Synergistic Coupling of Metallic Cobalt Nitride Nanofibers and IrOx Nanoparticle Catalysts for Stable Oxygen Evolution

Su-Ho Cho,‡ Ki Ro Yoon,‡§ Kihyun Shin,‡ Ji-Won Jung ‡ Chanhoon Kim, ‡ Jun Young Cheong, ‡ Doo-Young Youn,† Seok Won Song,† Graeme Henkelman,‡ and Il-Doo Kim†,*

‡Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea

†Department of Chemistry and the Institute for Computational Engineering and Science, University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information

ABSTRACT: The utilization of sustainable water electrolysis for hydrogen production is currently limited by sluggish kinetics of the oxygen evolution reaction (OER). The development of stable, highly active, and cost-effective OER catalyst supports would facilitate commercialization of water electrolysis technologies. In this study, we report for the first time the use of metallic cobalt nitride (Co₄N) nanofibers (NFs) as highly stable and conductive scaffolds for supporting Ir nanoparticles (NPs). The Ir catalysts supported on Co₄N NFs exhibit high OER activity and stability in alkaline media as compared with Ir catalysts supported on other materials (Co₃O₄ or carbon NFs) and commercial Ir/C. These results are attributed to the (i) efficient charge or mass transport between Ir NPs and metallic one-dimensional (1D) Co₄N NFs or interfibers, (ii) maintenance of the active oxidation state (Ir³⁺) of Ir NPs induced by synergistic charge compensation between catalyst and support during OER, and (iii) long-term stability induced by strong metal–support interactions.

1. INTRODUCTION

The concern about ever-growing energy costs and global warming associated with fossil fuel use has prompted the development of sustainable approaches for energy production. Among the possible alternatives, hydrogen energy has recently gained attention and is gradually replacing fossil fuels in some applications such as fuel cell vehicles because it has been considered as an abundant, clean, and renewable resource with no harmful emission. Water electrolysis is a promising way to generate hydrogen gas from water, but the sluggish reaction kinetics of the oxygen evolution reaction (OER) and the corresponding large overpotential at the anode limit the efficiency of water electrolyzers. As a consequence, tremendous effort has been devoted to find better materials to efficiently catalyze OER for water electrolysis.

Typically, noble metal based catalysts including Ir, Ru, and their oxides (IrO₂ and RuO₂) have been widely utilized as anode materials due to their outstanding OER activities and reasonable stabilities. However, the high cost and scarcity of such noble metals limit their widespread industrial application. To address these issues, the expensive metals can be partially substituted by cheaper materials (e.g., Cu-doped IrOₓ, IrCuₓ, IrNi₂, IrNi₄, IrNiOₓ, etc.) to reduce the cost of the catalyst as well as enhance the catalytic activity. Additionally, precious metal catalysts can be combined with robust support materials to provide homogeneous distribution of catalysts.

Carbon materials are most widely utilized as support materials due to their high surface area, high electrical conductivity, and their tunable pore structure. However, carbon materials are very corrosive at high potential (>1.5 V vs RHE), resulting in oxidation and irreversible loss of surface area. Metal oxides are the second most prevalent support material, since they usually have exceptional durability toward corrosion or dissolution, stabilization of catalyst particles against agglomeration, and increased catalytic activity, which can be attributed to the strong interaction between metals (catalysts) and metal oxides (supports). To date, Ir or IrO₂ nanoparticles (NPs) have been combined with robust oxide supports including TiO₂, Nb-doped TiO₂, Sb-doped SnO₂, and ZnO. Although enhanced electrochemical stability and performance have been achieved, key requirements such as sufficient electrical conductivity, available surface area, and structural stability under long-term operation should be further enhanced to make these support materials technically and economically viable.

Received: May 16, 2018
Revised: August 8, 2018
Published: August 9, 2018
Metal carbides or metal nitrides have recently attracted much attention as supports or catalytic materials by themselves in electrocatalysis due to their superior chemical and physical robustness and high metallic conductivity. Among them, cobalt nitride (Co3N) exhibits superior OER activity and stability in alkaline medium among other cobalt-based compounds. The outstanding performance of Co4N is attributed to the metallic electrical conductivity of Co3N cores and stable surface active sites that can facilitate oxidation of OH− into O2. Nonetheless, the possibility of Co3N as a support material has rarely been investigated in water electrolysis.

