

Experimental section

Synthesis of small-sized ZIF-8 particles (with average diameter of 50 nm): Zn(NO₃)₂ (258 mg) was dissolved into methanol (20 mL) to form a solution. 2-methylimidazole (263 mg) was dissolved in methanol (20 mL) to generate another clear solution. Then, both of them were mixed together, and stirred for 5 min. The solution was aged at room temperature for 24 hours. After that, white powders were precipitated. The powders were washed very carefully with methanol and dried.

Synthesis of middle-sized ZIF-8 particles (with average diameter of 300 nm): Dried powders of both Zn(CH₃COO)₂ (175 mg) and 2-methylimidazole (263 mg) were mixed together. Then, methanol (40 mL) was added to dissolve the mixed powders. The solution was stirred for 5 min. Then, the solution was aged at room temperature for 24 hours. After that, white powders were precipitated. The powders were washed very carefully with methanol and dried.

Synthesis of large-sized ZIF-8 particles (with average diameter of 1 μm): Zn(CH₃COO)₂ (175 mg) was dissolved into methanol (20 mL) to form a solution. 2-methylimidazole (263 mg) was dissolved in methanol (20 mL) to generate another clear solution. Then, both of them were mixed together, and stirred for 5 min. The solution was aged at room temperature for 24 hours. After that, white powders were precipitated. The powders were washed very carefully with methanol and dried.

Direct carbonization of ZIF-8 particles: ZIF-8 powders (200 mg) were directly heat-treated under nitrogen flow to remove the organic parts (C-N). The temperature was increased to 800 °C with a heating rate of 5 °C·min⁻¹. Then, the powders were annealed at 800 °C for 5 hours. After that, the obtained samples were washed extensively by conc. HCl solution (35 wt%) to remove residual Zn component.

Characterization: SEM images were taken with a Hitachi S-4800 scanning microscope at an accelerating voltage of 10 kV. TEM observation was performed using a JEM-2010 TEM system that

was operated at 200 kV. Wide-angle powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT 2500X diffractometer using monochromated Cu K α radiation (40 kV, 40 mA) at a scanning rate of 1 $^{\circ}\cdot\text{min}^{-1}$. Nitrogen adsorption-desorption isotherms were measured by using a Quantachrome Autosorb Automated Gas Sorption System at 77 K.

Preparation of quartz crystal microbalance (QCM) electrodes: Prior to the film deposition process, the quartz crystal microbalance (QCM) electrodes were firstly sonicated in a mixture of ethanol and water for 1 h. After being rinsed with water and dried under a gentle stream of N₂ gas, the frequency was recorded as initial frequencies for these electrodes (F_0). To prepare the electrodes for toluene vapor adsorption, the suspensions containing carbon samples (1 mg·mL⁻¹) with different particle sizes and Nafion (0.1 wt%) were deposited by drop-coating directly onto the QCM electrodes at room temperature. After drying in a gentle nitrogen flow at room temperature, the electrode surfaces were rinsed with pure water. Subsequently, the electrodes were dried under vacuum for 2 hour at 60 $^{\circ}\text{C}$.

QCM study for toluene vapor adsorption: QCM electrodes coated with carbon samples were then fixed inside the QCM instrument. All measurements were carried out in a glass cell with an internal volume of 320 ml. A 100 μL microliter syringe (SGE Analytical Science) was used for the injection toluene solvent. Prior to a measurement, the QCM electrodes coated with the samples recorded a stable baseline in N₂ gas stream ($\pm 2 \text{ Hz}\cdot\text{min}^{-1}$). Then the valve was switched to introduce the injected toluene vapor using a small pump at a constant volumetric flow rate of 100 ml·min⁻¹ and the frequency of crystal was recorded every 0.1 s until a stable response was obtained. After the exposure, the valve was switched again and a constant flow rate of N₂ gas stream was purged through the cell to recover the electrode to obtain a baseline response. The backshift of the crystal frequency to its initial value was taken as an indication of full desorption. The time-dependence of the frequency shift (ΔF) was plotted during the alternate exposure and removal of the toluene molecules. The

frequency was automatically recorded by a PC-supported measurement system. All experiments were carried out in an air-conditioned room at 22 °C.

