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Electrochemical Activated of CoNi/BSCF/N-doped Carbon: A Highly-Active Bifunctional Electrocatalyst for Water Splitting

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Abstract

Perovskite-type oxides are generally considered as promising electrocatalysts to replace noble metals, their activity of electrochemical water splitting, however, is somehow limited. Here, we report a facile approach to promote the water splitting kinetics of a perovskite oxide, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), through constructing a core-shell structured composite, CoNi/BSCF/NC, by coupling BSCF with CoNi nanoparticles and N-doped carbon. CoNi/BSCF/NC exhibits an extremely high activity, with a small overpotential, a shallow Tafel slope, and an excellent long-term durability toward both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), as compared to pristine BSCF and many other reported catalysts. A symmetric alkaline electrolyzer using CoNi/BSCF/NC as both cathode and anode delivers a current density of 10 mA/cm^2 at a small operating voltage (1.53 V), superior to the prototype using state-of-the-art materials (RuO_2 and Pt/C) (1.58 V). The performance of the CoNi/BSCF/NC composite is one of the best among reported catalysts, showing its great potential as a highly-active and cost-effective catalyst for electrochemical water splitting.

Introduction

Electrochemical water splitting is one of the most promising approaches to produce H_2 , which is a clean, renewable, and efficient energy carrier¹⁻⁶. Oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are the two global half reactions necessary for overall water splitting in an electrolyzer. The efficiency of such an electrolyzer, however, is critically hampered by the sluggish kinetics of OER and HER. In particular, OER is a major bottleneck because of its inefficient four proton-coupled electron transfer^{2,7}. Even using RuO_2 (or IrO_2), the benchmark catalyst for OER, a relatively large overpotential is still required to reach a current density higher than 10 mA/cm^2 . On the other hand, Pt supported on carbon (Pt/C) is generally considered as the benchmark catalyst for HER⁸. However, Pt/C, as well as RuO_2 (or IrO_2), are far too expensive and scarce for commercial purpose and usually suffer from a poor operating durability. Therefore, novel and effective catalysts are urgently needed to replace noble metals, with a special focus on lowering the cost and enhancing the activity and stability.

In recent years, a number of research works found that transition metal oxides, especially perovskite-type oxides with a formula of ABO_3 , display a promising OER activity in alkaline media⁹⁻¹². In particular, it was discovered that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is one of the most active OER catalysts¹²⁻¹⁴. Unfortunately, BSCF, similar with

other oxides^{8,15}, shows limited HER activity. A few researchers attempted to promote the HER activity, as well as the OER activity, of BSCF^{6,11,14,16}. For example, Xu *et al.* found that the HER activity of BSCF can be greatly enhanced by doping Pr into the A-site¹⁶. Hua *et al.* reported that both HER and OER activity of BSCF can be improved by La/Ca co-doping into the A-site⁶. Nevertheless, an overpotential at 10 mA/cm² of ~432 mV was still observed for overall water splitting⁶. It was reported previously that metal cobalt and nickel have been calculated to have a relatively low energy barrier for H adsorption^{8,17-20} in HER process, thus cobalt or nickel metal-based catalysts may have promising HER activity. Therefore, aside from modifying the composition of BSCF, coupling BSCF with cobalt and nickel metals may be an effective way to realize efficient overall water splitting. However, BSCF suffers from poor durability. Thus, we protected BSCF by wrapping it with carbon materials from the harsh electrolyte environment. This approach enhances the durability and boosts the electrical conductivity of the composite.

In this work, we report a core-shell structured composite containing BSCF, cobalt and nickel bimetal nanoparticles (CoNi), and N-doped carbon (NC) as a bifunctional catalyst for overall water splitting. This composite, CoNi/BSCF/NC, displays remarkable OER and HER activity and stability, as compared to pristine BSCF and

some of the state-of-the-art catalysts. The excellent OER and HER performance of CoNi/BSCF/NC is related to its unique composition and structure: (1) the core-shell structure maximizes interfacial interactions between each component and facilitates the charge transfer; (2) CoNi metals could be oxidized electrochemically, which synergistically works with BSCF and significantly improves the OER activity; (3) OH⁻ produced in HER process preferentially attaches to BSCF sites, which enables efficient adsorption of H atoms on CoNi sites and improves the HER kinetics. Due to above factors, a small voltage of 1.53 V is demanded to drive a current density of 10 mA/cm² in a prototype electrolyzer using CoNi/BSCF/NC as both electrodes.

