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Formation of Ni-Fe Mixed Diselenide Nanocages as a Superior Oxygen Evolution Electro catalyst

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Abstract

Exploring effective electrocatalysts is a crucial requirement for boosting the efficiency of water splitting to obtain clean fuels. In this work, we report a self-templated strategy to synthesize Ni-Fe mixed diselenide cubic nanocages for the electrocatalytic oxygen evolution reaction (OER). The diselenide nanocages are derived from corresponding Prussian-blue analogue nanocages, which are firstly obtained by treating the nanocube precursor with a site-selective ammonia etchant. The resulting Ni-Fe mixed diselenide nanocages perform as a superior OER electrocatalyst, which affords a current density of 10 mA cm^{-2} at a small overpotential of 240 mV, and a high current density, mass activity, and turnover frequency (TOF) of 100 mA cm^{-2} , 1000 A g^{-1} , and 0.58 s^{-1} , respectively, at the overpotential of 270 mV, a Tafel slope as small as 24 mV dec^{-1} , and excellent stability in alkaline medium.

Keywords: Prussian-blue analogue; diselenide; nanocages; electrocatalysis; oxygen evolution reaction.

To address the urgent need for clean and sustainable energy, electrochemical water splitting for the generation of hydrogen and oxygen is an environmentally friendly alternative to obtain clean fuels from renewable energy sources.^[1] Yet, the realization of efficient water splitting is greatly hindered by the oxygen evolution reaction (OER), which is a bottleneck half-reaction involved with multistep proton-coupled electron transfer and is kinetically sluggish.^[2] Exploring effective OER electrocatalysts is therefore a crucial requirement to reduce the activation barriers, expedite the reaction and thus enhance the energy conversion efficiency.^[3] Although the state-of-the-art precious metal based materials (e.g., RuO₂ or IrO₂) are the benchmark catalysts for OER, they are very costly due to their limited resources on earth. Over the last few decades, extensive efforts have been devoted to design and synthesize highly active, durable and low-cost 3d-metal based alternatives.^[4-7] Apart from the well-developed metal oxides and (oxy)hydroxides catalysts,^[8-14] metal selenides have recently arisen as another type of earth-abundant electrocatalysts with high catalytic activity towards the OER.^[15-21] The excellent electrocatalytic performance of some of these materials, such as CoSe₂,^[17-19] Co_{0.85}Se,^[20] and NiSe₂,^[21] are reported to benefit from their intrinsic metallic properties. Unfortunately, as the emerging OER electrocatalysts, metal selenides still suffer insufficient development, especially in those novel and facile routes for synthesizing highly efficient electrocatalysts of such materials with well-defined nanostructures.

The synthesis of new classes of nanostructures with high complexity is not only important for a wide range of applications but also significant for developing the modern synthetic methodology.^[22,23] Open cage/frame-like nanostructures are a unique family of these complex architectures. Numerous studies have been made to fabricate this kind of nanostructures made of noble metals,^[24-29] metal

oxides,^[30,31] and metal sulfides.^[32] For the purpose of electrocatalysis, the open constructions are generally considered as an advantage over the solid counterparts. This is because the open structures could provide a larger surface for the electrocatalysts to contact the electrolyte to form a favorable catalytic interface, benefited from which the electrocatalytic performance would be significantly improved. For instance, Chen and co-workers demonstrated that a Pt₃Ni rhombic dodecahedral nanoframe enables a three-dimensional (3D) surface molecular accessibility.^[25] The highly open-framework constructions diminish the number of buried nonfunctional metal atoms, and their uncommon geometry provides a pathway for tailoring electronic properties, endowing a substantial improvement in activity towards the oxygen reduction reaction.

Due to their intriguing stimuli-responsive electron transfer properties, Prussian-blue analogue (PBA) materials have attracted research interests for long time.^[33-37] Recently, nanostructured PBAs are converted to functional metal oxides, sulfides, and phosphides, which can retain their original nanostructures and find promising applications in electrochemical storage and conversion.^[30,32,38-41] Herein, we report a strategy to synthesize metal selenide open nanocages derived from PBA materials for the electrocatalytic OER. Briefly, Ni-Fe PBA nanocubes are first prepared, followed by a facile site-selective etching process by ammonia at room temperature to obtain the Ni-Fe PBA nanocages with open construction and unique hollow interior space. After selenization of the Ni-Fe PBA nanocages in Se vapor, the Ni-Fe mixed diselenide nanocages can be formed in this self-templated approach, which shows superior electrocatalytic performance towards the OER.

