# Controlled phosphating: an novel strategy toward $NiP_3@CeO_2$ interface engineering for efficient oxygen evolution electrocatalysis

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## Experimental section

### Materials and chemicals

Nickel foam (NF, Kunshan Guangjiayuan Electronic Material), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, Sigma Aldrich), cerous nitrate nonahydrate ($Ce(NO_3)_3 \cdot 9H_2O$, Alfa Aesar), sodium hypophosphite ($NaH_2PO_2$, Alfa Aesar), urea ($CO(NH_2)_2$, Promega Corporation) were used without further purification and all aqueous solutions were prepared using deionized water.

### Materials synthesis

In a typical synthesis process, $Ni(NO_3)_2 \cdot 6H_2O$ (1.019 g), $Ce(NO_3)_3 \cdot 9H_2O$ (0.76 g), and $CO(NH_2)_2$ (1.051 g) were dissolved in deionized water (60 mL). After continuously stirring for 30 min, the solution was then transferred to a 100 mL Teflon-lined stainless steel autoclave with a piece of Ni foam (2 cm × 3 cm). Then autoclave was sealed and maintained at 120 °C for 10 h in an oven. After the autoclave cooled down to room temperature, the sample was taken out and thoroughly washed with deionized water and ethanol several times alternatively, then dried at 60 °C for 6 h in air. After that, the sample was calcinated at 350 C for 2 h and grey $NiO@CeO_2$ was obtained. Next, the $NiO@CeO_2$/NF was placed in an alumina boat and the other alumina boat containing 700 mg $NaH_2PO_2$ was placed at the upstream of the tube furnace. The two alumina boats were calcined at 300 °C for 2 h with a heating speed of 2 °C min$^{-1}$ under Ar flow and then cooled down to room temperature naturally. $NiP_3$/NF were made under identical conditions with no cerium salts added for hydrothermal preparation.

### Structural characterization

The purity and phase data for the $NiP_3@CeO_2$ materials were researched by X-ray diffraction (XRD, Rigaku D/MAX-2200PC X-ray diffractometer with Cu Kα radiation). The scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS) mapping and transmission electron microscopy (TEM) were obtrained by LEO 1525 and JEOL 2010F. The X-ray photoelectron spectroscopy (XPS) was acquired using a PHI 5000 VersaProbe (ULVAC PHI, Japan) with an Al monochromatic Kα source.

### Electrochemical characterization

Electrochemical measurements were conducted (CHI660e electrochemical station, Shanghai Chenhua) using a typical three-electrode system in an alkaline medium. The graphite rod and Ag/AgCl electrode was used as the counter electrode and the reference electrode and $NiP_3@CeO_2$ was used as the working electrode. All of potentials reported were converted to a reversible

hydrogen electrode (RHE) according to the equation: $E_{RHE}= E_{Ag/AgCl} + 0.197 + 0.059*pH$. Linear sweep voltammetry (LSV) curves were performed to obtain characterization of basic electrochemical data at a scan rate of 5 mV s$^{-1}$ with iR compensation. The overpotential ($\eta$) for OER was calculated by $\eta(V) = E_{RHE} -1.23$ V and the Tafel slope (b) was calculated by $\eta= a + b$ log(j), where b is the Tafel slope and j is the current density. The double-layer capacitance ($C_{dl}$) was evaluated by electrochemically active surface area (ECSA) and cyclic voltammetry (CV) in a non-faradaic region. The $C_{dl}$ was calculated as half of the slope by curve plotting the current density against the scan rate. Electrochemical impedance spectroscopy (EIS) was researched at an overpotential of 300 mV from 0.01 Hz to 100 kHz at an alternating current voltage amplitude of 10 mV. The 1000 CV cycles were done between 1.2 and 1.7 V vs. RHE at a scan rate of 5 mV s$^{-1}$ during stability testing, and the LSV curves were preformed before and after the CV cycles. Chronopotentiometric tests were done at 8 mA cm$^{-2}$ for 10 h to study the stability of the material.