Results and discussion

Physical properties

CoNi/BSCF/NC composite was prepared through a three-step route: sol-gel synthesis of BSCF, hydrothermal treatment followed by heat treatment in N₂ atmosphere to get CoNi nanoparticles (NPs) and N-doped carbon (CoNi/NC), and then mechanical ball milling of two prepared components. For better comparison, pristine BSCF and CoNi/NC are also ball milled separately. Figure S1a shows the X-ray powder diffraction (XRD) pattern of BSCF synthesized in the first step. The XRD pattern can be well indexed to a cubic phase with a space group of $Pm\bar{3}m$, which is in good agreement

with literature^{14,21}. The experimental pattern of the prepared BSCF well matches the calculated profile obtained by Rietveld refinement analysis, suggesting the presence of little impurities. The XRD pattern and Rietveld refinement analysis of CoNi alloy NPs prepared in the second step is shown in Figure S1b, where no other phases are present. CoNi NPs also show a cubic phase ($Pm\bar{3}m$), consistently with a previous report²².

Figure 1a displays the XRD pattern of the as-obtained CoNi/BSCF/NC composite, where we can see the cubic phase of BSCF through the peaks at 22.4 °, 31.8°, 39.2 °, 45.7 °, 56.6 °, and 66.1°. In addition to the signals of BSCF, peaks at 44.5°, 51.9°, and 76.5° are also clearly observed and could be assigned to CoNi (111) and (200) planes, respectively. A weak bump at around 25° suggests the presence of carbon material in the composite, while Raman spectra (Figure S3) shows the existence of a substantial number of defects in the carbon material, indicating a relatively low graphitization degree. These results confirm that CoNi/BSCF/NC consists of BSCF particles, CoNi NPs, and a carbon matrix. The composite structure is further revealed by high-resolution transmission electron microscopy (HR-TEM). As shown in Figure 1b, the lattice fringes of BSCF are well observed with a d-spacing of 0.28 nm, which corresponds to the (011) plane of BSCF. Moreover, we can see that uniform CoNi NPs are evenly supported on BSCF particles (Figure 1b and 1c). The average particle size

of CoNi NPs are around 3 nm (Figure 1e), much smaller than that of BSCF particle, which is in the 60 - 120 nm range as shown in Figure S2. Furthermore, the overall CoNi/BSCF particles are completely encapsulated in the carbon material (Figure 1d), suggesting that CoNi/BSCF/NC composite has a core-shell structure.

Figure 1. (a) The XRD pattern of CoNi/BSCF/NC; (b, c) the high-magnification and (d) low-magnification TEM images of CoNi/BSCF/NC; and (e) the particle size distribution of CoNi nanoparticles. The X-ray photoelectron of (f) Co 2p and (g) Ni 2p spectra of CoNi/BSCF/NC, BSCF and CoNi/NC.

The existence of metallic Co and Ni on the surface of CoNi/BSCF/NC is further confirmed by X-ray photoelectron spectroscopy (XPS). As shown in Figure 1f, the two fitted peaks at around 778.2 eV and 780.1 eV in Co 2p_{3/2} band of CoNi/NC could be

attributed to metallic Co (Co^0) and oxidized Co ($\text{Co}^{2+}/\text{Co}^{3+}$), respectively, in good agreement with previous reports^{15,23}. However, it is difficult to fit the Co 2p bands of CoNi/BSCF/NC and BSCF because they are strongly overlapped with Ba 3d band. We can see from Figure 1f that the Co 2p_{3/2} band of CoNi/BSCF/NC covers characteristic peaks for both oxidized Co and metallic Co, while the Co 2p_{3/2} band of BSCF locates at a higher binding energy, which is barely intersected with the characteristic peak of metallic Co. Moreover, Co 3p band, as seen in Figure S4a, of CoNi/BSCF/NC is also shifted to a lower energy as compared to original BSCF, showing a lower oxidation state of Co at the surface of the composite. These results may indicate the presence of metallic Co on the surface of CoNi/BSCF/NC. Figure 1g shows Ni 2p band of CoNi/BSCF/NC, where a strong peak can be observed at around 852.2 eV, corresponding to the Ni metal²³. This clearly shows the presence of metallic Ni on the surface of the composite. The peak at around 855.1 eV refers to Ni(OH)₂/NiOOH species^{3,24,25}, which come from partial oxidation and water adsorption of its outside surface.