The morphology of the as-prepared Ni-Fe PBA nanocubes is characterized by field-emission scanning electron microscopy (FESEM). The FESEM image shows that the Ni-Fe PBA nanocubes

are highly uniform with a size of around 200 nm (Figure S1a, see Supporting Information). The crystal structure and composition of the nanocubes are characterized by X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX), respectively. The XRD result (Figure S1b, see Supporting Information) displays a typical PBA-type pattern with the face-centered cubic structure. The EDX spectrum (Figure S1c, see Supporting Information) confirms the Ni-Fe combination in this PBA-type material.

We then employed these Ni-Fe PBA nanocubes as the precursor in a self-templated approach to create cage-like nanostructures.^[42] Specifically, the solid nanocubes can be converted to hollow nanocages by treating with an appropriate amount of ammonia solution for 5 min at room temperature. XRD and EDX analyses confirm the as-treated product is still Ni-Fe PBAs with cubic crystal structure and nearly the same Ni/Fe atomic ratio with that of nanocubes (Figure S2, see Supporting Information). Overview FESEM image in **Figure 1a** shows that the product consists of uniform and high-quality nanocages without impure particles. High-magnification FESEM images of the typical nanocages are shown in Figure 1b,c to provide a clear view of these architectures from different directions. The cage-like nanoparticles have a cubic structure with an average size of ~ 200 nm, which well inherit the morphology and dimension of the nanocube templates. Cavities are observed at the corners of the cube-shaped nanoparticles, suggesting an open structure of the nanocages. From a topological view, a cubic nanocage is an ensemble braced by six nummular nanodisks, each of which serves as a wall and provides four parts to attach neighbouring nanodisks to construct a 3D architecture. A unique hollow interior can be seen directly from a cracked nanocage as shown in Figure 1d. This image also reveals an asymmetrical wall structure with a flat external surface and

pyramid-like internal one. The shape and construction of the hollow interior space of the nanocages are further studied by TEM, as displayed in Figure 1e,f. Highly uniform nanocages can be observed from Figure 1e, which is in agreement with the FESEM findings. The unique shape of the inner space is clearly delineated by the ensemble of the internal surface profile of the pyramid-like walls (Figure 1f). These walls are about 60 nm in thickness at the center and about 30 nm at the sides.

Time-dependent microscopy experiments are carried out to study the structural conversion from nanocubes to nanocages. **Figure 2** displays the morphology and structure of the intermediate products obtained at different reaction stages when treating the nanocubes with ammonia solution. As shown in Figure 2a,e, slightly truncated structures can be seen on the corners of the nanocubes, where the locations should possess more defects and higher reactivity than those on the faces of the nanocubes.^[32] After the treatment with ammonia for 1 min, the corners of each nanocube are all etched, while the faces remain nearly unchanged (Figure 2b,f). With the reaction time proceeding, a further etching prefers along a diagonal way to hollow out the nanocubes, leading to obvious cavities on the corners (Figure 2c). Meanwhile, the caving tunnels inside the nanocubes become deeper and wider, as shown in Figure 2g. Eventually, these eight tunnels converge at the center of each nanocube to form a hollow cage-like nanostructure when the reaction time reaches 5 min (Figure 2d,h). Figure 2i clearly illustrates the cube-to-cage conversion process regarding the external and internal structural evolution, which starts with the corners etching of the nanocubes and ends with the hollow interior space shaped as a concave-cube within the open nanocages. It should be noted that the nanocages could collapse to be disk-like nanoparticles if the reaction time prolongs to 10 min in the ethanol system (Figure S3a,b, see Supporting Information). These nanodisks should be derived from the

pyramid-like walls of the nanocages, but with smaller size and thinner thickness due to the further chemical etching. Another control experiment shows that under the similar etching conditions except in the water system, the final etched product would also become nanodisks in just 5 min, indicating a faster etching rate in water than that in ethanol (Figure S3c,d, see Supporting Information). Surprisingly, these nanodisks are still PBA-type material with the Ni-Fe combination, revealed by the XRD and EDX results (Figure S4, see Supporting Information).

