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Supporting Information

Mesoporous Ni-Fe oxide multi-composite hollow nanocages for efficient electrocatalytic water oxidation reactions

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Experimental

Synthesis of $Ni_3[Fe(CN)_6]_2$ prussian blue analogue (PBA) nanocube precursors and mesoporous $NiO/NiFe_2O_4$ multi-composite hollow nanocages (NCs).

We synthesized uniform $Ni_3[Fe(CN)_6]_2$ PBA nanocube precursors by modifying an established procedure.[1] In a typical synthesis, we dissolved 0.1374 mmol of Nickel (II) acetate tetrahydrate (97 %, $Ni(CH_3COO)_2 \cdot 4H_2O$, DAEJUNG, Korea), 0.7174 mmol of Sodium dodecylbenzenesulfonate (SDBS) (technical grade (Aldrich), $C_{18}H_{29}NaO_3S$, Sigma-Aldrich, USA) in 25 ml of D. I. water to form solution A. We dissolved 0.1502 mmol of Potassium hexacyanoferrate (III) (ACS reagent, ≥99.0 %, $K_3[Fe(CN)_6]$, Sigma-Aldrich, USA) in 25 ml of D. I. water to form solution B. Solutions A and B were heated at 60 °C oil bath with stirring for 1 h, respectively. Then solutions A and B were mixed and stirred in 60 °C oil bath for 3 h. After collection by centrifugation and washing with ethanol several times, the precipitates were dried in 60 °C oven overnight. Using the hydrothermal method, the prepared monodispersed $Ni_3[Fe(CN)_6]_2$ PBA nanocube precursors were calcined in air at 500 ~ 700 °C with a heating rate of 5 °C min^{-1} for 1 hour to transform them into mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs. In addition, pure $NiFe_2O_4$ and $NiO/NiFe_2O_4$ nanoparticles were prepared at 500 °C for 5 h in Air atmosphere by using liquid phase precursor method.[2]

Materials characterization.

We observed the surface morphology of the $Ni_3[Fe(CN)_6]_2$ PBA nanocube precursors and mesoporous $NiO/NiFe_2O_4$ multi-composite hollow CNs by field-emission scanning electron microscopy (FESEM, JEOL 7500F). We carried out high-resolution transmission electron

microscopy and energy dispersive spectroscopy (EDS) mapping using a JEM2100F with an accelerating voltage of 200 kV. The crystallinity and structure of the $Ni_3[Fe(CN)_6]_2$ PBA nanocube precursors and mesoporous $NiO/NiFe_2O_4$ multi-composite hollow CNs were examined by powder X-ray diffraction (Bruker D8 FOCUS) using CuKα radiation. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR, Bruker IFS-66/S) spectroscopy were employed to analyze the chemical bonding within the materials. Thermogravimetry and differential thermal analysis (TG-DTA, Seiko Exstar) was performed in air at a heating rate of 5 °C min^{-1} from 30 to 1000 °C, to confirm the reaction of $Ni_3[Fe(CN)_6]_2$ PBA nanocubes and the crystallization of $NiO/NiFe_2O_4$ multi-composite. We measured the Brunauer–Emmett–Teller specific surface areas and the Barrett–Joyner–Halenda pore size distributions of the samples on the surface area by using a pore size analyzer (Autosorb-iQ 2ST/MP) at 77 K with N_2 gas.

Electrochemical measurements.

All electrochemical experiments were conducted on a CHI 660D (ALS, Japan) electrochemistry workstation using a three-electrode cell. SCE (Saturated Calomel Electrode) was used as the reference electrode, and graphite rod was used as the counter electrode. The working electrode was prepared by mixing $NiO/NiFe_2O_4$ powder, carbon black (Vulcan XC 72R) as a conductive agent, and nafion as a binder (8:1:1 in weight ratio) in 1 mL of 2:1 v/v water/isopropanol mixed solvent. After sonication for 30 min, the slurry was coated onto carbon paper (1 cm × 1 cm, Toray, Japan), and dried at room temperature. The catalyst loading for $NiO/NiFe_2O_4$ was about 1 mg cm^{-2}. The polarization curves were obtained in 1 M KOH with a scan rate of 5 mV s^{-1} at room temperature. All potentials were iR-compensated and converted to a reversible hydrogen electrode

(RHE) scale via calibration. And the presented current density was normalized to the geometric surface area.

