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A Novel Emulsion-Based Replica Method for the Synthesis of Mesoporous Carbon

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We present a novel approach for the synthesis of large-pore mesoporous carbon with a highly porous structure, based on an oil/water (O/W) emulsion templating method. For the formation of oil-in-water emulsions with nanoscale oil droplets, polyvinylpyrrolidone was used as an emulsifier. Mesoporous carbon materials with large mesopores were successfully synthesized via a three-step process: (1) polymerization in the oil-in-water emulsion, (2) filtration, and (3) carbonization. We confirmed that the pore size of the carbon can be significantly reduced through a modified O/W emulsion method. The mesoporous carbon materials prepared without an activation step exhibited an appreciable surface area (705 m^2/g) and a noticeable capacitive performance of ~100 F/g at 2.0 A/g. We believe that the approach presented here can be widely applied to the synthesis of mesoporous carbon using various carbon sources, and the structural properties of the mesoporous carbon can be improved through proper optimization.

Keywords: Polyvinylpyrrolidone, Emulsion Method, Large-Pore Mesoporous Carbon.

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1. INTRODUCTION

Mesoporous carbon materials have attracted considerable attention in many potential applications such as drug delivery, adsorption/separation, catalysis and energy storage.[1–3] Several mesoporous carbon materials have been successfully prepared via various methods.[4–6] However, the reproducible synthesis of mesoporous carbon with large mesopores remains a challenge. To date, hard and soft template approaches are the most commonly used strategy for the synthesis of mesoporous carbon. Typically, commercial silica nanoparticles were used as a hard template.[7] Emulsion methods can often be used to prepare macro-/mesoporous carbon materials.[8–11] Here, a surfactant not only acts as an emulsifier to disperse the oil phase in the water phase but also acts as a micelle template in the oil/water (O/W) emulsion.

After carbonization, the oil phase can be removed, and the corresponding pores are formed. Inspired by the formation mechanism of macropores, we hypothesize that if the diameter of an oil phase droplet is tuned to the nanometer-sized range, then the removal of the oil phase during the thermal decomposition process can generate large mesopores. Therefore, our primary goal is to develop a new synthetic strategy for the fabrication of porous carbon with large mesopores based on an emulsion method without using a hard template.

Polyvinylpyrrolidone (PVP) is known as an excellent water absorber and an O/W emulsifier, which has been both used as an additive and blended with other carbon precursors to produce porous carbon materials.[12–14] However, this emulsifier has not been used for the preparation of mesoporous carbon materials, especially those that are based on an emulsion method. In this work, we attempted to minimize the size of an oil droplet by adding PVP as the emulsifier of the O/W emulsion and prepare porous carbon with large mesopores, as illustrated in Figure 1. Scanning electron microscopy (SEM) and nitrogen adsorption/desorption analysis methods were used to characterize the carbon material's morphology and pore structure. Finally, the electrochemical capacitive performance of the sample was evaluated by charge/discharge tests.

2. EXPERIMENTAL DETAILS

All chemicals (analytical grade) were purchased from Daejung Chemicals and Metals Co., Ltd. (KOREA). To synthesize mesoporous carbon with large mesopores, 4.7 g of resorcinol and 7.1 g of formaldehyde were dissolved in 5 mL of distilled water. 1.0 g of polyvinylpyrrolidone

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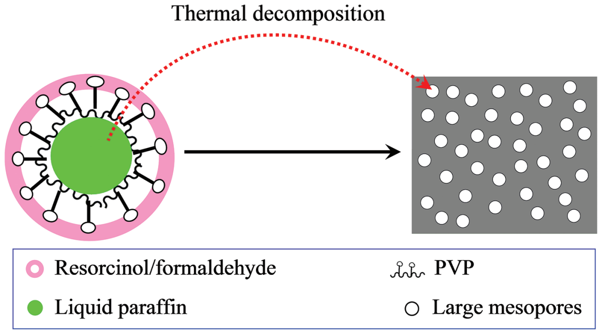

Figure 1. Schematic of the synthesis of mesoporous carbon via an O/W emulsion method with a PVP emulsifier.

