Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

$NiFe_2O_4$ hollow nanoparticles with small size on carbon nanotubes for oxygen evolution

Jianyu Kang,[a] Feng Yan,[a] Chunyan Li,[a] Lihong Qi,[a] Bo Geng,[b] Yue Wang,[a] Chunling Zhu*[b] and Yujin Chen*[ac]*

[a] *Key Laboratory of In-Fiber Integrated Optics, Ministry of Education, and College of Physics and Optoelectronic Engineering, Harbin Engineering University, Harbin 150001, China*

[b] *College of Chemistry and Chemical Engineering, Harbin Engineering University, Harbin, 150001, China*

[c] *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China*

*Corresponding authors.

E-mail addresses: yanfeng@hrbeu.edu.cn (F. Yan), zhuchunling@hrbeu.edu.cn (C. Zhu) and chenyujin@hrbeu.edu.cn (Y. Chen).

Experimental Section

Preparation of $NiFe_2O_4$-HNP /CNTs. $NiFe_2O_4$-HNP/CNTs were fabricated through a facile method based on Kirkendall effect. First, 1.0 g of CNTs was dispersed in 100 mL of hydrogen peroxide and heated to 140°C for 2 h to obtain surface-active CNTs. 27.0 mg of surface-active CNTs were dispersed into 72.0 mL of ethanol, then 150.0 mg of nickel acetate and 57.0 mg of iron acetylacetonate were added. After 15 min ultrasonic treatment, 2.0 mL of ammonia and 3.6 mL of distilled water were added to the above mixture. The mixture was sealed and heated to 80°C in water bath for 10 h under stirring. The precipitate was washed with ethanol and water for several times, and then NiFe hydroxide/CNTs were obtained. Second, the NiFe hydroxide/CNTs were heated in a tube furnace at 350°C for 3 h under a H_2/Ar flow, and then at 200°C for 3 h and 280°C for another 3 h at air atmosphere, respectively. After the tube furnace was cooled to room temperature, $NiFe_2O_4$-HNP/CNTs were fabricated.

Preparation of $NiFe_2O_4$-NP/CNTs and $NiFe_2O_4$-NPs. Compared with $NiFe_2O_4$-HNP /CNTs, the $NiFe_2O_4$-NP/CNTs were synthesized under the same conditions except the precursor of NiFe hydroxide/CNTs were directly annealed at 200°C for 3 h and 280°C for another 3 h at air atmosphere. Similarly, compared with $NiFe_2O_4$-NP /CNTs, the $NiFe_2O_4$-NPs was fabricated under the same conditions except the addition of CNTs.

Preparation of NiO-HNP/CNTs and Fe_2O_3-NP/CNTs. Compared with $NiFe_2O_4$-HNP /CNTs, all the synthesis process were under the same conditions except the only nickel acetate (190.2 mg) or iron acetylacetonate (212.9 mg) was added to the solution in the first step, and after the same heat treatment, the corresponding NiO-HNP/CNTs and Fe_2O_3-NP/CNTs were synthesized, respectively.

Structural characterization. A JSM 7401F scanning electron microscope (SEM) operated at 3.0 kV and a JEM2010 high-resolution transmission electron microscope (TEM) were used to characterize the morphology. X-ray diffraction (XRD) patterns were measured using a Bruker D8 Advance diffractometer. X-ray photoelectron spectroscopy (XPS) patterns were characterized using a PHI 5700 ESCA System.

Electrochemical measurements. 5.0 mg of $NiFe_2O_4$-HNP/CNTs were dispersed in 350 μL of ethanol. After 1 h of ultrasound, 50.0 μL of nafion was added to the above mixed solution and continued ultrasound for another 1 h. Then, 3.1 μL of the mixed solution dripped onto the surface of a glassy carbon disk electrode with a catalyst loading of around 0.2 mg cm^{-2}. A standard three-electrode system was performed by using the as-prepared catalyst as work electrode, graphite rod as the counter electrode and Ag/AgCl electrode as the reference electrode. All the electrochemical measurements were executed in both 1.0 M KOH solution after purging the electrolyte with N_2 gas for 30 min. All potentials measured were calibrated to RHE using the following Equation: E(RHE) =E(Ag/AgCl) + 0.21 V + 0.059 × pH. All current densities presented are corrected against ohmic potential drop.

