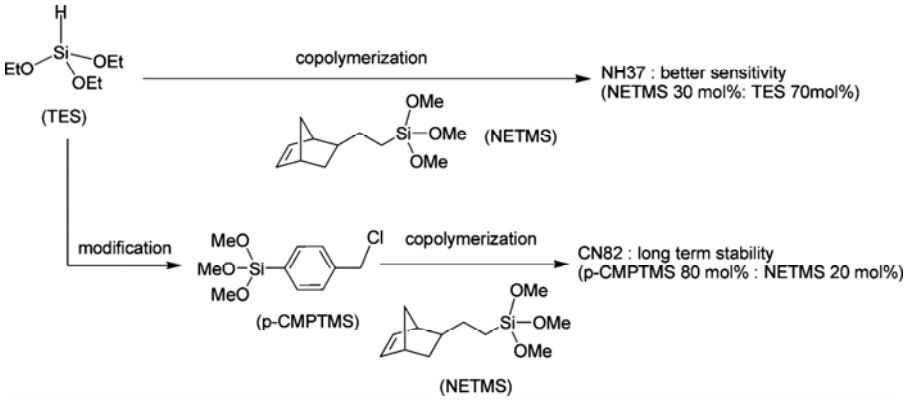
fibers compared to the nanoparticle films. As a result, transport of photoinjected electrons to the back contact was faster and recombination with the electrolyte slowed down significantly. To further improve device efficiency, the researchers are interested in decreasing the diameter of the nanofibers to increase the roughness factor of the films. To enhance the durability of the DSSC devices, the group also intends to employ ionic liquid electrolytes to obtain long-term stability at full sunlight intensity.

MELISSA A. HARRISON

Functionalized Silsesquioxanes Show High Sensitivity and Stability for Next-Generation E-Beam Lithography Resists

One of the most prevalent methods for creating submicron patterns is e-beam lithography (EBL). Electron optics can produce electron beams with a diameter of a few nanometers. The spatial resolution of EBL (typically ≈10s nm) is limited by scattering in the photoresist. Thus, it remains a challenge to create EBL resists which maintain high contrast below 20 nm. Hydrogen silsesquioxane (HSQ) has shown promise as a negative resist due to its ability to create sub-20 nm features with high contrast and fidelity. However, HSQ has low sensitivity and is not stable for long periods of time.

J.H. Sim of Seoul National University, H.-J. Lee of the National Institute of Standards and Technology, and their colleagues propose a solution to these problems in the May 25 issue of *Chemistry of Materials* (DOI: 10.1021/cm9035456; p. 3021). Sim and coresearchers created two compositions of functionalized HSQ resists (shown in Scheme 1). Norbornene-modified HSQ is created by co-polymerizing triethoxysilane (TES) with norbornene ethyltrimethoxysilane (NETMS). Norbornene-co-chloromethylphenyl functionalized silsesquioxane is obtained by co-polymerizing *p*-chloromethylphenyl trimethoxysilane and norbornene ethyltrimethoxsilane.



Scheme 1. Schematic showing compounds used for creating norbornene-functionalized HSQ (top line) and norbornene-co-chloromethylphenyl functionalized silsesquioxane (bottom line). Reproduced with permission from *Chemistry of Materials* **22** (10) (2010) 3021; DOI:10.1021/cm9035456. © 2010 American Chemical Society.

Contrast curves demonstrate that the norbornene and norbornene-co-chloromethylphenyl resists become insoluble at 58% and 75% of the electron dose for standard HSQ, respectively. Scanning electron micrographs qualitatively show that these resists also maintained high-resolution patterning at low electron dosages. The norbornene-functionalized resists produced 15 nm lines and norbornene-co-chloromethylphenyl resists produced 20 nm wide lines. While functionalizing HSQ with norbornene increased the shelf life in solution from approximately five days to 10 days, functionalizing with norbornene-co-chloromethylphenyl allowed the molecule to be stable for over a year without forming a gel.

The researchers conclude that by functionalizing the HSQ molecule, resists can be created with higher sensitivity and stability than currently possible, without sacrificing nanometer-scale resolution. According to the researchers, the ability to create more sensitive resists opens the door to creating large-area patterns using EBL.