In this regard, we have devised a novel composite material involving Co3N nanofibers (NFs) as support materials and small Ir NPs as the primary OER catalytic components. The combination of one-dimensional (1D) fibers scaffold and 0D catalysts is known to be an ideal configuration in electrocatalysis because of (i) high exposure and dispersion of the catalytic particles on the surface of the supporting material, (ii) directional and fast charge transfer along the 1D fiber channels, and (iii) efficient mass (electrolyte) diffusion between interfiber spaces. Scheme 1 illustrates the method used to synthesize the Co3N NFs supported Ir NPs (Ir@Co3O4 NFs) catalysts. Co3O4 NFs were obtained from conventional electrosprinning followed by a two-step heat treatment: calcination and nitridation. The Ir NPs of 2.6 nm in diameter were prepared via a conventional polyol method. The premade Co3N NFs were soaked in Ir NPs dispersed solution and stirred vigorously. Finally, the Co3N NFs-supported Ir NPs (Ir@Co3O4 NFs) were obtained.

For the synthesis of Co3O4 NFs, the Co3O4 NFs were placed in an Ar-filled tube furnace and nitridized at 450 °C for 2 h (7.5 °C min−1) with a continuous NH3 gas flow (100 sccm). After cooling down the furnace to room temperature, the Co3N NFs were washed with a mixture of lower aliphatic alcohols and water and isopropyl alcohol (IPA) to remove any metal nanoparticles and carbon from the surface. The as-spun Co(OAc)2/PVP composite NFs were calcined at 600 °C for 2 h with a ramping rate of 2 °C min−1 and the solution was kept at 150 °C for 1 h. After cooling down, acetone was added to the Ir solution (acetone/Ir solution = 2:1 v/v), and the Ir colloidal solution was dispersed using an ultrasonicator for 20 min. The segregated supernatant was discarded and replaced with ethanol. The Ir colloidal solution was then diluted to 0.894 mg mL−1 in ethanol for use.

For the synthesis of Ir@Co3O4 NFs, the as-spun and calcined Ir NPs dispersed solution was evaporated at 50 °C for 12 h, followed by annealing at 300 °C for 1 h in an Ar atmosphere.

The Ir@Co3N NFs exhibited excellent electrocatalytic activity for OER in alkaline media and superior electrochemical stability compared to Ir catalysts supported on Co3O4 NFs and carbon nanofibers (CNFs) (Ir@Co3O4 and Ir@CNFs) and commercial Ir/C catalysts. We have demonstrated that the outstanding performance of Ir@Co3N NFs in OER could be attributed to (i) the unique 1D metallic Co3N NFs for efficient charge transport, (ii) synergistic charge compensation for maintaining the catalytic active phase of Ir NPs, and (iii) improved durability of Ir NPs on robust supports induced by a strong metal–support interaction.

2. EXPERIMENTAL SECTION

2.1. Materials. Cobalt(II) acetate tetrahydrate (Co(OAc)2·4H2O, Sigma-Aldrich), poly(vinylpyrrolidone) (PVP, Mw ~ 1 300 000, Sigma-Aldrich), and N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich) were prepared for the synthesis of Co3O4 and Co3N NFs. Hexachloroiridic acid hydrate (H2ClIr-xH2O, 99.98%, Sigma-Aldrich), ethylene glycol (EG, 99.5%, SAMCHUN Chemical), and PVP (Mw ~ 10 000, Sigma-Aldrich) were prepared for the synthesis of monodispersed Ir NPs. Nafion solution (Nafion 117 solution, ∼5% in a mixture of lower aliphatic alcohols and water) and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich.

2.2. Preparation of Co3O4 NFs and Co3N NFs. The Co3O4 NFs were synthesized via a simple electrosprinning method and a subsequent calcination step. Amounts of 3 g of Co(OAc)2·4H2O and 1 g of PVP (Mw ~ 1 300 000) were dissolved in 8 g of DMF at 50 °C with magnetic stirring at 500 rpm for 12 h. The homogeneously mixed viscous solution was transferred into a plastic syringe with a stainless steel needle (25 gauge) that was equipped on the electrosprinning machine (Nano NC, Korea). A stainless steel foil was used as a grounded current collector that was placed at a distance of 15 cm from the needle tip. A high dc voltage (15 kV) was applied on the tip of needle, and the electrosprinning solution was subsequently pulled out with the flow rate of 30 μL min−1. Then, elongated as-spun fibers were collected on the stainless steel foil. The as-spun Co(OAc)2/PVP composite NFs were calcined at 600 °C for 1 h with a ramping rate of 5 °C min−1 in an air atmosphere. After calcination, black Co3O4 NFs were obtained.

