Nanoporous-carbon: A Revolutionary New Material for Chemical Microsensors

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Motivation—Gas-phase sensors for rapid detection of airborne chemicals are critical to public health and national security. Chemical sensors depend on sorbent coatings compatible with environmental parameters, such as temperature, humidity, and chemical back-ground. Such coatings need to be sensitive, reproducible, and stable for long-term use. Unfortunately, typical polymer and sol-gel coatings are constrained by stresses to sub-micron thicknesses, limiting the available sorption, and degrade with time and repeated thermal cycling. Surface acoustic wave (SAW) devices respond to gas-phase analytes by decreasing the oscillating frequency as a function of analyte concentration due to an increase in the sorbent mass. To be useful for SAWs, the coating must have both high surface area and rigidity. Nanoporous-carbon (NPC) uniquely combines these critical properties. NPC grows at room temperature with negligible residual stress on any substrate to any thickness. Purely graphitic and nanocrystalline, NPC is chemically robust and stable to temperatures > 600 ˚C, well above any thermal cycling used for devices.

Accomplishment—NPC grows via pulsed-laser deposition by focusing 248 nm excimer radiation to ablate a graphite target with an energy density just above the ablation limit. The ablated species kinetic energy is further attenuated via a controlled argon pressure during deposition, resulting in a lower average NPC mass density. Figure 1 shows transmission electron microscope images for NPC with densities of 0.25 and 1.0 g/cm^3. Films with the lowest densities have nm-sized voids, as shown by the arrow in Fig. 1(a); however, all NPC films have interplanar spacings between graphene sheet fragments greater than that of crystalline graphite. The spacing decreases with increasing density. Both of these structural features add useful surface area for analyte sorption. Intercalation into graphite is well known, and increasing the interplanar spacing should ease diffusion both in and out of the coating.

Figure 2(a) shows SAW performance detecting acetone sorption into various density NPC films. The power law relationship infers that while low-density NPC has greater adsorption of acetone at high concentrations, such films lose sensitivity at lower analyte concentrations, with the slopes predicting the sensitivity of coatings at low analyte concentrations. Figure 2(b) shows that the acoustic loss of NPC-coated SAW devices in air decreases with increasing mass density, i.e., the greater the film rigidity, the better the ultimate signal-to-noise (s/n) ratio. The NPC acoustic loss correlates with the isotherm slope, demonstrating that the acoustic loss (film rigidity) relates to sensitivity in very dilute analyte concentrations.

Figure 3(a) compares the adsorption isotherm for NPC with several commonly used sorption coatings for a common toxic chemical, chlorobenzene. Figure 3(b) extrapolates this power-law behavior toward infinite dilution, providing a prediction of the limits of detection. The y-axis minimum is set 10x above the s/n limit of the measurement system. The x-axis minimum is set to an analyte concentration of parts-per-billion (ppb). Only NPC exceeds this desired limit, and is > 6 orders of magnitude more sensitive than the best polymeric sensor coating. Similar data exist for many other gas analytes.

Significance—NPC-coated SAW devices offer the first hope toward ppb microsensor chemical detection. Compared to all existing sorbent coatings, NPC enhances sensitivity by multiple orders-of-magnitude and promises greater lifetime and field applications, including Homeland Defense, ES&H, and Industry.

Sponsors for various phases of this work include: Laboratory Directed Research & Development

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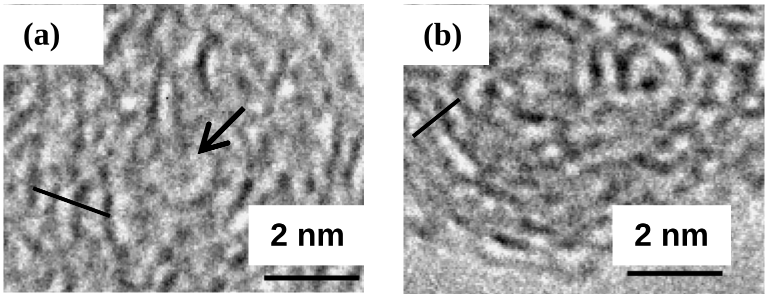

Figure 1. TEM images of NPC films with varying mass density: (a) 0.25 g/cm^3 and (b) 1.0 g/cm^3. The arrow in (a) points to a fullerene-sized void. The lines in each image show several aligned graphene sheet fragments.

