. 6(a), the TiO₂/ITO electrode began to give out an anode current under no illumination when the applied voltage was more than 1.4 V vs. Ag/AgCl; however, under illumination it exhibited an anode current only when the applied voltage was greater than 1.2 V vs. Ag/AgCl, and the anode current density was approximately 0.3 mA cm⁻² and the photocurrent density was approximately 0.2 mA cm⁻² at the applied voltage of 1.5 V vs. Ag/AgCl. For the AgPW₁₁-TiO₂/ITO electrode (Fig. 6(b)), the anode current density reached 1.4 mA cm⁻², i.e., 4.6 times as high as that of the TiO₂/ITO electrode at 1.5 V vs. Ag/AgCl under illumination. The photocurrent density of the

Fig. 6. Current density-time curves of TiO₂/ITO electrodes (a) and AgPW₁₁-TiO₂/ITO electrodes (b) with light on-off under simulated AM 1.5 illumination (100 mW cm⁻²) in Na₂SO₄ aqueous solution (0.1 mol L⁻¹) with varying bias potentials of 0.01, 0.60, 1.20, 1.40, 1.44 and 1.50 V vs. Ag/AgCl.

AgPW₁₁-TiO₂/ITO electrode was approximately 0.3 mA cm⁻². Because the oxidation of water is a slow reaction, the illumination could not improve the photocurrent greatly and we observed tailed photocurrent peaks [33].

To determine the stability of AgPW₁₁-TiO₂/ITO electrode, we examined reuse of the electrode. Fig. 7 shows the anode current density of the AgPW₁₁-TiO₂/ITO electrode after 15 reuses. The anode current was more than three times as high as that of the TiO₂/ITO electrode although the values decreased slightly as the number of uses increased. Thus, the AgPW₁₁-TiO₂/ITO electrode was relatively stable. For reuse of the AgPW₁₁-TiO₂/ITO electrode, EDX analysis showed the relative element composition. As shown in Table S1, the content of P, W and Ag remained identical for the reused electrodes. Furthermore, AgPW₁₁ was retained on the electrode after multiple catalysis reactions. To determine the amount of Ag adsorbed from AgPW₁₁ and AgNO₃ onto the TiO₂ anode, ICP measurements were performed, as listed in Table S2. The amounts of Ag adsorbed for AgPW₁₁ and AgNO₃ on AgPW₁₁-TiO₂/ITO and AgNO₃-TiO₂/ITO electrodes were similar at 1.2756 and 1.3259 ppm, respectively. Hence, the difference in the catalytic activity could be attributed to the polyoxometalate ligand.

3.4. Electrocatalytic water oxidation mechanism of [H₃Ag(H₂O)PW₁₁O₃₉]³⁻

In the phosphate buffer solution (pH = 6.0, 0.1 mol L⁻¹), with the use of a glassy carbon electrode as the working electrode, the cyclic voltammetry of AgPW₁₁ at concentrations of 0, 0.05, 0.10, 0.15 and 0.20 mmol L⁻¹ were studied under the conditions of 1.0–1.6 V vs. Ag/AgCl at a scanning speed of 100 mV s⁻¹. As shown in Fig. 8, the anode currents were considerably enhanced in the solution containing AgPW₁₁, and the larger concentration of AgPW₁₁ resulted in greater enhancement of the anode currents when the applied voltage was more than 1.25 V vs. Ag / AgCl. In the range of 1.1–1.6 V vs. Ag/AgCl, a pair of redox peaks A₁ and C₁ (*E*_{pa} ≈ 1.31 V, *E*_{pc} ≈ 1.23 V) appeared with

Fig. 7. Current density-time curves of AgPW₁₁-TiO₂/ITO electrodes with light on-off under simulated AM 1.5 illumination (100 mW cm⁻²) in aqueous Na₂SO₄ solution (0.1 mol L⁻¹) with bias potential held at 1.5 V vs. Ag/AgCl after reuse 1, 2, 3, 4, 5, 10 and 15 times.

Fig. 8. Cyclic voltammogram of AgPW₁₁ at different concentrations in phosphate buffer (0.1 mol L⁻¹, pH = 6.0) at a scan rate of 100 mV s⁻¹.

a ΔE_p value of more than 58 mV, indicating that the electrochemical reaction is quasi-reversible at the electrode surface.

