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# A Novel Template Route for Synthesizing Mesoporous Carbon Materials

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A novel template route by mixing ZnO nanoparticle templates and a polyacrylamide carbon source with mechanical stirring and followed by carbonization and template removal is first reported for synthesizing mesoporous carbon materials.

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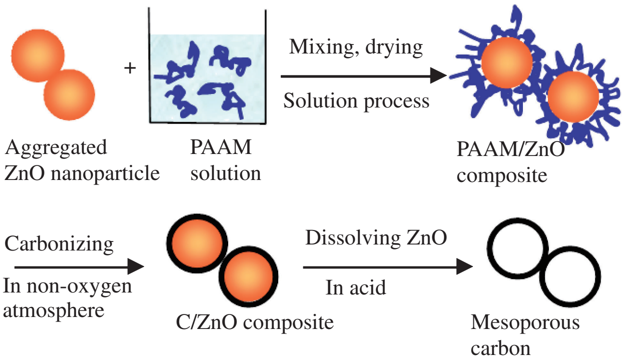
Mesoporous carbon (MC) materials are scientifically and technologically important for finding new advanced materials and for various immediate applications such as in supercapacitors, adsorbents of bulky pollutants, and the immobilization of biomolecules for biosensors.[1] Template methods are most promising for the preparation of MCs with controlled narrow pore size distribution (PSD). A recent study reported a soft-templating method by using a thermosetting polymer and a thermally decomposable surfactant to form a periodic ordered nanocomposite.[2] Mesoporous silicate and silica nanoparticles called hard templates have previously been used for the synthesis of MCs.[3–8] For obtaining MCs with the same particles size distribution of silica templates, the key point is to infiltrate the organic precursors around individual silica nanoparticles. Han et al. studied the effects of dispersion of silica in organic precursors on PSD of MCs.[3,6] They use a 12-nm silica nanoparticles as templates. They showed clearly that the resulting carbon has a broader PSD than the particle size of silica when using the silica nanoparticles without dispersion. They later improved the process by stabilizing the silica particles, and the resulting carbon showed a narrow PSD with the most probable pore size of about 10 nm, corresponding to the size of the templates. The silica nanoparticles are excellent templates because their dispersion behavior in solvent is well studied and easily controlled. However, dissolution of silica templates uses poisonous HF acid, and the by-product of the dissolution, $SiF_4$, is rarely recycled and environmentally unfriendly. MgO and its compounds are also developed as hard templates for synthesized porous carbons.[9] However, the templates could not perfectly control pore sizes of obtained porous carbons.

In this study, a novel hard template of ZnO nanoparticles is first reported to be used for synthesis of MC, with organic polyacrylamide (PAAM) carbon source. The process is illustrated in Scheme 1. The aggregated ZnO nanoparticles can be dispersed individually in PAAM matrix by a simple solution process. After carbonization of PAAM in non-oxygen atmosphere, a carbon network formed around the ZnO nanoparticles. Finally, mesopores were formed by dissolving the ZnO nanoparticle template in acetic acid. The process is simple and controlled easily.

The raw material of ZnO nanoparticles (0.02 µm, Wako Practical Grade) and polyacrylamide solution (PAAM, 10 wt %, molecular weight of (6–10) × $10^5$) purchased from Wako Co., Ltd. were used as received without any treatment. 3 g of ZnO nanoparticles was added to 25 $cm^3$ of distilled water followed by stirring at 700 rpm for 1 h, then 10 g of PAAM solution was added. The suspensions were stirred at 700 rpm for 4 h. Finally, the suspensions were dried at 373 K for 12 h to obtain a PAAM/ZnO composite. Then, the PAAM/ZnO composite was heated at 700 °C for 3 h in a tube electric furnace in $N_2$ gas containing 3% $H_2$ with a flow rate of 50 $cm^3\,min^{-1}$ for carbonization of PAAM. A black C/ZnO composite was obtained after cooling. A mesoporous carbon product was obtained by treating the C/ZnO composite in 50 wt % acetic acid for 4 h with the mole ratio of $H^+/ZnO = 2.5$ after washing and drying at 373 K. A mixture of KOH and the product (1:10 weight ratio) was heated at 800 °C for 10 h then dissolved in HCl solution for zinc analysis by atomic adsorption spectrometry (Shimadzu, A7000). Differential thermal and thermogravimetric analysis (DTA-TG) curves were obtained on a Shimadzu DTG-50 thermal analyzer at a heating rate of 10 $K\,min^{-1}$. Nitrogen adsorption/desorption isotherms at 77 K were obtained on a QUANTACHROME AUTOSORB 1-C apparatus with a sample outgassed for 2 h below $10^{-3}$ mmHg at 527 K. The total specific surface area ($S_{BET}$) was calculated by the Brunauer–Emmett–Teller (BET) method. The PSD was analyzed by the Dollimore–Heal (DH) method from desorption isotherms. The total pore volume ($V_{total}$) was calculated to be $P/P_0 = 0.99$, and the microporous specific volume ($V_{micro}$) estimated by t-plot. The mesopore volume ($V_{meso}$) was calculated as the difference between $V_{total}$ and $V_{micro}$.



