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Fluorographdiyne: A Metal-free Catalyst for Applications in Water Reduction and Oxidation

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Dedication ((optional))

Abstract: A highly efficient bi-functional metal-free catalyst was prepared by growth of three-dimensional porous fluorographdiyne networks on carbon cloth (p-FGDY/CC). Our experiments and density functional theory (DFT) calculations show the 3D p-FGDY/CC network is highly active and it is a high potential metal-free catalyst for hydrogen evolution reaction (HER), oxygen evolution reaction (OER), as well as overall water splitting (OWS) under both acidic and alkaline conditions. The experimental and theoretical results show very good consistency, for example, in the HER process, p-FGDY/CC exhibits small overpotentials of 82 and 92 mV to achieve 10 mA cm⁻² in both alkaline and acidic conditions, respectively. This ensures an even higher selectivity for various O/H intermediate species adsorption/desorption. The essential key promotion accomplishes a tetra-functional H₂O redox performance application within pHuniversal electrochemical conditions.

Introduction

Platinum (Pt)/ruthenium (Ru) based catalysts have long been considered as the best electrocatalyst for the hydrogen/oxygen evolution reactions (HER/OER).^[1] Unfortunately, however, the scarcity and high cost of them have been shown to be the main obstacles to the large-scale commercialization. From vision of advanced catalyst in the future, development of earth-abundant and cost-effective catalysts for HER/OER under low overpotentials (η) is one of the long-standing goals. Recently, numerous of transition metal-based materials have been synthesized as effective catalysts for water splitting,^[2] as we know, they actually suffer from inherent corrosion susceptibility to

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acidic electrolytes. Despite to tremendous efforts, highperformance water splitting with an efficient and stable catalyst remains a key challenge in efficient energy conversion systems.

Metal-free carbon materials are a promising class of catalysts, featuring intriguing advantages for water splitting because of their abundance, tunable chemical/electronic structures, and high tolerance to acidic/alkaline conditions.^[3] Several carbon materials, such as graphene,^[4] nitrogen-doped graphene,^[5] nitrogen-doped carbon nanotubes,^[6] nitrogen-doped carbon,^[7] and polyimidebased electrode,^[8] have been reported as metal-free catalysts for water splitting. However, the synthesis of conventional carbon materials suffers from the complicated and time- and energyconsuming pyrolysis process, easily resulting in the formation of ambiguous chemical and electronic structures, which seriously hinders the correct understanding of the active sites and catalytic mechanisms of the catalysts. Besides, the conventional metalfree catalysts can scarcely function concurrently in OER and HER in both alkaline and acidic conditions because of their intrinsically reactive and unstable nature in an unfavorable pH environment. Therefore, the development of easy to prepare, stable carbon materials in both alkaline and acidic system as a highly efficient catalyst is an urgent need to solve the key issues in the field of electrocatalysis. To the best of our knowledge, experimental and theoretical studies on a carbon material with clear chemical and electronic structures, which can concurrently function as HER-OER bifunctional catalysts in both alkaline and acidic conditions. have never been reported.

Graphdiyne (GDY) is a new carbon allotrope that features the coexistence of sp- and sp²-hybridized carbon atoms, the uneven surface charge distribution causes many active sites. In electrocatalysis, GDY has a unique advantage over that of only sp²-hybridized atom carbon. Owing to the unique chemical and electronic structures result in superior properties, GDY has been successfully applied in many fields^[9] including catalysis,^[9h-9m,10] electronics, and energy, since its first successful synthesis in 2010 by Li and coworkers.^[11] An important research direction for GDY is to expand its family. Several GDY derivatives (e.g., nitrogen-,^[12] hydrogen-,^[13] chlorine-,^[14] and boron-GDY,^[15]) have been reported and applied in different fields. But no reports focused on OWS process. Most importantly, the GDY derivatives obtained through only tuning of the monomer's structure have clear chemical and electronic structures. This provides us an ideal opportunity for study the exact HER/OER mechanisms of metalfree carbon materials.

