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Electronic Supplementary Information

Promoting the electrocatalytic activity through introduction of oxygen vacancies to core-shelled NiO hollow spheres catalysts for efficient oxygen evolution

Long Li, Mengcong Jiao, Ben Xu, Shengrong Guo* and Qiang Hu*

Department of Chemistry, Lishui University, Lishui 323000, P. R. China.

E-mail: guosr9609@lsu.edu.cn, qihu@z-etech.cn

1 Chemicals and reagents

Cobalt nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), potassium hydroxide (KOH), isopropanol, glycerol, ethanol and Nafion were procured from Sigma-Aldrich. All the chemicals were of analytical grade and used without any further modification. Deionized water (DI) was obtained from Thermo Scientific Barnstead Pacific TII Water Purification System (18 MΩ cm).

2 Materials characterizations

The phase formation was identified using powder X-ray diffraction (XRD) (Bruker D8, Cu-Kα). The morphologies of the catalysts were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). The linear scanning energy-dispersive X-ray spectrometry (EDX) and EDX elemental mappings were taken on TEM. The X-ray photoelectron spectroscopy (XPS) spectra were measured on ESCALAB 250 spectrometer (Perkin-Elmer). Raman spectra were analyzed using in-Via Raman spectrometer.

3 Electrochemical measurements

The electrochemical tests were conducted on CHI 760E electrochemical workstation. The Ag/AgCl (saturated KCl solution) as used as the reference electrode, a graphite rod was served as the counter electrode, and all NiO spheres catalysts were utilized as working electrode. All electrochemical tests were performed in 1 M KOH aqueous electrolyte and the catalysts were dissolved in ethanol solution and then uniformly cast onto glassy carbon working electrode with a total loading of 0.4 mg cm^{-2}. All the linear sweep voltammetry (LSV) measurements were taken at a scan rate of 5 mV s^{-1} to obtain the polarization curves. Chronoamperometric measurements were performed at corresponding potential to deliver a current density of 10 mA cm^{-2}. The Tafel slope was calculated according to the Tafel equation $\eta = b \log (j/j_0)$ (η is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density). Potentials were referenced to a reversible hydrogen electrode (RHE) using the following equation: Potentials were referenced to a reversible hydrogen electrode (RHE) using the following equation: E (RHE) =E (Ag/AgCl) + (0.205 + 0.059pH) V. The double layer capacitance (C_{dl}) was obtained using cyclic voltammetry (CV) scanning from 1.22 to 1.28 V vs. RHE with different scan rates from 20 to 60 mV s^{-1} for OER. The electrochemical impedance spectroscopy (EIS) measurements were carried out by ranging the frequency from 100 k Hz to 0.1 Hz.

4. Supplementary figures

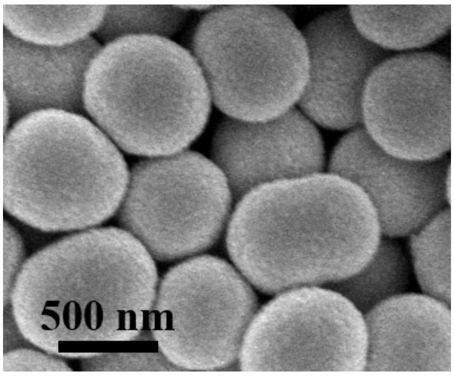

Fig. S1 SEM image of the Ni-precursor sample.

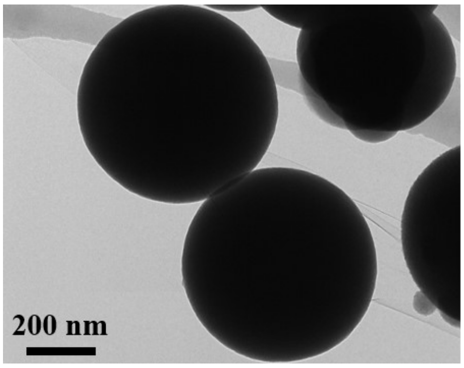

Fig. S2 TEM image of the Ni-precursor sample.

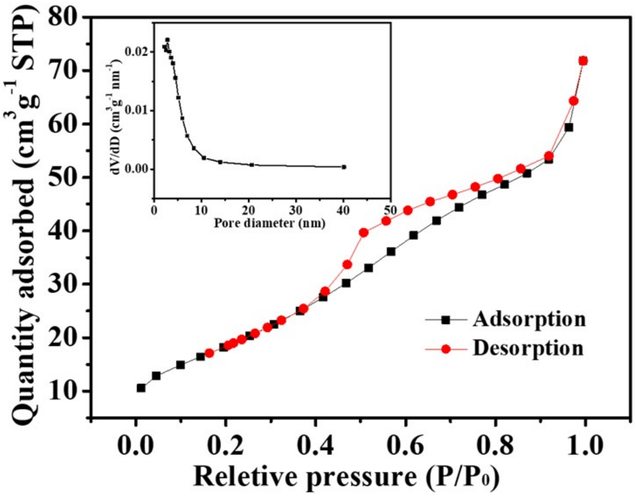

Fig. S3 N_2 adsorption-desorption isotherm, and the corresponding pore size distribution (inset) of the core-shell NiO_{1-x}-M hollow spheres.

