Supporting Information

Facile Deposition of Nanostructured Cobalt Oxide Catalyst from Molecular Cobaloximes for Efficient Water Oxidation

Ali Han, Haotian Wu, Zijun Sun, Hongxin Jia and Pingwu Du*

CAS Key Laboratory of Materials for Energy Conversion & Department of Materials Science and Engineering, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, China 230026

* Corresponding author: dupingwu@ustc.edu.cn

Experimental Methods

Materials. Cobalt chloride hexahydrate, potassium hydroxide, dimethylglyoxime ($dmgH_2$), 4-(dimethylamino)pyridine(4-Me_2N-py), pyridine, potassium hexafluorophosphate, acetone, triethylamine, methanol, were commercially available without further purification (J&K Chemicals). All electrolyte solutions were prepared with deionized water (Blue water Industry, resistivity: 18 MΩ·cm). The borate buffers (0.1 M Bi, 0.3 M Bi, 0.5 M Bi) were prepared starting with boric acid, deionized water and potassium hydroxide. The cobalt complexes Co(4-Me_2N-py)Cl (**1**), Co(dmgH)($dmgH_2$)Cl_2 (**2**), Co$(dmgH)_2$pyCl (**3**), Co$(dmgH)_2(py)_2PF_6$ (**4**) were synthesized according to reported method.[1, 2]

Electrochemical methods. All electrochemical experiments were performed at room temperature with a 660D CH Instrument potentiostat (purchased from Shanghai Chen Hua Instrument Co., Ltd.). The Ag/AgCl electrode (3 M KCl, the potential is 0.210 V vs. NHE) was used as the reference electrode, Pt wire as the counter electrode and fluorine doped tin oxide (FTO) electrode or glassy carbon electrode as the working electrodes. 0.1 M borate buffer (pH=9.2) was used as the electrolyte except as otherwise noted. Electrolysis was carried out at variable potentials without iR compensation. All potentials reported in this paper were converted to the Ag/AgCl reference scale.

Cyclic voltammetry. Glassy carbon electrode was used as the working electrode to obtain cyclic voltammograms. Prior to experiments, the GC electrode was successively polished with 1 μm, 0.3 μm, and 0.05 μm Al_2O_3 powder and cleaned with deionized water for three times. All the cyclic voltammograms were measured at 100 mV/s in 0.1 M electrolytes containing 1.0 mM cobalt complex (or cobalt complex-free for comparation). The CV scans were recorded in a range of 0 V - +1.5 V. There were iR compensations and no stirring were used for the CV tests.

Bulk electrolysis. The films deposition were performed at +1.1 V or +1.5 V in Bi solution at pH 9.2 containing 1 mM cobaloximes **1-4**, respectively. After deposition at +1.1 V or +1.5 V, the films deposited FTO were washed with deionized water and dried in the air and then transferred to a fresh aqueous solution with no cobalt complexes for bulk electrolysis at +1.1 V to compare the catalytic activities of films deposited from different cobalt precursors. Prior to tests, the FTO electrodes were ultrasonicated in deionized water, ethanol and deionized water for 5 minutes successively and dried in the air.

The Faradaic efficiency. A fluorescence-based oxygen sensor (Ocean Optics) was used for the quantitative detection of O_2. The experiment was performed in a gas-tight electrochemical cell. The solution was degassed by bubbling with high purity N_2 for 2 hours with vigorous stirring. CoOx-**1** was prepared by electrodeposition at +1.5 V for 7 hours. The reference electrode was positioned several mm from the working electrode. The phase shift of the O_2 sensor on the FOXY probe, recorded at 1s intervals, was converted into the partial pressure of O_2 in the headspace. After recording the partial pressure of O_2 for 2 hours in the absence of an applied potential, electrolysis was initiated at +1.1 V without iR drop compensation.

Scanning electron microscopy (SEM). The morphology and composition of the catalysts were examined using a SIRION200 Schottky field emission scanning electron microscope (SFE-SEM). The detected samples were rinsed with deionized water and dried in the air and then coated with Au to make the samples conducting before loading into the instrument. Images were obtained with an acceleration voltage of 5 kV.

X-ray photoelectron spectroscopy (XPS). The elemental composition of the catalyst on the top of FTO and the valence states of metal elements were probed with the ESCALAB 250 X-ray photoelectron spectroscopy (XPS). The sample used for XPS was prepared by electro-deposition for 7 hours. The survey scan and the high resolution Co 2p were shown in Figure 6. The spectra are referenced to the C1s peak (285.0 eV).

