In situ surface engineering of nickel inverse opal for enhanced overall electrocatalytic water splitting†

Qingwen Zhou, Jun Pu, Xiaolei Sun, Chao Zhu, Jiachen Li, Jian Wang, Shaozhong Chang and Huigang Zhang

High-efficiency non-precious catalysts are important for hydrogen and oxygen evolution reactions (HER and OER). Practical water splitting needs not only intrinsically active catalyst materials but also the maximization of their electrocatalytic capability in a real electrolyzer. Here, we report for the first time a Ni/Ni2P inverse opal architecture fabricated by surface engineering. The superior HER properties are enabled by maximum active crystallographic plane exposure and vertical alignment of Ni2P nanosheets on nickel inverse opal. It requires an overpotential of only 73 mV to drive a HER current density of ~20 mA cm−2. After doping with Fe, the resulting Fe:Ni/Ni2P inverse electrode shows excellent OER performance with a very low overpotential (285 mV) at a current density of 20 mA cm−2. An alkaline electrolyzer using the two 3D structured electrodes could split water at 20 mA cm−2 with a low voltage of ~1.52 V for 100 h. The catalytic activity is even superior to that of the noble metal catalyst couple (IrO2–Pt/C). This work provides a surface engineered opal structure to maximize the electrocatalyst properties in the systems with coupled electron transfer and mass transport.

Introduction

Three-dimensional ordered macroporous structures have been widely explored for many important applications such as photonics, catalysis, sensors, energy storage, and so on.1–3 They are generally prepared by inverting self-assembled opal templates. Silica, polystyrene (PS), and poly(methyl methacrylate) have been used to grow opal templates. The inversion of these templates usually involves electrodeposition, chemical vapor deposition, and sol-gel techniques. The resulting macroporous structure has an adjustable pore structure (such as size, interconnectivity, and surface properties)4–6 and could provide large surface area and interconnected channels for rapid species transport. Such properties are highly desired for surface reaction and mass transport coupled systems.4,5,8 Metals,4,8 metal oxides,11,26 and polymers12,13 have been applied to inverse opal structures to form monolithic electrodes, which demonstrated improved properties for photo-electrochemistry,14–17 sensing,18 energy storage,2,3,6 and water splitting.7,9,14 In this work, we take advantage of inverse opal structures to enhance electrocatalytic water splitting.

A high-efficiency water splitting system requires low overpotentials in both anode and cathode.19–21 Transition metal phosphides have been recently reported to exhibit superior hydrogen evolution reaction (HER) activities as compared to their oxides or hydroxides.22–25 For example, Ni5P nanoparticles exhibit one of the highest HER activities among non-noble metal electrocatalysts.26 In particular, experimental and theoretical investigations have revealed that the Ni5P {001} planes display great catalytic activities. Nanostructuring Ni5P to increase active plane exposure has been reported to enhance the HER properties.26–28 However, the maximized exposure of Ni5P {001} planes has not been realized yet.

Many attempts have been made to enhance catalytic performance through exploration of novel materials.21,23,24 Concurrent consideration of high active surface area, optimal electron pathway, and efficient mass transport is needed for further enhancement.9,19–21 A metallic inverse opal architecture is able to provide large surface area and mass transport channels. Preliminary research9 on Ni inverse opal has demonstrated that the catalytic activities for HER and OER increase with the layers of inverse opals, indicating that the architecture of inverse opals plays important roles in enhancing the electrocatalytic activities. Ni–Fe hydroxide catalysts have been known to be highly active for OER.20–23 It has been reported that Fe(III) incorporation into Ni based catalysts significantly enhances the OER catalytic activity, although the role of Fe is still ambiguous.21,23,24–26
Herein, we combined the crystallographic plane design of catalysts and architecture construction of electrodes to enhance the performance of the most active non-noble metal electrocatalyst and realize high-efficiency HER and OER. A Ni/Ni₂P inverse opal is constructed by the in situ surface phosphorization of a Ni inverse opal. The phosphorization process generates vertically aligned Ni₂P nanosheets on the surface of the Ni inverse opal. The nanosheets expose their most active {001} planes. The resulting Ni/Ni₂P inverse opal is then soaked in a Fe(NO₃)₃ aqueous solution to introduce Fe (denoted as Fe:Ni/Ni₂P inverse opal) through cation exchange. These two inverse opals respectively demonstrate superior HER and OER catalytic activities because of the most active site exposure, rapid electron pathway, and mass transport channels. The in situ conversion route enables the close interface adhesion of Ni₂P nanosheets to the nickel inverse opal. Thus, the inverse opal electrodes are able to demonstrate stable water electrolysis for even 100 h without significant degradation.