For the synthesis of Co3N NFs, the Co3O4 NFs were placed in an Ar-filled tube furnace and nitridized at 450 °C for 2 h (7.5 °C min−1) with a continuous NH3 gas flow (100 sccm). After cooling down the furnace to room temperature, the Co3N NFs were washed with a mixture of lower aliphatic alcohols and water and isopropyl alcohol (IPA) to remove any metal nanoparticles and carbon from the surface. The as-spun Co(OAc)2/PVP composite NFs were calcined at 600 °C for 2 h with a ramping rate of 2 °C min−1 and the solution was kept at 150 °C for 1 h. After cooling down, acetone was added to the Ir solution (acetone/Ir solution = 2:1 v/v), and the solution was centrifuged at 3000 rpm for 10 min. The segregated supernatant was discarded and replaced with ethanol. The Ir colloidal solution was then diluted to 0.894 mg mL−1 in ethanol for use.

2.4. Preparation of Ir@Co3N NFs. For the synthesis of the Co3N NFs-supported Ir NPs (Ir@Co3N NFs), certain amounts of Co3N NFs were added to the Ir colloidal solution and dispersed using sonication for 1 h. The resulting suspension was stirred for 30 min and kept in a convection oven at 50 °C for 12 h to evaporate the solvent. The dried mixture of Ir NPs and Co3N NFs was thermally treated at 300 °C for 1 h in an Ar atmosphere. For purposes of comparison, CNFs- and Co3O4 NFs-supported Ir NPs (Ir@CNFs and Ir@Co3O4 NFs) were prepared using the same procedure described above.

2.5. Materials Characterization. The morphologies and structures of the catalysts were examined by scanning electron microscopy (SEM, XL-30 SFEG, Philips, U.S.A.) and field emission transmission electron microscopy (FE-TEM, Tecnai G2 F30 S-Twin, FEI, Netherlands) with energy-dispersive X-ray spectrometry (EDS) analysis. The X-ray diffraction (XRD) patterns of Co3O4 NFs, Co3N NFs, and Ir@Co3N NFs were measured by an X-ray diffractometer (D/MAX-2500, Rigaku, Japan) using Cu Kα (λ = 1.54 Å) radiation. The amounts of Ir NPs in the catalysts were analyzed by inductively coupled plasma mass spectrometer (ICP-MS, Agilent ICP-MS 7700S, Agilent, U.S.A.). The surface analysis of catalysts was performed by X-
ray photoelectron spectroscopy (XPS) measurement (Thermo VG Scientific, Germany) with Kα radiation as excitation source.

2.6. Electrochemical Tests of Ir@Co₄N NFs. Electrochemical measurements were performed in a three-electrode system on single-channel potentiostat (ZIVE SP1, Wonatech, Korea). In a typical procedure, the catalyst ink suspension contained 50 μL of Nafion solution (5%) and 5 mg of catalyst dispersed in 1.25 mL of solvent composed of DI water and IPA with 3:1 v/v. The ink suspension was sonicated for 30 min, and then dropped on a glassy carbon electrode (GCE) with a catalyst loading mass of 0.285 mg cm⁻². The catalyst-loaded GCE was equipped on the potentiostat as the working electrode. Pt coil and Hg/HgO (filled with 1 M NaOH, \( E_{Hg/HgO} = 0.140 \) V vs RHE) were used as the counter and reference electrode, respectively. All electrochemical measurements were performed in an O₂-saturated 0.1 M KOH solution (pH = ~13). The measured potentials reported in our work were converted to the reversible hydrogen electrode (RHE) through the Nernst equation, \( E_{\text{RHE}} = E_{Hg/HgO} + 0.140 \) V + 0.059pH, and have been corrected by IR compensation. Linear sweep voltammetry (LSV) was conducted in the potential range of 0.0–1.0 V (vs Hg/HgO) with a scan rate of 5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) tests were performed by applying an ac voltage with a 10 mV amplitude in a frequency range from 1 MHz to 0.1 Hz. To investigate the stability of the catalysts, cyclic voltammetry (CV) scanning was carried out for 1000 cycles in a potential range from 0.0 to 0.8 V (vs Hg/HgO) with a scan rate of 100 mV s⁻¹, and chronoamperometric experiments were performed at 1.6 V (vs RHE) for 24 h.