When a small amount of mass is adsorbed onto a quartz electrode surface, the oscillating frequency of the quartz is changed. At steady state, the amount of adsorbed gas molecules onto/into the sensing film is determined from the interaction between gas molecules and the film of coating material. Sauerbrey's equation is used to relate the frequency change (ΔF) to the mass loading of the sample (Δm) [1].

$$\Delta F = -\frac{2NF_0^2}{\sqrt{\rho\mu}} \frac{\Delta m}{A} \quad \text{--- (1)}$$

where N , F_0 , ρ , μ , and A are the harmonic overtone, the fundamental resonance frequency, the crystal density, the elastic modulus of the crystal, and the surface area, respectively.

The amount of nanoporous carbons samples deposited onto QCM electrodes were calculated according to eq. 1, as $12.43 \text{ } \mu\text{g cm}^{-2}$ and $11.93 \text{ } \mu\text{g cm}^{-2}$ for large-sized and small-sized nanoporous carbon particles, respectively.

Particle sizes influence the characteristic rate of uptake of toluene vapor, which is controlled by diffusion, defined as D/r^2 (where D is the diffusion coefficient and r is the diffusion length, which is controlled by the diffusion coefficient and surface area (geometry). During the adsorption process, the surface concentration may reach its equilibrium in a time much shorter than other characteristic times in the system. In this case, we can assume that the surface is always at a constant concentration and calculate the time-dependence of the frequency shift (ΔF) upon uptake of toluene vapor. This constant surface concentration model is a simple linear model of adsorption commonly used in the literature, also known as the Fickian model [2]. Thus, the solutions of short time (t) behavior can be

derived from Fick's law for diffusion for a concentration into a homogeneous sphere of radius r , with D being the diffusion coefficient inside the sphere.

$$\frac{\Delta F_t}{\Delta F_\infty} = 6 \sqrt{\frac{D}{\pi}} \frac{t^{1/2}}{r^2} \quad \text{---(2)}$$

where ΔF_t and ΔF_∞ are the frequency changes at any time t and equilibrium state at the end of the adsorption process, respectively. The frequency change-time dependency is given by $\Delta F_t/\Delta F_\infty = (F_t - F)/(F_\infty - F)$ (F is the frequency of the electrode before injection at $t = 0$.).

References

- [1] G. Sauerbrey, Z. Phys. (1959) 155, 206.
- [2] J. Crank, The Mathematics of Diffusion, 2nd Edition. Clarendon Press, Oxford (1975) 414.