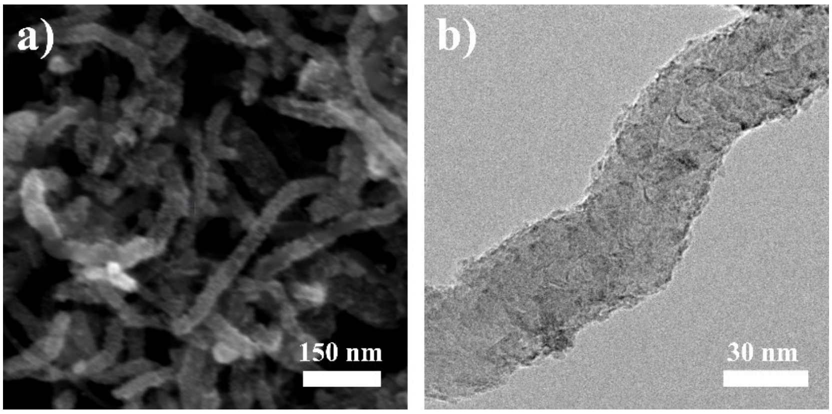

Fig. S1 a) SEM and b) TEM images of nickel and iron hydroxides grown on the surfaces of the CNTs.

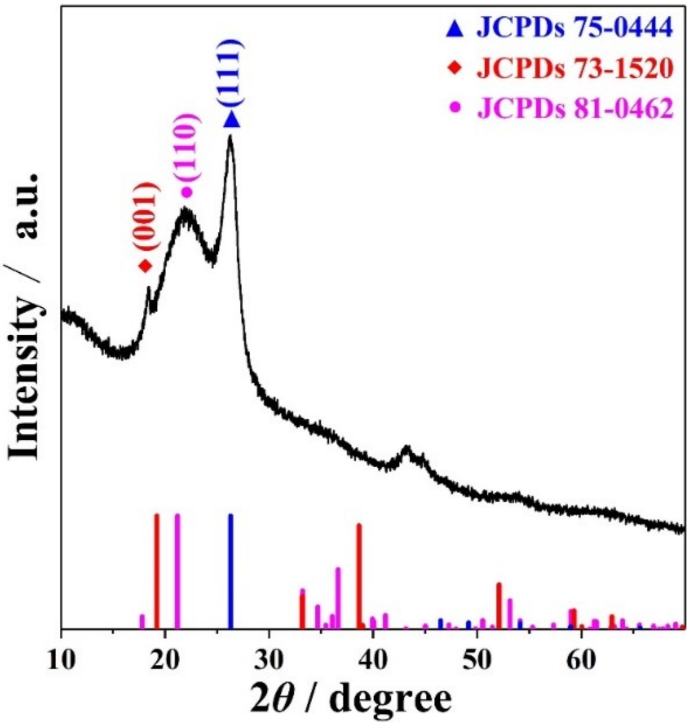

Fig. S2 XRD pattern of nickel and iron hydroxides.

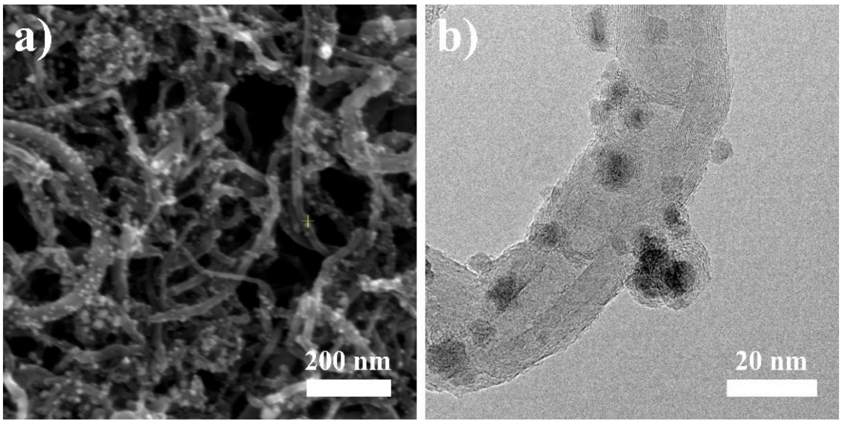

Fig. S3 a) SEM and b) TEM images of NiFe alloy NP/CNTs.

