Synthesis of Mesostructured Conducting Polymer-Carbon Nanocomposites and Their Electrochemical Performance

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Abstract: A conducting polymer layer was introduced into the pore surface of mesoporous carbon via vapor infiltration of a monomer and subsequent chemical oxidative polymerization. The polypyrrole, conducting polymer has attracted considerable attention due to the high electrical conductivity and stability under ambient conditions. The mesoporous carbon-polypyrrole nanocomposite exhibited the retained porous structure, such as mesoporous carbon with a three-dimensionally connected pore system after intercalation of the polypyrrole layer. In addition, the controllable addition of pyrrole monomer can provide the mesoporous carbon-polypyrrole nanocomposites with a tunable amount of polypyrrole and texture property. The polypyrrole layer improved the electrode performance in the electrochemical double layer capacitor. This improved electrochemical performance was attributed to the high surface area, open pore system with three-dimensionally interconnected mesopores, and reversible redox behavior of the conducting polypyrrole. Furthermore, the correlation between the amount of polypyrrole and capacitance was investigated to check the effect of the polypyrrole layer on the electrochemical performance.

Keywords: capacitor, conducting polymer, mesoporous carbon, nanocomposite.

Introduction

Recently, the incorporation of conducting polymer into carbon materials has attracted much attention because of their potential applications to the electrode materials.[1] To date, several conducting polymer-carbon composites have been prepared using conducting polymer and carbon nanotubes. Importantly, polypyrrole (PPy)[2] is a representative conducting polymer[3] with relatively high electrical conductivity and stability under ambient condition. In addition, PPy can be synthesized by simple chemical oxidative polymerization. For various electrochemical applications,[4] the mesoporous carbon-PPy (MC-PPy) nanocomposites could provide significant advantages such as high surface area, open pore system with three-dimensionally interconnected mesopores, and reversible redox behavior of conducting PPy. However, there is the limited information concerning the incorporation of conducting polymers into the framework of mesoporous carbons with their open pore structures.[5]

Herein, we report the synthesis of different MC-PPy nanocomposites as a function of PPy feeding amounts. Synthesized MC-PPy nanocomposites apply for the electrode

materials in electrochemical double-layer capacitor (EDLC). Furthermore, the relationship between specific capacitance and PPy loading in MC-PPy nanocomposites was investigated. Pyrrole monomer was introduced to the mesoporous carbons and polymerized to form the thin layers on their pore wall surfaces. The MC-PPy nanocomposites with controlled PPy amounts were obtained with the thickness variation of PPy coating on the pore surfaces.

Results and Discussion

The overall synthetic procedure for the MC-PPy nanocomposite is depicted in Figure 1. The mesoporous carbon was prepared by our previous method.[6] This mesoporous carbon was impregnated with pyrrole monomers through vapor phase infiltration[7] to obtain uniformly adsorbed monomer layers on the microporous mesopore walls. The impregnation process could be precisely controlled so that the pore surfaces were coated with ultrathin monomer layers in a different thickness by varying the loading amount of monomer. The subsequent polymerization of pyrrole resulted in the MC-PPy nanocomposites with different PPy loadings of 31, 43, and 55 wt%. The weight percent of PPy in the MC-PPy nanocomposite was calculated from the elemental analysis (EA). In addition, the FT-IR analysis of MC-PPy nano-

