Controlled synthesis of Co_3O_4@$NiMoO_4$ core-shell nanorods arrays for efficient water splitting

Xiaoqiang Du,[a*] Nai Li,[a] and Xiaoshuang Zhang[b*]

Sample preparation

In a typical synthesis,0.8g of $Co(NO_3)_2$. $6H_2O$ and 0.8g of $CO(NH_2)_2$ were dissolved in 70mL of deionized water under stirring to form a clear solution.The above solution and apiece of pre-treated Ni foam were transferred in to a 100mL autoclave and maintained at 100 °C for 8h.The product was rinsed with deionized water and annealed at 350 °C for 2h in air.The wire-like Co_3O_4 arrays were obtained on the Ni foam. Then, the obtained Co_3O_4 arrays on Ni foam were loaded in a solution containing 80mL of deionized water 2mmol Na_2MoO_4 .$2H_2O$ and $Ni(NO_3)$. $6H_2O$. The reaction was conducted for 12h and then cooled naturally.There resulting product was finally annealed at 400 °C for 2h in air.The rod-like Co_3O_4@$NiMoO_4$ nanostructures were obtained .

The resulting Co_3O_4@$NiMoO_4$ materials with different treatment times (t_R= 8 h) were named as Co_3O_4@$NiMoO_4$/NF-8h.

Material characterization

The crystal composes of the synthetized samples were determined by Powder X-ray diffraction (PXRD) using a PANalytical X'Pert Pro Diffractometer with Cu Kα radiation (step size: 0.017°, step time: 10.34 s) operating at 40 kV and 60 mA. The morphologies of the catalysts were characterized by Scanning electron microscopy (SEM) images equipped with a Hitachi S-4800 microscope (scanning voltage, 7 kV). X-ray photoelectron spectra (XPS) measurements were performed by ESCALAB250xi with 150 W Al Kα radiation.

Electrochemical tests

Electrochemical measurement was performed with a CHI 660E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai, China) in a standard three-electrode system using Co_3O_4@$NiMoO_4$/NF as the working electrode and it's working area for OER is ~ 1.0 cm^{-2}, platinum wire electrode as a counter electrode, and a Ag/AgCl as a reference electrode. All linear-sweep voltammograms (LSV) were performed in 1 M KOH acquire electrolyte. For OER performamce, linear sweep voltammetry (LSV) polarization curves were recorded from 0.2-0.8 V versus saturated Ag/AgCl at a scan rate of 2 mV s^{-1}. Chronoamperometric measurements were tested on corresponding potential to support a current density of about 4 mA cm^{-2} for 12 h. All potentials in this work were noted versus the reversible (RHE), which were converted using equation $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$ (1 M KOH, pH ~ 13.6), in which the E_{RHE} is the potential referred to RHE and $E_{Ag/AgCl}$ is measured potential against the reference electrode. The electrochemical active surface areas (ECSAs) was evaluated from the electrochemical double-layer capacitance (C_{dl}) through collecting cyclic votlammogram (CVs) in the potential range without Faradaic process at various scan rates including 10, 20, 30, 40, 50 mV s^{-1} in the potential range from 0.02-0.12 V versus Ag/AgCl. The overpotential (η) is calculated using the following equation: $\eta = E_{RHE} - 1.23V$.

Table S1. Comparison of water oxidation performance for Co_3O_4@$NiMoO_4$/NF with other non–noble–metal WOCs under alkaline conditions.

Catalyst	**j (mA cm^{-2})**	**η (mV)**	**Ref.**
Co_3O_4@$NiMoO_4$/NF	15	330	This work
Co_3O_4 /NF	15	370	This work
$NiMoO_4$/NF	15	440	This work
RuO_2 /NF	15	330	This work
$CoMoO_4$/NF	10	312	Chem. Commun., 2015, 51, 14361
$FeMoO_4$/NF	50	293	Inorg. Chem. Front., 2018, 5, 665
$CaMoO_4$/NF	50	345	Chem. Commun. 2018, 54, 5066
NiFe/NF	20	264	Int. J. Hydrogen Energy, 2016, 41, 8785
NiSe/NF	20	270	Angew. Chem., Int. Ed., 2015, 54, 9351
2D CuO	10	350	J. Mater. Chem. A, 2017, 5, 12747
NiFeMn–LDH	10	310	Chem. Commun., 2016, 52, 908
$NiCo_2O_4$@Ni–Co–B/CC	10	270	Inorg. Chem. Front., 2017, 4, 1546
$Ni_{0.75}V_{0.25}$–LDH	57	350	Nature Commun., 2016, 7, 11981
$NiCo_2S_4$@NiFe LDH/NF	60	201	ACS Appl. Mater. Interfaces, 2017, 9, 15364