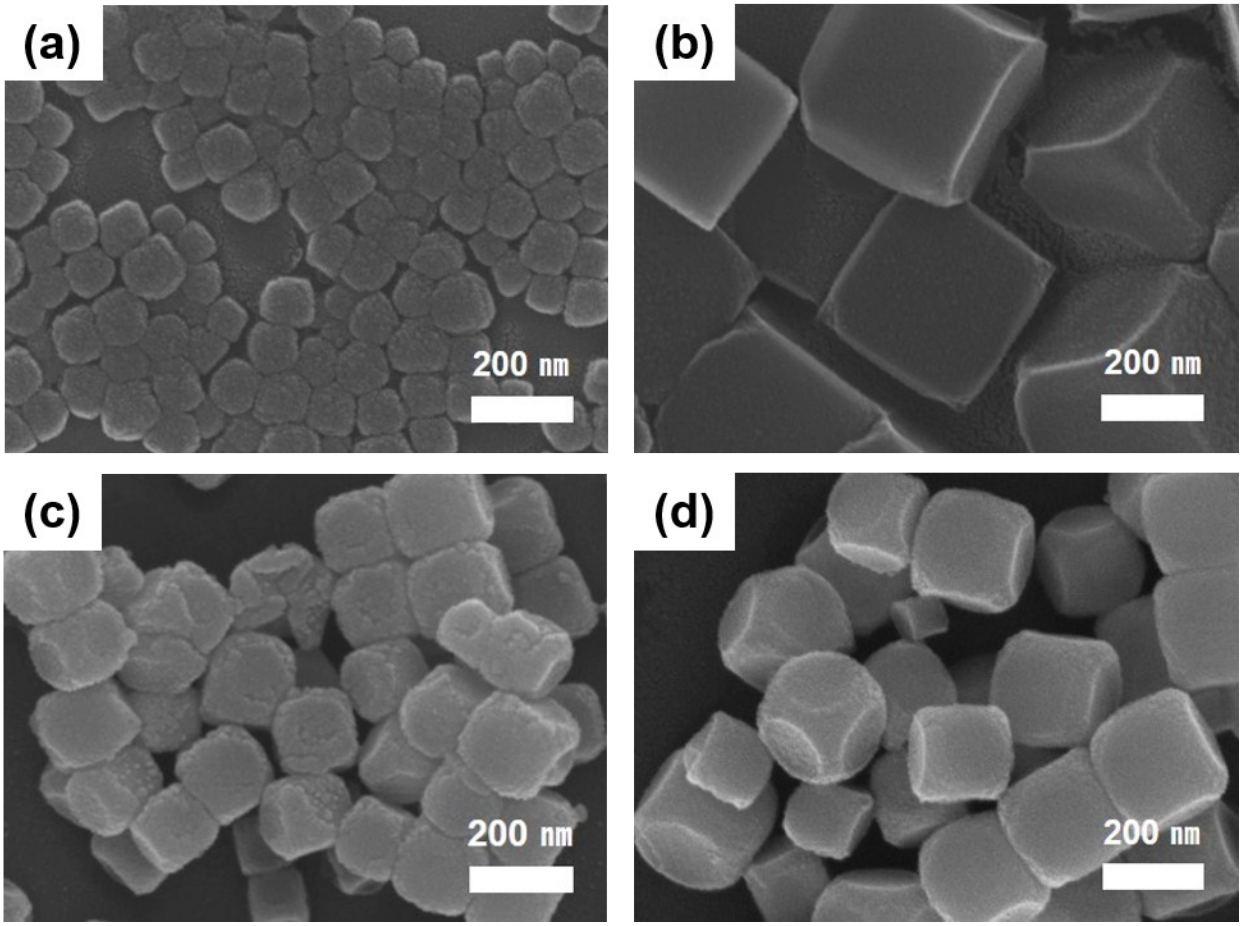

Fig. S1. FESEM images of synthesized $Ni_3[Fe(CN)_6]_2$ PBA nanocubes; concentration of SDBS (a) 0.3587 and (b) 1.4348 mmol at 60 °C, temperature (c) 50 and (d) 70 °C with concentration of SDBS 0.7174 mmol.

