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Cobalt tetramethoxyphenylporphyrin functionalized graphene for oxygen reduction reaction in neutral media

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ABSTRACT

Graphene was modified with cobalt tetramethoxyphenylporphyrin (CoTPP) by an ultrasonic treatment and was used as a non-noble catalyst for oxygen reduction reaction (ORR) in neutral media. The resulting CoTPP–graphene was characterized by scanning electron microscopy (SEM), UV–vis spectroscopy, Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy, which confirmed that CoTPP could be strongly supported onto graphene through π–π interaction. The electrochemical activity of CoTPP–graphene towards ORR was evaluated by cyclic voltammogram (CV). The CV results suggested the excellent catalytic activity of CoTPP–graphene in neutral electrolytes. Compared to electrodes modified with the mechanical mixture of graphene and CoTPP (N-CoTPP–graphene), the peak potential of ORR detected at the CoTPP–graphene electrode was more positive and the peak current was much higher, implying the necessary of ultrasonic and the enhanced activity of CoTPP after adsorbing on graphene surface. Thus, the CoTPP–graphene can be used as a good catalyst for ORR.

1. Introduction

Due to its high oxidation potential, low cost and clean reaction product, oxygen is an ideal electron acceptor in the fuel cells [1]. However, the poor kinetics of the oxygen reduction reaction (ORR) hinders its application at neutral media. Platinum (Pt) has been used extensively as the ORR catalyst, but there are several limitations such as high cost, scarcity and possible poisoning by the substrate. Thus, it is highly necessary to search for non-Pt ORR catalysts. Transition metal macrocycle compounds, such as phthalocyanines and porphyrins, have been researched widely as the most promising catalysts to replace Pt [2–5]. Zhang et al. reported that carbon black EC 300J (KB) modified with cobalt tetramethoxyphenylporphyrin (CoTPP) pyrolyzed at 900 °C had excellent catalytic performance for ORR [6]. Herrmann and co-workers found that CoTPP pyrolyzed with sulfur could be used as an electrocatalyst for ORR in acid media [7]. However, in this traditional way, these compounds need to be heated in inert atmosphere to improve the catalytic activity and stability, which may increase the cost and the complexity of the operation.

Graphene exhibits fascinating physical and chemical properties, such as excellent conductivity, high surface area and extraordinary electrocatalytic activities etc. [8,9]. Therefore, it has been used as a suitable supporting material for catalyst [10–12]. However, due to the van der Waals interaction [13], graphene tends to aggregate or even restack to form graphite, which may adversely affect its catalytic activity. To prevent the aggregation of graphene, CoTPP, an aromatic macromolecule with nitrogen atoms, which contains rich π electrons, can be combined with graphene though π–π conjugation. In addition, the resulting CoTPP–graphene compound possesses C, N and Co, so it might have good catalytic activity for ORR.

In this study, graphene was used as the supporting material and combined with CoTPP in a simple method in which no heating was required. The prepared CoTPP–graphene was used as a catalyst for ORR, and the catalytic activity was investigated. The experimental results indicated that the CoTPP–graphene might be a potential Pt alternative catalyst for ORR in neutral media.

2. Experimental section

Chemicals and materials: Nafion (5%), CoTPP and graphite were purchased from Sigma-Aldrich. The rest of the chemicals were all purchased from local chemical agents.

Synthesis of graphene and CoTPP–graphene: Graphene was prepared by a chemical oxidation method as previously described [14]. First, 5 g of graphite was slowly added into a mixture of concentrated sulfuric (87.5 mL) and nitric acid (45 mL) under

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continuous stirring in an ice-water bath. Then, 55 g of $KClO_3$ was carefully added into the mixture. The mixture was kept stirring for 96 h to obtain graphite oxide. After filtration and drying, graphene oxide was exfoliated in water by ultrasonic treatment for 2 h to form graphene oxide suspension. Finally, the graphene oxide suspension was reduced by hydrazine monohydrate at 80 °C for 24 h to obtain the graphene sheets.

The CoTPP–graphene catalyst was prepared as follows. 10 mg of CoTPP was first dissolved in 10 mL N,N-Dimethylformamide (DMF). Then 30 mg of graphene was dispersed in the mixture.

