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A facile approach to prepare crumpled CoTMPyP/electrochemically reduced graphene oxide nanohybrid as an efficient electrocatalyst for hydrogen evolution reaction

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ABSTRACT

Elaborate design and synthesis of efficient and stable non-Pt electrocatalysts for some renewable energy related conversion/storage processes is one of the major goals of sustainable chemistry. Herein, we report a facile method to fabricate Co porphyrin functionalized electrochemically reduced graphene oxide (CoTMPyP/ERGO) thin film by direct assembly of oppositely charged tetrakis(N-methylpyridyl) porphyrinato cobalt (CoTMPyP) and GO nanosheets under mild conditions followed by an electrochemical reduction procedure. STEM analysis confirms that CoTMPyP nanoaggregates are homogeneously distributed over the graphene surface. The electrochemical properties of CoTMPyP/ERGO were investigated by cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy. The results demonstrate that CoTMPyP/ERGO nanohybrid film can serve as excellent electrocatalyst for hydrogen evolution in alkaline solution with high activity and stability. The intimate contact and efficient electron transfer between CoTMPyP and ERGO, as well as the crumpled structure, contribute to the improvement of the electrocatalytic performance.

Keywords: Co porphyrin; electrochemically reduced graphene oxide; electrocatalysis; hydrogen evolution

1. Introduction

Hydrogen evolution reaction (HER) via electrochemical splitting of water has attracted worldwide attention because it can be realized using renewable energies [1]. Besides, the zero emission of

carbonaceous species from hydrogen utilization makes hydrogen an ideal candidate for the replacement of fossil fuel energy in the future [2]. Pt-group noble metals have proven to be the most efficient electrocatalysts for HER. Unfortunately, the prohibitive cost and scarcity significantly hinders their large scale commercial application [3, 4]. Thus, the exploration of highly active non-precious alternative catalysts has become a main research focus for the practical use of hydrogen.

Cobalt has emerged as an interesting non-noble metal for its catalytic power toward hydrogen evolution, and great efforts have been devoted to developing Co-based macrocyclic complexes as HER catalysts in the past [5-7]. Most of these studies were, however, performed smoothly only in nonaqueous solvents, which greatly limits their application in water-splitting devices. Therefore, a great deal of research has been carried out to develop highly active cobalt complexes which could work efficiently in aqueous solutions. Cobalt porphyrins have also been previously demonstrated to act as efficient photocatalyst for HER [8, 9] and electrocatalysts for the oxygen reduction reaction [10-12] and oxygen evolution reaction [13]; while the exploration of cobalt porphyrins based HER electrocatalysts has received much less attention. Dong *et al.* [14] developed metalloporphyrin-polyoxometalate hybrid films by the layer-by-layer method and investigated their catalytic properties for HER in acid media. Hung *et al.* [15] reported the use of a water-soluble CoTPPS as a stable and active catalyst for HER from neutral H₂O without any organic additives. However, the catalytic activity of these electrocatalysts usually suffers from the lower electrical conductivity and/or limited amount of exposed active sites. It is now well-accepted that two effective strategies to improve the HER performance of electrocatalysts are: (1) the incorporation of catalytic materials with conductive networks; (2) the construction of special structures, such as hollow, porous, or hierarchical architectures [16, 17].

Graphene, a one-atom-thick sheet of sp^2 -bonded carbon atoms in a honeycomb crystal lattice, has been widely investigated recently as a support for HER catalysts due to its huge surface area, excellent electron conductivity and outstanding mechanical strength [18-20]. Wang et al. successfully developed Co porphyrin and graphene multilayer films by using layer-by-layer technique [21]. However, this method involves tedious steps and the electrocatalytic performance of the multilayer films for HER needs to be improved. Thus, the development of a simple and efficient procedure is in demand. Herein, we demonstrate that Co porphyrin and electrochemically reduced graphene oxide hybrid film (CoTMPyP/ERGO) can be fabricated by the direct assembly of CoTMPyP and GO nanosheets followed by an electrochemical reduction procedure. The CoTMPyP/ERGO with abundant crumples ensures the high exposure of Co porphyrin on the high conductive graphene support for electrocatalytic reactions, and exhibits excellent catalytic activity toward HER in alkaline media (Fig. 1).

Fig. 1. Schematic illustration of possible HER process based on CoTMPyP/ERGO.

2. Experimental

2.1. Materials and reagents

Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. GO was prepared by a modified Hummer's method [22]. Free-base porphyrin H_2TMPyP was purchased from TCI. Cobalt porphyrin (CoTMPyP) was prepared through metallation by refluxing H_2TMPyP with $CoCl_2 \cdot 3H_2O$ as described by Hambright et al [23]. All other chemicals were analytical grade and were used as received.

from the suppliers without further purification. All aqueous solutions were prepared using ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore).

2.2. Preparation of CoTMPyP/GO

A GO aqueous colloidal suspension (0.2 mg mL^{-1}) was prepared by ultrasonically dispersing GO in distilled water. For the preparation of CoTMPyP functionalized graphene oxide (CoTMPyP/GO), 0.5 mg mL^{-1} of CoTMPyP aqueous solution was added with the mass ratio of GO to CoTMPyP (3:1) and stirred vigorously at 50°C for 12 h. The product was purified by centrifugation steps with water. The precipitate was dispersed into water under ultrasonication to form a homogeneous ink at a concentration of 2 mg mL^{-1} .

2.3. Preparation of CoTMPyP/ERGO

The glassy carbon electrodes (GCE, $\phi = 3 \text{ mm}$, CHI) were polished to a mirrorlike surface with 0.3, and $0.05 \text{ }\mu\text{m}$ alumina slurry in turn, and sequentially double-distilled water and anhydrous ethanol, and dried in air naturally. The modification of the working electrode was achieved by drop-casting $8 \text{ }\mu\text{L}$ CoTMPyP/GO dispersion containing 0.5% (w/w) Nafion on the pretreated GCE. Then, CoTMPyP/GO was electrochemically reduced by 30 successive cyclic voltammograms in an electrochemical cell containing a 0.05 M PBS (pH 5) solution over a potential range of 0 to -1.5 V at a scan rate of 50 mV s^{-1} [24]. For comparison purpose, ERGO modified electrode was prepared by drop-casting 2 mg mL^{-1} GO solution on a GCE following an electrochemical reduction procedure.

