

Ni(OH)₂ Nanoparticles Embedded in Conductive Microrod Array: An Efficient and Durable Electrocatalyst for Alkaline Oxygen Evolution Reaction

Xiaoxi Guo, Rong-Mei Kong, Xiaoping Zhang, Huitong Du, and Fengli Qu*®

College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong China

Supporting Information

ABSTRACT: It is extremely important to develop earth-abundant and stable oxygen evolution reaction (OER) electrocatalysts with excellent performance in alkaline media. In this work, we describe the in situ electrochemical conversion of microrod array of Ni(tetracyano-quinodimethane)₂, Ni(TCNQ)₂, into Ni(OH)₂ nanoparticles embedded in a conductive TCNQ microrod array via anode oxidation. Such Ni(OH)₂-TCNQ microarray shows OER activity needing overpotentials of 322 and 354 mV to attain current densities of 50 and 100 mA cm⁻² in 1.0 M KOH, respectively. It is also extremely durable with its electrocatalytic performance being kept for at least 20 h. This work points out a stimulating approach to explore the utilization of TCNQ array as a conductive matrix for electrochemical applications.



KEYWORDS: TCNQ array, Ni(OH)₂ nanoparticles, embedding, electrocatalysis, oxygen evolution reaction

G rowing environmental concerns and the increasing energy crisis have boosted the search for clean and high-efficient energy carrier alternatives to fossil fuels.^{1,2} Hydrogen is considered as an appealing candidate with high energy density and CO₂-free features.^{3–7} Alkaline water electrolysis offers a promising pathway to produce pure hydrogen extensively, but the sluggish kinetics of the anodic oxygen evolution reaction (OER) hampers its widespread application, and thus, high-efficiency OER electrocatalysts must be used to make the entire water-splitting process less energy-intensive.^{8–15} Noble metal oxides, RuO₂ and IrO₂, possess the highest catalytic activity,^{16–19} but the high cost and scarcity of such catalysts limit their widespread applications. It is therefore of significant importance to design and develop low-cost OER catalysts for efficient water oxidation electrocatalysis in alkaline media.

Among transition-metal oxides and hydroxides, NiO and Ni $(OH)_2$ show promising OER activities but suffer from poor electric conductivity.^{20–26} Incorporating nanocatalysts into suitable conductive hosts not only accelerates charge transfer and transport but also effectively avoids nanoparticles aggregation during electrochemical operation, thereby enhancing the catalytic activity and stability. Although metal–carbon hybrid catalysts can be directly derived from metal–organic frameworks where nanocatalysts are well embedded in conductive carbon matrix,^{27,28} their preparation needs high-temperature thermal annealing and is not energy-efficient. On the other hand, direct growth of array catalyst on a conductive substrate increases the electrode stability, lowers the series resistance, exposes more active sites, and facilitates the diffusion of electrolyte and gas.^{29,30} Thus, it is highly desired to construct

nanoscale NiO or Ni $(OH)_2$ encapsulating conductive array via a thermal annealing free preparative strategy, which, however, still remains a huge challenge.

Tetracyanoquinodimethane, referred to as TCNQ, is a waterinsoluble organic conductor^{31,32} and an attractive material for catalyst hybridization, but its use as a conductive matrix for nanocatalysts encapsulation still remains challenging. In this Letter, we demonstrate an easy in situ electrochemical encapsulation of Ni(OH)₂ nanoparticles in TCNQ microrod array on copper foam (Ni(OH)2-TCNQ/CF) at room temperature. During anodization process in the presence of OH⁻, TCNQ⁻ in Ni(TCNQ)₂ microarray was oxidized into a water-insoluble TCNQ microarray, and Ni²⁺ in Ni(TCNQ)₂ was in situ transformed into Ni(OH)₂ nanoparticles effectively entrapped in TCNQ matrix. Figure 1a shows a schematic diagram to illustrate the whole fabrication process, and preparation details are given in Supporting Information. As a 3D electrode, such Ni(OH)2-TCNQ/CF shows superior electrocatalytic property with low overpotentials of only 322 and 354 mV to afford geometrical catalytic current densities of 50 and 100 mA cm⁻² in 1.0 M KOH, respectively. In addition, it also demonstrates strongly long-term electrochemical stability with its performance being kept for at least 20 h, achieving high turnover frequency (TOF) up to $0.24/0.67 \text{ s}^{-1}$ at overpotential of 400/500 mV.