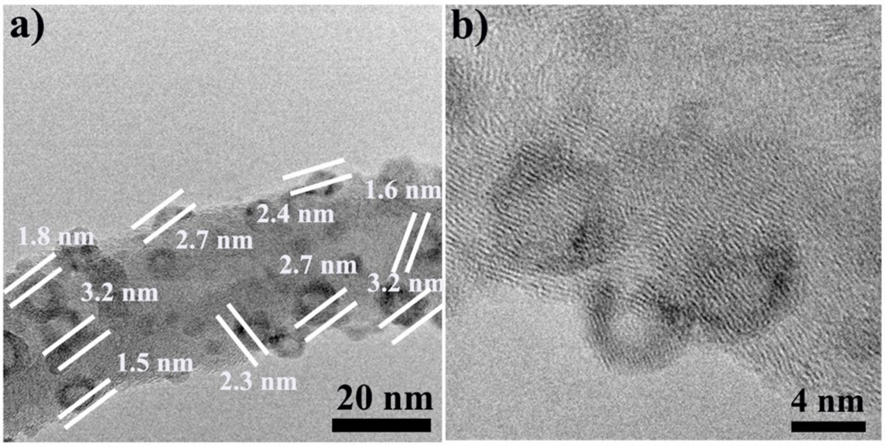

Fig. S4 a) TEM and b) HRTEM images of $NiFe_2O_4$-HNP/CNTs.

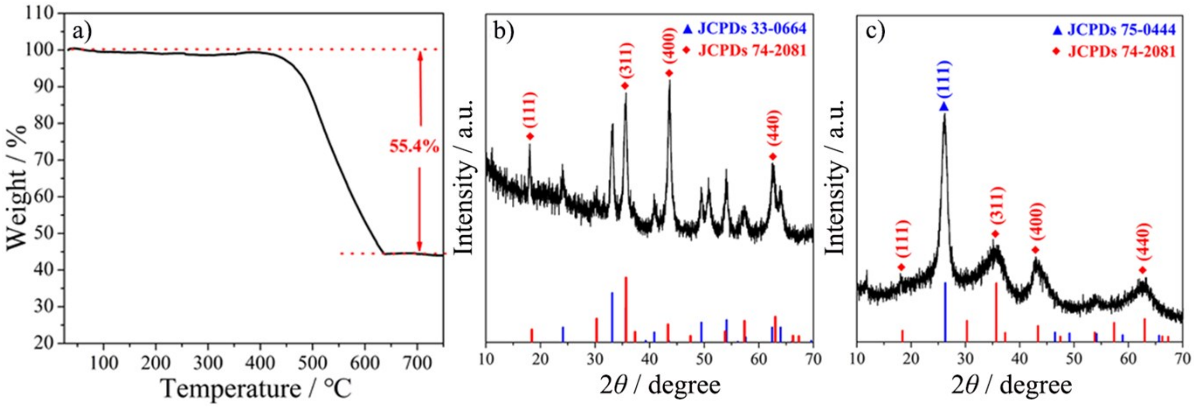

Fig. S5 a) TGA curve of $NiFe_2O_4$-HNP/CNTs. XRD patterns of b) $NiFe_2O_4$-NPs and c) $NiFe_2O_4$-NP/CNTs.