2.4. Characterization

X-ray diffraction (XRD) was carried out using a Bruker D8 Advance X-ray diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). UV-vis absorption spectra were recorded with a SHIMADZU UV-2501 spectrometer. X-ray photoelectron spectra (XPS) measurements were performed on a Phoibos

100 spectrometer. Field-emission scanning electron microscope (FESEM) and scanning transmission electron microscope (STEM) images were collected on a JSM-6700F Field emission scanning electron microscope operating at 5 kV and JEOL JEM-2100F transmission electron microscope operating at 200 kV, respectively. For XRD, FESEM and STEM measurements, samples were assembled onto FTO (Fluorine doped tin oxide) substrates.

2.5. Electrochemical measurements

Electrochemical measurements, including cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed on a CHI 660D electrochemical workstation with a three electrode cell system, in which the modified GCE with a catalyst was employed as working electrode, Pt wire as auxiliary electrode, and Ag/AgCl as reference electrode. The electrochemical impedance spectroscopy (EIS) measurements were obtained on an Autolab electrochemical workstation in a frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 pH + E_{Ag/AgCl}^{\circ}$$

where $E_{Ag/AgCl}^{\circ} = 0.1976$ V at 25 °C.

3. Results and discussion

3.1. Preparation and characterization of CoTMPyP/ERGO

In this work, we developed a facile two-step strategy for the synthesis of CoTMPyP/ERGO hybrid film. In the first step, graphite oxide was dispersed in the deionized water to form GO sheets, which are highly negatively charged because of the ionization of the carboxylic acid and phenolic hydroxyl groups on their edges and surface [25]. When the positively charged CoTMPyP ions were added, the electrostatic interaction provides a strong driving force for the assembly of GO sheets and CoTMPyP

cations. As in situ observed (Fig. 2, inset), the dark brown flocculent precipitation was formed after a certain amount of CoTMPyP solution reacted with GO aqueous dispersion. Additional interactions, such as π - π stacking and van der Waals force between GO and cobalt porphyrin, can improve the stability of the obtained composite [12]. To enhance the conductivity in the HER process, hybrid film was subsequently reduced by electrochemical method. As a result, the CoTMPyP/ERGO composite was obtained.

Fig. 2. UV-vis absorption spectra of (a) CoTMPyP solution, (b) GO dispersion and (c) CoTMPyP/GO dispersion.

Inset: images of CoTMPyP solution (left), GO dispersion (middle), and the corresponding mixture (right).

Fig. 2 shows UV-vis absorption spectra of CoTMPyP, GO and CoTMPyP/GO dispersion. CoTMPyP displays a strong typical Soret band at 432 nm, together with a weak Q band at 542 nm, respectively. In the GO spectrum, a broad peak at around 230 nm corresponds to the π - π^* transition of aromatic C-C bonds and a shoulder at around 300 nm was due to the n - π^* transition of C=O bonds. The UV-vis spectrum of CoTMPyP/GO shows typical absorptions of both moieties of the composite. However, the obvious red-shift of the Soret and Q bands of cobalt porphyrin in the composite can be observed clearly, which suggests π - π stacking interactions between the individual components [26].

The crystal structures of the samples are characterized by XRD. Fig. 3 shows the XRD patterns recorded for graphite, GO, CoTMPyP/GO and CoTMPyP/ERGO, respectively. The feature diffraction

peak of exfoliated GO appears at 10.0° (002) with d -spacing of 0.88 nm. For CoTMPyP functionalized GO, the peak is shifted to 8.0° , corresponding to an interlayer spacing of 1.10 nm. The enlarged interlayer spacing reveals that the formation of the CoTMPyP pillared CoTMPyP/GO composite [9]. After the electrochemical reduction process, the as-prepared CoTMPyP/ERGO shows a broad (002) peak centered at around 26.6° , and the peak located at 8.0° disappears, confirming the great reduction of GO and the exfoliation of graphene nanosheets [24].

Fig. 3. XRD patterns of (a) Graphite, (b) exfoliated GO, (c) CoTMPyP/GO and (d) CoTMPyP/ERGO on FTO

CV was also performed to monitor the transformation of GO to ERGO by the electrochemical current for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe. The CVs of CoTMPyP/ERGO, CoTMPyP/GO and bare GC electrodes in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ are given in Fig. S1. A reversible redox couple corresponding to the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe was observed on the bare GC electrode. For the electrode modified with the CoTMPyP/GO hybrid film, the anodic/cathodic peak currents were seriously suppressed because the substantial sp^3 fraction in GO renders the material insulating [24]. However, after electrochemical reduction procedure, the resulting CoTMPyP/ERGO modified electrode exhibited a largely increased redox peak current and a decreased peak separation compared to those of the GC electrode due to an augmenting of conductivity and the reactive edge defects on ERGO.

To gain a deeper insight into the changes in the chemical composition of CoTMPyP/ERGO by the electrochemical reduction, X-ray photoelectron spectroscopic (XPS) measurements were carried out. As shown in Fig. 4a, the C1s spectrum of CoTMPyP/GO shows the characteristic peaks of C-C/C=C (284.8 eV), C-O (286.8 eV) and C=O (288.4 eV), which indicate the presence of epoxide, hydroxyl and carboxyl groups in CoTMPyP/GO composite. The oxygen content in the XPS spectrum of CoTMPyP/ERGO is dramatically decreased, owing to the sp^2 carbon-network recovered by electrochemically reduction of GO sheet (Fig. 4b). In the spectrum of N 1s (Fig. 4c), the main peak at 399.5 eV corresponds to pyrrole-like nitrogen, while the two peaks at 398.2 eV and 400.8 eV correspond to pyridine-like nitrogen [27]. Co 2p XPS spectrum of CoTMPyP/ERGO (Fig. 4d) exhibits two characteristic peaks at 781.1 and 796.5 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ levels. The difference of 15.4 eV between Co $2p_{3/2}$ and $2p_{1/2}$ peaks and the absence of a shakeup satellite signal are clear evidence of the presence of the Co(III) ion [28].

