



Iron tetrasulfophthalocyanine functionalized graphene nanosheets for oxygen reduction reaction in alkaline media



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ABSTRACT

A Fe-based macromolecule composite was synthesized by functionalizing graphene nanosheets (GNs) with iron tetrasulfophthalocyanine (FeTSPc), a non-noble electrocatalyst for oxygen reduction reaction (ORR) in alkaline media in a simple and greener way. Utilizing GNs as a support can avoid FeTSPc being washed away from the electrode surface and catalyze ORR in alkaline media. The predominant properties of GNs not only make Fe center in the N4-ring protrude to serve as a catalyst, but also increase the active sites, resulting in excellent ORR catalytic activity in alkaline electrolytes. Conversely, by taking advantage of the excellent solubility of FeTSPc which helps to prevent the aggregation of GNs, the composite (demonstrated as GNs-FeTSPc) showed a long-term stability in alkaline aqueous solution and maintained the catalytic activity. Better yet, the composite GNs-FeTSPc is insensitive to CO due to the special structure of FeTSPc and can facilitate ORR with a direct four-electron process which was demonstrated by the rotating disc electrode (RDE) results. Clearly, our nanohybrid catalysts show great potential in the large-scale practical application of alkaline fuel cells (AFCs).

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1. Introduction

Electrocatalytic oxygen reduction reaction (ORR) has attracted considerable attention due to its slow kinetics and key role in controlling the performance of fuel cells [1–3]. Platinum (Pt) is the most commonly used catalyst to facilitate ORR with a direct four-electron process [4], however, it is charged for several drawbacks, including high cost, susceptibility to time-dependent drift and CO deactivation [5–7]. In contrast, non-precious metal catalysts (NPMCs) have shown great promise in virtue of lower cost, more abundant supply and relatively better activity [8–11]. Inspired by these characteristics, researchers are very interested in applying NPMCs in ORR investigations since the work researched by Jasinski on metal phthalocyanines in 1960s [12]. Nowadays, most research work involving NPMCs focuses on nitrogen-coordinated iron in a carbon matrix (referred to as Fe/N/C) [13–15], especially iron (II) phthalocyanine (FePc), which has been fixed on a variety of carbon materials for ORR, has drawn particular attention [16–20]. However, the synthesis of these catalysts generally requires high temperature pyrolysis, special equipment or organic solution [13–15,21–26], resulting in difficulty of mass production. Therefore, exploring a more convenient, efficient and greener method to

fabricate low-cost catalysts based on the transition metal macrocycles is imperative.

Graphene [27–29], as a new material with high specific surface area for metal-catalyst support, extraordinary electronic transport properties, good mechanical properties, superb thermal stability, especially easy preparation and low production cost in mass production, shows extraordinary advantages for the application in fuel cells under both ambient and harsh conditions. Meanwhile, iron tetrasulfophthalocyanine (FeTSPc), another transition-metal phthalocyanine, shows the potential to catalyze ORR effectively in alkaline media. However, the extremely good water-solubility of FeTSPc makes it too easy to be washed away from electrodes surface which has been a long-stand setback and has limited its fundamental studies and further applications on heterogeneous electrocatalysis in aqueous environment [30].

Herein, to overcome this problem without the help from high temperature pyrolysis or organic solvent, we coated FeTSPc onto GNs under ultrasonication to successfully avoid FeTSPc being washed away in an aqueous solution. By taking advantage of strong π - π interaction we have formed a Fe-based nanocomposite catalyst (demonstrated as GNs-FeTSPc) with GNs and FeTSPc to serve as the essential carbon content in the catalyst precursor and matrix of Fe and N which are identified as the factors required for producing active Fe-based NPMCs for ORR [13–15,23,24]. Compared to the synthesis methods reported previously, this is a simple and green way which could be used for mass production. Moreover, utilizing

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the hydrophilicity and special structure of FeTSPc, the as-formed GNs-FeTSPc catalyst not only has a long-term stability towards alkaline aqueous solution with no aggregations of GNs but also possesses better resistance against CO and methanol crossover. By getting helping hands from each other, the catalyst GNs-FeTSPc can facilitate ORR with a direct four-electron process in alkaline media which has not been reported yet.

2. Experimental

2.1. Chemicals and materials

FeTSPc and tetrasulfophthalocyanine (TSPc) were purchased from Sigma-Aldrich. GNs was synthesized by the chemical oxidation-reduction treatment of graphite [31,32]. In a typical procedure, 5 g of graphite was slowly added into a stirred mixture of concentrated sulfuric (87.5 mL) and nitric acid (45 mL) in an ice-water bath. Subsequently, 55 g of KClO_3 was carefully added into the mixture. All the processes were carried out in the fume hood. The mixture was kept stirring for 4 days at room temperature. Then 4 L of water was added to the slurry and the mixture was filtered to obtain graphite oxide. After dried at 80°C , graphene oxide was exfoliated in de-ionized water by ultrasonic treatment for 2 hours (h) to form a colloidal graphene oxide suspension. Finally, the graphene oxide suspension reacted with hydrazine monohydrate ($1\ \mu\text{L}$: 3 mg GNs oxide) for 24 h at 80°C to obtain the GNs. Pt/C (40 wt %) were purchased from Johnson Matthey Co. Potassium hydroxide was purchased from Chemical Reagent Co. Ltd. (Ruoyang, China). N_2 (99.5%), O_2 (99.2%) and CO (99.9%) and flow meter ($10\text{--}100\ \text{ml}\ \text{min}^{-1}$) were purchased from local gas company. All the materials and chemicals were at least analytical grade and used as received. Purified water ($0.07\ \mu\text{S}/\text{cm}$) was used throughout.

