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Co$_3$Mo$_3$N—An efficient multifunctional electrocatalyst

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Graphical abstract

Public summary
- Porous Co$_3$Mo$_3$N can act as a multifunctional electrocatalyst for OER, ORR, and HER
- Co$_3$Mo$_3$N performs better than precious metal catalysts
- Cobalt oxide-rich activation surface layer is shown to aid OER activity
- Better ORR and HER performance of Co$_3$Mo$_3$N is due to Co and Mo d-states
Efficient catalysts are required for both oxidative and reductive reactions of hydrogen and oxygen in sustainable energy conversion devices. However, current precious metal-based electrocatalysts do not perform well across the full range of reactions and reported multifunctional catalysts are all complex hybrids. Here, we show that single-phase porous Co$_3$Mo$_3$N prepared via a facile method is an efficient and reliable electrocatalyst for three essential energy conversion reactions; oxygen evolution reaction (OER), oxygen reduction reaction (ORR), and hydrogen evolution reaction (HER) in alkaline solutions. Co$_3$Mo$_3$N presents outstanding OER, ORR, and HER activity with high durability, comparable with the commercial catalysts RuO$_2$ for OER and Pt/C for ORR and HER. In practical demonstrations, Co$_3$Mo$_3$N gives high specific capacity (850 mA h g$_{zn}$$^{-1}$ at 10 mA cm$^{-2}$) as the cathode in a zinc-air battery, and a low potential (1.63 V at 10 mA cm$^{-2}$) used in a water-splitting electrolyzer. Availability of Co and Mo d-states appear to result in high OER and HER performance, while the OER properties result from a cobalt oxide-rich activation surface layer. Our findings will inspire further development of bimetallic nitrides as cost-effective and versatile multifunctional catalysts that will enable scalable usage of electrochemical energy devices.

**KEYWORDS:** ternary nitrides; multifunctional electrocatalysts; rechargeable Zn-air batteries; water splitting

**INTRODUCTION**

Electrode reactions are involved in new energy technologies for efficient energy conversion, storage, and management, such as fuel cells, metal-air batteries, and water-splitting electrolyzers. However, sluggish kinetics with high overpotential tends to limit these technologies. Typically, these challenges escalate further when multi-electron transfer processes are associated with the electrocatalytic reactions. Noble metal-based catalysts (such as Pt, Ru, and Ir) are currently considered as the state-of-the-art catalysts. Pt is used in oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Ru/Ir-based materials on the other hand are useful for oxygen evolution reaction (OER). However, high cost, scarcity, and unsatisfactory durability of these noble metal-based materials limit their viability and scalable use for renewable energy technologies.

Cheap and multifunctional catalysts that can accelerate all three ORR, HER, and OER would be desirable. Examples include rechargeable metal-air batteries that combine ORR and OER, and water electrolyzers that combine HER and OER. This also has significant implications for scalability since single-phase multifunctional catalysts can reduce materials flow concerns and simplify the manufacture of the system. Thus far, the few reports on multifunctional catalysts involve complex hybrids (e.g., graphitic-shell Fe$_x$Co$_{1-x}$Ni$_2$ alloys, GO-Cu-MOF, Mo-N/C@MoS$_2$, Co$_2$P/CoN/C, and defect graphene). Interstitial metal nitrides are an interesting class of materials with their unique mechanical, magnetic, electrical, and catalytic active properties.

In a number of cases, the catalytic performance of nitrides is analogous with that of noble metals, due to their very similar Fermi energy and electronic structure to that of group VIII noble metals. However, until now no single-phase nitride has demonstrated multifunctional electrocatalysis. As Co$_3$Mo$_3$N, has already found catalytic use in lithium-O$_2$ batteries, CO$_2$ reforming, hydrazine synthesis, hydrosulfurization, ammonia synthesis, and decomposition. We have investigated its use as a multifunctional electrocatalyst. Here, a porous Co$_3$Mo$_3$N catalyst is synthesized via a simple and generally applicable strategy and demonstrates high activity for OER, HER, and OER.