Fig. 4. High-resolution XPS spectra of C 1s of CoTMPyP/GO (a), C 1s (b), N 1s (c) and Co 2p (d) of CoTMPyP/ERGO.

Fig. 5. SEM images of ERGO (a), CoTMPyP/GO (b), SEM images in different magnifications of CoTMPyP/ERGO (c and d). (e-g) Bright-field STEM, dark-field STEM images and elemental mapping of Co element in CoTMPyP/ERGO.

The morphology and structure of ERGO, CoTMPyP/GO and CoTMPyP/ERGO were investigated through SEM and STEM observations. ERGO consists of large, transparent and rippled sheets (Fig. 5a), whereas CoTMPyP/GO shows several folded layers stacked on top of one another (Fig. 5b). As for CoTMPyP/ERGO, abundant crumples with many nano-/micro- sized voids distributed inside and between the graphene sheets are discernible (Fig. 5c and d). The CVs of a CoTMPyP/GO modified GCE in a potential range from 0.0 to -1.5 V are shown in Fig. S2. In the first cycle, the electrochemical reduction of the surface oxygen-containing functional groups of GO in the hybrid film occurs at a more positive potential (-0.85 V) than that of pure GO (-1.0 V). The characteristic peak disappears in the successive scans, demonstrating the quick and irreversible reduction of surface-oxygenated species. At the same time, hydrogen bubbles on the hybrid film modified electrode surface associated with the reduction procedure can be observed (Fig. S3), which does not occur in the case of GO. This implies that hydrogen diffusive release during the electrochemical reduction process may contribute to the

in-situ formation of the crumpled structure for CoTMPyP/ERGO. Such unique nanostructure could support fast mass and electron transport, thus providing the basis for potential application in HER. STEM images and Co map further show that Co porphyrin nanoaggregates[29] with an average size of around 6 nm are homogeneously immobilized on the surface of graphene sheets (Fig. 5e-g).

3.2. Electrochemical performance of the HER catalyst

To investigate the electrocatalytic properties, a well-defined amount of prepared nanocomposite was drop-casted onto the surface of a GC electrode and measured in alkaline media at room temperature. The use of the GC electrode is advantageous because it has a rather large overpotential (vs. RHE) for the HER, and thus, does not interfere with measurements. For comparison, we also prepared a sample of ERGO without any metalloporphyrin, so that we could obtain a good estimation of the origin of the electrocatalytic properties. The results of our measurements are illustrated in Fig. 6.

The electrocatalytic activity of CoTMPyP/ERGO thin film for HER was first evaluated by LSV in alkaline solutions (0.1 and 1 M KOH) at a scan rate of 2 mV s^{-1} , as shown in Fig. 6a. The blank GCE gives no observed current or hydrogen evolution, even when the overpotential was increased to 600 mV. CoTMPyP/ERGO exhibits significantly higher current density and more positive onset potential than that of ERGO in both solutions, indicating the principal contribution of Co porphyrin to HER. In 0.1 M KOH solution, CoTMPyP/ERGO shows a onset potential at 220 mV (vs. RHE) and achieves the current density of 1 mA cm^{-2} at the overpotential of 347 mV, which is much lower than that of the diamine-dioxime cobalt catalyst (590 mV) [28] and [ERGO@CoTMPyP]₇ catalysts (474 mV) [21], demonstrating the high activity of CoTMPyP/ERGO thin film toward HER in alkaline solution. Furthermore, in 1 M KOH solution, the overpotential needed for the current density of 1 mA cm^{-2} is decreased to 315 mV.

Fig. 6. LSV polarization curves for HER on a GC electrode modified with CoTMPyP/ERGO and ERGO catalysts in 0.1 and 1 M KOH at a scan rate of 2 mV s^{-1} . (b) The Tafel curves of CoTMPyP/ERGO and ERGO in 0.1 and 1 M KOH. (c) CV curves in double layer region at scan rates of 5, 10, 15, 20, 25, 30, 35, 40, 45 mV s^{-1} of CoTMPyP/ERGO. (d) The capacitive currents at 0.15 V as a function of scan rate for CoTMPyP/ERGO and ERGO ($\Delta j = j_a - j_c$). (e) Impedance spectra of CoTMPyP/ERGO modified GC electrode in 1 M KOH solution at different applied overpotentials. The inset shows the equivalent circuit. (f) Polarization curves of CoTMPyP/ERGO initially and after 1000 potential cycles in 1 M KOH.

Tafel plot is applied to evaluate the efficiency of the catalytic reaction in alkaline solutions (0.1 and 1 M KOH), which is derived from the polarization curves using the Tafel equation $\eta = b \log(-j) + a$, where η is overpotential, j is the current density and b is the Tafel slope. The Tafel slopes of CoTMPyP/ERGO catalyst (96 mV dec^{-1} in 1 M KOH and 99 mV dec^{-1} in 0.1 M KOH) are lower than those of previously reported CoP/CC (129 mV dec^{-1} in 1 M KOH) [30], commercial Pt/C (109 mV

dec⁻¹ in 1 M KOH) [31] and [ERGO@CoTMPyP]₇ hybrid (116 mV/decade in 0.1 M KOH) [21], implying its favorable HER catalytic kinetics. According to the previous reports [32], the mechanism of HER process in alkaline solution can be regarded as a combination of three basic steps: (1) The electroreduction of water molecules with hydrogen adsorption (Volmer reaction: $M + H_2O + e^- \rightarrow M-H_{ads} + OH^-$), (2) the electrochemical hydrogen desorption (Heyrovsky reaction: $M-H_{ads} + H_2O + e^- \rightarrow M + H_2 + OH^-$), and/or (3) the chemical desorption (Tafel reaction: $2M-H_{ads} \rightarrow 2M + H_2$), where M stands for an metal atom, and H_{ads} represents a H atom absorbed at an active site of the catalyst. The Tafel slopes obtained for CoTMPyP/ERGO are close to the theoretical one for the Volmer-Heyrovsky mechanism (the value equal to 118 mV dec⁻¹).