2.7. Density Functional Theory Calculations. The adsorption energies of Ir NPs on the Co₄N and turbostratic doped carbon were calculated to evaluate the durability of the supported catalysts. Ir NPs consisting of 4, 5, 9, 10, and 21 Ir atoms were considered, to determine trends in the adsorption energy as a function of particle size. A Co₄N (111) surface was constructed with a 3 × 3 supercell containing six atomic layers with the bottom two layers fixed in their bulk positions. We considered turbostratic doped carbon to describe CNF; detailed information about the turbostratic doped carbon model has been described in our previous study. Both systems contained a 10 Å vacuum gap to isolate the slabs from their periodic images.

GGA-level spin-polarized density functional theory (DFT) calculations were performed with the Vienna ab initio simulation package (VASP). The Perdew–Burke–Ernzerhof (PBE) functional

Figure 1. TEM images of Ir NPs with (a) low and (b) high magnifications. (c) Particle size distribution of Ir NPs. SEM images of (d) Co₄N NFs and (e) Ir@Co₄N NFs (scale bar in inset is 200 nm). TEM images of Ir@Co₄N NFs with (f) low (g) medium, and (h) high magnifications. (i) SAED patterns of Ir@Co₄N NFs. EDS elemental maps of Ir@Co₄N NFs: (j) Co, (k) N, and (l) Ir atoms.
was employed to describe electronic exchange and correlation. The interaction between the ionic cores and the valence electrons were treated within the projector augmented wave framework. In this study, the cutoff energy was set to 400 eV and the Brillouin zone was sampled at $2 \times 2 \times 1$ with the Monkhorst–Pack scheme. The convergence criteria for the electronic structure and geometry were set to $10^{-5}$ eV and $0.01$ eV Å$^{-1}$, respectively. Adsorption energies of Ir NPs were calculated as

$$E_{\text{ads}} = E_{\text{IrNP} + \text{Support}} - E_{\text{Support}} - E_{\text{IrNP}}$$

Here, $E_{\text{ads}}$ is the adsorption energy of a supported Ir NP, $E_{\text{IrNP} + \text{Support}}$ is the total energy after binding of the Ir NP on the support, $E_{\text{Support}}$ is the total energy of isolated clean support, and $E_{\text{IrNP}}$ is the total energy of an isolated Ir NP.

3. RESULTS AND DISCUSSION

The microstructures of the synthesized Ir NPs, Co$_4$N NFs, and Ir@Co$_4$N NFs were characterized by SEM and TEM measurements (Figure 1). As shown in Figure 1a, the ir colloid solution prepared by the polyol method contained uniform and monodispersed Ir NPs due to the capping effect of PVP. The observed interplane distances in the NPs are between 2.19 and 2.22 Å, corresponding to the (111) facet of metallic Ir (Figure 1b). The average size of the Ir NPs was 2.6 nm (Figure 1c).

Figure S1 shows that Co$_3$O$_4$ NFs have a clear 1D structure with an average diameter of 270 nm. The Raman spectrum of CNFs (Figure S3b) shows two major peaks at 1332 and 1588 cm$^{-1}$ corresponding to the vibration modes of CO$_2$ and CO$_3$ in CNFs. These results indicate that the CNFs have a polycrystalline structure.

After Ir NPs loading, the surface of the Co$_4$N NFs became rougher, but the overall morphology of the NFs was well-maintained (Figure 1e). We could confirm the existence of mesopores in the Co$_4$N NFs through TEM observation as indicated by white arrows (Figure 1f). As shown in the extended TEM image (Figure 1g), the spherical Ir NPs are observed on the surface of the Co$_4$N NFs. From the HRTEM image (Figure 1h), we confirm that the Ir NPs were crystalline, exhibiting (111) planes of metallic Ir (red dashed circles). As a catalyst support material, Co$_4$N NFs were also preserved after loading of Ir NPs with a well-defined lattice spacing of 2.07 Å, corresponding to the (111) plane of Co$_4$N. The clear ring patterns in the SAED result (Figure 1i) also support the coexistence of both Ir and Co$_4$N species as polycrystalline structures. Energy-dispersive X-ray spectroscopy analysis (Figure 1j) reveals the complete formation of nitride compounds (Co$_4$N) and a uniform distribution of Ir species on the Co$_4$N NFs. These comprehensive results indicate that ~2.6 nm sized Ir NPs were supported on the surface of mesoporous Co$_4$N NFs without significant aggregation.