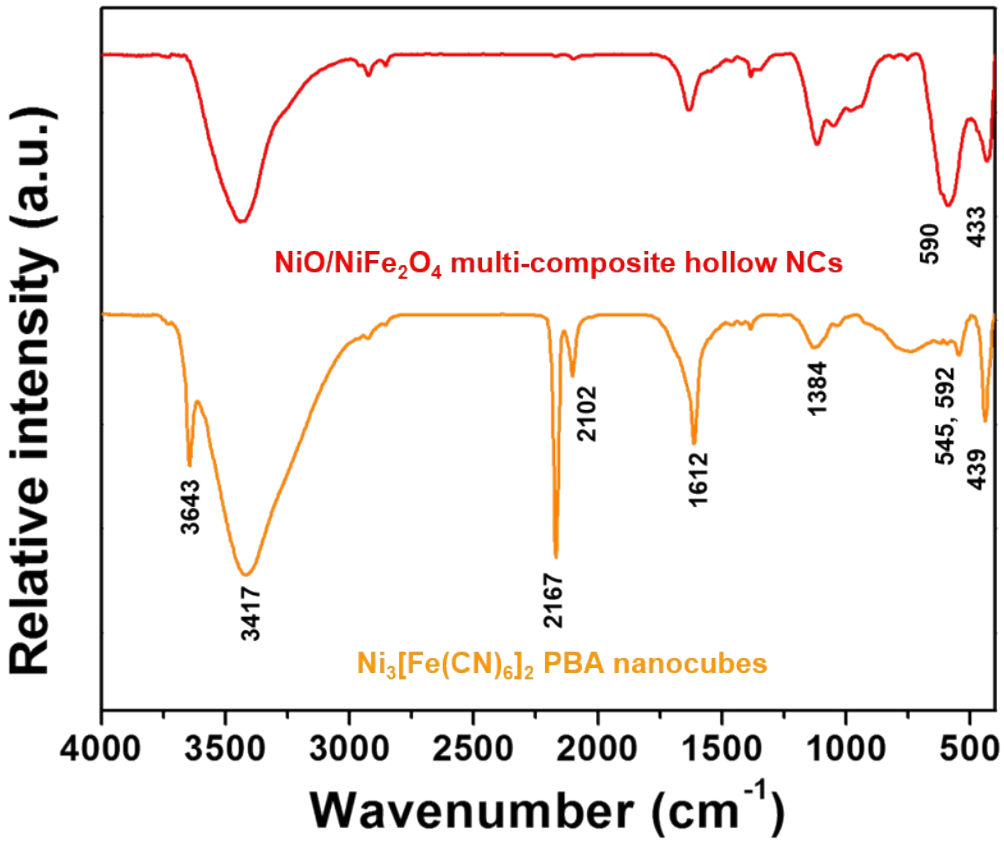

Fig. S2. FTIR spectra of the as-prepared $Ni_3[Fe(CN)_6]_2$ PBA nanocubes and mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs.