**RESULTS AND DISCUSSION**

Co$_3$Mo$_3$N is prepared in a straightforward manner through ammonolysis of CoMoO$_4$ at 800°C (Figures S1 and S2A). As shown in the Rietveld refinement results, the as-prepared Co$_3$Mo$_3$N forms an intermediate nitride with an η-carbide-like cubic structure (in space group: Fd-3m, a = 11.0132(1) Å) (Figure 1A, Table S1). In fact there are two interpenetrating networks of corner-shared NMo$_2$ octahedra and Co[Mo$_x$Co$_{1-x}$]$_2$[Mo$_x$Co$_{1-x}$]$_2$ pseudo-icosahedra in the Co$_3$Mo$_3$N structure (Figure S3). Co$_3$Mo$_3$N comprises one-dimensional porous rods with diameters in the range 100–300 nm (Figures 1, S2B, and S4). Also, the results of high-resolution transmission electron microscopy (HR-TEM) and elemental energy loss spectroscopy (EELS) mapping suggest that there is no distinct phase or shell on the surface (Figures 1D and 1E). The polycrystalline nature of Co$_3$Mo$_3$N is proven using selected area electron diffraction pattern with diffraction spots as shown in Figure S5, and the percentages of elements in Co$_3$Mo$_3$N are determined by an inductively coupled plasma optical emission spectrometer and an elemental analyzer (Tables S2 and S3).

The electrocatalytic performance for three energy conversion processes (ORR, HER, and OER) of Co$_3$Mo$_3$N was investigated under standard conditions with the alkaline electrolyte (Figure 2). Figure 2A shows the ORR polarization curves of Co$_3$Mo$_3$N, measured in 0.1 M KOH. Co$_3$Mo$_3$N$_2$ (see the supplemental information and Figure S6 for more details) and the commercial 20 wt.% Pt/C (the industry standard ORR catalyst) are tested using same conditions for comparison. The half-wave potential ($E_{1/2}$) of Co$_3$Mo$_3$N (0.75 V) is lower than that of commercial Pt (0.80 V), but more positive than those of the binary nitrides CoN (0.65 V) and MoN$_2$ (0.66 V). In the range of 0.2–0.8 V, almost ideal four-electron reduction takes place (calculated number of transferred electrons $n = 3.8$) and the peroxide yield observed is low (6%–10%) (Figure S7). Koutecky-Levich analysis confirms this mechanism, as seen in the deduced $n = 3.9$ (Figure S8). The reaction dynamics can be
studied using the Tafel slope. As seen in Figure 2B, CoMo3N displays a smaller Tafel slope (57 mV dec⁻¹) when compared with than 20 wt.% Pt/C (81 mV dec⁻¹), demonstrating better ORR catalytic kinetics.

The HER activity of the same materials is also evaluated in the alkaline electrolyte (1.0 M KOH), and all polarization curves are corrected for internal Ohmic losses (iR-corrections). From the linear sweep voltamograms (LSVs) (Figure 2C), it is seen that an overpotential to achieve a catalytic current density of 10 mA cm⁻² (η₁₀) is −0.10 V for CoMo3N compared with −0.01 V for Pt/C under identical conditions. However, and importantly, the current densities of CoMo3N and Pt/C reach the same value at −0.30 V, demonstrating excellent properties of the CoMo3N catalyst under large currents. CoMo3N also shows much higher activity than Co4N (η₁₀ = −0.16 V) and Mo3N2 (η₁₀ = −0.21 V). The Tafel slope of CoMo3N (49 mV dec⁻¹) is lower than those of Co4N (111 mV dec⁻¹) and Mo3N2 (81 mV dec⁻¹) as shown in Figure 2D. This is evidence of improved kinetics and better HER activity through the use of CoMo3N.

