Supporting Information

Ultra-tiny $Co(OH)_2$ particles supported on graphene oxide for highly efficient electrocatalytic water oxidation

Experimental details

Materials

All reagents were analytical grade (Sinopharm Chemical Reagent Co.,Ltd) and used without further purification. Graphene oxide (GO) sheets were provided by Nanjing XF Nano Materials Tech Co., Ltd, Nanjing, People's Republic of China.

Synthesis of $Co(OH)_2$/GO

GO was dispersed in the anhydrous ethanol (EtOH). The concentration of GO in the EtOH was 0.33 mg/ml. At the first step, the reaction mixture was prepared by adding 9 ml of 0.049 M $Co(Ac)_2$ aqueous solution to 180 ml of GO-EtOH suspension at 0℃, followed by the addition of 4 ml of concentrated ammonia. The solution was stirred for 20 minutes at 0 ℃, followed by the addition of 5.25 ml of de-ionized water. The reaction mixture kept at 0 ℃ with vigorous stirring for 10 h. The resulting product was filtrated and washed with EtOH and water, followed by vacuum drying at 60 ℃.

Synthesis of Co_3O_4/GO

The reaction mixture was firstly prepared by adding 9 ml of 0.2 M $Co(Ac)_2$ aqueous solution to 180 ml of GO-EtOH suspension, followed by the addition of 4 ml of concentrated ammonia. The solution was stirred for 20 minutes at room temperature, followed by the addition of 5.25 ml of de-ionized water. The reaction mixture was kept at ~80℃ with vigorous stirring for 10 h. The resulting product was filtrated and washed with EtOH and water, followed by vacuum drying at 60 ℃.

Synthesis of HT-Co_3O_4/GO

To prepare HT-Co_3O_4/GO, the resulting reaction mixture from above steps for synthesis of Co_3O_4/GO was transferred to a autoclave for hydrothermal reaction at

150 ℃ for 3 h. After cooling the autoclave to room temperature, the product was filtrated and washed with EtOH and water, followed by vacuum drying at 60 ℃.

Characterization of $Co_xO_yH_z$/GO composite

The compositions and phases of $Co_xO_yH_z$/GO were identified by powder wide angle X-ray diffraction (XRD) using Rigaku Ultima IV diffractometer with Cu Kα radiation (λ= 0.154178 nm). The infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer from ThermoElectron Corporation. The morphologies and crystal structures of $Co_xO_yH_z$/GO were characterized by a FEI Tecnai G2 transmission electron microscopy (TEM). Detailed X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo Scientific K-Alpha XPS spectrometer. A monochromatic Al Kα X-ray source was used. The C 1s photoelectron binding energy was set at 284.8 eV and used as reference for calibrating others peak positions. The thermal stabilities of $Co_xO_yH_z$/GO were examined by thermogravimetric analysis (TGA) on a TG analyzer in dry air in the range of 40-900℃ with a heating rate of 10 ℃/min.

Electrochemical measurements

5 mg of catalyst powder were dispersed in 1 ml of 3:1 v/v water/isopropanol solution. Subsequently, 16 μl of 5 wt% Nafion solution was added. The mixed solution was sonicated for 30 min to obtain a homogeneous ink. The working electrode was prepared by uniformly drop casting 20 μl of the catalyst ink onto 1 cm^2 carbon paper and then being baked at 60℃ for 30 min. Electrochemical measurements were performed in a typical 3-electrode configuration with a Pt plate as the counter electrode and an Ag/AgCl (3 M KCl) electrode as the reference electrode. The electrolyte was 1 M KOH aqueous solution. Linear scan voltammograms with a scanning rate of 50 mV/s were conducted to evaluate the OER performances of catalyst at 25℃.

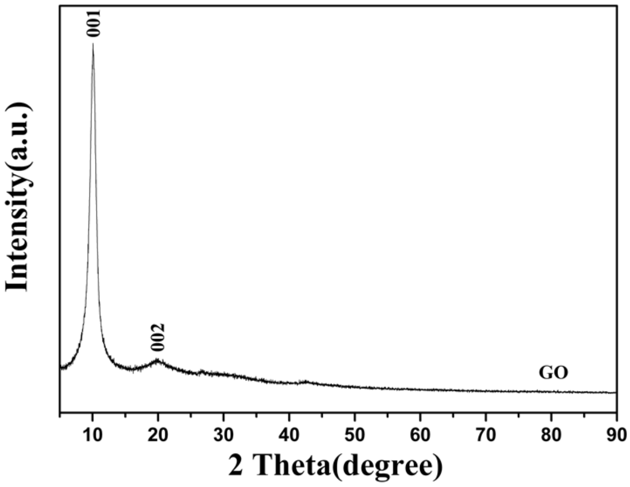

Figure S1. XRD spectra of GO.