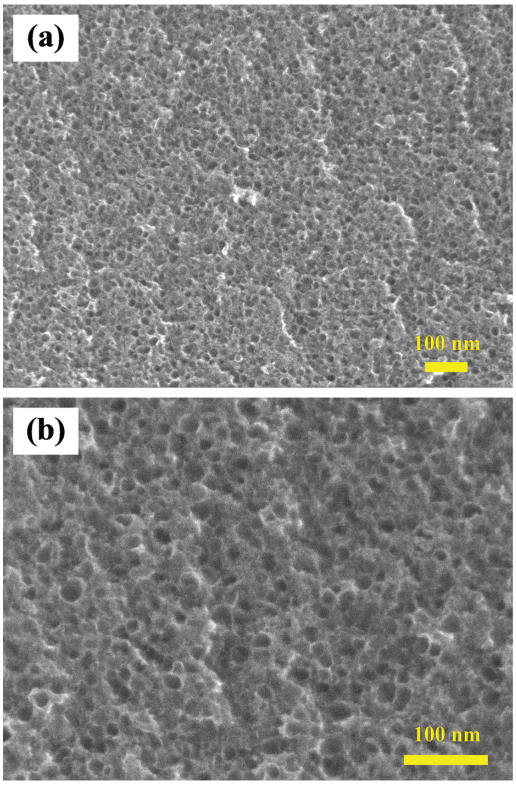

Figure 2. (a) Low- and (b) high-magnification FESEM images of the mesoporous carbon.

(MW = ca. 40000) was added into the aqueous solution. This mixture was stirred to obtain a homogeneous solution at room temperature. The resulting solution was added dropwise into a flask containing 5 g of liquid paraffin under vigorous stirring at 40 °C to obtain an oil in water (O/W) emulsion solution. After stirring for 30 min, NaOH was added into the flask for catalytic polymerization. The prepared polymers were filtered and dried at 100 °C for 24 h, followed by carbonization at 850 °C for 2 h under an argon gas flow.

Scanning electron microscopy (SEM) images were collected using a JEOL JSM-7500F instrument. N_2 adsorption–desorption isotherms at 77 K were taken by a Tristar II 3020 adsorption analyzer. The surface area and pore size distribution of the prepared mesoporous carbon materials were estimated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

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All electrochemical measurements were tested in a coin-type cell with two identical carbon electrodes and a glass fiber membrane separator. A slurry that was composed of 80 wt% mesoporous carbon, a 10 wt% polytetrafluoroethylene binder, and 10 wt% acetylene black was dispersed in isopropyl alcohol, coated onto a Ni mesh, and dried at 100 °C. The charge and discharge tests for the coin cells with a 6.0 M KOH electrolyte solution were performed at a current density of 2 A/g.

3. RESULTS AND DISCUSSION

According to the FESEM images, the mesoporous carbon has abundant large mesopores that were randomly distributed in the amorphous carbon matrix (Fig. 2). The results indicate that much smaller pore sizes can be achieved when adding PVP in the solution compared with those of the previously prepared carbon materials via a similar O/W emulsion method where conventional surfactants were used (Fig. 2). This result clearly indicates that PVP would be a highly beneficial material for the creation of O/W emulsion template with nanoscale oil droplets. Note that a stable emulsion that consists of carbon sources and paraffin can be formed without adding PVP. It is thought that the unique chemical nature of PVP with hydrophilic and hydrophobic groups directly contributed to the formation of a highly stable O/W emulsion solution. In addition, the small pore size can be attributed to the viscosity effect of PVP in the emulsion solution.[15–17] A proper viscosity not only divides the oil phase into smaller droplets but also inhibits the aggregation of droplets. The surface area and microstructure of mesoporous carbon were examined by N_2 adsorption/desorption tests.