Experimental

Chemicals and reagents

Ti foil (thickness: 0.4 mm) was purchased from Suzhou Maikerui Metal Co., Ltd. Polystyrene (PS) spheres (8% w/v, 8.3 g/100 mL) were purchased from Invitrogen Co., Ltd. Ni plating solution (SN-10) was purchased from Transene Corp. Tetrahydrofuran (99 wt%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. NaH₂PO₂ (99 wt%), Fe(NO₃)₃·9H₂O (99.99 wt%) and 1-octadecene (90 wt%) were purchased from Shanghai Aladdin Corp. Ethyl alcohol (99.7 wt%) was purchased from Shanghai Hesen Electric Co., Ltd. IrO₂ (99.9 wt%) was purchased from Shanghai Adamas Reagent Co., Ltd.

Fabrication of Ni inverse opal

Ti foil was used as the substrate to grow PS opal. After pre-treating in forming gas (5% H₂ and 95% Ar) at 550 °C for 2.5 h, the Ti foil was vertically placed into a vial with a suspension containing about 0.2 wt% PS microspheres. The temperature of PS suspension was maintained at 55 °C. After about 95 vol% of water evaporated, the sample was removed out of the vial and dried at room temperature. A following heat treatment at 95 °C for 2 h was applied to form the annealing neck between adjacent PS microspheres. The annealed opal was then placed into a commercial Ni plating solution (SN-10, Transene Corp.). Using a Ni plate as the counter electrode, Ni was electroplated into the 3D PS opal structure at a current density of ~1.5 mA cm⁻² for ~4 h.

After the electrodeposition, the sample was washed with deionized water and dried. The PS template was removed using tetrahydrofuran, yielding the Ni inverse opal structure. The weight of the nickel mass was determined by the difference in Ti foil weight before electroplating and after electroplating. The nickel loading on the Ni inverse opal electrode is about 4.5 mg cm⁻².

Surface phosphorization

The in situ phosphorization setup for the Ni inverse opal is illustrated in Fig. S1 of the ESI†. The obtained Ni inverse opal and about 0.3 g NaH₂PO₂ were first placed in the middle and bottom of a 20 mL quartz test tube, respectively. The quartz tube was then sealed with a ground stopper and gently placed into a tube furnace. When heated at 300 °C for 20 min in forming gas, the surface of the Ni inverse opal was phosphorylated by the phosphine generated from the decomposition of NaH₂PO₂. The final product is the Ni₂P/Ni inverse opal. The Ni₂P/Ni inverse opal electrode has a Ni₂P loading of ~1.9 mg cm⁻². The resulting Ni₂P/Ni inverse opal was washed with water thoroughly and then soaked in 1 mM Fe(NO₃)₃ aqueous solution for 24 h. Then the Fe:Ni₂P/Ni inverse opal electrode was obtained after rinsing with water and ethanol several times.

The bulk Ni/Ni₂P structures as the control samples were prepared using two phosphorization techniques. A flat Ni film was first electroplated on Ti foil. The bulk Ni/Ni₂P electrode has a Ni₂P loading amount of 2.1 mg cm⁻². The Ni-coated Ti foil was heated with NaH₂PO₂ under the same fabrication conditions as in the fabrication of the Ni/Ni₂P inverse opal. The resulting sample is denoted as bulk Ni/Ni₂P. The second control sample was phosphorized using TOP as a phosphorus source. The Ni-coated Ti foil, 10 mL 1-octadecene, and 0.5 mL TOP were placed in a round-bottomed flask. After heating at 120 °C for 1 h, the system was purged with Ar and heated to 300 °C for 20 min. Finally, the obtained sample was washed with hexane and ethanol several times and is denoted as bulk Ni/Ni₂P(TOP).