For the purpose of comparison, we also prepared Ir NPs supported on CNFs (Ir@CNFs). The CNFs, that were prepared by electrospinning and a subsequent carbonization annealing, exhibited a 1D structure with a smooth surface and an uniform diameter of 630 nm (Figure S3a). The Raman spectrum of CNFs (Figure S3b) shows two major peaks at
approximately 1348 and 1590 cm\(^{-1}\), assigned to the D and G bands. The relative intensity of the D and G band peaks (\(I_D/I_G\)) is used to estimate the amount of disorder in the carbon structure, and the \(I_D/I_G\) value of 0.963 is similar to the turbostratic carbon structure predominant in electrospun CNFs as reported in the literature.\(^3\) In order to prepare Ir@CNFs, Ir NPs were attached on the CNFs in the same manner with Ir@Co\(_4\)Ns, and their microstructures are displayed in Figure S4.

The chemical and structural properties of Co\(_3\)O\(_4\) NFs, Co\(_4\)N NFs, and Ir@Co\(_4\)N NFs were investigated with XRD and XPS. As shown in Figure 2a, the Co 2p spectra of Co\(_3\)O\(_4\) NFs can be deconvoluted into Co\(^{3+}\), Co\(^{2+}\), and satellite peaks at 780.53, 783.43, and 786.53 eV, respectively.\(^3\) The coexistence of Co\(^{3+}\) and Co\(^{2+}\) is attributed to the spinel-type Co\(_3\)O\(_4\) as illustrated in Figure 2c. After the nitridation process, the binding energy of metallic Co\(^0\) bond centered at 778.58 eV was detected in Co\(_4\)N NFs. The existence of mixed valence of cobalt ions (Co\(^{3+}\) and Co\(^{2+}\)) in Co\(_3\)O\(_4\) NFs implies that the surface of Co\(_3\)O\(_4\) NFs includes slightly oxidized species (CoO\(_x\)) as reported in previous studies.\(^3\) Their binding energies were maintained when the Ir NPs were introduced at the surface. In the N 1s region (Figure 2b), no specific bonds were detected in Co\(_3\)O\(_4\) NFs, while clear Co–N bond appeared in Co\(_4\)N NFs and Ir@Co\(_4\)N NFs. These results indicate that the surface chemical composition was changed and that N species were definitely introduced in the nitridation step. From the XRD patterns, we could observe clear crystalline changes from Co\(_3\)O\(_4\) to Co\(_4\)N after the nitridation process (Figure 2d). The XRD pattern of Co\(_3\)O\(_4\) NFs was well-matched with previously reported spinel-type Co\(_3\)O\(_4\) (JCPDF no. 42-1467).\(^4\) For Co\(_4\)N NFs, the XRD patterns were matched with Co\(_3\)N phases through (111), (200), and (220) planes at 44.2°, 51.5°, and 75.9°, respectively, as reported in the literature.\(^5\) The Co\(_3\)N is known to have a face-centered crystal (fcc) structure in which four Co atoms are close-packed and a N atom is placed at the center of the unit cell as illustrated in Figure 2f. The crystalline structure of Co\(_3\)N was not significantly changed after Ir loading, evidenced by our XPS and XRD results. The Co\(_3\)N NFs exhibit a positive temperature-dependent resistance behavior, consistent with metallic conduction (Figure S5). The metallic property of Co\(_3\)N NFs results in electron delocalization and brings efficient charge transfer between the surface of the catalysts and the current collector, which is a critical requirement of an effective support material for electrocatalysis. For Ir@Co\(_3\)N NFs, the spectrum of Ir 4f was dominated by Ir\(^{4+}\) bonds (1.59 atom %) and followed by Ir\(^0\) (0.7 atom %) and Ir\(^{3+}\) (0.44 atom %) bonds, implying the evolution of oxidized iridium (IrO\(_x\)) covering the metallic Ir core in NPs.\(^4\) Considering the probe depth of the X-ray in the XPS analysis, the thickness of this oxide layer should be less than 2 nm.