In addition, as the HER process involves gas-liquid-solid three phases, active surfaces and efficient mass and charge transport properties are preferable for an electrocatalyst. To estimate the effective electrochemically active surface area (ECSA) of CoTMPyP/ERGO, we measured the electric double layer capacitance (C_{dl}) [33, 34]. The CV curves were collected in the region of 0.1–0.2 V, where the current response is only due to the charging/discharging of the double layers (Fig. 6c and Fig. S4). The measured capacitive current densities are plotted as a function of scan rates and shown in Fig. 6d. The linear slope is equivalent to twice of that of C_{dl}. The calculated capacitances of CoTMPyP/ERGO and ERGO are 23.5 and 10 mF cm⁻², respectively. Therefore, CoTMPyP/ERGO modified electrode has an active surface area 2.4 times that of ERGO. Indeed, as observed in SEM and STEM images, the crumpled graphene nanosheets in the CoTMPyP/ERGO hybrid film provide a large surface area for good dispersion of the supported Co porphyrin, favoring the exposure of more active sites for the HER.

Table 1 Equivalent circuit parameters of hydrogen evolution reaction on CoTMPyP/ERGO modified GC electrode in 1 M KOH solution at different overpotentials

Overpotential (V)	R_s ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	Q_1 ($\text{mS cm}^{-2} \text{ s}^n$)	n_1	R_2 ($\Omega \text{ cm}^2$)	Q_2 ($\text{mS cm}^{-2} \text{ s}^n$)	n_2	R_{ct} ($\Omega \text{ cm}^2$)
0.33	8.87	127.5	0.38	0.55	264.4	0.83	1	391.9
0.34	8.98	138.1	0.36	0.56	223	0.87	1	361.1
0.35	8.96	143.6	0.34	0.56	185.6	0.91	1	329.2
0.36	9.07	150.5	0.31	0.57	162.1	0.97	1	312.6

EIS measurements were then employed to further probe the interfacial reactions and electrode kinetics in HER, which was carried out with a frequency range from 100 mHz to 100 kHz. Fig. 6e shows Nyquist plots for the CoTMPyP/ERGO catalyst obtained at different overpotentials in 1 M KOH. All of the Nyquist plots exhibit two semicircles. The first semicircle at medium- and high- frequencies with a diameter (resistance) R_1 is related to hydrogen adsorption. The second one at low frequency with resistance R_2 is assigned to the HER kinetics [35-37]. The impedance responses can be modeled by the equivalent circuit presented in Fig. 6e (inset) where the overall impedance was characterized by a parallel combination of capacitance and resistance of two charge-transfer processes. The total charge-transfer resistance, R_{ct} , equals $R_1 + R_2$. The circuit elements Q_1 , R_1 , Q_2 and R_2 were related to the high and the low frequency capacitive loops, respectively. R_{ct} is related to the electrocatalytic kinetics, and a lower value corresponds to a faster reaction rate. The resultant EIS parameters used to simulate the impedance data are given in Tables 1. It can be seen that the R_{ct} values decrease with increasing overpotentials, which implies that CoTMPyP/ERGO exhibits good electron transfer ability at high potential [38].

To investigate durability under electrocatalytic operation, we conducted continuous CV sweeps between 0 and -0.5 V versus RHE with a scan rate of 100 mV s^{-1} in 1 M KOH for 1000 cycles. As shown in Fig. 3f, the polarization curves of CoTMPyP/ERGO are similar before and after 1000 cycles

and a positive shift of only 7 mV for η to achieve 10 mA cm^{-2} was observed, demonstrating the superior stability of CoTMPyP/ERGO in alkaline condition. The excellent catalytic performance for CoTMPyP functionalized ERGO could be rationalized as follows: (1) The electrostatic interaction as well as π - π stacking provide an intimate contact between them, facilitating flow of electrons from ERGO to CoTMPyP during cathodic polarization; (2) ERGO, as a good conductor of electricity, favors fast electron transport; (3) The crumpled structure with the voids distributed inside and between the graphene sheets not only leads to the exposure of more active sites but also facilitates sufficient transport of reactants and products.

4. Conclusions

In summary, electrostatic self-assembly of Co porphyrin and GO nanosheets under mild condition followed by the electrochemical reduction procedure has been proven as a simple and efficient strategy for preparing crumpled CoTMPyP/ERGO nanocomposite. The obtained nanocomposite was investigated as an active electrocatalyst for efficient HER in 1 M KOH aqueous solution using polarization, CV and impedance measurements. An excellent electrocatalytic activity was observed for CoTMPyP/ERGO, even after 1000 sweep cycles. A Tafel slope of 96 mV dec^{-1} indicated a Volmer-Heyrovsky mechanism for the HER involved, which is among the best records over the metalloporphyrin-based catalysts. It is envisaged that this work may provide a simple route to design a wide range of low-cost and high-performance organic moieties functionalized graphene with potential applications in water splitting and other energy related technologies.