Received: October 7, 2017 Revised: December 9, 2017 Published: December 15, 2017



Figure 1. (a) Schematic diagram to expound the fabrication process for $Ni(OH)_2$ -TCNQ/CF. (b) XRD patterns for $Ni(TCNQ)_2$ and $Ni(OH)_2$ -TCNQ. (c) FTIR spectra for $Ni(TCNQ)_2$ and $Ni(OH)_2$ -TCNQ. SEM images for (d) $Ni(TCNQ)_2/CF$ and (e) $Ni(OH)_2$ -TCNQ/CF. (f) HAADF-STEM image of $Ni(OH)_2$ -TCNQ. (g) TEM and HRTEM (inset) images of $Ni(OH)_2$ -TCNQ.

Figure 1b displays the X-ray diffraction (XRD) patterns for Ni(TCNQ)₂ and Ni(OH)₂-TCNQ scratched down from CF. The peaks of Ni(TCNQ)₂ are consistent with a previous report,³³ indicating the Ni(TCNQ)₂ is successful synthesized via cation exchange used as-made CuTCNQ nanorod array precursor (CuTCNQ/CF).³⁴ After anodization treatment, $Ni(OH)_2$ -TCNQ shows the diffraction peaks at 19.5° (001), 33.4° (100), 38.4° (101), and 39.1° (002) belonging to Ni(OH)₂ planes (JCPDS No. 14-0117) and other peaks are attributed to pure TCNQ³⁵ implying the successful conversion of Ni(TCNQ)₂ to Ni(OH)₂-TCNQ. Figure 1c shows the Fourier transform infrared (FTIR) spectroscopies of Ni-(TCNQ)₂ and Ni(OH)₂-TCNQ. Vibrational modes at 2057, 2137, and 2198 cm⁻¹ accord to $v(C \equiv N)$ stretching of the TCNQ, π (C=C) wing stretching at 1506 cm⁻¹ and δ (C-H) bending vibrations at 823 cm^{-1.36} Those absorption peaks are lower in energy than that of the TCNQ molecule at 2222 cm^{-1} , revealing that the product contains pristine TCNQ.³⁷ Among these vibrational modes, the shift of the 823 cm⁻¹ peak in Ni(TCNQ)₂ to 863 cm⁻¹ in pure TCNQ is quite crucial.³⁵ These results demonstrate that the TCNQ⁻ is changed into TCNQ after anodization treatment. Figure S1 illustrates the Raman spectra of Ni(TCNQ)₂ and Ni(OH)₂-TCNQ. Clearly, four intense Raman vibrations at 1206, 1388, 1607, and 2216 cm⁻¹ are obtained from TCNQ⁻, which show some differences after anodization treatment. In particular, the wavelength of the 1388 cm⁻¹ C–CN stretch in TCNQ⁻ would shift to 1454 cm⁻¹ when TCNQ is formed. The C \equiv N stretching band (2216 cm⁻¹) in TCNQ⁻ should shift to a higher frequency of 2225 cm⁻¹ after anode oxidation.³⁸ Those shifts confirm the presence of TCNQ in the generated material. Figure S2 displays the scanning electron microscopy (SEM) image of CuTCNQ/CF. Figure 1d shows the SEM image of Ni(TCNQ)₂/CF, revealing the surface of Cu foam is completely covered by a $Ni(TCNQ)_2$ microrod array with a diameter of $1-2 \mu m$. Impressively, $Ni(OH)_2$ -TCNQ/CF still retains an array feature after