Preparation of Pt/C and IrO₂ electrodes

About 20 wt% Pt on Vulcan carbon (Johnson Matthey Corp.) was used for comparison of HER properties. First, 8 mg Pt/C catalyst was dispersed into isopropanol (50 μL) to form a slurry. Second, 7.7 μL solution was drop-cast onto Ti foil within an area of 0.25 cm² (4.9 mg cm⁻²). After naturally drying in air, 2 μL Nafion solution (0.3%) was cast on top of the electrode to protect the film. IrO₂ (Adamas Reagent, Ltd.) was used for comparison of OER properties. The preparation procedure for the IrO₂ electrode was the same as that for the Pt/C electrode.

Materials characterization

Morphology observation and elemental mapping were conducted using a Zeiss Ultra 55 field emission scanning electron microscope. Transmission electron microscopy (TEM) characterization, selected area electron diffraction (SAED) pattern, scanning transmission electron microscopy (STEM) images, and corresponding EDX spectra were obtained using an FEI Tecnai G2 20 microscope at 200 kV. X-ray diffraction (XRD) patterns were collected using a Rigaku D/MAX 2500 V with Cu Kα radiation (1.5418 Å). X-ray photoelectron spectroscopy (XPS)
analysis was performed on an ESCALab MKII spectrometer with Mg Kα X-ray as the excitation source.

**Electrochemical measurements**

The electrochemical measurements were conducted using a VSP potentiostat (Bio-Logic Corp., France) with a three-electrode setup. Ag/AgCl (3 M KCl) was used as the reference electrode. A carbon rod and Pt wire were used as the counter electrodes in the HER and OER tests, respectively. The potentials were converted to the reversible hydrogen electrode (RHE) via the following equation:

\[
E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times \frac{\text{pH}}{2} + 0.210 \text{ V}
\]

The electrolytes (1 M KOH) were deaerated using Ar (for HER) and oxygen (for OER) bubbles through the experiments. In all the experiments, the working surface area of the electrode was controlled around 0.25 cm². The LSV tests were conducted at a scan rate of 2 mV s⁻¹. The obtained LSV curves were corrected for ohmic drop obtained via impedance measurements. The long-term durability test was performed using chro-nopotentiometric measurements.

**Results and discussion**

The fabrication procedure for the Ni/Ni₂P inverse opal is illustrated in Fig. 1. PS microspheres are first deposited on a Ti foil to form an opal structure. The obtained PS opal is sintered to enhance the connection between PS microspheres. A Ni electrodeposition is carried out to fill the void in the PS template. After removing the PS using tetrahydrofuran (THF), the resulting Ni inverse opal is heat-treated together with NaH₂PO₂ in forming gas (5% H₂ and 95% argon). The decomposition of NaH₂PO₂ generates PH₃, which corrodes the Ni inverse opal to form a thin layer of Ni₃P on the Ni surface (see Fig. S1 in the ESI† for the setup illustration). The fabrication details of the Ni inverse opal are available in our previous publications.²,³ The Fe:Ni/Ni₂P inverse opal is subsequently obtained by soaking the as-prepared Ni/Ni₂P inverse opal in 1 mM Fe(NO₃)₃ aqueous solution for 24 h.³⁵

Fig. 2a and b show the scanning electron microscope (SEM) images of the Ni inverse opal prior to and after surface phosphorization. The highly porous opal structure has a pore size of 500 nm and window size of ~150 nm between two adjacent spherical voids. The pore structure could be tuned by using different microsphere sizes. The specific surface area of the Ni inverse opal in this work was estimated to be 2.06 m² g⁻¹ (see Fig. S2 and discussion in the ESI† for details). When Ni atoms on the surface of the inverse opal react with phosphine during heat treatment, the smooth surface becomes rough because of the formation of surface phosphides. As shown in Fig. 2c, about 15 nm thick nanosheets are vertically aligned on the surface of the Ni inverse opal. The elemental mapping in Fig. 2d indicates the uniform distribution of nickel and phosphorus atoms. The XRD patterns in Fig. 2e show the peaks of the substrate Ti and Ni. The remaining peaks are in agreement with the hexagonal Ni₂P (JCPDS no. 865-1989), indicating the partial conversion of the Ni inverse opal to Ni₃P and the formation of the Ni/Ni₃P heterostructure. For the resulting Fe:Ni/Ni₂P inverse opal, the main phase is still the hexagonal Ni₃P (ESI, Fig. S3†). Elemental

![Fig. 1](image1.png)  
**Fig. 1** Schematic illustration of the fabrication procedure of the inverse opal electrodes and the overall water splitting using the Fe:Ni/Ni₂P and Ni/Ni₃P inverse opal as OER and HER catalysts, respectively.