References:

1 P. Du, J. Schneider, G. Luo, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 4952-4962.

2 M. Razavet, V. Artero, M. Fontecave, *Inorg.Chem.* **2005**, *44*, 4786-4795.

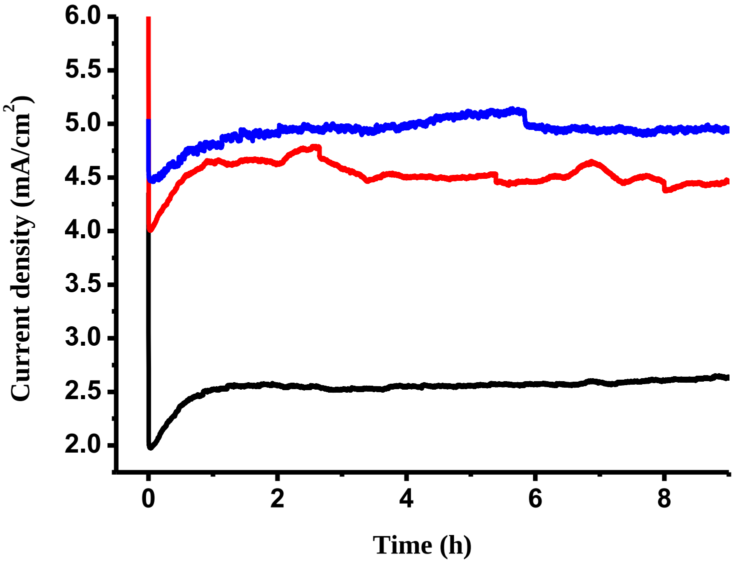

Figure S1. Current density profile of CoO$_X$-**1** catalyst (deposited at +1.5 V) for bulk electrolyses at 1.1V in a cobaloxime-free solution: 0.1 M KBi (black plot), 0.3 M KBi (red plot), 0.5 M KBi (blue plot).

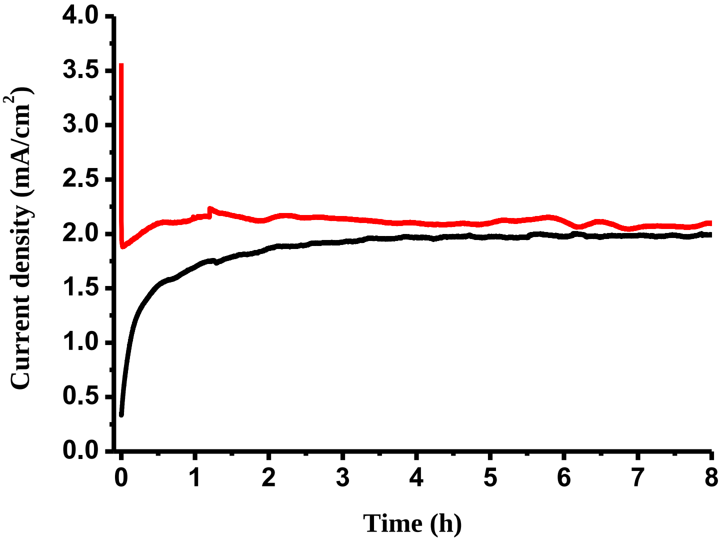

Figure S2. Current density profiles of electrodeposition at +1.1 V containing 1.0 mM cobaloxime **1** (black plot) and current density profiles of the as-synthesized CoOx-**1** for bulk electrolysis at +1.1 V in a cobaloxime-free solution (red plot).

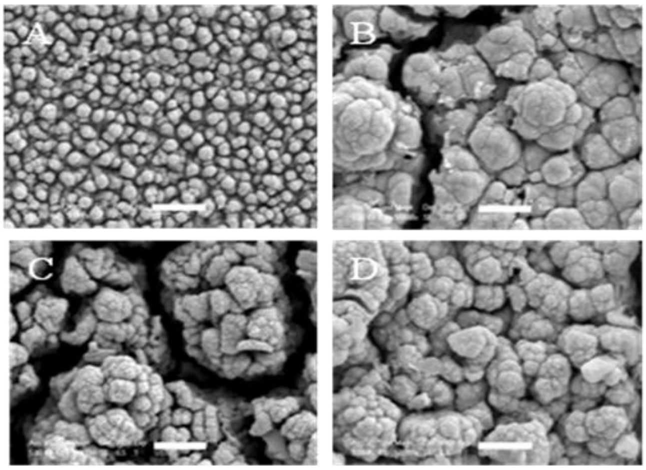

Figure S3. SEM micrographs of catalysts deposited on FTO surface after 7 h of electrolysis at +1.5 V vs Ag/AgCl with 1 mM cobaloximes in a 0.1 M borate buffered solution at pH 9.2. The initial cobaloximes are: (A) 1, (B) 2, (C) 3, (D) 4. Scale bar: 1 μm.