The OER activity of CoMo3N was also evaluated using linear sweep voltammetry. The results for Co4N, Mo3N2, CoMoO4, and RuO2 (one of the best known active OER catalysts) are used as a benchmark for comparison (Figures 2E and S9). The LSV curves with iR-correction indicate that the OER activity of CoMo3N is better than those of Co4N, Mo3N2, and CoMoO4. In fact, the performance even exceeds that of RuO2 significantly. To generate a catalytic current density of 10 mA cm⁻², η₁₀ values required for CoMo3N, Co4N, Mo3N2, CoMoO4, and RuO2 are 0.29, 0.33, 0.43, 0.41, and 0.35 V, respectively (Figure 2E inset). And their respective Tafel slopes are 60, 75, 93, 102, and 86 mV dec⁻¹ (Figures 2F and S9). Hence, CoMo3N outperforms RuO2 as well as the binary nitrides (Co4N and Mo3N2) and oxide (CoMoO4) for OER. Above all, CoMo3N exhibits small overpotentials and high currents for all three electrocatalytic reactions and is more stable compared with the commercial precious metal-based catalysts (Figure S10).

The good ORR and HER performances can be explained by the electronic structures. Binary transition metal nitrides (such as iron, cobalt, and nickel nitrides) have previously been studied as non-precious-metal catalysts. The electrocatalytic activity of cobalt hydroxide toward HER and OER was investigated theoretically, showing that the hybridization of 2p states of O atom and 3d states of Co atoms plays crucial roles in charge transfer and also increases the metallic property of the Co hydroxide layer. Moreover, density functional theory (DFT) calculations were applied to explore the active sites of CoMo3N toward hydrogen adsorption on top of the (111) surfaces. The results show that molecular hydrogen would be adsorbed mostly on the MoN3 framework, binding through the Mo atoms, and dissociative hydrogen adsorptions would occur on exposed cobalt atoms of Co8 clusters or occur on Mo3 clusters that are close to N vacancies. DFT calculations also have indicated that heavier transition metals, such as molybdenum or tungsten, modify the electronic structure of nitrides favorably. This leads to near-optimal adsorption of intermediates in electrochemical reactions and hence improved catalytic activity. CoMo3N, with an η-carbide structure, is a metallic nitride with enhanced d-states density near the Fermi level, as shown in Figure S11. This is in contrast to Co4N, whose electronic states are more p-like around the Fermi level (contributed from nitrogen). After adding Mo atoms to the Co4N structure, there is a charge transfer from Mo to Co species (Figures S11A and S11C). In comparison with Mo3N2, a lower Mo valence in CoMo3N is due to the lower occupation of Mo in the d-band. This in fact is expected to give an electron-donating ability to the CoMo3N crystal, and therefore enhancing kinetics of ORR and HER. Hence its unique electronic structure makes CoMo3N a promising candidate for ORR and HER (as also evidenced by experiment). In addition, it is noted that the d-band center is a good gauge in designing active oxygen and hydrogen reaction catalysts. This measure involves the determination of the first moment of the projected d-band density of states relative to the Fermi level. By considering this parameter, CoMo3N (with a d-band center of −1.61 eV) should be a better OER catalyst than Ru (whose d-band center is around −1.42 eV). This too is consistent with our experimental results.