Figure S1

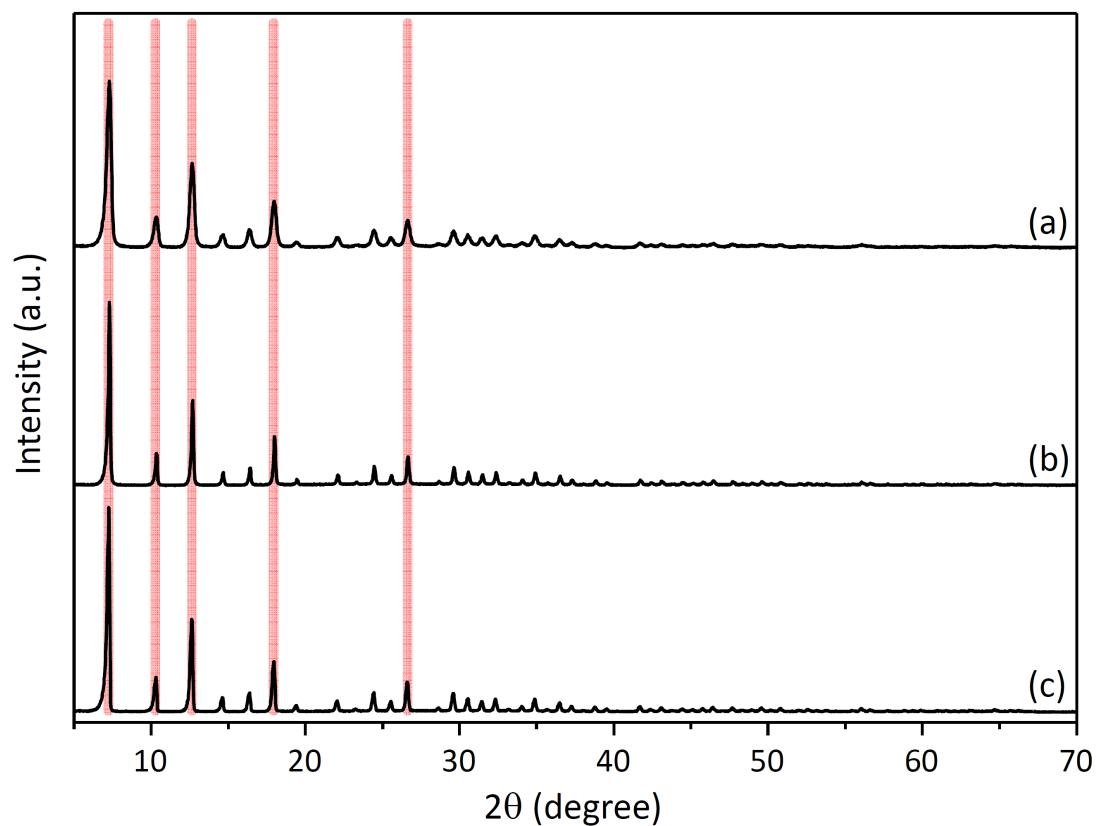


Figure S1 Wide-angle XRD profiles of ZIF-8 crystals with different sizes ((a) small-sized, (b) middle-sized, and (c) large-sized ZIF-8 crystals, respectively.).

Figure S2

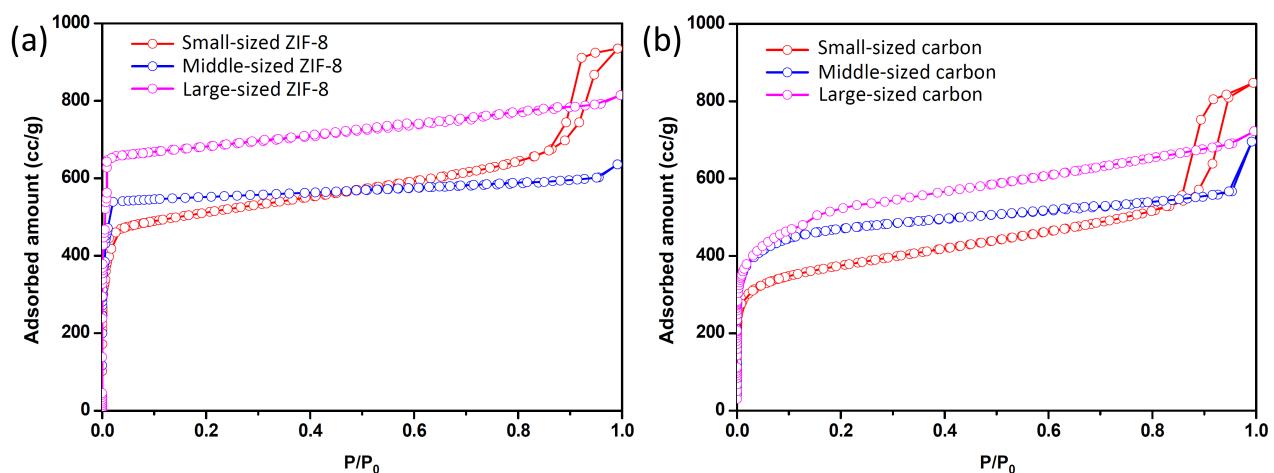


Figure S2 Nitrogen adsorption-desorption isotherms of (a) ZIF-8 crystals and (b) nanoporous carbon particles with different sizes.

