Facile Templating Methods to Remarkable Architectures of Nanoporous Carbon Spheres

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A colloidal crystal fabricated from monodispersed mesoporous silica spheres (MMSS) has been employed as a sacrificial template to prepare nanoporous carbon architectures. The mesostructure of MMSS was well replicated, even when they were fabricated to the colloidal crystal, in the nanopores of the carbon spheres. By changing the filtration process slightly, the 3D-packed nanoporous carbon colloidal crystal and the novel "ball in cup" carbon hierarchical structure were successfully obtained.

In recent years, carbon materials with well-ordered porous structures are expected to be used in many applications, such as gas storage, catalyst supports, and electrode materials.[1–3] Among the various methods for creating porous carbons, nanocasting strategy is one of the most promising techniques.[4–8] We have previously reported the adaptation of this nanocasting procedure to monodispersed mesoporous silica spheres[9] (by the acronym MMSS hereafter), resulting in carbon spheres, which well replicated the internal structure of MMSS.[10] By conducting a layer-by-layer technique (LBL)[11] on the mesoporous silica (MMSS)/carbon composite to enhance its dispersibility in water, the close-packed arrays from these composite particles have been fabricated via self-assembly. Following the removal of the coated electrolytes and dissolution of MMSS templates in hydrofluoric acid, three-dimensional (3D) close-packed colloidal crystals of nanoporous carbon have been obtained. However, to reach the ultimate goal, many procedures and time were essential. It would be more useful if 3D-packed colloidal crystals of nanoporous carbon could be fabricated by more simple and efficient methods.

In addition to the 3D-packed arrays, a hierarchical porous carbon architecture has received a great deal of attention. These hierarchical carbons are mainly composed of macroporous carbon (ca. inverse opal carbon) with mesoporous walls.[12,13] The combination of macropores and mesopores is very attractive, because of the enhancements in mass transportation and specific surface area. However, the location of the mesopores is almost limited to the carbon walls, owing to their fabrication method. A brand-new-hierarchical porous architecture will definitely open new perspectives for increased applications. Here, we report a simple and facile nanocasting method to obtain two types of ordered carbon structure; 3D-packed colloidal arrays and hierarchical porous colloidal structures (novel "ball in cup" architecture) by the use of a close-packed colloidal crystal of MMSS as a template.

MMSS was prepared using a cetyltrimethylammonium chloride as a structure directing agent and a tetramethoxysilane (TMOS) as a silica source, according to our previous report.[9] In our facile nanocasting method, a colloidal crystal from MMSS, with a diameter of 560 nm and a standard deviation of 3.8%, was used as a sacrificial scaffold. To obtain well-ordered arrays of MMSS, an electrophoretic deposition (EPD) process[14] was performed to an aqueous dispersion of MMSS, employing both cathode and anode electrodes of ITO. The deposited film was carefully peeled from the cathode electrodes and dried at room temperature. The film obtained was annealed at 1073 K to create necks[15] between MMSS, which means the MMSS template was solidified. To accomplish the 3D-packed nanoporous carbon arrays, the colloidal film of MMSS was immersed in furfuryl alcohol for 3 h at ambient temperature. Filtration was performed to remove a residual carbon precursor, which occupied interstitial spaces within the MMSS by adding drops of ethanol, followed by polymerization in air at 423 K. This procedure was repeated twice and finally, the composite colloidal arrays were carbonized at 1173 K in nitrogen flow. Hydrofluoric acid etching was carried out to give the colloidal crystals of nanoporous carbon spheres by dissolving MMSS colloidal crystal template.

The preparation of a novel "ball in cup" carbon hierarchical architecture was similar to that of 3D-packed structures. The differences were that the filtration process was not conducted sufficiently and the second immersion time was longer (12 h), in order to leave the carbon precursor in the interstices of MMSS in the colloidal film. After the final polymerization step, the subsequent process was the same as that of the former one.[16]

Figure 1 shows the SEM images of the colloidal crystal of MMSS (a) and the resultant 3D-packed carbon arrays (b), (c). In both structures, highly ordered hexagonal arrays can be observed over relatively large domains. From EDX analysis, the ratio of C/Si of the carbon colloidal crystal was estimated to be 98.1/1.9, indicating that almost all the silica template was removed. The size of the replicated carbon spheres decreased to almost half (ca. 300 nm) that of MMSS template. However, as was observed in our previous report, the 3D-close-packed

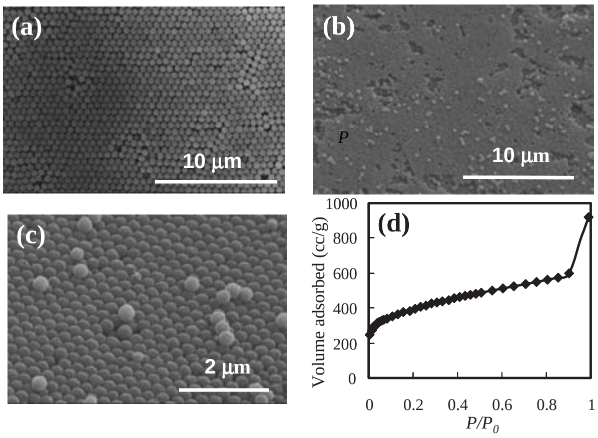

Figure 1. (a) SEM image of MMSS colloidal crystal template. (b)–(d) Structural characterization of the resultant 3D-packed nanoporous carbon arrays [(b)–(c) SEM images. (d) nitrogen adsorption isotherm.].