Interestingly, the shape of the interior hollow space is uncommon and distinct from other cubic hollow nanostructures, e.g., nanoboxes with flat internal walls.^[38-40] We speculate that the ammonia should work as a cavity creator in the cube-to-cage conversion process by means of site-selective chemical etching. Fourier transform infrared (FTIR) spectra are performed to trace the chemical composition change of the products at different reaction times (Figure S5 and Table S1, see Supporting Information). As the etching time goes from 0 to 5 min, we observe a significant decrease of the $\nu(\text{CN})$ peak at 2166 cm^{-1} for $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{III}}$, relative to the $\nu(\text{CN})$ peak at 2097 cm^{-1} for $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{II}}$.^[33] This indicates the ammonia etching occurs mainly at the $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{III}}$ sites rather than $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{II}}$ ones. Basically, compared with Fe^{II} , the Fe^{III} species has stronger affinity with the -CN- group. This means the electron donating ability of the N atom in the $\text{-N}\equiv\text{C-Fe}^{\text{III}}$ species is weaker than that in the $\text{-N}\equiv\text{C-Fe}^{\text{II}}$ ones. Therefore, the bonding between Ni^{II} and $\text{-N}\equiv\text{C-Fe}^{\text{III}}$ should be weaker and easier to be broken than that between Ni^{II} and $\text{-N}\equiv\text{C-Fe}^{\text{II}}$. The following reactions are probably involved in the etching process:

As can be seen from the above equations, the Ni^{2+} species from the $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{III}}$ sites can be stabilized by coordinating with ammonia in a ligand exchange reaction (eq. 1). Besides, a redox reaction could also be involved in the etching process (eq. 2). A $\nu(\text{NH})$ peak for NH_4^+ at 1415 cm^{-1} in the FTIR spectra emerges at the later stages of the etching process (Figure S5 and Table S1, see Supporting Information), further proving the occurrence of the redox reaction (eq. 2) during the ammonia treatment. Combining the TEM and FTIR analysis above, we can infer that the $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{III}}$ and the $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{II}}$ species should co-exist in the nanocubes, but they may distribute inhomogeneously. The $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{III}}$ species could distribute mainly at the center of the nanocubes, while the $\text{Ni}^{\text{II}}\text{-N}\equiv\text{C-Fe}^{\text{II}}$ one locates near the surface of the nanocubes.

By selenizing the Ni-Fe PBA nanocages in Se vapor at $350\text{ }^\circ\text{C}$ for 2 h,^[19,43] Ni-Fe based selenide nanocages can be obtained. XRD result in **Figure 3a** demonstrates that the product is a diselenide mixture, mainly composed of cubic pyrite-phase NiSe_2 (JCPDS card No. 88-1711) and FeSe_2 (JCPDS card No. 65-2570). EDX spectrum (Figure S6, see Supporting Information) reveals the molar ratio of these two components is around 1:0.77 (NiSe_2 : FeSe_2). The formation of Ni-Fe mixed diselenide is further supported by X-ray photoelectron spectroscopy (XPS). As revealed in Figure 3b, the peak at 853.1 eV in the Ni $2p_{3/2}$ spectrum has a binding energy between the NiO_x species (855.4 eV) and nickel metal (852.6 eV), indicative of Ni^{2+} in nickel selenides.^[16] Similarly, the peaks at 706.9 and 708.2 eV in the Fe $2p_{3/2}$ spectrum (Figure 3c) suggest the Fe^{2+} and Fe^{3+} species, respectively, in the iron selenides.^[16] The Se 3d peaks of the Ni-Fe mixed diselenide nanocages are located at 54.2 and 55.2 eV (Figure 3d), which are red-shifted from 55.4 eV for elemental Se and should be assigned to the Se species binding with Fe^{3+} and $\text{Ni}^{2+}/\text{Fe}^{2+}$, respectively. Some peaks attributed to related oxides

