



Supporting Information

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## Supporting Information

### A Layered Mesoporous Carbon Sensor Based on Nanopore-Filling Cooperative Adsorption in Liquid Phase

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#### Experimental details

##### 1. Materials.

Sodium polystyrene sulfonate (PSS, 30 wt% in water), polydiallyldimethylammonium chloride (PDDA, 20 wt% in water) and tannic acid were purchased from Sigma-Aldrich. Caffeine and octadecanethiol were purchased from Wako Pure Chemical Co. and Tokyo Chemical Ind., respectively. Water used in the experiments was purified through a Purelab Prima system to a resistivity of 18.2 M $\Omega$  cm.

##### 2. Preparation and characterization of mesoporous carbon materials

Synthesis and characterization of mesoporous carbon (CMK-3) were described in detail elsewhere (1). Oxidation of CMK-3 was performed according to our previous report (2). In a typical oxidation experiment, 100 mg of CMK-3 was added to 6 g of ammonium persulfate solution (0.125 or 1 M in 2 M H<sub>2</sub>SO<sub>4</sub>). The mixture was stirred for 24 hours at 20 °C. All the oxidized samples were filtered, washed several times with distilled water until the washings contained no sulfate, and dried overnight in a vacuum oven. Only traces of sulfur were detected in the oxidized samples by elemental analysis (C, H, N, and S) and Energy Dispersive X-ray (EDX) analysis. All the mesoporous carbon materials were analyzed using powder X-ray diffraction (XRD; Rigaku 3070E model) with CuK $\alpha$  ( $\lambda = 0.154$  nm) radiation, nitrogen adsorption and desorption isothermometry measured at -196 °C using a Quantachrome Autosorb-1C instrument, and FT-IR spectroscopy using a Nexus 670 FT-IR spectrometer. Selected samples were subjected to scanning electron microscopic (SEM) observation. The samples were coated with Pt (Hitachi E-1030 ion sputterer, 10 mA/10 Pa) under argon atmosphere. Accelerating voltage of the SEM observation was 5.0 kV. High-resolution transmission electron microscopy (HR-TEM) was performed by using a JEOL-JEM2000 operating at 200 kV. Aqueous dispersions of silica capsules were dropped onto a carbon-coated copper grid, and excess water was allowed to evaporate at room temperature.

1. M. Hartmann, A. Vinu, *Langmuir* **2002**, *18*, 8010-8016.
2. A. Vinu, K. Z. Hossian, P. Srinivasu, M. Miyahara, S. Anandan, N. Gokulakrishnan, T. Mori, K. Ariga, V. V. Balasubramanian, *J. Mater. Chem.* **2007**, *17*, 1819-1825.

##### 3. Quartz crystal microbalance (QCM) and layer-by-layer (LbL) assembly

The QCM technique was used for detection of mass change during the assembly process and guest sensing. In order that they could act as electrodes, the QCM resonators (USI System, Japan) used were coated by vapor deposition of silver or gold on both surfaces. The resonance frequency was 9 MHz (AT-cut) and frequency decreased ( $-\Delta F$ ) proportionally with increase in mass ( $\Delta m$ ) according to the Sauerbrey equation (3). Using intrinsic parameters for AT cut quartz plate and electrode area, the equation  $\Delta m$  (Hz) = 0.95 x ( $-\Delta F$ ) (ng) holds. The QCM frequency was stable within  $\pm 2$  Hz during 1h. All experiments were carried out in an air-conditioned room at 20 °C.

For the LbL assembly, aqueous solutions of PDDA (3 mg mL<sup>-1</sup>) and PSS (3 mg mL<sup>-1</sup>), and an aqueous dispersion of the oxidized CMK-3 (5 mg mL<sup>-1</sup>) were used. In the first LbL adsorption stage, four pairs of polyion (PDDA/PSS) layers were assembled as precursor layers on the QCM resonators, and the precursor film formation terminated at the PDDA adsorption step giving a positively charged surface. Subsequently, LbL assembly of the oxidized CMK-3 and PDDA was performed. Adsorption time of all the steps was set at 10 minutes, followed by rinsing with deionized water and drying under a gentle stream of nitrogen.

For control experiments, a self-assembled monolayer (SAM) was prepared on a gold-coated QCM plate by immersion of the QCM plate in 10 mM ethanolic solution of octadecanethiol for 24 hours.

3. C. K. O'Sullivan, G. G. Guilbault, G. G. *Biosens. Bioelectron.* **1999**, *14*, 663-670.

#### **4. Sensing experiment**

Prior to guest sensing experiments, LbL film-coated QCM plates were soaked in salt-free pure water (15 mL, 20 °C) and equilibrated. After the frequency of the QCM was stabilized, a solution of the guest was injected by syringe (0.02 to 0.2 mL) under stirring of the whole solution to ensure efficient diffusion of the guests. Frequency shifts were monitored continuously using a frequency counter that transmitted data to a PC computer in *in-situ* mode (UQ-200-BK1 system).