Electrochemical activation toward OER

The OER activity of CoNi/BSCF/NC was evaluated by RDE measurements using a conventional three-electrode system in 0.1 M KOH solution saturated with O₂. Figure

2a shows the cyclic voltammetry (CV) profile of CoNi/BSCF/NC. It is exciting to note that its OER activity is gradually activated by CV cycling. The OER current density of CoNi/BSCF/NC at an overpotential of 0.4 V is gradually improved 2.7 times after 100 cycles and 6.8 times after 200 cycles (Figure 2b). Moreover, as shown in Figure 2c, the onset overpotential and the overpotential at 10 mA/cm² both decreases with increasing cycle number and tend to stabilize after approximately 200 cycles. As comparison, we also conducted an identical CV test with pristine BSCF and CoNi/NC. Different with CoNi/BSCF/NC, this electrochemical activation is not observed with BSCF, as shown in Figure S6a, where the OER current of BSCF decreases continuously with increasing cycle number. We also found that CoNi/NC shows slightly improved OER activity during CV cycling (Figure S6b and S6c). However, unlike CoNi/BSCF/NC, the improved OER activity of CoNi/NC is limited and only observed in the first 10-20 cycles.

To investigate the reasons of the electrochemical activation of CoNi/BSCF/NC, we conducted XPS to study the changes of its surface chemical properties. Figure 2d shows Ni 2p spectra of CoNi/BSCF/NC before and after electrochemical activation through 200 CV cycles. It is clear to see that the peak showing metallic Ni (at 852.2 eV) disappears after activation, and is replaced by a peak at higher binding energy. This

shift suggests that the Ni metal in the composite was oxidized electrochemically. Moreover, both Co 2p band (Figure S5a) and Co 3p band (Figure S5b) slightly shifted to higher energy after activation, suggesting that metallic Co may also be partial oxidized. Actually, the electrochemical activation has also been observed with other Ni-containing catalysts and was attributed to the simultaneous oxidation of Ni in previous works²⁶⁻²⁸. It is demonstrated that even for metallic catalysts, such as Ni and Co (actually passive oxide covers the metal), oxygen evolution always occurs on the oxide surface²⁹. This is mainly because positive charged metal ions are more capable of adsorbing OH than their metallic counterparts^{-8,15,30,31}. Therefore, electrochemical oxidation of metallic Ni and Co leads to increased catalytically active sites.

Notably, the observed oxidized Ni groups in Figure 2d do not pertain to Ni oxides, which usually have a characteristic peak at around 853.2 eV^{25,32}, but rather Ni(OH)₂/NiOOH groups (855.1 eV)^{3,24,25}. Consistent result could be obtained from O 1s spectra (Figure S5c). We can see clearly that the relative amount of lattice oxygen has been reduced after activation, while the content of metal-OH groups increases. Corrigan *et al* show that Fe ions can readily incorporate into Ni(OH)₂/NiOOH during electrochemical measurements in KOH electrolyte³³. Boettcher and Bell both reveal that Fe ions have an extreme sensitive and positive effect on the OER performance of

Ni(OH)₂/NiOOH^{24,28,34,35}, even though the role of Fe in the electrochemical process is still under investigation. The ICP results (Table S3, haven't got the results) shows the elemental leaking from the composite into the electrolyte. Therefore, it is possible that a small amount of Fe ions leak from BSCF particles and incorporate into Ni(OH)₂/NiOOH groups, leading to significantly enhanced OER activity. Moreover, the fact that CoNi/NC, which is Fe-free, only shows limited improvement during CV cycling, from a side, confirms the huge impact of Fe ions on the OER activity of Ni-containing catalysts.