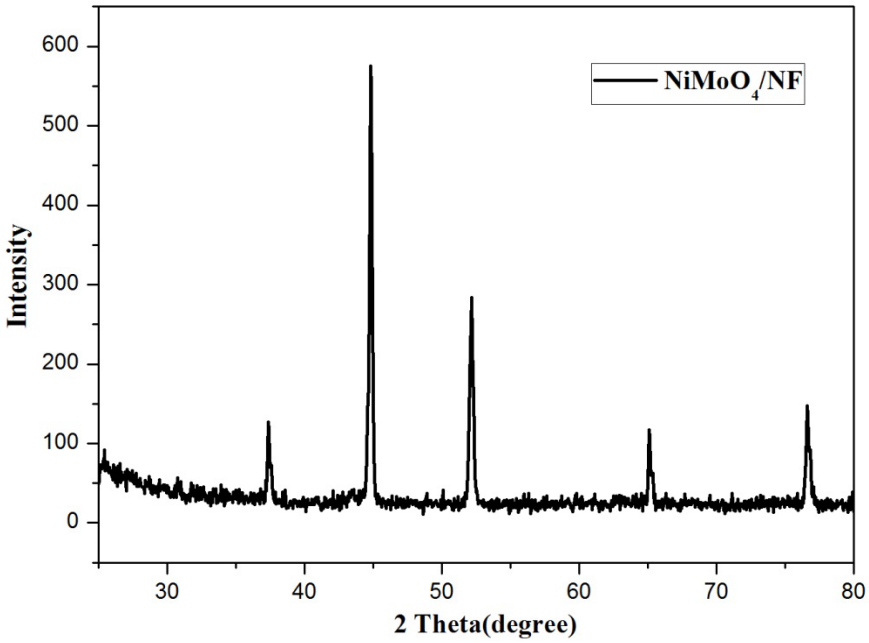

Fig. S1 XRD of $NiMoO_4$/NF.

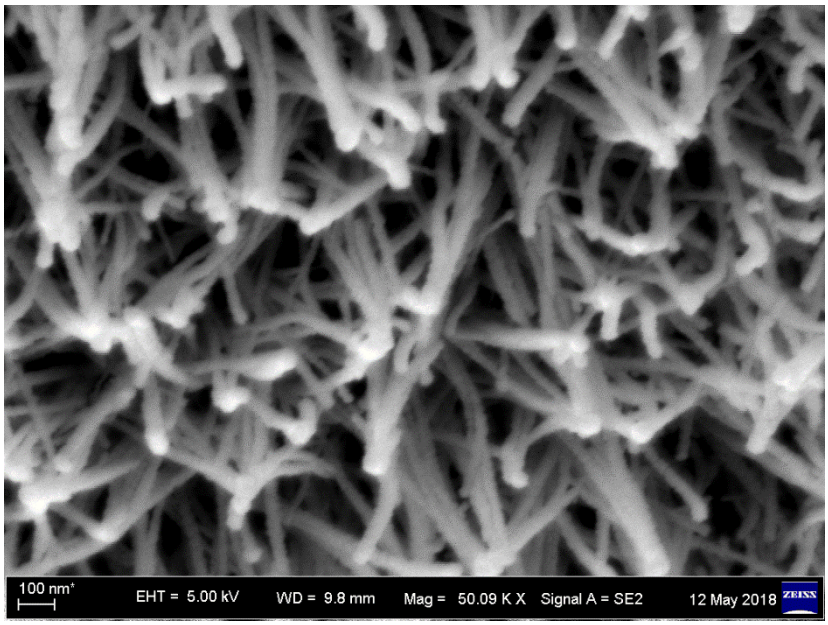

Fig. S2 SEM of Co_3O_4/NF.