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A facile approach to prepare crumpled CoTMPyP/electrochemically reduced graphene oxide nanohybrid as an efficient electrocatalyst for hydrogen evolution reaction

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ABSTRACT

Elaborate design and synthesis of efficient and stable non-Pt electrocatalysts for some renewable energy related conversion/storage processes is one of the major goals of sustainable chemistry. Herein, we report a facile method to fabricate Co porphyrin functionalized electrochemically reduced graphene oxide (CoTMPyP/ERGO) thin film by direct assembly of oppositely charged tetrakis(N-methylpyridyl) porphyrinato cobalt (CoTMPyP) and GO nanosheets under mild conditions followed by an electrochemical reduction procedure. STEM analysis confirms that CoTMPyP nanoaggregates are homogeneously distributed over the graphene surface. The electrochemical properties of CoTMPyP/ERGO were investigated by cyclic voltammetry, linear sweep voltammetry and electrochemical impedance spectroscopy. The results demonstrate that CoTMPyP/ERGO nanohybrid film can serve as excellent electrocatalyst for hydrogen evolution in alkaline solution with high activity and stability. The intimate contact and efficient electron transfer between CoTMPyP and ERGO, as well as the crumpled structure, contribute to the improvement of the electrocatalytic performance.

Keywords: Co porphyrin; electrochemically reduced graphene oxide; electrocatalysis; hydrogen evolution

1. Introduction

Hydrogen evolution reaction (HER) via electrochemical splitting of water has attracted worldwide attention because it can be realized using renewable energies [1]. Besides, the zero emission of

carbonaceous species from hydrogen utilization makes hydrogen an ideal candidate for the replacement of fossil fuel energy in the future [2]. Pt-group noble metals have proven to be the most efficient electrocatalysts for HER. Unfortunately, the prohibitive cost and scarcity significantly hinders their large scale commercial application [3, 4]. Thus, the exploration of highly active non-precious alternative catalysts has become a main research focus for the practical use of hydrogen.

Cobalt has emerged as an interesting non-noble metal for its catalytic power toward hydrogen evolution, and great efforts have been devoted to developing Co-based macrocyclic complexes as HER catalysts in the past [5-7]. Most of these studies were, however, performed smoothly only in nonaqueous solvents, which greatly limits their application in water-splitting devices. Therefore, a great deal of research has been carried out to develop highly active cobalt complexes which could work efficiently in aqueous solutions. Cobalt porphyrins have also been previously demonstrated to act as efficient photocatalyst for HER [8, 9] and electrocatalysts for the oxygen reduction reaction [10-12] and oxygen evolution reaction [13]; while the exploration of cobalt porphyrins based HER electrocatalysts has received much less attention. Dong *et al.* [14] developed metalloporphyrin-polyoxometalate hybrid films by the layer-by-layer method and investigated their catalytic properties for HER in acid media. Hung *et al.* [15] reported the use of a water-soluble CoTPPS as a stable and active catalyst for HER from neutral H₂O without any organic additives. However, the catalytic activity of these electrocatalysts usually suffers from the lower electrical conductivity and/or limited amount of exposed active sites. It is now well-accepted that two effective strategies to improve the HER performance of electrocatalysts are: (1) the incorporation of catalytic materials with conductive networks; (2) the construction of special structures, such as hollow, porous, or hierarchical architectures [16, 17].

Graphene, a one-atom-thick sheet of sp^2 -bonded carbon atoms in a honeycomb crystal lattice, has been widely investigated recently as a support for HER catalysts due to its huge surface area, excellent electron conductivity and outstanding mechanical strength [18-20]. Wang et al. successfully developed Co porphyrin and graphene multilayer films by using layer-by-layer technique [21]. However, this method involves tedious steps and the electrocatalytic performance of the multilayer films for HER needs to be improved. Thus, the development of a simple and efficient procedure is in demand. Herein, we demonstrate that Co porphyrin and electrochemically reduced graphene oxide hybrid film (CoTMPyP/ERGO) can be fabricated by the direct assembly of CoTMPyP and GO nanosheets followed by an electrochemical reduction procedure. The CoTMPyP/ERGO with abundant crumples ensures the high exposure of Co porphyrin on the high conductive graphene support for electrocatalytic reactions, and exhibits excellent catalytic activity toward HER in alkaline media (Fig. 1).

Fig. 1. Schematic illustration of possible HER process based on CoTMPyP/ERGO.

2. Experimental

2.1. Materials and reagents

Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. GO was prepared by a modified Hummer's method [22]. Free-base porphyrin H_2TMPyP was purchased from TCI. Cobalt porphyrin (CoTMPyP) was prepared through metallation by refluxing H_2TMPyP with $CoCl_2 \cdot 3H_2O$ as described by Hambright et al [23]. All other chemicals were analytical grade and were used as received

from the suppliers without further purification. All aqueous solutions were prepared using ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$, Millipore).

2.2. Preparation of CoTMPyP/GO

A GO aqueous colloidal suspension (0.2 mg mL^{-1}) was prepared by ultrasonically dispersing GO in distilled water. For the preparation of CoTMPyP functionalized graphene oxide (CoTMPyP/GO), 0.5 mg mL^{-1} of CoTMPyP aqueous solution was added with the mass ratio of GO to CoTMPyP (3:1) and stirred vigorously at 50°C for 12 h. The product was purified by centrifugation steps with water. The precipitate was dispersed into water under ultrasonication to form a homogeneous ink at a concentration of 2 mg mL^{-1} .

2.3. Preparation of CoTMPyP/ERGO

The glassy carbon electrodes (GCE, $\phi = 3 \text{ mm}$, CHI) were polished to a mirrorlike surface with 0.3, and $0.05 \text{ }\mu\text{m}$ alumina slurry in turn, and sequentially double-distilled water and anhydrous ethanol, and dried in air naturally. The modification of the working electrode was achieved by drop-casting $8 \text{ }\mu\text{L}$ CoTMPyP/GO dispersion containing 0.05% (w/w) Nafion on the pretreated GCE. Then, CoTMPyP/GO was electrochemically reduced by 30 successive cyclic voltammograms in an electrochemical cell containing a 0.05 M PBS (pH 5) solution over a potential range of 0 to -1.5 V at a scan rate of 50 mV s^{-1} [24]. For comparison purpose, ERGO modified electrode was prepared by drop-casting 2 mg mL^{-1} GO solution on a GCE following an electrochemical reduction procedure.