Herein, for the first time we synthesized 3D porous fluorographdiyne nanostructures on carbon cloth (p-FGDY/CC), as bifunctional catalysts for both HER and OER, as well as OWS in both acidic and alkaline electrolytes. This strategy maximizes the active surface area and the number of active sites of the

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catalyst. Owing to the unique chemical and electronic structures of FGDY and the constructed 3D hierarchical porous electrode, the novel P-FGDY/CC electrode shows outstanding catalytic activities towards HER, OER, and OWS, respectively, together with superior long-time stabilities from acidic to alkaline conditions.



Figure 1. a) Schematic of the structure of FGDY. b) The photograph of the p-FGDY/CC material. SEM images of c),d) pure CC and e-f) p-FGDY/CC. h) Contact angle measurements of p-FGDY/CC. i) Photographs of the p-FGDY/CC electrode with bended morphology exhibiting its flexibility nature. Photographs of j) the three-electrode system (WE: working electrode; RE: reference electrode; CE: counter electrode) and k) enlarged image of the WE of the marked in j).

Results and Discussion

Similar to graphdiyne, FGDY features a two-dimensional (2D) one-atom-thick planar structure (Figure 1a), possessing diacetylenic bond (sp carbon), benzene rings (sp² carbon) and fluorine atoms homogeneously distributed in each benzene ring. By using a facile in-situ growing procedure from 1,3,5-triethynyl-2,4,6-trifluorobenzene precursor (Supporting Information, Figure S1), a film of p-FGDY nanostructures uniformly grown on the smooth surface of CC (Figure 1b,c). The scanning electron microscopy (SEM) images (Figure 1d-f; Supporting Information, Figure S2) clearly show that the p-FGDY comprises of nanobelts cross-linked together, forming a 3D porous network, which may effectively facilitate the electron and mass transfer during the water splitting reactions. The contact angle measurements for the materials reveal the super-hydrophilicity nature of p-FGDY/CC (CA is 0°, complete wetting; Figure 1g), while the CC surface is highly hydrophobic (CA \approx 116°; Supporting Information, Figure S3). The super-hydrophilic surfaces can facilitate the transport of reactants and products at the electrolytecatalyst interface, and thus can help improving the performance of a catalyst. In combination with the high flexibility nature of the p-FGDY/CC (Figure 1h), it is very suitable as a working electrode for water splitting (Figure 1i).



Figure 2. a,b) TEM images and c) high-resolution TEM image of p-FGDY. Inset in a) is the selected area electron diffraction. d) Scanning TEM image, corresponding elemental mapping of e) C and f) F, and g) the overlapping image. h) Raman spectrum of p-FGDY/CC. XPS i) C 1s and j) F 1s spectra of p-FGDY/CC.

geometric structure of FGDY was Detailed further characterized by the transmission electron microscope (TEM, Figure 2a-c), which revealed the same porous morphology to the SEM (Figure 1e-g) results. The selected-area diffraction (SAED) pattern for FGDY nanosheet (Figure 2f) indicates the amorphous feature, as confirmed by the X-ray diffraction (XRD) results (Supporting Information, Figure S4). The magnified TEM images (Figure 2b,c) further verify that the FGDY structure is porous connected by nanobelts. The porous and edge/defect-rich structures are also clearly observed (Supporting Information, Figure S5). Figure 2c shows the high-resolution TEM image of FGDY, giving an interplanar spacing of 0.360 nm. The scanning TEM and corresponding elemental mapping results (Figure 2d-g) show the homogeneous distribution of carbon and fluorine over the whole nanosheet. Raman spectrum (Figure 2h) represents typical peaks at 1371 cm⁻¹ (D band) and 1591 cm⁻¹ (G band), together with the characteristic peaks at 2198 cm⁻¹ corresponding to the vibration of the diacetylenic linkage. No peaks corresponding to the stretching of terminal alkyne could be observed from the Raman spectrum, suggesting that all precursor formed the π-conjugated diacetylenic linkage. The high intensity of the D band further confirmed the presence of high-density defects in the sample. In typical XPS spectra, pure CC shows the existence of C and O species (Supporting Information, Figure S6). For p-FGDY, only C and F peaks could be observed (Supporting Information, Figure S7a), demonstrating the successful synthesis