To obtain more insights of the electrochemical activation of CoNi/BSCF/NC, the electrochemically active surface area (EASA) of the CoNi/BSCF/NC composite was also estimated before and after activation in a non-Faradic region of 1.06 - 1.12 V vs. RHE (Figure S7). As seen in Figure 2f, the electrochemical double-layer capacitance (C_{dl}) after activation is calculated to be 1.02 mF/cm², a value two times greater than that of the initial composite (0.45 mF/cm²). And the corresponding EASA of CoNi/BSCF/NC before and after activation are 25.5 cm² and 11.25 cm², respectively. The larger EASA of the composite after electrochemical activation enables more active sites to be exposed at catalyst surface, which leads to enhancement in OER activity. The electrochemical impedance spectroscopy (EIS) measurement was also conducted,

as seen in Figure 3e. The charge transfer resistance (R_{ct}) of this composite is greatly reduced from 87.6Ω to 32.1Ω after activation through 200 CV cycles. As a result, CoNi/BSCF/NC possesses an increasing charge-transfer rate during CV test, which is likely due to the increase of the active sites and leads to an improved OER activity. Therefore, we may conclude that the significant OER self-improvement of CoNi/BSCF/NC is ascribed to factors including (1) metallic Ni and Co oxidation, (2) Fe ions incorporation into $NiOOH/Ni(OH)_2$, and (3) the increased EASA and the reduced R_{ct} .

Figure 2. (a) The CV profile over 1000 cycles, (b) the LSV curves after certain numbers of CV cycles, and (c) the overpotential changes with CV cycle numbers of CoNi/BSCF/NC. (d) The Ni 2p X-ray photoelectron spectra, (e) the measured capacitive current density at different scan rates, and (f) the electrochemical impedance spectroscopy of CoNi/BSCF/NC before and after CV test. All tests (except XPS) are

conducted in 0.1M KOH solution saturated with O₂.

OER activity and stability

The OER activity of self-improved CoNi/BSCF/NC is further studied and compared with BSCF, CoNi/NC, the physical mixture of BSCF and CoNi/NC, and the benchmark catalyst RuO₂. Figure 3a shows the linear scan voltammogram (LSV) of five catalysts at a rotation speed of 1600 rpm. It is clear to see that CoNi/BSCF/NC exhibits a much sharper increase in current density starting from its onset potential as compared to BSCF and other catalysts. This onset potential of CoNi/BSCF/NC is measured to be 1.48 V vs. RHE, which is 0.08 V smaller than original BSCF (1.56 V) and is a relatively small value in comparison to most OER catalysts reported so far (Table S4)^{10,11,14,23,27,36-41}. Impressively, the OER activity of CoNi/BSCF/NC even outperforms that of noble-metal catalyst RuO₂ with much smaller overpotential and higher current density. The overpotentials of CoNi/BSCF/NC necessary to achieve a current density of 10 mA/cm² and 50 mA/cm² are only 320 mV and 370 mV; these values are 50 mV and 190 mV smaller than those of RuO₂, respectively. Moreover, the OER performance of CoNi/BSCF/NC far surpasses that of the physical mixture of BSCF and CoNi/NC (Figure 3a and 3b). This may due to the strong interaction between each component in CoNi/BSCF/NC and the effective charge-transfer of the core-shell structure. EIS

measurements were conducted to confirm this hypothesis; as shown in Figure S8a, the charge transfer resistance (R_{ct}) of CoNi/BSCF/NC is much smaller than that of the physical mixture. Figure 3b shows the Tafel plots, which indicates the kinetic activity of the catalysts. The Tafel slope of CoNi/BSCF/NC is measured to be 57 mV/dec, which is not only greatly improved as compared to BSCF (120 mV/dec), but also among the best of recently reported OER catalysts (Figure 3d and Table S4)^{10,11,14,23,27,36-41}. Moreover, we also studied the OER catalytic behavior of CoNi/BSCF/NC in a more concentrated electrolyte. As displayed in Figure S9a, the OER current of CoNi/BSCF/NC also increases with CV cycling in 1 M KOH solution. And the activated composite shows greatly improved OER activity (Figure S9b) and reduced R_{ct} (Figure S9c), as compared to initial one.

Furthermore, the stability of CoNi/BSCF/NC is evaluated by CV and chronopotentiometry (CP) measurements, and is compared with original BSCF and RuO₂. The OER activity drop of CoNi/BSCF/NC (Figure S10a) over 1000 cycles of CV scan is almost negligible, while the OER currents of BSCF (Figure S10b) and RuO₂ (Figure S10c) reduce obviously after 1000 cycles. The CP test of three catalysts at a current density of 10 mA/cm² is shown in Figure 3c. While BSCF displays an increase in overpotential by almost 200 mV after 10,000 s continuously operation,

CoNi/BSCF/NC shows an excellent durability with no obvious potential increase. This stability improvement of CoNi/BSCF/NC as compared to original BSCF may be ascribed to the protection of carbon shell. Therefore, CoNi/BSCF/NC, with relatively small overpotential and Tafel slope, and excellent stability, is one of the best OER catalysts developed so far in alkaline solution (Figure 3d and Table S4).

