Ionic-Liquid-Assisted One-Step Synthesis of CoO Nanosheets as Electrocatalysts for Oxygen Evolution Reaction

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ABSTRACT: The sluggish oxygen evolution reaction (OER) hinders the development of electrocatalytic water splitting for energy conversion and storage. Therefore, it is imperative to explore the cost-effective and highly efficient noble-metal-free electrocatalysts for OER. Herein, we are introducing such OER electrocatalyst based on Co, fabricated through an ionic-liquid-assisted one-step synthesis, where ionic liquid played a dual role as solvent cum structure-directing agent. Besides possessing large-accessible surface area and numerous active sites, the as-prepared stable CoO nanosheets exhibited excellent electrochemical activity through establishing an extensive contact with the electrolyte. Under alkaline conditions, the overpotential to achieve a current density of 10 mA cm$^{-2}$ is only 320 mV, and the Tafel slope is as small as 70 mV dec$^{-1}$. Thus, our work provides a new pathway for designing and engineering the highly efficient non-noble metal OER electrocatalysts by using ionic liquids.

1. INTRODUCTION

The oxygen evolution reaction (OER), as a half reaction of water splitting, has been extensively studied in recent years. However, the OER is a complicated reaction as four electrons are needed for the formation of an oxygen molecule, which makes it kinetically sluggish and requires large overpotential. Therefore, from a practical point of view, highly efficient OER electrocatalyst is crucial to accelerate this reaction. Presently, ruthenium oxide (RuO$_2$) and iridium oxide (IrO$_2$) are the state-of-the-art OER electrocatalysts. However, as precious metals, the scarcity and high cost limit their applications in industry. Therefore, research on earth-abundant, environmental-friendly, and cost-effective non-noble metal compounds as efficient electrocatalysts for OER is of great significance.

Transition metal oxides, phosphides, hydroxides, sulfoxides, double hydroxide hybrids, and so forth, have been reported as efficient electrocatalysts for OER. Among them, the cobalt (Co)-based compounds are considered as the promising candidates because of their high intrinsic catalytic activity, low-cost, earth abundance, and environmental benign nature. However, their catalytic activity is generally restricted by their structure, limited number of active sites, and poor conductivity, especially, in case of cobalt oxides. Several strategies were employed in the past to improve the catalytic activity of Co-based OER electrocatalysts, for example, doping with heteroatoms, manufacturing defect-rich structures, lowering the size, and forming the composites. However, these protocols are often complicated or limited to specific cases. Thus, a simple and feasible strategy to increase the number of active sites for improving the catalytic performance of Co-based electrocatalysts is urgently needed. It is well-known that two-dimensional (2D) structure can not only expose maximum active sites but also expand the contact area between the catalysts and the electrolyte. Hence, it is promising for improving the catalytic activity of electrocatalysts for OER. Numerous efforts have been devoted to explore effective methods for preparing 2D cobalt oxide materials as electrocatalysts for OER. However, all previous attempts faced insurmountable challenges to some extent. Ironic liquids (ILs) are referred to as “designer solvents” with tunable physicochemical properties and desired functions by changing their components. Owing to their high fluidity, low-melting temperature, high-boiling temperature, and very low-vapor pressure properties, they have been used so far as structure-directing agents in the synthesis of nanostructured materials such as CuO, SnS$_2$, and CuS. Recently, our group also employed ILs successfully for fabricating one-dimensional hierarchical MoO$_2$ an efficient hydrogen evolution reaction electrocatalyst. However, ILs are used rarely in the synthesis of OER electrocatalysts.

Herein, we describe an IL-assisted synthetic method for making cobalt oxide (CoO) electrocatalyst for OER. We fabricated CoO nanosheets through a one-step ionothermal method by using cobalt(III) acetylacetonate (Co(acac)$_3$) and 1-butyl-3-methylimidazolium-bis[(trifluoromethyl)sulfonyl]imide ([BMIM][NTf$_2$]). The IL—[BMIM][NTf$_2$] acts as a solvent and structure-directing agent during the synthetic process. When tested for OER activity, the as-prepared CoO nanosheets exhibited superior electrocatalytic performance with notable stability under alkaline conditions. Thus, the...
present synthetic strategy provides a new way for preparing the highly performable OER electrocatalysts.

2. RESULTS AND DISCUSSION

The molecular structures of the precursors used in this report are shown in Figure 1A, and Figure 1B illustrated the simple synthetic procedure involved. Direct heating of the mixture of precursors under N2 atmosphere yielded the CoO nanosheets, where the IL played a dual role as a solvent and a structure-guiding agent.