Figure S3

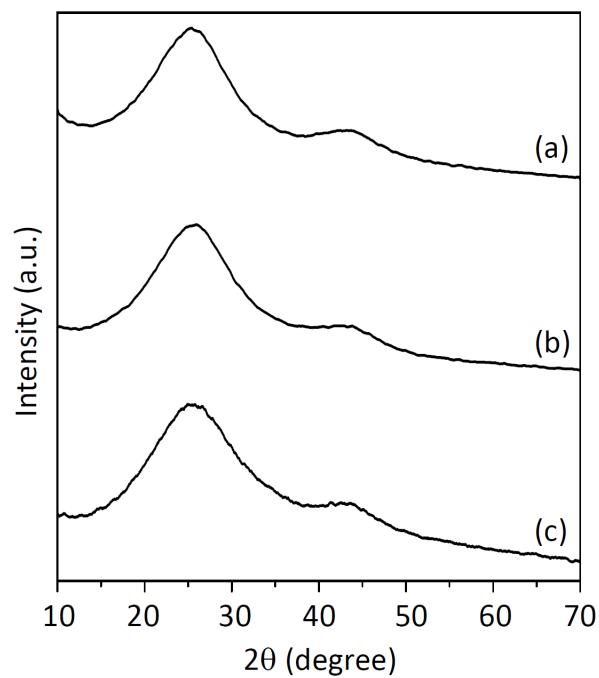


Figure S3 Wide-angle XRD profiles of nanoporous carbon particles with different sizes ((a) small-sized, (b) middle-sized, and (c) large-sized carbon particles, respectively.).

Figure S4

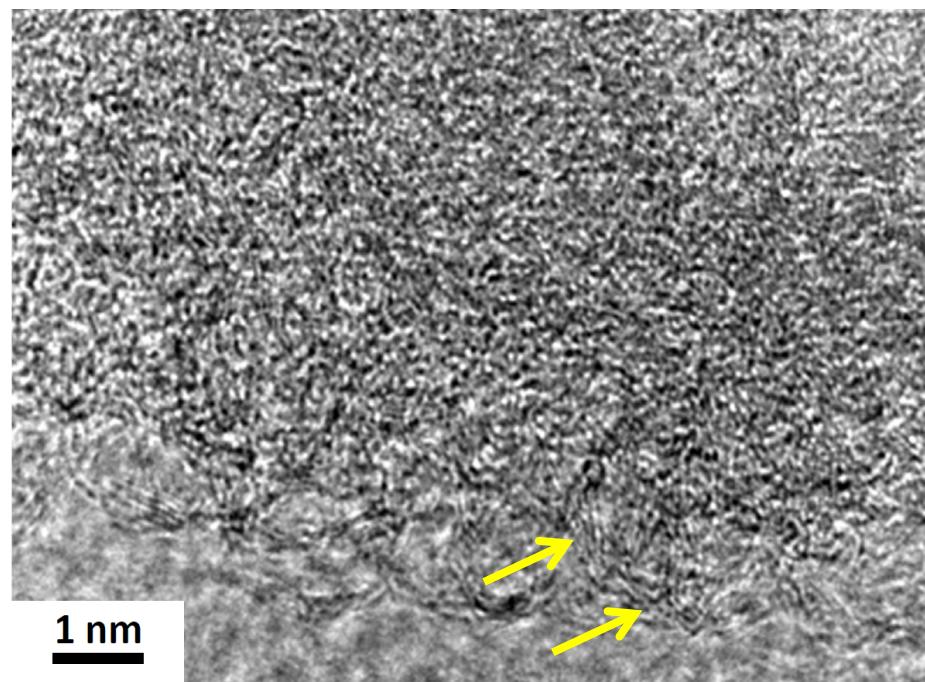


Figure S4 High-resolution TEM image of small-sized nanoporous carbon particles.