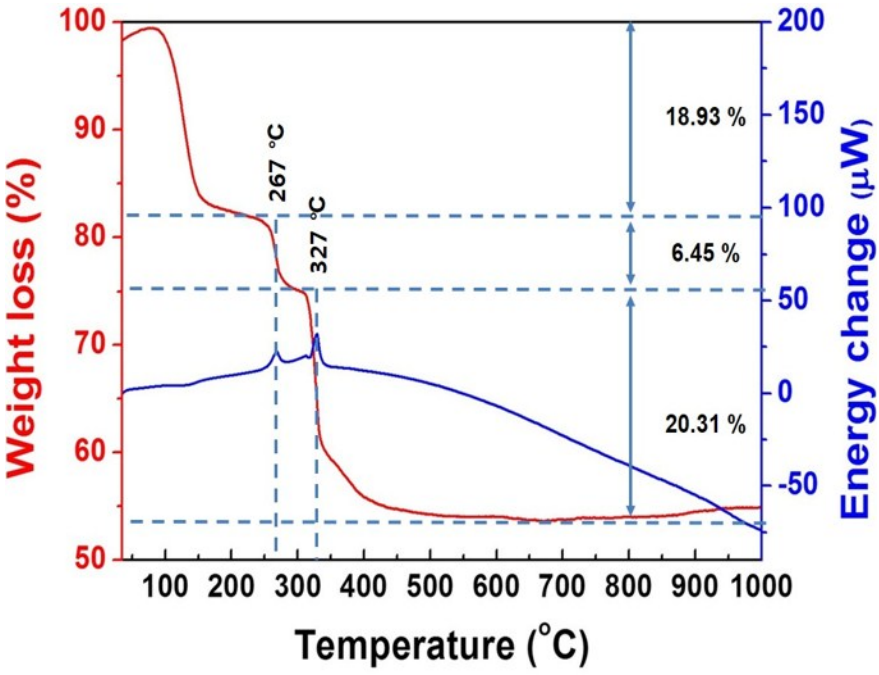

Fig. S3. TG-DTA curves of $Ni_3[Fe(CN)_6]_2$ PBA nanocubes.

