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Article

# 중간세공을 갖는 껍질로 구성된 속이 빈 마이크로 탄소입자의 합성 및 이들의 전기화학적 특성

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# Synthesis of Hollow Carbon Microspheres with Mesoporous Shell and Vacant Core Structure and Their Electrochemical Properties

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**초 록**

본 연구에서는 구형의 폴리스티렌 구슬을 틀로 사용하여, 크기분포가 좁으면서 속은 비어있고 벽이 다공성인 구조의 탄소 마이크로 캡슐을 합성하였다. 폴리스티렌의 표면은 무기물인 실리카졸이 쉽게 입혀질 수 있도록 폴리비닐피롤리돈(PVP)을 코팅하여 변조하였다. PVP가 코팅된 PS 마이크로 입자표면에 SBA-16 졸을 부착시킨 다음, 실리카층에 존재하는 중간 크기의 세공 내에 탄소원을 채워 넣는 음각식 형뜨기법을 적용함으로써 속이 빈 구조의 탄소 마이크로캡슐을 제조하였다. 탄화과정을 거치고 틀로 사용한 다공성 실리카입자를 HF로 용해하면, 좁은 입자크기분포를 갖는 중간세공이 함유된 계란껍질형의 탄소입자를 얻을 수 있었다. 계란껍질형 탄소 마이크로캡슐 입자의 다공성과 전기화학적 특성은 XRD, SEM, TEM, 질소분자 흡/탈착분석법 및 cyclic voltammetry법으로 평가하였다. 이들 탄소입자는 슈퍼캐패시터와 같은 전자재료로서 유효하게 사용될 만한 높은 전기전도도와 용량을 나타내었다.

**Abstract**

In this study, highly monodispersed porous carbon microcapsules with a hollow core were synthesized using polystyrene (PS) beads as a hard template. The surface of PS was first modified with polyvinylpyrollidone (PVP) for the easy attachment of inorganic silica sol. After coating the surface of PVP modified PS microspheres with SBA-16 sol, the carbon microcapsules with a hollow macroporous core were fabricated through reverse replication method by filling carbon sources in the mesopores of silica mold. The hollow carbons having a mesoporous shell structure and narrow particle size distribution could be obtained after the carbonization of carbon source and the dissolution of silica mold by HF solution. The mesoporous characteristics and electrochemical properties of hollow carbon microcapsules were characterized by XRD, SEM, TEM, $N_2$ adsorption/desorption analysis and cyclic voltammetry. They showed the high electric conductivity and capability for use as efficient electro-materials such as a supercapacitor.

***Keywords:*** *SBA-16 sol, hollow porous carbon, super capacitor, microcapsules*

## 1. Introduction

Enormous research interests have been focused on the synthesis and application of nanoporous carbons. Their unique physicochemical properties are suitable for various applications as fuel cell electrodes[1], lithium ion batteries[2], hydrogen storage vehicles[3], chemical sensors[4] and super capacitors[5]. The electrochemical capacitor is one of the important components in high power electric devices used for the development of hybrid vehicles. Super capacitors (SCs) have attracted considerable attention in recent years due to the increasing demand for novel electrical energy accumulators with a high specific power and durability[6]. Carbon-based pseudo-capacitor materials have been used to store the charges via fast Faradaic reactions and also by double-layer charging. Accordingly, carbonaceous materials such as carbon nanotubes[7-11] and mesoporous carbon[12-15] were used widely as the electrode materials of electric double layer type capacitors because of their high chemical and physical stability, good conductivity, and availability. To achieve high performance as SCs, both micro- and meso-pores should be formed in the carbon matrix to provide high