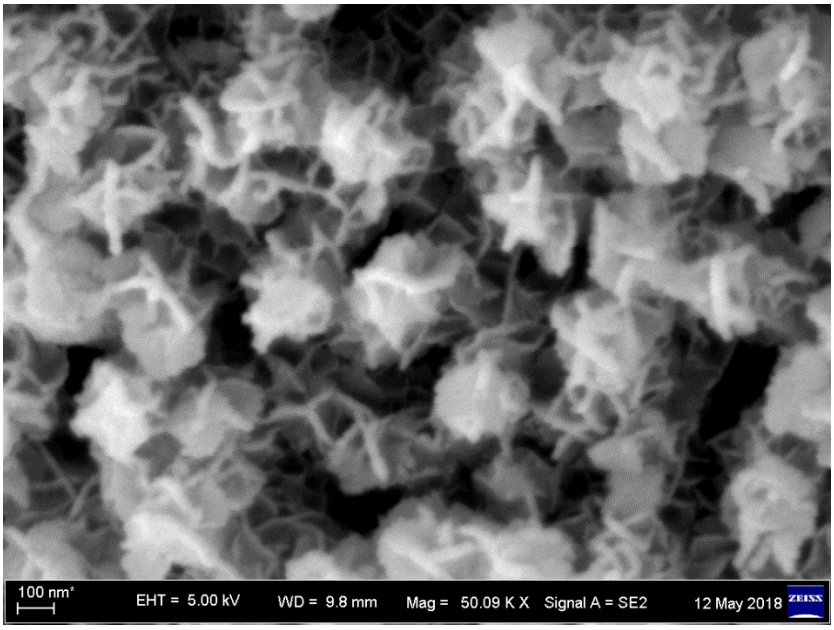

Fig. S3 SEM of Co_3O_4@$NiMoO_4$/NF.

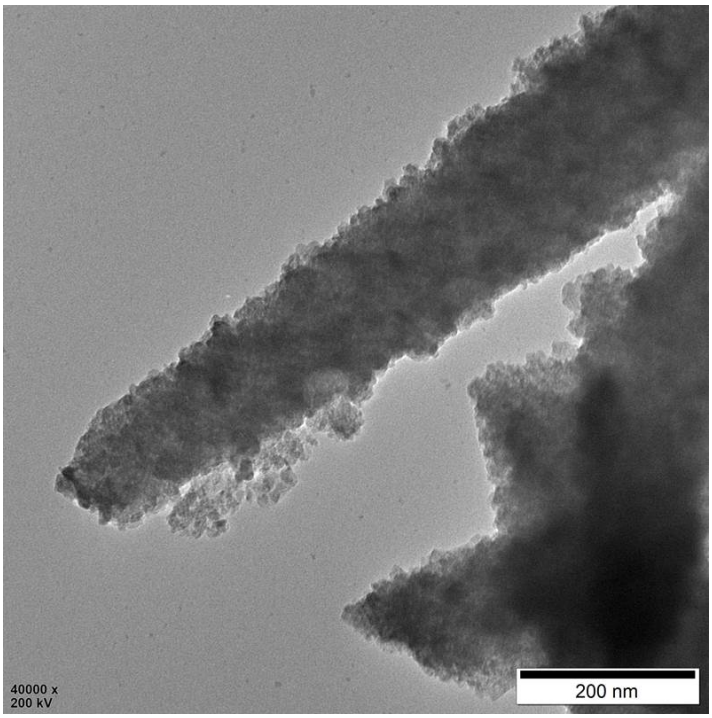

Fig. S4 TEM of Co_3O_4@$NiMoO_4$/NF.

