Scalable processing method using waste polystyrene to produce nitrogen-enriched porous carbon for boosting supercapacitor performance

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ABSTRACT

A high-efficiency rational design of a durable material produced from waste materials for sustainable energy generation and storage systems is a formidable challenge. This paper describes the large-scale synthesis of nitrogen-doped porous carbon (PS-C) from waste polystyrene with a short processing time using the thermal plasma method. The as-synthesized PS-C exhibited an electrochemical capacitance of 482 Fg^{-1} at a current density of 1 Ag^{-1} and a capacitance retention of 95% at a current density of 6 Ag^{-1} after 5000 charge–discharge cycles. This reported specific capacitance and cyclic performance are attributed to the morphology, nitrogen doping, and structural integrity resulting from the synergy of the material.

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1. Introduction

Ever-increasing environmental pollution and the rising demand for energy have created a need for sustainable "wastes to energy" processes. A prospective method to address this energy dilemma and environmental pollution issues, is to develop renewable energy storage materials from solid waste. Designing efficient electrode materials for electrochemical energy storage devices or carbon-based supercapacitors with low cost, long life, and high storage throughput is challenging. However, the creation of highly efficient carbon materials in bulk quantities requires reliable and low-cost precursors and scalable, environmentally friendly processes.

The mechanisms for the synthesis of porous carbon materials from polystyrene for pollutant absorption [1,2], hydrogen storage [3], and electrochemical energy storage applications [4,5] have been extensively reported. However, all such studies were based on a complicated template-based synthesis method wherein MgO [3], SiO_2 [6], transition metal oxides, or complex [3,7,8] particles are used as the template for the synthesis of carbon materials, and the removal of the template then produces porous carbon. This study reports a scalable method with minimal processing time for the treatment of polystyrene waste to produce electronic-grade nitrogen-doped carbon (PS-C) for supercapacitor applications. Thermal plasma-based processing exhibits tremendous potential for treating materials in a controlled atmosphere with ample-tuned thermal enthalpy. Notably, this process can generate a hierarchical macroporous network structure with an adequate amount of microporosity. The as-prepared nitrogen-doped PS-C electrode displayed a high specific capacitance of 482 Fg^{-1} at a current density of 1 Ag^{-1} and excellent rate capability and cycle stability.

2. Materials and methods

Sodium hydroxide 97% (NaOH), urea 98% (CH_4N_2O), and hydrochloric acid 37% (HCl) were purchased from Himedia and used without further purification. A PS-C sample was prepared

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using a typical synthesis method by treating a 200 g mixture of waste polystyrene (PS) and urea with a weight ratio of 1:1 in a plasma reactor for 10 min. The plasma reactor and its working conditions are presented schematically in Scheme 1 and described in detail in our previous work [9,10]. In this study, argon was used as the plasmagen gas at a current of 250 A and a voltage of 50 V. The resulting carbon material was ground into a fine powder using a mortar and pestle. The as-synthesized product was washed using a 2 M HCl-in-water solution repeatedly until the pH was neutral and dried further in a vacuum oven overnight. The dried product was used for subsequent characterizations and tests. The details of the physical characterizations, electrode preparation, and electrochemical calculations are provided in the supplementary section (SI-1). The obtained nitrogen-doped carbon nanomaterials are denoted hereinafter as PS-C.

3. Results and discussion

The scanning electron microscopy (SEM) images of the PS-C samples, at different magnifications, are shown in Fig. 1a and 1b. The low-magnification image depicts a broader area of uniform pore morphology after plasma treatment (Fig. 1a). Additionally, the high-magnification image clearly depicts the nested mesoporous morphology of the sample (Fig. 1b). This uniform-size mesoporous morphology facilitates the infiltration of electrolytic ions during electrochemical reactions and is highly desirable for supercapacitor applications. The structural changes in the material were observed before and after plasma treatment and compared using X-ray diffraction (XRD) patterns and Raman spectroscopy data. Fig. 1c shows the comparative XRD patterns of the PS and PS-C samples.

