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Fe(TCNQ)₂ Nanorod Array: A Conductive Non-Noble-Metal Electrocatalyst toward Water Oxidation in Alkaline Media

Xiaoxi Guo, Shuyun Zhu, Rong-Mei Kong, Xiaoping Zhang, and Fengli Qu*

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

Supporting Information

ABSTRACT: It is extremely desired to develop cost-effective and highefficient water oxidation electrocatalysts in alkaline electrolytes. In this Letter, we report the topotactic conversion of Cu(tetracyanoquinodimethane) nanoarray, denoted as Cu(TCNQ), into Fe(TCNQ)₂ nanoarray via lowtemperature cationic exchange. As a 3D electrode, such Fe(TCNQ)₂ possesses superior oxygen evolution reaction (OER) performance needing over-potentials as low as 321 and 353 mV to afford 20 and 50 mA cm⁻² in 1.0 M KOH, respectively. Remarkably enough, such a catalyst shows good durability in the long term electrochemical process with its catalytic activity being retained for 25 h at lowest. This work demonstrates that $Fe(TCNQ)_2$ nanoarray may open up new possibilities for OER application.



KEYWORDS: Fe(TCNQ), Nanorod array, Low-temperature cationic exchange, Electrocatalysis, Oxygen evolution reaction

■ INTRODUCTION

The exhaustion of fossil fuels, energy shortage and environmental pollution is becoming more and more serious, which gradually restricts the social and economic sustainable development.¹⁻³ It is of great urgency to search for clean and renewable energy alternatives. Hydrogen, a renewable and clean energy carrier, is considered as an appealing substitute to fossil fuels.^{4,5} Alkaline water electrolysis is an environmentally friendly method to produce sustainable hydrogen on a large scale.^{6,7} However, the oxygen evolution reaction (OER) is affected by intrinsically slow reaction kinetics, which requires highly efficient catalysts to achieve high current densities at low overpotentials (η) .^{8,9} Currently, precious metal oxides, such as RuO₂ and IrO₂, possess excellent OER performance, but the high cost, scarcity and poor durability are greatly restricted their widespread applications.¹⁰ Accordingly, it is extremely expected to explore and design cheap and earth-abundant alternative catalysts under alkaline conditions.

Given that Fe is a low-cost and natural-abundant transition metal, it has been widely used as an effective dopant to enhance the OER activities;^{11–13} however, pure Fe-based catalysts have not been broadly investigated.¹⁴ A metal–organic framework (MOF), metal ions or clusters combined with organic linkers, has high surface area, controllable porosity and diversity in metal and functional groups, which are beneficial for OER.¹⁵ Moreover, the nanoarray catalyst is capable of increasing the electrode stability, lowering the series resistance, exposing more active sites and facilitating the diffusion of the reactants and products.^{16–19} In particular, Fe(tetracyanoquinodimethane)₂ $(Fe(TCNQ)_2)$, an exceptional MOF, possesses outstanding electric conductivity^{20,21} but has not been applied for OER before. Hence, the development of a conductive Fe-based catalyst is of great need for high-efficient OER electrocatalysis. In this Letter, we demonstrate the development of Fe(TCNQ)₂ nanorod array on copper foam (Fe(TCNQ)₂/ CF) via low-temperature cationic exchange. Scheme 1

Scheme 1. Fabrication of Fe(TCNQ)₂/CF Electrocatalyst



illustrates the whole formation process, and preparation details are given in Supporting Information. In this process, Fe²⁺ exchanged with Cu⁺ in Cu(TCNQ) nanorod array grown on Cu foam (Cu(TCNQ)/CF) to fabricate Fe(TCNQ)₂/CF. Serving as a conductive electrode for water electrolysis, such postsynthetic ion exchange of Fe(TCNQ)₂/CF gives obviously enhanced OER performance with low overpotentials of 321 and 353 mV at 20 and 50 mA cm^{-2} in 1.0 M KOH, respectively. In

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addition, it has excellent long-term catalytic stability with its performance being kept for 25 h at lowest.

RESULTS AND DISCUSSION

Figure 1a displays the X-ray (XRD) patterns of Cu(TCNQ) and $Fe(TCNQ)_2$ scratched down from CF. The peaks of



Figure 1. (a) XRD patterns for Cu(TCNQ) and Fe(TCNQ)₂. (b) FT-IR spectroscopy for Fe(TCNQ)₂. SEM images for (c) Cu-(TCNQ)/CF and (d) Fe(TCNQ)₂/CF.