For quasi-reversible processes, the transferred electrons can be calculated by the formula: $\Delta E_p = E_{pa} - E_{pc} = 58/n$ (mV, 25 °C). As shown in Fig. 8, when the sweep speed was 100 mV s⁻¹, $\Delta E_p = E_{pa} - E_{pc} = 1.31 - 1.23 = 0.08$ V, from which *n* was determined to be 0.73. Therefore, the number of electrons transferred in the A₁–C₁ process was considered to be 1. Thus, we deduced that the electrode process was a Ag^I/Ag^{II} redox process. The peak at 1.5 V could be assigned to the silver transformation Ag^{II} → Ag^{III} (AgO⁺) [34]. Furthermore, the cyclic voltammogram of AgPW₁₁ was compared with that of AgNO₃ in Fig. S3. We found that the redox peaks of AgNO₃ were similar to those of AgPW₁₁ in the positive potential region, which corresponded to the redox processes of silver. Furthermore, AgPW₁₁ featured a higher peak current and lower peak potential.

Fig. 9(a) is a cyclic voltammetry curve of AgPW₁₁ at different sweep rates in the range of 1.0–1.4 V vs. Ag/AgCl. When the sweep speed was increased from 100 to 900 mV s⁻¹, the cathode reduction potential (C₁) moved to negative potential and the anodic oxidation potential (A₁) moved to a more positive potential. These shifts resulted in an increase of the peak-to-peak potential difference (ΔE_p) of the oxidation peak A₁ and the reduction peak C₁ increased. These results suggest that the diffusion speed could not keep up with the scanning speed at excessively fast scanning speeds. Furthermore, the A₁–C₁ electrode process was a quasi-reversible process. The A₁, C₁ peak current values are plotted against the square root of sweep rates ($v^{1/2}$), as shown in Fig. 9(b); the *R*² values of linear fits were 0.99507 and 0.99851, respectively. This good linear relationship indicated that the A₁–C₁ electrode process was mainly controlled by diffusion [34,35].

To investigate the effect of pH on the AgPW₁₁ catalysis, eight groups of phosphate buffer solutions with different pH were prepared, and an equal amount of 0.2 mmol L⁻¹ of AgPW₁₁ was added. Fig. 10(a) shows cyclic voltammetry curves measured in solutions of different pH. The peak potentials shifted in a negative direction with increasing pH. As shown in Fig. 10(b), *E*_{pc} exhibited a linear relationship with the pH values with a slope

Fig. 9. (a) Cyclic voltammogram of 0.2 mmol L⁻¹ AgPW₁₁ in phosphate buffer (0.1 mol L⁻¹, pH = 6.0) at different sweep speeds, from inside to out followed by 100, 200, 300, 400, 500, 600, 700, 800, and 900 mV s⁻¹; (b) Curve of the peak current value of the redox peak A₁–C₁ versus the square root of the sweep speed. The applied voltage of the cyclic voltammogram was 1.0–1.4 V vs. Ag/AgCl.

Fig. 10. (a) Cyclic voltammogram of 0.2 mmol L⁻¹ AgPW₁₁ in different phosphate buffers having different pH values; from left to right: pH = 5.3, 5.5, 5.7, 5.9, 6.1, 6.3, 6.5 and 6.7. (b) Curve of E_{pc} vs pH.

of -0.08882 . According to the Nernst equation [36] $S = 2.303RTm/(anF)$, where S is the slope of E_{pc} , m is the number of transferred protons, T is the temperature, n is the number of transferred electrons, R and F are constants, and α is the transfer coefficient (usually 0.5 for quasi-reversible processes). Hence, the number of transferred protons was deduced to be 1. Therefore, the electrode process of A₁–C₁ was considered to be $1e^- \sim 1H^+$ for $[H_3Ag^I(H_2O)PW_{11}O_{39}]^{3-}$, expressed below as:

In the cyclic voltammetry curves, an oxidation process of Ag^{II}/Ag^{III} was not found; however, we noted that the oxidation current of Ag^I→Ag^{II} was obviously higher than that of the reduction current of Ag^{II}→Ag^I. The disproportionation reaction of Ag^{II} has been reported [37]. Combined with our previous result [27], we deduced that the following disproportionation reaction likely occurred:

followed by water oxidation:

where Eq. (3) is the rate-determined reaction. (3)

4. Conclusions

In the paper, the electrocatalytic and photoelectrocatalytic effects of AgPW₁₁ for water oxidation have been investigated through its immobilization on a TiO₂ electrode. We found that the AgPW₁₁-TiO₂/ITO electrode produced anode currents respectively 10 and 2 times as high as those of the TiO₂/ITO electrode and the AgNO₃-TiO₂/ITO electrode. At higher applied voltages, AgPW₁₁ catalyst exhibited improved catalytic activity. The catalytic effect was attributed to the capacity of the AgPW₁₁-TiO₂/ITO electrode to transfer electrons at the electrode-electrolyte interface. This result proves the critical role of the polyoxometalate ligand in transferring protons and electrons during water oxidation process. However, the photocurrent was not noticeably enhanced under illumination. The AgPW₁₁-TiO₂/ITO electrode was relatively stable. A mechanism for the electrocatalytic water oxidation by AgPW₁₁ is proposed

