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Layer-by-Layer Films of Dual-Pore Carbon Capsules with Designable Selectivity of Gas Adsorption

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Establishing removal technologies of environmentally deleterious substances is currently one of the most urgent and important issues especially for removal of hydrophobic aromatic compounds, some of which are known to be potentially carcinogenic or mutagenic.[1] Nanostructured materials with regular pore geometries, such as mesoporous materials,[2] metal organic frameworks,[3] and patterned films,[4] have received much attention as effective media for materials sensing, sorption, and storage due to their huge surface areas and pore volumes per unit mass. On the other hand, nano- and microcapsules[5] have been recently re-evaluated as attractive media for materials storage and drug delivery. Therefore, systems featuring a combination of the relevant characteristics, i.e., dual-pore core−shell materials with a capsule interior and nanoporous wall, should be ideal for materials' sequestration and/or storage. For these purposes, we have recently developed silica capsules possessing mesoporous walls and fabricated them into thin films[6] for automodulated materials release using layer-by-layer (LbL) techniques.[7] Subsequent efforts have recently resulted in the preparation of innovative carbon-based mesoporous capsules (dual-pore carbon capsule).[8] In this work, the dual-pore carbon capsules were incorporated into an LbL assembly for adsorption of aromatic vapor phase guests (Figure 1). In addition, we have succeeded in tuning the guest selectivity of the carbon capsule film by impregnation of additional components, resulting in designable selectivity of volatile materials adsorption.

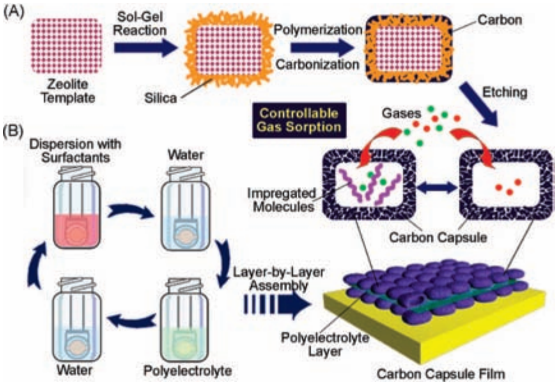

Figure 1. Schematic illustration of (A) the synthesis of carbon capsules and (B) the carbon capsule film by the LbL process.

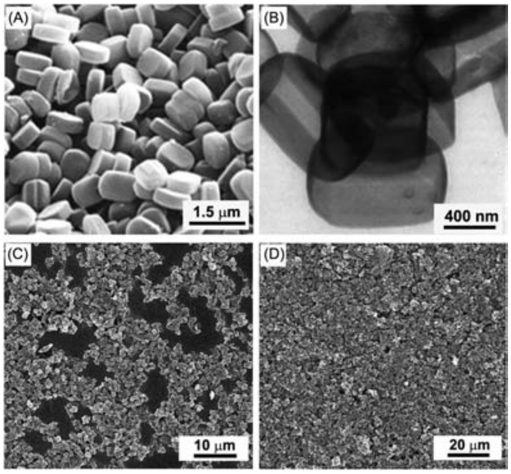

Figure 2. (A, B) SEM and TEM images of the carbon capsules. SEM images of the carbon capsule compartment films fabricated by LbL methods using carbon capsule dispersions with (C) CTAB and (D) SDS. The films were prepared using 20 LbL cycles.

Carbon capsules were synthesized using zeolite crystals as templates according to our previous reports (Figure 1A).[8] The capsules have homogeneous dimensions (1000 × 700 × 300 nm^3) with 35-nm-thick mesoporous walls with a uniform pore size distribution centered at 4.3 nm in diameter and a specific surface area of 918 m^2 g^{-1} (Figure 2A and B). Carbon capsules (4 mg) were dispersed in water with the aid of surfactants, dodecyltrimethylammonium bromide (DTAB), cetyltrimethyl- ammonium bromide (CTAB), sodium dodecyl sulfonate (SDS), and sodium alkyl benzene sulfonate (SABS) (1 mM, 4 mL) under sonication for 20 min. The dispersions obtained are stable for at least 1 week.[9] Surfactant-stabilized carbon capsules were then deposited alternately with counterionic polyelectrolytes, poly(diallyldimethylammonium chloride) (PDDA), or poly(styrene sulfonate) (PSS), resulting in LbL films assembled on quartz crystal microbalance (QCM) electrodes (Figure 1B), as confirmed by measuring the frequency shifts by QCM.[9] It should be noted that surfactant covering enables assembly of a noncharged substance in the LbL process. Scanning electron microscopic (SEM) images of the carbon capsule LbL films (Figure 2C and D)[9] indicate a variable film morphology. QCM resonators were coated homogeneously if SDS- or SABS-covered carbon capsules were employed, while an uneven distribution was observed for LbL films with DTAB- and CTAB-covered carbon capsules. This is most likely due to differing coating orientations for SDS and SABS compared to DTAB or CTAB on the surface of carbon substances[10] and affects their aggregated structures during LbL adsorption cycles.

