

left the regime of possible slow light propagation in an opaque spectral region above the long-wavelength cutoff. To efficiently couple the waveguide modes with longer wavelengths (in the slow light regime) into the bends, the average refractive index at the bend was effectively increased by producing a waveguide with smaller hole radii in the bend vicinity. For waveguide structures with  $r = 0.33a$ , the blueshift in long-wavelength cutoff was reduced from 15 nm to 6 nm when the radii of four holes in the vicinity of the bends were decreased, allowing for some light transmission in the slow

light spectral region. The researchers said that the blueshift can be completely compensated and all of the wavelengths commensurate with slow light propagation can be incorporated into the high-transmission region of the waveguide if the refractive index is further increased by decreasing the radii of 16 nearby holes instead of four in the bend vicinity. According to the researchers, this demonstration makes photonic crystal waveguides very promising devices for slow light applications such as all-optical data storage and quantum computing.

TUSHAR PRASAD

### Virtual-Detector-Based Photoacoustic Microscopy Improves *In Vivo* Imaging

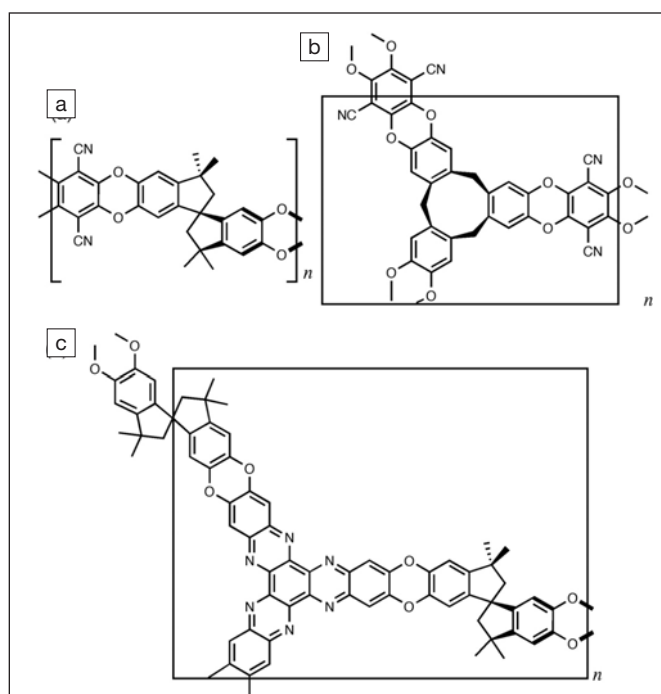
Photoacoustic microscopy (PAM) is a promising, noninvasive imaging technique that shows potential for applications in dermatology and related cancer research. The technique employs the absorption of laser pulses to produce a thermoelastic expansion of biological media and ultimately emitting a photoacoustic (PA) signal. Large-numerical-aperture (NA) ultrasound transducers detect the acoustic signal. Lateral and axial resolution is obtained from the focused

### Polymers with Intrinsic Microporosity Engineered for Hydrogen Storage

Safe and efficient onboard hydrogen storage for cars cannot currently be based on reversible  $H_2$  adsorption in microporous materials like zeolites, carbon, or in materials based on a metalorganic framework, because the quantity of adsorbed  $H_2$  is insufficient. Organic polymers have heretofore not been considered, because their free volumes are generally much too small. Recently, however, N.B. McKeown of Cardiff University, P.M. Budd of the University of Manchester, D. Book of Birmingham University, and their colleagues have hypothesized that their recently reported “polymers of intrinsic microporosity” (PIMs) would be good candidates for  $H_2$  storage because they form solids with large, interconnected free volume with accessible internal surface areas in the range of 500–900  $m^2/g$ . The rigidly contorted macromolecular structures formed by PIMs pack inefficiently and are a consequence of their fused-ring subunits, one of which typically contains a site of contortion, for example, a rigid, non-planar unit.

As reported in a recent issue of *Angewandte Chemie International Edition* (Vol. 45, Issue 11, DOI: 10.1002/anie.200504241; p. 1804), McKeown and co-researchers tailored the micropore structure of PIMs by using monomers that contain preformed cavities to provide appropriately sized sites for hydrogen adsorption. The researchers incorporated a bowl-shaped receptor monomer—cyclotricatechylene (CTC)—within a network PIM by using a benzodioxane-formation reaction between CTC and tetrafluoroterephthalonitrile, designating the new PIM as CTC-network-PIM. More conventional PIMs (PIM-1 and HATN-network-PIM; see Scheme I) were synthesized in order to compare gas adsorption properties. Structures for all three PIMs were confirmed by elemental analysis, infrared spectroscopy, and, in the case of the soluble PIM-1,  $^1H$  and  $^{13}C$  nuclear magnetic resonance. Nitrogen adsorption measurements showed that while all three PIMs have Brunauer–Emmett–Teller (BET) surface areas of about 800  $m^2/g$  with pore distributions biased in the range of 0.6–0.7 nm, the bias for CTC-network-PIM is particularly dramatic, which the researchers attribute to the internal dimensions of the CTC subunit. This finding suggests to the researchers that the choice of monomer precursor can be used to tune the pore size distributions within PIMs.

