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One-step synthesis of hollow nanostructured aniline oligomers and their derived nitrogen doped carbon

Shuangxi Xing[a], Lin Chen[a], Lei Huang[a], Tian Wang[b], Xiaodan Yu[a], Yuxin Zhang[b,*], Yan Xing[a,*]

[a] Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China
[b] National Key Laboratory of Fundamental Science of Micro/Nano Devices and System Technology, College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China

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ABSTRACT

Hollow nanostructured aniline oligomers are generated via a one-step route using copper acetate and *p*-phenylenediamine as oxidant and accelerator at room temperature. An Ostwald ripening process for the nuclei with high energy and low polymerization degree has been adopted for the cavity formation. The carbonized aniline oligomers with a well-maintained hollow structure presents a specific capacitance of 192 F g^{-1} at a current density of 2 A g^{-1} and 13% capacitance fading after 3000 cycles. In principles, the hollow structure can relieve the expansion/contraction of the electrode materials and the nitrogen doping properties can provide additional pseudocapacitance.

1. Introduction

Hollow micro/nanostructured polymerized aniline, including polyaniline (PANI) and aniline oligomers have received much attention in diverse applications, including supercapacitors, batteries, sensors and absorbent, as such structure renders the materials excellent performance [1–4]. Since aniline oligomers are non-conducting, they are typically useful for application in the fields that do not require conductivity [5]. In order to construct a hollow structure, a sacrificial template, such as polystyrene, silica and metal oxide is usually adopted [6–8]. In this way, a kind of *in situ* sacrificial oxidative template should be pointed out, where the template is capable of oxidizing aniline to make them polymerized on its surface and its product is dissolvable in the system, leading to the formation of hollow structure [9,10]. The self-assembly process with the aid of specific acids is another facile way to achieve hollow PANI. In detail, salicylic acid, *β*-naphthalene sulfonic acid or perfluorooctane sulfonic acid was used as both dopant and structure-directing reagent to construct unique soft template for the generation of hollow structure [11–13]. It should be noted that hollow PANI could also be obtained by using H_2O_2 and Fe^{3+} via a hydrothermal method, where the Fe^{3+} ions act as catalyst and H_2O_2 as oxidant with its decomposed O_2 to facilitate the formation of cavity [14].

On the other hand, conducting polymers often act as source materials for the preparation of nitrogen-containing carbons through the pyrolysis treatment, which show great potential applications in absorbent, CO_2 capture and energy storage and conversion [15–17]. Indeed, the well-dispersed uniform conducting polymer nanostructures ensure the generation of carbon materials with high specific surface area and activity. In some cases, a hard template, such as polystyrene or silica, was utilized to support the PANI growth followed by carbonization [18,19]. The nitrogen component was considered to enhance the capacitance by virtue of contributing pseudocapacitance. Despite these improvements, it remains a challenge to develop rational designing a proper conducting polymer nanostructure, e.g., hollow one at room temperature for electrode materials. Besides, an activation process exists in most cases in order to produce porous structure and increase the specific surface area thereby. Actually, the specific capacitance is greatly enhanced owing to the large amounts of active sites. However, the utilization of acid or base solution with high concentration does not appear time-consuming. Therefore, it is anticipated to obtain carbon materials with good electrochemical performance while in the absence of post-treatment on activation.

Here, we reported a facile route to synthesize hollow aniline oligomers in nanosize by just using copper acetate as oxidant in the presence of *p*-phenylenediamine, which played a role of accelerator to keep the generation of aniline oligomers in uniform distribution via a kinetically controlled process. Furthermore, the nanostructured hollow aniline oligomers were transferred into hollow carbon spheres through a pyrolysis process (Fig. 1A). The as-obtained carbon materials without typical KOH activation treatment exhibited a specific capacitance of 208 F g^{-1} at a current density of 1 A g^{-1} and gave 13% loss of initial

* Corresponding authors.
E-mail addresses: zhangyuxin@cqu.edu.cn, 45070833@qq.com (Y. Zhang), xingy202@nenu.edu.cn (Y. Xing).