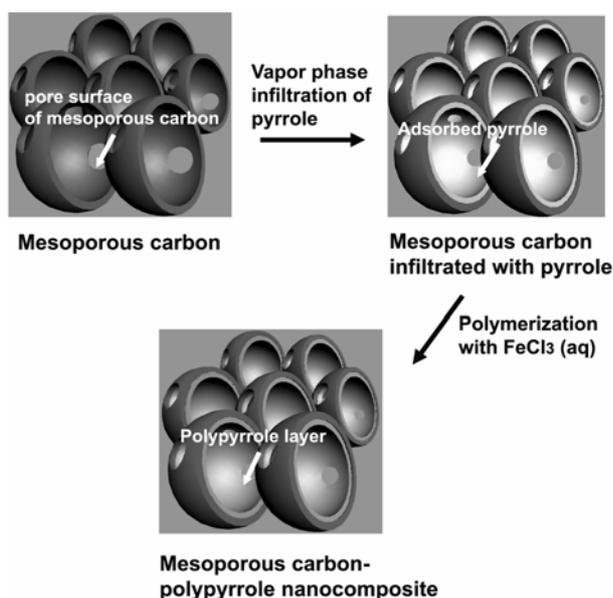*Corresponding Author. E-mail: jsjang@plaza.snu.ac.kr

Figure 1. Schematic representation of the synthetic procedure for mesoporous carbon-polypyrrole (MC-PPy) nanocomposite.
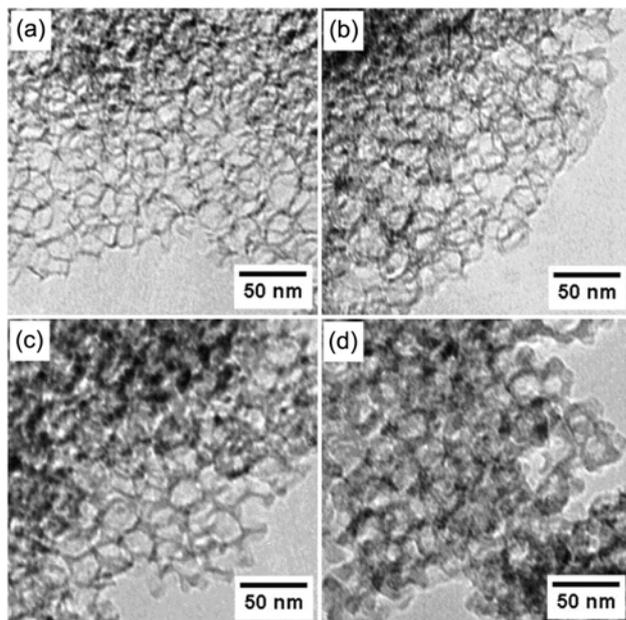

Figure 2. TEM images of (a) the mesoporous carbon with 22 nm pore diameter and the corresponding MC-PPy nanocomposites with (b) 31, (c) 43, and (d) 55 wt% PPy loadings.

Figure 3. Pore size distribution curves of (a) the mesoporous carbon with 22 nm pore diameter, the corresponding MC-PPy nanocomposites, (b) the mesoporous carbon with 12 and 7 nm pore diameter and their MC-PPy nanocomposites with 43 wt% PPy loadings. The dV and dD are differential pore volume and differential pore diameter, respectively. The normalized dV/dD was introduced to clarify the decrease of pore diameter.

composite exhibited the characteristic PPy peaks of ring-stretching bands at 1469, 1485, and 1549 cm^{-1} and N-H stretching band at 3403 cm^{-1}, which demonstrated the successful polymerization of pyrrole monomer.[5]