To assess the electrochemical properties of the pristine support materials, we first carried out OER tests by comparing Co\(_3\)O\(_4\) NFs, Co\(_4\)N NFs, and CNFs without Ir catalysts. Figure 3a compares the current–potential response of Co\(_3\)O\(_4\) NFs, Co\(_4\)N NFs, and CNFs in an O\(_2\)-purged 0.1 M KOH solution. Co\(_4\)N NFs and Co\(_3\)O\(_4\) NFs show OER overpotentials (\(\eta\)) of 0.44 and 0.53 V at 10 mA cm\(^{-2}\) respectively, while a negligible response was observed for the pristine CNFs. The OER performance of Co-based catalysts can be explained by the presence of Co\(^{3+}/Co^{2+}\) redox surface sites, and the OER activity of the pristine Co\(_4\)N NFs is comparable to what has recently been reported for a Co\(_4\)N catalyst.\(^3\) Figure 3b depicts the Nyquist plots of EIS for Co\(_4\)N NFs, Co\(_3\)O\(_4\) NFs, and CNFs. The OER performance of Co-based catalysts can be explained by the presence of Co\(^{3+}/Co^{2+}\) redox surface sites, and the OER activity of the pristine Co\(_4\)N NFs is comparable to what has recently been reported for a Co\(_4\)N catalyst.\(^3\) Figure 3c depicts the Nyquist plots of EIS for Co\(_3\)O\(_4\) NFs, Co\(_4\)N NFs, and CNFs. The OER activity of the pristine Co\(_4\)N NFs is comparable to what has recently been reported for a Co\(_4\)N catalyst.\(^3\) Figure 3d depicts the Nyquist plots of EIS for Co\(_3\)O\(_4\) NFs, Co\(_4\)N NFs, and CNFs. The OER activity of the pristine Co\(_4\)N NFs is comparable to what has recently been reported for a Co\(_4\)N catalyst.\(^3\)
Figure 3c. The slight shoulder appeared at around 1.2 V in Ir@Co4N NFs was attributed to the electrochemical oxidation of Co4N under the positive bias, which was similarly observed in the polarization curves of pristine Co4N NFs (Figure 3a). The shoulder was not observed after further cycling test (Figure 4a), which means that the superficial layer of Co4N was slightly oxidized to catalytically active CoOx without excessive oxidation of the core Co4N phase, as previously reported.31

Interestingly, the Ir@CNFs system shows the best OER activity followed by Ir@Co4N NFs, Ir/C, and Ir@Co3O4 NFs with overpotential values to drive 10 mA cm−2 of 0.310, 0.336, 0.354, and 0.365 V, respectively. The superior performance of Ir@CNFs can be explained by the highest electrical conductivity of CNFs (∼20 Ω sq−1) among the samples.37 The specific activity of Ir@Co4N NFs, Ir@Co3O4 NF, Ir@CNFs, and Ir/C obtained at a potential of 1.6 V were 17.68, 10.87, 30.40, and 13.34 mA cm−2, respectively (Figure 3d, left column). When we considered the Ir mass activity in the catalysts, calculated from the inductively coupled plasma optical emission spectrometry (ICP-OES, Table S1), Ir@CNFs still exhibited the highest activity of 0.87 A mgIr−1 followed by Ir/C (0.68 A mgIr−1), Ir@Co4N NFs (0.65 A mgIr−1), and finally Ir@Co3O4 NFs (0.39 A mgIr−1). These results indicate that the initial OER activity at high potential is largely affected by the electrical conductivities of the support materials. Nevertheless, the mass activity of Ir@Co4N NFs exhibits a high value among the reported values of Ir-based catalysts supported by various materials in previous literatures (Table S4).

To check the stability of the prepared samples (Ir@Co4N, Ir@Co3O4 NFs, and Ir@CNFs), we conducted LSV tests after 1000 cyclic potential sweeps between 0.9 and 1.7 V. For Ir@Co4N NFs, the OER curve exhibited a similar shape with 2.8% increased current density at 1.6 V after cycling test (Figure 4a). On the other hand, Ir@Co3O4 NFs shows a drastic performance decline by 60.2% after 1000 cycles (Figure 4b). Compared to the stable performance of pristine Co3O4 NFs after 1000 cycles (Figure S6), there is a significant reduction of OER performance of Ir@Co3O4 NFs. The Ir catalysts supported on carbon-based materials (Ir@CNFs and Ir/C) exhibit drastic degradation after the cycling test. As can be seen in the inset of Figure 4c, almost 94.5% loss of initial current density was measured after the stability test. Similarly, the OER performance of the Ir/C catalyst showed a performance decline by 73.7% at 1.6 V after cycling (Figure 4d). The results show that there is a correlation between improved OER stability of catalysts and support materials.