It is surprising to have good OER activity as well as desirable ORR and HER performances in one material. To help explain the high activities of CoMo3N, the catalysts are investigated using XRD and X-ray photoelectron spectroscopy (XPS) analysis before and after cycling. The XRD pattern of CoMo3N (Figure S12) shows the additional peaks compared with the initial sample, which proves that the surface oxidation occurs during the OER process without morphology changes (Figures S12 and S13). Also, there is no obvious
change for both Co 2p and Mo 3d after ORR and HER processes (Figures S14 and S15), but change is observed after OER. Hence, we perform analysis using TEM. Deconvolution of Co 2p spectra can be ascribed to Co-N species and Co2+ (Co-O) with a pair of satellite peaks (Figure 3).28,41 Co-N peaks disappear after OER testing, which indicates oxidation of Co atoms occurs on the Co3Mo3N surface. Mo 3d region XPS spectra can be resolved into three types of peaks associated to Mo-N, Mo4+, and Mo6+, respectively.42 All types of Mo 3d (including Mo-N) peaks remain, although with weaker intensity (Figure S15), suggesting that Mo atoms coordinated by N are present in the subsurface. Detailed analysis of the surface layer of Co3Mo3N after OER cycles is further confirmed using TEM. The as-prepared sample shows no additional surface layer but, after the OER, an amorphous oxide/hydroxide layer (~3–6 nm) appears on the surface. The HR-TEM image, high-angle annular dark field-scanning TEM (HAADF-STEM) image and the corresponding EELS elemental mappings show that the topmost part of the surface oxide layer is enriched in Co (Figures 3C–3E). According to this, an amorphous cobalt oxide-rich activation surface layer is generated on Co3Mo3N during OER process, which offers the active sites for OER.33,45 Specifically, the Mo atoms shift toward the inner bulk forming short bonding with N atoms to compensate the influence of dangling bonds in surface. The surface Co atoms get more freedom to be oxidized, which are also expected to offer flexible valence during OER runs, and hence is likely the key source of catalytic activity (Figure 3A). The electronic states of Co in the oxide-rich surface can be tuned by the local oxide/nitride composition which shifts the position and width of the d-electron band. The deprotonation of OH for OER over the Ni/Co-based materials is normally considered the potential determining step. The cobalt oxide-rich surface can offer favorable energetics for the deprotonation of OH.47 Meanwhile, the surface Mo atoms can transfer charges and facilitate the reaction continuity as an electron pump.47 These, in fact, are expected to offer the appropriate energetics and electronic structures for advanced catalytic efficiency.

Inspired by the remarkable half-cell performance of Co3Mo3Na as a multifunctional catalyst for ORR, HER, and OER simultaneously, a circuit consisting of a rechargeable zinc-air battery and a water electrolyzer has been built (Video S1). This was done to demonstrate the utility of the multifunctional Co3Mo3N electrocatalyst in practical applications. The zinc-air battery with a Co3Mo3N cathode was fabricated as shown in Figure S16A. As a rechargeable battery, the charging process of the zinc-air battery is supported by OER on the cathode side, while ORR happens in the discharging process. Thus, efficient catalysts for both ORR and OER simultaneously are vital in this case. Conventionally, the fabrication of the electrode uses a mixture of ORR and OER catalysts. Here, we offer a simpler manufacturing approach, as the as-synthesized single-phase Co3Mo3N is the only catalyst for anode and cathode fabrication. For comparison, a control zinc-air battery was fabricated with a precious metal-based air-cathode using the commercial Pt/C and RuO2 composite. As illustrated in Figure 4A, the Co3Mo3N-driven zinc-air battery shows a smaller voltage gap in the charge and discharge polarization curves compared with the commercial Pt/C and RuO2 composite catalyst demonstrating excellent cyclability. Galvanostatic discharge curves of a Co3Mo3N-driven zinc-air battery at various current densities from 2 to 50 mA cm−2 are illustrated to explore the discharge rate performance. As shown in Figure S16B, the discharge potential recovers when the current density goes back to 2 mA cm−2, suggesting good rate capability. Specific capacity can
be obtained according to the consumption of zinc. At 10 mA cm\(^{-2}\), the Co\(_3\)Mo\(_3\)N-driven zinc-air battery gives a specific capacity of 850 mA h g\(\text{Zn}^{-1}\), which outperforms the Pt/C and RuO\(_2\) battery (755 mA h g\(\text{Zn}^{-1}\)) (Figure S16C). For stability, the charge-discharge voltage gap of the commercial Pt/C and RuO\(_2\) composite system increases greatly after 100 h; on the other hand, the voltage gap for Co\(_3\)Mo\(_3\)N remains stable at a current density of 2 mA cm\(^{-2}\) (Figure 4B). Compared with the voltage gap (0.84 V) after 50 h, the discharge-charge potential gap of Co\(_3\)Mo\(_3\)N-based battery only increases by 0.05 and 0.12 V after 150 and 260 h, respectively. To examine the air-cathode’s cycling stability at a higher current density, we tested the two batteries at a current density of 10 mA cm\(^{-2}\) (Figure S16D). Co\(_3\)Mo\(_3\)N-based battery still shows a slightly increased potential gap demonstrating the ultralong cycling ability, while a commercial Pt/C and RuO\(_2\) based battery displays a significant variation in both charge and discharge voltages. This result shows the stability of Co\(_3\)Mo\(_3\)N when employed in operation as a cathode of zinc-air battery.