such as NiO_x , FeO_x , and SeO_x can also be observed in the XPS spectra (Figure 3b-d), indicating a certain degree of oxidation on the surface of metal selenides.^[16] It can be seen from **Figure 4a-d** that the as-formed Ni-Fe mixed diselenides well retain the cage-like nanostructures as those of their Ni-Fe PBA template, but rougher surfaces are observed for the former ones. Elemental mapping images in Figure 4e show a homogenous distribution of the Ni, Fe, and Se elements in the nanocage. In control experiments, we also convert the Ni-Fe PBA nanocubes and nanodisks to corresponding Ni-Fe mixed diselenide nanostructures by a similar annealing route. XRD and EDX analyses confirm that the products are also Ni-Fe diselenide mixtures (Figure S7a,b and Figure S8a,b, see Supporting Information). FESEM and TEM images show that these Ni-Fe mixed diselenides are still either cube- or disk-shaped solid nanoparticles (Figure S7c,d and Figure S8c,d, see Supporting Information).

The electrocatalytic OER performance of Ni-Fe mixed diselenide nanocages (denoted as Ni-Fe-Se cages) is investigated in an alkaline solution (1.0 M KOH) in a standard three-electrode system. A glassy carbon electrode modified with the catalyst, a Ag/AgCl electrode and a Pt wire are used as the working electrode, reference electrode, and counter-electrode, respectively. For comparison, the electrochemical properties of the Ni-Fe-Se disks and cubes, as well as Ni-Fe PBA cages, disks, and cubes are also studied. **Figure 5a** shows the iR -compensated polarization curves recorded by linear sweep voltammetry (LSV) of all the six catalysts. The iR -uncompensated polarization curves are also provided for reference (Figure S9, see Supporting Information). It can be observed that the selenide nanomaterials give obviously lower onset potential and higher current density for the OER than the PBA ones. To reach a current density of 10 mA cm^{-2} , which is a common criterion to evaluate the OER activity, the Ni-Fe-Se cages and disks need the same potential of 1.47 V, corresponding to an

overpotential of only 240 mV (Figure 5b). On the other hand, 30, 140, 150, and 190 mV higher overpotentials are required for the Ni-Fe-Se cubes, Ni-Fe PBA cages, disks, and cubes, respectively, to achieve the same current density. Moreover, the current densities of the selenides rise much faster than those of the PBAs. Specifically, the current density of the Ni-Fe-Se cages could increase to 100 mA cm^{-2} at the overpotential of 270 mV, which is 10 and 60 mV lower than those of the Ni-Fe-Se disks and cubes, respectively, to reach the same current density (Figure 5b). In contrast, the PBA catalysts cannot afford such a high current density (100 mA cm^{-2}) in the applied potential range. At the overpotential of 270 mV (Figure 5c), the current density of the Ni-Fe-Se cages (100 mA cm^{-2}) is much higher than that of the Ni-Fe-Se disks (63 mA cm^{-2}), which is even 10-fold and more than 50-fold higher than those of Ni-Fe-Se cubes and other three PBA catalysts, respectively.

Furthermore, the mass activity is another quantitative parameter used to define the activity of a catalyst. This value is calculated using the formula: $\text{mass activity} = j/c$, where j is the current density at a given overpotential, c is the loading of catalysts on the electrode (kept at 0.1 mg cm^{-2} in this work). Therefore, one can find a similar sequence of the mass activities for these six catalysts at the overpotential of 270 mV (Figure 5d) with that of the current densities shown in Figure 5c. It should be noted that the mass activity of the Ni-Fe-Se cages can reach to 1000 A g^{-1} at this given overpotential (Figure 5d). A different activity metric is the turnover frequency (TOF), which is calculated by assuming that all the metal sites (both Ni and Fe) in the catalysts are active (see Supporting Information). Note that this TOF is a conservative estimate because not all of the metal sites are electrochemically accessible. Particularly, the TOF is as high as 0.58 s^{-1} associated with the Ni-Fe-Se cages at an overpotential of 270 mV (Figure 5e). This value is much higher than those of