The phase and crystallinity of the CoO sample prepared under ionothermal conditions at 280 °C for 5 h (hereafter, denoted as CoO-280-5) were examined by powder X-ray diffraction (XRD). As shown in Figure 2A, the XRD diffraction pattern is in good agreement with the standard hexagonal CoO (P63mc, PDF no. 80-0075), indicating the existence of single hexagonal CoO phase. The peaks at around 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, and 67.8° can be assigned to the (100), (002), (101), (102), (110), (103), and (112) crystal planes of hexagonal CoO phase, respectively. The weak peak intensities indicate low crystallinity, which is owing to the weak oxidation conditions. To further explore the representative morphology of CoO-280-5, TEM image was obtained (Figure 2B), which demonstrated the formation of the well-defined 2D structure. More importantly, the low contrast between the near transparent nanosheets and background indicates that the CoO nanosheets are very thin. Further, the atomic force microscopy analysis confirmed the nanosheet-like morphology (Figure S1, thickness ≈ 3–5 nm), where some nanosheets are composed of several parallel-stacked ultrathin sheets. Such 2D nanosheets can not only provide numerous electroactive sites but also result in shorter ion-diffusion pathways and larger contact area with the electrolyte. Thus, these CoO nanosheets are promising candidates as electrocatalysts for OER.

To investigate the fabrication process of the CoO nanosheets, a time-dependent study was carried out. Two samples were prepared under conditions similar to CoO-280-5, except the reaction times were 1 h for CoO-280-1 and 2 h for CoO-280-2. Subsequent, powder X-ray analysis revealed (Figure 3A) that both samples have the same hexagonal CoO phase similar to CoO-280-5 (P63mc, PDF no. 80-0075) but with much poorer crystallinity. The TEM analysis of CoO-280-1 indicated an aggregated structure with very few inconspicuous primary sheets in the outer region (Figure 3B), whereas these nanosheets were grown much denser and distant in the case of CoO-280-2 (Figure 3C). Furthermore, many nanosheets started exfoliating from the aggregates. Upon increasing the reaction time to 5 h, the well-defined 2D nanosheets were formed, as shown in Figure 2B (i.e., CoO-280-5). On the basis of the aforementioned results, the growth process of the CoO nanosheets may be inferred as follows: at the initial stage, the cobalt oxide nanoparticles generated and aggregated to form conglomeres. However, owing to the sorption of [BMIM][NTf2] on the particles, the aggregate of the particles is metastable. It is well-known that 1,3-dialkylimidazolium-based ILs are able to self-organize into polymeric supramolecular structures which can act as the template for the formation of the sheetlike architectures. Therefore, the nanoparticles relocated to sheet structure gradually. Thus, the primary nanosheets come into being in the outer region of the conglomeres, as shown in Figure 3B. With the prolongation of the reaction time, the aggregated particles are consumed and the CoO nanosheets are formed finally.

As the stability and viscosity of ILs are significantly affected by the temperature, we investigated the influence of reaction temperature in our case by preparing samples at another four different temperatures (250, 300, 330, and 350 °C) by keeping the time period and other reaction conditions intact. The XRD results (Figure 4) suggested that when the reaction temperature was below 300 °C, the products are mainly cobalt oxide, whereas at 330 °C or higher, the products became the mixtures of cobalt sulfides (Co9S8 and Co3S4) and cobalt oxide. The product obtained at 250 °C (CoO-250-5) has a very poor crystallinity, almost amorphous in nature. For the samples obtained at 330 °C (Co9S8-330-5) and 350 °C (Co3S4-350-5), the peaks at 2θ = 29.8°, 31.2°, and 52.1° belong to the (311), (222), and (440) planes of Co9S8 (PDF no. 65-6801), respectively. Also, the peaks at 26.7° and 55° can be assigned, respectively, to the (220) and (440) planes of another cobalt sulfide—Co3S4 (PDF no. 42-1448). However, the peaks at...
34.1° can be indexed to the (111) plane of the CoO. The generation of cobalt sulfides can be attributed to the partial decomposition of [BMIM][NTf2] at high temperatures, which serves as a sulfur source for the cobalt sulfides. The decomposition of [BMIM][NTf2] at high temperatures will inevitably lead to damped function on structure engineering, which will be confirmed by the TEM analysis. The TEM image of CoO-250-5 (Figure 5A) consists of aggregated structures only because of the high viscosity of [BMIM][NTf2] and the low-reaction temperature which restricts the growth of the nanosheets. Although in the case of CoO-300-5 (Figure 5B), a stacked morphology composed of several parallel-stacked sheets is observed. This is due to the diminished protection of [BMIM][NTf2] for the nanosheets at high temperature. The initial-formed CoO nanosheets are unable to keep dispersed owing to the decreased viscous nature of [BMIM][NTf2] or insufficient adsorption of [BMIM][NTf2] on the nanosheets. When the ionothermal temperature is increased further to 330 °C and 350 °C, that is, in the cases of Co_S_y-330-5 and Co_S_y-350-5, respectively, cobalt sulfides were produced and the nanosheets are thicker and cracked down, as shown in Figure 5C and 5D, respectively. These results demonstrate that when the reaction temperature is higher than 300 °C, the stabilizing and structure-guiding functionality of [BMIM][NTf2] wears off.