Graphical Abstract

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Catalytic effects of $[\text{Ag}(\text{H}_2\text{O})(\text{H}_3\text{PW}_{11}\text{O}_{39})]^{3-}$ on a TiO_2 anode for water oxidation

Jiansheng Li, Lei Wang, Wansheng You *, Meiying Liu *, Lancui Zhang, Xiaojing Sang
Liaoning Normal University

$[\text{H}_3\text{Ag}^{\text{I}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$ was immobilized on a TiO_2/ITO electrode, and showed enhanced electrocatalytic activity for water oxidation to O_2 . Our results indicate that the $[\text{H}_3\text{PW}_{11}\text{O}_{39}]^{4-}$ ligand plays an important role in transferring electrons and protons in water oxidation process.

based on our CV studies. The oxidation of AgPW_{11} is a quasi-reversible process related to one proton and one electron transfer. We deduced that disproportionation of $[\text{H}_2\text{Ag}^{\text{II}}(\text{H}_2\text{O})\text{PW}_{11}\text{O}_{39}]^{3-}$ might occur, resulting in $[\text{H}_3\text{Ag}^{\text{III}}\text{OPW}_{11}\text{O}_{39}]^{3-}$, which oxidizes water to O_2 .

References

- [1] M. G. Walter, E. L. Warren, J. R. Mckone, S. W. Boettcher, Q. X. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.*, **2010**, 110, 6446–6473.
- [2] X. Sala, I. Romero, M. Rodríguez, L. Escriche, A. Llobet, *Angew. Chem. Int. Ed.*, **2009**, 48, 2842–2852.
- [3] H. Yamazaki, A. Shouji, M. Kajita, M. Yagi, *Coord. Chem. Rev.*, **2010**, 254, 2483–2491.
- [4] R. Brimblecombe, G. C. Dismukes, G. F. Swiegers, L. Spiccia, *Dalton Trans.*, **2009**, 9374–9384.
- [5] W. C. Xu, H. X. Wang, *Chin. J. Catal.*, **2017**, 38, 991–1005.
- [6] X. Q. Du, J. W. Huang, Y. Y. Feng, Y. Ding, *Chin. J. Catal.*, **2016**, 37, 123–134.
- [7] H. Lv, Y. V. Geletii, C. Zhao, J. W. Vickers, G. Zhu, Z. Luo, J. Song, T. Lian, D. G. Musaev, C. L. Hill, *Chem. Soc. Rev.*, **2012**, 41, 7572–7589.
- [8] A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N. D. McDaniel, S. Bernhard, M. Bonchio, *J. Am. Chem. Soc.*, **2008**, 130, 5006–5007.
- [9] M. Orlandi, R. Argazzi, A. Sartorel, M. Carraro, G. Scorrano, M. Bonchio, F. Scandola, *Chem. Commun.*, **2010**, 46, 3152–3154.
- [10] Y. V. Geletii, Z. Q. Huang, Y. Hou, D. G. Musaev, T. Q. Lian, C. L. Hill, *J. Am. Chem. Soc.*, **2009**, 131, 7522–7523.
- [11] Y. V. Geletii, C. Besson, Y. Hou, Q. S. Yin, D. G. Musaev, D. Quiñero, R. Cao, K. I. Hardcastle, A. Proust, P. Kögerler, C. L. Hill, *J. Am. Chem. Soc.*, **2009**, 131, 17360–17370.
- [12] A. Sartorel, P. Miró, E. Salvadori, S. Romain, M. Carraro, G. Scorrano, M. Di Valentin, A. Llobet, C. Bo, M. Bonchio, *J. Am. Chem. Soc.*, **2009**, 131, 16051–16053.
- [13] M. Murakami, D. Hong, T. Suenobu, S. Yamaguchi, T. Ogura, S. Fukuzumi, *J. Am. Chem. Soc.*, **2011**, 133, 11605–11613.
- [14] P. E. Car, M. Guttentag, K. K. Baldrige, R. Alberto, G. R. Patzk, *Green Chem.*, **2012**, 14, 1680–1688.
- [15] X. B. Han, Z. M. Zhang, T. Zhang, Y. G. Li, W. B. Lin, W. S. You, Z. M. Su, E. B. Wang, *J. Am. Chem. Soc.*, **2014**, 136, 5359–5366.
- [16] Q. S. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle, C. L. Hill, *Science*, **2010**, 328, 342–345.
- [17] Z. Q. Huang, Z. Luo, Y. V. Geletii, J. W. Vickers, Q. S. Yin, D. Wu, Y. Hou, Y. Ding, J. Song, D. G. Musaev, C. L. Hill, T. Q. Lian, *J. Am. Chem. Soc.*, **2011**, 133, 2068–2071.
- [18] M. Natali, S. Berardi, A. Sartorel, M. Bonchio, S. Campagnac, F. Scandola, *Chem. Commun.*, **2012**, 48, 8808–8810.
- [19] S. Tanaka, M. Annaka, K. Sakai, *Chem. Commun.*, **2012**, 48, 1653–1655.
- [20] F. Y. Song, Y. Ding, B. C. Ma, C. M. Wang, Q. Wang, X. Q. Du, S. Fu, J. Song, *Energy Environ. Sci.*, **2013**, 6, 1170–1184.
- [21] J. Soriano-López, S. Goberna-Ferrón, L. Vígara, J. J. Carbó, J. M. Poblet, J. R. Galán-Mascarós, *Inorg. Chem.*, **2013**, 52, 4753–4755.
- [22] M. K. Kanan, D. G. Nocera, *Science*, **2008**, 321, 1072–1075.
- [23] J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodríguez, C. Viæas, T. Parella, A. Llobet, *Angew. Chem. Int. Ed.*, **2008**, 47, 5830–5832.
- [24] R. Brimblecombe, G. F. Swiegers, G. C. Dismukes, L. Spiccia, *Angew. Chem. Int. Ed.*, **2008**, 47, 7335–7338.
- [25] F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. R. Gonzalez, H. Amenitsch, T. Da Ros, L. Casalis, A. Goldoni, M. Marcaccio, G. Scorrano, G. Scoles, F. Paolucci, M. Prato, M. Bonchio, *Nat. Chem.*, **2010**, 2, 826–831.
- [26] S. M. Lauinger, J. M. Sumliner, Q. S. Yin, Z. H. Xu, G. J. Liang, E. N. Glass, T. Q. Lian, C. L. Hill, *Chem. Mater.*, **2015**, 27, 5886–5891.
- [27] Y. Cui, L. Shi, Y. Y. Yang, W. S. You, L. C. Zhang, Z. M. Zhu, M. Y. Liu, L. C. Sun, *Dalton Trans.*, **2014**, 43, 17406–17415.
- [28] C. Brevard, R. Schimpf, G. Tourné, C. M. Tourne, *J. Am. Chem. Soc.*, **1983**, 105, 7059–7063.
- [29] S. Ito, P. Chen, P. Comte, S. Ito, P. Chen, P. Comte, M. K.