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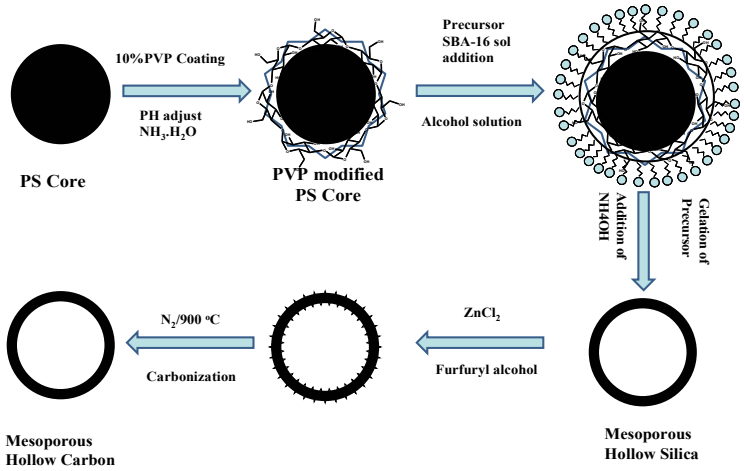



**Scheme 1. Fabrication of mesoporous carbons using PS template and SBA-16 silica-sol by sacrificial core method.**

surface areas, which plays an important role in charging the electrical double layer and providing easy electrolyte diffusion for accessibility[12,15]. Most activated carbon commercially available contains micropores, allowing only slow ion transportation rates through the small pores. On the other hand, the presence of interconnected regular mesopore channels probably may provide the large surfaces favorable for charging the electric double-layer through improved electrolyte transport[11-14].

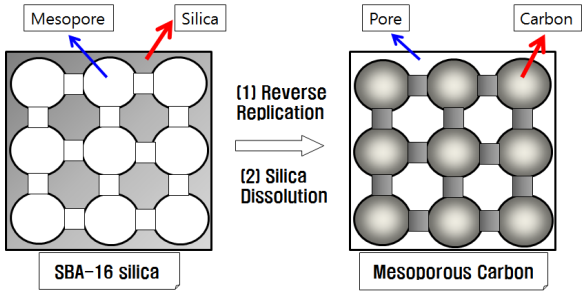
In addition, the porous carbons have been commonly used in organic synthesis for the fine chemicals as a catalyst support due to their many unique properties, such as excellent chemical stability in both acidic and basic media. These active porous carbons are highly porous enough to allow the fine dispersion and stabilization of small metallic particles. However, they have a very broad pore size distribution from micro to macroscopic range. Ordered mesoporous carbon (OMC) materials may overcome this obstacle, because they exhibit the large size of pore with a narrow pore size distribution and higher surface areas. In recent years, there was a growing interest in the synthesis of OMCs by using porous inorganic templates as a mold[16-19]. Particularly, the synthesis of OMC that employs ordered mesoporous silicas as templates has attracted much attention due to the structural ordering of pores and tailored porosity, as well as easy functionalization of mesostructures. These features shed light on future perspectives for the development of new adsorbents[20], catalysts[21], electrode materials [19] and templates for ordered mesoporous inorganic materials[22]. The OMS templates have offered a big benefit from the viewpoint of structural order and diversity in achieving novel carbon structures. We have fabricated OMCs containing hexagonally ordered mesopores through reverse replication method by using mesoporous silica such as SBA-15 particles as a mold[23,24]. Porous carbons could be fabricated by the nanocasting method, using inorganic silicas as a mold[25-30]. This type of carbons could be applied in many fields including catalysis, separation and energy storage due to their uniform pore structure with a large pore volume[31]. The core-shell type microcapsules have shown various efficient properties owing to their unique structures. They were applicable to a wide variety of materials for electronics and biologically active agents. Consequently, some recent research efforts have been paid to the synthesis of spherical hollow particles with a narrow size distribution[32-34].