The transmission electron microscopy (TEM) images of pristine mesoporous carbon and MC-PPy nanocomposites confirmed that pore diameter and wall thickness were con-
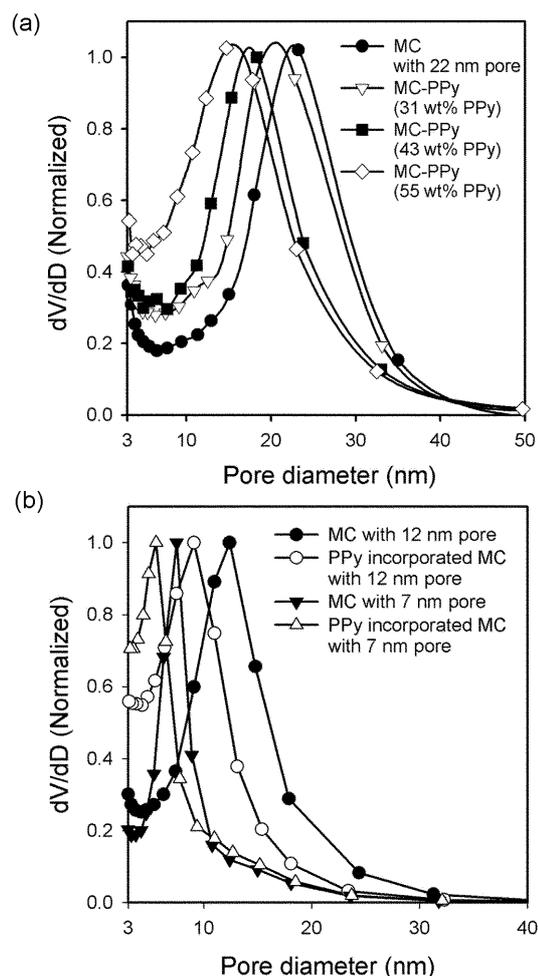
trolled as a function of PPy loading. The MC-PPy nanocomposites clearly showed the gradual increment in pore wall thickness with increasing PPy loadings (Figures 2(a)-(d)). These phenomena represented that the polymerization indeed occurred on the pore walls of the mesoporous carbon. It was noteworthy that the MC-PPy nanocomposites retained the original textural properties from the mesoporous carbon without mesopore blockage even at high PPy loading.

The MC-PPy nanocomposites showed the narrow distributions in pore sizes as well as the mesoporous carbon (Figure 3(a)). The pore structures of the mesoporous carbon and MC-PPy nanocomposites were analyzed by nitrogen adsorption-desorption isotherms at 77 K. The pore diameter of pristine mesoporous carbon was ca. 22.2 nm, which was calculated

by BJH method from adsorption branch. In the case of MC-PPy nanocomposites, the pore size systematically decreased with increasing PPy loading: 20.3 nm (31 wt%), 17.3 nm (43 wt%), and 15.5 nm (55 wt%). From these data, it could be concluded that pore diameter tunable mesoporous carbon nanocomposites were successfully fabricated by precisely controlled incorporation of PPy loading.

To verify the feasibility of our above-mentioned approach, mesoporous carbons with 12 and 7 nm diameters were infiltrated with 43 wt% of PPy loading. In the case of mesoporous carbon with 12 and 7 nm pore diameter, the narrow pore size distributions of nanocomposites were exhibited and the resulting pore sizes of nanocomposites were 9.1 and 5.6 nm, respectively (Figure 3(b)). The corresponding nanocomposites represented that the ultrathin PPy layer was also formed onto the pore surface of mesoporous carbons without pore blocking. Therefore, our fabrication strategy endows the incorporation of PPy into mesoporous carbons with various pore diameters.

Cyclic voltammetry measurements were performed to investigate the EDLC performance of MC-PPy nanocom-

Figure 4. Cyclic voltammograms of (a) mesoporous carbon with 22 nm pore diameter, the corresponding MC-PPy nanocomposites, (b) PPy incorporated mesoporous carbon (12 nm pore diameter) nanocomposite, and PPy incorporated mesoporous carbon (7 nm pore diameter) nanocomposite. The scan rate was 5 mV/s.