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of FGDY and the dopant-free nature of the p-FGDY/CC sample. The trace O peak mainly originated from the adsorption of air (Supporting Information, Figure S7b), similar to other reported carbon materials such as graphdiyne^[16] and graphene.^[17] The C 1s can be deconvoluted into three peaks at 284.4, 285.0, and 286.6 eV (Figure 2i), which are ascribable to C=C (sp²-C), C≡C (sp-C) and C–F, respectively. The integrated peak area ratio of sp²-C versus sp-C is 1.0, in accordance with the chemical composition of FGDY. The fluorine peak (687.4 eV, Figure 2j) can be ascribed to the semi-ionic C–F bond with high polarity,^[18] which benefits to the enhancement of the catalytic activity.^[19] This is further verified by our density functional theory (DFT) results (as discussed later). The XPS spectra of the reference sample, 2D FGDY, are in accordance with that of p-FGDY (Supporting Information, Figure S8).



Figure 3. a) Polarization curves of the catalysts for HER in 1.0 M KOH. (inset: Enlarged view of the polarization curves near the onset region). b) Comparison of the HER performances of the p-FGDY/CC with reported metal-free and metal-based catalysts. c) Long-term stability tests of the p-FGDY/CC in 1.0 M KOH during the HER process. d) Polarization curves of the catalysts for HER in 0.5 M H₂SO₄. e) Comparison of the HER performances of the p-FGDY/CC with reported catalysts in 0.5 M H₂SO₄. f) Long-term stability tests of the p-FGDY/CC with reported catalysts in 0.5 M H₂SO₄. f) Long-term stability tests of the p-FGDY/CC in 0.5 M H₂SO₄ during the HER process. g) Polarization curves of the catalysts for OER in 1.0 M KOH. h) Comparison of the OER performances of the p-FGDY/CC with the reported catalysts. i) Long-term stability tests of the p-FGDY/CC with the reported catalysts. j) Long-term stability tests of the p-FGDY/CC with the reported catalysts. j) Long-term stability tests of the catalysts. k) CV curves of FGDY in the region of $-0.14 \text{ V} \sim -0.04 \text{ V}$ vs. RHE at various scan rates. l) Corresponding capacitive current densities as a function of scan rates for p-FGDY.

Electrocatalytic HER performance of the p-FGDY/CC was assessed using a three-electrode electrochemical cell at a scan rate of 1 mV s⁻¹ (see Supporting Information for details). The catalytic performances of CC substrate, 2D FGDY film, and

20wt% Pt/C were also tested for comparison. CC substrate and 2D FGDY film showed negligible HER activities at applied potentials in both alkaline (Figure 3a) and acidic (Figure 3c) conditions. As shown in Figure 3a, p-FGDY/CC shows an excellent HER activity with a low onset overpotential of 82 mV versus the reversible hydrogen electrode (RHE) at the current density (J) at 10 mA cm⁻² in 1.0 M KOH, which is better than all reported metal-free catalysts such as NCP/G NS,[20] EBP@NG(1:4)^[21] and even comparable to the metal-based ones (Figure 3b; Supporting Information, Table S1). As analyzed from the Tafel plots, p-FGDY/CC shows a smaller Tafel slope (139 mV dec⁻¹) than that of 2D FGDY film (241 mV dec⁻¹) and pure CC (202 mV dec⁻¹) (Supporting Information, Figure S9). Stability tests for p-FGDY/CC electrode were performed under HER conditions. The overpotentials at 10 mA cm⁻² were measured after every 500 cycles for several independent experiments (Supporting Information, Figure S10). There was a slight variation in the overpotential during the testing process over 8500 cycles ($\eta_{initial}$ = 82 \pm 14 mV; $\eta_{8500cycles}$ = 80 \pm 9 mV; Figure 3c). At a constant applied potential of 170 mV, p-FGDY/CC showed approximate 100% retention of the initial J even after 60 h (Figure 3c). The XPS and SEM results revealed that the structural composition and morphologies were well preserved during the long-term stability test (Supporting Information, Figure S11), indicating the excellent stability of the p-FGDY/CC. Even in the strong acidic condition (0.5 M H₂SO₄), the 3D P-FGDY/CC still shows an excellent HER performance with a small overpotential (92 mV at 10 mA cm⁻²; Figure 3d), which is much smaller than the reference catalysts, benchmarked metal-free catalysts, and even compared favorable to the metal-based catalysts (Figure 3e; Supporting Information, Table S2) measured in acidic conditions. Besides, 3D p-FGDY/CC exhibits a smaller Tafel slope of 157 mV dec⁻¹ (Supporting Information, Figure S12). After 3000 cycles, the p-FGDY/CC electrodes showed modest changes in $\eta_{10 \text{ mA cm}^{-2}}$ every 200 cycle intervals over 3000 cycling tests (Figure 3f; Supporting Information, Figure S13). And there is no decrease in J after 9hour electrolysis at an applied potential of 120 mV. The XPS and SEM analysis on the sample obtained after the stability tests further confirmed the high stability of the p-FGDY/CC electrode in strong acidic condition (Supporting Information, Figure S14).