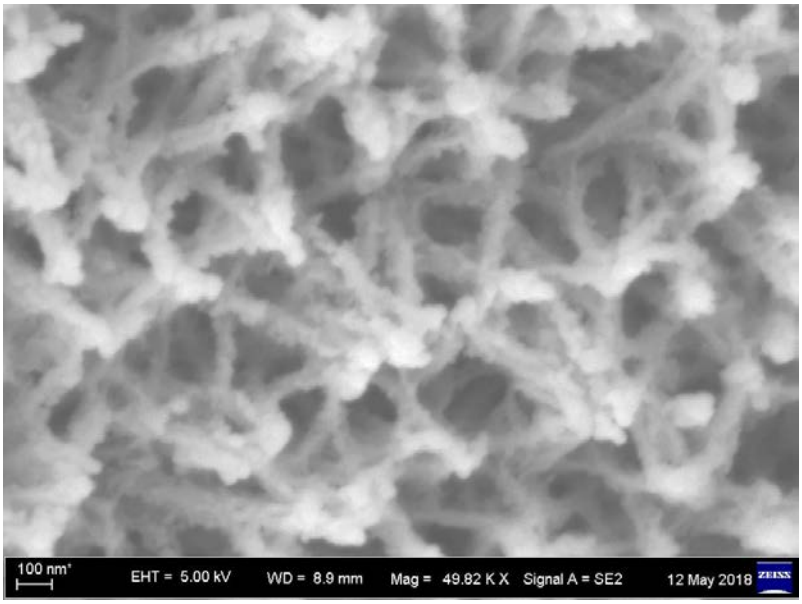

Fig. S5 SEM of Co_3O_4@$NiMoO_4$/NF-8h.

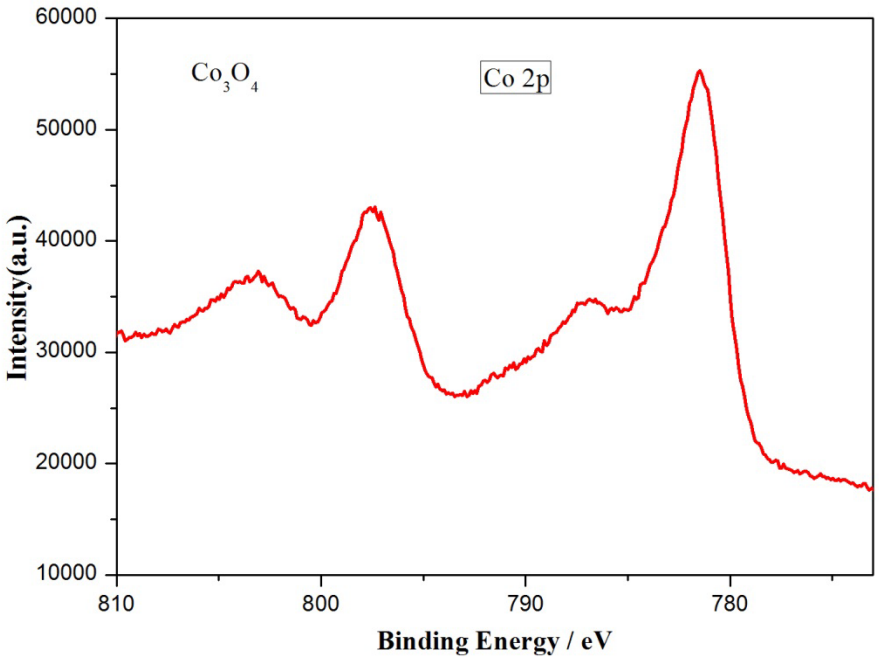

Fig. S6 XPS spectra of the Co 2p for Co_3O_4 /NF.

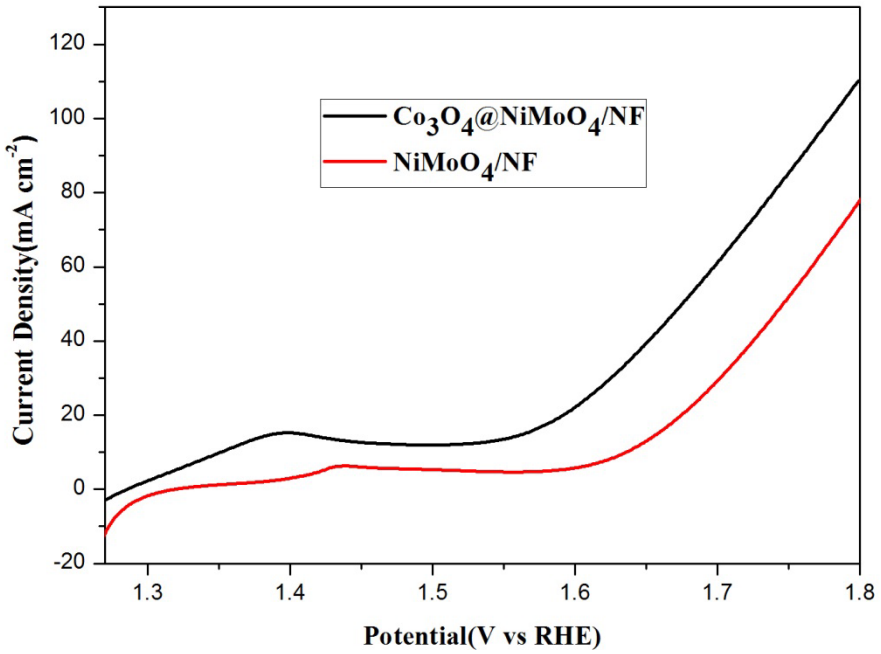

Fig.S7 OER polarization curves for the Co_3O_4@$NiMoO_4$/NF and $NiMoO_4$/NF.