As a typical procedure, inorganic hollow microspheres can be synthesized by sacrificial core method for which nano-sized inorganic particles are coated on the surfaces of polystyrene (PS) spheres by controlled precipitation of inorganic precursor molecules. The template polymers are subsequently removed by selective dissolution in the proper solvents or by calcination in air to generate the inorganic hollow spheres. In this respect, a general synthetic strategy for mesostructured hollow carbons guided by host-guest chemistry is much desired. Here in this work, the fabrication of carbon microcapsules with hollow macroporous core and mesoporous shell structure is presented. PS beads with a monodispersed size distribution were used as a template core for the synthesis of hollow carbon. However, the porous carbons are well known as fundamental candidates for raw electrochemical materials. As a result, the mesoporous hollow type carbons fabricated in this study can be used as a efficient material because they have unique structure with a mesoporosity in the shell wall and vacant cores, providing the improved diffusivity of big molecules in application.

## 2. Experimental

### 2.1. SBA-16 sol coating on PVP modified PS

The SBA-16 silica sol was prepared according to the method reported previously in the literature[34]. The triblock copolymer, Pluronic F-127 (Aldrich), was used as a surfactant and tetraethylorthosilicate (TEOS, 98%, Alchich) as a silica source, respectively. The starting composition in molar ratio for the synthesis of high grade SBA-16 sol was fixed as 1.0 TEOS : 0.011 F-127 : 10.1 Ethanol : 0.24 HCl : 10 $H_2O$. This sol was coated on the surfaces of PS microspheres for the synthesis of silica microcapsules with hollow macroporous core/mesoporous shell structure in a narrow particle size distribution. The general procedure to fabricate the hollow carbon microcapsules is shown in Scheme 1. The prior modification of PS surfaces by coating a polyvinylpyrollidone (PVP) polymer was critical for the successful




**Scheme 2. Concept of mesoporous carbon formation from SBA-16 silica by reverse replication.**

deposition of hydrophilic precursor (inorganic sol) on the polymer surfaces. PS bead with a size distribution in 0.4～0.6 micrometer scale was used as a template core in the synthesis. First of all, PS polymer was coated by PVP at the amount of 10 wt%. This sample was dried at 80 ℃ under vacuum for 12 h. The PVP modified PS particles (2.0 g) were dispersed in the solution of octanol (10 mL) with stirring for 0.5 h, and SBA-16 sol (8 mL) was added dropwise to the suspended solution. Then methanol (60 mL) was additionally introduced into the mixture. Deposition of silica sol to form the mesoporous shells has been performed for 6 h under a vigorous stirring at 50 ℃. Finally, ammonia water (0.3 mL) was added into the solution with stirring. The silica sol coated PS composite was filtered, dried at 100 ℃ for 48 h, and then the block copolymer F127 in the pore of as-synthesized hollow silica was extracted in the refluxing methanol solvent (300 mL) acidified with HCl (35%, 2 mL).

### 2.2. Synthesis of mesoporous hollow carbon microcapsules

The reverse replication of mesoporous silica by infiltration of pores with furfuryl alcohol and $ZnCl_2$ has been performed for the synthesis of carbon replica of hollow microcapsules, as shown in Scheme 2. The mixed composite sample was dried at 150 ℃ for 12 h after filling the pores by incipient wetness method, and heated in a muffle furnace from room temperature to 900 ℃ with a temperature heating rate of 5 ℃/min. The temperature was maintained at 900 ℃ for 5 h, and was then cooled down to room temperature. Finally the silica template was removed using an aqueous 10 wt% HF solution (50 wt%; Duksan Pure Chemicals Co. Ltd.). The porous carbon microcapsule products were recovered by filtration after washing with the mixture of distilled water and methanol.

### 2.3. Characterization

X-ray powder diffraction (XRD) data were acquired on a D/MAX 2500V/PC diffractometer using CuK$\alpha$ radiation. The morphology and microstructures of as-prepared and calcined samples were characterized by field emission (FE) TEM (S-4200), and FE-SEM (JEM-2100F). The nitrogen adsorption/desorption analysis was performed at -196 ℃ by using a surface area and porosity analyzer equipment (Micromeritics, ASAP 2010) to determine BET surface area and the mean pore size. Electrochemical properties of mesoporous metal oxides were tested by Cyclic voltammetry (Autolab 128N).

