Supporting information

Cobalt Porphyrin Electrode Films for Electrocatalytic Water Oxidation

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Figure S1. The CV scans were recorded by using bare FTO as working electrodes in 0.1 M TBAH (in 40 mL anhydrous DMF) containing 20 nmol **CoP-1/CoP-2** by gradually adding a certain amount of water. The scan rates were 50 mV/s and there were iR compensations (about 3-8 ohms). a, **CoP-1**; b, **CoP-2**.



Figure S2. (a). CVs of the FTO electrode in a 0.91 mM ferricyanide solution at virous scan rates. (b) Plot of maximum peaks of anodic current (ferro/ferricyanide couple) versus $v^{1/2}$.



Figure S3. EDX data for FTO coated with CoP-1 film before bulk electrolysis.



Figure S4. The profiles of bulk electrolysis at 1.3 V for **CoP-1** in 0.5 M and 0.1 M Bi solutions. The working electrodes were FTO coated with 20 nmol **CoP-1**. Black plot: 0.1 M Bi solution; red plot: 0.5 M Bi solution.



Figure S5. The absorption spectra (a for **CoP-1** and b for **CoP-2**) of the FTO electrodes. Black plot: the bare FTO; red plot: the FTO coated with cobalt porphyrin films; blue plot: the FTO after electrolysis and washed by THF.



Figure S6. HRMS spectrometry of **CoP-1** before electrolysis (a) and after electrolysis (b) and **CoP-2** before electrolysis (c) after electrolysis (d).



Figure S7. (a) SEM images for bare FTO and (b) FTO coated with **CoP-2** after bulk electrolysis and washed by THF. (c) EDX data for FTO coated with **CoP-2** after bulk electrolysis and washed by THF.



Figure S8. (left) Cyclic voltammograms obtained using FTO coated with 20 nmol/cm^2 CoP-1 as the working electrode in a 0.5 M Bi solution. Red plot: CoP-1 deposited FTO; blue plot: clean FTO. The black plot was recorded as the control test in the electrolyte solution using a bare FTO as the working electrode. The scan rate is 50 mV/s with iR compensation. (right) The charges passed through the working electrode during 1 hour electrolysis in a 0.5 M Bi solution at 1.3 V (vs Ag/AgCl). Black plot: bare FTO; red plot: CoP-1 deposited FTO; blue plot: clean FTO.



Figure S9. (a) TEM images for the solution after bulk electrolysis using FTO coated with **CoP-1** film as the working electrode. (b) EDX data for the sample measured in (a).



Figure S10. Cyclic voltammograms obtained in a 0.5 M Bi solution containing 20 nmol Co^{2+} by using bare FTO as the working electrodes. After several CV scans, to the electrolyte solution was added excess bpy (80 µmol). black plot- the CV plot with no bpy, red plot- the CV plot with bpy. Both CV scans used the bare FTO as the working electrode. The scan rate is 50 mV/s and there is iR compensation (about 3-8 ohms).



Figure S11. The charge passed through the working electrode during 1 hour electrolysis of **CoP-1** film under different pH solutions at 1.3 V, black plot: pH=4.7; red plot: pH=9.2; green plot: pH=13.0.



Figure S12. The recyclability of **CoP-1** catalyst film for water oxidation under the controlled potential at 1.3 V in a 0.5 M Bi solution. The black plot represented the passed charge and the red plot displayed the current density during electrolysis. For the whole process, the GCE electrode (d= 3 mm) coated with **CoP-1** film was used, washed with THF after 1 hour electrolysis and reused for another cycle of electrolysis.