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Mesoporous Sensors

A Layered Mesoporous Carbon Sensor Based on Nanopore-Filling Cooperative Adsorption in the Liquid Phase[**]

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The behavior of molecules in nanospaces has become one of the central issues of nanoscience.[1] In particular, spatially confined species experience enhanced intermolecular interactions because of low entropic losses, which results in highly cooperative phenomena. The mechanism of gas sorption in nanochannels,[2] for example capillary condensation, is a widely studied example, whereas cooperative adsorption within the nanospaces formed in liquid phases has not been extensively investigated despite its fundamental importance in various chemical and biological events. Such cooperative adsorption might also permit improved detection limits for size-matched biomaterials in aqueous systems with respect to conventional sensors based only on surface interactions. In order to investigate cooperative adsorption within nanospaces, and in the aqueous phase, for the development of sensitive detector systems, herein we demonstrate the layer-by-layer (LbL) assembly[3] of mesoporous carbon materials[4] on a quartz crystal microbalance (QCM) plate with the aid of polyelectrolyte binders and the use of the resulting structure for in situ sensing of nonionic aqueous guests (Figure 1 A). The work described herein includes the following key features: 1) the first example of LbL assembly of mesoporous carbon; 2) highly selective sensor for tea components; and 3) highly cooperative nanopore-filling adsorption in the liquid phase (Figure 1 B). We selected tea components as guests due to their biological importance—tannic acid has been reported to have anticancer and related properties.[5]

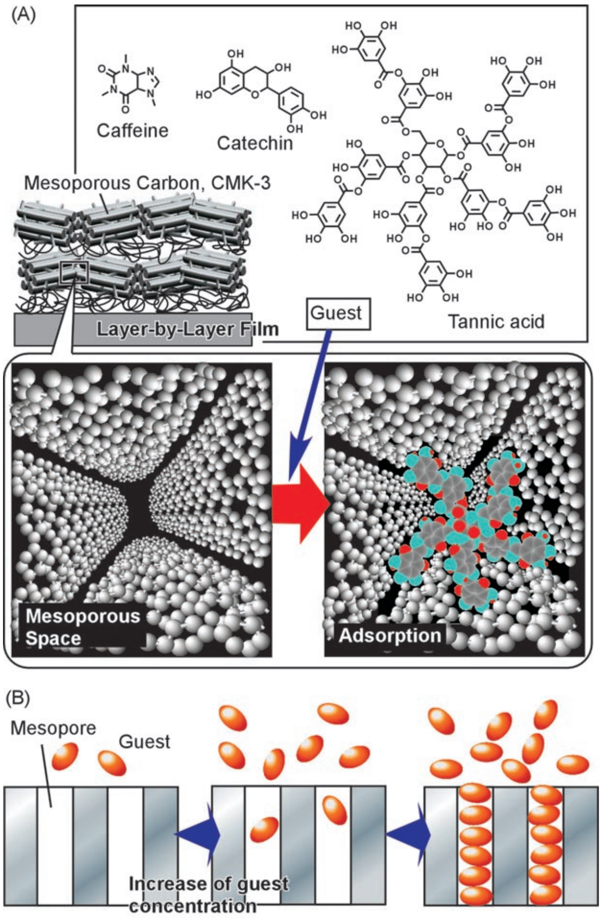

Figure 1. The mesoporous carbon CMK-3 LbL film and guests (A) and the cooperative adsorption of guest molecules into a mesopore at a certain guest concentration (B).

Although nonionic mesoporous carbon materials were previously considered unsuitable for LbL assembly, the surface oxidation of carbon using ammonium persulfate[6,7] enabled us to introduce negative carboxylate groups onto mesoporous carbon (CMK-3). The regular structure of CMK-3 was maintained after oxidation with 0.125 or 1 M acidified ammonium persulfate solution at room temperature for 24 h, as illustrated in the TEM images of different cross-sections (Figure 2 B). The textural parameters of the resulting materi-

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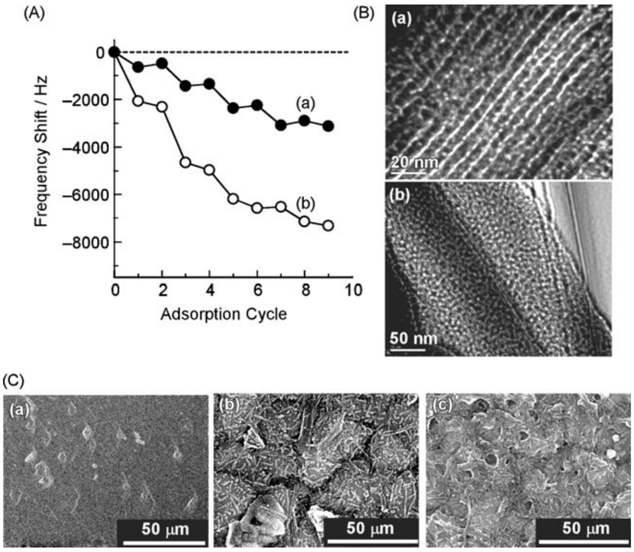

Figure 2. A) QCM frequency shifts of the LbL assembly between oxidized CMK-3 (5 mg mL^{-1}, even steps) and PDDA (3 mg mL^{-1}, odd steps): a) oxidized CMK-3 prepared with 1 M ammonium persulfate; b) oxidized CMK-3 prepared with 0.125 M ammonium persulfate. B) HR-TEM images of oxidized CMK-3 from different directions. C) SEM images of the CMK-3 LbL films: a) bare QCM surface; b) five-layer film; c) ten-layer film. See the Supporting Information for details.