- Nazeeruddin, P. Liska, P. Péchy, M. Grätzel, *Prog. Photovoltaics*, **2007**, 15, 603–612.
- [30] N. Lu, Y. H. Zhao, H. B. Liu, Y. H. Guo, X. Yuan, H. Xu, H. F. Peng, H. W. Qin, *J. Hazard. Mater.*, **2012**, 199–200, 1–8.
- [31] J. S. Li, X. J. Sang, W. L. Chen, L. C. Zhang, Z. M. Zhu, Y. G. Li, Z. M. Su, E. B. Wang, *J. Mater. Chem. A*, **2015**, 3, 14573–14577.
- [32] M. Nakogaki, Translated by J. W. Xu, Z. Yan, *Basic of Membrane Science*, Shanghai Science Press, Shanghai, **1984**, 203.
- [33] R. Brimblecombe, A. Koo, G. C. Dismukes, G. F. Swiegers, L. Spiccia, *J. Am. Chem. Soc.*, **2010**, 132, 2892–2894.
- [34] Q. L. Li, X. Y. Liu, *Anal. Chim. Acta*, **1992**, 258, 171–175.
- [35] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, 2009.
- [36] P. Zuman, *The Elucidation of Organic Electrode Processes*, Academic Press, New York, **1969**, 1–167.
- [37] A. Kumar, P. Neta, *J. Phys. Chem.*, **1979**, 83, 3091–3095.