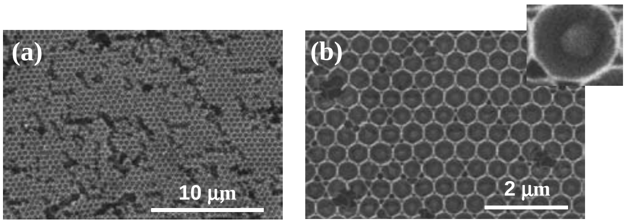

Figure 2. SEM images of a novel "ball-in-cup" carbon nanostructure. The inset is corresponding local magnification.

structure was maintained, even after immersion in the hydrofluoric acid solution, in spite of the considerable shrinkage of the spheres. A colloidal opalescence is definitely observed on the obtained ordered arrays of the carbon replica. A nitrogen adsorption isotherm of the colloidal crystal of carbon is shown in Figure 1d, which was a typical type I, indicating the development of microporosity. We were able to confirm the presence of the micropore (ca. 1.2 nm) directly by the DFT analysis. The BET specific surface area was $1300\,\mathrm{m^2\,g^{-1}}$ and the total pore volume was $0.75\,\mathrm{cm^3\,g^{-1}}$.

Figure 2 shows the SEM images of the novel "ball in cup" carbon hierarchical structure. This structure is constructed from an inverse opal backbone, in which each macropore is partially occupied by a small ball. In the EDX analysis, the estimated ratio of C/Si is 98.2/1.8, revealing that this attractive architecture was entirely built-up from carbon. The validity that the small carbon ball replicates the porous structure is also confirmed by the nitrogen adsorption measurement. Although the BET specific surface area is $620\,\mathrm{m^2\,g^{-1}}$, which is smaller than that of 3D-packed colloidal crystal type, a steep increase derived from microporosity was observed. The evaluation successfully supports that the replicated carbon architecture has a hierarchical porosity: macropores providing pathways for fast mass transfer and micropores promising high surface area and pore volume.

The formation mechanisms of the ordinary type of 3D-packed colloidal crystal and the new type of opal with the hierarchical porosity (ball in cup) are considered as follows. When the colloidal crystal of MMSS is immersed in furfuryl alcohol, the mesopores of MMSS are first filled with furfuryl alcohol by capillary condensation. As for preparing the 3D-packed colloidal carbon, to enable subsequent infiltration of the carbon precursor, the residual carbon source, which occupies the interstices between MMSS, must be removed before the polymerization process. By contrast, when the carbon precursor remains in the interstices between MMSS, subsequent polymerization results in solidified inverse-opal backbone which blocks the second infiltration of furfuryl alcohol into the mesopores. This assumption is supported by the difference in the carbon sphere size observed in the SEM images. The particle size of the 3D-packed carbon colloidal crystal is about 300 nm, being larger than that of the small ball (200 nm) in the new hierarchical carbon colloidal structure. As well as the filtration process after first immersion of furfuryl alcohol, the size of interconnecting pore is also a key determinant to obtain the "ball in cup" carbon hierarchical structure. When the sintering temperature was relatively high or heating time was longer, interconnected pore grew larger, resulting in failure to encage the small carbon ball inside the inverse-opal carbon backbone.[16] Although, the optimized route to the "ball in cup" carbon structure still remains a challenge, this hierarchical architecture, to the best of our knowledge, has been reported for the first time. It is reasonable to expect that this architecture has a potential to open new perspectives for application in catalyst, electrochemical systems, or photonic devices. Study is underway to clarify the possibility of the emerging practical applications as well as to optimize the fabrication conditions.

In conclusion, a simple and facile nanocasting method, in which MMSS colloidal crystal was used as a sacrificial scaffold, has been successfully employed to prepare nanoporous carbon architectures. Even when fabricated to the colloidal crystal, the mesostructure of MMSS was well replicated in the nanopores of the carbon colloidal crystal. The 3D-packed colloidal crystal and the novel "ball in cup" carbon hierarchical structure were obtained by merely changing the filtration process slightly. The colloidal structures prepared, especially the "ball in cup" carbon hierarchical structure, are expected to open up the possibility for emerging applications.

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