We next evaluated the OER performances of the p-FGDY/CC in both alkaline and acidic electrolytes, in comparison with 2D FGDY film, CC substrate and RuO₂. In 1.0 M KOH, P-FGDY/CC exhibits a low onset potential of 1.54 V (vs. RHE) and needs a potential of 1.69 V (vs. RHE) to reach 10 mA cm⁻² (Figure 3g). These values are smaller than that of 2D FGDY film (2.5 V), CC (2.03 V), and most of the reported benchmarked metal-free catalysts such as pyridinic-N-doped graphene (1.68 V)^[22] and NCNF-1000 (1.84 V),^[23] (Figure 3h). The Tafel slopes of the p-FGDY/CC, 2D FGDY film and CC are 128, 213, and 670 mV dec⁻¹. respectively, confirming the superior catalytic kinetics of the p-FGDY/CC electrode (Supporting Information, Figure S15). The durability tests showed that the OER activities of p-FGDY/CC could be maintained after 2000 continuous cycling test (Figure 3i) and an 9-hour electrolysis test (Figure 3i), indicating the metalfree p-FGDY/CC is a robust OER catalyst in alkaline condition. The XPS measurements on the samples after the durability test further confimed the robust nature of the p-FGDY/CC (Supporting Information, Figure S16). The OER properties of the p-FGDY/CC

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were also studied in 0.5 M H₂SO₄. As shown in Figure S17, P-FGDY/CC shows an onset potential of 1.54 V (vs. RHE), and it can deliver 10 mA cm⁻² at the potential of 1.8 V (vs. RHE). The Tafel slope is calculated to be 192 mV dec⁻¹. There is no obvious variation in the potentials at 10 mA cm⁻² after every 200 cycles over the whole course of the cycling test (Supporting Information, Figure S18). Additonal XPS results of the sample after stability test in 0.5 M H₂SO₄ revealed that there are no any changes in its chemical structure (Supporting Information, Figure S19). Moreover, the catalytic performances of the catalysts were determined in neutral conditions (1.0 M PBS, pH = 7). The p-FGDY/CC exhibits small overpotentials of 380 and 623 mV at the J of 2 and 10 mA cm⁻², respectively, and Tafel slope of 300 mV dec⁻¹ (Supporting Information, Figure S20), which are smaller than that of 2D FGDY film (674 mV at 2 mA cm⁻²; Tafel slope: 467 mV dec⁻¹), and superior to that of non-metal and transition metal based electrocatalysts (Supporting Information, Table S3). The electrochemical performance of the 1st and 2000th cvcles are almost the same revealing the good stability of the p-FGDY/CC in neutral condition (Supporting Information, Figure S21). As shown in Figure S22, the p-FGDY/CC also possesses good OER catalytic activities and durability. These results confirmed the excellent catalytic nature of the p-FGDY/CC.

