Electronic Supplementary Information (ESI)

Regulating Active Species of Ni(OH)₂ by CeO₂: 3D CeO₂/Ni(OH)₂/Carbon Foam as an Efficient Electrode for Oxygen Evolution Reaction

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Experimental Section

Preparation of N, O, S Doped CF: Firstly, commercial melamine foam (MF) was cut into small pieces. A piece of MF was put into a tube furnace and heated to 700 °C for 1 h under protection of nitrogen atmosphere. Then the as-prepared carbon foam (CF) was cooled down to room temperature. Secondly, a piece of as-prepared CF was immersed completely in the (4 mL 65% HNO₃ + 12 mL 98% H₂SO₄) mixed acid solution at 35 °C for 6 h. The obtained NOSCF was washed by deionized water till the pH of solution was neutral.

Growth of Ni(OH)₂ Nanosheets on NOSCF: 5.26 g of NiSO₄·6H₂O, 1 g of K₂S₂O₈ and 100 mL of deionized (DI) water (H₂O) were added in a 150 mL beaker at room temperature. A piece of as-prepared NOSCF was used as a substrate, and immersed into the above clear green solution. Then 3 mL of NH₃·H₂O solution was added drop by drop with stirring for a few seconds, let set for 1 h without stirring at room temperature.

Colloidal Synthesis of Monodispersed CeO₂ NPs: The 3.3 nm-sized CeO₂ NPs was prepared by one pot colloidal synthesis method. 2 mmol (109.6 mg) of (NH₄)₂Ce(NO₃)₆, 20 mmol (5.36 g) of OM and 20 mmol (5.05 g) of ODE were added into a 100 mL three-necked flask, removed water and oxygen by heating up to 120 °C. Then the resulting slurry was heated to designed reaction temperature of 300 °C under nitrogen atmosphere, and reacted for 40 min. After cooling to room temperature, the CeO₂ product was precipitated by excess ethanol and separated by centrifugation (10,000 rpm, 8 min), followed by dispersed in 5 mL hexane and removed long-chain ligand by adding 5 mL Na₂S (50 mg mL⁻¹) solution.

Decoration of CeO₂ NPs on Ni(OH)₂/NOSCF to Form the CeO₂/Ni(OH)₂/NOSCF Electrode: Electrophoretic deposition method was used for depositing CeO₂ NPs on Ni(OH)₂/NOSCF. Firstly,
the surfaced modified CeO₂ NPs were re-dispersed in acetone with various concentrations. The electrophoretic deposition process was performed with a two-electrode system. Ni(OH)₂/NOSCF was used as working electrode and Pt foil was used as counter electrode in the CeO₂ NPs dispersion. A constant voltage of 100 V/cm was applied for 10 mins.

Characterizations: The shapes of NOSCF and Ni(OH)₂/NOSCF were examined through a Quanta F250 scanning electron microscope (SEM). The morphologies of CeO₂ were characterized by a Hitachi HT−7700 transmission electron microscope (TEM, Japan), operating at 100 kV. High−resolution TEM (HRTEM) images were obtained by a Philips Tecnai F20 FEG−TEM (USA), operating at 200 kV. The podwer X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX−RB with Cu Kα radiation (λ=1.5418 Å). FT-IR spectra were measured by a Nicolet 6700 FT-IR spectrometer. X-ray photoelectron spectra (XPS) were conducted by a PHI Quantera SXM spectrometer. UV-vis absorption spectra were measured by a PerkinElmer Lambda 35 UV−vis spectrophotometer.

Electrocatalytic Measurements for OER: The electrochemical measurements were carried out in an O₂ -saturated solution of 1.0 M KOH on an AUTOLAB PGSTAT204 electrochemistry workstation by using a typical three-electrode electrochemical cell. A saturated calomel electrode (Hg/HgCl₂ in saturated KCl) and Pt plate were used as the reference electrode and the counter electrode, respectively. The as prepared CeO₂/Ni(OH)₂/NOSCF directly served as working electrode. CV and LSV curves with a scan rate of 10 and 5 mV s⁻¹ were conducted, respectively. EIS results were recorded in the frequency range from 1.0 to 100 kHz at an open circuit potential with a 5 mV amplitude. Stability of CeO₂/Ni(OH)₂/NOSCF was conducted by chronoamperometry method under different overpotentials (vs. SCE) of 0.55, 0.60, 0.65, 0.70, 0.75, 0.80 V for continuous testing of 6 h.
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**Fig. S1** EDS elemental mapping for C, N, O and S elements recorded on the pure carbon foam.

