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Metal−Organic Frameworks as Sensors: A ZIF-8 Based Fabry−Pérot Device as a Selective Sensor for Chemical Vapors and Gases

Guang Lu and Joseph T. Hupp*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received February 17, 2010; E-mail: j-hupp@northwestern.edu

Permanently microporous metal−organic framework (MOF) materials[1] have attracted considerable attention on account of their large internal surface areas, uniform channels, (sub)nanometer-sized cavities, thermal stability, and chemical tailorability.[2] Among the potential applications for which proof-of-concept reports have proliferated are gas storage,[3] chemical catalysis,[4] and small-molecule separations.[5] At first glance MOFs would also appear to be attractive for chemical sensing. Nevertheless, reports of MOF-based sensing are comparatively few.[6] The challenge is signal transduction: the cavities of MOFs are generally too small to tailor with reporter molecules, i.e. moieties that can readily signal analyte-binding events via changes in color, redox potential, or other properties. In the handful of cases where sensing has been described, advantage has generally been taken of *framework* luminescence,[7] with signal transduction consisting of luminescence quenching.[6,8]

Here we describe an alternative approach that circumvents the need for molecular-level reporters and instead relies upon a readout of changes in a macroscopic property of the sensing material, the refractive index. Specifically, we have configured the material as a transparent thin film on an appropriate support material (glass or silicon) and optically monitored the energies of Fabry−Pérot interference peaks as a function of analyte exposure.[9] These peaks are observable when the thickness of a supported material is comparable to the wavelength of light (λ). Importantly, their energies also depend on the film's refractive index.

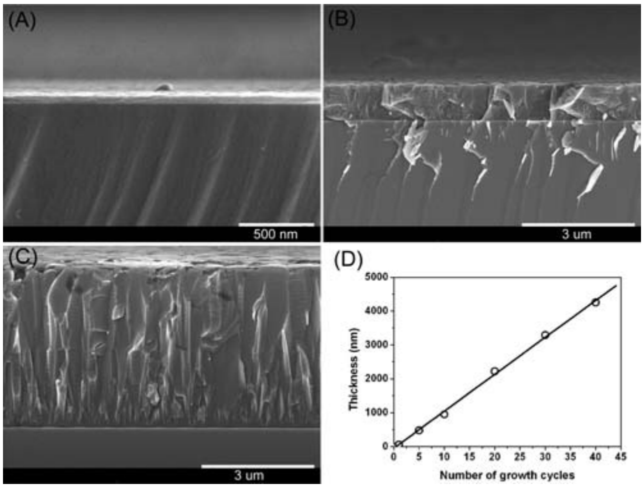

Figure 1. Cross-sectional SEM images of ZIF-8 films grown on silicon substrates with cycles of (A) 1, (B) 10, and (C) 40; (D) thickness of ZIF-8 film versus numbers of growth cycles.

As the sensing material we chose a zeolitic imidazolic framework, ZIF-8. This chemically robust and thermally stable material is characterized by the sodalite (SOD) zeolite-type structure with large cavities (11.6 Å) and small pore apertures (3.4 Å).[10] Diverse protocols[10] are available to produce ZIF-8 crystals with sizes from micrometers to nanometers.[10d] While dense ZIF-8 membranes have recently been synthesized on porous supports using solvothermal conditions for the purpose of gas separation,[11] it is not easy to precisely control thicknesses of films on the submicrometer scale using these conditions. Several strategies have been developed to prepare MOF thin films,[12] but they either produce poor morphologies[13] or are time-consuming[14] to grow with thicknesses over 100 nm. In our experiments, ZIF-8 was obtained in thin-film form (Figure 1A) simply by immersing glass or silicon slides in a freshly prepared methanolic solution of 2-methylimidazole and $Zn(NO_3)_2$ at room temperature (see Supporting Information (SI)). Quartz crystal microgravimetry experiments (gold surfaces; see SI) show initially rapid film growth that subsequently slows and is largely complete after 30 min. Thicker films can be obtained by repeating the process with fresh solutions (Figure 1B and 1C). Cross-sectional scanning electron microscopy (SEM) images demonstrate that the films thicken by ca. 100 nm per growth cycle (Figure 1D). (The initial cycle, however, yields a ca. 50 nm thick film.) X-ray diffraction measurements (see SI) establish that the films comprise ZIF-8.

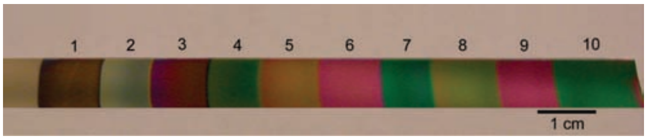

Figure 2. Photograph of a series of ZIF-8 films of various thicknesses grown on silicon substrates.