The water-splitting performance of Co\(_3\)Mo\(_3\)N catalyst has been further discussed in a two-electrode setup fabricated with both a Co\(_3\)Mo\(_3\)N-based anode and cathode. As illustrated in the LSV curves (Figure 4C), a current density of 10 mA cm\(^{-2}\) can be obtained at around 1.63 V for Co\(_3\)Mo\(_3\)N-based electrodes. Although a slightly lower potential (1.61 V) is required to achieve 10 mA cm\(^{-2}\) in the commercial RuO\(_2\) and Pt/C-based electrolyzer, the observed current density reaches the same value as the Co\(_3\)Mo\(_3\)N at 1.68 V. For stability, Co\(_3\)Mo\(_3\)N when operated at an applied potential of 1.63 V to reach 10 mA cm\(^{-2}\), shows only a slight degradation over a 24 h testing period (Figure 4D). The excellent results for practical devices further demonstrate the high promise of the reported single-phase ternary nitride electrocatalyst. It offers a way toward cost-effective, stable, and high-performance electrocatalytic materials.

Conclusions

In summary, single-phase porous Co\(_3\)Mo\(_3\)N is found to be an excellent multifunctional electrocatalyst for ORR, HER, and OER. Co\(_3\)Mo\(_3\)N shows better ORR and HER performance than the corresponding binary nitride phases and Pt/C due to the presence of both 3d and 4d contributions to the band structure. A cobalt oxide-rich surface layer offers flexible valence, modifying the band energy for good OER activity, which shows more advanced performance than most of the reported catalysts and the RuO\(_2\) benchmark. We demonstrate the multifunctional nature of Co\(_3\)Mo\(_3\)N in a practical combination of a rechargeable zinc-air battery and water electrolyzer where stability and performance indicators surpass the state-of-the-art precious metal-based catalysts. It will reveal a new direction for future design of multifunctional catalysts using bimetallic nitrides as cost-effective, stable, and versatile materials that will offer prospects for scalable usage of electrochemical energy devices.
REFERENCES

1. Yang, M., Guarecuco, R., and DiSalvo, F.J. (2013). Mesoporous chromium nitride as a high performance catalyst support for methanol electrooxidation. Chem. Mater. 25, 1783–1787.

2. Strasser, P., Koh, S., Aminyev, T., et al. (2010). Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. Nat. Chem. 2, 454–460.

3. Xiao, J., Mei, D., Li, X., et al. (2011). Hierarchical porous graphene as a lithium-air battery electrode. Nano Lett. 11, 5071–5078.

4. He, P., Wang, Y., and Zhou, H. (2011). Titanium nitride catalyst cathode in a Li-air fuel cell with an acidic aqueous solution. Chem. Commun. 47, 10701–10703.

5. Park, S., Shao, Y., Liu, J., et al. (2012). Oxygen electrocatalysts for water electrolyzers and reversible fuel cells: status and perspective. Energ. Environ. Sci. 5, 9331–9344.

6. Zou, X., and Zhang, Y. (2015). Noble metal-free hydrogen evolution catalysts for water splitting. Chem. Soc. Rev. 44, 5148–5180.

7. Zhu, Y.P., Guo, C., Zheng, Y., et al. (2017). Surface and interface engineering of noble-metal-free electrocatalysts for efficient energy conversion processes. Acc. Chem. Res. 50, 915–923.