Cu(TCNQ) and Fe(TCNQ)₂ match well with previous reports,²²⁻ which imply the successful synthesis of Fe- $(TCNQ)_2$ via cationic exchange using as-made Cu(TCNQ)precursor. Figure 1b displays the Fourier transform infrared (FT-IR) spectroscopy for Fe(TCNQ)₂. Three resolved bands at 2067, 2147 and 2209 cm⁻¹ accord with the C \equiv N band, indicating the presence of TCNQ^{-.25} Meantime, two representative peaks at 1505 and 826 cm⁻¹ are attribute to $v_{c=c}$ and δ_{C-H} bending bands of TCNQ⁻.²⁶ The presence of a broad band at 3373 cm⁻¹, along with a weak peak at 1615 cm⁻¹, suggests the postsynthetic material contains coordinated water molecules.²⁷ The FT-IR results support the formation of the Fe(TCNQ)₂. The scanning electron microscopy (SEM) image of Cu(TCNQ) shows the surface of Cu foam is completely covered by Cu(TCNQ) nanorod (Figure 1c). As is shown in Figure 1d, the $Fe(TCNQ)_2$ still remains nanoarry feature after cationic exchange and we can obviously observed that the nanorod gets thicker. The energy-dispersive X-ray (EDX) elemental mapping images (Figure S1) confirm the presence of Fe, C, N elements within Fe(TCNQ)₂/CF. Taken together, all these characterizations manifest the successful synthesis of Fe(TCNQ)₂.

As shown in Figure 2a, the X-ray photoelectron spectroscopy (XPS) survey spectrum of $Fe(TCNQ)_2$ indicates the catalyst consists of Fe, C and N elements. The presence of O element may arise from contamination or surface oxidation of the product²⁸ and the single of Cu derive from the substrate.²⁹ In Figure 2b, the two major binding energies (BEs) at 711.2 and 724.5 eV for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ correspond to $Fe^{2+.30}$ In the C 1s region (Figure 2c), the BEs at 284.7 and 286.1 eV are observed, which stem from carbon bonds and CN group in TCNQ respectively. In addition, a shakeup satellite (identified as Sat.) at 288.1 eV is due to the unsaturated carbon bonds.^{31,32}



Figure 2. (a) XPS survey spectrum for $Fe(TCNQ)_2/CF$. (b) Fe 2p, (c) C 1s and (d) N 1s regions for $Fe(TCNQ)_2/CF$.

In Figure 2d, N 1s BE occurs at ca. 398.9 eV along with a shakeup feature at 400.3 eV, which are lower than that of reported neutral TCNQ. 33,34

Polarization curves for $Fe(TCNQ)_2/CF$ ($Fe(TCNQ)_2$ loading: 3.3 mg cm⁻²), Cu(TCNQ)/CF, RuO₂ (Figures S2 and S3, see Supporting Information for preparation details) on Cu foam (RuO₂/CF with the same catalyst loading) and bare Cu foam were recorded via linear sweep voltammetry (LSV) with a scan rate of 2 mV s⁻¹ in 1.0 M KOH (Figure 3a), which



Figure 3. (a) LSV curves of bare Cu foam, RuO_2/CF , Cu(TCNQ)/CF and $Fe(TCNQ)_2/CF$. (b) Tafel plots of RuO_2/CF , Cu(TCNQ)/CF and $Fe(TCNQ)_2/CF$ for OER. (c) Multicurrent process of $Fe(TCNQ)_2/CF$ in 1.0 M KOH. (d) EIS spectra of $Fe(TCNQ)_2/CF$ and Cu(TCNQ)/CF.

were employed to estimate the OER activity. All experimental data were corrected with ohmic potential drop losses arising from solution resistance^{35,36} and potentials were reported on a reversible hydrogen electrode (RHE) scale except specifically explained. Apparently, the RuO₂/CF exhibits marvelous catalytic performance with a low overpotential of 231 mV to afford 20 mA cm⁻², but the bare Cu foam shows the poor activity. Besides, Cu(TCNQ)/CF also has OER catalytic activity with the overpotential of 355 mV to deliver 20 mA

cm⁻². Impressively, Fe(TCNQ)₂/CF shows a superior property, only demanding 321 and 353 mV to attain 20 and 50 mA cm⁻², respectively. Note that the Fe(TCNQ)₂/CF possesses favorable behavior compared to other Fe-based catalysts under alkaline conditions (Table S1). Because commercial alkaline water electrolysis usually operates in strongly alkaline media, OER test in 30 wt % KOH was also performed and such Fe(TCNQ)₂/CF catalyst shows excellent activity, requiring a much lower overpotential of 183 mV to drive 20 mA cm⁻² (Figure S4). Figure 3b shows the Tafel plots for Fe(TCNQ)₂/CF, Cu(TCNQ)/CF and RuO₂/CF and their values are 77, 141 and 87 mV dec⁻¹, respectively. As observed, the Tafel plot of Fe(TCNQ)₂/CF is much smaller than that of Cu(TCNQ)/CF, implying more favorable catalytic reaction kinetics of Fe(TCNQ)₂/CF.

