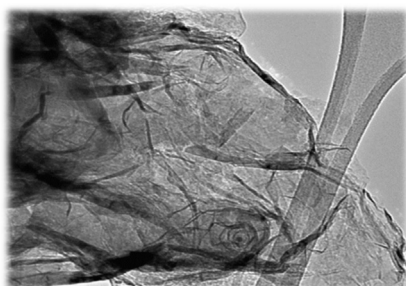
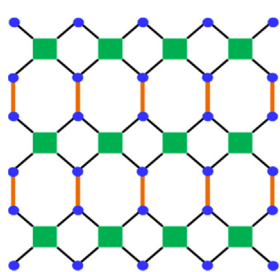


Regular Article

Controllable synthesis of carbon nanosheets derived from oxidative polymerisation of *m*-phenylenediamineLiyuan Zhang^a, Liyuan Chai^b, Mengran Wang^b, Yuekun Lai^{c,d}, Yanqing Lai^b, Xiaoyan Li^{a,*}^a Environmental Engineering Research Centre, Department of Civil Engineering, The University of Hong Kong, Hong Kong, China^b School of Metallurgy and Environment, Central South University, Changsha 410083, China^c College of Chemical Engineering, Fuzhou University^d College of Textile and Clothing Engineering, Soochow University, Suzhou 215006, China

GRAPHICAL ABSTRACT

A sustainable synthesis of carbon nanosheets is achieved by Fe³⁺-*m*-phenylenediamine redox reaction and coordination followed by a carbonisation. The porosity of the carbon nanosheets can be tuned by the solvent composition.



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ABSTRACT

Synthesis of high-quality carbon nanosheets with superior physicochemical properties is of particular importance for environmental and catalytic applications. In this research, carbon nanosheets with tunable porosity were successfully synthesized using two-dimensional (2D) poly(*m*-phenylenediamine) (PmPD) as precursor. The flat polymer precursor was acquired by oxidative polymerisation of *m*-phenylenediamine coupled with iron ions coordination, which confined an anisotropic growth of polymer within the 2D directions. Moreover, the addition of H₂O after the polymerisation is able to indirectly regulate the porosity of the carbon nanosheets. The carbon nanosheets with controllable porosity realize comparable electrocatalytic activity for oxygen reduction reaction as compared with commercial Pt/C, indicative of great potential to serve as noble metals candidates in the application of zinc/air batteries.

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1. Introduction

Graphene has been a hot research topic because of its outstanding mechanical, optical, electronic and thermal properties [1–4].

Meanwhile, analogues of graphene (or carbon nanosheets) have also attracted increasing attention owing to their relatively low-cost synthesis [5–8]. To date, template methods (e.g., based on graphene oxide, C₃N₄, FeCl₃, boron oxide) [9–14], molten salt methods [15–23], chemical vapour deposition [24], blowing processes [25,26], organic salt carbonisation [27–29] and several other strategies [30–39] have been developed to the preparation of

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carbon nanosheets. Based on these developments, the prospect of large-scale production of carbon nanosheets has become feasible. The current focus is now gradually moving towards the regulation of texture properties (e.g., porosity) to manipulate the activity of carbon nanosheets, for which much more effort is required to achieve breakthroughs [26,40,41].

Nitrogen-containing conjugated polymers (NCPs) are multifunctional organic materials that have been applied in a variety of areas such as energy storage, adsorption and catalysis [42–48]. They are also ideal sources of carbon nanostructures owing to their high char yield [44,49]. In particular, polypyrrole, polyaniline, poly(phenylenediamine)s, poly(naphthalenediamine)s and their derivatives are promising candidates [50–55]. In general, the morphology of NCPs hardly changes after carbonisation [44], and it is therefore feasible to fabricate carbon nanosheets by tuning the NCP morphology. However, the synthesis of thin NCP nanostructures (e.g., nanosheets, nanobelts) without hard or soft templates remains challenging owing to the strongly disordered assembly of rigid macromolecular chains inducing isotropic polymer growth [56,57]. In addition, the existing methods for porosity regulation of NCP-derived carbon are ineffective. These challenges make necessary the novel synthesis described herein.

In this research, we developed a novel method to synthesise carbon nanosheets using 2D poly(*m*-phenylenediamine) (PmPD) as the carbon source. The flat PmPD was prepared via Fe³⁺-monomer redox reaction and Fe^{2+/3+}-PmPD coordination. This method does not require any templates (*Note*: the carbon source itself possesses sheet-like morphology), and the porosity of the resulting carbon nanosheets can be tuned indirectly by adjusting the solvent composition. Besides, *m*-phenylenediamine is of the lowest price and risk amongst the three phenylenediamines (*Note* S1) and PmPD is advantageous in production yield [44]. Moreover, polymerisation of *m*-phenylenediamine can be well controlled to manipulate the structure and morphology of the products [57–60].