In the case of the PS sample, a broad peak was observed in the range of 20° to 30° in the XRD pattern (black line in Fig. 1c). After plasma treatment, two broad peaks were observed at 26.2°and 43.3°, which correspond to the typical (0 0 2) and (1 0 1) crystal planes of graphitic carbon, respectively. Additionally, submerged low-intensity peaks, which correspond to two different crystal phases of C_3N_4 (JCPDF file numbers 78-1747 and 87-1526), were observed on the broad peak. Thus, the structural data confirmed the carbonization, surface modification, and phase formation of the raw polystyrene after plasma processing. Furthermore, the Raman spectroscopy spectra comparison corroborated the afore-

described findings. Fig. 1d shows the Raman spectrum of the PS sample with typical signature Raman bands of C=C in polystyrene. However, after plasma treatment, three broad peaks were observed at 1339, 1598, and 2616 cm^{-1}, corresponding to the D, G, and 2D bands, respectively. The D and G bands are assigned to the defects/disorders in carbon, and the in-plane E_{2g} optical mode at the center of the Brillouin zone, respectively, while the 2D band is a second-order Raman scattering of an in-plane transverse optical mode near the K point of the Brillouin zone [11]. One additional peak at 1016 cm^{-1}, corresponding to the CN$_x$ vibrations [12], was observed in the PS-C sample.

A three-electrode system with a 1 M aqueous KOH solution as the electrolyte, was used to test the electrochemical storage capabilities of the plasma-processed sample (Fig. 2). A synthetic material, Hg/HgO, and Pt foil were used as the working, reference, and counter electrodes, respectively. Compared with the raw polystyrene electrode, the PS-C electrode exhibited a significant increase in the current density, as observed from the cyclic voltammetry (CV) curves, at a scan rate of 70 mVS^{-1}, thus reflecting its superior electrochemical charge storage capability in comparison to that of the PS electrode (Fig. 2a). Thus, the electrochemical performances of the PS-C sample only is discussed in details in further sections.