![Fig. 2](image2.png)  
**Fig. 2** (a) SEM image of the Ni inverse opal. (b, c) SEM images of the Ni/Ni₂P inverse opal at different magnifications. (d) SEM image and elemental mapping of the Ni/Ni₃P inverse opal. (e) XRD patterns of the Ni and Ni/Ni₃P inverse opal. (f, g) XPS spectra of the phosphorized sample: (f) Ni 2p₃/2 and (g) P 2p. (IO: inverse opal).
mapping and EDX analysis in STEM suggested a homogeneous incorporation of Fe into Ni$_2$P layers (ESI, Fig. S4 and S5†).

Fig. 2f and g present the XPS data of the Ni/Ni$_2$P inverse opal. The peak around 852.7 eV in the Ni 2p$_{3/2}$ spectrum is typically due to Ni phosphide. The peak at a higher binding energy of 855.5 eV is usually attributed to NiO, indicating the surface oxidation. The weak and broad peak around 860.2 eV is regarded as the satellite of the Ni 2p$_{3/2}$ component that originates from nickel phosphate. The P 2p spectrum (Fig. 2g) has two characteristic peaks around 129.5 and 133.4 eV, which have been attributed to phosphorus in phosphide and phosphate species, respectively. These results are in agreement with previous reports. In XPS around the Fe 2p binding energy region, Fe:Ni/Ni$_2$P inverse opal shows an obvious protuberant baseline, while just a smooth baseline is observed in the Ni/Ni$_2$P inverse opal (ESI, Fig. S6†), suggesting the successful incorporation of Fe.

To further investigate the microstructure of Ni$_2$P nanosheets, the phosphorized inverse opal was peeled off the Ti substrate and ground into pieces. The Ni$_2$P nanosheets were detached off the inverse opal by ultrasonication and then collected for TEM observation. Fig. 3a clearly shows the planar morphology of phosphorized nanoparticles. The magnified observation of the box region in Fig. 3a indicates lattice fringes of 0.51 nm (Fig. 3b), which corresponds to the interplanar distance of (100) planes of Ni$_2$P. The SAED pattern was collected on a nanosheet crystal. It reveals the typical hexagonal pattern, which has reflection spots with the reciprocal distance of 0.196 nm$^{-1}$. The hexagonal spots (red circles) were indexed to the (100) planes, indicating the zone axis of [001]. In conjunction with morphology observation and diffraction analysis, it indicates that the exposed surface of Ni$_2$P nanosheets is the {001} plane, which has been predicted to have great potential for HER electrocatalysis because of its electronic and structural analogy with the active site of [NiFe] hydrogenase.

![Fig. 3](image-url) (a) TEM and (b) high-resolution TEM image and (c) SAED pattern of a Ni$_2$P nanosheet. (d) Top-down view of the Ni$_2$P (001) plane and a two-dimensional flake of Ni$_2$P.

The HER and OER electrocatalytic activities of the inverse opal electrodes were characterized in a three-electrode system and compared with bulk Ni, phosphorized bulk Ni, Ni inverse opal, and the benchmark catalysts (commercial Pt/C for HER and IrO$_2$ for OER), respectively. Fig. 4a shows the linear sweep voltammetry (LSV) polarization curves of the samples for HER. The ohmic potential drops (iR) that originated from the electrolyte resistance are corrected for all the LSV curves using the R values obtained via the electrochemical impedance spectroscopy (EIS) measurements. The overpotentials at 20 and 100 mA cm$^{-2}$ are denoted as $\eta_{20}$ and $\eta_{100}$, respectively. As expected, Pt/C exhibits the highest HER activity with a near-zero onset overpotential, beyond which the current density increases sharply. The bulk Ni sample shows the worst catalytic performance because of the largest overpotentials under various current densities. After phosphorization, the electrocatalytic properties are significantly improved as the $\eta_{20}$ and $\eta_{100}$ are decreased to 306 and 387 mV, respectively. Contrast, the $\eta_{20}$ and $\eta_{100}$ for the Ni/Ni$_2$P inverse opal are 73 and 145 mV, which are substantially lower than those for the Ni inverse opal (330 mV and 434 mV) and phosphorized bulk Ni. The large differences of overpotentials between original and phosphorized Ni inverse opal indicate that the HER driving force is significantly reduced by the surface phosphorization of the Ni inverse opal.