**DFT calculation**

In this study, the Cambridge Serial Total Energy Package module of Materials Studio was used for DFT calculation. The interactions of electrons were calculated by the generalized gradient approximation functions of Perdew-Burke-Emzerh (GGA-PBE). The (200) and (111) plane optimal structures of $NiP_3$ and $CeO_2$ were calculated by setting a cutoff energy of 450 eV and 3×3×1 k-points grid. The structures were also optimized for energy and force convergence choosing as $2.0×10^{-5}$ eV/atom and 0.05 eV/A, respectively. The vacuum space was up to 0.002 A to eliminate periodic interactions.

**Table S1.** The atomic percent of $NiP_3@CeO_2$

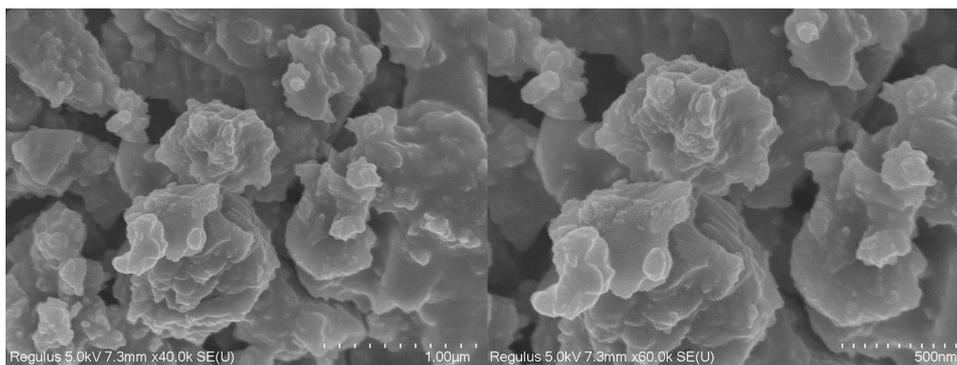| Element | Line Type | k Factor | Atomic % |
|---------|-----------|----------|----------|
| O | K series | 2.020 | 50.25 |
| P | K series | 1.052 | 17.02 |
| Ni | K series | 1.164 | 6.38 |
| Ce | L series | 2.044 | 26.35 |
| Total: | | | 100.00 |

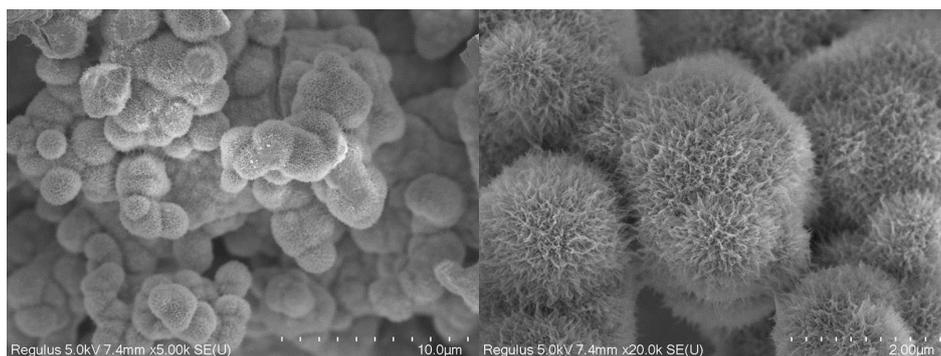**Fig. S1** SEM of the resulting NiP$_3$/NF.