8. Li, M., Zhao, Z., and Chen, T., et al. (2016). Ultrafine jagged platinum nanowires enable ultra-high mass activity for the oxygen reduction reaction. Science 354, 1414–1419.

9. Chen, A., and Holt, H.P. (2010). Platinum-based nanostructured materials: synthesis, properties, and applications. Chem. Rev. 110, 3767–3804.

10. Retuerto, M., Pascual, L., Calle-Vallejo, F., et al. (2019). Na-doped ruthenium perovskite electrocatalysts with improved oxygen evolution activity and durability in acidic media. Nat. Commun. 10, 2041.

11. Escudero-Escibano, M., Mallard, P., Hansen, M.H., et al. (2016). Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction. Science 352, 73–76.

12. Tian, X., Luo, J., Nan, H., et al. (2016). Transition metal nitride coated with atomic layers of Pt as a low-cost, highly stable electrocatalyst for the oxygen reduction reaction. J. Am. Chem. Soc. 138, 1575–1583.

13. Kang, P., Zhang, S., Meyer, T.J., et al. (2014). Rapid selective electrocatalytic reduction of carbon dioxide to formate by an iridium pincer catalyst immobilized on carbon nanotube electrodes. Angew. Chem. Int. Ed. 53, 8709–8713.

14. Guo, X., Liu, P., Han, J., et al. (2015). 3D nanoporous nitrogen-doped graphene with encapsulated RuO2 nanoparticles for Li-O2 batteries. Adv. Mater. 27, 6137–6143.

15. Khani, H., Grundish, N.S., Wipf, D.O., et al. (2019). Graphitic-shell encapsulation of metal electrocatalysts for oxygen evolution, oxygen reduction, and hydrogen evolution in alkaline solution. Adv. Energy. Mater. 10, 1903215.

16. Jahan, M., Liu, Z., and Loh, K.P. (2013). A graphene oxide and copper-centered metal alloy electrocatalysts by means of the lanthanide contraction. Science 340, 1857–1862.

17. Hunter, S.M., McKay, D., Smith, R.I., et al. (2010). Topotactic nitrogen transfer: structural transformation in cobalt molybdenum nitrides. Chem. Mater. 22, 2898–2907.

18. Chen, P., Xu, K., Fang, Z., et al. (2015). Metallic Co3N porous nanowire arrays activated by surface oxidation as electrocatalysts for the oxygen evolution reaction. Angew. Chem. Int. Ed. 54, 14710–14714.

19. Pillai, S.B., Bariya, B.A., Upadhyay, D., et al. (2020). Catalytic activity and underlying atomic rearrangement in monolayer COOH towards HER and OER. Int. J. Hydrogen Energy. 45, 23900–23907.

20. Racski, S.A., Zhang, B., Anbalgam, K., et al. (2018). Synthesis and application of nanostructured metal nitrides and carbides: a review. Prog. Solid State Chem. 50, 1–15.

21. Ham, D.J., and Lee, J.S. (2009). Transition metal carbides and nitrides as electrocatalysts for low temperature fuel cells. Energies 2, 873–899.

22. Li, J. (2016). Porous Co3M4N nanorods as an effective electrocatalyst for Li-O2 battery. Int. J. Electrochem. Sci. 11, 498–505.

23. Zhang, K.L.Z., Dong, S., and Cui, G. (2013). In fabrication and application of metallic nitrides as cathode electrocatalysts for rechargeable Li-O2 batteries. Adv. Optoelectron. Energy Environ.

24. Zha, Z., Cai, S., Wang, D., et al. (2013). Review on air cathode in Li-air batteries. J. Technol. Innov. Renew. Energ. 2, 293–305.

25. Fu, X., Xu, H., Yin, W., et al. (2017). Bimetallic molybdenum nitride Co3Mn: a new promising catalyst for CO2 reforming of methanol. Catal. Sci. Technol. 7, 1671–1678.

26. Zeinalipouryazdi, C.D., and Catlow, C.R.A. (2017). A computational study of the heterogeneous synthesis of hydrazine on Co3M4N. Catal. Lett. 147, 1820–1826.