Ni-Fe-Se disks (0.38 s^{-1}), Ni-Fe-Se cubes (0.07 s^{-1}), Ni-Fe PBA cages (0.008 s^{-1}), Ni-Fe PBA disks (0.007 s^{-1}), and Ni-Fe PBA cubes (0.006 s^{-1}). Remarkably, the TOF of Ni-Fe-Se cages is boosted to 1.06 s^{-1} at an overpotential of 280 mV, exhibiting the largest enhancement (0.48 s^{-1}) among these six catalysts with only a 10 mV overpotential increase (Figure 5e). The Tafel plots of the catalysts are further investigated to get additional insight into their OER performance. The Tafel plots are derived from the polarization curves via the Tafel equation ($\eta = b \times \log j + a$, where η is the overpotential, j is the current density, and b is the Tafel slope). As can be seen in Figure 5f, the Ni-Fe-Se cages obviously exhibit enhanced kinetics for OER, which is proved by its much lower Tafel slope of 24 mV dec^{-1} compared with other catalysts such as Ni-Fe-Se disks (26 mV dec^{-1}), Ni-Fe-Se cubes (59 mV dec^{-1}), Ni-Fe PBA cages (120 mV dec^{-1}), Ni-Fe PBA disks (127 mV dec^{-1}), Ni-Fe PBA cubes (199 mV dec^{-1}). Therefore, the OER activity of the Ni-Fe-Se cages is the best among the six catalysts and superior in comparison of other selenide-based or Ni-Fe-based electrocatalysts (Table S2, see Supporting Information).

It can be concluded from any activity metric mentioned above that the Ni-Fe mixed diselenides are much better than the Ni-Fe PBAs, which might be attributed to better electronic conductivity of the metal selenides derived from their intrinsic metallic properties.^[17-21] The electrochemical impedance spectroscopy (EIS) data further prove that Ni-Fe mixed diselenides have much smaller charge-transfer resistance than the Ni-Fe PBAs (Figure S10, see Supporting Information).

Interestingly, Ni-Fe mixed diselenides present an OER activity trend in terms of the nanostructures, i.e., cages > disks > cubes. To explore the possible reason for this activity trend, we estimate the electrochemically active surface area (ECSA) of the catalysts based on their double-layer

capacitances (C_{dl}), since the ECSA is generally proportional to the C_{dl} of the electrocatalysts.^[44] Specifically, scan-rate dependence of cyclic voltammograms (CVs) is performed in the potential range of 1.177-1.277 V without redox processes, to obtain the capacitive current associated with double-layer charging for the Ni-Fe-Se cages, disks, and cubes (Figure S11, see Supporting Information). Then the C_{dl} can be obtained by plotting the $\Delta j = j_a - j_c$ at 1.24 V *vs.* RHE against the scan rate (the linear slope is twice of the C_{dl}),^[44] as shown in Figure 5g. The results show that the linear slopes follow the sequence of cages > disks > cubes, implying that the highest electrocatalytic OER activity of the cages could be attributed to their largest ECSA, which benefits from the high electrocatalyst-electrolyte contact interface area provided by their open and hollow nanostructures. The slight difference of the charge-transfer resistance among these three selenides should also contribute to this activity trend (Figure S10, see Supporting Information). Additionally, the rougher surface composed of small nanoparticle building blocks could also offer sufficient electrochemically active sites for the electrocatalysis. To ensure that the observed current of the catalyst (e.g., Ni-Fe-Se cages) in Figure 5a originates from oxygen evolution rather than side reactions, the OER Faradaic efficiency is investigated by a rotating ring-disk electrode (RRDE) technique. A ring potential of 0.40 V *vs.* RHE is applied to detect the generated O₂ molecules by the electrochemical oxygen reduction reaction (ORR), rendering a continuous OER (on glassy carbon (GC) disk electrode) → ORR (on Pt ring electrode) process (illustrated as the inset of Figure 5h). As shown in Figure 5h, when a constant current ($i_{disk} = 0.7$ mA) is applied to the disk electrode for O₂ generation, a ring current of around 0.14 mA can be detected, verifying that the observed catalytic oxidation current can be exclusively

attributed to the oxygen evolution with a high Faradaic efficiency of 98.9%-99.7% (see Supporting Information for the calculation method).^[7,8,13]