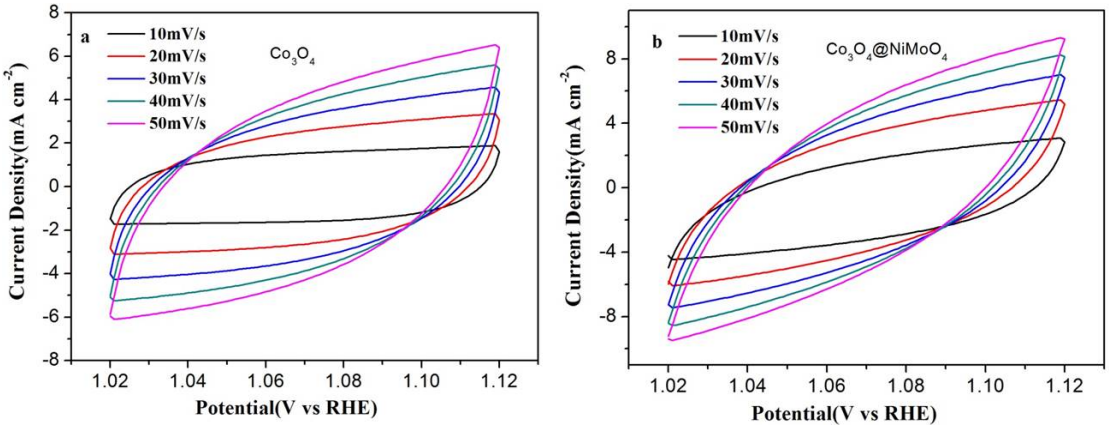

Fig. S8 CV_S of Co_3O_4 /NF and Co_3O_4@$NiMoO_4$/NF with different scan rates (10-50 mV s^{-1}) in the region of 1.02-1.12V *vs* RHE.

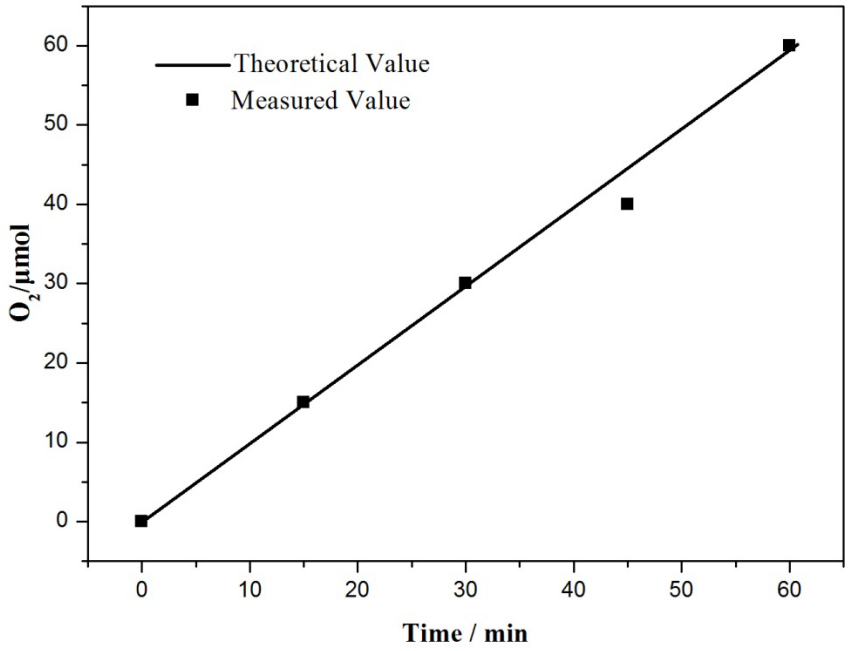

Fig. S9 Electrocatalytic efficiency of O_2 production over Co_3O_4@$NiMoO_4$/NF at a potential of ca. 1.55 V, measured for 60 min.