2. Experimental section

2.1. Synthesis

All of the raw materials used in this study were from Sigma. 1.0 g of *m*-phenylenediamine was dissolved into 10 mL of ethanol (99.5%). 3.0 g of FeCl₃ anhydrous was dissolved in 30 mL of ethanol (99.5%). The FeCl₃ was used as oxidant and its solution was poured into the monomer solution to initiate the polymerisation. The polymerisation system was placed steadily for additional 2 h to complete the reaction and then solution was put into an oven at 105 °C to constant weight to obtain the dark brown solid intermediate (or PmPD-based mixtures).

The solid was put into a furnace, in which the air was replaced by ultrapure N₂ (99.999%). The temperature was gradually increased to 800 °C with ramp of 10 °C min⁻¹. The isothermal duration at 800 °C lasts for 1 h and after that, the furnace was cooled naturally to room temperature in ambient conditions.

The black solid product was treated by ball milling to obtain the uniform powder. The milling liquid was 1:1 HCl solution. The ball milling rate is 500 rpm while time is 2 h. The carbon powder was captured by vacuum filtration and then rinsed with deionized water until the pH is close to 7. After freeze drying, the carbon nanosheets were obtained, which was stored in N₂ for further use.

2.2. Characterisations

The morphology of the as-prepared samples and intermediates were characterized by field emission scanning electron microscope (SEM) (Hitachi 4800S, accelerated voltage of 5 kV) and high-

resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2, accelerated voltage of 150 kV). X-ray photoelectron spectroscopy (XPS) (ESCALAB 250 Xi) was applied to analyse the chemical compositions of the products. The phase compositions were revealed by X-ray diffraction (XRD) (Rigaku D/Max III diffractometer with Cu K α radiation). The pore-size distribution was tested and calculated from N₂ adsorption-desorption isotherm by Micromeritics ASAP[®] 2420 Accelerated Surface Area and Porosimetry System. Atomic force microscopy (AFM) (Bruker MultiMode 8) is used to measure the thickness of the carbon nanosheets.

2.3. Electrochemical tests

The electrocatalytic activities for oxygen reduction reaction (ORR) of the as-prepared samples were evaluated using a rotating disk electrode (RDE) in 0.1 M KOH solution. The spiral Pt wire was served as counter electrode and the Ag/AgCl was performed as reference electrode. The working electrode was prepared as follow: 8 mg catalyst was dispersed into 2 mL mixed solvent (ethanol/water = 1/1, volume ratio) to form uniform catalyst ink; then 5 μ l ink was dropped on a clean glassy carbon electrode and subsequently dried at room temperature. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) was recorded from 0.2 V to –1.0 V in O₂ or N₂ saturated 0.1 M KOH.

To extend the application of as-prepared electrocatalyst, alkaline zinc/air batteries were fabricated. The catalytic layer was assembled by firstly mixing catalyst, acetylene black, active carbon and polytetrafluoroethylene together with a weight ratio of 3:1:3:3 and subsequently roll-forming. To form sample-loaded electrode, catalytic layer, gas diffusion layer and Ni foam were rolled into one piece. The adoptive electrolyte is 6 M KOH solution and pure Zn plate was employed as anode. The battery measurements were carried out on a LAND CT2001A battery-testing instrument. All battery testing measurements are operated under atmospheric air.

The Koutecky-Levich (K-L) equation is shown as below:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_l} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_k} \quad (1)$$

$$B = 0.2nF(D_0)^{\frac{2}{3}}\nu^{-\frac{1}{6}}C_0 \quad (2)$$

where J_k stands for the kinetic current density, J_l is the limited diffusion current density, ω represents the RDE rotation rate (rpm), F is the Faraday constant (96485 C mol⁻¹), D_0 is the diffusion coefficient and the bulk O₂ concentration is denoted as C_0 , ν is the kinetic viscosity of the electrolyte, and B can be acquired from the slope of the fitting line. Based on the K-L equation, n (electron transfer number) can be calculated from the B value.

3. Results and discussion

The synthetic procedure is illustrated in Fig. 1A. Pure ethanol was used as the solvent to prepare the Fe³⁺ and monomer solutions. The role of pure ethanol will be discussed below. The Fe³⁺ solution was poured into the monomer solution to initiate the polymerisation of *m*-phenylenediamine. In this step, Fe³⁺ was reduced to Fe²⁺ [61] while the monomer was oxidised to cation radicals. In general, the cation radicals result in chain propagation through an electrophilic substitution reaction [44]. Fe²⁺ from the reduction of Fe³⁺ could be re-oxidized to Fe³⁺ by the oxidants (e.g., dissolved oxygen), which would oxidise the remaining monomers [62]. The solid polymer was obtained by drying the suspension at 105 °C, and the dried solid material was then carbonised in a tube furnace under ultrapure N₂ (99.999%). The synthesis in this research is benefited by the simple polymerisation process, full utilization of the raw materials and high quality of the product. In

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