



# Synthesis of N-doped carbon nanosheets from collagen for electrochemical energy storage/conversion systems

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## ARTICLE INFO

### Article history:

Received 26 September 2010

Received in revised form 7 November 2010

Accepted 7 November 2010

Available online 12 November 2010

### Keywords:

Collagen

N-doped

Carbon nanosheets

Supercapacitors

Oxygen reduction

## ABSTRACT

This study proposes a simple method for synthesizing carbon nanosheets doped with nitrogen through carbonization of collagen. Collagen, the most abundant protein in mammals, was cross-linked with paraformaldehyde and subsequently heated in vacuum at 800 °C to obtain N-doped carbon nanosheets with a high specific surface area of 695 m<sup>2</sup> g<sup>-1</sup>. With the contribution of N-doped structures, the carbon nanosheets show ideal capacitive behavior with 80% capacitance retention in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1000 mV s<sup>-1</sup>. In comparison with a commercial electrocatalyst, 20% Pt on Vulcan XC-72, carbon nanosheets display a positive shift in the onset potential and superior electrocatalytic activity toward the oxygen reduction reaction (ORR). The above excellent electrochemical performances render the N-doped carbon nanosheets a promising material for electrochemical energy storage/conversion systems.

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## 1. Introduction

Recently, several efforts have been devoted to change the physicochemical properties of carbonaceous materials by introducing heteroatoms, especially the nitrogen atom, to the graphitic or graphite-like structures. For example, nitrogen-doped carbon materials have been found to enhance the performances of several electrochemical energy storage or conversion systems, such as electric double-layer capacitors (EDLCs) [1–6] and fuel cells [7–12]. The N-doped structures are believed to provide pseudocapacitance contributed from the redox faradaic reactions of these electrochemically active functional groups. Moreover, certain N-doped functional groups can enhance the electronic conductivity of carbon materials for EDLCs [6,13,14]. As a result, N-doped carbon materials are considered to be promising EDLC electrode materials that are used practically as power sources/energy storage devices to supply/deliver pulsed current. More recently, these unique N-containing functional groups have been found to be the electrocatalytic sites for the ORR in fuel cells [7,15–17]. Accordingly, several studies showed the potential of N-doped carbonaceous materials to replace the commonly used yet much more expensive platinum as the electrocatalyst for the ORR.

N-doped carbonaceous materials have been prepared through the post-treatment, e.g., ammoxidation, of carbon samples [2,3] or the employment of an N-containing precursor. The latter procedure is preferred because it is easier, more cost-effective, and more controllable

for the N-doping content [1,4–6,18]. Among many N-containing precursors, biomaterials, such as proteins, have been reported as suitable precursors for synthesizing N-doped carbonaceous materials because of their amino group-bountiful nature [19–21]. Accordingly, collagen [22,23], the most abundant protein in mammals, was utilized as the precursor to prepare N-doped carbon materials in this work. Material analyses confirmed the existence of N-doped structures and characterized the collagen-derived material as carbon nanosheets. The N-doped carbon nanosheets showed a near ideal EDLC behavior with high power performances. Furthermore, they were able to catalyze the ORR with a higher catalytic activity and more positive onset potential in comparison with the commercial electrocatalyst, 20% Pt on Vulcan XC-72. Therefore, the excellent capacitive performance and activity toward the ORR established the potential of collagen-derived N-doped carbon nanosheets for the electrochemical applications.

## 2. Experimental

A collagen solution (5 mg ml<sup>-1</sup>) was obtained by dissolving collagen powder (Sigma-Aldrich, USA) in an acetic acid solution (0.02 M). With the addition of phosphate buffered saline (PBS, Sigma-Aldrich, USA) and sodium hydroxide, collagen gel was formed after 24-h incubation at 37 °C. After being cross-linked with a 4% paraformaldehyde solution for 15 min, the soaked gel was heated in vacuum at a rate of 4 °C min<sup>-1</sup> to 800 °C and kept at this temperature for 6 h.

XPS measurement was performed on the Kratos Axis Ultra DLD (Kratos analytical, USA) which employed Al monochromator ( $h\nu = 1486.69$  eV) irradiation as the photosource. The scanning electron microscopic (SEM) and transmission electron microscopic (TEM)

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images of carbon nanosheets were obtained by Hitachi S-4700I (Hitachi, Japan) and JEM-2010 (JEOL, Japan), respectively.

The electrochemical performances of the collagen-derived carbon material were investigated by CHI 633A (CH Instruments, USA) in a three-compartment cell. An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs. standard hydrogen electrode at 25 °C) was used as the reference electrode, and platinum wire was employed as the counter electrode. A Luggin capillary was used to minimize errors due to ohmic potential drop in the electrolyte. The potentials for the ORR are referred to a reversible hydrogen electrode (RHE).

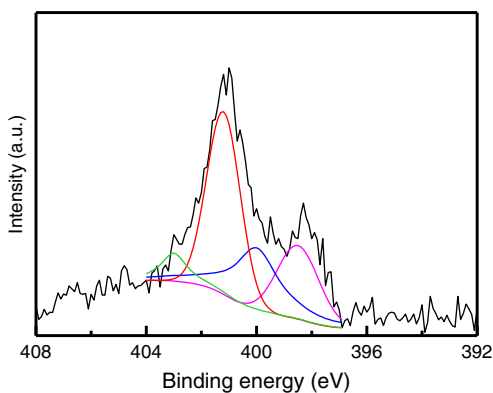
The material for the working electrode was a mixture consisting of the collagen-derived carbon material and polyvinylidene in the weight ratio of 10:1. The mixture (ca. 1 mg) was homogeneously suspended in N-methyl-2-pyrrolidone and coated on a graphite substrate with an exposed surface area of 1 cm<sup>2</sup>. The electrolyte for evaluating capacitive performances is a 0.5 M sulfuric acid solution, whereas it is a 0.1 M potassium hydroxide solution for investigating the ORR activity. A commercial electrocatalyst, 20% Pt on Vulcan XC-72 (E-TEK, USA), was also applied (also ca. 1 mg) for the comparison of oxygen reduction activity.