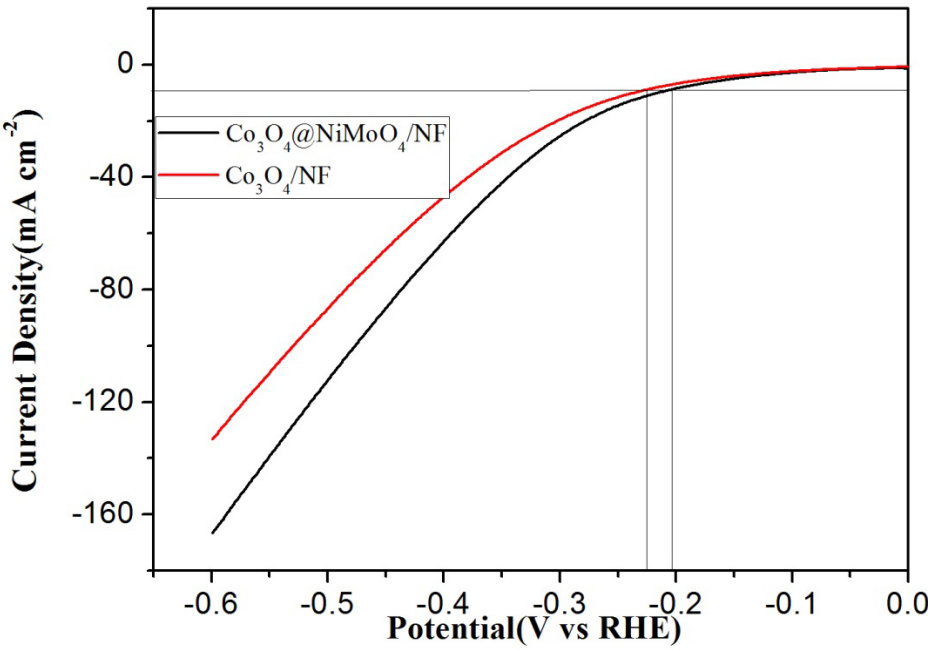

Fig. S10 HER polarization curves for the Co_3O_4@$NiMoO_4$/NF and Co_3O_4/NF.