To determine the surface chemical states of the constituents in the products, CoO-280-5 and Co_S_y-350-5 were subjected to XPS (X-ray photoelectron spectroscopy) analysis. Figure 6A−C shows the high-resolution XPS spectra of Co 2p region, O 1s region, and S 2p region of CoO-280-5, respectively. The Co 2p spectrum exhibits two prominent peaks at 780.4 and 797.4 eV corresponding to the Co 2p3/2 and Co 2p1/2 peaks of CoO. The peaks at 785 and 803.4 eV correspond to the satellites of Co 2p3/2 and Co 2p1/2. The peaks at 529.6 and 532.7 eV in O 1s spectrum are attributed to the lattice Co−O of CoO and the hydroxyl groups on the surface. The peak located at 531.1 eV is associated with oxygen vacancies. When the ultrathin sheets structure and weak oxidation environment are taken into account, it is reasonable that the nanosheets are rich in defects.31,54,55 The peaks located at 162, 164.9 eV can be indexed to S 2p3/2 and S 2p1/2 of C−S group, respectively; in addition, the peaks at 167.8 and 170.3 eV in S 2p region belong to the S−O group. The above superficial groups may be derived from the surface adsorption or carbonization of [BMIM][NTf2]. For Co_S_y-350-5, the high-resolution XPS spectrum of Co 2p region was presented in Figure 6D. The peaks at 778.8 and 796.4 eV can be ascribed to the Co 2p3/2 and Co 2p1/2 of Co_S_y suggesting the existence of Co_S_y phase. The peaks at 778.8 and 793.4 eV were derived from Co3+ and Co2+ of Co3S4. The peaks at 785 and 802 eV are satellite peaks. The peak at 782.2 eV can be assigned to the Co−O. The 2p XPS spectrum of Co_S_y-350-5 can be deconvoluted into six peaks (Figure 6F). The peaks at 160.2 and 162.5 eV can be assigned to S 2p1/2 and S 2p3/2 of Co3S4. The peaks at 160.4 and 164.5 eV corresponded to the S 2p1/2 and S 2p3/2 orbital of Co3S4. The peak at 167.8 and 171.1 eV can be indexed to S 2p1/2 and S 2p3/2 of SOx, which may be owing to the surficial oxidation. The high-resolution XPS spectrum of O 1s region for Co_S_y-350-5 (Figure 6E) also includes three peaks corresponding to Co−O (529.6 eV), the hydroxyl groups on the surface (533.0 eV), and the oxygen vacancies (531.2 eV).
a mixture of Co₉S₈, Co₃S₄, and surficial CoO, which is in good agreement with the XRD results.