We investigated the catalytic kinetics of the catalysts at electrode/electrolyte interface by electrochemical impedance spectroscopy (EIS). The recorded impedance data were fitted by using a circuit model (Supporting Information, Figure S22). The p-FGDY/CC has the smallest solution resistance ($R_s = 4.5 \Omega$) and charge-transfer resistance ($R_{ct} = 277 \Omega$) among the catalysts (Figure 3g; Supporting Information Table S4), indicating the fastest charge-transfer behavior which benefits to the improvements of the catalytic performances. After the stability test, both R_s and R_{ct} increased to the higher values (R_s = 4.8 Ω , R_{ct} = 293 Ω ; Supporting Information, Figure S23), revealing that the activity of the catalyst decreased after long-term stability test. We further estimated the electrochemical active surface area (ECSA) of catalysts by determining the double-layer capacitances (Cdl) via cyclic voltammetry (CV) method (Figure 3h,3i; Supporting Information, Figure S24). The p-FGDY/CC shows the largest Cdl value of 3.5 mF cm⁻² than that of 2D FGDY film (0.12 mF cm⁻²) and CC (0.27 mF cm⁻²). Accordingly, the p-FGDY/CC has the largest ECSA value 87.5 cm², which is 29.2 and 12.9 times larger than 2D FGDY film (3.0 cm²) and CC (6.75 cm²), respectively, indicating the direct growth of 3D p-FGDY networks can effectively increase the active surface area, the number of active sites and thus enhance the catalytic activity.



Figure 4. a-c) The real spatial contour plots for bonding and anti-bonding orbitals near EF, regarding the a) pristine FGDY, b) H-adsorption, and c) initial H2O-adsorption. d) PDOSs of s- and p-bands for FGDY system. e) Individual site-dependent PDOSs of C1, C2, and C3 sites, as well as the C site bonding with F (CF). f) PDOSs of adsorbing O/H-species. g) Alkaline HER energetic pathway comparison between pristine GDY and FGDY. h) Transition state comparison of H₂O splitting between pristine GDY and FGDY. i) OER pathway within acidic and alkaline conditions at the electrode U=0 V for FGDY. j) OER pathway within acidic and alkaline conditions at the electrode U=1.23 V for FGDY.

To gain deep insight into the high catalytic activity of p-FGDY, DFT calculations were carried out. The bonding and anti-bonding orbitals near the Fermi level (E_F) are demonstrated for indicating the active electronic orbitals that are responsible for site-to-site electron-transfer. In FGDY, the strong C-F bonding induces the charge-polarization (Figure 4a), which will further enhance the degree of electron-localization near the C2 site. Accordingly, the C2 site of the F-GDY system exhibits a strong electron-rich character which is the active site for efficient electron-transfer with H^+ (Figure 4b) and the initial H_2O -adsorption (Figure 4c). The projected partial density of states (PDOSs) of FGDY demonstrates that the dominant p-band peak is more close to the E_F than the s-band peak (Figure 4d), indicating that the localized p-electronic orbitals are more active for electron-transfer to adsorbing species. Individual site-dependent PDOSs analysis (Figure 4e) illustrates that the p-band of C2 site is the active orbital for efficient electron-transfers, where covers the bandwidth from E_V -0.1 eV to E_V -2.0 eV (E_V =0 for E_F). Accordingly, the C2 site is confirmed to be predominant active site for catalysis. From the PDOSs analysis on the individual adsorbing O/H-related species (Figure 4f), we found all adsorbing O-species (i.e. H₂O, H/2H, O, and O₂) present substantial p-p overlapping (E_V-0.1 eV to E_V-2.0 eV). Especially to the adsorbate at the potential determining step (OOH), an offset effect (~0.3 eV) has also been observed between the adsorbing OOH and C2 site, indicating an efficient desorption without p-p over-binding. Meanwhile, the p-p offset is more evident between OH and C2 site implying no related over-binding has been found.