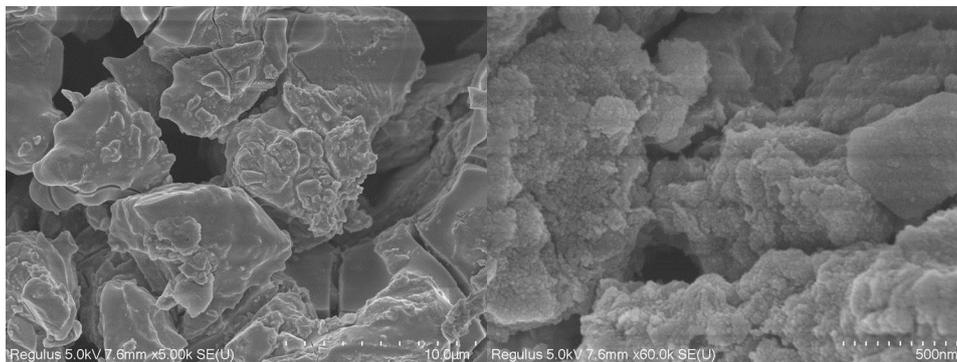**Fig. S2** SEM of the resulting NiO@CeO$_2$/NF.



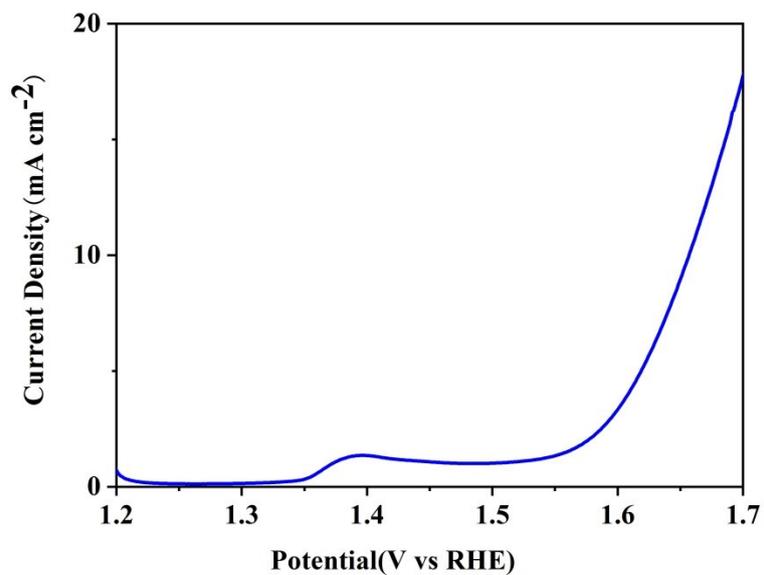**Fig. S3** SEM of the resulting NiP$_3$@CeO$_2$/NF.

**Fig. S4** Polarization curve of the Ni foam for OER with a scan rate of 5 mV s$^{-1}$ in 1 M KOH.
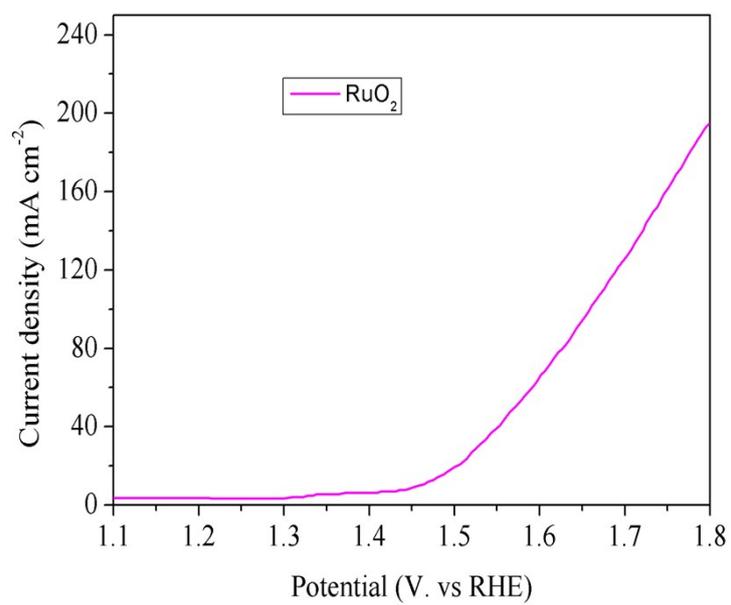