anodization treatment (Figure 1e). Figure 1f displays the high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of Ni(OH)₂-TCNQ, showing its detailed structure. Energy-dispersive X-ray (EDX) elemental mapping images (Figure S3) confirm the presence of Ni, C, N, O elements within Ni(OH)₂-TCNQ/CF. Figure 1g displays the transmission electron microscopy (TEM) image of Ni(OH)2-TCNQ, indicating that abundant Ni(OH)2 nanoparticles with a size of ca. 6.5 nm are uniformly embedded in TCNQ. In addition, the TEM images of Ni(TCNQ)₂ anodized for 250, 500, 750, 1000 cyclic voltammetry (CV) cycles are displayed in Figure S4 and the sizes of $Ni(OH)_2$ are about 4.9, 6.5, 6.7, 6.4 nm, respectively. Before 500 CV cycles anodization treatment, the size of Ni(OH)₂ gradually increases and then maintains at ca. 6.5 nm after 500 CV cycles anodization treatment. The high-resolution TEM (HRTEM) image confirms the formation of $Ni(OH)_2$ with (101) plane, which corresponds to the lattice fringe width of 0.237 nm. Taken together, all these characterizations imply the successful synthesis of $Ni(OH)_2$ -TCNQ and the formation of $Ni(OH)_2$ nanoparticles embedded in the TCNQ microrod array.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the covalent state of elements. The spectra of Ni(TCNQ)₂ and Ni(OH)₂-TCNQ show binding energies (BEs) corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ positioned at 855.6 and 873.3 eV, respectively, which confirm the presence of Ni²⁺ (Figure 2a).³⁹ As shown in Figure 2b, the peak exhibits no obvious shift after anode oxidation in the C 1s region. However, the small peaks display many differences. The C 1s spectrum of the sample Ni(OH)₂-TCNQ locates at 284.8, 286.8, and 288.7 eV, and these BEs are for C 1s of the ring, wings including the cyano groups, and the shakeup satellite of neutral TCNQ, separately.⁴⁰ The spectrum of Ni(TCNQ)₂ for the N 1s region shows a shift of 1.5 eV to higher BE (Figure 2c). An accompanying shift in the shakeup symbol is at 2.1 eV higher BE⁴¹ after anodization treatment. In the O 1s spectrum,



Figure 2. (a) Ni 2p, (b) C 1s, (c) N 1s, and (d) O 1s regions for $Ni(TCNQ)_2$ and $Ni(OH)_2$ -TCNQ.

the appearance of a significant sign at 529.9 eV indicates the presence of Ni–O species due to the air oxidation. The Ni(OH)₂-TCNQ shows three peaks at 529.8, 531.1, and 532.6 eV which are consistent with previous reports.⁴² The XPS results indicate that Ni(TCNQ)₂ successfully converts to Ni(OH)₂-TCNQ via anodization.

The OER activity of Ni(OH)₂-TCNQ/CF (loading: 5.6 mg cm⁻²) was assessed via linear scan voltammetry (LSV) using a standard three-electrode system with a scan rate of 2 mV s⁻¹ in 1.0 M KOH. RuO₂ on Cu foam (RuO₂/CF), Ni(TCNQ)₂/CF, Ni(OH)₂-TCNQ/CF, and bare Cu foam were also conducted for comparison. Figure 3a exhibits LSV curves for Ni(OH)₂-TCNQ/CF, Ni(TCNQ)₂/CF, RuO₂/CF, and bare copper foam. Predictably, copper foam is not active to OER, and RuO₂/CF displays an excellent OER property with a low overpotential of 225 mV at 20 mA cm⁻². Impressively, the Ni(TCNQ)₂/CF is capable of catalytic OER activity reaching



Figure 3. (a) LSV curves of Ni(OH)₂-TCNQ/CF, Ni(TCNQ)₂/CF, RuO₂/CF, and bare copper foam. (b) Corresponding Tafel plots for Ni(OH)₂-TCNQ/CF, Ni(TCNQ)₂/CF and RuO₂/CF. (c) Multistep chronopotentiometric curve of Ni(OH)₂-TCNQ/CF. (d) EIS spectra of Ni(OH)₂-TCNQ/CF and Ni(TCNQ)₂/CF.