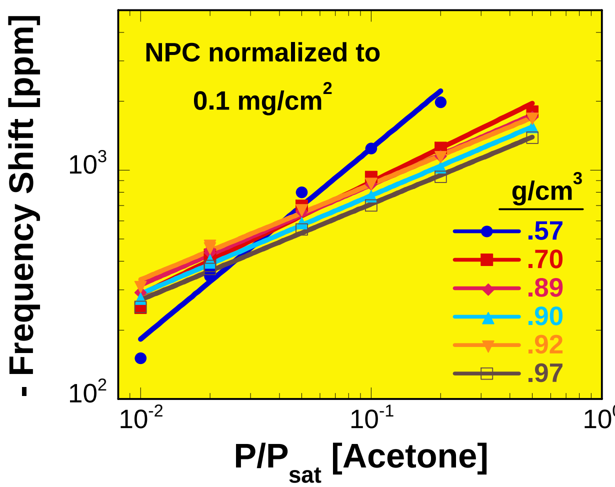

Figure 2(a). Log-log representation of acetone adsorption isotherms from SAW sensor devices coated with varying average NPC mass densities.

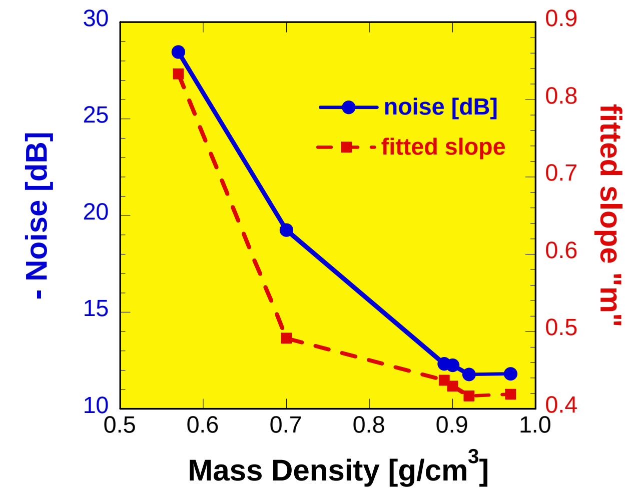

Figure 2(b): Network analysis of SAW acoustic loss and the fitted slopes from Fig. 2(a) as functions of average NPC mass density.

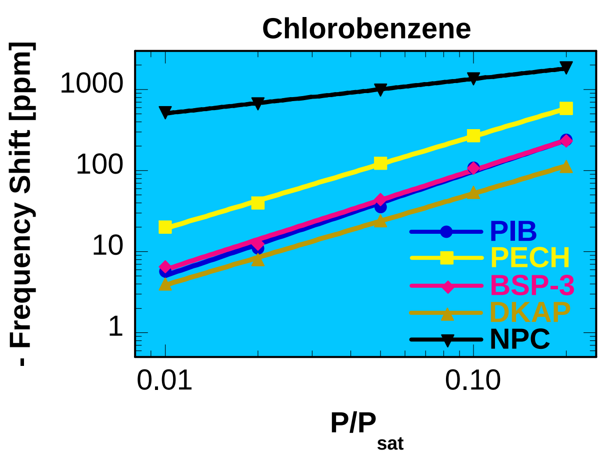

Figure 3(a). Log-log (power law) representation of SAW frequency shifts for various coatings responding to chlorobenzene from 1 – 20 % of its saturation pressure.

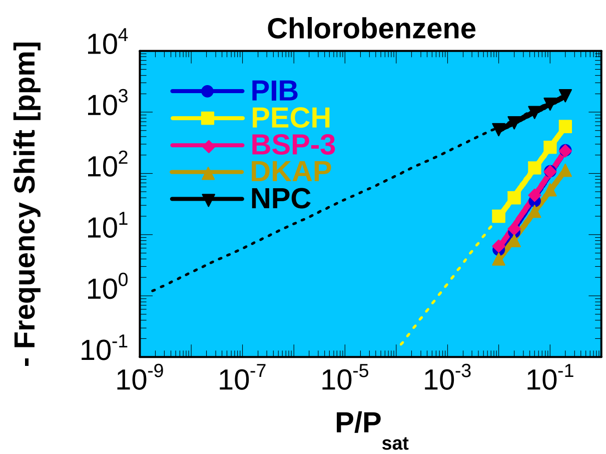

Figure 3(b). Extrapolation of power-law functions of isothermal adsorption data to very low (ppb) dilution limits for a variety of SAW sensor coatings.