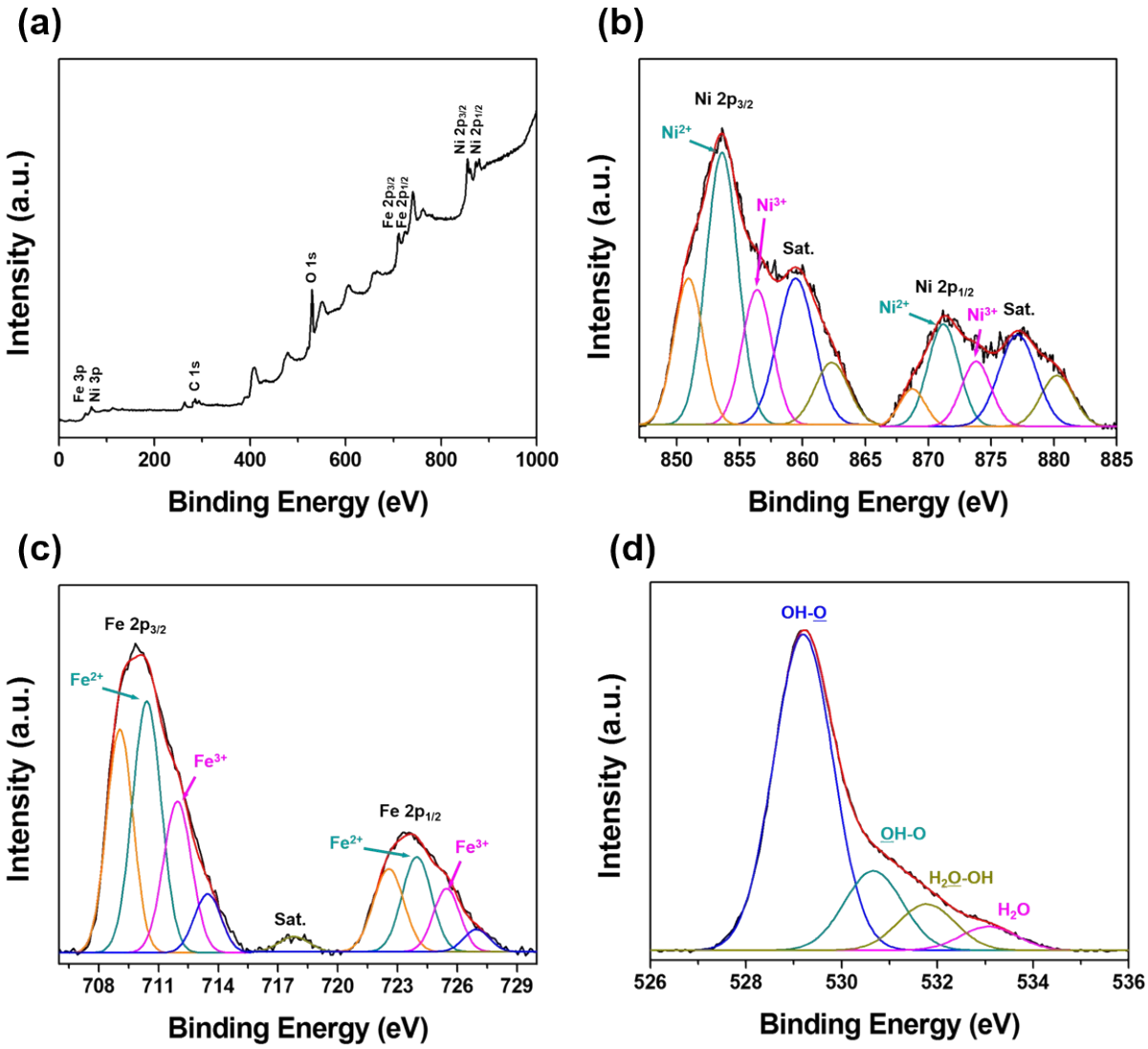

Fig. S4. (a) XPS survey scan of $NiO/NiFe_2O_4$ multi-composite hollow NCs after 1 h of calcination in air at 500 °C. XPS spectra of (b) Ni 2p, (c) Fe 2p, and (d) O 1s of $NiO/NiFe_2O_4$ multi-composite hollow NCs sample.