The OER catalytic activities of the electrocatalysts synthesized at different temperatures were measured by linear scanning voltammetry (LSV) method in 1 M aqueous KOH solution. Figure 7A shows the polarization curves of all of the electrocatalysts studied for OER. The CoO nanosheets (CoO-280-5) show the highest catalytic activity, which is close to commercial RuO₂. The corresponding overpotential at the current density of 10 mA cm⁻² is only 320 mV, which is lower than that of CoO-250-5 (349 mV), CoO-300-5 (338 mV), CoₓSᵧ-330-5 (359 mV), and CoₓSᵧ-350-5 (387 mV). The OER kinetics of the studied electrocatalysts was estimated by using Tafel plots derived from the corresponding polarization curves (Figure 7B). The Tafel slopes are 60, 70, 83, 85, 95, and 97 mV dec⁻¹ for RuO₂, CoO-280-5, CoO-250-5, CoO-300-5, CoₓSᵧ-330-5, and CoₓSᵧ-350-5, respectively, which indicate that the CoO nanosheets possess a faster OER kinetics. In addition, the onset potential of the CoO-280-5 electrocatalyst is 1.472 V versus reversible hydrogen electrode (RHE), which is also lower than that of all of the other studied electrocatalysts (CoO-250-5: 1.534 V, CoO-300-5: 1.517 V, CoₓSᵧ-330-5: 1.549 V, and CoₓSᵧ-350-5: 1.582 V). These results demonstrate that the CoO nanosheets possess the highest electrocatalytic activity among all of the studied electrocatalysts in this work. Furthermore, the catalytic performance of CoO-280-5 is also superior to the majority of the previously reported cobalt oxide and sulfide-based electrocatalysts, as listed in Table S1. To better understand the high OER catalytic activity of the nanosheets, the cyclic voltammetry (CV) studies (Figure S2) were carried out to determine the electrochemical surface areas (ECSAs) of the as-prepared electrocatalysts. Among the estimated double-layer capacitances \( C_{dl} \) of all of the electrocatalysts (Figure 7C), CoO-280-5 exhibited the highest value (26.5 mF cm⁻²). On the basis of the linear relationship between the \( C_{dl} \) and ECSA, we can conclude that the CoO-280-5 nanosheets possess more exposed active sites than the other studied electrocatalysts. Thus, the high OER catalytic activity of the as-synthesized CoO-280-5 nanosheets can be explained as follows: on one hand, when compared with the stacked nanosheets or bulk structure, the ultrathin nanosheet structure can expose a large amount of superficial active sites; in addition, the ultrathin nanosheets with poor crystallization possess numerous defect sites, such as oxygen vacancies, edges, stacking faults, and so forth, as shown in Figure 6B, which could serve as highly active species for enhanced OER catalysis.⁶⁵ On the other hand, in comparison with the bulk phase, the ultrathin nanosheet structure not only offers a large effective surface area for sufficient electrode-material/current-collector contact but also decreases the length of the ion-diffusion paths and increases the contact area between the surface of the electrocatalyst and the electrolyte, which is favorable for an efficient mass transfer, especially the escape of O₂.⁶⁶ Moreover,
the intimate electronic contact between the electrode and catalyst plays an important role in determining the catalytic activity and durability; compared with the bulk or stacked structure, the ultrathin nanosheets are inclined to form most intimate contact with electrode, preventing the detachment of the catalyst, which ensures the unhindered operation of the electrode reaction.

As the stability is one of the prominent factors in determining the practicability of electrocatalysts, we probed CoO-280-5 by continuous CV sweeps in 1 M aqueous KOH solution from 1.0 to 1.6 V versus RHE at a scan rate of 50 mV/s and I-t measurements at 1.6 V versus RHE for 12 h. The polarization curve (Figure 7D) shows a slight decay in current density after 1000 continuous CV cycles. In addition, the I-t measurements (Figure 7E) indicated an almost steady current density without any significant decay during the 12 h of continual OER. However, in the end, a slight increase in the current density resulted from desorption of the adsorbed IL. These results suggest that the CoO-280-5 electrocatalyst possesses notable stability which can be attributed to the close acquaintance generated between the CoO nanosheets and the electrolyte.

3. CONCLUSIONS

In summary, we have successfully engineered a high-performance stable OER electrocatalyst (CoO-280-5), composed of hierarchical CoO nanosheets prepared through a simple single-step IL-assisted reaction. The structure-guiding nature of IL played a vital role in developing the suitable nanosheet-like architecture for the electrocatalyst. Its excellent OER performance is even comparable to the state-of-the-art nonprecious metal electrocatalysts. Thus, this report provides a new strategy for the fabrication and exploration of novel electrocatalysts.

4. EXPERIMENTAL SECTION

4.1. Materials. Cobalt(III) acetylacetonate (Co(acac)3) was purchased from Aladdin, 1-butyl-3-methylimidazolium-bis[(trifluoromethyl)sulfonyl]imide ([BMIM][NTf2]) was bought from Lanzhou Greenchem and ILs from LICP, CAS, China. Nafion solution (5 wt %) was purchased from Sigma-Aldrich. Carbon cloth (CC) was provided by Ce Tech. Co., Ltd. Commercial RuO2 (99.99%) was provided by Shanghai Macklin Biochemical Co., Ltd. Potassium hydroxide was supplied by Sinopharm Chemical Reagent Co., Ltd, and ultrapure (99.999%) nitrogen was bought from Jinan Deyang Gas Co., Ltd. All chemicals were used as received.

4.2. Synthesis of Cobalt-Based Electrocatalsysts. Prior to use, the [BMIM][NTf2] was degassed in vacuum at 120 °C for 20 min. In a typical synthetic process, 50 mg of Co(acac)3 and 1.0 g of [BMIM][NTf2] were mixed in a glass bottle. Then, the glass bottle was placed into the tube furnace and flushed with N2 gas for 20 min. Subsequently, the temperature of the furnace was raised from room temperature to 280 °C with a rate of 2 °C/min and maintained at 280 °C for 5 h. After cooling down to room temperature, the precipitate was washed with ethanol and distilled water for three times and then dried in vacuum. To put an insight into the growth mechanism of the nanosheets, two more samples were prepared through the same process and just maintained at 280 °C for 1 or 2 h. For exploring the influence of the reaction temperature, another four samples were prepared through the same process just at different temperatures: 250, 300, 330, and 350 °C, respectively.

