Supporting Information

Low-temperature Synthesis of Small-size High-entropy Oxide for Water Oxidation

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Experimental Section

Chemicals and Materials: $Co(Ac)_2 \cdot 4H_2O$, $Ni(Ac)_2 \cdot 4H_2O$, $Mn(Ac)_2 \cdot 4H_2O$ and hexamethylenetetramine (HMTA) were purchased from Sinopharm Chemical Reagent Co., Ltd. $Cu(Ac)_2 \cdot H_2O$ was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. $Fe(Ac)_2$ was obtained from Saan Chemical Technology (Shanghai) Co., Ltd. polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO₂₀–PPO₇₀–PEO₂₀, Pluronic P123) was purchased from Shanghai Maclean Biochemical Co., Ltd. Ethylene glycol and absolute ethanol were purchased from Shanghai Titan Scientific Co., Ltd. Multi-walled carbon nanotubes (MWCNT) were purchased from Shenzhen Nanotech Port Co. Ltd. Deionized water (18.25 M Ω cm resistivity) was obtained via a ultrapure water equipment in laboratory. All the chemicals were directly used after purchase without further purification. *Synthesis of high entropy oxides (HEO)* : In a typical synthesis, 0.6 g polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO₂₀–PPO₇₀–PEO₂₀, Pluronic P123) was first dissolved in 11.25 mL ethanol, then 7.5 mL H₂O, and 36 mL ethylene glycol were added to form a homogeneous solution. Next, 0.3mmol Co(Ac)₂·4H₂O, 0.3mmol Ni(Ac)₂·4H₂O, 0.3mmol Mn(Ac)₂·4H₂O, 0.3mmol Fe(Ac)₂, 0.3mmol Cu(Ac)₂·H₂O and 0.21 g hexamethylenetetramine (HMTA) were added into the mixed solution under vigorous stirring for 45 min. After that, the solution was transferred into a 100 mL stainless-steel Teflon-lined autoclave and heated at 170 °C for 15 h. It was then cooled to room temperature, and the product was washed several times with water and ethanol and finally dried at 60 °C, yielding the high entropy oxide precursor. The HEO nanoparticles were finally obtained by calcinating the precursor at 400 °C for 2h. In addition, mix metal oxides with less elements are also prepared by this method.

Synthesis of high entropy oxides on multi-walled carbon nanotubes substrates (HEO/MWCNT): In a typical synthesis, firstly, multi-walled carbon nanotubes are treated by O₂ plasma (commercial 13.56 MHz RF source) for 30 min with the power of 200 W before use, this step can remove impurities on the surface and at the same time it can improve its hydrophilicity. Secondly, 0.6 g polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO₂₀–PPO₇₀–PEO₂₀, Pluronic P123) was first dissolved in 11.25 mL ethanol, then 7.5 mL H₂O, and 36 mL ethylene glycol were added to form a homogeneous solution. Next, 0.1516 g multi-walled carbon nanotubes (MWCNT) were added to the above solution under vigorous stirring. The rest synthesis process was the same as that of high entropy oxides mentioned above.

Synthesis of traditional high entropy oxide (Reverse co-precipitation process): The traditional high entropy oxide was synthesized according to methods already reported. In brief, the concentration of the precursor solution was 0.1 M. A base solution with initial pH 10 was prepared by adding 25 ml of ammonia (NH3, Merck, 25%) in 200 ml of deionized water. The precursor solution was added to the ammonia solution in a controlled fashion along with continuous stirring of the mixture at ambient conditions. Ammonia solution was added externally to the mixture at regular intervals in order to maintain the pH level at 10. After filtering, the precipitate was dried at 120 °C for 4 h and lightly ground in an agate mortar and finally calcined at 1000 °C for 1 h to obtain desired crystalline oxide phase. The pH, rate of addition of precursors' solution into the base and temperature of calcination were the factors affecting the crystal structure, morphology and crystallite size of the powder synthesized.

Materials characterization: The morphology and microstructure of all samples was characterized by scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscope (TEM, FEI, F20 S-TWIX). The crystal phase of the products was examined by X-ray diffraction (XRD) (Bruker, D8-Advance X-ray diffractometer, Cu K α , $\lambda = 1.5406$ Å). The actual metal content (Co, Cu, Fe, Mn and Ni) in the catalysts was determined by inductively coupled plasma optical emission spectroscopic (XPS) measurements were carried out with an ESCALAB 250Xi using a monochromic Al X-ray source (200 W, 20 eV). The thermogravimetric analysis (TGA) was carried out by a STA449C instrument with a heating rate of 5 °C /min in air.

Electrochemical measurements: All of the electrochemical measurements were performed with a CHI 760D electrochemical workstation with a three-electrode system at the room temperature. The catalyst dropped on a glassy carbon electrode (5 mm in diameter, 0.196 cm²) was used as the working electrode, graphite rod was used as the counter electrode and saturate calomel electrode (SCE) was used as the reference electrode in 1 M KOH electrolyte. The electrochemical activity of HEO and HEO/MWCNT electrocatalysts was measured for oxygen evolution reaction. Generally, 4 mg of electrocatalyst sample was ultrasonically dispersed in 450 μ L ethanol, 500 μ L deionized water and 50 μ L Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink followed by dropping 10 μ L of the electrocatalyst ink onto the surface of a glass carbon electrode (GCE) and dried under room temperature. The scan rate for linear sweep voltammetry (LSV) was kept at 5 mV/s to minimize the capacitive current. All the polarization curves in this work were corrected by eliminating iR drop with respect to the ohmic resistance of the solution.



Figure S1. XRD pattern of control samples was obtained by pyrolyzing the precursor at 500, 600, 700, 800, 900 and 1000 °C.



Figure S2. XRD diffractograms of the HEO.



Figure S3. (a) The EDX spectroscopy of HEO, (b) The EDX spectroscopy of HEO/MWCNT.



Figure S4. (a, b) SEM image of the HEO prepared by the traditional reversible coprecipitation, (c, d) SEM image of the HEO/MWCNT.



Figure S5. Raman spectrum of HEO before (left) and after (right) stability test.



Figure S6. XPS survey spectrum of HEO before (left) and after (right) water oxidation.



Figure S7. iR-corrected LSV curves of the HEO, HEO/MWCNT and control samples in O_2 -saturated 1 M KOH electrolyte at a scan rate of 5 mV s⁻¹.

Figure S8. Thermogravimetric analysis of HEO/MWCNT in air.

Figure S9. (a) XRD diffractograms of mix metal oxides with less elements, (b) iR-corrected LSV curves of mix metal oxides with less elements in O_2 -saturated 1 M KOH electrolyte at a scan rate of 5 mV s⁻¹.

Figure S10. Time-dependent current density curves of HEO at 1.63V vs. RHE in 1.0 M KOH.

Figure S11. Cyclic voltammetry curve (CV) of HEO in 1.0 M KOH.

Figure S12. (a) CVs of cycled HEO at various scan rates during OER testing, (b) Plot of double layer charging current density vs the scan rate of HEO during OER testing, (c) CVs of cycled HEO at various scan rates after OER testing, (d) Plot of double layer charging current density vs the scan rate of HEO after OER testing.

Figure S13. The equivalent series resistance (ESR) of the HEO.

element	Content (wt.%)
Со	11.9
Cu	26.0
Fe	8.42
Mn	17.8
Ni	9.47

Table S1. Detection of the actual Co, Cu, Fe, Mn and Ni contents in HEO by ICP-OES analysis.