Fig. 4b shows the Tafel plots of these five samples. The linear portions of these curves are fitted with $\eta = b \log|j| + a$ ($\eta$ is the overpotential, $j$ is the current density, $b$ is the Tafel slope, and $a$ is a constant). The Ni/Ni$_2$P inverse opal shows a much lower Tafel slope (76 mV dec$^{-1}$) than the Ni inverse opal (85 mV dec$^{-1}$). The exchange current density of the Ni/Ni$_2$P inverse opal (~6.2 × 10$^{-3}$ A cm$^{-2}$) is two orders of magnitude higher than that of the Ni inverse opal (~3.4 × 10$^{-5}$ A cm$^{-2}$). A low Tafel slope together with a high exchange current density is usually...
desired to drive a high HER current density under low overpotentials, demonstrating high electrocatalytic activity. Both the Tafel slope and exchange current density results show that the Ni/Ni₂P inverse opal is a superior non-precious electrocatalyst.

It has been reported that nickel phosphide has better HER electrocatalytic properties than metallic Ni. This partly explains why phosphorization increases the HER electrocatalytic activities for either bulk Ni or inverse opal. A control sample of bulk Ni was phosphorized by TOP and is denoted as Ni/Ni₂P(TOP). The detailed characterizations are given in the ESI, Fig. S7 and S8. The bulk Ni/Ni₂P(TOP) is the aggregate of polycrystals with exposure of various crystallographic planes. It shows much worse electrocatalytic performance (~102 mV higher overpotentials at 100 mA cm⁻²) than the bulk Ni/Ni₂P nanosheet sample prepared using PH₃ (ESI, Fig. S9 and Table S1). The PH₃ route generates the Ni₂P nanosheets with exposed \{001\} planes which are the most active. Conversely, the bulk Ni/Ni₂P(TOP) has a mixed crystal plane exposure. The performance difference could be ascribed to the maximum active crystallographic plane exposure.

In comparison to the flat Ni sample, the performance improvement of the Ni inverse opal could be attributed to the porous structure, which provides a relatively large accessible surface area. Similarly, the Ni/Ni₂P inverse opal demonstrates higher activity than phosphorized bulk Ni because of the increased surface area, which is corroborated by the double-layer capacitance measurements in Fig. S10. For an electrocatalytic process, the surface reactions and mass transport are coupled in series. A large surface area definitely promotes the transformation from reagents to products. The influence of electrode microstructure cannot be neglected. To clarify the role of the porous structure, the Ni/Ni₂P inverse opal was ground to destroy the porous structure. The obtained powder was slurry-cast on Ti foil. The LSV curves of the samples with and without the inverse opal structure are compared in Fig. S11. The \(\eta_{100}\) for HER increased to 168 mV after the loss of the inverse opal structure. In other words, the inverse opal structure could facilitate the mass transport and decrease the overpotentials because of its interconnected pore structure. The Ni/Ni₂P heterostructure has the most active Ni₂P \{001\} planes exposed. However, once the inverse opal structure is destroyed, the exposed active planes are embedded inside the electrode. The electrocatalysis is limited by the accessible surface area (sites) and mass transport (species). This may be further corroborated by the electrochemical impedance spectroscopy (EIS) measurements. Fig. S12–S14 present the Nyquist and Bode plots of bulk Ni/Ni₂P, Ni and Ni/Ni₂P inverse opals. Their reaction resistances are calculated and summarized in Table S2. Due to the interconnected pores and Ni/Ni₂P heterostructure, the Ni/Ni₂P inverse opal exhibits much lower reaction resistances at varied overpotentials. Therefore, it can be deduced that tuning the activities by crystallographic plane design plays a vital role in preparing a high-efficiency electrocatalyst and engineering the electrode structure is of equal importance to unleash the electrocatalytic potentials, which high active planes could provide.

