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Communication

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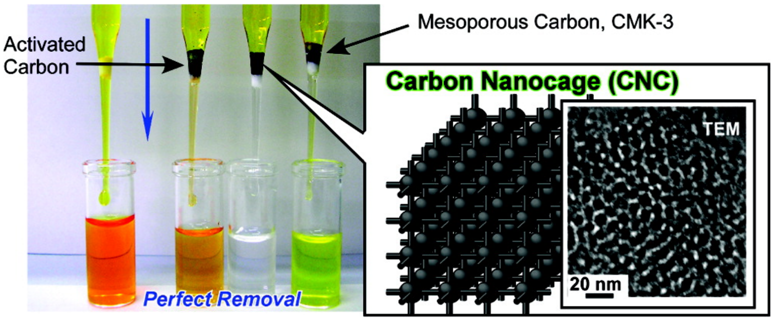

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One-Pot Separation of Tea Components through Selective Adsorption on Pore-Engineered Nanocarbon, Carbon Nanocage

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Selective sensing, extraction, and separation of bioactive components from beverages and foods are certainly important processes in industrial technology and have also attracted fundamental scientific investigations, leading to development of various functional molecules and functioning systems, which can operate in solution[1] and at interfaces.[2] Despite these advances, simple, economical, and environmentally friendly processes are still crucial requirements both from industrial and ecological standpoints. The direct adsorption of target components onto an appropriate medium could be superior to sophisticated sensors or chromatography despite these latter being scientifically more highly evaluated. For example, conventional adsorbents such as activated carbons are still used widely since structural modification of the adsorbents can be applied to alter guest selectivity.[3] However, such strategies would be much improved if advanced pore-engineered materials, such as mesoporous materials[4] and coordination polymers,[5] were to be applied. One-pot separation of bioactive materials using adsorbents containing pores of precisely controlled dimensions, as products of current nanotechnology, could furnish more advanced processes while maintaining technical simplicity. In order to realize this concept, we here report a simple, cheap, and toxic-solvent-free one-pot separation of the tea components catechin and tannic acid using a novel pore-engineered nanocarbon, the carbon nanocage (CNC),[6,7] which contains regularly structured cage-type mesopores. Extremely high separation selectivity (ca. 95%) has been realized for tannic acid. This compound possesses antioxidant properties[8] for antimutagenic and anticarcinogenic activities and for suppression[9] of potentially fatal diseases including cancer,[9c] human immunodeficiency virus (HIV) disease,[9d] and severe acute respiratory syndrome (SARS).[9e]

CNC materials were synthesized, as previously reported by us,[6] by using cage-type mesoporous silica KIT-5[10] as a hard template. KIT-5 has pore and cage diameters of 5.2 and 15.0 nm, respectively.[6] Specific surface area and specific pore volume were 1600 $m^2\ g^{-1}$ and 2.10 $cm^3\ g^{-1}$, respectively,[6] and far exceed those observed for conventional mesoporous carbon CMK-3.[11] Regularity of pore geometry was confirmed by using transmission electron microscopy (TEM)[6] (see image inserted in Figure 1 with the CNC structural cartoon). The superior adsorption capability of the CNC materials for small molecules was demonstrated, as shown in Figure 1A, by a simple adsorption experiment of a dyestuff (Alizarin Yellow) and reflects the widespread demand for sequestration of organic dyes.[12] An aqueous solution (2 g L^{-1}, ca. 5 mL) was passed through a bed of the respective carbon material (2.5 mg) deposited on top of a cotton plug in a pipet and with application of a slight pressure.[13] When compared with the control test without carbon (a), the CNC materials completely removed the dye (c), while activated carbon powder (AC, Kanto Chem., Japan, <2 nm) (b) and CMK-3 (3 nm) (d) were not effective for removal of the dye under these conditions.

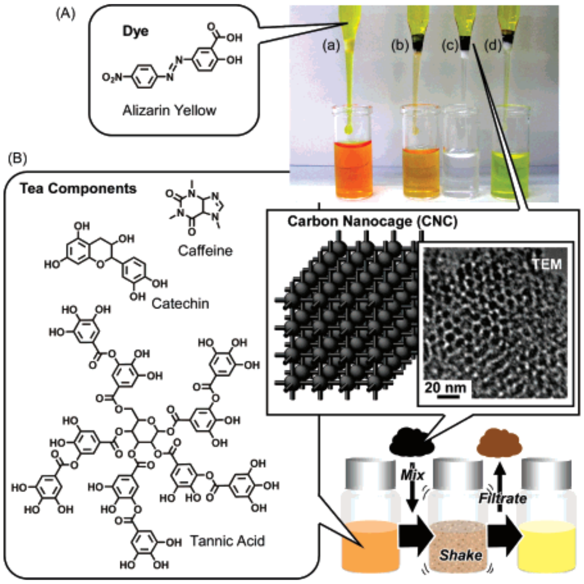

Figure 1. (A) Filtration of Alizarin Yellow by carbon adsorbents: (a) none; (b) AC; (c) CNC; (d) CMK-3. (B) Outline of tea component adsorption experiment with formula of guests structure of CNC.

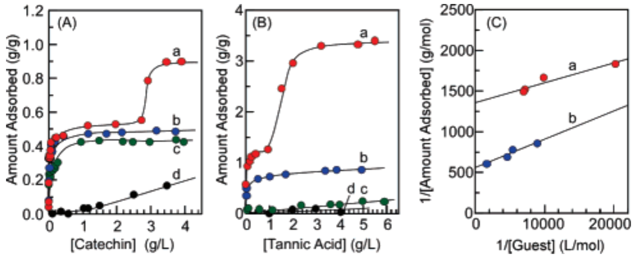

Figure 2. Adsorption isotherms of (A) catechin and (B) tannic acid: (a) CNC; (b) CMK-3; (c) AC; (d) SBA-15. (C) Linear Langmuir plot for adsorption of (a) tannic acid and (b) catechin to CNC.

