

Facile deposition of cobalt oxide based electrocatalyst on low-cost and tin-free electrode for water splitting

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Abstract

Facile deposition of a water-splitting catalyst on low-cost electrode materials could be attractive for hydrogen production from water and solar energy conversion. Herein we describe fast electrodeposition of cobalt-based water oxidation catalyst (Co-WOC) on simple graphite electrode for water splitting. The deposition process is quite fast, which reaches a plateau in less than 75 min and the final current density is $\sim 1.8 \text{ mA/cm}^2$ under the applied potential of 1.31 V at pH = 7.0. The scanning electron microscopy (SEM) study shows the formation of nanometer-sized particles (10–100 nm) on the surface of the electrode after only 2 min and micrometer-sized particles (2–5 μm) after 90 min of electrolysis. X-ray photoelectron spectroscopy (XPS) data demonstrate the as-synthesized ex-situ catalyst mainly contains Co^{2+} and Co^{3+} species incorporating a substantial amount of phosphate anions. These experiments suggest that cost-efficient cobalt oxide materials on graphite exhibit alluring ability for water splitting, which might provide a novel method to fabricate low-cost devices for electrochemical energy storage.

Key words

electrocatalyst; water splitting; water oxidation; hydrogen production

1. Introduction

The catalytic oxidation side of water splitting coupled with four electrons and four protons has been considered as the major scientific challenge in artificial photosynthesis, which is very important to the future development of solar hydrogen technologies and hydrogen-based fuel cells [1,2]. In nature, photosystem II (PS II) utilizes a cube-like CaMn_4O_5 active site to mediate catalytic water oxidation. The structure and function of PS II inspired many scientists to study model complexes and mimic the function of PS II, but most examples have limited efficiency in water oxidation [3–6]. Recently, a simple in-situ electrodeposition of cobalt-based water oxidation catalyst (Co-WOC) on indium tin oxide (ITO) or fluorine-doped tin oxide (FTO) electrodes has been developed in aqueous neutral phosphate solution [7–11]. Co-WOC shows good activity ($\sim 1.1 \text{ mA/cm}^2$ current density on ITO) for oxygen evolution at a moderate overpotential ($< 500 \text{ mV}$). Because of its many fascinating features, such as robustness, benign operating conditions for catalysis (pH 7.0, room tem-

perature), self-healing properties, and elemental abundance, Co-WOC attracts much attention for fundamental research and shows possibility of practical applications in “personalized energy” concept [12]. Some other cobalt oxide water oxidation catalysts (Co_3O_4 , Co_2O_3 et al.) are also reported [13–21]. Subsequently, photodeposition of Co-WOC on a variety of semiconductors (ZnO [22], WO_3 [23], Fe_2O_3 [24,25], BiVO_4 [26,27], TaON [28], TiO_2 [29]) has been provided in the literature for solar-driven water splitting. The functionalized photoanodes by Co-WOC clearly exhibit their abilities by utilizing the photogenerated holes for enhancing solar-driven oxygen production. More recently, the work has been done to couple Co-WOC with visible light-absorbing materials (p-type/n-type silicon materials) to make an “artificial leaf” for photoelectrochemical water splitting [30–32].

ITO and FTO have been widely used as conductive electrodes in the above-mentioned water oxidation systems and many optoelectronic devices, such as solar cells and organic light emitting diodes [31,33–36]. However, the limited availability of indium and tin elements could significantly increase the cost. The instability of ITO/FTO in the presence of base

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or acid may cause serious problems in the practical applications of these devices [37]. The structural defects in FTO could also result in serious current leakage [38–40]. Moreover, the fabrication of ITO/FTO films requires cost-inefficient techniques, such as physical vapor deposition, chemical vapor deposition and magnetron sputtering. Thus, the search for alternative electrodes with low-cost and high stability to replace ITO and FTO is a crucial goal for electrochemical- and/or solar-driven water splitting.

In the present study, we report the method of direct deposition of Co-WOC on cheap graphite materials for catalytic water splitting. The deposition process is quite fast and reaches equilibrium in less than 75 min when the applied potential is 1.31 V versus normal hydrogen electrode (NHE). The final current density is $\sim 1.8 \text{ mA/cm}^2$, which is higher than the values obtained from ITO or FTO electrodes under the same applied potential.

2. Experimental

Materials. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%), KH_2PO_4 (99.5%) and $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All electrolyte solutions were prepared with deionized water (Blue Water Industry, resistivity: $18 \text{ M}\Omega\cdot\text{cm}$). Graphite rod was purchased from Alfar Aesar (diameter: 6.15 mm, 99.9995% (metals basis)).