As shown in Figure 4e, Ir@Co4N NFs has similar η values before and after cycling, with only a slight change from 0.336 to 0.331 V, while the other samples exhibited significantly increased η values after the cycling test. In particular, the Tafel slope of the Ir@Co4N NFs increased slightly from 94.5 to 102.92 mV dec−1 (Figure 4f). In contrast, drastic increases of the Tafel slopes for Ir@Co3O4 NFs (from 103.42 to 154.25 mV dec−1) and Ir/C (from 108.52 to 166.82 mV dec−1) were observed after cycling (Figure 4f).
mV dec\(^{-1}\)), Ir@CNFs (from 70.53 to 240.02 mV dec\(^{-1}\)), and Ir/C (from 114.73 to 158.92 mV dec\(^{-1}\)) were observed.

Oxidation states of Ir NPs in Ir@Co\(_4\)N NFs, Ir@CNFs, Ir/C before and after potential cycling tests were investigated with XPS. As shown in Figure 5a−c, the Ir 4f spectrum for all samples can be deconvoluted into a contribution of Ir\(^0\) (60.9 eV), Ir\(^{4+}\) (61.4 eV), and Ir\(^{3+}\) (62.4 eV) species along with their respective satellites.\(^{10,45}\) It is noteworthy that the 4f spectrum of Ir@Co\(_4\)N NFs and Ir@CNFs exhibited different shapes, indicating that the electronic structure of the Ir NPs is changed on the different support materials. The relative quantities of Ir 4f spectra before and after cycling test are summarized in Table S2.

In their initial state, the majority of Ir 4f states correspond to Ir\(^{4+}\) for all samples. However, sharp Ir\(^{4+}\) peaks were detected in Ir@CNFs and Ir/C, implying that Ir NPs tend to be more oxidized on the carbonaceous surface. For Ir@Co\(_4\)N NFs, a significant amount of Ir\(^{3+}\) associated with oxygen vacancies increased, while other peaks (Ir\(^{4+}\) and Ir\(^0\)) decreased after the cycling test (Table S2). On the other hand, the Ir\(^{4+}\) peaks were maintained in Ir@CNFs and Ir/C after cycling (Figure 5, parts b and c).

To determine the origin of the lower oxidation state (Ir\(^{3+}\)) in Ir@Co\(_4\)N NFs, we monitored changes in the Co 2p spectra before and after potential cycling. As shown in Figure 5d (lower column), the Co 2p spectra appeared similar to Co\(^0\), Co\(^{3+}\), and Co\(^{2+}\) states at binding energies of 778.4, 780.1, and 783.0 eV in the initial Ir@Co\(_4\)N NFs sample. After potential cycling, the surface of Co\(_4\)N had more oxidized species including Co\(^{3+}\) and Co\(^{2+}\), or more quantitatively, the "Co\(^0\)/ (Co\(^{2+}\) + Co\(^{3+}\))" ratio decreased from 8.0% to 3.3% upon cycling (Figure S8). Furthermore, the O 1s XPS spectra (Figure 5e) show an increase in the binding energy ranging from 530 to 531.5 eV, alluding to the evolution of CoO\(_x\) species as well as IrO\(_x\)(OH)\(_y\) on the surface, which are known to catalytically active for OER.\(^{7,10,14,46,47}\) On the basis of the above observation, it is reasonable to assert that there is a direct correlation between the chemical changes of the Co\(_4\)N NFs surface and Ir NPs. As evidenced by XPS, the surface oxidation of Co\(_4\)N during OER plays a significant role in preserving the active Ir\(^{3+}\) state of Ir NPs.

Figure 5. XPS Ir 4f spectra of (a) Ir@Co\(_4\)N NFs, (b) Ir@CNFs, and (c) commercial Ir/C catalysts before and after cycling tests (1000 cycles). (d) XPS Co 2p and (e) O 1s spectra of Ir@Co\(_4\)N NFs before and after cycling tests. (f) Relative quantities of Ir atoms in Ir@Co\(_4\)N NFs, Ir@CNFs, and commercial Ir/C catalysts before and after cycling tests.

Figure 6. (a) Adsorption energy of Ir\(_x\) NPs on the Co\(_4\)N and turbostratic doped carbon. (b) Chronoamperometric response of Ir@Co\(_4\)N NFs at 1.6 V (vs RHE).
One of the critical factors causing performance degradation of the catalysts from their initial performance is detachment or dissolution of the catalytic material from their supports during OER.\(^{19,48}\) Figure 5f compares the relative amount of Ir in the catalyst before and after cycling. The calculated Ir losses of Ir@Co\(_4\)N NFs, Ir@CNFs, and Ir/C were 3.2%, 98.3%, and 28.6% of their initial Ir composition, respectively. These results imply that Ir NPs were well-anchored to the Co\(_4\)N NF support even after vigorous OER cycling, while Ir NPs were easily detached from the CNFs and the commercial Vulcan carbon in the Ir/C catalyst during OER testing. Overall, these results provide evidence that the Ir component has better sustainability on the Co\(_4\)N NFs as catalyst support compared to other carbonaceous supports.