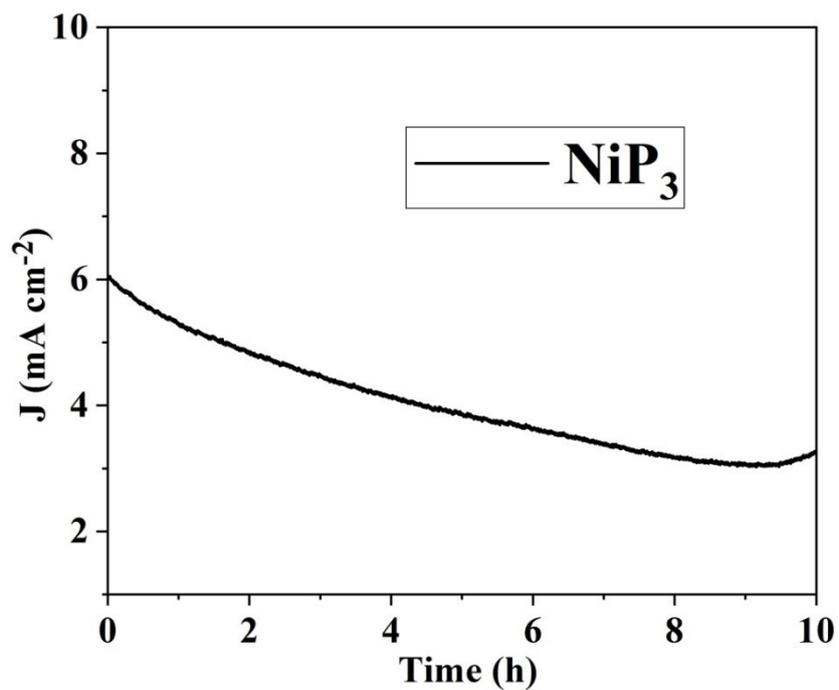**Fig. S5** Polarization curve of the RuO$_2$ for OER with a scan rate of 5 mV s$^{-1}$ in 1 M KOH.

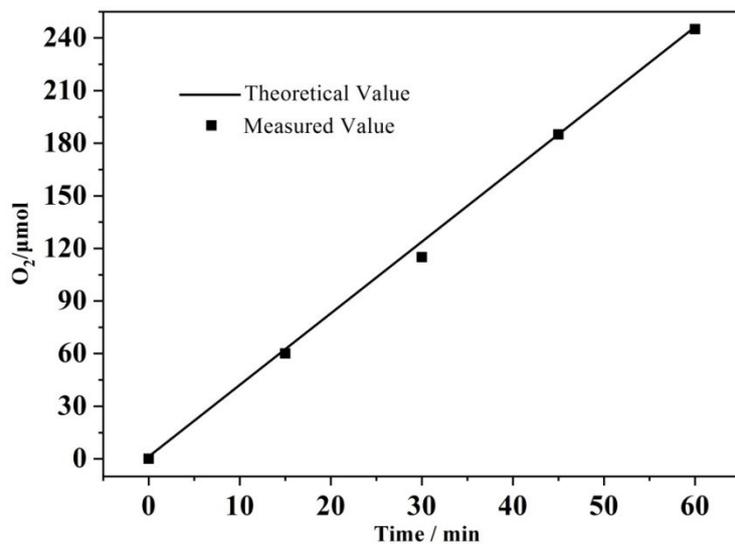**Fig. S6** Chronopotentiometric curve of $NiP_3$ at a constant potential of 1.50V.