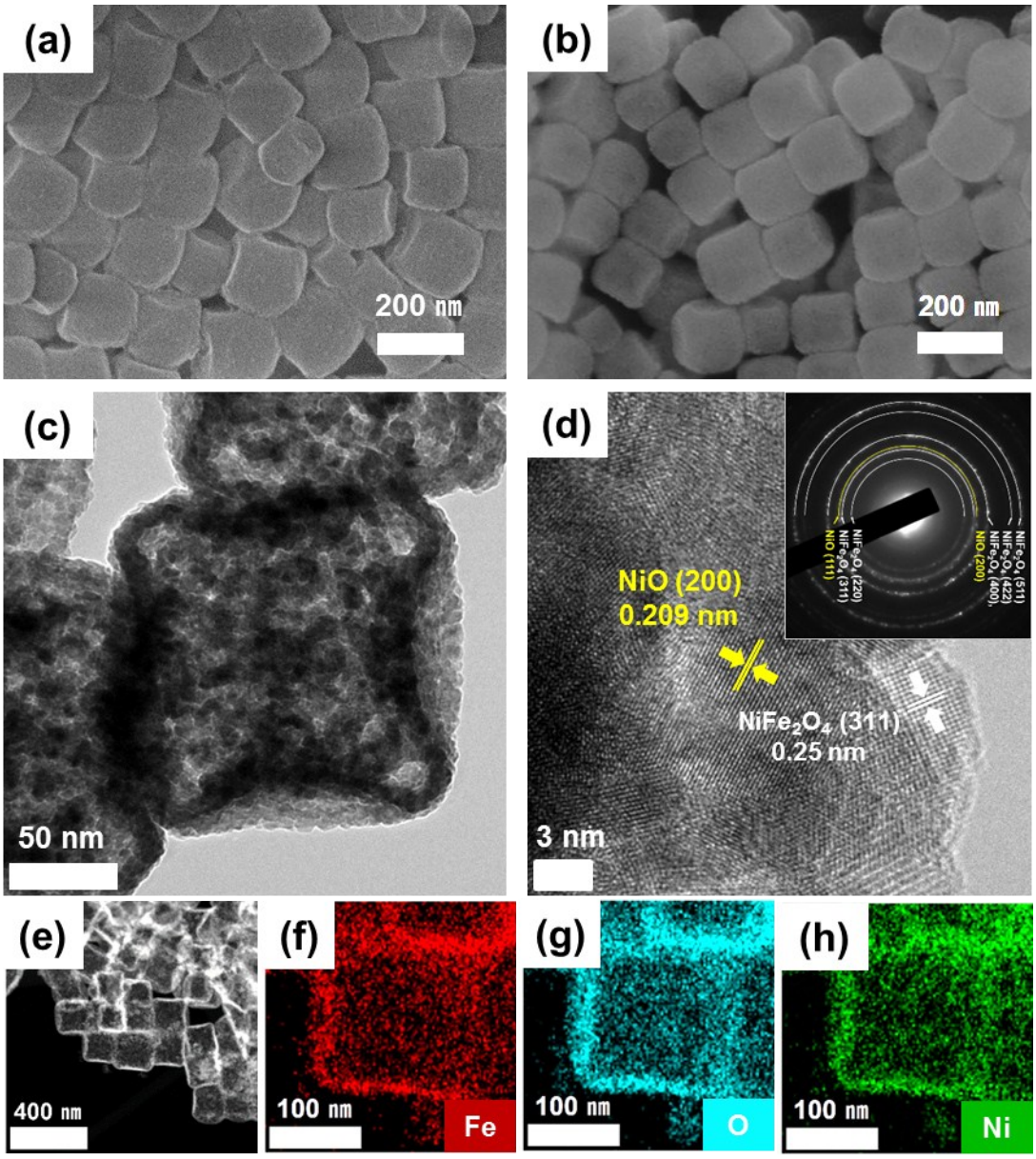

Fig. S5. (a) and (b) FESEM images of $NiO/NiFe_2O_4$ multi-composite hollow NCs after 1 h of calcination in air at 600 and 700 °C. (c) TEM and (d) HRTEM images (the inset shows the corresponding selective area diffraction pattern) of mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs after 1 h of calcination in air at 600 °C. (e)-(h) STEM-EDS of mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs.

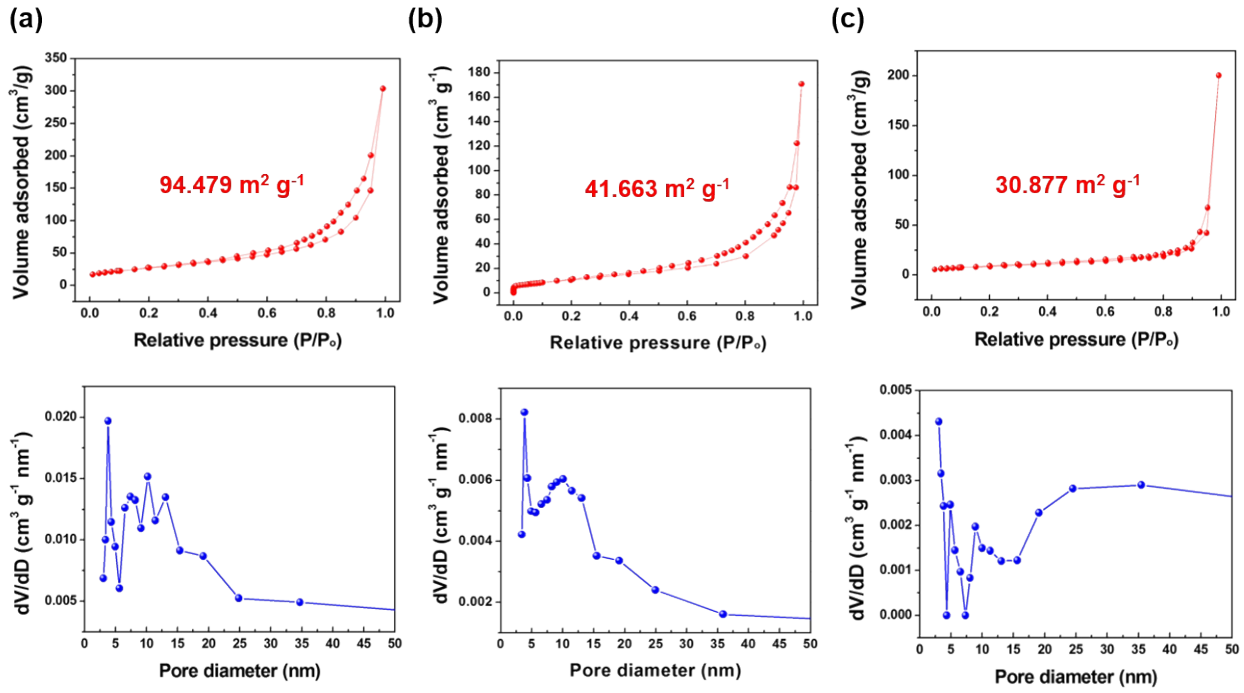

Fig. S6. Nitrogen adsorption-desorption isotherms and pore size distribution of mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs; (a) 500 °C, (b) 600 °C, and (c) 700 °C for 1 hour at air atmosphere.