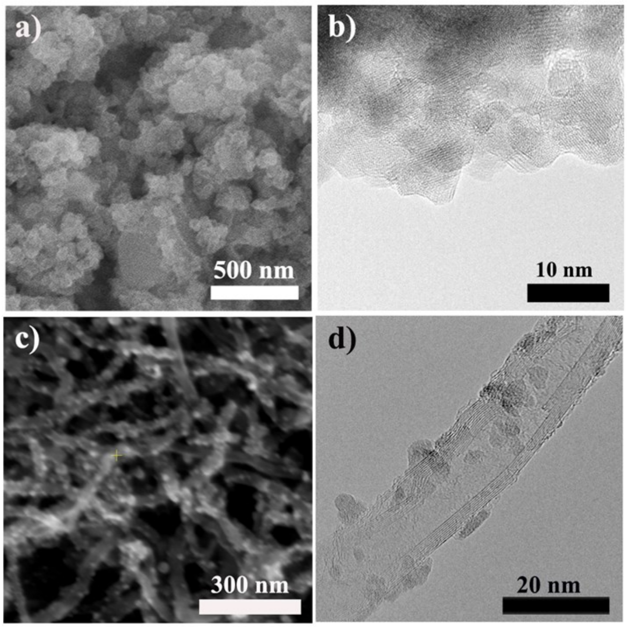

Fig. S6 a) SEM and b) TEM images of $NiFe_2O_4$-NPs. c) SEM and d) TEM images of $NiFe_2O_4$-NP/CNTs.

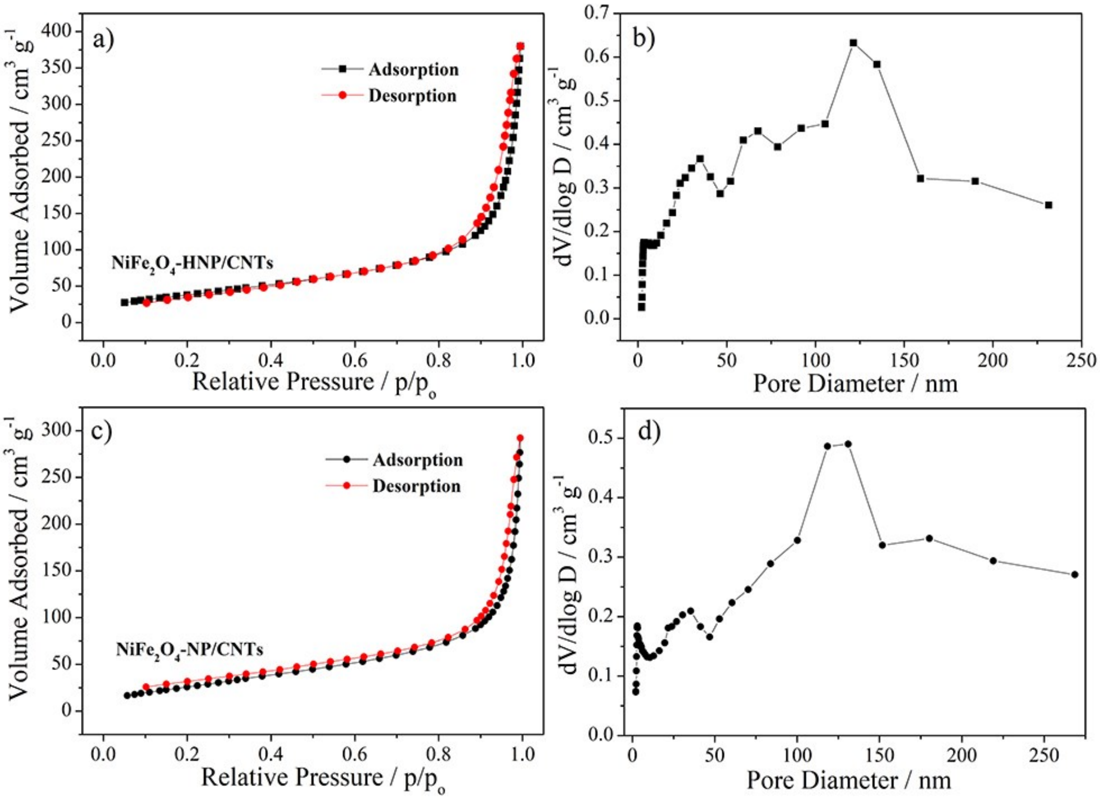

Fig. S7 a, c) Nitrogen adsorption and desorption isotherms and b, d) the corresponding pore-size distribution calculated of $NiFe_2O_4$-HNP/CNTs and $NiFe_2O_4$-NP/CNTs.