### 3. Results and discussion

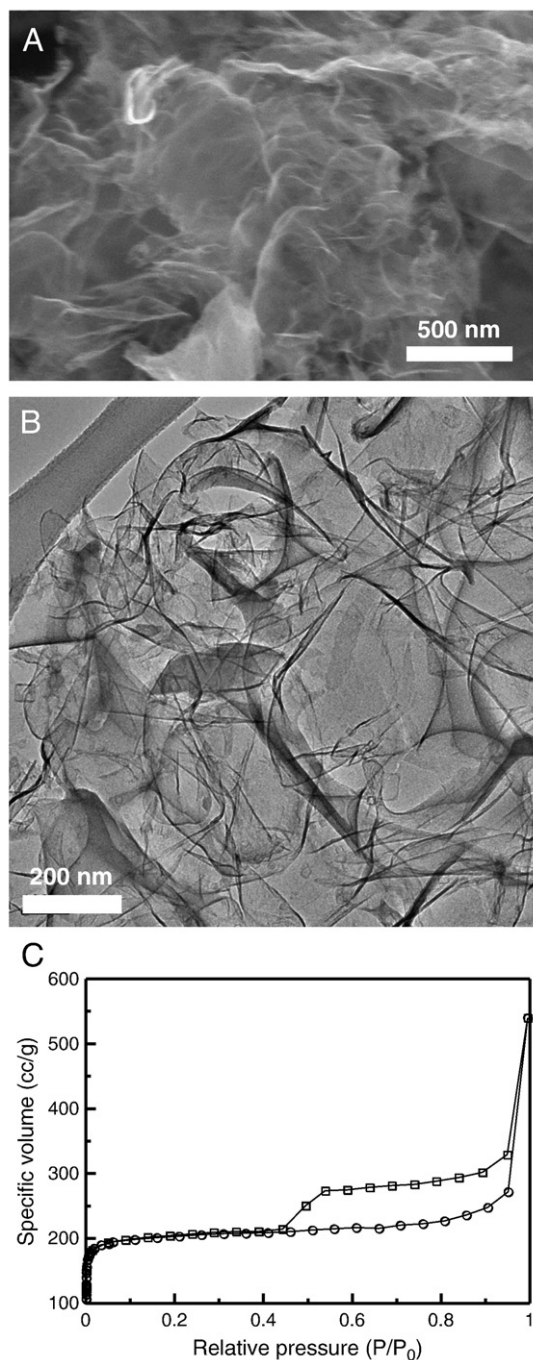
XPS analysis was performed to evaluate the nitrogen content of the collagen-derived carbon material. Owing to the presence of amino groups in collagen, the atomic ratio of nitrogen for the carbonized material is about 1%. Fig. 1 reveals the existence of pyridinic-N (398.5 eV, 21.4 at.%), pyrrolic-N (400 eV, 28.1 at.%), quaternary-N (401.2 eV, 42.8 at.%), and pyridine-N-oxide (403 eV, 7.7 at.%) [1,5,6]. This result confirmed that the collagen-derived carbon material contains N-doped structures.

The surface morphology of the N-doped carbonaceous material was examined by the SEM image, as shown in Fig. 2A. The loose and layered structure characterized the carbonaceous material as carbon nanosheets. The sheet-like morphology was confirmed in the TEM image (Fig. 2B). The above results reveal the formation of a highly porous N-doped carbonaceous material. As shown in Fig. 2C, the porosity of N-doped carbon nanosheets was investigated by the analysis of N<sub>2</sub> adsorption/desorption isotherms. In addition to micropores, the hysteresis loop between adsorption and desorption isotherms demonstrates the existence of slit-like mesopores, which agrees well with the morphology. The presence of both micropores and mesopores contributes to the high specific surface area (695 m<sup>2</sup>g<sup>-1</sup>) of the carbon nanosheets.

To unravel the capacitive performance of the N-doped carbon nanosheets, cyclic voltammograms at different scan rates were carried



**Fig. 1.** N 1s core-level XPS spectra of the collagen-derived carbon material. The black line is the raw spectrum; the pink, blue, red, and green lines correspond to pyridine-N, pyrrolic-N, quaternary-N, and pyridine-N-oxide, respectively.



**Fig. 2.** (A) SEM and (B) TEM images, and (C) N<sub>2</sub> adsorption/desorption isotherms of the N-doped carbon nanosheets.

out, as shown in Fig. 3A. With its high specific surface area, the N-doped carbon nanosheets possess a nearly ideal double-layer behavior with a specific capacitance of 102 Fg<sup>-1</sup> at 25 mV s<sup>-1</sup>, which is comparable to that of activated carbons. In addition, perfect reversibility and stability are observed with varying the scan rate. Only 20% loss in capacitance is found when changing the scan rate from 25 to 1000 mV s<sup>-1</sup> (Fig. 3B), indicating that the N-doped carbon nanosheets are a high power material. Previous studies [6,13,14] proposed that with the modified electron donor/acceptor properties, pyridinic-N and pyrrolic-N in carbon materials could induce Faradaic pseudocapacitance, whereas quaternary-N and pyridine-N-oxide could improve the ability of electron transfer in carbon materials. Since the redox peaks in the CV diagrams are not obvious, the contribution of pseudocapacitance from

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