Adsorption of various volatile substances onto the carbon capsule LbL films (5 layers, 2.4 mg) in vapor-saturated atmospheres (at 20 °C) was investigated by *in situ* frequency decrease (mass increase) of the QCM resonator used as the film support (Figure 3A). The guest substances used here have different vapor pressures, while aromatic hydrocarbons such as benzene (e) and toluene (f) are better adsorbed than water (a), aliphatic hydrocarbons (b, cyclohexane), or aromatic hydrocarbons containing a polar group (c, pyridine; d, aniline). In

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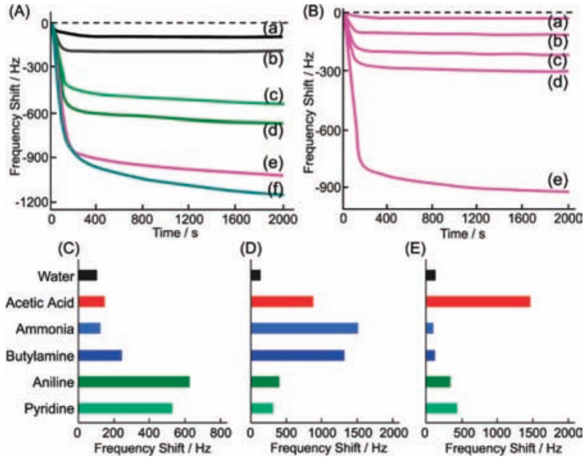

Figure 3. QCM frequency shift upon (A) adsorption of vapor phase (a) water, (b) cyclohexane, (c) pyridine, (d) aniline, (e) benzene, and (f) toluene in carbon capsule films. (B) Benzene vapor adsorption in (a) polyelectrolyte, (b) silica capsule, (c) activated carbon, (d) CMK-3, and (e) carbon capsule films, which were similarly fabricated. The gas-phase adsorptions of water, acetic acid, ammonia, butylamine, aniline, and pyridine were investigated using (C) carbon capsule, (D) lauric-acid-loaded carbon capsule, and (E) dodecylamine-loaded carbon capsule films. Films were prepared using 5 LbL cycles.

particular, the amount of benzene adsorbed at equilibrium is ca. 5 times larger than that of cyclohexane, despite their very similar vapor pressures, molecular weights, and structures, and indicating the crucial role of $\pi-\pi$ interactions[11] on volatiles' adsorption in the carbon capsule film. Carbon capsule films clearly adsorb benzene more effectively than they do cyclohexane (Figure 3B(e)). Adsorbed quantities are also apparently greater than those for polyelectrolyte LbL films (a) and even than those for LbL films of silica capsules (b),[6] activated carbon (c), and mesoporous carbon CMK-3 (d).[12] These results indicate the importance of the inner cage structure of the carbon capsule films.

Of the functional group-bearing guests (water, acetic acid, ammonia, butylamine, aniline, and pyridine), the carbon capsules have large affinities for aromatic guests such as aniline and pyridine (Figure 3C). However, selectivity could be easily tuned by impregnation with additional recognition components (about 7−8 wt%), introduced after film preparation.[9] The carbon capsule film impregnated with lauric acid showed the greatest affinities for nonaromatic amines and the second highest affinity for acetic acid (Figure 3D). Interestingly, selectivity between nonaromatic amines and aromatic amines is completely reversed in the presence of the lauric acid additive, probably reflecting the different basicity of these amines. Impregnation of dodecylamine into the carbon capsule films resulted in a strong preference for acetic acid (Figure 3E).

Exposure of the nonimpregnated carbon capsule films to ambient atmosphere[9] resulted in rapid reversion of the QCM frequency to starting values in the case of nonaromatic guests such as cyclohexane. For aromatic guests, small quantities tend to remain within the capsule films even after exposure of the film to ambient conditions, suggesting strong interaction between aromatic guests and the carbon bulk. Moreover, the impregnated capsule films retain selected guests even in guest-free atmosphere, enabling analysis of guest-included films. FTIR spectra of the lauric acid impregnated capsule film[9] indicates that ammonia adsorption causes a shift in ν(C=O) from 1702 cm^{-1} (original) to 1736 cm^{-1} (after adsorption) with the appearance of new peaks at 1670 cm^{-1} (δ(NH), H-bonded)) and 1559 cm^{-1} (COO^{-}), suggesting strong entrapment of amines through acid−base interactions.

To conclude, we have successfully prepared layer-by-layer films of dual-pore carbon capsules that exhibit excellent adsorption capabilities for volatile guests such as aromatic hydrocarbons. In addition, the selectivity of gas adsorption can be controlled flexibly by impregnation with second recognition sites. It is anticipated that these materials will find widespread applications as sensors or filters because of their designable guest selectivity. As the used carbon materials are stable in water, this system can also be used for removal of toxic materials from water.

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Supporting Information Available: Experimental details, SEM images and QCM data on adsorption/desorption, and FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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