**Fig. S7** Electrocatalytic efficiency of $O_2$ production over $NiP_3@CeO_2/NF$ at a potential of ca. 1.48 V, measured for 60 min.
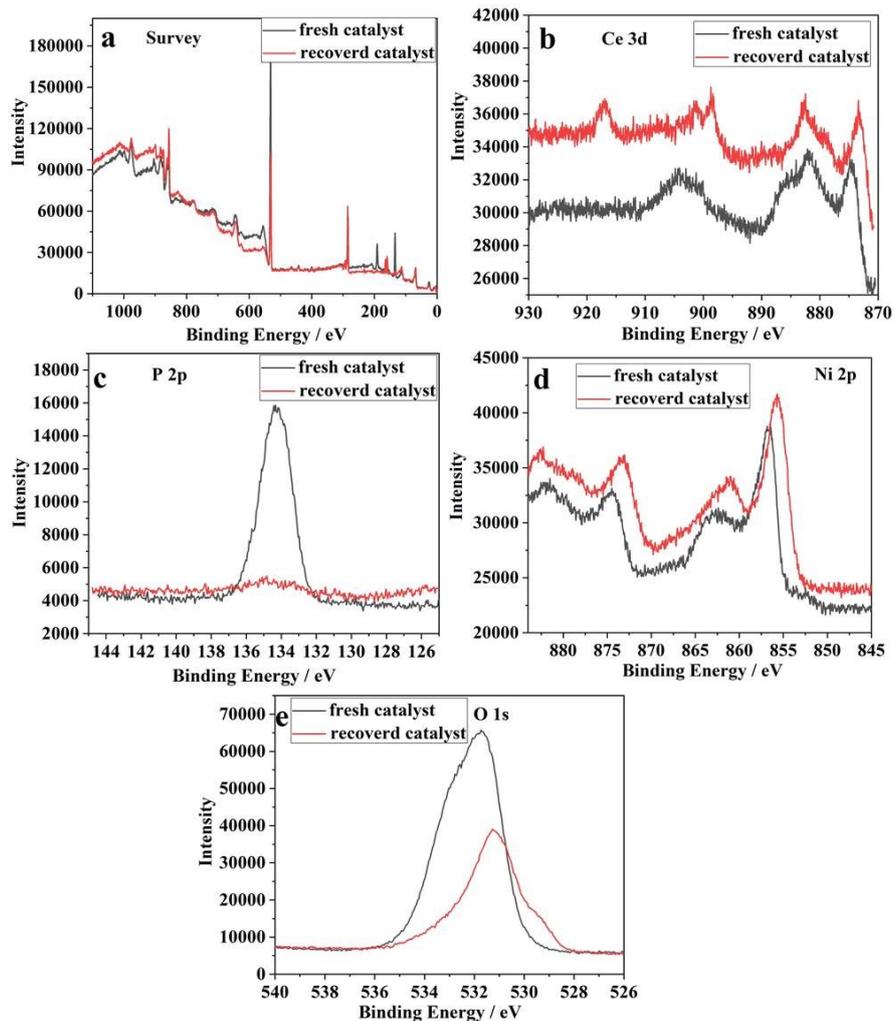
**Fig.S8** XPS of the fresh and recovered $NiP_3@CeO_2/NF$ (a) Survey, (b) Ce 3d, (c) P 2p, (d) Ni 2p and (e) O1s.
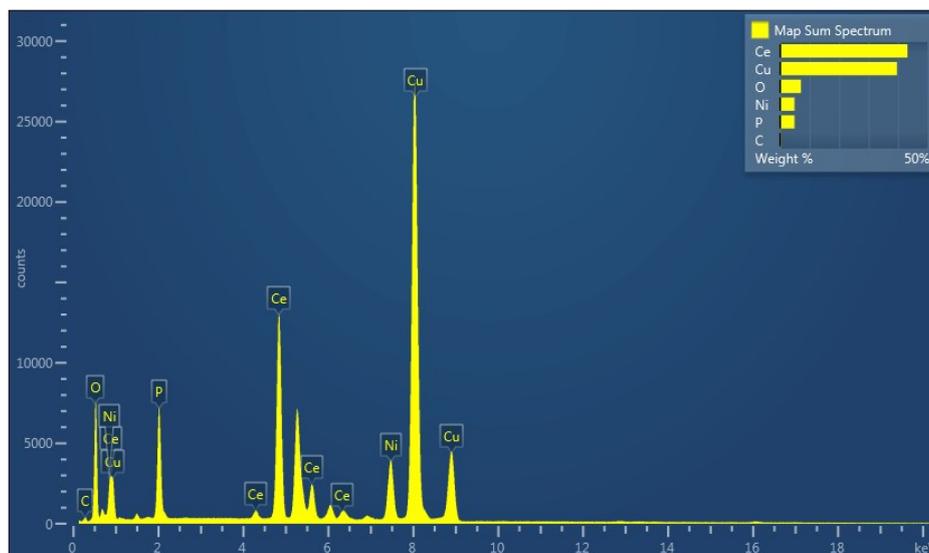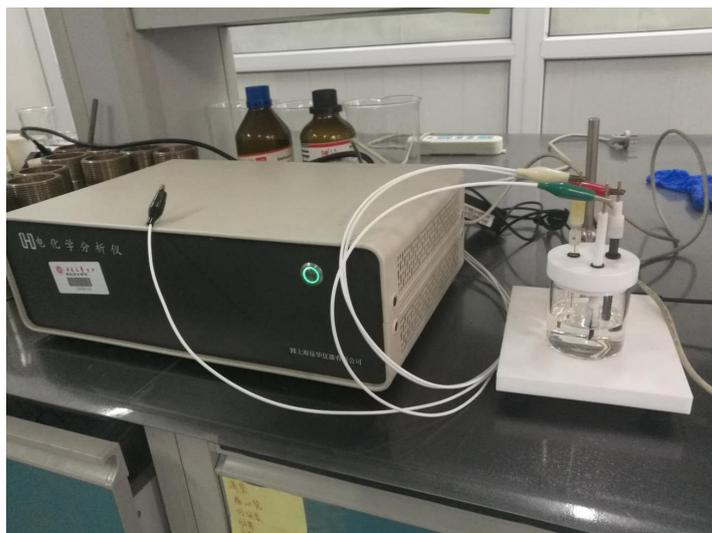