Hydrogen adsorption is both rapid and reversible, which



Scheme I. Soluble “polymers of intrinsic microporosity”: (a) PIM-1, (b) HATN-network-PIM, and (c) CTC-network-PIM. Reproduced with permission from *Angewandte Chemie International Edition* 45 (11) (2006) DOI: 10.1002/anie.200504241; p. 1804. © 2006 Wiley-VCH Verlag GmbH & Co KG.

the researchers expected for physisorption on a microporous material. All three PIMs adsorb a maximum of 1.4–1.7% by mass at pressures of >10 bar. The number of hydrogen molecules adsorbed per ring—0.5 for PIM-1, 0.43 for HATN-network-PIM, and 0.56 for CTC-network-PIM—suggests to the researchers that  $H_2$  adsorption is enhanced by the greater predominance of ultramicropores that result from the incorporation of the bowl-shaped CTC subunits. The researchers said that they “believe that optimization of PIMs for  $H_2$  adsorption presents additional opportunities towards achieving the U.S. Department of Energy’s ambitious 2010 target of a practical storage system that holds 6.0%  $H_2$  by mass.”

STEVEN TROHALAKI

laser spot, and the information from scans of the sample is later converted to a two-dimensional image. One problem inherent in large-NA systems is a reduction in the depth of focus, causing a deterioration of image quality in the out-of-focus region. The synthetic-aperture focusing technique (SAFT), which employs a point detector such as a needle hydrophone, was developed to reduce this phenomenon. In the February 15 issue of *Optics Letters* (p. 474), M.L. Li of Texas A&M University and co-researchers have introduced a virtual detector for PAM that allows the SAFT to be applied to the large-NA transducer without losing depth of focus and eliminates the need for the point detector.

In this system, the focal point of the transducer is considered to be a virtual point detector. Li and colleagues said, "Photoacoustic (PA) waves that are generated within a certain solid angle are assumed to be detected by the virtual detector." Linear scanning of both the laser and the transducer creates a superposition of the PA waves produced by the biological tissue. This superposition, coupled with a coherence factor, facilitates synthetic-aperture focusing and is the basis for improved lateral resolution and signal-to-noise ratio.

The researchers offered a brief description of the PAM system, but focused largely on advances made using the new virtual point detector. First, a proof-of-principle study of a 6- $\mu\text{m}$  carbon fiber immersed in 1% Intralipid solution was performed. In this study, "depth-independent lateral resolution of the carbon fiber" was achieved, "without affecting the axial resolution." Second, *in vivo* experiments were carried out on the scalps of rats. According to the researchers, the technique provides a much clearer vascular distribution that is attributed to improved lateral resolution and signal-to-noise ratio.

KEVIN P. HERLIHY

### 3D Nanostructures in Hydrogen Silsesquioxane Achieved by Proton Beam Writing

The most commonly used technique for three-dimensional (3D) nanolithography is e-beam writing. Therefore, different resists have been developed to define high-resolution features. Among them is  $(\text{HSiO}_3/2)_8$ , a hydrogen silsesquioxane (HSQ) from Dow Corning. In HSQ, resolution below 20 nm has been reported and single lines down to 7 nm wide have been observed. Recently, it has been shown that HSQ can also be used as an extreme ultraviolet (EUV) resist using 13.4-nm wavelength, and 26-nm wide lines have been demonstrated. In the March 8 issue of *Nano Letters* (DOI: 10.1021/nl052478c; p. 579), J.A. van Kan, A.A. Bettiol, and F. Watt from the Centre for Ion Beam Applications at the National University of Singapore have presented their results on high-energy proton-beam writing (p-beam writing) in HSQ resist at the 20-nm level.

Their method employs a focused mega-electronvolt proton beam scanned in a predetermined pattern over a suitable resist that is subsequently chemically developed. The researchers said that in both electron-beam (e-beam) and p-beam writing, the energy loss of the primary beam is dominated by energy transfer to substrate electrons. Nevertheless, unlike the high-energy secondary electrons generated during e-beam writing, secondary electrons induced by the primary proton beam have low energy, typically less than 100 eV. Hence, the secondary electrons have a limited range, resulting in minimal proximity effects, thus enabling the fabrication of high-density 3D micro- and nanostructures with well-defined vertical, smooth side walls.

In this study, layers of HSQ deposited by spin-coating on silicon wafers were evaluated. They were pre-baked for 120 s at 150°C before p-beam exposure. After exposure, they were developed in a tetramethylammonium hydroxide (TMAH) solution. Squares of 5  $\mu\text{m}$   $\times$  5  $\mu\text{m}$  were written with a focused 2-MeV p-beam, and the

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