27. Hada, K., Tanabe, J., Omori, S., et al. (2002). Characterization of cobalt molybdenum nitrides as cathode electrocatalysts for rechargeable Li-O2 batteries. Adv. Funct. Mater. 12, 1496–1506.

28. Jacobsen, C.J., Dahl, S., Clausen, B.S., et al. (2001). Catalyst design by intercalation in the periodic table: bimetallic ammonia synthesis catalysts. J. Am. Chem. Soc. 123, 8404–8405.

29. Amar, I.A.A., Lan, R., Petit, C.T., et al. (2015). Electrochemical synthesis of ammonia based on Co3M4N catalyst and LiAlO2-(Li,Na,K)2CO3 composite electrolyte. Electrochemistry 6, 286–294.

30. Sun, T., Wu, Q., Che, R., et al. (2015). Alloyed Co-Mn nitride as high-performance electrocatalyst for oxygen reduction in acidic medium. ACS Catal. 5, 1837–1862.

31. Hunter, S.M., McKay, D., Smith, R.I., et al. (2010). Topotactic nitrogen transfer: structural transformation in cobalt molybdenum nitrides. Chem. Mater. 22, 2898–2907.

32. Chen, P., Xu, K., Fang, Z., et al. (2015). Metallic Co3N porous nanowire arrays activated by surface oxidation as electrocatalysts for the oxygen evolution reaction. Angew. Chem. Int. Ed. 54, 14710–14714.

33. Feng, L., Liu, H., Li, W., et al. (2016). A new promising catalyst for CO2 reforming of methanol. Catal. Sci. Technol. 7, 1671–1678.

34. Pillai, S.B., Bariya, B.A., Upadhyay, D., et al. (2020). Catalytic activity and underlying atomic rearrangement in monolayer COOH towards HER and OER. Int. J. Hydrogen Energy. 45, 23900–23907.

35. Zeinalipouryazdi, C.D., Hargreaves, J.S.J., and Catlow, C.R.A. (2016). DFT-D3 study of molecular N2 and H2 activation on Co3M4N surfaces. J. Phys. Chem. C 120, 21390–21398.

36. Zeinalipouryazdi, C.D., Hargreaves, J.S.J., and Catlow, C.R.A. (2016). Alkaline Electrolyzer for CO2 Reduction with a Pulse Cycling Interval of 30 Min per Cycle. Int. J. Hydrogen Energy. 42, 29071–29078.

37. Chen, Z., Song, Y., Cai, J., et al. (2018). Tailoring the d band centers enables Co3M4N nanoarrays to be highly active for hydrogen evolution catalysis. Angew. Chem. Int. Ed. 57, 5076–5080.

38. Zhang, B., Zheng, X., Voznyy, O., et al. (2016). Homogeneously dispersed multimetal oxygen-evolving catalysts. Science 352, 333–337.

39. Hammer, B., and Norskoy, J.K. (1995). Electronic factors determining the reactivity of metal surfaces. Surf. Sci. 343, 211–220.

Figure 4. Zinc-air batteries and water-splitting electrolysers using Co3M4N or combined Pt/C and RuO2 catalysts (A) Charge and discharge polarization curves of the zinc-air batteries. (B) Long-term cycling curves at a constant current density of 2 mA cm−2 with a pulse cycling interval of 30 min per cycle. (C) Polarization curves of an alkaline electrolyzer for the overall water-splitting reaction. (D) Potentiostatic electrolysis for water-splitting reaction at a constant voltage of 1.63 V.
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AUTHOR CONTRIBUTIONS

M.Y., F.J.D., and J.P.A. conceived and coordinated the research. Y.Y. synthesized and characterized the materials. S.A. performed electronic structure calculations. Y.Y., T.T., J.W., H.G., and J.C. carried out and analyzed the electrochemical measurements and co-wrote the paper with M.Y., F.J.D., and J.P.A. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing financial interests.

SUPPLEMENTAL INFORMATION

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