**Fig.S9** EDS spectroscopy of the $NiP_3@CeO_2/NF$.

**Fig.S10** A photograph showing generation of $O_2$ bubbles on the $NiP_3@CeO_2/NF$ electrodes.
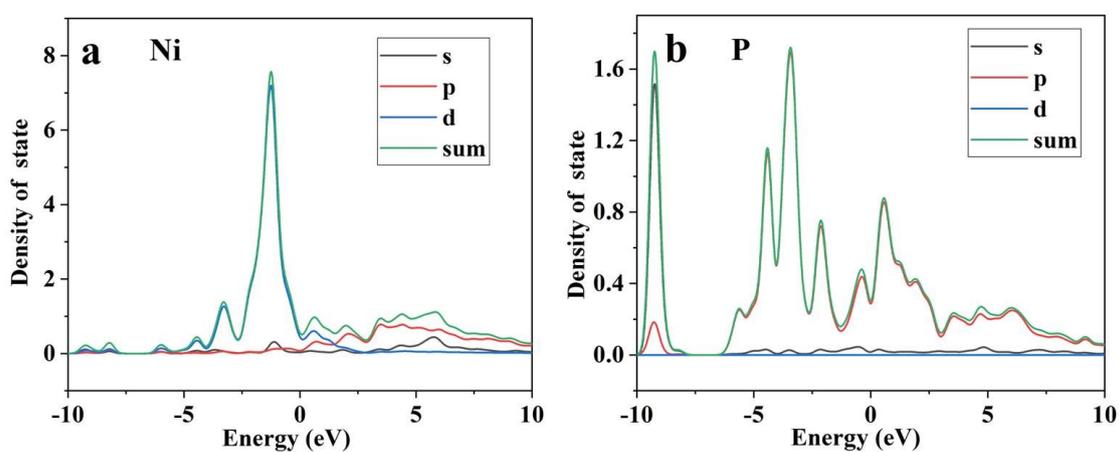