The CV characteristics of the PS-C sample were obtained in the potential range of 0 to – 1 V at different scan rates ranging from 5 to 100 mVs^{-1} (Fig. 2b). All the curves exhibit similar oval-type shapes without any notable changes, thus confirming the high rate capability and electric double-layer capacitor-dominated characteristics of the material [13]. The galvanostatic charge–discharge (GCD) behavior of the PS-C material at different current densities is presented in Fig. 2c. The highest specific capacitance of 482 Fg^{-1} was estimated at a current density of 1 Ag^{-1}. This specific capacitance decreased from 482 to 277 Fg^{-1} when the current density increased from 1 to 6 Ag^{-1}, thus indicating good charge storage and rate capability of the material as a supercapacitor electrode (Fig. 2d). Further, the cycle stability of the material was tested for the long-run charge–discharge and is presented in Fig. 3a. After the completion of 5000 charge–discharge cycles at the current density of 6 Ag^{-1}, the material retained 95% of its initial specific capacitance. The comparative GCD plot indicated the above-stated retention percentage of the specific capacitance after the completion of 5000 GCD cycles (inset in Fig. 3a). The electrochemical impedance spectroscopy (EIS) measurement of the sample was
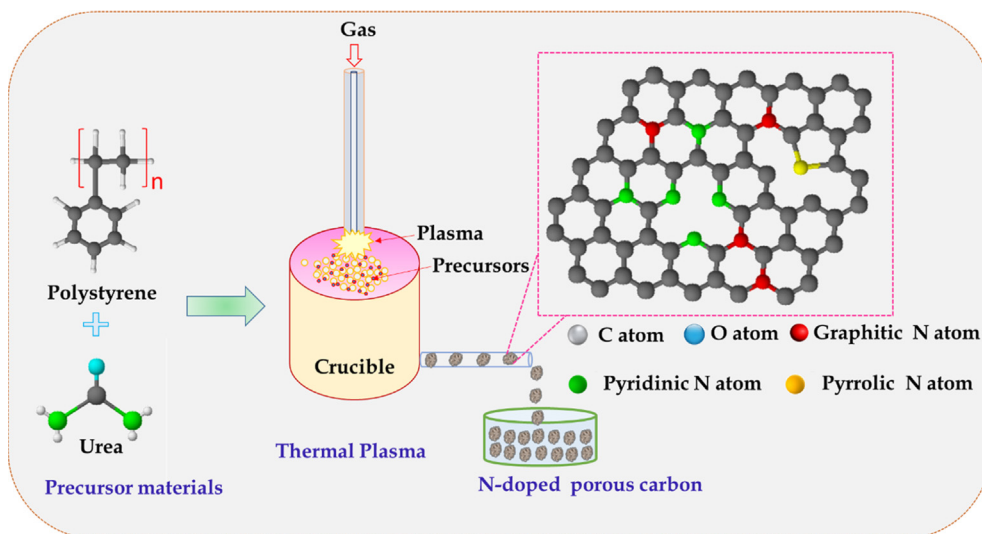
Scheme 1. Schematic of the process and the molecular representation of the product.
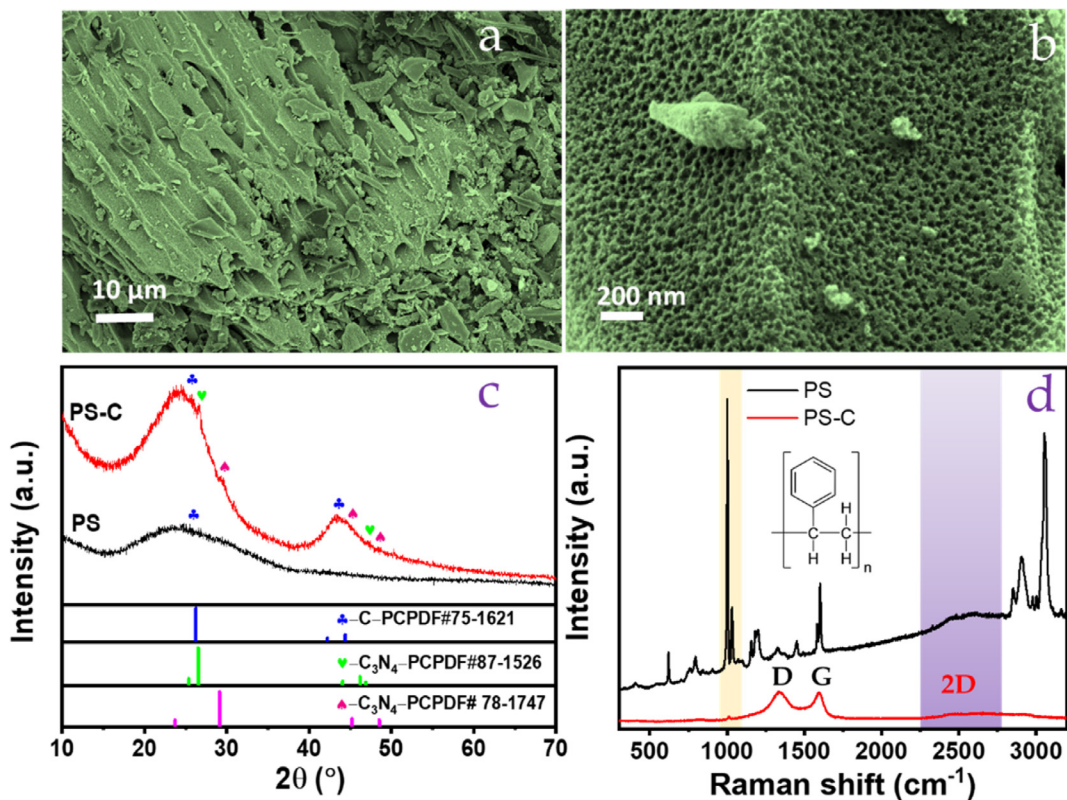
Fig. 1. Low magnification and (a) corresponding high magnification (b) SEM images of PS–C sample. Comparative XRD patterns and (c) Raman spectroscopy spectra of (d) PS and PS–C samples, respectively.
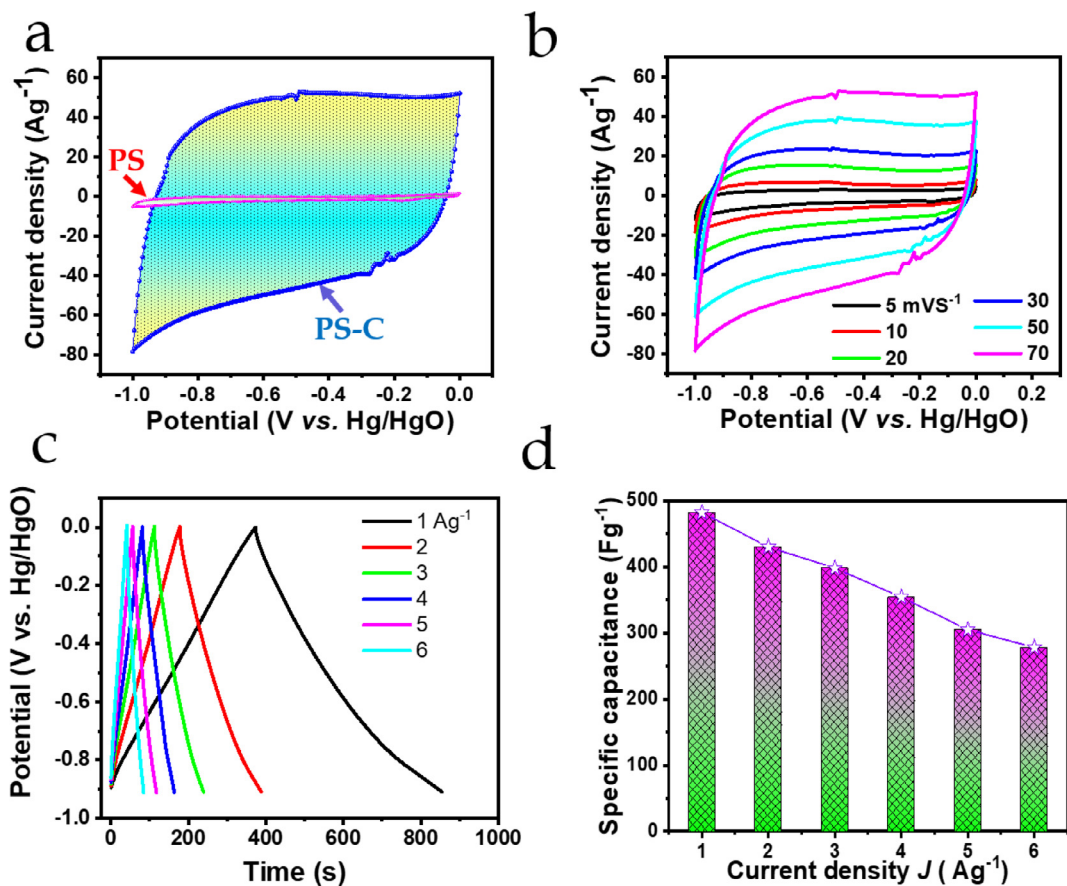