4.3. General Characterization. The powder XRD patterns were measured using a Rigaku D/max-rc X-ray diffractometer with Ni-filtered Cu Kα (λ = 1.5418 Å) radiation. TEM was carried out on a JEM 1400 TEM operating at 120 KV. The XPS analysis was tested on an ESCALAB 250 photoelectron spectrometer.

4.4. Electrochemical Test. The electrochemical measurements were carried out on a CHI600B three-electrode electrochemical workstation (Shanghai Chenhua, China) at room temperature. The saturated calomel electrode (SCE) and carbon rod were used as the reference electrode and the counter electrode, respectively. The electrocatalysts-loaded CC was used as the working electrode. The potentials vs. SCE in this work was converted to an RHE according to the Nernst equation (E_{RHE} = E_{SCE} + 0.059 p[H] + 0.197) for 25 °C.12,42 Before use, CC was cut into rectangular pieces. Then, the CC pieces were cleaned by sonication in acetone, deionized water, and ethanol for 30 min each and then dried in vacuum.31 Electrolyte powder (5 mg) was dispersed in the solution containing 900 μL of distilled water and 100 μL of 5 wt % Nafion solution. Then, the mixture was ultrasonicated for 10 min to form a homogeneous ink. Then, total 60 μL of the ink was dripped onto the CC and dried in vacuum acting as the working electrode (the loading mass is about 1 mg/cm2). The OER activities of all of the synthesized electrocatalysts were evaluated by the LSV in 1 M aqueous KOH solution with a potential range from 1.2 to 1.7 V versus RHE and a scan rate of 5 mV/s. All of the recorded polarization curves were iR corrected. Before LSV measurement, CV was performed at a scan rate of 50 mV/s in 1 M aqueous KOH solution from 1.0 to 1.6 V versus RHE for 20 cycles to reach a stable current density. The durability test was performed with a CV between 1.2 and 1.7 V versus RHE for 1000 continuous cycles. The electrochemically active surface areas (ECSAs) were estimated through CV at the potential between 1.1 and 1.2 V versus RHE with scan rates of 20, 30, 40, 50, 60, 70, and 80 mV/s.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01394.

Atomic force microscopy image of the CoO-280-5; cyclic voltammograms of all studied electrocatalysts; and table of the electrocatalytic activities of many previously reported CoO- and cobalt sulfides-based electrocatalysts for OER under alkaline conditions.

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Notes

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REFERENCES

(1) Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chen, H.; Yang, S. A Strongly Coupled Graphene and FeNi Double Hydroxide Hybrid as an Excellent Electrocatalyst for the Oxygen Evolution Reaction. Angew. Chem. 2014, 126, 7714−7718.
(2) Favaro, M.; Yang, J.; Nappini, S.; Magnano, E.; Toma, F. M.; Crumlin, E. J.; Yano, J.; Scharf, I. D. Understanding the Oxygen Evolution Reaction Mechanism on CoOx using Operando Ambient-Pressure X-ray Photoelectron Spectroscopy. J. Am. Chem. Soc. 2017, 139, 8960−8970.
(3) Lu, Z.; Chen, G.; Li, Y.; Wang, H.; Xie, J.; Liao, L.; Liu, C.; Liu, Y.; Wu, T.; Li, Y.; Luntz, A. C.; Bajdich, M.; Cui, Y. Identifying the Active Surfaces of Electrochemically Tuned LiCoO2 for Oxygen Evolution Reaction. J. Am. Chem. Soc. 2017, 139, 6270−6276.
(4) Zhao, Y.; Zhang, Y.; Ding, Y.; Chen, M. Hexagonal nanoplates of NiO/Co3O4 composite acting as an efficient photocatalytic and electrocatalytic water oxidation catalyst. Dalton Trans. 2015, 44, 15628−15635.
(5) Rosen, J.; Hutchings, G. S.; Jiao, F. Ordered Mesoporous Cobalt Oxide as Highly Efficient Oxygen Evolution Catalyst. J. Am. Chem. Soc. 2013, 135, 4516−4521.
(6) Zheng, X.; Yao, Y.; Qiao, S. Z. Engineering of Carbon-Based Electro catalysts for Emerging Energy Conversion: From Fundamental to Functionality. Adv. Mater. 2015, 27, 5372−5378.
(7) Wang, S.; Yu, D.; Dai, L. Polyelectrolyte Functionalized Carbon Nanotubes as Efficient Metal-free Electro catalysts for Oxygen Reduction. J. Am. Chem. Soc. 2011, 133, 5182−5185.
(8) Barman, B. K.; Nanda, K. K. A Noble and Single Source Precursor for the Synthesis of Metal-Rich Sulphides Embedded in an N-Doped Carbon Framework for Highly Active OER Electro catalysts. Dalton Trans. 2016, 45, 6532−6536.
(9) Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. Synthesis and Activities of Rutile IrO2 and RuO2 Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions. J. Phys. Chem. Lett. 2012, 3, 399−404.
(10) Zhu, Y.-P.; Liu, Y.-P.; Ren, T.-Z.; Yuan, Z.-Y. Self-Supported Cobalt Phosphide Mesoporous Nanorod Arrays: A Flexible and Bidirectional Electro catalyst for Highly Active Electrocatalytic Water Reduction and Oxidation. Adv. Funct. Mater. 2015, 25, 7337−7347.
(11) Chang, J.; Liang, L.; Li, C.; Wang, M.; Ge, J.; Liu, C.; Xing, W. Ultrathin Cobalt Phosphate Nanosheets as Efficient Bifunctional catalysts for a Water Electrolysis Cell and the Origin for Cell Performance Degradation. Green Chem. 2016, 18, 2287−2295.
(12) Jiang, Y.; Li, X.; Wang, T.; Wang, C. Enhanced electrocatalytic oxygen evolution of α-Co(OH)2 nanosheets on carbon nanotube/polyimide films. Nanoscale 2016, 8, 9667−9675.
(13) Shen, M.; Ruan, C.; Chen, Y.; Jiang, C.; Ai, K.; Lu, L. Covalent Entrapment of Cobalt-Iron Sulphides in N-Doped Mesoporous Carbon: Extraordinary Bifunctional Electro catalysts for Oxygen Reduction and Evolution Reactions. ACS Appl. Mater. Interfaces 2015, 7, 1207−1218.
(14) Wu, J.; Ren, Z.; Du, S.; Kong, L.; Liu, B.; Xi, W.; Zhu, J.; Fu, H. A Highly Active Oxygen Evolution Electro catalyst: Ultrathin CoNi Double Hydroxide/CoO Nanosheets Synthesized via Interface-Directed Assembly. Nano Res. 2016, 9, 713−725.
(15) Wang, Y.; Xie, C.; Zhang, Z.; Liu, D.; Chen, R.; Wang, S. In Situ Exfoliated N-Doped, and Edge-Rich Ultrathin Layered Double Hydroxides Nanosheets for Oxygen Evolution Reaction. Adv. Funct. Mater. 2018, 28, 1703363.
(16) Wang, Y.; Yan, D.; El Hankari, S.; Zou, Y.; Wang, S. Recent Progress on Layered Double Hydroxides and Their Derivatives for Electrocatalytic Water Splitting. Adv. Sci. 2018, 5, 1800064.
(17) Zhou, X.; Shen, X.; Xia, Z.; Zang, Z.; Li, J.; Ma, Y.; Qu, Y. Hollow Fluffy Co3O4 Cages as Efficient Electrocatalytic Materials for Supercapacitors and Oxygen Evolution Reaction. ACS Appl. Mater. Interfaces 2015, 7, 20322−20331.