an overpotential of 401 mV at 100 mA cm⁻². It is worth mentioning that the as-prepared Ni(OH)₂-TCNQ/CF exhibits superior performance with overpotentials as low as 322 and 354 mV at 50 and 100 mA cm^{-2} , respectively. Furthermore, we investigated the effect of different anodization treatments on OER performance of Ni(OH)₂-TCNQ/CF. In Figure S5a, the different Ni(TCNQ)₂/CF samples are anodized via CV for 250, 500, 750, 1000 cycles with a scan rate of 100 mV s⁻¹ at the region of +0.4 to +0.8 V vs Hg/HgO in 1.0 M KOH. Apparently, the sample anodized after 500 CV cycles shows the optimized activity. Additionally, the Ni(OH)2-TCNQ/CF catalyst is better than most non-noble-metal catalysts documented in literature under alkaline condition (Table S1). Tafel-plot analysis is an important parameter to obtain an insight into the OER kinetics.^{43,44} In Figure 3b, the Tafel slopes of Ni(OH)2-TCNQ/CF, Ni(TCNQ)2/CF, and RuO2/CF are calculated to be 110, 219, and 86 mV dec⁻¹, respectively, indicating Ni(OH)2-TCNQ/CF possesses the superior rate for O_2 evolution.

Figure 3c displays the multicurrent process of Ni(OH)₂-TCNQ/CF in the current densities ranging from 64 to 304 mA cm⁻² with an increment of 24 mA cm⁻² per 500 s. At the start of 24 mA cm⁻², the potential immediately levels off at 0.683 V versus Hg/HgO and remains constant for the surplus 500 s. The remaining steps have the identical result to the first one, suggesting superior mass transport properties, conductivity, and mechanical robustness of Ni(OH)₂-TCNQ/CF.^{45,46} Further electrochemical impedance spectroscopy (EIS) analysis manifests that Ni(OH)₂-TCNQ/CF possesses a smaller semicircle radius than that of Ni(TCNQ)₂/CF (Figure 3d), which implies a smaller charge transfer resistance (R_{ct}) and more rapid catalytic kinetics for Ni(OH)₂-TCNQ/CF due to the excellent conductivity of TCNQ.

The polarization curve of Ni(OH)2-TCNQ/CF after 1000 cycles shows no obvious change compared with the initial one, as shown in Figure 4a. Long-term electrolysis at 50 mA cm⁻² further demonstrates that such catalyst holds its high catalytic performance for 20 h at lowest (Figure 4b). Furthermore, Ni(TCNQ)₂/CF obtained by anodization treatment with 250, 750, and 1000 CV cycles also exhibit excellent stability (Figure S5b). The XRD patterns and Raman spectra of the catalyst before and after OER test show no obvious difference, revealing the structural stability of the as-prepared Ni(OH)₂-TCNQ sample (Figure S6). After OER electrolysis, the EDX elemental mapping images demonstrate that Ni, C, N, O elements are still present in the microarray (Figure S7). As shown in Figure 4c, Ni(OH)₂-TCNQ/CF still preserves an array feature after the durability test. Moreover, the HRTEM image taken from the Ni(OH)₂-TCNQ microrods shows high dispersion of Ni(OH)₂ nanoparticles in TCNQ without noticeable aggregation (Figure 4d). These results suggest this high-performance catalyst is highly durable and robust during OER, promising its application in real water-splitting devices.

TOF is employed to estimate the intrinsic catalytic activity of catalysts according to previously reported method (see Supporting Information for details).⁴⁷ Figure S8a shows the CVs of Ni(OH)₂-TCNQ/CF under different scan rates. Assuming oxidation of Ni centers in Ni(OH)₂-TCNQ/CF is an one-electron process,^{48,49} the concentration of surface active site can be derived from the linear dependence between the oxidation peak current and scan rate from CVs (Figure S8b). Then the TOF of Ni(OH)₂-TCNQ/CF can be calculated up to 0.24/0.67 mol O₂ s⁻¹ at overpotential of 400/500 mV (Figure



Figure 4. (a) LSV curves for Ni(OH)₂-TCNQ/CF before and after 1000 CV cycles. (b) Chronopotentiometric curve of Ni(OH)₂-TCNQ/CF at 50 mA cm⁻² (without *iR* correction). (c) SEM for Ni(OH)₂-TCNQ/CF after durability test. (d) HRTEM images take from Ni(OH)₂-TCNQ microrod after durability test.