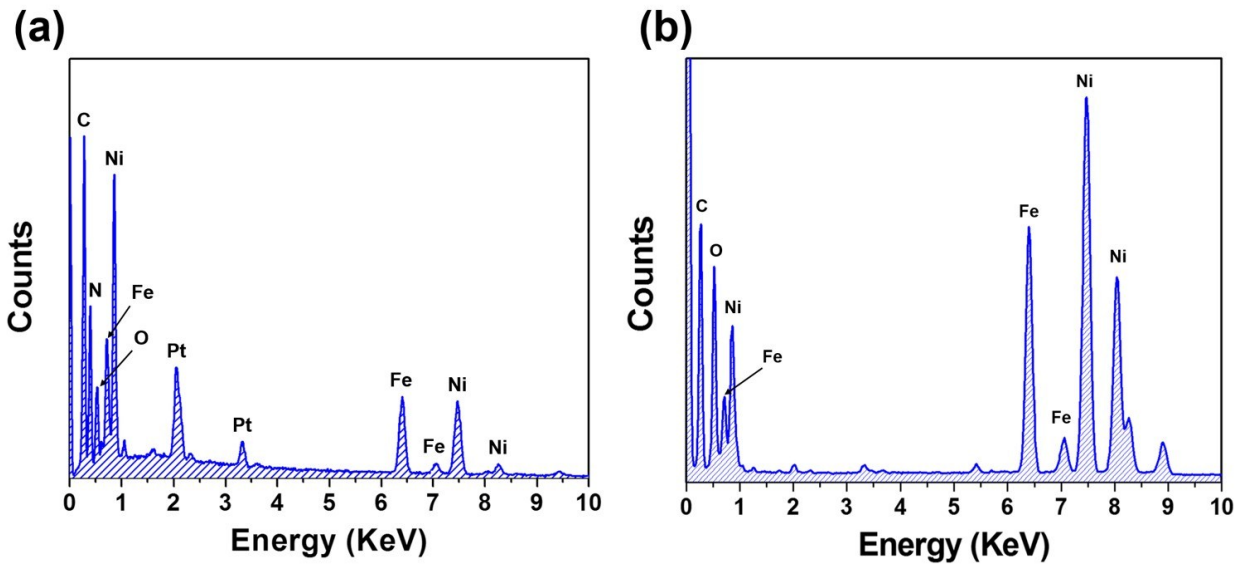

Fig. S7. The EDS spectra of the as-prepared (a) $Ni_3[Fe(CN)_6]_2$ PBA nanocubes and (b) mesoporous $NiO/NiFe_2O_4$ multi-composite hollow NCs after calcined at 500 °C for 1 hour.