Figure 2 shows a series of ZIF-8 films of various thicknesses, l, grown on silicon substrates. While ZIF-8 itself is colorless, the silicon-supported thin films are not. The variable coloration is a manifestation of film-thickness-dependent optical interference in the visible region. At normal incidence the wavelengths of the (reflected) interference peaks are given by

$$m\lambda = 2nl \qquad (1)$$

where m is an integer and n is the thin film's refractive index.

The key to chemical sensing is the tunability of n. For a microporous MOF, n is a volume-weighted average of the indices for the cavities (vacuum, $n_{\text{vac}} = 1$) and the framework ($n_{\text{fram}} > 1$). Inserting into the cavity any polarizable molecule will displace vacuum and increase the overall refractive index. From eq 1, this will result in red shifts of the interference peaks.

Fabry−Pérot fringes for transmission of visible light through a ca. 1000 nm thick film (10-cycle growth) of ZIF-8 on glass were monitored to demonstrate the sensing properties.[15] Exposure to propane shifts the visible-region fringes by up to 49 nm (Figure 3A). The extents of the shifts are sensitive to the propane partial pressure (Figure 3B). The analyte-induced shift occurs within 1

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min and is reversed by replacing analyte with pure nitrogen gas (see SI). From the magnitudes of the shifts in the interference fringes, we calculated that the volume fraction of analyte in the framework is ∼0.13 for pure propane at 1 atm.

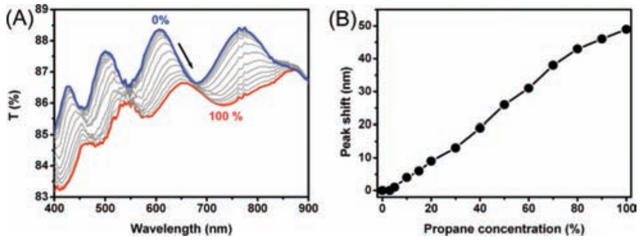

Figure 3. (A) UV−vis transmission spectra of 10-cycle ZIF-8 film grown on glass substrate after exposure to propane of various concentrations (blue curve for 0% and red curve for 100%) and (B) corresponding interference peak (originally at 612 nm) shift versus propane concentration. The propane concentration is expressed as a percentage of the total gas flow where nitrogen is used as diluent.

While responsive to a range of vapors and gases, the ZIF-8 sensor does display some chemical selectivity. For example, linear *n*-hexane is readily sensed, but the sterically more demanding cyclohexane is not, consistent with the small portal size for ZIF-8 cavities. Consistent with the known hydrophobicity of ZIF-8,[10a] the sensor is unresponsive to water vapor. In contrast, ethanol is readily detected (Figure 4A). Exposure to the vapor above ethanol/water mixtures of various ethanol contents gives rise to ethanol-concentration-dependent responses, with the sensor response saturating at ca. 40% ethanol (Figure 4B). We have taken advantage of this observation to calculate the volume fraction of analyte in the framework: 0.25 for pure ethanol, which agrees reasonably well with the void volume fraction (0.20) indicated by single-crystal X-ray structural measurements.[16]

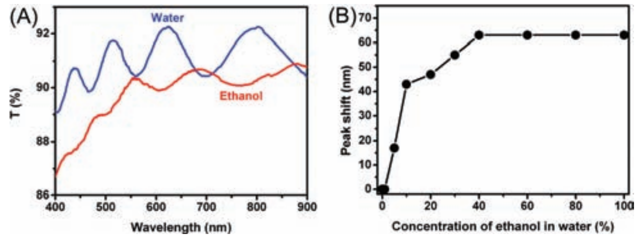

Figure 4. (A) UV−vis transmission spectra of 10-cycle ZIF-8 film grown on glass substrate on exposure to vapors of ethanol and water. (B) Interference peak (originally at 612 nm) shift versus ethanol concentration in ethanol/water solutions. The concentration is expressed as a volume percentage.

The detection limit depends, in part, on the resolution of the spectrophotometer. For 1 nm resolution, the estimated detection limit for ethanol in water is ca. 0.3 vol %, corresponding to an ethanol vapor concentration of ca. 100 ppm.

In summary, we have constructed MOF-based Fabry−Pérot devices that function as selective sensors for chemical vapors and gases. To obtain suitable devices we rely upon a simple, but controllable and effective, method for fabricating ZIF-8 films. Virtues of this method include gentle reaction conditions (room temperature), rapid growth rate (∼100 nm/30 min), good control over thickness (∼ 100 nm/cycle), no special requirements for surface modification of substrates, and ease of removal of solvent (methanol).

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Supporting Information Available: Materials and methods, QCM, XRD, EDXS, FT-IR, TGA, N_2 gas sorption, gas- and vapor-testing data, and effective refractive index and volume fraction calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) From the interference fringes, the refractive index of evacuated ZIF-8 is ∼1.39.

(16) The accessible void volume fraction in ZIF-8 framework is estimated in the CALC SOLV routine in PLATON using a default value of 1.20 Å for the probe radius.

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