(18) Reddy, N. K.; Winkler, S.; Koch, N.; Pinna, N. Electrochemical Water Oxidation of Ultrathin Cobalt Oxide-Based Catalyst Supported onto Aligned ZnO Nanorods. ACS Appl. Mater. Interfaces 2016, 8, 3226−3232.
(19) Li, X.; Fang, Y.; Wen, L.; Li, F.; Yin, G.; Chen, W.; An, X.; Jin, J.; Ma, J. Co@Co3O4 core-shell particle encapsulated N-doped mesoporous carbon cage hybrids as active and durable oxygen-evolving catalysts. Dalton Trans. 2016, 45, 5575−5582.
(20) Koza, J. A.; He, Z.; Miller, A. S.; Switzer, J. A. Electrodeposition of Crystalline Co3O4-A Catalyst for the Oxygen Evolution Reaction. Chem. Mater. 2012, 24, 3567−3573.
(21) Zhao, Y.; Zhang, Y.; Ding, Y.; Chen, M. Hexagonal nanoplates of NiO/Co3O4 composite acting as an efficient photocatalytic and electrocatalytic water oxidation catalyst. Dalton Trans. 2015, 44, 15628−15635.
(22) Jin, H.; Wang, J.; Su, D.; Wei, Z.; Pang, Z.; Wang, Y. In Situ Cobalt-Cobalt Oxide/N-Doped Carbon Hybrids as Superior Bifunctional Electro catalysts for Hydrogen and Oxygen Evolution. J. Am. Chem. Soc. 2015, 137, 2688−2694.
(23) Dou, S.; Tao, L.; Wang, R.; El Hankari, S.; Chen, R.; Wang, S. Plasma-Assisted Synthesis and Surface Modification of Electrode Materials for Renewable Energy. Adv. Mater. 2018, 30, 1705880.
(24) Chen, D.; Qiao, M.; Lu, Y.-R.; Hao, L.; Liu, D.; Dong, C.-L.; Li, Y.; Wang, S. Preferential Cation Vacancies in Perovskite Hydroxide for the Oxygen Evolution Reaction. Angew. Chem., Int. Ed. 2018, 57, 8691−8696.
(25) Xiao, Z.; Wang, Z.; Huang, Y.-C.; Wei, Z.; Dong, C.-L.; Ma, J.; Shen, S.; Li, Y.; Wang, S. Filling the oxygen vacancies in Co3O4 with phosphorus: an ultra-efficient electrocatalyst for overall water splitting. Energy Environ. Sci. 2017, 10, 2563−2569.
(26) Yan, X.; Tian, L.; Atkins, S.; Liu, Y.; Murowchick, J.; Chen, X. Converting CoMoO4 into CoO/MoOx for Overall Water Splitting by Hydrogenation. ACS Sustainable Chem. Eng. 2016, 4, 3743−3749.
(27) Yuan, W.; Zhao, M.; Yuan, J.; Li, C. M. Ni Foam Supported Three-Dimensional Vertically Aligned and Networked Layered CoO Nanosheet/Graphene Hybrid Array as a High-Performance Oxygen Evolution Electro catalyst. J. Power Sources 2016, 319, 159−167.
(28) Liu, T.; Guo, Y.-F.; Yan, Y.-M.; Wang, F.; Deng, C.; Rooney, D.; Sun, K.-N. CoO Nanoparticles Embedded in Three-Dimensional Nitrogen/Sulfur co-Doped Carbon Nanofiber Networks as a Bifunctional Catalyst for Oxygen Reduction/Evolution Reactions. Carbon 2016, 106, 84−92.
(29) Wang, Y.; Qiao, M.; Li, Y.; Wang, S. Tuning Surface Electric Configuration of NiFe LDHs Nanosheets by Introducing Cation Vacancies (Fe or Ni) as Highly Efficient Electro catalysts for Oxygen Evolution Reaction. Small 2018, 14, 1800136.
(30) Zhang, X.; Liu, Q.; Meng, L.; Wang, H.; Bi, W.; Peng, Y.; Yao, T.; Wei, S.; Xie, Y. In-Plane Coassembly Route to Atomically Thick Inorganic-Organic Hybrid Nanosheets. ACS Nano 2013, 7, 1682−1688.
(31) Bao, J.; Zhang, X.; Fan, B.; Zhang, J.; Zhou, M.; Yang, W.; Hu, X.; Wang, H.; Pan, B.; Xie, Y. Ultrathin Spinel-Structured Nanosheets Rich in Oxygen Deficiencies for Enhanced Electrocatalytic Water Oxidation. Angew. Chem. 2015, 127, 7507−7512.
(32) Wang, Y.; Tao, L.; Xiao, Z.; Chen, R.; Jiang, Z.; Wang, S. 3D Carbon Electro catalysts In Situ Constructed by Defect-Rich Nanosheets and Polyhedrons from NaCl-Sealed Zeolitic Imidazolate Frameworks. Adv. Funct. Mater. 2018, 28, 1705356.
(33) Liu, R.; Wang, Y.; Liu, D.; Zou, Y.; Wang, S. Water-Plasma-Enabled Exfoliation of Ultrathin Layered Double Hydroxide Nanosheets with Multivacancies for Water Oxidation. Adv. Mater. 2017, 29, 1701546.
(34) Gao, M.-R.; Yuan, J.; Antonetti, M. Ionic Liquids and Poly(ionic Liquid)s for Morphosynthesis of Inorganic Materials. Chem.—Eur. J. 2017, 23, 5391−5403.
(35) Li, Z.; Jia, Z.; Luan, Y.; Pu, T. Ionic Liquids for Synthesis of Inorganic Nanomaterials. Cur. Opin. Solid State Mater. Sci. 2008, 12, 1–8.