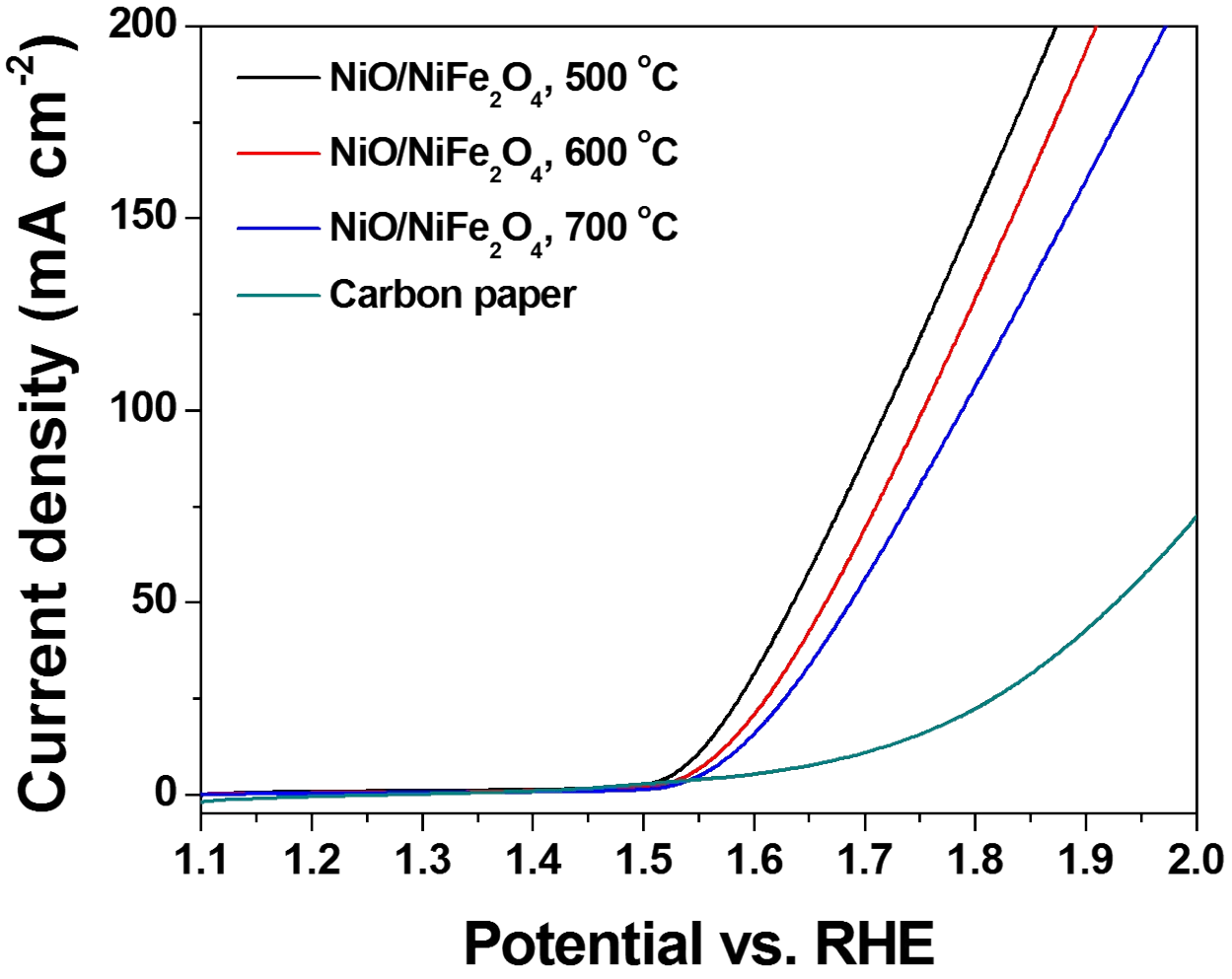

Fig. S8. Comparison of electrocatalytic properties of $NiO/NiFe_2O_4$ multi-composite hollow NCs (500, 600, and 700 °C), and pristine substrate. OER polarization curves recorded in 1 M KOH solution at a scan rate of 5 mV s^{-1} without iR compensation.

Table S1. Comparison of electrocatalytic properties of $NiO/NiFe_2O_4$ multi-composite hollow NCs (500, 600, and 700 °C), pure $NiFe_2O_4$, NiO and mixed $NiO/NiFe_2O_4$.

Sample	Overpotential (mV) at 10 mA cm^{-2}	Tafel polt (mV dec^{-1})
$NiO/NiFe_2O_4$ multi-composite hollow NCs (500 °C)	303	58.5
$NiO/NiFe_2O_4$ multi-composite hollow NCs (600 °C)	322	64.9
$NiO/NiFe_2O_4$ multi-composite hollow NCs (700 °C)	335	67.8
$NiFe_2O_4$	323	54
$NiO/NiFe_2O_4$	327	73
NiO (commercial)	423	96
NiO (commercial)/$NiFe_2O_4$	334	89

Supporting References

1. P. Nie, L. Shen, H. Luo, B. Ding, G. Xu, J. Wang and X. Zhang, *J. Mater. Chem. A.*, 2014, **2**, 5852.

2. B. K. Kang, M.-O. Kim, D. H. Yoon, Mater. Lett., 2012, **79**, 170.