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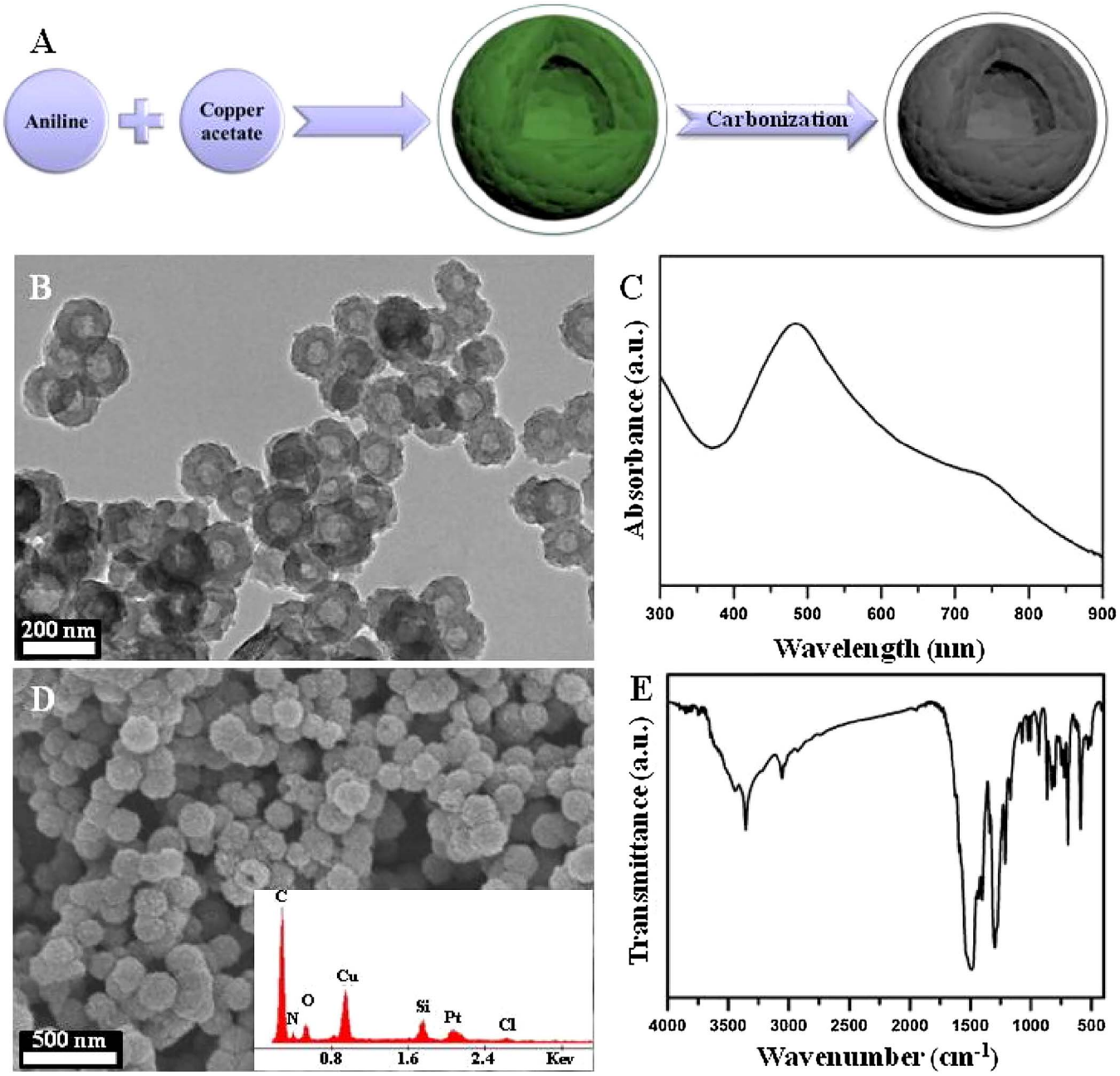

Fig. 1. A) Scheme for the generation of hollow aniline oligomers and their carbonized products; TEM (B) and SEM (B) images of hollow aniline oligomers (inset of Fig. D: EDX spectrum of hollow aniline oligomers); UV–vis (C) and FTIR (E) spectra of hollow aniline oligomers.

value after 3000 cycles at 2 A g^{-1}.

2. Experimental

2.1. Materials

Aniline (98%, J & K Chemical Ltd) was distilled before use and stored at 4 °C. Copper acetate (98.0%, Aldrich) and *p*-phenylenediamine (99 + %, Acros) were used as received. All solutions were prepared using ultrapure water (resistivity > 18 MΩ cm^{-1}).

2.2. Synthesis of hollow nanostructured aniline oligomers

Typically, 4 mL ypically, 4 mL of aniline aqueous solution (50 mM) was mixed with 6 μL of hydrochloric acid (1 M) and 2 μL of *p*-phenylenediamin/ethanol solution (20 mg in 1 mL of ethanol). Afterwards, 4 mL of copper acetate aqueous solution (40 mM) was dropped to induce the polymerization of aniline. The final concentration of aniline, hydrochloric acid and copper acetate is 33.3, 1 and 26.6 mM, respectively. After 10 h, the reaction solution was centalic > -phenylenediamin/ethanol solution (20 mg in 1 mL of ethanol). Afterwards, 4 mL of copper acetate aqueous solution (40 mM) was dropped to induce the polymerization of aniline. The final concentration of aniline, hydrochloric acid and copper acetate is 33.3, 1 and 26.6 mM, respectively. After 10 h, the reaction solution was centrifuged and the isolated products were dried in vacuum at 50 °C for 24 h.

2.3. Preparation of hollow nanostructured carbon

The aniline oligomers product was ground and heated to 800 °C with a rate of 5 °C min^{-1} and maintained at 800 °C for 2 h under a N_2 atmosphere. To get rid of the possible influence from the Cu element