Figure S5

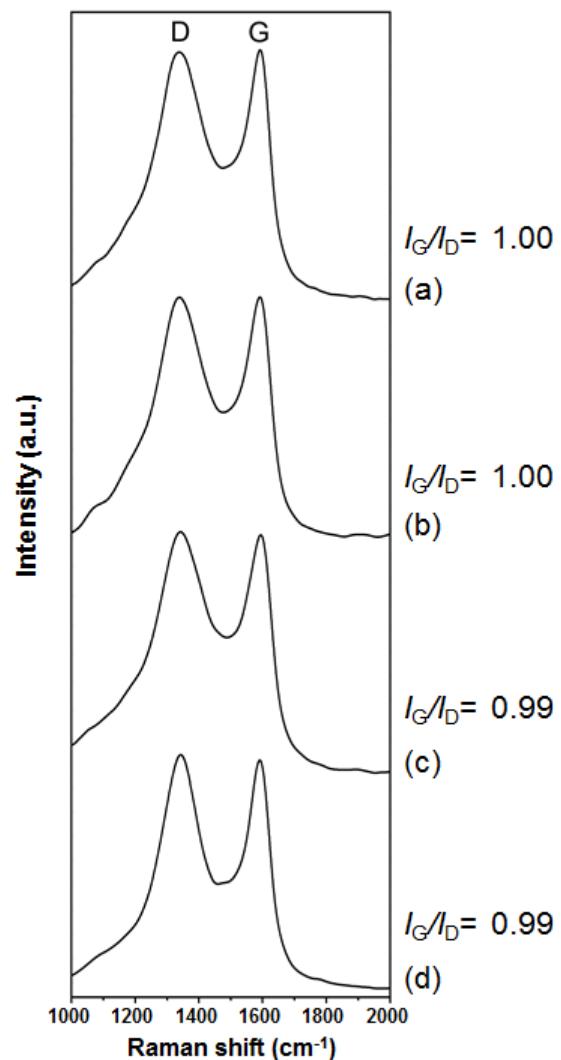


Figure S5 Raman spectra of the nanoporous carbons treated at 800°C : (a) small-sized, (b) middle-sized, (c) large-sized and (d) commercially available activated carbon.

Figure S6

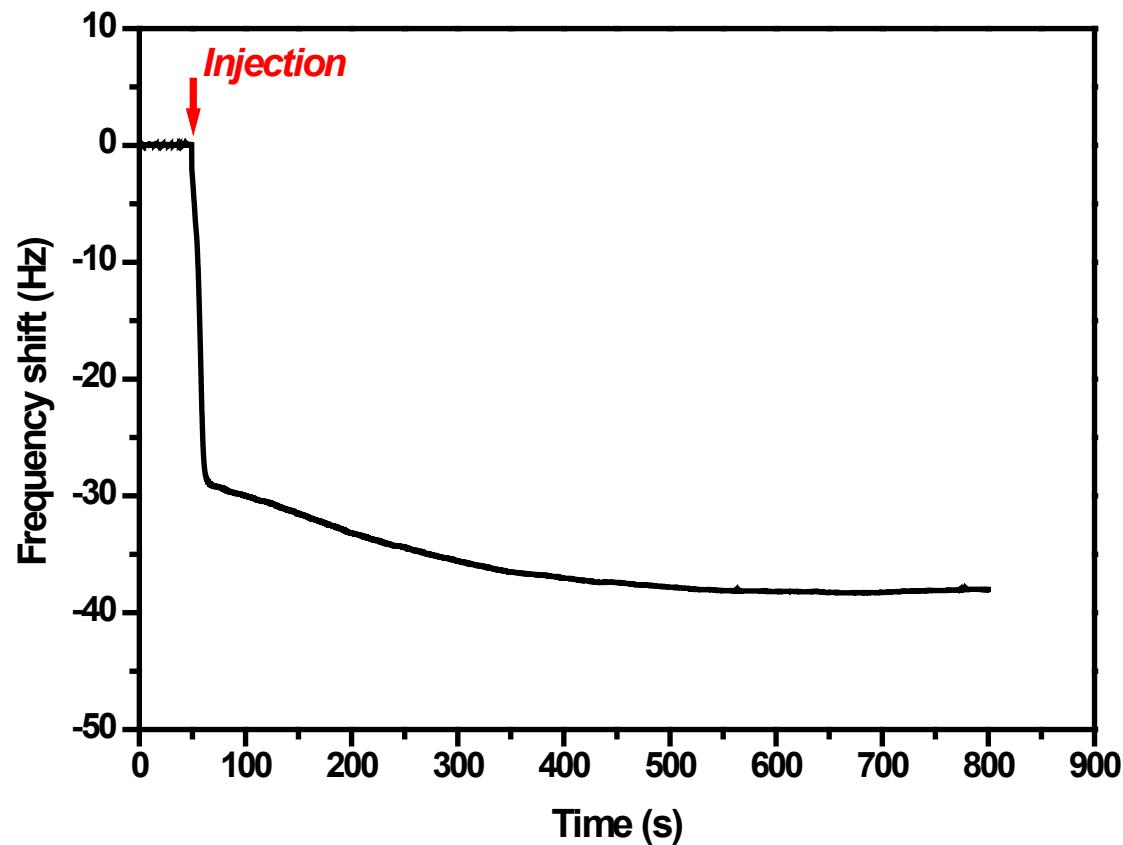


Figure S6 Mass-normalized time-dependent frequency shift of QCM coated with Nafion layer ($2.56 \mu\text{g cm}^{-2}$) upon toluene vapor adsorption.