**Fig. S2** (a) High-resolution O 1s XPS spectra of NOSCF and further oxidized NOSCF. (b) XPS spectrum of N, O and S doped carbon foam (NOSCF), the contents of C, N, O and S elements in NOSCF were measured to be about 66.8, 4.3, 24.5 and 0.42 atom %, respectively.

**Fig. S3** The enlarged SEM image of Ni(OH)$_2$ nanosheets grown on NOSCF.
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Fig. S4 The loading percentage of Ni(OH)$_2$ in the Ni(OH)$_2$/NOSCF was determined by thermogravimetric analysis (TGA). As shown in Fig. S2, the sample weight decreases slowly between 50 and 150°C; this is mainly due to the removal of chemically adsorbed H$_2$O. The slight weight loss of 3.75% between 300 and 350 °C is believed that the reaction of Ni(OH)$_2$ → NiO+H$_2$O occurs in this region. With continue to increase the temperature to more than 450 °C, an obvious weight loss of 50.8 % is present between 450 and 660 °C, indicating the NOSCF begins to convert into CO$_2$. Through analysis of the TGA data, the loading percentage of Ni(OH)$_2$ in the Ni(OH)$_2$/NOSCF composite was estimated to be ~63%.

![Ni(OH)$_2$/NOSCF TGA](image)

Fig. S5 FTIR spectra (Nicolet 6700) of oleylamine, as-prepared CeO$_2$ NPs and surface modified CeO$_2$ NPs. The presence of acyclic C-H stretching at 2923 cm$^{-1}$ and 2854 cm$^{-1}$ indicate the existence of oleylamine. The three sharp peaks at 1314, 1054 and 810 cm$^{-1}$ in the IR spectrum of CeO$_2$ NPs were indexed to C–N stretch of oleylamine, respectively. Based on the FTIR analysis of CeO$_2$ NPs, it is confirmed that these CeO$_2$ NPs are coated by oleylamine organic molecule. Note here, after surface modified treatment, the intensity of characteristic peaks of oleylamine obviously decreased, indicating a successful removal of organic capping ligands from the surface of CeO$_2$ NPs.

![FTIR spectra](image)

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Fig. S6 (a) TEM image of CeO₂ NPs after surface modification. The interplanar spacing of 0.16 nm can be observed, which is corresponding to the (111) crystal plane of CeO₂ NPs. (b) Digital photo for surface modified-CeO₂ NPs dispersed in water solution.

Fig. S7 (a) EIS Nyquist plots showing the electrode kinetics of Ni(OH)₂/NOSCF and CeO₂/Ni(OH)₂/NOSCF. (b) Enlarged EIS Nyquist plots derived from a).
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**Fig. S8** Polarization curves recorded on CeO$_2$/Ni(OH)$_2$/NOSCF electrode with different content of CeO$_2$ NPs in CeO$_2$/Ni(OH)$_2$/NOSCF. The loading mass ratio of CeO$_2$ NPs on Ni(OH)$_2$/NOSCF were 5%, 10%, 30% and 50%, potential scan rate is 5 mV s$^{-1}$.

**Table S1.** Comparisons of the OER activity for CeO$_2$/Ni(OH)$_2$/NOSCF electrocatalyst with some representative OER catalysts under basic condition.

<table>
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<th>Catalysts</th>
<th>Electrolyte</th>
<th>Onset potential</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Ref.</th>
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<tr>
<td>CeO$_2$/Ni(OH)$_2$/NOSCF</td>
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<td>57</td>
<td>Our work</td>
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References: