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New Electro-Fenton Gas Diffusion Cathode based on Nitrogen-doped Graphene@Carbon Nanotube Composite Materials

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ABSTRACT

For the development of a highly active and energy-effective electro-Fenton process, a novel nitrogen-doped graphene@carbon nanotube composite material (N-G@CNT) is prepared, characterized, investigated for the oxygen reduction reaction (ORR), and employed for dimethyl phthalate (DMP) degradation in aqueous solution. It is found that N-G@CNT's ORR activity towards H_2O_2 production is significantly improved in terms of increased current density and more positive onset potential. Moreover, −0.2 V (*vs.* SCE) is the lowest cathodic potential, to our best knowledge, in which DMP degrades over N-G@CNT GDE (*Gas Diffusion Electrode*) more effectively than over: i) graphite GDE or ii) graphene GDE or iii) CNT GDE. The apparent rate constant of DMP degradation is found to be 0.0322 min^{-1}, about 14, 19, and 54 times higher than those measured on the above three types of GDEs, respectively. It is also found that, at the lower potential (−0.2 V), the energy consumption (EC) for the half-life time degradation of DMP over the studied GDEs, is as follows (in $J\,mg^{-1}$): N-G@CNT = 2.56 < graphite = 10.61 < graphene = 12.23 < CNT = 38.35. The lower onset potential could be attributed to both the bridge between graphene and CNT and the nitrogen doping. The as-prepared N-G@CNT exhibits high activity and desirable stability, and represents a potential candidate material as electro-Fenton cathode for energy-effective wastewater treatment.

1. Introduction

Among various *advanced oxidation processes* (AOPs), *electro-Fenton* (EF) process is an effective technique for degrading persistent organic pollutants, which are resistant to biological processes in the wastewater treatment [1–6]. It is based on the continuous in-situ electrochemical generation of H_2O_2 in acidic solution through 2-electron process of *oxygen reduction reaction* (ORR) at the cathode (Eq. (1)) [7]. Meanwhile, Fe^{2+} is added into the system to react with the generated H_2O_2 for hydroxyl radicals ($^{\bullet}OH$) production via Fenton reaction (Eq. (2)) [8]. The $^{\bullet}OH$ radical, as a non-selective oxidant reagent for destructing organic contaminants, has a high standard electrode potential (2.80 V *vs.* SHE (*standard hydrogen electrode*)) and it is the second strongest oxidant species, just next to fluorine (2.87 V *vs.* SHE) [9].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \; 0.695\,V\ (vs.\ SHE) \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \tag{2}$$

Taking into consideration of Eqs. (1) and (2), H_2O_2 generation via ORR at the cathode (Eq. (1)) plays an important role in the EF process [1]. As it is known, the electrocatalytic mechanism and kinetics of ORR is strongly dependent on the electrode materials. Accordingly, the efficiency of H_2O_2 generation is directly related to the types and structures of the cathode materials. At present, the investigated cathodes for EF system are mainly made of various carbonaceous materials including graphite [10], carbon felt [11], graphite felt [12], carbon sponge [13], activated carbon fiber [14], carbon@PTFE (*Polytetrafluoroethylene*, PTFE) composite *gas diffusion cathode* (GDE) [15–17], and so on.

In carbon@PTFE composite GDEs, PTFE serves to bind the carbon particles into a cohesive layer and impart some hydrophobic characteristics. GDEs have a thin and porous structure favoring the improvement of O_2 mass transfer, leading to a fast O_2 reduction and to high accumulation concentration of H_2O_2. Consequently, the

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EF system using GDEs could exhibit better performance for the degradation of organic contaminants in wastewater treatment [1].

For the preparation of carbon@PTFE GDEs, various carbon materials have been investigated, including graphite [18], mesoporous carbon [19], carbon aerogel [20], and carbon nanotubes (CNT) [21], and so on. The electrochemical active surface area and the oxygen mass transfer to the cathode electrode could be further improved by exploiting the structure properties of carbon materials. However, due to the limitation of the intrinsic catalytic activity of traditional carbonaceous materials, the overpotential for ORR remains high, and thus the cathode can only work at relatively negative applied potentials (from −0.5 V to −1.2 V (*vs.* SCE)) [18,22–24]. This high applied cathode potential could result in a big cell voltage of the EF system and at the same time it could induce the side reaction of hydrogen evolution, leading to a low current efficiency [25,26]. Consequently, it is beneficial for decreasing the *energy consumption* (EC) of EF system – and thus enhancing its operation economy and the ORR catalytic activity, lowering the overpotential of the cathode. In this way the cell voltage will also be decreased.

Recently, it has been reported that *nitrogen doped graphene* (N-G) possesses high ORR catalytic activity, attracting also much attention for ORR electrocatalysis for fuel cells applications [27–31]. Qu et al. [32] synthesized N-G by chemical vapor deposition of methane in the presence of ammonia. The resultant N-G was adopted as the ORR cathode, with a much higher electrocatalytic activity, long-term operation stability, and good tolerance to fuel crossover effect. Geng et al. [33] synthesized N-G material using heat treatment and found that its electrocatalytic activity and durability for ORR was comparable and even better than that of the commercial Pt/C. Moreover, in order to further enhance the electrocatalytic performance, composite materials containing graphene and CNT have been synthesized [34–37].

The CNT between graphene nanosheets not only prevents graphene from restacking and increases basal spacing, but also bridges the defects for electron transfer and improves the electrical conductivity [38]. In the field of ORR, Yu et al. [39] reported the synthesis of bridged graphene and CNT to obtain the G@CNT composite materials with microscopic three-dimensional structure. These materials possessed higher electrochemical surface area and thus they favored the ORR in fuel cells. However, to our best knowledge, no investigations have been devoted to the performance of *nitrogen-doped graphene@CNT* (N-G@CNT) composite materials as cathodes for an efficient EF process.

In the present investigation, we focused on the fabrication and characterization of a N-G@CNT composite material based GDE. A N-G@CNT composite (as active material) was synthesized through an hydrothermal method and together with PTFE (as binder and hydrophobic agent) were used for the preparation of the GDE. The chemical composition and the structure of N-G@CNT were studied, and its electrocatalytic activity toward the ORR in EF system was investigated. Herein, DMP was used as a model substrate to evaluate the performance of EF process using N-G@CNT GDE in terms of reaction kinetics and energy efficiency.

It is well known that, *dimethyl phthalate* (DMP) – a representative of di-alkyl phthalate esters – is widely used as an indispensable additive of plastics to increase the flexibility. The annual world production of plastics is estimated to be around 100 million tons. As a result, a great amount of DMP is drained into the aquatic environment through the disposal of manufacturing wastewater. DMP belongs to the endocrine-disrupting chemicals, whose ubiquity in the environment has brought a great concern to the public and environmental researchers. DMP has been listed as one of the priority pollutants in many countries and has been used in rapid performance assessment of some AOPs including EF reactions [40].

2. Experimental

2.1. Preparation of N-G@CNT

The N-G@CNT was obtained through the hydrothermal process in ammonia aqueous solution, which is schematically illustrated in Fig. 1 and described in details below [32]. The CNTs were provided with oxygen-containing functional groups through oxidation. CNTs (0.5000 g) and $NaNO_3$ (0.3750 g) were mixed together and then 15.0 mL H_2SO_4 (98.0 wt%) was slowly added with magnetic stirring. After that, 1.0000 g $KMnO_4$ powder was added into the above solution within 0.5 h. After stirring for 24 h, 3.0 mL H_2O_2 (30 wt%) and 50.0 mL deionized water were added. After stirring for another 30 min, the product was filtered, washed with deionized water three times and dried in a vacuum oven at 80 °C for 12 h. Graphene was prepared by chemical oxidation and exfoliation of natural graphite under acidic conditions according to Hammer's method [41]. To prepare N-G@CNT, the above treated CNT (21.0 mg) and graphene (30.0 mg) were added into 20.0 mL deionized water with magnetic stirring. After that, 0.5 mL ammonia (25 wt %) was gradually added into the above suspension, which was then transferred into an autoclave for hydrothermal process at 180 °C for 12 h. The solid product was obtained by centrifugation, washed with water and ethanol, and then dried at 80 °C for 12 h in a vacuum oven. For comparison, the composite G@CNT was also prepared through the same preparation process as that of N-G@CNT except that ammonia was not introduced.

2.2. Physico-chemical characterization of N-G@CNT

The morphology of the N-G@CNT was obtained by *transmission electron microscopy* (TEM) (Tecnai G2 spirit, FEI, Holland) operating

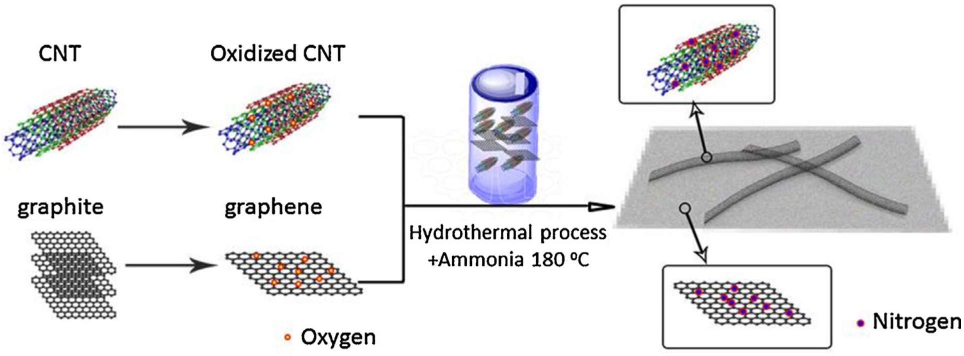

Fig. 1. Schematic illustration for the preparation of N-G@CNT composites.