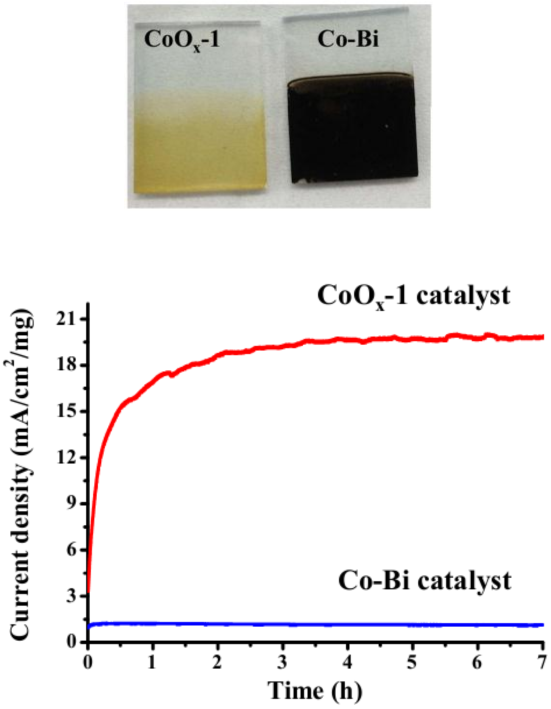

Figure S4. Current density profiles by weight of CoO$_x$-1 (red plot) and Co-Bi (blue plot) catalyst electrodeposited under the same conditions in borate buffer at pH 9.2.

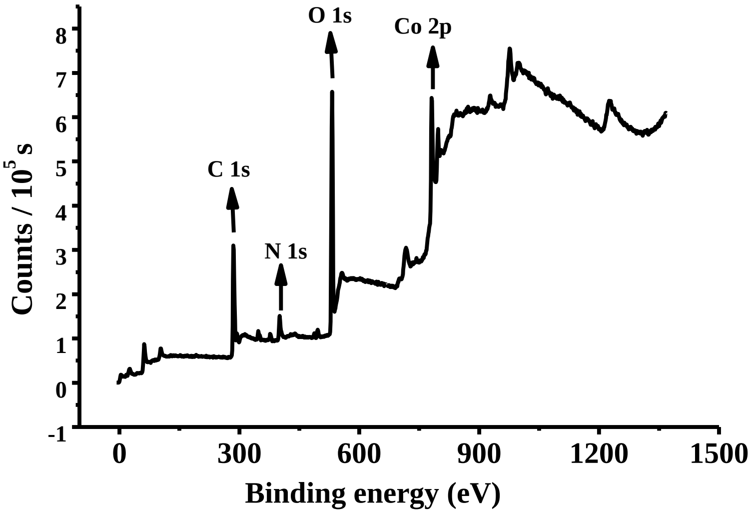

Figure S5. The XPS survey data of CoO_x-**2** electrodeposited at +1.5 V in borate buffer at pH 9.2.

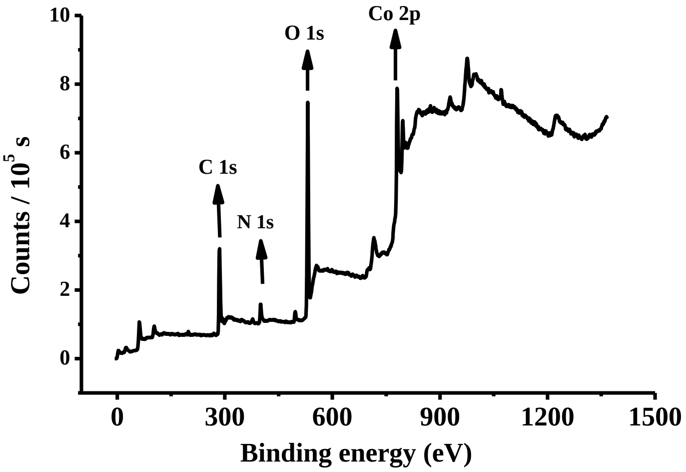

Figure S6. The XPS survey data of CoO_x-**3** electrodeposited at +1.5 V in borate buffer at pH 9.2.

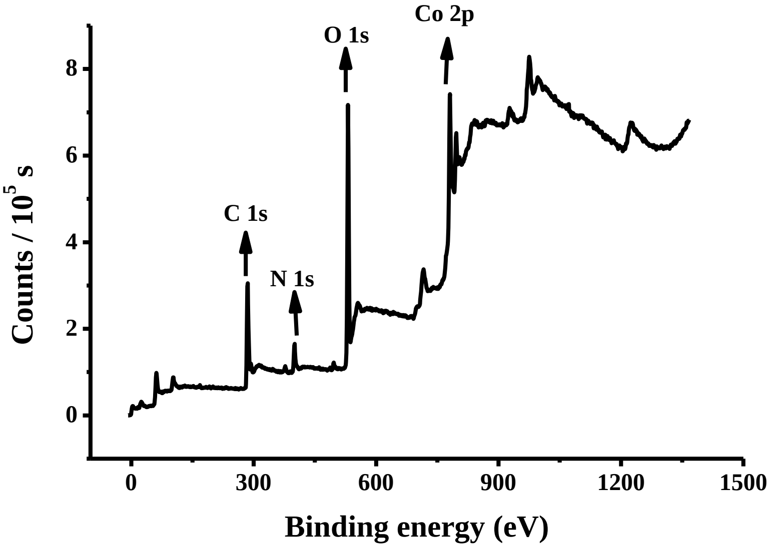

Figure S7. The XPS survey data of CoO_x-**4** electrodeposited at +1.5 V in borate buffer at pH 9.2.