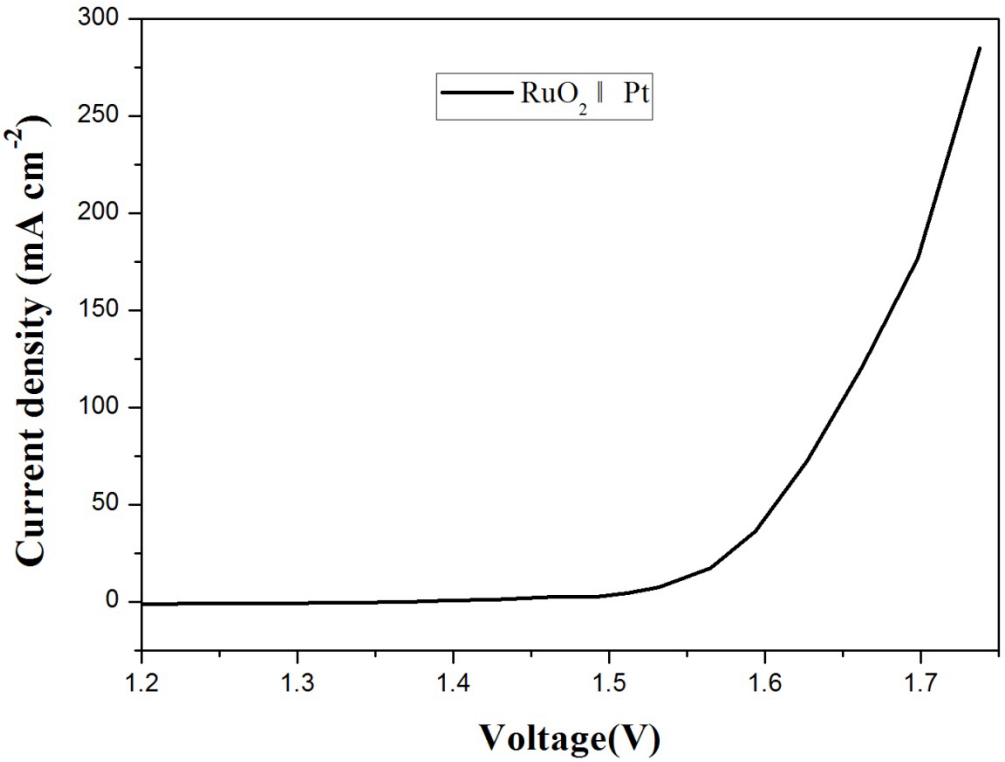

Fig. S11 Polarization curve of the RuO_2 and Pt for water splitting with a scan rate of 5 mV s^{-1} in 1 M KOH.

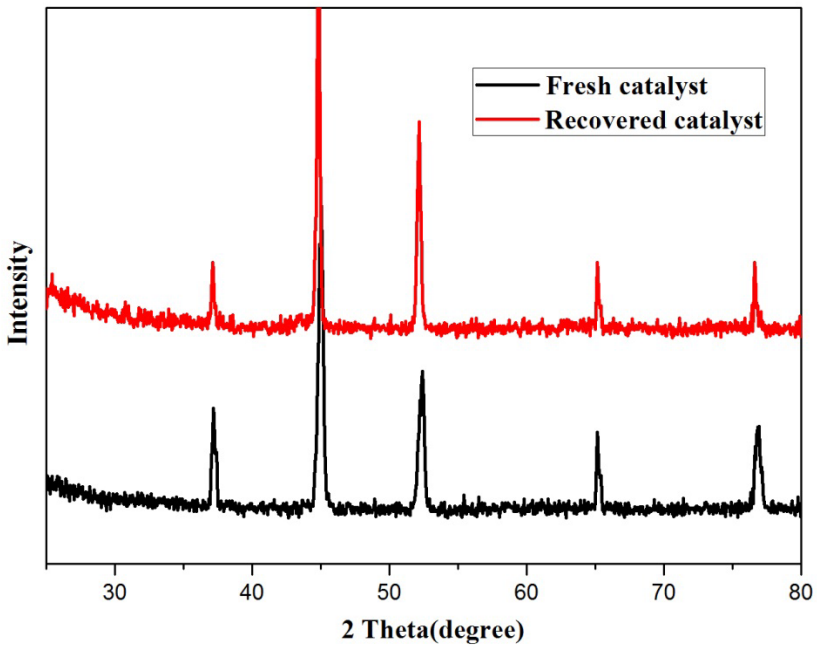

Fig. S12 XRD of fresh catalyst and recovered catalyst.

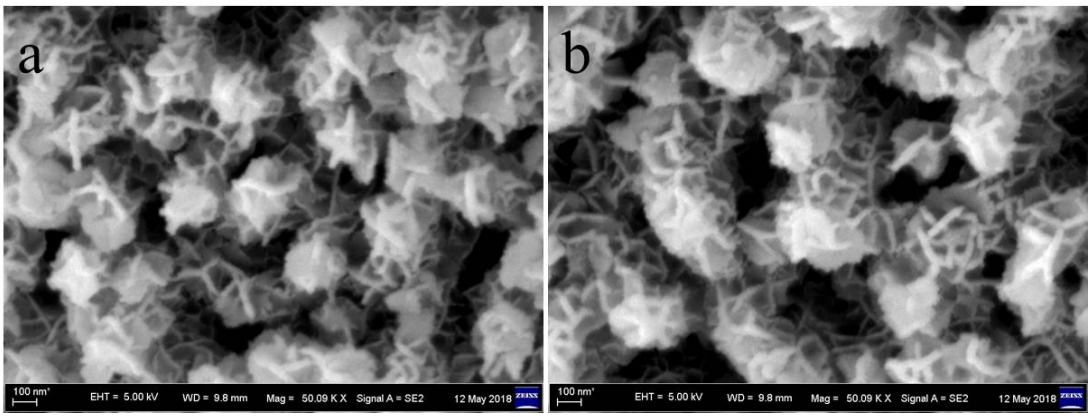

Fig. S13 SEM of fresh catalyst (a)and recovered catalyst(b).

