Enhanced Electron Collection Efficiency Observed in Dye-Sensitized Solar Cells with Hollow TiO_2 Nanofiber Photoanodes

Dye-sensitized solar cells (DSSCs) are fabricated and studied in an attempt to replace current solar cell technologies with cheaper and more efficient devices to better utilize solar energy. DSSCs have been presented as a cost-effective alternative to conventional silicon solar cells, employing mesoporous, anatase TiO_2 films. The TiO_2 photoanode has been previously fabricated as interconnected, spherical nanoparticle films and more recently using TiO_2 nanotube arrays. Now E. Ghadiri and N. Taghavinia of Sharif University of Technology, Iran; and S.M. Zakeeruddin, M. Grätzel, and J.-E. Moser of the Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, have employed nanostructured, TiO_2 hollow fibers as photoanodes in DSSCs which demonstrate improved electron transport properties as compared to mesoporous, spherical nanoparticle films.

In the May 12 issue of *Nano Letters* (DOI: 10.102/nl904125q; p. 1632), Ghadiri and coworkers described their facile and novel preparation of TiO_2 nanofibers using low-cost cellulose fibers as a template. Aqueous solutions of $(NH_4)_2TiF_6$ and boric acid at a temperature of 50°C were used to deposit titania on cotton fibers. The samples are heated to 500°C for 3 h in air to remove the cellulose template.

TiO_2 nanofibers were employed in conjunction with the ruthenium complex Na–Ru^{II} (4,4′-bis(5-hexylthiophen-2-yl)-2,2′-bipyridine)(4-carboxylic acid-4′-carboxylate-2,2′-bipyridine)$(NCS)_2$ (C101) to produce 6 μm films for DSSCs. The volatile redox-active electrolyte used was comprised of 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 0.03 M I_2, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85/15,v/v). In the blue-green region of the spectrum (λ = 400–550 nm), the absorptance (α) of the film was close to α = 0.8 and peaked at α = 0.81 at λ_{max} = 550 nm. At λ = 550 nm, the incident photon-to-current conversion efficiency of the photovoltaic device was 0.77 and the absorbed photon-to-current efficiency exceeded 90% in the 550–650 nm range of the spectrum. The highest photovoltaic power conversion efficiency of η = 7.15% was measured with TiO_2 nanofiber films of 9 μm thickness.

Carrier trapping was observed to be reduced in the designs employing hollow

SNAPSHOT

Perspectives on Future Nanowire Technologies

Semiconductor nanowires became one of the most active nanoscience research areas in the late 1990s. Since then, semiconductor nanowire research activity, as measured by the number of publications, has increased exponentially. Discovery and hypothesis-driven research have emerged in several subfields, including nanowire electronics, nanowire photonics, energy conversion and storage, and interfacing nanowires with living cells. Extensive worldwide research activities quickly followed the publication of research papers that introduced the original ideas and concepts in these subfields. Recently, in a short perspective article, P. Yang, R. Yan, and M. Fardy at the University of California, Berkeley and Lawrence Berkeley National Laboratory examined the latest nanowire-research trends and activities while interjecting their personal views and speculations in order to stimulate more creative thinking and even more innovative ideas about nanowire research itself.

In their perspective published in the May 12 issue of *Nano Letters* (DOI: 10.1021/nl100665r; p. 1529), Yang, Yan, and Fardy said that the nanowire community often places more importance on the novelty of new research over whether or not it offers improvement when, in their view, both are equally important for the advancement of nanowire technology. In addition, the researchers examined how the fundamental understanding of nanowires has been advanced with both the bottom-up and top-down approaches to fabrication (the first consists of chemical assembly, such as Langmuir–Blodgett techniques, while the latter include lithographic processes). The researchers also offered their opinion on three applications particularly suited for nanowires and for which great progress can be made relatively soon.

Integrated nanophotonics would allow the manipulation of light pulses within submicrometer volumes, which are necessary if highly integrated light-based devices, such as optical computers, are to be realized. Assembly of photonic circuits from nanowire elements that assume various functions—light creation, routing, and detection—is currently feasible. Furthermore, because current nanowire materials include active, passive, nonlinear optical, and semiconducting inorganic crystals, the assembly of multifunction components on the same substrate using bottom-up schemes should be pursued.

Nanowire-based single cell endoscopy is possible with the development of a nanoscopic coherent light source and nanowire probe. *In situ* imaging would allow investigation of intracellular biological processes *in vivo* and greatly improve our fundamental understanding of cell functions, physiological processes, and cellular signal pathways. These nanowire probes could also be used for spot-delivery of chemicals or extraction of proteins and DNA from single living cells with much better spatial resolution compared to conventional methods.

Another potential nanowire application is the generation of fuels by the direct conversion of solar energy by a fully integrated system that is efficient, durable, and reasonably inexpensive to manufacture. The researchers said that key features in photosynthetic systems, such as spatial and directional arrangement of the light-harvesting components, should serve as design guides. Both gas-phase and solution-phase methods produce large quantities of nanowires that are readily processed into interconnected meshes or membranes with roll printing, casting, or automated drawdown. The nanowires' large surface areas and tunable bandgaps will allow them to act as effective photoelectrodes.

The researchers said, "We can be confident that we will continue to see many more fundamental new discoveries and science based on this unique class of nanoscale building blocks. Meantime, the future of nanowire technology will be largely dependent on how well we can balance the issues of cost, performance, and stability of the nanowire-based devices and systems."

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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.

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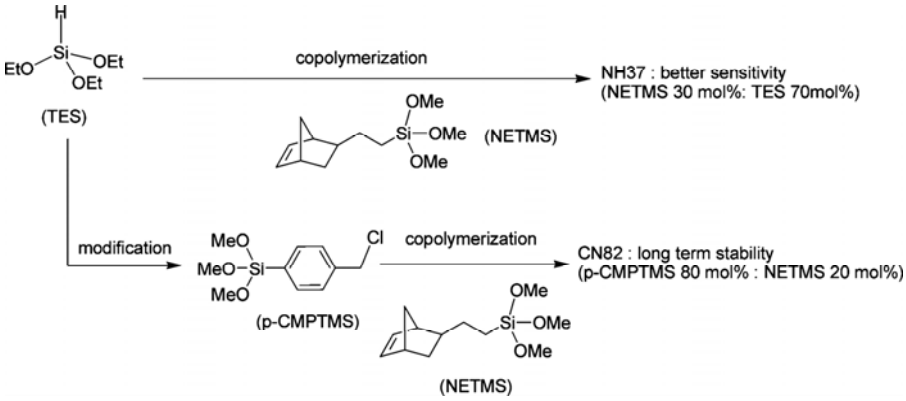
Functionalized Silsesquioxanes Show High Sensitivity and Stability for Next-Generation E-Beam Lithography Resists

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