2.2. Apparatus and measurements

Scanning electron microscope (SEM) characterization was performed with a LEO 1530 VP (LEO, Germany) at 15 kV, and for the SEM study, the nanomaterials were directly pasted onto the ITO electrode through conductive paste in their power forms. Raman spectra were obtained on a LabRAM Aramis (HJY, France) with the excitation wavelength of 632.8 nm. Fourier transform infrared spectroscopy (FTIR) measurements were performed on Vector 33 (Bruker, Germany). X-ray photoelectron spectroscopic (XPS) measurements were performed with a Kratos AXIS Ultra (DLD). UV-vis absorption spectra were recorded with a Hitachi 3010 spectrometer (Japan). Photographs were taken with a Canon IXUS105 digital camera. Electrochemical measurements were performed using a computer-controlled potentiostat (CHI 660 C, CH Instrument, USA) with a typical three-electrode cell. Pt wire was used as counter electrode. All potentials were referred to a 3.0 M KCl Ag/AgCl electrode. GC electrode was polished with 0.3- and 0.05- μm alumina slurry on a polishing cloth, cleaned under bath sonication for 5 min in acetone and distilled water, and thoroughly rinsed with doubly distilled water.

2.3. Preparation of electrodes

The GNs-FeTSPc nanocomposite used for the experiment was prepared as the previous method [33,34]. Typically, a mixture consisting of 5 mg GNs and 1 mg FeTSPc in 5 mL distilled water was suspended under ultrasonication for 8 h at room temperature. The resulting suspension was filtered with a Millipore porous filter (0.45 μm , Millipore). The obtained sample was first thoroughly rinsed with distilled water to remove the non-adsorbed FeTSPc and then dried at 60°C overnight to obtain the GNs-FeTSPc nanocomposite. The nanocomposite was redispersed in water to give a

homogeneous suspension ($2\ \text{mg}\ \text{mL}^{-1}$) under ultrasonication for subsequent experiments. The same procedure was used to prepare GNs-TSPc. About $4\ \mu\text{L}$ of the prepared suspension was dropped onto glassy carbon electrodes (GC, 3-mm diameter) to obtain the modified electrodes for electrochemical measurements. The same procedures were applied to prepare GNs-TSPc/GC, GNs/GC and Pt-C/GC and all the current density were normalized by the GC electrode's geometric area. Especially, for the experiments of the crossover, poisoning effects and long-term durability, the GNs-FeTSPc/GC and Pt-C/GC were overcoated with Nafion (0.5% in ethanol).

3. Results and discussion

The noncovalent functionalization of GNs with FeTSPc via π - π stacking interaction is illustrated in Scheme 1. Typically, the functionalization can be achieved by ultrasonic treatment of GNs and FeTSPc (structure shown in Fig. 1A) aqueous solution, and then dried at 80°C for 3 h (see methods information). As shown in Fig. 1B, GNs obtained by the chemical oxidation-reduction treatment of graphite is a translucent film which suggests the sample comprises of very thin graphene layers. This is also proved by the Raman spectra (Fig. 1B, inset) of which the D band around $1288\ \text{cm}^{-1}$ corresponding to sp^2 domains isolated by oxidized carbon atoms, and G band around $1536\ \text{cm}^{-1}$ is attributed to first order scattering of the E_{2g} mode, a characteristic band of crystalline graphite. The 2D band of graphene in Raman spectra is sensitive to stacking of graphene layers. For single-layer graphene, the 2D band centers appear at $2641\ \text{cm}^{-1}$ (at 633 nm), when for multilayer graphene the 2D band appears as a broadened peak with upshift to higher wavenumbers [35–39]. The 2D band of GNs indicated in Fig. 1B is centered on $2642\ \text{cm}^{-1}$ corresponding to the single-layer characteristic of the synthesized sheets. However, a peak broadening along with a tail toward the higher wavenumbers is observed for the GNs, indicating a slight aggregation of the GNs. Meanwhile, as a Fe heterocyclic molecule containing N4-chelate structure, FeTSPc bears fairly uniform electron density distribution and abundant π -conjugation system. Therefore, it can be tethered to GNs surface via π - π stacking interaction readily [40]. Unlike the blocky morphology of FeTSPc (Fig. 1C), GNs-FeTSPc nanocomposites (Fig. 1D) is composed of pieces of GNs combined with tiny FeTSPc particles (Fig. 1D, inset) and thus has a rougher surface which indicates that FeTSPc nanoparticles have been obviously grown on the surface of GNs and GNs-FeTSPc nanohybrids indeed formed [33,34].

UV-vis spectroscopy of FeTSPc aqueous solution (0.1 mM) before (short dot) and after (solid) addition of GNs (0.2 mg) followed by ultrasonic treatment for 8 h at room temperature was displayed in Fig. 2. The peak at 632 nm (Q band of phthalocyanine) corresponds to the π - π transition of the tetrasulfophthalocyanine ligand, characteristic of FeTSPc monomeric species whereas the shoulder at 578 nm (Q band) corresponds to the electronic absorption of dimeric species of FeTSPc. The peak at 326 nm was the characteristic B band of FeTSPc at lower wavelengths [41,42]. The peak absorbance at 632 nm decreases obviously after sonication (solid), because part of FeTSPc has been adsorbed onto GNs. In addition, the π - π stacking between FeTSPc and GNs makes the electron cloud overlap and the scope of conjugate expand, resulting in a red shift in the π - π band [43]. Unlike the insoluble pristine GNs due to strong π - π stacking and van der Waals interaction, the GNs-FeTSPc nanocomposites exhibit excellent water solubility and can be stored in the dark for weeks without precipitation (Fig. 2, inset, C). The excellent dispersion property also indicates the interaction between GNs and FeTSPc and makes it available either to print, brush or spray-coat the catalyst onto the electrode of fuel cells.

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