Fig. 2. (a) Comparative CV graph of PS and PS–C samples at 70 mVs^{-1}, (b) CV, (c) GCD, and (d) rate capability of PS–C sample.
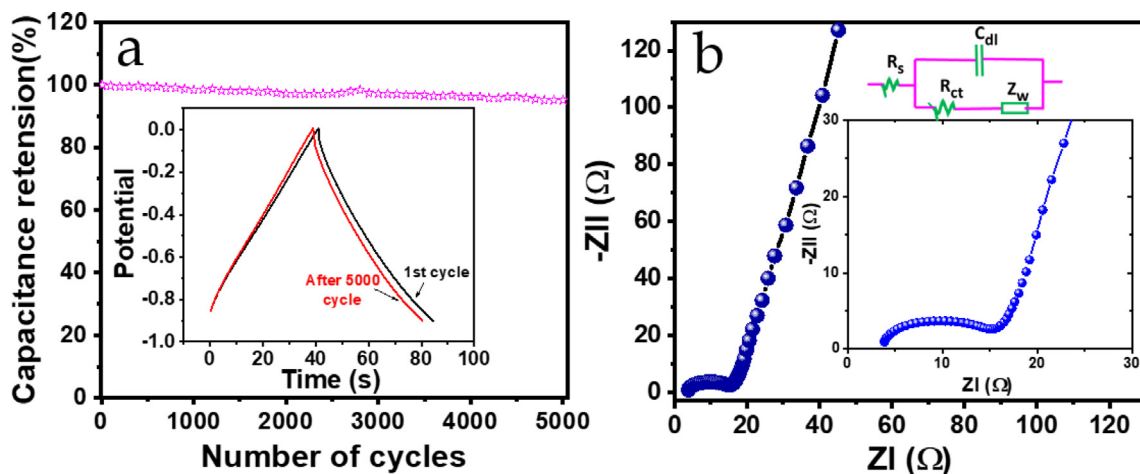
Fig. 3. (a) EIS plot with insert showing the magnified high-frequency part of the EIS and equivalent circuit diagram, (b) cyclic stability of PS-C sample at current density of 6 Ag^{-1}.