S8c), which are higher than those of other Ni-based catalysts like Ni α/γ (0.23 s⁻¹, η = 700 mV),⁵⁰ MWCNTs/Ni(OH)₂ (0.015 s⁻¹, η = 490 mV),⁵¹ Ni₂P@C/G (0.1 s⁻¹, η = 350 mV),⁵² Ni NPs@N-CNTs (~0.01 s⁻¹, ~ 539 mV)⁵³ implying the high catalytic activity of Ni(OH)₂-TCNQ/CF. Faradaic efficiency (FE) is employed to evaluate the OER activity of catalysts. We determined the FE of the Ni(OH)₂-TCNQ/CF by comparing the amount of actually generated oxygen with theoretically calculated oxygen. The amount of O₂ increases during continuous electrolysis, and the FE of such catalyst electrode is measured as nearly 100% in alkaline media (Figure S9).

In summary, anodization treatment of Ni(TCNQ)₂ microrod array is confirmed to be an effective method for in situ synthesis of Ni(OH)₂ nanoparticles embedded in the TCNQ array. The high conductivity of TCNQ and the well dispersibility of Ni(OH)₂ nanocatalysts enable Ni(OH)₂-TCNQ/CF as a superior OER catalyst capable of driving 50 and 100 mA cm⁻² at overpotentials of 322 and 354 mV in 1.0 M KOH, respectively. Such catalyst shows strong long-term electrochemical stability for at least 20 h, with TOF up to 0.24/0.67 s⁻¹ at overpotential of 400/500 mV. The present work not only provides us a promising electrocatalytic material for alkaline water oxidation but also opens up a new opportunity for developing a nanoscale transition-metal encapsulating TCNQ microarray as a conductive 3D electrode for applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03406.

Experimental details, Raman spectra, XRD patterns, SEM images, LSV curves, i-t curves, CV curves, $j_{c-\nu}$ curve, EDX elemental mapping images, TOF curve, Faradaic efficiency curve, and Table S1 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: fengliquhn@hotmail.com.

ORCID 0

Fengli Qu: 0000-0001-6311-3051

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 201775089, 21375076), the Key Research and Development Program of Shandong Province (2015GSF121031) and the Natural Science Foundation Projects of Shandong Province (Nos. ZR2017JK010, ZR2017QB008).

REFERENCES

(1) Crabtree, G. W.; Dresselhaus, M. S.; Buchanan, M. V. *Phys. Today* **2004**, *57*, 39–44.

- (2) Nocera, D. G. Acc. Chem. Res. 2012, 45, 767-776.
- (3) Service, R. F. Science 2009, 324, 1257-1259.
- (4) Zhang, G.; Liu, H.; Qu, J.; Li, J. Energy Environ. Sci. 2016, 9, 1190–1209.
- (5) Lu, X.-F.; Gu, L.-F.; Wang, J.-W.; Wu, J.-X.; Liao, P.-Q.; Li, G.-R. Adv. Mater. 2017, 29, 1604437.
- (6) Feng, J.-X.; Ye, S.-H.; Xu, H.; Tong, Y.-X.; Li, G.-R. Adv. Mater. **2016**, 28, 4698–4703.

(7) Tian, T.; Huang, L.; Ai, L.; Jiang, J. J. Mater. Chem. A 2017, 5, 20985–20992.

- (8) Walter, M. G.; Warren, E. L.; Mckone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. *Chem. Rev.* **2010**, *110*, 6446–6473.
- (9) Wang, J.; Cui, W.; Liu, Q.; Xing, Z.; Asiri, A. M.; Sun, X. Adv. Mater. 2016, 28, 215–230.
- (10) Zhu, W.; Zhang, R.; Qu, F.; Asiri, A. M.; Sun, X. ChemCatChem 2017, 9, 1721–1743.
- (11) Xie, L.; Tang, C.; Wang, K.; Du, G.; Asiri, A. M.; Sun, X. Small **2017**, *13*, 1602755.
- (12) Ma, T. Y.; Dai, S.; Jaroniec, M.; Qiao, S. Z. Angew. Chem., Int. Ed. 2014, 53, 7281–7285.