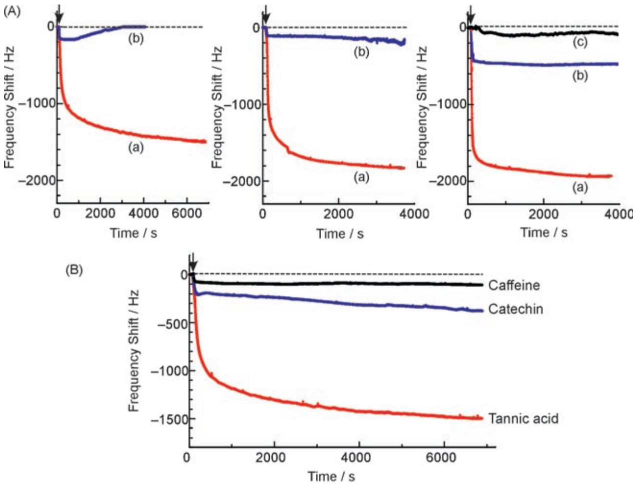

Figure 3. A) QCM frequency shifts upon tannic acid adsorption to a) a two-layer mesoporous carbon film, b) an SAM of octadecanethiol, and c) a four-layer PDDA/PSS LbL film at 20 °C and tannic acid concentrations of 0.013 (left), 0.053 (middle), and 0.27 g L^{-1} (right). B) QCM frequency shifts upon guest (0.13 g L^{-1}) adsorption to a two-layer mesoporous carbon film at 20 °C. Black arrows indicate guest injection.

als are dependent on oxidant concentration, with pore diameters of between 3.3 and 3.9 nm, specific surface areas of between 700 and 1260 m^2 g^{-1}, and specific pore volumes of between 0.48 and 1.1 cm^3 g^{-1}. The LbL assembly of oxidized CMK-3 was performed using poly(diallyldimethyl chloride) (PDDA) on a QCM plate. The QCM frequency decreases proportionally with mass increase at the surface.[7] Figure 2 A shows the frequency shifts of the LbL films of CMK-3/PDDA upon mass increase. Continuous film growth was confirmed for both oxidized CMK-3 samples, although film growth was not as uniform as that observed for the charged mesoporous silica materials.[8] The SEM images (Figure 2 C) also revealed an increasing surface coverage of the QCM plate as LbL assembly proceeds. Thicker films displayed good surface coverage (image c) while coverage was incomplete for films with fewer layers (image b). As imperfect surface coverage is expected to be advantageous for the diffusion of guest molecules, we decided to use two-layered films (weight corresponding to about 1500 Hz) for subsequent sensing, where CMK-3 oxidized with 0.125 M ammonium persulfate was used to minimize the contribution of carboxylate groups to guest adsorption.

The red plot in Figure 3 A shows an immediate frequency shift due to adsorption of tannic acid onto the CMK-3 LbL films after injection of tannic acid.[7] For reference, adsorption of tannic acid onto the SAM surface of octadecanethiol was also measured and found to result in a much less significant frequency shift (blue plot in Figure 3 A). An LbL film composed only of polyelectrolyte (PDDA and poly(sodium styrenesulfonate) (PSS)) also displayed a poor adsorption capacity for tannic acid even at the highest concentration examined (black plot in Figure 3 A, right). As shown in Figure 3 B, the frequency shifts upon adsorption of tannic acid (red plot) greatly exceed those for catechin (blue plot) and caffeine (black plot). The resulting sensitivity ratios of tannic acid to catechin or caffeine are around 3.9 and 13.6, respectively. The superior adsorption capacity for tannic acid likely originates in its molecular structure, in other words the multiple phenyl rings of the tannic acid molecule can interact with the carbon surface through π–π interactions and hydrophobic effects. As the amount of residual carboxylate groups is negligible under the oxidation conditions used,[6] the contribution of hydrogen bonding is not likely to be significant. In addition, the size fitting of tannic acid (a circular molecule with an approximate diameter of 3 nm) to the CMK-3 nanochannel may result in enhanced interactions between the guests themselves and/or the guest and carbon surface. The comparable frequency shift for adsorbed tannic acid and that for immobilized CMK-3 suggests that most of the pores are filled by tannic acid molecules (based on a pore volume of 1 cm^3 g^{-1}).