posites. The cyclic voltammograms (CVs) of the mesoporous carbon with 22 nm pore diameter and related MC-PPy nanocomposites are presented in Figure 4(a). The CVs of MC-PPy nanocomposites displayed a steep increase in the current over the potential range of 0.0-0.1 V, which a steepness of current is an important behavior in ideal supercapacitor. In ideal capacitor, energy must be abruptly retrievable and storable over the switching potential in discharging and charging, which is shown in steepness of current. Specific capacitances of MC-PPy nanocomposites at 31 and 43 wt% of PPy loadings were 176.5 and 222.7 F/g, respectively. MC-PPy nanocomposite at 55 wt% of PPy loading exhibited the specific capacitance of 233.6 F/g, which was a two-fold higher value compared with the mesoporous carbon (102.6 F/g). High specific capacitance of MC-PPy nanocomposites could be associated with the retained pore structure and inherent pseudo-capacitance property of conducting PPy.[1] It was found that the capacitances of MC-PPy nanocomposites increased with increasing PPy loadings. In general carbon-conducting polymer composites, conducting polymer and carbon serve as electron donor and electron acceptor, respectively.[8] These charge-transfer complexes between carbon and conducting polymer afforded the enhanced electrochemical performance. Additionally, the conductivity of pristine PPy and MC-PPy nanocomposites was measured by the four-probe method. The conductivity of pristine PPy was 2.6 S cm^{-1} and MC-PPy nanocomposites exhibited the conductivity of 19.1 to 25.3 S cm^{-1}. This increase of conductivity in MC-PPy nanocomposites is attributed to mesoporous carbon framework with high conductivity compared to pristine PPy. In the MC-PPy nanocomposites of mesoporous carbons with 12 and 7 nm pore size, the CVs showed similar behaviors to nanocomposites of mesoporous carbon with 22 nm pore diameter (Figure 4(b)). The specific capacitances of these MC-PPy composites were measured to be 238.9 (12 nm mesoporous carbon) and 274.5 F/g (7 nm mesoporous carbon), respectively. Judging from these results, it was demonstrated that introduction of PPy layer into mesoporous carbons enhanced the performance of EDLC electrode and MC-PPy nanocomposites could be used as electrode materials for EDLC.

In summary, we synthesized the MC-PPy nanocomposites with controlled PPy loadings via vapor infiltration of pyrrole monomer and subsequent polymerization. The PPy was successfully coated onto the pore surface of mesoporous carbon up to 55 wt% of PPy loading. PPy incorporation into mesoporous carbon enhanced the specific capacitance of nanocomposites due to pseudo-capacity character of PPy layer and the specific capacitances had a strong dependency on the PPy feeding amounts. This methodology could provide the fabrication of small pore sized MC-polymer nanocomposites and might be expanded to allow the synthesis of various core-shell nanostructures composed of metallic, inorganic or organic materials.
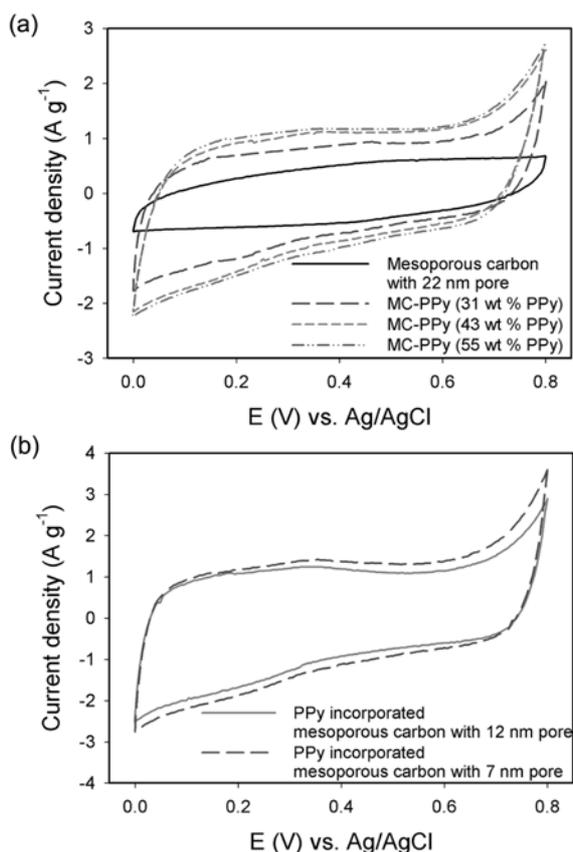
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