Figure 3. (a) The LSV curves and (b) the Tafel plots of CoNi/BSCF/NC, BSCF, CoNi/NC, the physical mixture of BSCF and CoNi/NC, and RuO_2 . (c) The chronopotentiometry (CP) of CoNi/BSCF/NC, BSCF, and RuO_2 . (d) A comparison of CoNi/BSCF/NC and some highly active OER catalysts reported so far^{10,11,14,23,37-43}.

HER activity and stability

The HER catalytic activity of CoNi/BSCF/NC was also evaluated and compared with some reference catalysts using RDE at 1600 rpm in 1 M KOH solution saturated with N₂. CoNi/BSCF/NC shows excellent HER activity (Figure 4a) with a small onset potential of 132 mV and achieves current density of 10 mA/cm² at an overpotential of 183 mV. These are superior values as compared other perovskite-based HER catalysts (Table S5), such as Pr_{0.5}BSCF¹⁶, La_{0.5}(Ba_{0.4}Sr_{0.4}Ca_{0.2})_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}/rGO⁶, and SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-δ}⁴. From the comparison, it emerges that CoNi/BSCF/NC is among the best perovskite-based HER catalysts in basic condition, as summarized in Figure 4d. Moreover, CoNi/BSCF/NC displays a favorable Tafel slope of 49 mV/dec, which is only slightly larger than that of Pt/C (20 wt% Pt on carbon black), showing an efficient HER kinetics of this composite. In addition, the operation durability of CoNi/BSCF/NC under HER condition was evaluated by chronoamperometric test at a current density of 10 mA/cm², as seen in Figure 4c. Negligible potential change of CoNi/BSCF/NC is observed over 14,000 s continuously operation.

To investigate the synergistic effect of two components and the impact of the core-shell structure, the HER activities of BSCF, CoNi/NC, and the physical mixture of the two were also tested and compared to CoNi/BSCF/NC (Figure 4a). BSCF shows limited

HER activity, with much larger onset potential and overpotential, while CoNi/NC is much more active than BSCF, indicating the pivotal role of metallic Co and Ni in HER catalysis. The HER activity, including the overpotential and Tafel slope, of CoNi/NC, however, is much inferior to that of CoNi/BSCF/NC, which suggests that BSCF may also plays certain role in HER. Notably, the HER activity of the physical mixture of BSCF and CoNi/NC is even worse than that of CoNi/NC, without observing any synergistic effect. This suggests that the excellent HER activity of CoNi/BSCF/NC might also be facilitated by the special core-shell structure of the composite, which enables stronger interfacial interaction between each component, and thus gives a faster charge transfer. Charge transfer resistance (R_{ct}) was obtained from EIS measurements (Figure S8b), where a reduced R_{ct} of 69 Ω is observed with CoNi/BSCF/NC as compared to the physical mixture of BSCF and CoNi/NC (153 Ω). Furthermore, deeper insights could be obtained from the analysis of HER pathway, which undergoes, in alkaline media^{42,43}, the Volmer-Heyrovsky process:

or Volmer-Tafel process:

