ing tip distance in a stepwise fashion, with a step value equal to the quantum of conductance, until the conductance value almost reached zero. Additional steps with step values of approximately integral multiples of 1/100 of the conductance quantum were observed for 1 mM 4,4'bipyridine in a 0.1 M NaClO₄ water solution. The researchers attribute these additional conductance steps to the formation of junctions with one, two, three, and more molecules. In order to confirm that the conductance steps were caused by the formation of stable molecular junctions, a solution of 2,2'-bipyridine molecules was tested. In 2,2'-bipyridine, the positions of two nitrogen atoms prevent the molecule from simultaneously binding to two electrodes, and no conduction steps were observed. The same experiments were performed for hexanedithiol, octanedithiol, and decanedithiol molecules in toluene. The conductance showed stepwise behavior, but the step size was smaller than in the case of 4,4'-bipyridine because of the higher resistance of *N*-alkanedithiol molecules as compared with 4,4'-bipyridine. The researchers said that the resistance of *N*-alkanedithiol molecules corresponds well with the widely accepted model of electron tunneling through the molecule.

MAXIM NIKIFOROV



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"Design Rules" of Silk Production Unraveled in Studies of *Bombyx mori* Cocoons

Traditionally, silk fibers produced by silkworms and spiders are harvested, disentangled, and then woven into fabrics. H.-J. Jin and D.L. Kaplan from Tufts University have begun to unravel the *in* vitro mechanism of silk processing in insects and spiders. As described in the August 28 issue of Nature, the researchers monitored the behavior of the silk fibroin solutions as a function of decreasing water content. Starting with the cocoons of the domestic silk moth Bombyx mori, the researchers "degummed" the cocoons to generate sericin-free fibroin fibers. The family of sericin proteins is hydrophilic and acts as the glue between fibroin fibers. The sericin in these aqueous fibroin solutions was substituted with polyethylene oxide (PEO). The silk fibroin and the PEO molecules preferentially vie for the water molecules in which the protein is dissolved. As the fibroin concentration is increased and the water content is lowered, micelles form first, ranging in diameter from 100 nm to 200 nm; subsequently, "globules" form as the water content is further decreased. Through scanning electron microscopy and atomic force microscopy, the researchers observed that these globules arise from phase separation between the hydrophilic and hydrophobic segments. Films of the fibroin aqueous solutions were cast and subsequently treated with methanol, physical shear, and stretching. The characteristics of the resulting silk structures depended critically upon the nature of the postprocessing.

The researchers describe a process that combines the primary sequence of the silk proteins and the biological environment of the gland during silk spinning to create silk fibers. These "design rules," said the researchers, apply to all silk proteins in terms of processing in aqueous environments, which can lead to materials engineering in aqueous systems of new silk-based materials with desired properties for potential applications in tissue engineering and biomaterials.

LARKEN E. EULISS

Carbon Nanocoil Supports Surpass Performance of Other Nanostructured Materials in Direct Methanol Fuel Cells

T. Hyeon of Seoul National University, Y.-E. Sung of Kwangju Institute of Science and Technology, and colleagues have developed carbon nanocoils as a catalyst support for the fabrication of direct methanol fuel-cell (DMFC) electrodes. They synthesized the carbon nanocoils by heat-treating solid composites of a carbon precursor (resorcinol formaldehyde gel), silica sol, and a transition-metal salt. The research team said that because the synthetic procedure is simple and inexpensive, it can be readily applied to cost-effective, large-scale production of the material. High surface area and good crystallinity are the characteristics needed for the catalyst support for DMFCs. As the researchers reported in the September 22 issue of Angewandte *Chemie*, their synthesized carbon material exhibited a high surface area of $318 \text{ m}^2/\text{g}$ and was composed of 5–10-nm-thick graphitic coils. The crystallinity of the material was comparable to that of carbon nanotubes. The researchers said that this was especially important because it is difficult to obtain crystalline carbon materials with a large surface area. For example, they said, many activated carbons have surface areas exceeding 1000 m^2/g , but they are noncrystalline and amorphous. Alternatively, graphite is highly crystalline, but has a very small surface area of $<10 \text{ m}^2/\text{g}$.

Carbon is a critical material for DMFCs because a good support exhibiting a homogeneous high dispersion of catalytic species is a key factor dominating the overall performance and stability of fuel cells. Hyeon and colleagues identified highly dispersed PtRu alloy catalysts of up to 60 wt% on their carbon support, resulting in higher catalytic activity for methanol oxidation. In a half-cell test for methanol oxidation at 0.6 V, the electrode using the carbon nanocoil had six times higher current than that of a commercialized fuel-cell carbon substrate.

The carbon nanocoil performed better as a support material for fuel cells than other nanostructured carbon materials. In particular, the nanocoils exhibited a current density that was three times higher at a given voltage than that of the graphitic carbon nanofiber, which was known to be one of the best catalyst supports for DMFC electrodes. In nanocoil experiments using a full fuel cell—composed of a cathode, anode, and polymer membrane electrolyte—the maximum power density increased by >85% over the standard commercial sample at 30°C.

Oxide Superlattices Containing Si Nanocrystals and Er Ions Luminesce Efficiently at 1.54 µm

M. Zacharias and colleagues from the Max Planck Institute of Microstructure Physics (Halle, Germany) have developed a means of controlling the size of silicon nanocrystals and custom-manufacturing these crystals on 4 in. wafers. The technique is based on a combination of superlattices—multilayer structures with layer thicknesses of a few nanometers and varying bandgaps—and phase separation in the ultrathin layers.

The superlattice structure of amorphous silicon oxide layers (SiO_x/SiO_2) was manufactured using a standard deposition technique. The researchers employed a variation of this technique by evaporating the silicon oxide either in a vacuum or in an oxygen-containing atmosphere. The resulting amorphous SiO/SiO₂ superlattice structure was then tempered in a nitrogen-containing atmosphere at 1100°C. Through the thermally activated phase separation, the SiO in the ultrathin sublayers transformed into pure silicon nanocrystals and amorphous SiO₂,





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