**Scheme 1.** Synthetic procedure of mesoporous carbons with ZnO nanoparticles template route.

The raw ZnO nanoparticles are aggregated particles as shown in Figure 1a. ZnO nanoparticle suspensions in distilled water gave rise to precipitate immediately after stirring was stopped. The ZnO nanoparticles form flocs immediately after dropping in PAAM solution; however, the flocs disappear speedily with stirring. Finally, well dispersed, stable suspensions of ZnO nanoparticles were created. We found that the suspensions did not precipitate for 24 h after stirring was stopped, and

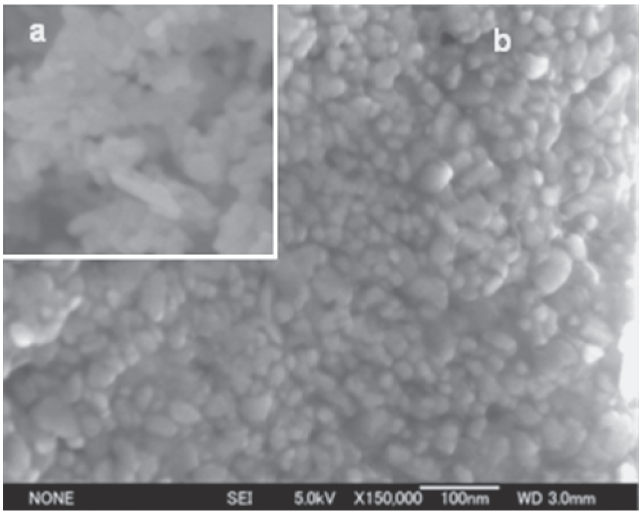


**Figure 1.** HRSEM images of the ZnO raw material (a) and the PAAM/ZnO composite (b).

even by centrifuging at 5000 rpm for 40 min. The ZnO nanoparticles can be dispersed well in PAAM solution without any pretreatment of the raw materials by only mechanical stirring. PAAM molecules permeate into interfaces between the aggregated ZnO nanoparticles by capillary percolation to separate the nanoparticles aggregated in the solution and then adsorbed on the surface to stabilize colloidal suspension by a mechanism called steric stabilization.[10]

HRSEM observation of the PAAM/ZnO composite obtained after drying the suspension showed that the ZnO nanoparticles dispersed well in the PAAM matrix as shown in Figure 1b. The ZnO nanoparticles can be clearly observed individually in Figure 1b, different from the ZnO raw materials in Figure 1a. This shows that ZnO nanoparticles could be dispersed individually in PAAM matrix using this process. PAAM plays an important role in the dispersion of ZnO nanoparticles. The particle size measured from the HRSEM image shows a size distribution of the ZnO nanoparticles from 13 to 25 nm with the largest value of 18 nm as given in Figure 2a.

The results of TG-DTA analysis indicate that the main pyrolytic reactions of PAAM and the PAAM/ZnO composite ended at around 450 °C in atmosphere of $N_2$ containing 3% $H_2$. The heating temperature of 700 °C in this study is high enough for the carbonization of PAAM.

The mesoporous carbon product shows ZnO content lower than 0.2 wt %. The $N_2$ adsorption/desorption isotherms of the mesoporous carbon product can be categorized as type IV with a typical mesoporous material.[11] The product has a $V_{\text{total}}$ of 2.33 $\text{cm}^3\,\text{g}^{-1}$ and a $V_{\text{meso}}$ of 2.12 $\text{cm}^3\,\text{g}^{-1}$ and $S_{\text{BET}}$ of 1102 $\text{cm}^2\,\text{g}^{-1}$. The PSD of the mesoporous carbon product is in the range of 8–22 nm as shown in Figure 2b, which is very close to 13–25 nm of the particle size distribution of the ZnO nanoparticles shown in Figure 2a. Because the mesopores are formed by ZnO removal, The $V_{\text{meso}}$ may be equal to the volume of the ZnO nanoparticle template dissolved. Because 1 g of the C/ZnO composite produces 0.077 g of the mesoporous carbon product, the volume of the ZnO template dissolved from 1 g of the product was 2.14 $\text{cm}^3$, using the ZnO density of 5.6 $\text{g cm}^{-3}$. This value is close to 2.12 $\text{cm}^3\,\text{g}^{-1}$ of the $V_{\text{meso}}$ described above. These agreements in the PSD and the volumes indicate that the dissolution reaction of the ZnO nanoparticle template takes place topotactically to form mesopores, in other words the ZnO nanoparticles transfer to the mesopores individually.

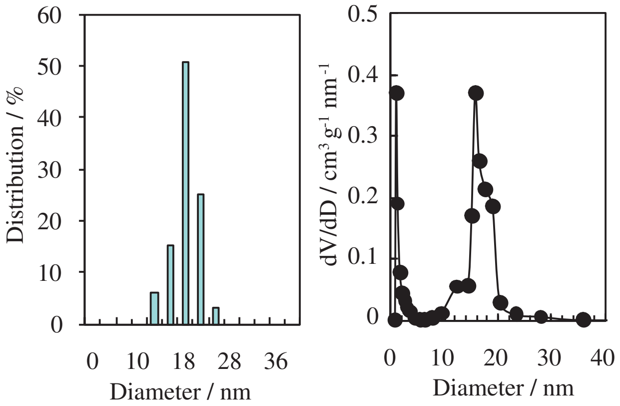


**Figure 2.** (a) Particle size distribution of the ZnO raw material obtained by measuring particle size in HRSEM image of Figure 1b. (b) PSD analyzed from the desorption isotherm.

ZnO nanoparticles were first used as a template with PAAM carbon source for synthesizing mesoporous carbons. This process is environmentally friendly and can be expected to reduce costs because $Zn^{2+}$ or $Zn(OH)_4{}^{2-}$ solutions by the dissolved by-products can be easy recycled for synthesis of ZnO nanoparticles by aqueous processes.[12]

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