To better understand the strong metal–support interaction, we calculated the adsorption energy of Ir NPs on Co\(_4\)N supports.\(^{39}\) As shown in Figure 6a, the \(E_{\text{ads}}\) of Ir NPs increases with the number of Ir atoms in the clusters. The \(E_{\text{ads}}\) of Ir\(_{21}\) NP (which has an estimated particle size of \(\sim 0.8\) nm) were \(-7.53\) eV on the Co\(_4\)N surface and \(-6.36\) eV at the defect site of turbostratic doped carbon. More negative \(E_{\text{ads}}\) values represent stronger binding of Ir NPs on the surface.\(^{28–30}\)

Although the particle sizes in our simulations are smaller than the synthesized Ir NPs in the experiment, there is a clear trend in Figure 6a showing that larger Ir NPs will have stronger binding energies on the Co\(_4\)N than that on the turbostratic doped carbon. The stability of the catalytic activity and the high durability of the catalyst can be attributed to a strong interaction between metal (Ir NPs) and support (Co\(_4\)N NFs), preventing aggregation or detachment of active particles. The various \(E_{\text{ads}}\) values for supported clusters with different number of Ir atoms (\(x = 4, 5, 9, 10, 21\)) are listed in Table S3.

Finally, we evaluated the long-term stability of Ir@Co\(_4\)N NFs by chronoamperometric response (Figure 6b), which was performed at 1.6 V (vs RHE). The Ir@Co\(_4\)N NFs exhibit excellent stability with no obvious decay for over 24 h. However, Ir@CNFs show fast degradation of their initial current density value (Figure S9). These results demonstrate that the Co\(_4\)N NFs act as a robust and promising support material for OER catalysts in terms of (i) high electrical conductivity due to the electron delocalization of Co\(_4\)N, (ii) stability of their active phase by synergistic charge compensation, and (iii) formation of strong adhesion between metal NPs and nitride NFs.

4. CONCLUSION

In this work, we first reported metallic Co\(_4\)N NFs as a stable and robust support material for efficient OER in water electrolysis. The Co\(_4\)N NFs were prepared via a facile electrospinning technique, and Ir NPs prepared by a polyol method were loaded onto the surface of Co\(_4\)N NFs. The prepared Ir@Co\(_4\)N NFs exhibit high OER activity and excellent stability (over 1000 cycles) in alkaline media as compared with commercial Ir/C. We demonstrated that Ir NPs maintain surface-active Ir\(^{39}\) when they are loaded on Co\(_4\)N NFs, which undergo surficial oxidation during OER. Furthermore, a strong metal–support interaction between Ir NPs and Co\(_4\)N NFs suppresses the dissolution or detachment of the Ir NPs from the Co\(_4\)N NF support, enabling long-term electrochemical stability. This work provides a new avenue for the development of a new class of supports which have high electrical conductivity, high compatibility with catalysts, and enhanced stability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b02061.

Graphical and tabular characterization information including a table of ICP-OES analysis, SEM images, TEM images, XRD, and additional graphical information on electrochemical measurement (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: idkim@kaist.ac.kr.

ORCID

Graeme Henkelman: 0000-0002-3036-7153
Il-Doo Kim: 0000-0002-9970-2218

Author Contributions

§S.-H.C. and K.R.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Korea CCS R&D Center (KCRC) grant funded by the Korea government (Ministry of Science, ICT and Future Planning) (No. 2014M1A8A1049303), the Wearable Platform Materials Technology Center (WMC) funded by the National Research Foundation of Korea (NRF), a Grant of the Korean Government (MSIP) (No. 2016R1A5A1009926), and the BRL Program funded by the NRF (No. 2014R1A4A1030712). This work is also supported by the Global Ph.D. Fellowship Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2015H1A2A1033952). The computational work done in Austin was supported by the Welch Foundation (F-1841) and the Texas Advanced Computing Center.

REFERENCES

Core-Shell Particles as Efficient, Cost-Effective, and Stable Catalysts

Chemistry of Materials
Article

2012

chemical water splitting. Evolution Reaction.

Tailoring ruthenium exposure to enhance the performance of fcc