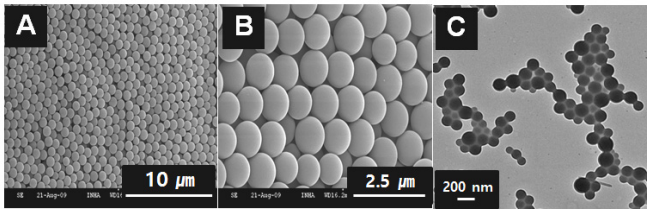



**Figure 1. SEM (A, B) and TEM (C) images for PS micro beads used as a hard template for the fabrication of hollow mesoporous silica and carbon microcapsules.**

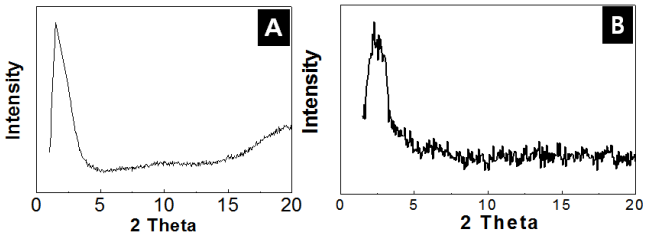



**Figure 2. XRD pattern of hollow mesoporous silica sphere (A) and carbon microcapsule (B).**

## 3. Results and Discussion

Figure 1 shows the SEM and TEM images for PS beads used as a hard template in this work. They have a narrow particle size distribution, showing the monodispersed mean diameter in the range of 0.4～0.6 μm. Because the surface nature of PS is hydrophobic, the prior modification of PS surfaces by coating PVP was critical for the successful deposition of inorganic SBA-16 sol. Coating of 10 wt% of PVP was adopted in this work.

After coating of PVP, the PS particles were used for attachment of SBA-16 sol on their surfaces. Through the reverse replication of mesoporous silica by infiltration of pores with furfuryl alcohol and $ZnCl_2$, the porous carbon microcapsule products could be obtained after removal of PS and silica walls by calcination in air and HF treatment, respectively.

To investigate and confirm the formation of mesoporous SBA-16 silica silica layer coated on the surfaces of PS, XRD analysis was performed, and the obtained diffractograms of SBA-16 silica shell wall and corresponding carbon shell fabricated after replication treatment are presented in Figure 2.

The XRD pattern of SBA-16 silica microcapsule shows no well-resolved peaks at $2\theta$ angles below 5°, which correspond to the cubic im3m space. This means the shell of hollow capsule is constructed by irregularly connected mesopores, due to losing the ordering of cubic structure. However, It is clear that both of SBA-16 silica and corresponding carbon samples have the mesoporosity in the shells, showing a big peak at near 2.5 degree.

Additionally, to confirm the structures of pores formed in the shell of silica and carbon, the nitrogen adsorption-desorption experiment was tested, and the results are listed in Figure 3. Figure 3 shows the nitrogen adsorption-desorption isotherms of the hollow-type porous silica and carbons synthesized in this work. Their isotherms are both type IV

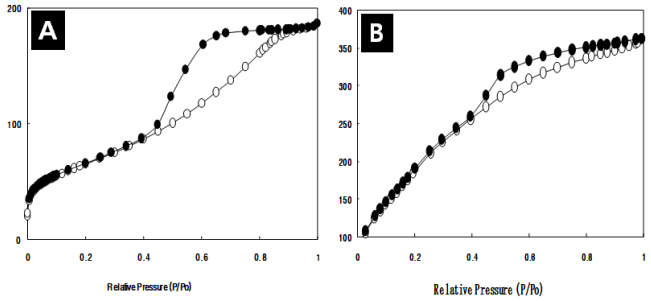



**Figure 3. Nitrogen adsorption/desorption isotherms for starting hollow type mesoporous silica (A) and mesoporous hollow carbon capsules (B) templated by PS.**