- (13) Chen, P.; Xu, K.; Fang, Z.; Tong, Y.; Wu, J.; Lu, X.; Peng, X.; Ding, H.; Wu, C.; Xie, Y. Angew. Chem. **2015**, *127*, 14923–14927.
- (14) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y. L.; Risch, M.; Hong, W. T.; Zhou, J.; Shao-Horn, Y. Nat. Commun. 2013, 4, 2439.
- (15) Feng, J.-X.; Xu, H.; Dong, Y.-T.; Ye, S.-H.; Tong, Y.-X.; Li, G.-R. Angew. Chem., Int. Ed. 2016, 55, 3694–3698.
- (16) Lee, Y.; Suntivich, J.; May, K. J.; Perry, E. E.; Shao-Horn, Y. J. J. Phys. Chem. Lett. **2012**, *3*, 399–404.
- (17) Lu, X.-F.; Liao, P.-Q.; Wang, J.-W.; Wu, J.-X.; Chen, X.-W.; He,
- C.-T.; Zhang, J.-P.; Li, G.-R.; Chen, X.-M. J. Am. Chem. Soc. 2016, 138, 8336-8339.
- (18) Jiang, J.; Liu, Q.; Zeng, C.; Ai, L. J. Mater. Chem. A 2017, 5, 16929–16935.
- (19) Ai, L.; Niu, Z.; Jiang, J. Electrochim. Acta 2017, 242, 355–363.
 (20) Smith, R. D. L.; Prévot, M. S.; Fagan, R. D.; Trudel, S.;
- Berlinguette, C. P. J. Am. Chem. Soc. 2013, 135, 11580–11586. (21) Kuai, L.; Geng, J.; Chen, C.; Kan, E.; Liu, Y.; Wang, Q.; Geng, B.
- Angew. Chem. 2014, 126, 7677–7681.
- (22) Fominykh, K.; Feckl, J. M.; Sicklinger, J.; Döblinger, M.; Böcklein, S.; Ziegler, J.; Peter, L.; Rathousky, J.; Scheidt, E. W.; Bein,
- T.; Fattakhova-Rohlfing, D. *Adv. Funct. Mater.* **2014**, *24*, 3123–3129. (23) Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan,
- Y. J. Am. Chem. Soc. 2014, 136, 7077-7084.
- (24) Kim, J.-H.; Kang, S. H.; Zhu, K.; Kim, J. Y.; Neale, N. R.; Frank, A. J. Chem. Commun. **2011**, 47, 5214–5216.
- (25) Sun, X.; Si, W.; Liu, X.; Deng, J.; Xi, L.; Liu, L.; Yan, C.; Schmidt, O. G. *Nano Energy* **2014**, *9*, 168–175.
- (26) Nardi, K. L.; Yang, N.; Dickens, C. F.; Strickler, A. L.; Bent, S. F. *Adv. Energy Mater.* **2015**, *5*, 1500412.
- (27) Dou, S.; Li, X.; Tao, L.; Huo, J.; Wang, S. Chem. Commun. 2016, 52, 9727–9730.
- (28) Hou, Y.; Wen, Z.; Cui, S.; Ci, S.; Mao, S.; Chen, J. Adv. Funct. Mater. 2015, 25, 872–882.
- (29) Jiang, P.; Liu, Q.; Liang, Y.; Tian, J.; Asiri, A. M.; Sun, X. Angew. Chem., Int. Ed. 2014, 53, 12855–12859.
- (30) Ren, Z.; Botu, V.; Wang, S.; Meng, Y.; Song, W.; Guo, Y.; Ramprasad, R.; Suib, S. L.; Gao, P. Angew. Chem., Int. Ed. 2014, 53, 7223–7227.
- (31) Bhardwaj, S. K.; Sharma, A. L.; Bhardwaj, N.; Kukkar, M.; Gill, A. A.S.; Kim, K.; Deep, A. Sens. Actuators, B **201**7, 240, 10–17.
- (32) Shvachko, Y. N.; Starichenko, D. V.; Korolyov, A. V.; Yagubskii, E. B.; Kotov, A. I.; Buravov, L. I.; Lyssenko, K. A.; Zverev, V. N.; Simonov, S. V.; Zorina, L. V.; Shakirova, O. G.; Lavrenova, L. G. *Inorg.*
- *Chem.* **2016**, *55*, 9121–9130. (33) Clérac, R.; O'Kane, S.; Cowen, J.; Ouyang, X.; Heintz, R.; Zhao,
- H.; Bazile, M. J., Jr; Dunbar, K. R. Chem. Mater. 2003, 15, 1840–1850.
 (34) Neufeld, A. K.; O'Mullane, A. P.; Bond, A. M. J. Am. Chem. Soc. 2005, 127, 13846–13853.
- (35) Ramanathan, R.; Walia, S.; Kandjani, A. E.; Balendran, S.; Mohammadtaheri, M.; Bhargava, S. K.; Kalantar-zadeh, K.; Bansal, V. *Langmuir* **2015**, *31*, 1581–1587.
- (36) Vickers, E. B.; Giles, I. D.; Miller, J. S. Chem. Mater. 2005, 17, 1667–1672.
- (37) Davoudi, Z. M.; Kandjani, A. E.; Bhatt, A. I.; Kyratzis, I. L.;
- O'Mullane, A. P.; Bansal, V. Adv. Funct. Mater. 2014, 24, 1047–1053.
 (38) Nafady, A.; Bond, A. M. Inorg. Chem. 2007, 46, 4128–4137.
- (39) Yan, J.; Fan, Z.; Sun, W.; Ning, G.; Wei, T.; Zhang, Q.; Zhang, R.; Zhi, L.; Wei, F. Adv. Funct. Mater. **2012**, 22, 2632–2641.
- (40) Higo, M.; Futagawa, T.; Mitsushio, M.; Yoshidome, T.; Ozono, Y. J. Phys. Chem. B **2003**, 107, 5871–5876.
- (41) Lindquist, J. M.; Hemminger, J. C. Chem. Mater. 1989, 1, 72–78.
- (42) Gund, G. S.; Dubal, D. P.; Jambure, S. B.; Shinde, S. S.; Lokhande, C. D. J. Mater. Chem. A 2013, 1, 4793-4803.
- (43) Liu, Q.; Xie, L.; Liu, Z.; Du, G.; Asiri, A. M.; Sun, X. Chem. Commun. 2017, 53, 12446–12449.
- (44) Xie, L.; Zhang, R.; Cui, L.; Liu, D.; Hao, S.; Ma, Y.; Du, G.; Asiri, A. M.; Sun, X. Angew. Chem. 2017, 129, 1084–1088.

