PHOTONIC STRUCTURES: NEW TECHNIQUE
CREATES PATTERNS IN UNIQUE CRYSTALS
FORMED FROM HYDROGEL NANOPARTICLES

Researchers have developed a laser-based technique for creating patterns in self-assembled colloidal crystals produced from hydrogel nanoparticles – soft spheres that respond to heat by changing size. The development could make possible the fabrication of waveguides, three-dimensional microlenses and other photonic structures from the unusual crystals.

In related work, the Georgia Institute of Technology researchers have also learned to use weak attractive forces between the soft spheres to produce uniform crystalline structures with particle concentrations much lower than possible with hard spheres. The developments were described September 10th at the 226th national meeting of the American Chemical Society in New York.

In April 2002, a research team led by Andrew Lyon, a professor in Georgia Tech’s School of Chemistry and Biochemistry, announced it had developed a family of hydrogel-based nanoparticles that could be used to create photonic crystals whose optical properties could be tuned by thermally adjusting the water content of the particles.

The soft, conformable spherical particles provided a unique system for producing self-assembled periodic structures that could be tuned to transmit specific wavelengths of light. Applications were expected in optical switching and optical limiting.

The work discussed at the ACS meeting moves the nanoparticles closer to practical application by providing a way to form complex patterns in the crystalline structures. The patterns could be useful as optical waveguides or lenses.

“This represents a fundamentally new method for patterning self-assembled photonic materials,” Lyon said. “By combining a photo-patterning method with a self-assembly
technique, we can rapidly make large volumes of very nice optical materials. This provides the best of both worlds – a good optical material that is easy to prepare, combined with a process that allows us to tell the material what kind of overall structure it should have.”

Lyon’s group creates the pattern with a frequency-doubled Nd:YAG laser whose beam applies specific amounts of heat to the poly-N-isopropylacrylamide nanoparticles, which average 224 nanometer in diameter. To produce the smallest possible features, the researchers include tiny gold nanoparticles with the hydrogels; the gold converts the laser light to heat, allowing precise thermal control.

The heat prompts phase transitions, causing the particles to shrink or swell depending on the temperature. That changes the crystalline structure.

“The gold particles allow us to use a very narrowly-focused laser beam to locally heat the material,” Lyon said. “We can have a very sharp temperature gradient between the center of the laser spot and the surroundings. Everything outside of the laser spot experiences mostly ambient conditions and stays crystallized. Everything inside the laser spot goes through a melting phase. Then, the effective cooling rate is very rapid as the laser moves away, trapping the material as an optically transparent, non-diffraction glassy material.”

The patterning could be used to create optical waveguides or microlenses.

“By controlling the beam intensity profile, we can create a wavefront gradient index lens,” Lyon explained. “Across the surface of the crystal, you would have a constantly varying refractive index which provides a lensing effect.”

The patterning process is reversible, however. Before they are locked into place in the final production step, patterns created in the soft spheres can be erased and redrawn. The technique can also be used as an annealing step to remove defects where they are not wanted.

“We are trying to push the limits of fidelity, trying to make very small line widths so we can get down toward a useful patterning length scale, which is on the order of five microns,” Lyon added. “That could be very useful for transmitting optical information through these structures.”

Such patterning would not be possible with hard spheres, whose size cannot be changed significantly once they are created.

Beyond developing the patterning technique, Lyon and collaborators Saet Byul Debord, Clinton Jones and Michael Serpe have also studied the fundamental physics governing formation of crystals from the nanoparticles. Because they are soft and conformable, the hydrogels perform in ways that are very different from hard spheres.

“We are changing the phase diagram dramatically,” Lyon said. “That opens up new opportunities for different ways to accomplish the self-assembly of optical materials because you are no longer limited by simple hard-sphere packing. With these spheres, we can have a material that displays self-assembly properties based on weak attractive forces – and still ends up as a crystal.”

For instance, attractive forces between the spheres cause them to deform, moving closer to one another to maximize particle-to-particle contact. That allows formation of crystals from solutions with particle contents as low as 12 percent – well below the 50 percent concentration required to create uniform crystals from hard spheres.

“This was completely unexpected,” Lyon added.

Before the hydrogel nanoparticles can be useful in photonic applications, however, the researchers must reduce the size of the spheres and refine the technology to create smaller features.

Lyon and his team have fabricated nearly 100 different types of monodisperse hydrogel nanoparticles, in sizes ranging from 50 nanometers to 10 microns in diameter. The temperature at which the particles transition to a crystalline state can be controlled chemically during the synthesis process in a range from 10 degrees C to 60 degrees C.

After synthesis and precipitation polymerization in aqueous media, the particles are separated from the surrounding water by simple centrifuging. The resulting glassy gelatinous material, which has a faint blue, green or red hue, is more viscous than honey.

To give it desirable optical properties, the material must be annealed by heating it past the volume phase transition temperature of the component hydrogel particles, at which the photonic crystal loses its order and the nanoparticles begin to give up water content.

After removing small amounts of water, the material is allowed to cool, re-absorb water and re-crystallize. This thermal cycling process, repeated several times, packs the soft hydrogel particles into an ordered 3-D hexagonal array, which produces the periodic dielectric structure needed for optical applications.

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