Figure 3c exhibits the multicurrent curve of Fe(TCNQ)₂/CF in the current densities ranging from 40 to 240 mA cm⁻² with an increment of 20 mA cm⁻² per 500 s. The initial potential instantly levels off at 0.725 V vs Hg/HgO at the start current density and maintains constant for the surplus 500 s. And the rest steps have the similar result to the first one, suggesting excellent mass transport properties, conductivity, and mechanical robustness of Fe(TCNQ)₂/CF electrode.^{37,38} Figure 3d shows the electrochemical impedance spectroscopy (EIS) analysis for Fe(TCNQ)₂/CF and Cu(TCNQ)/CF. As observed, Fe(TCNQ)₂/CF has a smaller semicircular diameter than that of Cu(TCNQ)/CF which indicates charge transfer resistance (R_{ct}) of Fe(TCNQ)₂/CF is smaller than that of Cu(TCNQ)/CF.

The $Fe(TCNQ)_2/CF$ durability tests were carried out by means of cyclic voltammetry (CV) and chronopotentiometric measurement 1.0 M KOH. As is shown in Figure 4a,



Figure 4. (a) OER polarization curves for $Fe(TCNQ)_2/CF$ before and after 500 CV cycles. (b) Chronopotentiometric curve of $Fe(TCNQ)_2/CF$ under a static current density of 20 mA cm⁻² for at least 25 h (without *iR* correction).

polarization curve after 500 cycles shows slight difference with the initial one. And the chronopotentiometric curve measured under a constant current density of 20 mA cm⁻² further demonstrates that $Fe(TCNQ)_2/CF$ remains its high electrocatalytic activity for 25 h at lowest (Figure 4b).

The high catalytic performance of $Fe(TCNQ)_2/CF$ may attribute to its high electrochemical active surface areas (ECSAs). Here, we further measure the double layer capacitance (C_{dl}) of $Fe(TCNQ)_2/CF$ and Cu(TCNQ)/CF to evaluate their ECSAs. The CVs with different scan rates at the region of +1.12 to +1.22 V were measured, where the current response was only due to the charging and recharging from the double layer (see Supporting Information for details). As exhibited in Figure S5, the C_{dl} for $Fe(TCNQ)_2/CF$ is 131 mF cm⁻² even bigger than that of Cu(TCNQ)/CF (32 mF cm⁻²), suggesting $Fe(TCNQ)_2/CF$ owns much higher ECSAs than that of Cu(TCNQ)/CF. And the open spaces between nanorods accelerate inward diffusion of electrolyte and outward diffusion of oxygen.^{39,40} Moreover, we tested the Faradaic efficiency (FE) of Fe(TCNQ)₂/CF for water oxidation by comparing the amount of experimentally measured O₂ with theoretically calculated ones.⁴¹ The amount of O₂ increases during electrolysis process and the measured value is basically in line with theoretical one, suggesting Fe(TCNQ)₂/CF has nearly 100% FE (Figure S6).

CONCLUSION

In summary, we investigate Fe(TCNQ)₂/CF fabricated via lowtemperature cationic exchange from Cu(TCNQ)/CF that can work as a high-performance OER catalyst. Serving as a robust 3D electrode, the as-made Fe(TCNQ)₂/CF enables high catalytic activity for OER in 1.0 M KOH, needing overpotentials of 321 and 353 mV to achieve 20 and 50 mA cm⁻², respectively. The low-cost and earth-abundant Fe(TCNQ)₂/ CF catalyst with a low overpotential, good stability and large anodic current density represents a promising catalyst for the OER application.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03962.

Experimental section; EDX elemental mapping images; XRD pattern; SEM image; LSV curves; CV curves; $j_c - \nu$ curve; Faradaic efficiency curve (PDF)

AUTHOR INFORMATION

Corresponding Author

*F. Qu. E-mail: fengliquhn@hotmail.com.

ORCID [©]

Fengli Qu: 0000-0001-6311-3051

Notes

The authors declare no competing financial interest.

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