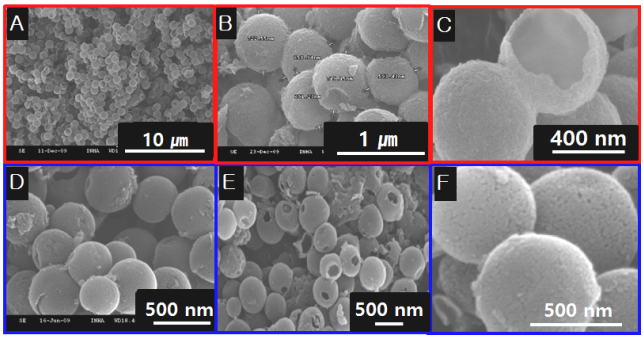



**Figure 4. SEM images of mesoporous hollow silica spheres (A, B, C) and hollow carbon spheres (D, E, F).**

with a hysteresis loop, indicating that the mesopore channels are present in the wall of hollow shell. The specific surface areas of mesoporous silica and the corresponding carbon microcapsules obtained after reverse replication treatment from the mesoporous silica are 320 $m^2/g$ and 500 $m^2/g$, respectively. The mesopores with average pore size of around 50 Å were formed inside the wall of silica and carbon shell. This result confirms that the introduction of mesostructured pore channels into the shell wall of mesoporous hollow silica and reversely replicated hollow carbon was performed successfully.

To show the successful fabrication of hollow type structure, the microspheres of silica and carbon were characterized by SEM and TEM. Figure 4 shows SEM images of various mesoporous silica and carbon microcapsules fabricated using PS beads with diameter of around 0.5 μm as core templates, respectively. We found that the monodisperse microcapsules could be synthesized very easily by our method. The microcapsules having a hollow core with mesoporous shell was generated after burning out the PS template in air. As shown in Figure 4, a hollow structure with vacant core was clearly investigated in the picture of (C) and (E). Some particles have partially broken shells, indicating the imperfect coverage of silica sol could happened during the coating step on PS surfaces. Optical microscope image also revealed that the calcined hollow silica and carbon microcapsules have the spherical shape with uniform size.

TEM images revealed that the shapes of calcined $SiO_2$ and carbon microcapsules with a mesoporous shell were spherical with nearly uniform size and thin walls. The shell of hollow core is composed of very

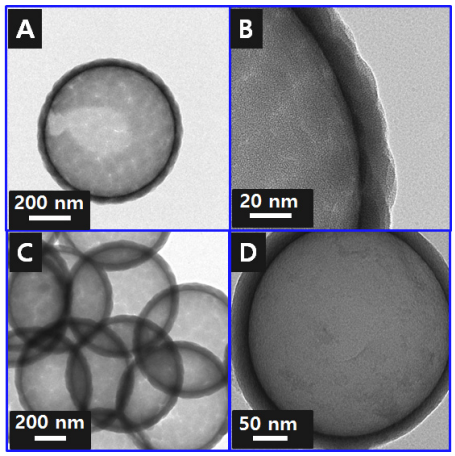



**Figure 5. TEM images of hollow silica sphere (A, B) and hollow carbon spheres (C, D).**

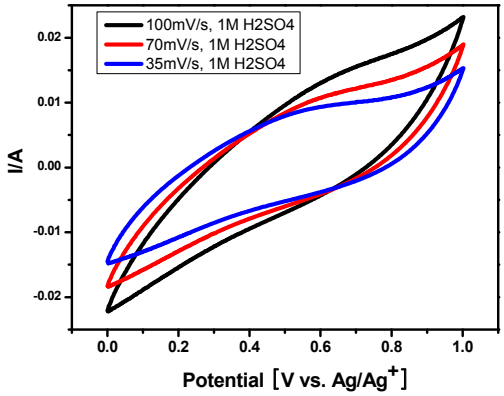



**Figure 6. Cyclic voltammograms of hollow carbon spheres.**

small mesopores as can be seen in Figure 5(B). The presence of mesoporous pores could be found clearly in the enlarged images of TEM.