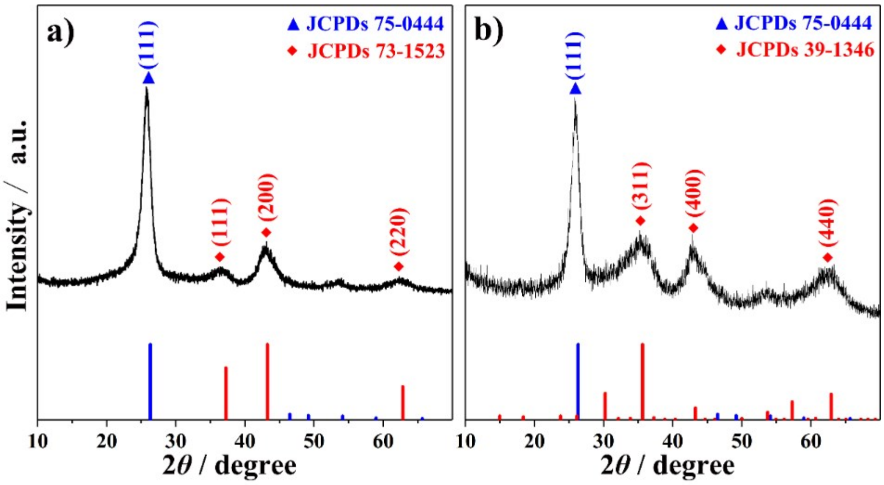

Fig. S8 XRD patterns of a) NiO-HNP/CNTs and b) Fe_2O_3-NP/CNTs.

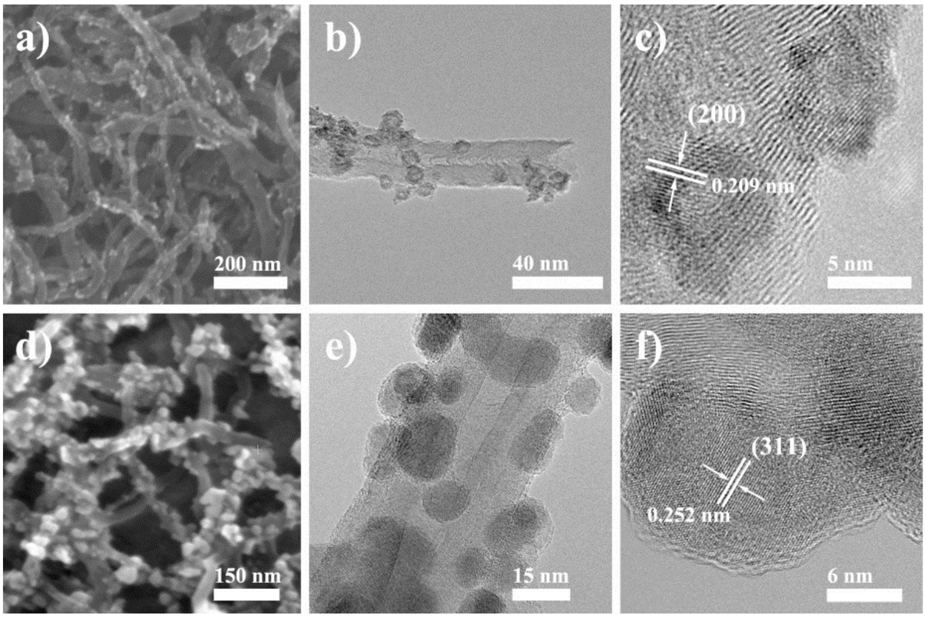

Fig. S9 a) SEM, b) TEM, and c) HRTEM images of NiO HNP/CNTs. d) SEM, e) TEM, and f) HRTEM images of Fe_2O_3 NP/CNTs.