Table S1. The loading of nanocomposites.

sample	loading (wt%)
$Co(OH)_2$/GO	30
Co_3O_4/GO	66
HT-Co_3O_4/GO	72

The loading of nanocomposites is calculated by the method as blow.

$35\% = (13\% \cdot m_{GO} + m_{Co3O4}) / (m_{Co3O4} + m_{GO})$

$= 13\% \cdot m_{GO} / (m_{Co3O4} + m_{GO}) + m_{Co3O4} / (m_{Co3O4} + m_{GO})$

$= 13\% \cdot (1-35\%) + m_{Co3O4} / (m_{Co3O4} + m_{GO})$

$m_{Co3O4} / (m_{Co3O4} + m_{GO}) = 27\%$

$3 \cdot m_{Co3O4} / M_{Co3O4} \cdot M_{Co(OH)2} = m_{Co(OH)2}$

$m_{Co3O4} = m_{Co(OH)2} \cdot M_{Co3O4} / (3 \cdot M_{Co(OH)2}) = m_{Co(OH)2} \cdot 240.8 / (3 \cdot 92.4)$

$= 0.87 \cdot m_{Co(OH)2}$

$m_{Co3O4} / (m_{Co3O4} + m_{GO}) = 0.87 \cdot m_{Co(OH)2} / (0.87 \cdot m_{Co(OH)2} + m_{GO}) = 27\%$

$0.87 / (0.87 + m_{GO} / m_{Co(OH)2}) = 27\%$

$m_{GO} / m_{Co(OH)_2} = 2.352$

$(m_{Co(OH)_2} + m_{GO}) / m_{Co(OH)_2} = 1 + m_{GO} / m_{Co(OH)_2} = 1 + 2.352 = 3.352$

$Co(OH)_2$ wt% ($Co(OH)_2$ /GO) = $m_{Co(OH)_2} / (m_{Co(OH)_2} + m_{GO}) = 1 / 3.352 = 30\%$

$70\% = (13\% \cdot m_{GO} + m_{Co_3O_4}) / (m_{Co_3O_4} + m_{GO})$

$= 13\% \cdot m_{GO} / (m_{Co_3O_4} + m_{GO}) + m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO})$

$= 13\% \cdot (1-70\%) + m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO})$

Co_3O_4 wt % (Co_3O_4/GO) = $m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO}) = 66\%$

$75\% = (13\% \cdot m_{GO} + m_{Co_3O_4}) / (m_{Co_3O_4} + m_{GO})$

$= 13\% \cdot m_{GO} / (m_{Co_3O_4} + m_{GO}) + m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO})$

$= 13\% \cdot (1-75\%) + m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO})$

Co_3O_4 wt % (HT-Co_3O_4/GO) = $m_{Co_3O_4} / (m_{Co_3O_4} + m_{GO}) = 72\%$

Table S2. OER activities of $Co(OH)_2$/GO, Co_3O_4/GO, and HT-Co_3O_4/GO at 1.5 V

catalyst	I ($A \cdot cm^{-2}$)	mass activity ($A \cdot g^{-1}$)	TOF (s^{-1})
$Co(OH)_2$/GO	0.326	17413.7	2.66
Co_3O_4/GO	0.309	6478.6	0.99
HT-Co_3O_4/GO	0.321	6168.3	0.94

Calculations of mass activity and turnover frequency

Table S2 reports mass activity and turnover frequency (TOF) for $Co(OH)_2$/GO, Co_3O_4/GO, and HT-Co_3O_4/GO. We define mass activity as the current passes per gram cobalt and define TOF as the number of O_2 molecules evolved per cobalt atom per second.[1] Using mass activity, we then calculate TOF.

$$mass\ \ activity = \frac{I(A \cdot cm^{-2})}{m_{Co}(g \cdot cm^{-2})}$$

$$TOF = \frac{I(C \cdot s^{-1} \cdot g^{-1}) M_{Co}(g \cdot mol^{-1})}{4(e^{-}) \cdot 1.602 \cdot 10^{-19}(C \cdot \frac{1}{e^{-}}) 6.022 \cdot 10^{23}(site \cdot mol^{-1})}$$

For example, mass activity of $Co(OH)_2$/GO is calculated as below.

$m_{Co} = m_{Co(OH)_2} \cdot M_{Co} / M_{Co(OH)_2}$

$= 20\ \mu l / (1000\ \mu l + 16\ \mu l) \cdot 0.005\ g \cdot 30\% \cdot M_{Co} / M_{Co(OH)_2} = 0.0000187209$

mass activity = $I / m_{Co} = 17413.7\ (A \cdot g^{-1})$

[1] GORLIN Y, CHUNG C-J, BENCK J D, et al. Understanding Interactions between Manganese Oxide and Gold That Lead to Enhanced Activity for Electrocatalytic Water Oxidation [J]. Journal of the American Chemical Society, 2014, 136(13): 4920-6.