Electrochemical methods. All electrochemical experiments were performed at room temperature with a CH Instruments potentiostat 660D (purchased from Shanghai ChenHua Instrument Co., Ltd.), while an Ag/AgCl electrode (3 mol/L KCl) was used as the reference electrode and a Pt wire as the counter electrode. The electrolyte was 0.1 mol/L potassium phosphate buffer (KPi) solution containing 0.5 mmol/L Co^{2+} at pH 7.0 unless otherwise noted. All potentials reported in this manuscript were converted to the NHE reference scale, using $E(\text{NHE}) = E(\text{Ag}/\text{AgCl}) + 0.210 \text{ V}$. All overpotentials were calculated by $\eta = E(\text{NHE}) - 0.82 \text{ V}$.

Cyclic voltammetry. A clear graphite rod was used as the working electrode and a Pt wire was used as the counter electrode in all cases. The cyclic voltammograms were collected at 100 mV/s in 0.1 mol/L KPi electrolyte containing 0.5 mmol/L Co^{2+} or no Co^{2+} at pH 7.0.

Bulk electrolysis and in situ catalyst formation. The bulk electrolysis was performed in an electrochemical cell (volume: 50–60 mL) with a graphite rod as the working electrode, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The cell typically contains 40 mL 0.1 mol/L KPi solution (pH 7.0). The concentration of cobalt ions is 0.5 mmol/L. Typically, a 2–3 cm^2 area of the graphite rod was immersed into the electrolyte. The electrolysis was carried out at variable potentials. The distance between the surface of graphite electrode and the reference electrode was controlled within 5–8 mm and no iR compensation was applied during electrolysis (i is the stable current, R is the compensating resistance). For determination of the quantity of oxygen generated during catalysis, oxygen was collected from

the headspace. The weight of as-synthesized catalyst on the graphite was obtained by calculating the difference before and after the bulk electrolyses.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). SEM images and EDX spectra were recorded on a JEOL JSM-7500F field emission scanning electron microscope. The samples were prepared via electrodeposition at a fixed potential. Subsequently, the catalyst samples were rinsed with deionized water and dried with exposure to air for a few hours. The images of the catalyst morphology on the surface of graphite for bulk electrolysis were examined after 0 min, 2 min, 5 min, 20 min, and 90 min, respectively.

X-ray photoelectron spectroscopy (XPS). XPS spectra were acquired by ESCALAB 250 (Thermo-VG Scientific). The sample was prepared after the electrodeposition for more than 10 h in 0.1 mol/L KPi electrolyte containing 0.5 mmol/L Co^{2+} at pH 7.0. The spectrum was calibrated by C 1s peak (285.0 eV).

3. Results and discussion

Figure 1(a) shows the cyclic voltammetry (CV) scans of a graphite rod as the working electrode in a 0.1 mol/L potassium phosphate buffer (KPi) solution containing 0.5 mmol/L Co^{2+} at pH = 7.0. The potential was measured against the Ag/AgCl electrode and converted to NHE potentials and a platinum wire was used as the counter electrode. The results demonstrate a strong oxidation curve with the onset at $\sim 1.1 \text{ V}$ versus NHE (note: all the potentials reported in this paper are versus NHE). A broad shoulder at ~ 1.0 – 1.3 V could be resulted from the oxidation of Co^{2+} ions ($E_p(\text{Co}^{2+}/\text{Co}^{3+}) = 1.13 \text{ V}$ [7]). The sharp increase of the current density after 1.3 V indicates strong catalytic water oxidation. Control experiment exhibits no appreciable catalytic curve at ~ 0.2 – 1.6 V in the absence of Co^{2+} ions, indicating the catalytic role of cobalt species when graphite materials are used as the working electrode.

Figure 1(b) shows the data of bulk electrolysis using a graphite rod as the working electrode in 40 mL neutral KPi solution containing 0.5 mol/L Co^{2+} . A rising current density is observed when the applied potential is 1.31 V and the plot rapidly levels off after 75 min, demonstrating a fast deposition process. During bulk electrolysis, a thin black film is clearly seen on the surface of the electrode, as shown in Figure 1(b) (inset). Meanwhile, gas bubbles are increasingly emerged around the rod and subsequently released out of the aqueous solution. The gas has been confirmed to be oxygen by gas chromatography and fluorescence-based oxygen sensor. The final current density is $\sim 1.8 \text{ mA/cm}^2$, which is higher than the value using ITO as the electrode for bulk electrolysis ($\sim 1.1 \text{ mA/cm}^2$). The CV scan of graphite electrode coated with Co-WOC film in KPi electrolyte solution gave a lower overpotential for water oxidation than that of the clean graphite electrode, further confirming the catalytic role of Co-WOC on the surface of graphite electrode.

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