To examine the electrochemical properties of mesoporous hollow type carbons, the Cyclic Voltametric tests were performed in 1.0 M aqueous $H_2SO_4$, and the obtained CV curves for the mesoporous hollow carbon microcapsules are listed in Figure 6. The electrode displays a capacitive charging current in both anodic and cathodic scanning directions across the potential range 0～1.0 V (versus Ag/AgCl reference electrode) at the scan rate of 35～100 mV/s. As shown in Figure 6, the high current intensity was measured for the porous hollow carbon microcapsules. This can be interpreted in terms of those materials have large surface areas due to the highly porous structure which can provide fast, non-faradic reactions through electric double layer charging.

Additionally, the electric conductivity in the organic solution containing the hollow carbon microcapsules has been investigated in this work. The electrorheological (ER) fluids were prepared by sonication using the dried hollow carbon microcapsules dispersed in silicone oil (10 vol%). No stabilizers were added to the microspheres dispersion in the silicone oil. A DC high voltage source was used to apply a voltage to the sample. The gap between the two parallel electrodes was fixed at 350 mm. The microstructure image of the ER fluid was obtained using an optical microscope. The behavior of the particle chain (so-called

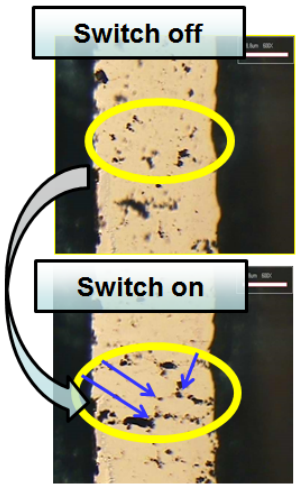



**Figure 7. Optical microscopic images of the hollow carbon microspheres dispersed in silicone oil before (up) and after (down) the application of an electric filed strength of 1.4 kV/mm. Both sides of the horizontal black stripes represent the electrodes. The gap distance between two parallel electrodes was 350 mm.**

'fibrillation'), based on the interfacial polarization within microspheres in silicone oil, was demonstrated under an applied electric field of 1.4 kV/mm for 5 sec. The hollow carbon microspheres formed the thin connecting chains of particles when the electric field was applied, and the structure remained stable as long as the field was applied. The fibrillated chains were observed and spanned between two electrodes as shown in Figure 7. It is possible that the fibrillated chains structure might provide a path for the mobile carrier transporting, and would determine the conducting behavior of ER fluids.

## 4. Conclusions

Highly monodispersed porous carbon microcapsules with a hollow core could be synthesized using PS beads as a hard template, in this work. After coating of SBA-15 sol on the surfaces of PVP modified PS microspheres, the mesoporrous carbon microcapsules with a vacant macroporous core was fabricated through reverse replication method by filling furfuryl alcohol and $ZnCl_2$ as a carbon source and a catalyst in the mesopores of silica mold, respectively. The carbons having a mesoporous shell structure and narrow particle size distribution could be obtained after carbonization of carbon source and dissolution of silica mold by HF solution. The mesoporous nature and the electrochemical properties of hollow carbon microcapsules were characterized by XRD, SEM, TEM, $N_2$ adsorption/desorption analysis and cyclic voltammetry. XRD result indicated that the shells of hollow capsule of silica and carbon were constructed by irregularly connected mesopores, and the hollow structure with vacant core could be clearly investigated in the images of TEM. TEM images also revealed that the shapes of calcined $SiO_2$ and carbon microcapsules were spherical and the particle distribution was very narrow. The obtained mesoporous hollow type carbons have shown the high electric conductivity and the capability for use as efficient electro-materials.

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