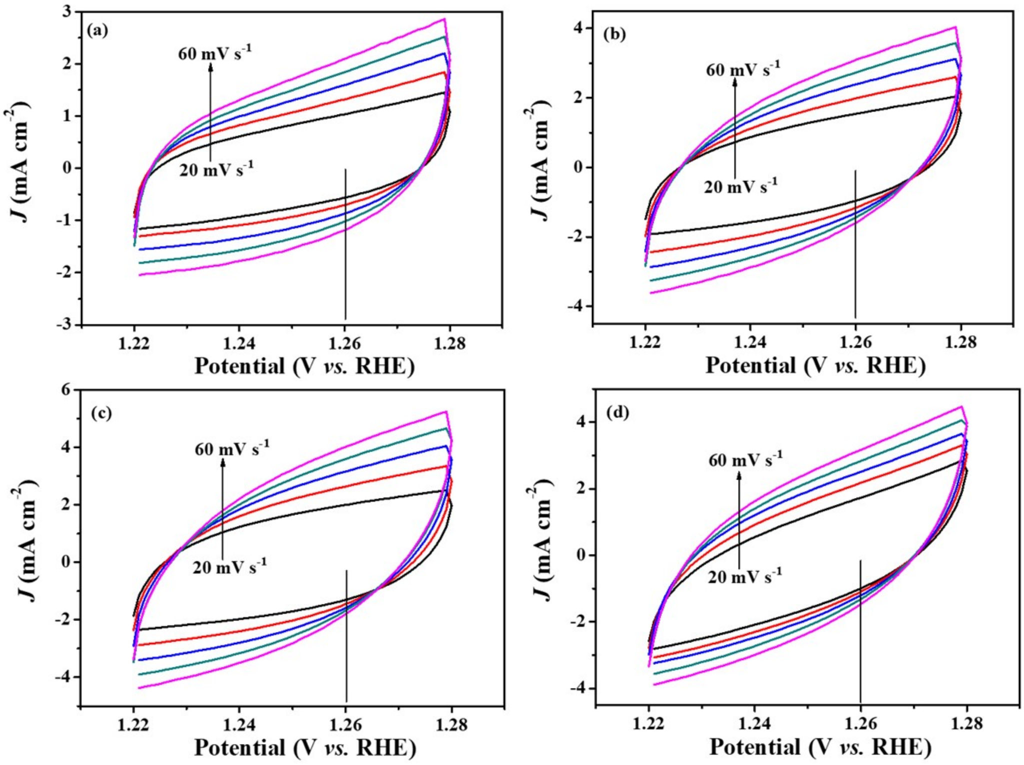

Fig. S4 CVs tested at the potential range of 1.22 –1.28 V vs. RHE with the scan rates increasing from 20 to 60 mV s^{-1} for (a) NiO, (b) NiO_{1-x}-L, (c) NiO_{1-x}-M and (d) NiO_{1-x}-H spheres.

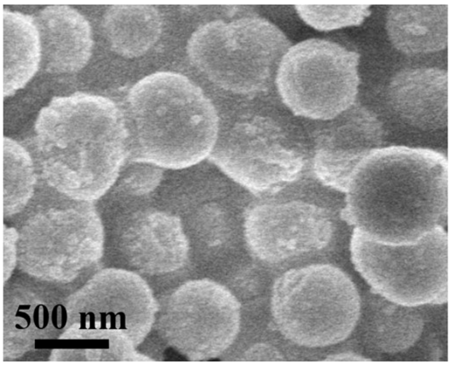

Fig. S5 SEM image of of the NiO_{1-x}-M catalyst after the cycling test.

Table S1 Comparison of OER performance in alkaline media for NiO_{1-x}-M spheres with other reported OER catalysts electrocatalysts.

Catalysts	Current density (j, mA cm^{-2})	η at the corresponding j (mV)	Tafel slope (mV dec^{-1})	Ref.
NiO_{1-x}-M spheres	10	360	103.9	this work
Fe-doped NiO	10	310	N.A.[a]	[1]
NiO-V_o nanosheet	10	138	138	[2]
Sm-NiO-E	10	409	81	[3]
porous NiO	10	310[b]	54	[4]
O-NiO@MCSN	10	410	93	[5]
NiO nanosheets	10	400	136	[6]
NiO NPs/g-C_3N_4	10	360	65	[7]
NiO/NiS	40	209[c]	60	[8]
Ni/NiO	10	470	58	[9]
NiO nanobelts	50	382	142	[10]
Se-Fe_2O_3@Ni/NiO/CC	10	205[c]	36	[11]
Ce-NiO-E	10	382	118	[12]
NiO/CuO nanosheet	10	234[b]	22	[13]
Co doped NiO	10	370	69	[14]
NiO nanosheets	10	380	299	[15]
NiO/CoFe alloy nanosheets	30	280[c]	77	[16]

a: not given
b: tested on nickel foam
c: tested on carbon cloth

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