2.4. Characterization

X-ray diffraction (XRD) was carried out using a Bruker D8 Advance X-ray diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). UV-vis absorption spectra were recorded with a SHIMADZU UV-2501 spectrometer. X-ray photoelectron spectra (XPS) measurements were performed on a Phoibos

100 spectrometer. Field-emission scanning electron microscope (FESEM) and scanning transmission electron microscope (STEM) images were collected on a JSM-6700F Field emission scanning electron microscope operating at 5 kV and JEOL JEM-2100F transmission electron microscope operating at 200 kV, respectively. For FESEM and STEM measurements, CoTMPyP/GO dispersion was dropped onto FTO (Fluorine doped tin oxide) substrates and electrochemically reduced in a similar manner with that on GCE.

2.5. Electrochemical measurements

Electrochemical measurements, including cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed on a CHI 660D electrochemical workstation with a three electrode cell system, in which the modified GCE with a catalyst was employed as working electrode, Pt wire as auxiliary electrode, and Ag/AgCl as reference electrode. The electrochemical impedance spectroscopy (EIS) measurements were obtained on an Autolab electrochemical workstation in a frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 pH + E_{Ag/AgCl}^{\circ}$$

where $E_{Ag/AgCl}^{\circ} = 0.1976$ V at 25 °C.

3. Results and discussion

3.1. Preparation and characterization of CoTMPyP/ERGO

In this work, we developed a facile two-step strategy for the synthesis of CoTMPyP/ERGO hybrid film. In the first step, graphite oxide was dispersed in the deionized water to form GO sheets, which are highly negatively charged because of the ionization of the carboxylic acid and phenolic hydroxyl groups on their edges and surface [25]. When the positively charged CoTMPyP ions were added, the

electrostatic interaction provides a strong driving force for the assembly of GO sheets and CoTMPyP cations. As in situ observed (Fig. 2, inset), the dark brown flocculent precipitation was formed after a certain amount of CoTMPyP solution reacted with GO aqueous dispersion. Additional interactions, such as π - π stacking and van der Waals force between GO and cobalt porphyrin, can improve the stability of the obtained composite [12]. To enhance the conductivity in the HER process, hybrid film was subsequently reduced by electrochemical method. As a result, the CoTMPyP/ERGO composite was obtained.

Fig. 2. UV-vis absorption spectra of (a) CoTMPyP solution (5×10^{-5} M), (b) GO dispersion and (c) CoTMPyP/GO dispersion. Inset: images of CoTMPyP solution (left), GO dispersion (middle), and the corresponding mixture (right).

Fig. 2 shows UV-vis absorption spectra of CoTMPyP, GO and CoTMPyP/GO dispersion. CoTMPyP displays a strong typical Soret band at 432 nm, together with a weak Q band at 542 nm, respectively. In the GO spectrum, a broad peak at around 230 nm corresponds to the π - π^* transition of aromatic C-C bonds and a shoulder at around 300 nm was due to the n - π^* transition of C=O bonds. The UV-vis spectrum of CoTMPyP/GO shows typical absorptions of both moieties of the composite. However, the obvious red-shift of the Soret and Q bands of cobalt porphyrin in the composite can be observed clearly, which suggests π - π stacking interactions between the individual components [26].

The crystal structures of the samples are characterized by XRD. Fig. 3 shows the XRD patterns recorded for graphite, GO, CoTMPyP/GO and CoTMPyP/ERGO, respectively. The feature diffraction peak of exfoliated GO appears at 10.0° (002) with d -spacing of 0.88 nm. For CoTMPyP functionalized GO, the peak is shifted to 8.0° , corresponding to an interlayer spacing of 1.10 nm. The enlarged interlayer spacing reveals that the formation of the CoTMPyP pillared CoTMPyP/GO composite [9]. After the electrochemical reduction process, the as-prepared CoTMPyP/ERGO shows a broad (002) peak centered at around 23.8° , and the intensity of the peak located at 8.0° decreases remarkably, confirming the great reduction of GO and the exfoliation of graphene nanosheets [24].

Fig. 3. XRD patterns of (a) Graphite, (b) exfoliated GO, (c) CoTMPyP/GO and (d) CoTMPyP/ERGO

CV was also performed to monitor the transformation of GO to ERGO by the electrochemical current for the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe. The CVs of CoTMPyP/ERGO, CoTMPyP/GO and bare GC electrodes in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ are given in Fig. S1. A reversible redox couple corresponding to the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ probe was observed on the bare GC electrode. For the electrode modified with the CoTMPyP/GO hybrid film, the anodic/cathodic peak currents were seriously suppressed because the substantial sp^3 fraction in GO renders the material insulating [24]. However, after electrochemical reduction procedure, the resulting CoTMPyP/ERGO modified electrode exhibited

a largely increased redox peak current and a decreased peak separation compared to those of the GC electrode due to an augmenting of conductivity and the reactive edge defects on ERGO.

Fig. 4. High-resolution XPS spectra of C 1s of CoTMPyP/GO (a), C 1s (b), N 1s (c) and Co 2p (d) of CoTMPyP/ERGO.