Besides the high activity, excellent stability of the electrocatalysts towards OER is also critical for energy conversion systems. To estimate the stability of the Ni-Fe-Se cages, successive CV scanning is performed for 500 cycles at a scan rate of 100 mV s⁻¹. At the end of the cycling, the obtained polarization curve is similar to the initial one, with only ~1% loss in the current density (Figure 5i). The long-term durability of the Ni-Fe-Se cages for OER is also tested by a chronopotentiometry (CP) measurement (inset of Figure 5i). Impressively, the nanocages could maintain the current density of 5 mA cm⁻² for 22 h with only ~0.7 % increase required for the potential. These data suggest superior stability of the Ni-Fe-Se cages catalyst. After the CP measurement, the composition and structure of the Ni-Fe-Se cages are further probed (Figure S12, see Supporting Information). Remarkably, the original textural features of the catalyst can be retained in terms of the diselenide composites, cage-like nanostructures and homogeneous elemental distribution, indicating the good structural robustness of this catalyst. In addition, both the Ni-Fe-Se disks and cubes also show excellent long-term durability in the alkaline electrolyte (Figure S13, see Supporting Information).

In summary, we have demonstrated a self-templated route to transform the Ni-Fe PBA nanocages to corresponding metal diselenide nanocages with an open structure and unique hollow interior. As the primary structure, the Ni-Fe PBA nanocages are found to be formed by a chemical etching process from their nanocube precursor, due to the possible structurally inhomogeneous distribution of the active sites for the ammonia-evoked etching. The final product of Ni-Fe mixed diselenide nanocages

shows superior OER performance, which affords a current density of 10 mA cm^{-2} at a small overpotential of 240 mV, a high current density, mass activity, and TOF of 100 mA cm^{-2} , 1000 A g^{-1} , and 0.58 s^{-1} , respectively, at the overpotential of 270 mV, a Tafel slope as small as 24 mV dec^{-1} , and excellent stability in alkaline medium.

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Figures and captions

Figure 1. a) Overview FESEM image of the Ni-Fe PBA nanocages with uniform dimensions. b,c) Magnified FESEM images of the nanocages from different directions. d) FESEM image of a cracked nanocage with the exposed interior. e) TEM image shows various perspectives of the nanocages. f) TEM image of a typical nanocage with the well-defined interior.

Figure 2. a-d) FESEM and e-h) TEM images of the products obtained in the etching procedure for the fabrication of the Ni-Fe PBA nanocages at a,e) 0 min, b,f) 1 min, c,g) 3 min, and d,h) 5 min. i) The corresponding schematics illustrate the structural evolution of the exterior and interior of the Ni-Fe PBA nanocubes to form nanocages.

Figure 3. a) XRD pattern and b-d) XPS spectra of b) $\text{Ni } 2p_{3/2}$, c) $\text{Fe } 2p_{3/2}$, and d) $\text{Se } 3d$ of the Ni-Fe mixed diselenide nanocages.

Figure 4. a) Overview FESEM image of the Ni-Fe mixed diselenide nanocages. b,c) Magnified FESEM images of the nanocages from different directions. d) TEM image of the nanocages. e) Dark-field TEM image and corresponding elemental mapping images of a typical Ni-Fe mixed diselenide nanocage.

Figure 5. a) LSV curves, b) overpotential required for $j = 10$ and 100 mA cm^{-2} , c) current densities at $\eta = 270 \text{ mV}$, d) mass activities at $\eta = 270 \text{ mV}$, e) TOFs at $\eta = 270$ and 280 mV , f) Tafel slopes of the six catalysts. g) Capacitive $\Delta j = j_a - j_c$ as a function of scan rate of the three diselenide catalysts. h) Ring currents when i_{disk} holds at 0 and 0.7 mA based on the RRDE and i) the stability measurements of the Ni-Fe-Se cages catalyst. The inset of h) shows the schematic setting of the RRDE experiment. The inset of i) exhibit the CP response at the current density of 5 mA cm^{-2} of the Ni-F-Se cages.

for Table of Content Entry

A self-template strategy is developed to synthesize Ni-Fe diselenide nanocages with the assistance of site-selective ammonia etchant. With the structural and compositional advantages, these unique nanocages exhibit superior electrocatalytic performance for the oxygen evolution reaction in alkaline medium.