We move on the energetic pathway of OER and HER. For the acidic HER (**Figure 4g,h**), the chemisorption gradually turns to be more and more favorable at the C2 site with the H-coverage increases. Especially at the high coverage rate, the H-

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chemisorption at the C2 site is -0.35 eV. For the alkaline HER pathway, the dominant barrier is shown at the step of adsorbing the H2O and H simultaneously. As shown in Figure 4g, the FGDY exhibits the barrier as low as the 0.09 eV. Overall the performance indicates an energetic downhill trend for the alkaline HER on the F-GDY system. Furthermore, the H₂O splitting within F-GDY system shows a low barrier level at the transition-state (TS) step (0.31 eV) and very energetic favorable (-0.63 eV) (Figure 4h). It is promising to advance the pH-universal applications. Further viewing on the OER performance (Figure 4i,j), the favorable bonding strengths of both C2-H2O and C2-OH guarantee adsorption/desorption of OOH to be rather energetic stable and lowers the barrier (0.22 eV at the U=1.23 V for alkaline) of forming [*OOH+H₂O+OH+3e⁻]. The acidic OER pathway exhibits a slightly higher barrier (0.61 eV at the U=1.23 V) at the step of initial H₂O splitting, which is attributed to the contrast bonding difference between H₂O and OH viewing from the PDOSs analysis. Therefore, overall OER performance from both alkaline and acidic conditions are well performed (Figure 4i,j). Therefore, the strong F-C bonding induced p-electronic orbital re-distribution enhances the electron-rich character at the C2 site and consequently elevates the electron-transfer ability. This ensures an even higher O/H selectivity for various intermediate species adsorption/desorption, and is also the essential key promotion accomplishing a tetra-functional H₂O redox performance application within pH-universal electrochemical conditions.

All of the experimental and theoretical results indicate the high catalytic performances of p-FGDY/CC toward HER and OER in both strong acidic and alkaline electrolytes. In light of this, we constructed a metal-free water splitting electrolyzer with p-FGDY/CC as both the anode and cathode (p-FGDY/CC||p-FGDY/CC) for OWS in alkaline and acidic electrolytes (Supporting Information, Figure S25). p-FGDY/CC||p-FGDY/CC requires low cell voltages of 1.75 V and 1.80 V to achieve 10 mA cm⁻² in 1.0 M KOH and 0.5 M H₂SO₄, respectively (Supporting Information, Figure S26). p-FGDY/CC electrolyzer also shows high long-term stabilities in both 1.0 M KOH (Supporting Information, Figure S27) and 0.5 M H₂SO₄ (Supporting Information, Figure S28). For example, the current density degradation is less than 5.0% at applied voltage of 1.76 V in alkaline media.

Conclusion

In summary, we report, for the first time, the in-situ, facile, and large-scale growth of 3D porous FGDY networks on carbon cloth. The unique structure endows the metal-free p-FGDY/CC electrode with highly active and stable HER, OER, as well as OWS performances under pH-universal electrochemical conditions, which superior to those of benchmarked metal-free or metal-based electrocatalysts. Our experimental and theoretical results reveal that such excellent catalytic performances might be due to the high electron-transfer ability high conductivity, edge/defect-rich structure and the direct contact between the FGDY and CC substrate. The strong F-C bonding modifies the local p-p coupling related electron-rich character at the C2 site and

consequently elevates the electron-transfer ability. This ensures an even higher selectivity for various O/H intermediate species adsorption/desorption, and is also the essential key promotion of overall water splitting. The design and synthesis of efficient and stable catalysts based on graphdiyne structure might be one of the optimal opportunities for high-performance electrode materials.

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Keywords: carbon material • fluorographdiyne • metal-free catalyst • oxygen evolution reaction • overall water splitting

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We report a three-dimensional porous fluorographdiyne networks on carbon cloth (p-FGDY/CC) as an active metal-free catalyst toward HER, OER and OWS under both acidic and alkaline conditions. The strong F-C bonding modifies the local p-p coupling related electronic orbital fillings, as the essential key promotion of overall water splitting.



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