The influence of accessible surface area and microstructures is applicable to both HER and OER. We characterized the OER properties of the Ni/Ni₂P inverse opal. As shown in Fig. 4c, the \(\eta_{20}\) and \(\eta_{100}\) overpotentials of the Ni/Ni₂P inverse opal are 331 and 380 mV, respectively. They are significantly more negative than the overpotentials of the Ni inverse opal, bulk Ni, and bulk Ni/Ni₂P, and even lower than those of the benchmark OER electrocatalyst (IrO₂). More interestingly, the Fe:Ni/Ni₂P inverse opal shows a more significant OER electrocatalytic performance. The corresponding overpotentials are 285 (\(\eta_{20}\)) and 317 mV (\(\eta_{100}\)), respectively. We also examined the catalytic kinetics for oxygen evolution. Fig. 4d shows the Tafel plots of the six electrodes. The Fe:Ni/Ni₂P inverse opal has a Tafel slope of 48 mV dec⁻¹, which is smaller than those of other four control samples and IrO₂. Table 1 summarizes the HER and OER electrocatalytic properties of various catalytic electrodes.

The durability of electrocatalysts is of vital importance for continuous HER and OER operations. To determine the long-term stability of the two inverse opal electrodes in HER and OER processes, chronopotentiometric measurements were conducted at ±20 mA cm⁻² for up to 100 h. Fig. 5a shows that the cathodic voltage remains around −0.073 V. During the 100 h test, the HER overpotential only increases by ~20 mV. The OER durability measurement shows that the anodic voltage remains at 1.52 V with a slightly increased overpotential of ~17 mV in 100 h. After the long-term stability tests, the electrodes were cleaned and observed by SEM. Fig. 5b and c show that the inverse opal structure and vertically aligned Ni₂P nanosheets are generally maintained. As shown in Fig. S15, the Ni and P

<table>
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<th>Sample</th>
<th>HER (\eta_{20}/\eta_{100}) [mV]</th>
<th>Tafel slope [mV dec⁻¹]</th>
<th>OER (\eta_{20}/\eta_{100}) [mV]</th>
<th>Tafel slope [mV dec⁻¹]</th>
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<tr>
<td>Ni/Ni₂P inverse opal</td>
<td>73/145</td>
<td>76</td>
<td>331/380</td>
<td>54</td>
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<td>85</td>
<td>285/317</td>
<td>48</td>
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<td>78</td>
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<td>Bulk Ni</td>
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<td>477/—</td>
<td>84</td>
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<tr>
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<td>41</td>
<td>378/—</td>
<td>66</td>
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signals of the Ni/Ni2P inverse opal after the HER tests resemble those prior to the tests, indicating the retention of the electrocatalyst. However, the partial oxidation of the Fe:Ni/Ni2P inverse opal is revealed by comparing the Ni, P and Fe XPS spectra (ESI, Fig. S16 and S17†) prior to and after the OER tests. The appearance of an oxide peak in the Raman spectra (ESI, Fig. S18†) further confirms the oxidation of the Fe:Ni/Ni2P inverse opal. The inverse opal electrodes were re-scanned for HER and OER tests with the LSV polarization technique. Fig. 5d and e show that before and after 100 h electrolysis, the LSV curves of the inverse opal electrodes overlap. It indicates that the as-prepared inverse opal electrodes have long-term electrocatalytic stability. In addition, the generated H2 and O2 gases from the Ni/Ni2P inverse opal electrodes at constant current densities for HER and OER, respectively. SEM images of (b) Ni/Ni2P inverse opal surface and (c) Fe:Ni/Ni2P inverse opal surface after HER and OER tests for 100 h, respectively. LSV polarization curves of (d) Ni/Ni2P inverse opal and (e) Fe:Ni/Ni2P inverse opal before and after HER and OER tests for 100 h, respectively.

Fig. 5 (a) Chronopotentiometric curves of Ni/Ni2P and Fe:Ni/Ni2P inverse opal electrodes at constant current densities for HER and OER, respectively. SEM images of (b) Ni/Ni2P inverse opal surface and (c) Fe:Ni/Ni2P inverse opal surface after HER and OER tests for 100 h, respectively. LSV polarization curves of (d) Ni/Ni2P inverse opal and (e) Fe:Ni/Ni2P inverse opal before and after HER and OER tests for 100 h, respectively.