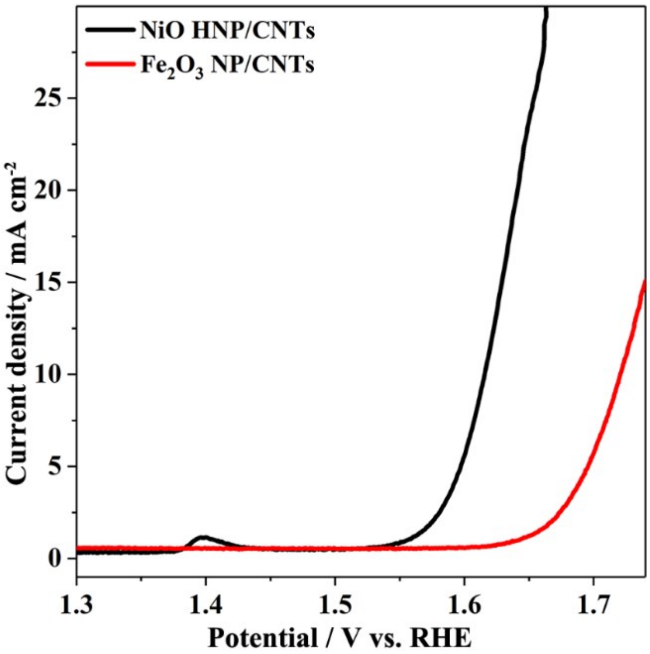

Fig. S10 polarization curves for NiO HNP/CNTs and Fe_2O_3 NP/CNTs for OER in 1.0 M KOH solution.

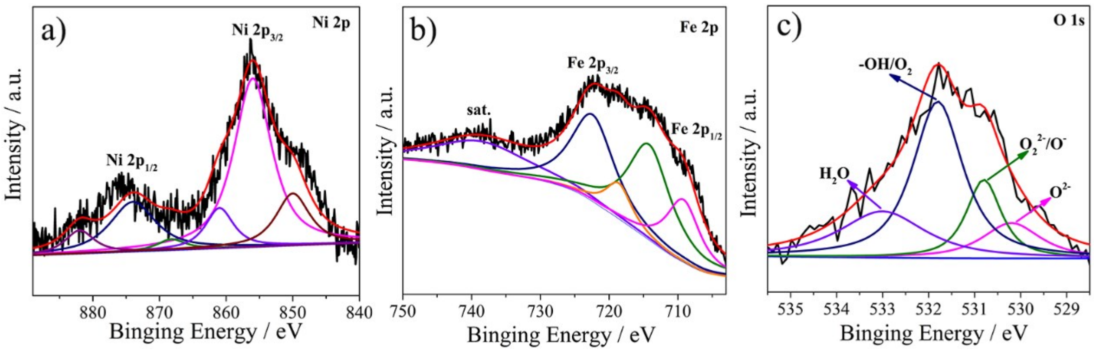

Fig. S11 XPS spectra of a) Ni 2p, b) Fe 2p, and c) O 1s after 3h OER measurement.

Table S1. Comparison of the OER activities of $NiFe_2O_4$ HNP/CNTs in 1.0 M KOH with recently published results.

Catalysts	Tafel slope (mV dec^{-1})	η_{10} (mV)	Electrolyte	Refs.
NiFe LDH-MOF	47	275.4	1.0 M KOH	*Adv. Funct. Mater.* 2019, 1903875
$FeNi_2S_4$/GA	66	273	1.0 M KOH	*J. Mater. Chem. A* 2018, 6, 19417
Ni-Fe LDH hollow nanoprisms	49.4	280	1.0 M KOH	*Angew. Chem. Int. Ed.* 2018, 57, 172
polyelemental (Co, Ni, Fe, W, B, P) hollow nanoparticles	30	110	1.0 M KOH	*Adv. Mater. Interfaces* 2019, 1900586.
CoFeNi-nanosheets array	44	240 (*j* =100 mA cm^{-2})	1.0 M KOH	*ACS Appl. Energy Mater.* 2019, 2, 8919.
FeB_2	52.4	296	1.0 M KOH	*Adv. Energy Mater.* 2017, 7, 1700513
Exfoliated NiFe LDH	89	270	1.0 M KOH	*Adv. Mater.* 2017, 29, 1700017
Ni_3FeN-NP	46	280	1.0 M KOH	*Adv. Energy Mater.* 2016, 6, 1502585
NiSe nanowire	64	270	1.0 M KOH	*Angew. Chem., Int. Ed.* 2015, 54, 9351
NiFeCr LDH/GC	131	280	1.0 M KOH	*Adv. Energy Mater.* 2018, 8, 1703189
Co-NiMoN NRs	73.48	294	1.0 M KOH	*ACS Appl. Mater. Interfaces* 2019, 11, 27751
$NiFe_2O_4$-HNP/CNTs	**40**	**260**	**1.0 M KOH**	**This work**