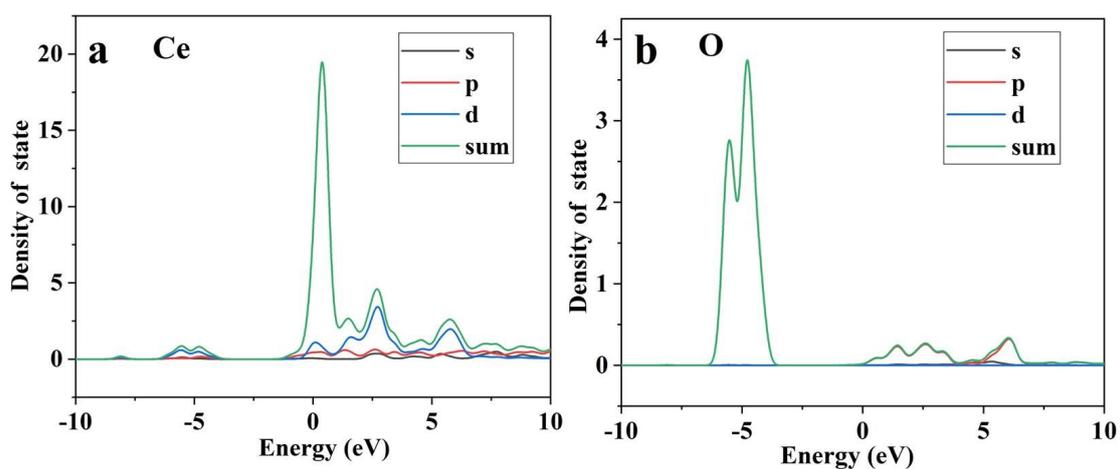**Fig. S11** Calculated density of states for Ni and P in $NiP_3$.



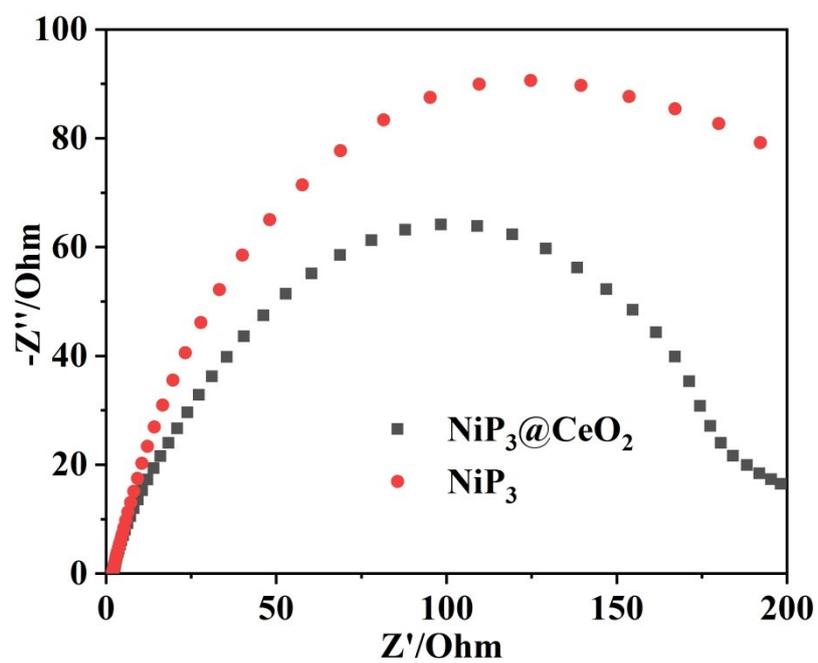**Fig. S12** Calculated density of states for Ce and O in $CeO_2$.

**Fig. S13** Nyquist plots of NiP$_3$/NF and NiP$_3$@CeO$_2$/NF.