- (45) Xie, M.; Yang, L.; Ji, Y.; Wang, Z.; Ren, X.; Liu, Z.; Asiri, A. M.; Xiong, X.; Sun, X. *Nanoscale* **2017**, *9*, 16612–16615.
- (46) Zhang, X.; Si, C.; Guo, X.; Kong, R.; Qu, F. J. Mater. Chem. A 2017, 5, 17211–17215.
- (47) Zou, X.; Goswami, A.; Asefa, T. J. Am. Chem. Soc. 2013, 135, 17242–17245.
- (48) Bediako, D. K.; Costentin, C.; Jones, E. C.; Nocera, D. G.; Savéant, J. M. J. Am. Chem. Soc. **2013**, 135, 10492–10502.
- (49) Surendranath, Y.; Kanan, M. W.; Nocera, D. G. J. Am. Chem. Soc. **2010**, 132, 16501–16509.
- (50) Yeo, B. S.; Bell, A. T. J. Phys. Chem. C 2012, 116, 8394-8400. (51) Zhou, X.; Xia, Z.; Zhang, Z.; Ma, Y.; Qu, Y. J. Mater. Chem. A
- **2014**, *2*, 11799–11806.
- (52) Wang, M.; Lin, M.; Li, J.; Huang, L.; Zhuang, Z.; Lin, C.; Zhou, L.; Mai, L. Chem. Commun. **2017**, 53, 8372–8375.
- (53) Han, H.; Chao, S.; Yang, X.; Wang, X.; Wang, K.; Bai, Z.; Yang, L. Int. J. Hydrogen Energy **2017**, 42, 16149–1615.