From Figure 3(a), the isotherms clearly belong to a typical Type IV curve, which has a capillary condensation step between relatively moderate and high pressures according to the IUPAC classification. A sharp increase in the adsorption volume at a low relative pressure of $p/p_0 < 0.01$ is observed, indicating the micropore filling.[18, 19]

The wider hysteresis loop with a large area is found at a relative pressure of greater than 0.43, which demonstrates the presence of many mesopores in these carbon materials. Capillary condensation will first occur in the smaller-sized mesopores during the adsorption process.[20] As the relative pressure increased, adsorption inside the large-sized mesopores will also cause capillary condensation in sequence until all pores have filled. In the desorption process, the condensation liquid inside the large-sized mesopores will first evaporate at a high relative pressure because the phase equilibrium pressure of liquid in the pore is proportional to the mesopore size. However, the condensation liquid inside smaller-sized mesopores can only be desorbed when

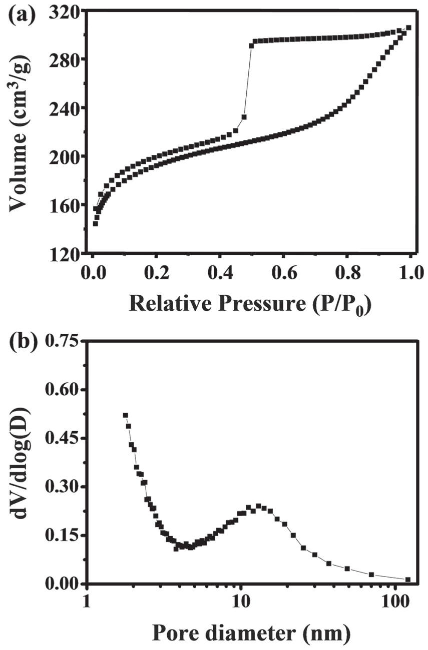

Figure 3. (a) N_2 sorption isotherms and (b) pore size distribution curves of the mesoporous carbon.

the relative pressure is low enough. Therefore, the width of hysteresis loop reflects the mesopore size distribution in the carbon. That is, the mesopore size distribution of mesoporous carbon is wider. In addition, this wider hysteresis loop belongs to Type H2, which often shows an inverted triangle with regard to the relative pressure, suggesting the existence of ink bottle-like pores.[20] These data indicate that mesoporous carbon possesses a high surface area of 705 m^2/g and a total pore volume of 0.46 cm^3/g.

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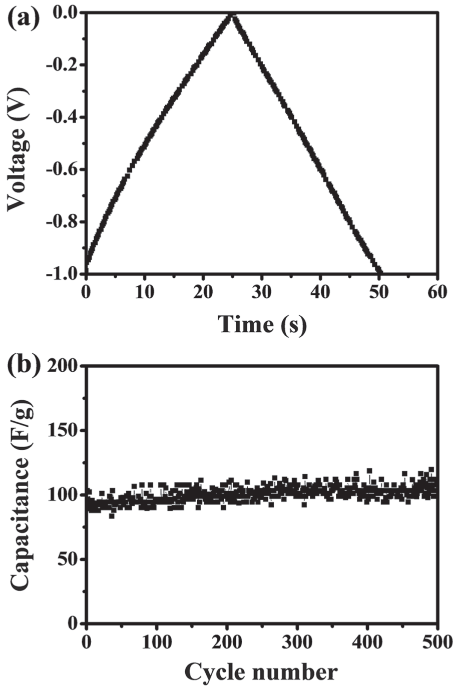

Figure 4. (a) Charge–discharge curves and (b) cycling performance of the mesoporous carbon.

One of the main applications for mesoporous carbon is its use as an electrode material in electrochemical energy storage. Figure 4(a) shows the charge–discharge profiles of the mesoporous carbon electrode at 2.0 A/g. It was found that the curves are linear without a voltage drop, demonstrating good electrochemical double-layer capacitance. The specific capacitance of the carbon electrode was measured at ∼100 F/g. After 500 cycles, the mesoporous carbon electrode exhibited excellent cycling performance with 100% retention.

4. CONCLUSION

Large-pore mesoporous carbon with a highly porous structure has been successfully synthesized via a modified emulsion method using a polyvinylpyrrolidone emulsifier. Unlike other porous carbon materials that were prepared through an O/W emulsion route, carbon materials with much smaller pore sizes were achieved. The prepared mesoporous carbon possessed various pore sizes, ranging from 2 to 100 nm. It was found that the mesoporous carbon exhibited a noticeable capacitive performance of ∼100 F/g, which is attributed to its large surface area (705 m^2/g). We believe that the electrochemical performance of mesoporous carbon can be significantly enhanced by the fine tuning of experimental parameters or a conventional activation step.

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