[Ag(H₂O)(H₃PW₁₁O₃₉)]³⁻修饰的TiO₂阳极对水氧化的催化作用研究

李健生, 王 蕾, 由万胜*, 刘美英#, 张澜萃, 桑晓静

辽宁师范大学功能材料化学研究所, 辽宁大连116029

摘要: 高效的水氧化是实现大规模分解水制氢的瓶颈, 开发稳定、经济、高效的水氧化催化剂是引人关注的. 早在上世纪中期Ag⁺作为水氧化催化剂就有报道, 但尚未见Ag⁺配合物作为分子基水氧化催化剂的报道. 本课题组选择缺位多酸阴离子[H₃PW₁₁O₃₉]³⁻作为配体, 成功研制了银-多酸配合物[H₃Ag^I(H₂O)PW₁₁O₃₉]³⁻(AgPW₁₁)分子基水氧化催化剂, 发现其对使用S₂O₈²⁻化学氧化水具有很好的催化作用, 这主要归功于多酸配体在传输电子和质子的作用, 对理解催化氧化水的机理有重要学术价值.

将分子基催化剂修饰到电极上是实现其电化学催化氧化水的必由之路. 本文采用浸渍法将AgPW₁₁修饰到TiO₂电极上, 成功制备了AgPW₁₁-TiO₂/ITO电极, 并通过XRD, SEM, EDX技术对AgPW₁₁-TiO₂/ITO电极进行了表征. 结果表明, AgPW₁₁被成功负载到TiO₂纳米粒子表面, 它的引入使得TiO₂电极表面的纳米粒子平均尺寸由10–40 nm增加到15–60 nm. 在0.1 mol L⁻¹ Na₂SO₄电解质溶液中利用线性扫描伏安、计时电流和电化学阻抗技术研究了AgPW₁₁-TiO₂/ITO阳极催化氧化水的性能, 结果发现, 当施加偏压大于1.3 V vs. Ag/AgCl时, 随电压升高, AgPW₁₁-TiO₂/ITO电极相比TiO₂/ITO电极有更显著的氧化电流; 当施加偏压在1.5 V vs. Ag/AgCl时, AgPW₁₁-TiO₂/ITO电极氧化电流比TiO₂/ITO电极和AgNO₃-TiO₂/ITO电极分别高出10倍和2.5倍, 这归因于AgPW₁₁-TiO₂/ITO电极上电极-电解质界面具有更低的电荷转移阻抗, 也说明多酸阴离子配体在催化过程中能够更好地传输电子和质子. 在光照条件(100 mW cm⁻²)下, AgPW₁₁-TiO₂/ITO电极有较高的阳极电流, 但光电流并没有明显增加, 这主要是由于修饰电极光生电子-空穴复合速率较快所致. AgPW₁₁-TiO₂/ITO阳极重复使用15次后, 电流密度仍然高出TiO₂/ITO电极3倍以上, 表明AgPW₁₁-TiO₂复合电极稳定性较好. 在0.1 mol L⁻¹磷酸缓冲溶液体系中研究了AgPW₁₁在不同浓度、不同pH值和不同扫速下的循环伏安曲线. 在1.1–1.6 V vs. Ag/AgCl扫描范围和100 mV s⁻¹扫速条件下, 在1.23和1.31 V vs. Ag/AgCl处出现的一对氧化还原峰, 归结为Ag^I/Ag^{II}的1e氧化还原过程. 在1.0–1.4 V vs. Ag/AgCl扫描范围内, 随扫速由100增至900 mV s⁻¹, 阴极还原峰电位负移而阳极氧化峰电位正移, 导致峰-峰电位差ΔE_p增加, 而且氧化峰电流与还原峰电流与扫速平方根呈线性关系, 说明该电极氧化还原过程受扩散控制. 对Ag^I/Ag^{II}的氧化还原过程, 随着pH值由5.3增加到6.7, 氧化还原峰电位负移, 并且E_{pc}与pH值呈现线性关系, 斜率为-0.08882, 根据能斯特方程S = 2.303 RTm/(nF), 推测转移的质子数为1. 由此可知, AgPW₁₁氧化是准可逆的、1电子和1质子转移过程. 推测[H₃Ag^I(H₂O)PW₁₁O₃₉]³⁻氧化生成的[H₂Ag^{II}(H₂O)PW₁₁O₃₉]³⁻可能发生歧化反应, 所生成[H₃Ag^{III}OPW₁₁O₃₉]³⁻进而氧化水放出氧气.

关键词: 水氧化; 电催化; 光电化学; 二氧化钛; 多金属氧酸盐; 银离子配合物

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*通讯联系人. 电话/传真: (0411)82159378; 电子信箱: wsyou@lnnu.edu.cn

#通讯联系人. 电话/传真: (0411)82159256; 电子信箱: myliu312@yahoo.com

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