performed at an open-circuit potential. The Nyquist plot (Fig. 3b) clearly shows a well-defined semicircle in the high-to-medium frequency region, followed by a linear portion in the low-frequency region. The equivalent circuit fitting of this plot is inserted in the right portion of Fig. 3b.

This equivalent circuit consists of the electrolytic resistance (R_s), charge transfer resistance (R_{ct}), Warburg impedance (Z_W), and double-layer capacitance (C_{dl}). The R_s ($\approx 3.6\ \Omega$) and R_{ct} ($\approx 15.1\ \Omega$) values, which were high, were estimated for this sample, thus confirming the improvement in the conductivity of the material after plasma treatment. In light of the aforedescribed analysis, it is suggested that (i) a finely distributed mesoporous structure provides a widely exposed surface area, which facilitates the infiltration of electrolytic ions and minimizes their diffusion pathways, and (ii) N-doping in the porous carbon matrix improves the electrical conductivity that boosts the transport kinetics of charge carriers at the electrolyte and electrode interface, thus resulting in a notable electrochemical charge storage performance.

4. Conclusions

N-doped carbon was successfully synthesized with high structural integrity, on a large scale with a minimal processing time of 5 min. Furthermore, the as-synthesized material exhibited a high specific capacitance of 482 Fg^{-1} at a current density of 1 Ag^{-1} and excellent cycle stability of 96% after the completion of 5000 charge–discharge cycles at a current density of 6 Ag^{-1}. Such notable electrochemical energy storage performance of the material highlighted the applicability and sustainability of the scaled-up synthesis of N-doped carbon from waste polystyrene.

CRediT authorship contribution statement

Rakesh K. Sahoo: Formal analysis, Investigation, Writing - review & editing. **Ramesh Kumar Chitumalla:** Formal analysis, Investigation, Writing - review & editing. **Arya Das:** Formal analysis, Investigation, Writing - review & editing. **Mamata Mohapatra:** Supervision, Conceptualization, Writing - review & editing. **Je Moon Yun:** Supervision, Conceptualization, Writing - review & editing. **Joonkyung Jang:** Supervision, Conceptualization, Writing - review & editing. **Kwang Ho Kim:** Supervision, Conceptualization, Writing - review & editing. **Saroj K. Singh:** Supervision, Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2021.130135.

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