As we can see from the above equations, both HER processes involve the adsorption of H_2O , reduction of H_2O into OH^- , release of OH^- , absorption of H intermediate, and formation of H_2 . Efficient release of OH^- is an important step to refresh the catalyst surface because OH^- occupies the H adsorption sites and catalytic active sites^{8,15}. And inefficient release of OH^- has been considered to be the reason why metallic Co and Ni fail to meet satisfactory in HER catalysis, even though they have relatively low H binding energy^{8,17-20}. As compared to Co and Ni metals, BSCF could more readily adsorb OH^- groups due to (i) the electrostatic affinity of cobalt and iron ions to negatively charged OH^- , (ii) more unfilled d-orbitals of cobalt and iron ions, and (iii) high content of oxygen vacancies of BSCF^{13,21}. O 1s spectra (Figure S4b and Table S2) of BSCF and CoNi/NC further confirm this hypothesis. The O 1s band can be deconvoluted into four characteristic peaks correspond to lattice oxygen (around 529.2 eV for O^{2-}), defect oxygen or highly oxidative oxygen species (around 530.4 eV), hydroxyl groups (around 531.6 eV for metal–OH), and adsorbed molecular water (around 533.4 eV for H_2O)^{16,44,45}. The molar ratio of different oxygen species were calculated from the relative area of the different characteristic peaks (Table S2). As compared to CoNi/NC, a larger amount of hydroxyl groups is attached on the surface of BSCF, suggesting a stronger interaction between the BSCF and OH^- in the electrolyte. Therefore, on a CoNi/BSCF interface, the formed OH^- groups could preferentially

attach to the BSCF site, while the nearby metallic CoNi site could be exposed to H atoms, and thus facilitate the Tafel or Heyrovsky process. In contrast, pristine BSCF is not active for HER due to its poor H adsorption, and CoNi/NC alone is not effective enough because of the inefficient desorption of OH^- . Additionally, we have to admit that the detailed mechanism of HER catalytic process of CoNi/BSCF/NC is not fully clear because of the difficulties in theoretical modelling of this complicated composite.

Figure 4. (a) The LSV HER curves and (b) Tafel plots of CoNi@BSCF/NC, BSCF, CoNi/NC, the physical mixture of BSCF and CoNi/NC, and Pt/C. (c) The chronopotentiometry (CP) of CoNi/BSCF/NC and Pt/C. All tests are conducted in 1 M KOH saturated with N_2 . (d) A comparison of CoNi/BSCF/NC and reported perovskite-

based HER catalysts^{4,6,16}.

Bifunctional performance toward overall water splitting

The excellent catalytic performance of CoNi/BSCF/NC towards OER and HER suggests that it could serve as both cathode and anode materials for overall water splitting. We then set up a prototype alkaline electrolyzer at room temperature using our composite (electrochemically activated) for both electrodes. 1 M KOH is used as electrolyte and Ni foam as the current collector. Benchmark catalysts Pt/C, RuO₂, and the original BSCF are also used as reference. Figure 5a shows the overall water splitting performance of the prototype electrolyzers using different catalysts. The voltage at 10 mA/cm² is observed at 1.53 V for CoNi/BSCF/NC - CoNi/BSCF/NC electrolyzer, which is even smaller than RuO₂ - Pt/C prototype and much smaller than BSCF – BSCF one. This is also a quite competitive value among many reported highly active bifunctional catalysts even though our catalyst loading is lower than most of the reported ones^{2-6,46-51} (Figure 5b and Table S6). The durability of the prototype electrolyzer with CoNi/BSCF/NC was also evaluated, as seen in Figure 5c, using chronopotentiometry (CP) measurement at 10 mA/cm². No obvious voltage increase is observed over 12,000 continuously test.

Figure 5. (a) The LSV curves and (c) the chronopotentiometry (CP) measurement of at 10 mA/cm² of prototype electrolyzers. (b) The comparison of the required voltage at 10 mA/cm² of CoNi/BSCF/NC with some of the most active bifunctional catalysts reported in 2017^{2-6,46-51}.

Conclusion

In this work, we reported a novel composite, CoNi/BSCF/NC, with a special core-shell structure as a highly active and stable bifunctional electrocatalyst for OER and HER. The unique composition and structure of CoNi/BSCF/NC enables the electrochemical activation of its OER activity in a great extent and the significantly enhanced HER activity by imparting synergistic HER process to BSCF-site and CoNi-site. The CoNi/BSCF/NC (activated) not only exhibits outstanding OER performance, which surpass most catalysts reported so far, but also shows excellent HER performance with small overpotential and Tafel slope in alkaline media. More impressively, the overall water splitting performance of CoNi/BSCF/NC is also superior to most bifunctional catalysts reported in 2017, with a small voltage of 1.53 V at 10 mA/cm². This is the first

time that the water splitting performance of BSCF is greatly promoted by cooperating with bimetal alloy nanoparticles and N-doped carbon materials. Therefore, this work might open new avenues to further improve the performance of some state-of-the-art electrocatalysts using a simple and cost-effective approach.

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