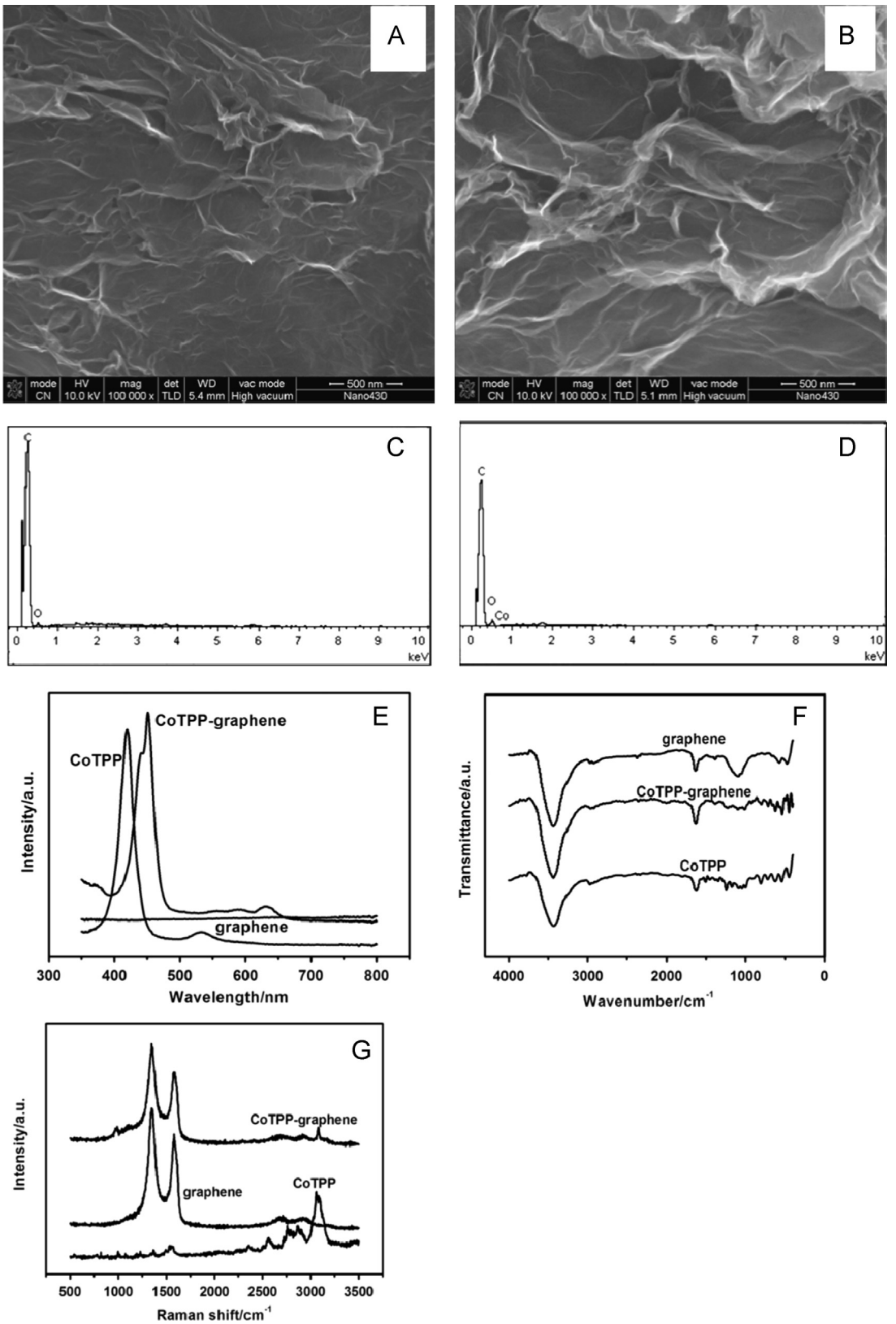

Fig. 1. SEM images of the graphene (A) and CoTPP–graphene (B). EDS images of the graphene (C) and CoTPP–graphene (D). UV–vis (E), FTIR (F) and Raman spectra (G) of graphene, CoTPP and CoTPP–graphene.