Tannic acid adsorption to the CMK-3 LbL films was investigated more closely by varying the guest concentrations (Figure 4 A). The adsorption quantities at equilibrium exhibit a sigmoidal profile at low concentrations (red plot (a) in Figure 4 B, expanded in the inset). This cooperative binding profile is absent for the adsorption of tannic acid to the SAM surface of octadecanethiol (blue plot (b) in Figure 4 B). As the QCM sensing experiments can provide in situ analysis of guest binding, we were able to observe a two-step adsorption behavior, the clearest case of which is illustrated in Figure 4 C. Step profiles are not always easy to observe, however, and the time-dependence of adsorption cannot be described by a single time constant in every case. For a simple analysis of the time-dependence of the adsorption process, the frequency shifts obtained were divided into two components (F_1 and F_2 in Figure 4 C) and plotted separately as a function of the guest concentration (Figure 4 D). While F_1 obeys a simple satura-

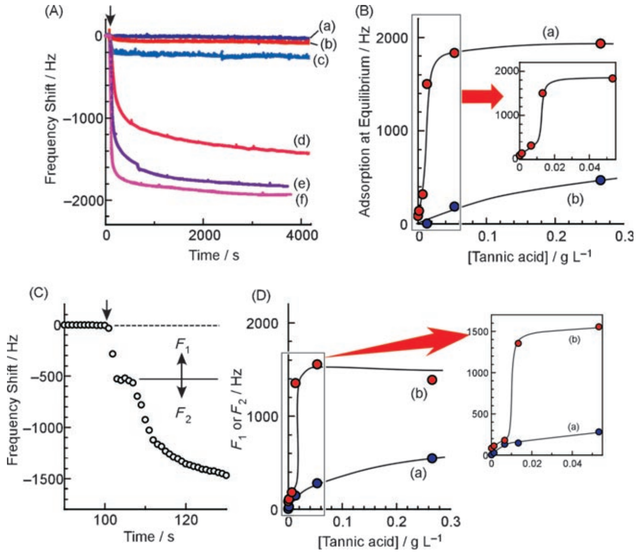

Figure 4. A) QCM frequency shifts upon adsorption of tannic acid to a two-layer mesoporous carbon film at 20 °C and a tannic acid concentration of 0.00013 (a), 0.0013 (b), 0.0067 (c), 0.013 (d), 0.053 (e), and 0.27 g L^{-1} (f). B) Saturated QCM shifts at various tannic acid concentrations: a) two-layer mesoporous carbon film; b) SAM of octadecanethiol. C) Typical time course of frequency shifts upon tannic acid adsorption to a two-layer mesoporous carbon film. D) First frequency change F_1 (a) and second frequency change F_2 (b) during the adsorption of tannic acid at various concentrations to a two-layer mesoporous carbon film. Black arrows indicate guest injection.

tion relationship (blue plot (a) in Figure 4 D), only F_2 behaves cooperatively, as indicated by its frequency shift profile.

To interpret this finding we assume that the initial rapid frequency drop is related to adsorption of the guest to the outer surface of the film and that the subsequent shifts reflect penetration of the guest into the nanochannels. The first adsorption component appears to be similar to a simple partition between solution and surface. The highly cooperative behavior of the latter component might result from confinement effects during adsorption. A similar inflection of adsorption isotherms for gas adsorption has been explained by citing structural changes of the host materials[9] or phase transitions of host–guest complexes.[10] However, neither of these phenomena can explain the sigmoidal adsorption isotherm observed in the present work because the carbon framework of CMK-3 is not flexible and the adsorbed guest cannot be complexed by the host. Snurr and co-workers have recently suggested that electrostatic guest–guest interactions are important during the cooperative adsorption of carbon dioxide into metal–organic frameworks.[11] Likewise, Kaneko and coworkers have proposed that cluster formation of guest (water) molecules is responsible for the sigmoidal shape of the adsorption isotherm.[12] Our case may be similarly explained by enhanced guest–guest interaction since the adsorbed tannic acid can form effective π–π and/or hydrophobic interactions when confined. The entropically favored release of the clustered water from the mesopores upon guest inclusion might induce this peculiar behavior for the guest adsorption. Our previous work on adsorption onto mesoporous carbon in the liquid phase revealed an unpredictable dependence on the guests being adsorbed. Thus, the adsorption of proteins generally obeys a simple Langmuir-type mechanism[13] whereas the adsorption of small molecules such as amino acids or vitamins is more complex with profiles typical of non-Langmuir-type adsorption[14] and multi-step adsorption.[15] In the latter cases, weak interactions between guest molecules may complicate the adsorption profile, as is seen in the present case.

In summary, the high sensitivity and selectivity of this QCM sensor coated with a CMK-3 LbL film has been demonstrated to originate from the highly cooperative adsorption of tannic acid in its size-comparable nanospaces. The results described herein will help our understanding of molecular interactions within nanospaces, especially nonspecific interactions in aqueous media, a full exploration of which might clarify important phenomena, including those of biological systems.

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