SCOTT COOPER

Method Developed for Producing Chitosan Nanoparticles Using Nanoporous Membranes

The drive to develop drug delivery systems that can be tailored for controlled release of pharmaceutical action continues to receive immense research, but the efficacy of many drugs is limited by their ability to reach the site of optimum therapeutic action. Recently, R.N. Zare of Stanford University and C.R. Martin of the University of Florida and their colleagues have developed a liquid–liquid separation approach using a nanoporous membrane to produce organic nanoparticles, which can be loaded with other organic guest molecules. To illustrate this technique, the researchers used chitosan, a pH-responsive polymer with biodegradable and biocompatible properties. These properties enable chitosan to be used in a wide range of applications in both pharmaceutical and biomedical fields.

As reported in the May 4 online edition of *Nano Letters* (DOI: 10.1021/nl101057d), the research team used track-etched polycarbonate (PCTE) and anodized aluminum oxide (AAO) nanoporous membranes having 10 nm and 20 nm cylindrical pores, respectively, as the separator or the liquid~liquid system. The pH of the feed and receiver solutions was adjusted independently so that chitosan is soluble in the feed solution and insoluble in the receiver solution. The feed solution was forced under pressure through the pores of the membrane into the receiver solution, as shown in Figure 1. When nanodroplets of the soluble chitosan were injected through the membrane into the receiver solution, nanoparticles of chitosan were formed at the exits of the nanopores and carried

away from the membrane by the constant gravity flow. The nanoparticles were collected from the receiver solution by filtration, rinsed with deionized water, and dried in air at room temperature.

The mean diameter of the nanoparticles was found to be 5 nm and 21 nm with the PCTE and AAO membranes respectively, with the larger mean diameter formed at the exit of the AAO membrane. The hydrodynamic diameters as determined by dynamic light scattering of the nanoparticles were 8 nm and 26 nm using PCTE and AAO nanoporous membranes, respectively. These values slightly differ because the first set was obtained after thorough drying of the particles, while the hydrodynamic diameter was obtained while the particles were still in solution. In addition, particle diameter was found to increase exponentially with flow rate.

This study demonstrated a general liquid–liquid separation approach to produce organic nanoparticles using a nanoporous membrane. Moreover, it was demonstrated that it was possible to incorporate host molecules (e.g., rhodamine 6G organic dye molecules) into the chitosan nanoparticles, which suggests the practical use of this approach in preparing pharmaceuticals in nanoparticle form for drug delivery, according to the researchers.

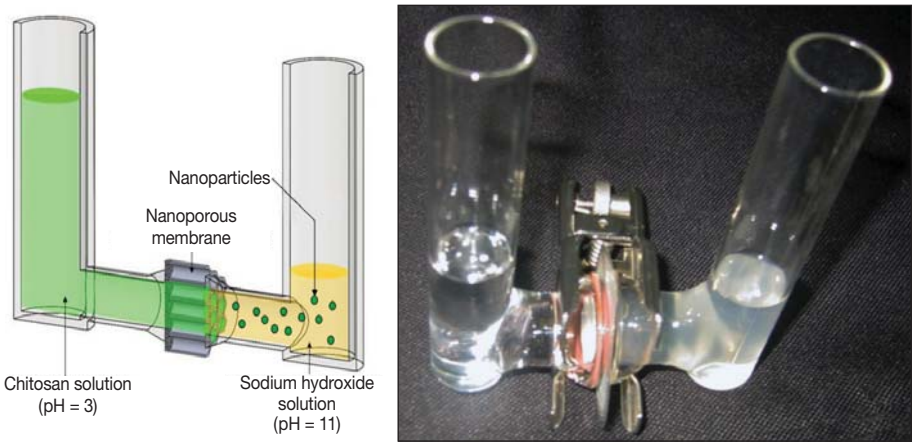


Figure 1. Method for producing chitosan nanoparticles by flow through a nanoporous membrane. (Images courtesy of Richard N. Zare, Chair, Department of Chemistry, Stanford University.)

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