To gain a deeper insight into the changes in the chemical composition of CoTMPyP/ERGO by the electrochemical reduction, X-ray photoelectron spectroscopic (XPS) measurements were carried out. As shown in Fig. 4a, the C1S spectrum of CoTMPyP/GO shows the characteristic peaks of C-C/C=C (284.8 eV), C-O (286.8 eV) and C=O (288.4 eV), which indicate the presence of epoxide, hydroxyl and carboxyl groups in CoTMPyP/GO composite. The oxygen content in the XPS spectrum of CoTMPyP/ERGO is dramatically decreased, owing to the sp^2 carbon-network recovered by electrochemically reduction of GO sheet (Fig. 4b). In the spectrum of N 1s (Fig. 4c), the main peak at 399.5 eV corresponds to pyrrole-like nitrogen, while the two peaks at 398.2 eV and 400.8 eV correspond to pyridine-like nitrogen [27]. Co 2p XPS spectrum of CoTMPyP/ERGO (Fig. 4d) exhibits two characteristic peaks at 781.1 and 796.5 eV, corresponding to the $2p_{3/2}$ and $2p_{1/2}$ levels. The Co 2p

energy position is very similar to the binding energy of Co(II) in oxide materials [28]. However, the satellite structures are not obvious here. Similar spectrum has been reported for the case of Co porphyrin functionalized carbon nanotube [29] and Co phthalocyanine on Au [30].

Fig. 5. SEM images of ERGO (a), CoTMPyP/GO (b), SEM images in different magnifications of CoTMPyP/ERGO (c and d). (e-g) Bright-field STEM, dark-field STEM images and elemental mapping of Co element in CoTMPyP/ERGO.

The morphology and structure of ERGO, CoTMPyP/GO and CoTMPyP/ERGO were investigated through SEM and STEM observations. ERGO consists of large, transparent and rippled sheets (Fig. 5a), whereas CoTMPyP/GO shows several folded layers stacked on top of one another (Fig. 5b). As for CoTMPyP/ERGO, abundant crumples with many nano-/micro-sized voids distributed inside and between the graphene sheets are discernible (Fig. 5c and d). The CVs of a CoTMPyP/GO modified GCE in a potential range from 0.0 to -1.5 V are shown in Fig. S2. In the first cycle, the electrochemical reduction of the surface oxygen-containing functional groups of GO in the hybrid film occurs at a more positive potential (-0.85 V) than that of pure GO (-1.0 V). The characteristic peak disappears in the successive scans, demonstrating the quick and irreversible reduction of surface-oxygenated species. At

the same time, hydrogen bubbles on the hybrid film modified electrode surface associated with the reduction procedure can be observed (Fig. S3), which does not occur in the case of GO. This implies that hydrogen diffusive release during the electrochemical reduction process may contribute to the *in-situ* formation of the crumpled structure for CoTMPyP/ERGO. Such unique nanostructure could support fast mass and electron transport, thus providing the basis for potential application in HER. STEM images and Co map further show that Co porphyrin nanoaggregates[31] with an average size of around 6 nm are homogeneously immobilized on the surface of graphene sheets (Fig. 5e-g).

3.2. Electrochemical performance of the HER catalyst

To investigate the electrocatalytic properties, a well-defined amount of prepared nanocomposite was drop-casted onto the surface of a GC electrode and measured in alkaline media at room temperature. The use of the GC electrode is advantageous because it has a rather large overpotential (vs. RHE) for the HER, and thus, does not interfere with measurements. For comparison, we also prepared a sample of ERGO without any metalloporphyrin, so that we could obtain a good estimation of the origin of the electrocatalytic properties. The results of our measurements are illustrated in Fig. 6.

The electrocatalytic activity of CoTMPyP/ERGO thin film for HER was first evaluated by LSV in alkaline solutions (0.1 and 1 M KOH) at a scan rate of 2 mV s^{-1} , as shown in Fig. 6a. The blank GCE gives no observed current or hydrogen evolution, even when the overpotential was increased to 600 mV. CoTMPyP/ERGO exhibits significantly higher current density and more positive onset potential than that of ERGO in both solutions, indicating the principal contribution of Co porphyrin to HER. In 0.1 M KOH solution, CoTMPyP/ERGO shows a onset potential at 220 mV (vs. RHE) and achieves the current density of 1 mA cm^{-2} at the overpotential of 347 mV, which is much lower than that of the diamine-dioxime cobalt catalyst (590 mV) [32] and [ERGO@CoTMPyP]₇ catalysts (474 mV) [21],

demonstrating the high activity of CoTMPyP/ERGO thin film toward HER in alkaline solution.

Furthermore, in 1 M KOH solution, the overpotential needed for the current density of 1 mA cm^{-2} is

decreased to 315 mV. The CV curve of CoTMPyP/ERGO modified GCE in 1 M KOH is given in Fig.

S4.

Fig. 6. LSV polarization curves for HER on a GC electrode modified with CoTMPyP/ERGO and ERGO catalysts in 0.1 and 1 M KOH at a scan rate of 2 mV s^{-1} . (b) The Tafel curves of CoTMPyP/ERGO and ERGO in 0.1 and 1 M KOH. (c) CV curves in double layer region at scan rates of 5, 10, 15, 20, 25, 30, 35, 40, 45 mV s^{-1} of CoTMPyP/ERGO. (d) The capacitive currents at 0.15 V as a function of scan rate for CoTMPyP/ERGO and ERGO ($\Delta j = j_a - j_c$). (e) Impedance spectra of CoTMPyP/ERGO modified GC electrode in 1 M KOH solution at different applied overpotentials. The inset shows the equivalent circuit. (f) Polarization curves of CoTMPyP/ERGO initially and after 1000 potential cycles in 1 M KOH.