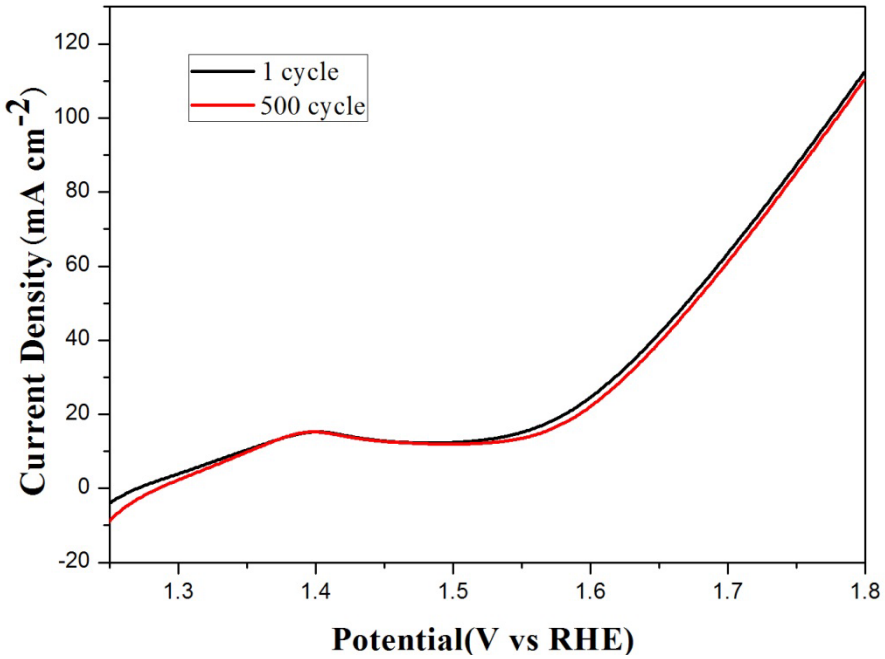

Fig.S14 OER polarization curves for the Co_3O_4@$NiMoO_4$/NF before and after 500 cycles of the accelerated stability test.

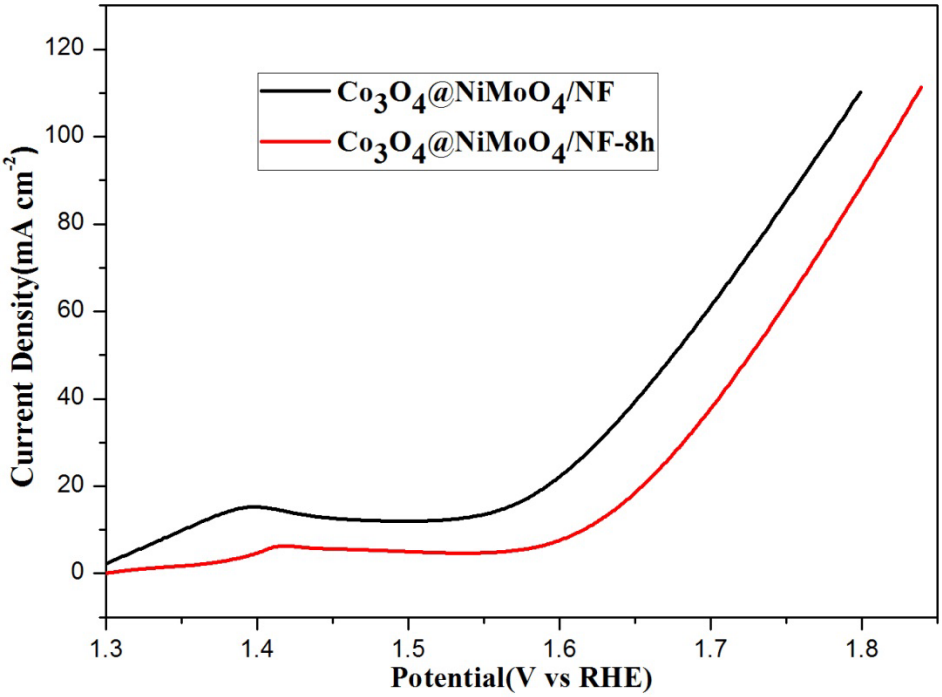

Fig.S15 OER polarization curves for the Co_3O_4@$NiMoO_4$/NF and Co_3O_4@$NiMoO_4$/NF-8h.