This straightforward result encouraged us to perform quantitative experiments on adsorption of the bioactive tea components, caffeine, catechin, and tannic acid (Figure 1B). The adsorbent [0.5 mg, CNC, AC, CMK-3 or mesoporous silica SBA-15 (pore diameter, 9.2 nm)[11]] was dispersed in an aqueous solution of the tea components (4 mL in 25 mM carbonate buffer at pH 5.8) with shaking (160 rpm) for 24 h at 20 °C.[13] Equilibrium concentration and amount of guest adsorbed were quantified by using UV−vis spectroscopy after filtration. All three carbon adsorbents had similar adsorption capacity for caffeine, although caffeine was hardly adsorbed by hydrophilic SBA-15.[13] Superior capacity of carbon adsorbents relative to SBA-15 was also evident for adsorption of catechin (Figure 2A). Interestingly, only CNC showed two-step adsorption and greater adsorption capacity at higher concentration. Variation in the behaviors of the adsorbents was much more obvious in isotherms for tannic acid adsorption (Figure 2B). The CNC material exhibited larger adsorption capacity for tannic acid with a

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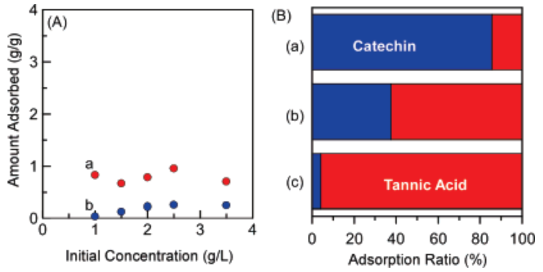

Figure 3. (A) Adsorption amount of (a) tannic acid and (b) catechin to CNC in competitive adsorption. (B) Adsorbed ratios of tannic acid (red) and catechin (blue) to carbon adsorbent at 1 g L^{-1} of initial concentration: (a) AC; (b) CMK-3; (c) CNC.

two-step adsorption, while CMK-3 showed lower capacity in single-step mode. Only poor adsorption capacity was detected for AC and SBA-15.

Differences in adsorption behaviors of these materials probably reflect hydrophobicity and structural dimensions of adsorbents and guests. A major driving force for adsorption should be hydrophobic interactions in aqueous media, so that SBA-15 has poor adsorption capability due to its hydrophilic silica surfaces. Molecular dimensions of catechin (0.8 × 1.3 nm) and of tannic acid (approximately circular diameter 3 nm) were estimated using molecular models.[13] Catechin can be contained in pores of CNC (pore diameter 5.2 nm and cage diameter 15 nm), CMK-3 (3.0 nm), and AC (<2 nm), but the larger tannic acid is not permitted to enter activated carbon micropores and may have difficulty diffusing within small CMK-3 mesopores. Larger cage-type pores of the CNC adsorbent promote its adsorption of both catechin and tannic acid in multilayer mode, and this may originate from interaction between adsorbed guests. The presence of tannic acid on the CNC adsorbent was confirmed by using FT-IR spectroscopy of the adsorbent after adsorption.[13] XRD (111) peaks[13] of the CNC adsorbent disappeared following guest adsorption, reflecting diminished electron density between framework and pores upon guest filling. Adsorption strengths of catechin and tannic acid on the CNC were estimated from linear plots of Langmuir isotherms for the initial adsorption steps (Figure 2C). Binding constants of 18 000 and 56 000 M^{-1} were obtained for catechin and tannic acid, respectively.

Competitive adsorption (guest selection) of catechin and tannic acid on the CNC adsorbent using solutions containing equal weights of the guests unexpectedly gave adsorption behaviors (Figure 3A) which departed significantly from those of the individual guests because of competitive adsorption. Catechin adsorption was suppressed drastically by the presence of tannic acid, especially at its lower concentrations. Diminished catechin adsorption is caused by preferential adsorption of tannic acid on CNC, as indicated by the difference in their binding constants, and could be due to stronger $\pi-\pi$ interactions between tannic acid and the surfaces of CNC. Interestingly, multilayer adsorption of tannic acid even at high concentrations could not be detected in the presence of catechin. Interaction of catechin and tannic acid molecules in the CNC pores might disturb multilayer adsorption of tannic acid. Finally, we found a highly selective separation of catechin and tannic acid by using appropriate conditions. Adsorption ratios between these tea components at 1 g L^{-1} are summarized in Figure 3B, where complete inversion in the selectivities for catechin and tannic acid is demonstrated going from AC, CMK-3 to CNC. Surprisingly, use of CNC as adsorbent provided a highly selective adsorption of tannic acid (ca. 95%) in a simple one-pot process. This process cannot be achieved by activated carbon or conventional mesoporous carbon, CMK-3.

This work strikingly demonstrates the importance of pore-engineering in carbon adsorbent design. Very high selectivity for adsorption of tea components (catechin and tannic acid) was achieved through a simple one-pot process using the novel nanocarbon, carbon nanocage (CNC). Availability of CNC for practical use will not be limited to the examples presented here. Although nonspecific hydrophobic interactions play a major role in the current case, functionalization at the cage interior should enable us to achieve a more specific molecular recognition. Since the structural dimensions of CNC are comparable with those of some proteins and peptides, CNC adsorbents could be used for efficient removal of hydrophobic toxic biomaterials such as amyloids and will have a great impact on biomedical fields.

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Supporting Information Available: Experimental details, adsorption isotherms of caffeine, CPK models of guests, XRD profile of CNC, and FT-IR spectra of CNC. This material is available free of charge via the Internet at http://pubs.acs.org.

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