Tafel plot is applied to evaluate the efficiency of the catalytic reaction in alkaline solutions (0.1 and

1 M KOH), which is derived from the polarization curves using the Tafel equation $\eta = b \log(-j) + a$, where η is overpotential, j is the current density and b is the Tafel slope. The Tafel slopes of CoTMPyP/ERGO catalyst (96 mV dec⁻¹ in 1 M KOH and 99 mV dec⁻¹ in 0.1 M KOH) are lower than those of previously reported CoP/CC (129 mV dec⁻¹ in 1 M KOH) [33], commercial Pt/C (109 mV dec⁻¹ in 1 M KOH) [34] and [ERGO@CoTMPyP]₇ hybrid (116 mV/decade in 0.1 M KOH) [21], implying its favorable HER catalytic kinetics. According to the previous reports [35], the mechanism of HER process in alkaline solution can be regarded as a combination of three basic steps: (1) The electroreduction of water molecules with hydrogen adsorption (Volmer reaction: $M + H_2O + e^- \rightarrow M-H_{ads} + OH^-$), (2) the electrochemical hydrogen desorption (Heyrovsky reaction: $M-H_{ads} + H_2O + e^- \rightarrow M + H_2 + OH^-$), and/or (3) the chemical desorption (Tafel reaction: $2M-H_{ads} \rightarrow 2M + H_2$), where M stands for an metal atom, and H_{ads} represents a H atom absorbed at an active site of the catalyst. The Tafel slopes obtained for CoTMPyP/ERGO are close to the theoretical one for the Volmer-Heyrovsky mechanism (the value equal to 118 mV dec⁻¹).

In addition, as the HER process involves gas-liquid-solid three phases, active surfaces and efficient mass and charge transport properties are preferable for an electrocatalyst. To estimate the effective electrochemically active surface area (ECSA) of CoTMPyP/ERGO, we measured the electric double layer capacitance (C_{dl}) [36, 37]. The CV curves were collected in the region of 0.1–0.2 V, where the current response is only due to the charging/discharging of the double layers (Fig. 6c and Fig. S5). The measured capacitive current densities are plotted as a function of scan rates and shown in Fig. 6d. The linear slope is equivalent to twice of that of C_{dl} . The calculated capacitances of CoTMPyP/ERGO and ERGO are 23.5 and 10 mF cm⁻², respectively. Therefore, CoTMPyP/ERGO modified electrode has an active surface area 2.4 times that of ERGO. Indeed, as observed in SEM and STEM images, the

crumpled graphene nanosheets in the CoTMPyP/ERGO hybrid film provide a large surface area for good dispersion of the supported Co porphyrin, favoring the exposure of more active sites for the HER.

Table 1 Equivalent circuit parameters of hydrogen evolution reaction on CoTMPyP/ERGO modified GC electrode in 1 M KOH solution at different overpotentials

Overpotential (V)	R_s ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	Q_1 ($\text{mS cm}^{-2} \text{ s}^n$)	n_1	R_2 ($\Omega \text{ cm}^2$)	Q_2 ($\text{mS cm}^{-2} \text{ s}^n$)	n_2	R_{ct} ($\Omega \text{ cm}^2$)
0.33	8.87	127.5	0.38	0.55	264.4	0.83	1	391.9
0.34	8.98	138.1	0.36	0.56	223	0.87	1	361.1
0.35	8.96	143.6	0.34	0.56	185.6	0.91	1	329.2
0.36	9.07	150.5	0.31	0.57	162.1	0.97	1	312.6

EIS measurements were then employed to further probe the interfacial reactions and electrode kinetics in HER, which was carried out with a frequency range from 100 mHz to 100 kHz. Fig. 6e shows Nyquist plots for the CoTMPyP/ERGO catalyst obtained at different overpotentials in 1 M KOH. All of the Nyquist plots exhibit two semicircles. The first semicircle at medium- and high- frequencies with a diameter (resistance) R_1 is related to hydrogen adsorption. The second one at low frequency with resistance R_2 is assigned to the HER kinetics [38-40]. The impedance responses can be modeled by the equivalent circuit presented in Fig. 6e (inset) where the overall impedance was characterized by a parallel combination of capacitance and resistance of two charge-transfer processes. The total charge-transfer resistance, R_{ct} , equals $R_1 + R_2$. The circuit elements Q_1 , R_1 , Q_2 and R_2 were related to the high and the low frequency capacitive loops, respectively. R_{ct} is related to the electrocatalytic kinetics, and a lower value corresponds to a faster reaction rate. The resultant EIS parameters used to simulate the impedance data are given in Tables 1. It can be seen that the R_{ct} values decrease with increasing overpotentials, which implies that CoTMPyP/ERGO exhibits good electron transfer ability at high potential [41].

To investigate durability under electrocatalytic operation, we conducted continuous CV sweeps

between 0 and -0.5 V versus RHE with a scan rate of 100 mV s^{-1} in 1 M KOH for 1000 cycles. As shown in Fig. 6f, the polarization curves of CoTMPyP/ERGO are similar before and after 1000 cycles and a positive shift of only 7 mV for η to achieve 10 mA cm^{-2} was observed, demonstrating the superior stability of CoTMPyP/ERGO in alkaline condition. The excellent catalytic performance for CoTMPyP functionalized ERGO could be rationalized as follows: (1) CoTMPyP plays a critical role in the hybrid film activity for HER, where Co-N₄ is the active center [15, 21]; (2) The electrostatic interaction as well as π - π stacking provide an intimate contact between them, facilitating flow of electrons from ERGO to CoTMPyP during cathodic polarization; (3) ERGO, as a good conductor of electricity, favors fast electron transport; (4) The crumpled structure with the voids distributed inside and between the graphene sheets not only leads to the exposure of more active sites but also facilitates sufficient transport of reactants and products.

4. Conclusions

In summary, electrostatic self-assembly of Co porphyrin and GO nanosheets under mild condition followed by the electrochemical reduction procedure has been proven as a simple and efficient strategy for preparing crumpled CoTMPyP/ERGO nanocomposite. The obtained nanocomposite was investigated as an active electrocatalyst for efficient HER in 1 M KOH aqueous solution using polarization, CV and impedance measurements. An excellent electrocatalytic activity was observed for CoTMPyP/ERGO, even after 1000 sweep cycles. A Tafel slope of 96 mV dec^{-1} indicated a Volmer-Heyrovsky mechanism for the HER involved, which is among the best records over the metalloporphyrin-based catalysts. It is envisaged that this work may provide a simple route to design a wide range of low-cost and high-performance organic moieties functionalized graphene with potential applications in water splitting and other energy related technologies.

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