The high electrocatalytic activities and long-term stability of the two inverse opal electrodes in the separate HER and OER tests intrigued us to investigate their electrolysis properties as bifunctional catalysts for overall water splitting. To test whether our newly developed heterostructure works for long-term practical applications, a water splitting electrolyzer was constructed using the Ni/Ni2P inverse opal as the cathode and the Fe:Ni/Ni2P inverse opal as the anode. The LSV polarization curve in Fig. 6a shows that the water splitting reaction at 20 mA cm\(^{-2}\) could be driven by 1.523 V, which is even 81 mV smaller than the benchmark cell using IrO2 and Pt/C electrodes. The overpotential of 1.604 V at 20 mA cm\(^{-2}\) for the IrO2/Pt/C catalytic couple in our work is comparable to previous reports (1.55–1.70 V)\(^{33–54}\) (ESI, Table S3†). In addition, the electrolyzer assembled using the Fe:Ni/Ni2P/Ni/Ni2P couple affords a current density of 100 mA cm\(^{-2}\) at 1.721 V, whereas the electrolyzer based on the IrO2/Pt/C catalytic couple gives 100 mA cm\(^{-2}\) at 1.858 V (consistent with the previously reported result\(^{41}\)). Fig. 6b demonstrates that the gas bubbles evolved from both cathode and anode when the current density reaches 20 mA cm\(^{-2}\). Moreover, the inverse opal electrode couple ran for 100 h without significant degradation. The cell voltage remained around 1.523 V with a subtle increase of overpotential during the 100 h of electrolysis, indicating the excellent stability of the water splitting system.

The electrocatalytic properties of Ni/Ni2P and Fe:Ni/Ni2P inverse opals have been summarized and compared with the state-of-the-art water splitting catalysts in Tables S4–S6†. Our newly designed Ni inverse opal-derived electrodes demonstrate high catalytic performance and long-term stability because of their unique hierarchical structure and the \textit{in situ} surface engineering. Ni2P nanocrystals show the most active {001} planes and nanosheet morphology, which maximize the active sites of Ni2P materials. The vertical alignment of Ni2P nanosheets enables the maximum exposure of active sites of Ni2P to the electrolyte. Meanwhile, the simple immersion treatment in a dilute Fe\(^{3+}\) solution ensures great improvement of OER performance for the Ni2P/Ni inverse opal, since the Ni–Fe based catalyst is in principle highly active for electrocatalytic OER. Furthermore, the \textit{in situ} growth of Ni2P on the Ni surface leads to a good electric contact between the Ni2P catalyst and the conducting network and decreases the electric resistances. The good contact between Ni2P and Ni also contributes to the long-term stability. In addition, the porous structure of Ni inverse
opal has two advantages. First, it significantly increases the accessible active surface per geometric area. The large internal surface enables more Ni$_2$P nanosheets to expose their active [001] planes for electrocatalysis. Second, the interconnected pore architecture facilitates the mass transport of species and decreases transport-related resistances. These results show that the Ni/Ni$_2$P inverse opal has great potential for long-term and energy-efficient water electrolysis.

Conclusions

In summary, we developed unique 3D Ni/Ni$_2$P and Fe:Ni/Ni$_2$P inverse opals by a series of in situ surface engineering treatments. The heterostructures exhibit high HER/OER electrocatalytic activities and long-term stability for water splitting. For HER, the Ni/Ni$_2$P inverse opal requires an overpotential of only 73 mV to drive a current density of 20 mA cm$^{-2}$. The Fe:Ni/Ni$_2$P inverse opal shows OER activity with a small overpotential of 285 mV to reach 20 mA cm$^{-2}$. Through the well-designed experiments, the superior catalytic property of the two inverse opal electrodes is attributed to the unique hierarchical structure and the in situ surface engineering. The Ni$_2$P nanosheets exhibit the most active sites for electrolysis reactions. The vertical alignment of nanosheets on the surface of the Ni inverse opal makes all active surface accessible to the electrolyte. The interconnected pore architecture facilitates the mass transport of chemical species. The metallic Ni network decreases the electron conduction and transfer resistance. The in situ growth route enables the close attachment of nanosheets to metallic scaffolds, which is instrumental to the long-term stability of electrocatalysts. Generally, our design and synthesis technique enable the synergistic effect of the control of crystallographic planes, the 3D architecture of electrodes, and rapid electron transfer networks. It may also provide insights into maximizing the electrocatalytic properties in other systems with coupled electron transfer and mass transports.

Acknowledgements

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