(36) Li, Z.; Liu, Z.; Zhang, J.; Han, B.; Du, J.; Gao, Y.; Jiang, T. Synthesis of Single-Crystal Gold Nanosheets of Large Size in Ionic Liquids. J. Phys. Chem. B 2005, 109, 14445–14448.

(37) Zhou, Y.; Antonietti, M. Preparation of Highly Ordered Monolithic Super-Microporous Lamellar Silica with a Room-Temperature Ionic Liquid as Template via the Nanocasting Technique. Adv. Mater. 2003, 15, 1452–1455.

(38) Duan, X.; Huang, H.; Xiao, S.; Deng, J.; Zhou, G.; Li, Q.; Wang, T. 3D Hierarchical CuO Mesocrystals from Ionic Liquid Precursors: Towards Better Electrochemical Performance for Li-ion Batteries. J. Mater. Chem. A 2016, 4, 8402–8411.

(39) Jana, M. K.; Rajendra, H. B.; Bhattacharyya, A. J.; Biswas, K. Green ionicothermal synthesis of hierarchical nanostructures of SnS2 and their Li-ion storage properties. CrystEngComm 2014, 16, 3994–4000.

(40) Yao, K.; Zhao, C.; Sun, N.; Li, W.; Zhang, Y.; Wang, H.; Wang, J. Freestanding CuS Nanosheets: ionic-liquid-assisted synthesis and prominent catalytic performance for the decomposition of ammonia percolate. CrystEngComm 2017, 19, 5048–5057.

(41) Zhang, B.; Xue, Y.; Jiang, A.; Xue, Z.; Li, Z.; Hao, J. Ionic Liquid as Reaction Medium for Synthesis of Hierarchically Structured One-Dimensional MoO2 for Efficient Hydrogen Evolution. ACS Appl. Mater. Interfaces 2017, 9, 7217–7223.

(42) Li, K.; Zhang, J.; Wu, R.; Yu, Y.; Zhang, B. Anchoring CoO Domains on CoSe2 Nanobelts as Bifunctional Electrocatalysts for Overall Water Splitting in Neutral Media. Adv. Sci. 2016, 3, 1500426–1500432.

(43) Wang, H.; Wang, X. Growing Nickel Cobaltite Nanowires and Nanosheets on Carbon Cloth with Different Pseudocapacitive Performance. ACS Appl. Mater. Interfaces 2013, 5, 6255–6260.

(44) He, X.; Song, X.; Qiao, W.; Li, Z.; Zhang, X.; Yan, S.; Zhong, W.; Du, Y. Phase- and Size-Dependent Optical and Magnetic Properties of CoO Nanoparticles. J. Phys. Chem. C 2015, 119, 9505–9559.

(45) Nam, K. M.; Shim, J. H.; Han, D.-W.; Kwon, H. S.; Kang, Y.-M.; Li, Y.; Song, H.; Seo, W. S.; Park, J. T. Syntheses and Characterization of Wurtzite CoO, Rocksalt CoO, and Spinel Co3O4 Nanocrystals: Their Interconversion and Tuning of Phase and Morphology. Chem. Mater. 2010, 22, 4446–4454.

(46) Sun, Y.; Hu, X.; Luo, W.; Huang, Y. Ultrathin CoO/Graphene Hybrid Nanosheets: a Highly Stable Anode Material for Lithium-Ion Batteries. J. Phys. Chem. C 2012, 116, 20794–20799.

(47) Lee, J. S.; Wang, X.; Luo, H.; Baker, G. A.; Dai, S. Facile Ionothermal Synthesis of Microporous and Mesoporous Carbons from Task Specific Ionic Liquids. J. Am. Chem. Soc. 2009, 131, 4596–4597.

(48) Dupont, J. On the Solid, Liquid and Solution Structural Organization of Imidazolium Ionic Liquids. Chem. Soc. 2004, 15, 341–350.

(49) Jiang, J.; Yu, S.-H.; Yao, W.-T.; Ge, H.; Zhang, G.-Z. Morphogenesis and Crystalization of Bi2S3 Nanosteelites by an Ionic Liquid-Assisted Templating Route: Synthesis, Formation Mechanism, and Properties. Chem. Mater. 2005, 17, 6094–6100.

(50) Ghosh, M.; Sampathkumaran, E. V.; Rao, C. N. R. Synthesis and Magnetic Properties of CoO Nanoparticles. Chem. Mater. 2005, 17, 2348–2352.

(51) Kundu, S.; Jayachandran, M. Shape-Selective Synthesis of Non-Micellar Cobalt Oxide (CoO) Nanomaterials by Microwave Irradiations. J. Nanopart. Res. 2013, 15, 1543–1555.

(52) Kundu, S.; Mukadam, M. D.; Yusuf, S. M.; Jayachandran, M. Formation of Shape-Selective Magnetic Cobalt Oxide Nanowires: Environmental Application in Catalysis Studies. CrystEngComm 2013, 15, 482–497.

(53) Liu, X.; Dong, C.; Dong, W.; Wang, X.; Yuan, X.; Huang, F. Co Nanoparticles Embedded in a 3D CoO Matrix for Electrocatalytic Hydrogen Evolution. RSC Adv. 2016, 6, 38515–38520.