

Strength in Silk is Driven by Critically Sized Nanocrystals

Silk has been a prized material for thousands of years, partially due to its high strength. This strength arises from protein nanocrystals folded into β -sheets, which act as a reinforcing phase within the silk fiber (see Figure 1). As described in the April issue of *Nature Materials* (DOI: 10.1038/nmat2704; p. 359), M.J. Buehler and co-researchers at the Massachusetts Institute of Technology used molecular simulations to identify ~ 3 nm as a critical dimension of nanocrystals, which directly affects the elastic modulus, strength, and toughness of silk fibers.

Buehler and graduate student S. Keten, postdoctoral associate Z. Xu, and undergraduate student B. Ihle used the crystalline protein sequence expressed by the mulberry silkworm, *Bombyx mori*, to simulate nanocrystals ranging in size from approximately 2 nm to 6.8 nm, in a series of molecular level computational experiments to probe the effect of crystal size on their mechanical properties. The results show that nanocrystals below ~ 3 nm are much stronger and tougher than those at larger dimensions. The researchers explain this observation by the increased significance of shear, which dominates the mechanics of nanocrystals below this size and that allows all hydrogen bonds to work concertedly. This results in a significant buildup of mechanical strength. Taking into account the effect of shear, the calculated values for elastic ($E = 22.6$ GPa) shear ($G = 4.6$ GPa) moduli correlated well to experimental values. Simulated pull-out tests, used to identify the nanocrystals' failure mechanisms, demonstrated that nanocrystals below a critical size of ~ 3 nm exhibit a highly dissipative slip-stick behavior. This slip-stick motion, enabled by the weak nature of hydrogen bonds, dissipates a significant amount of energy

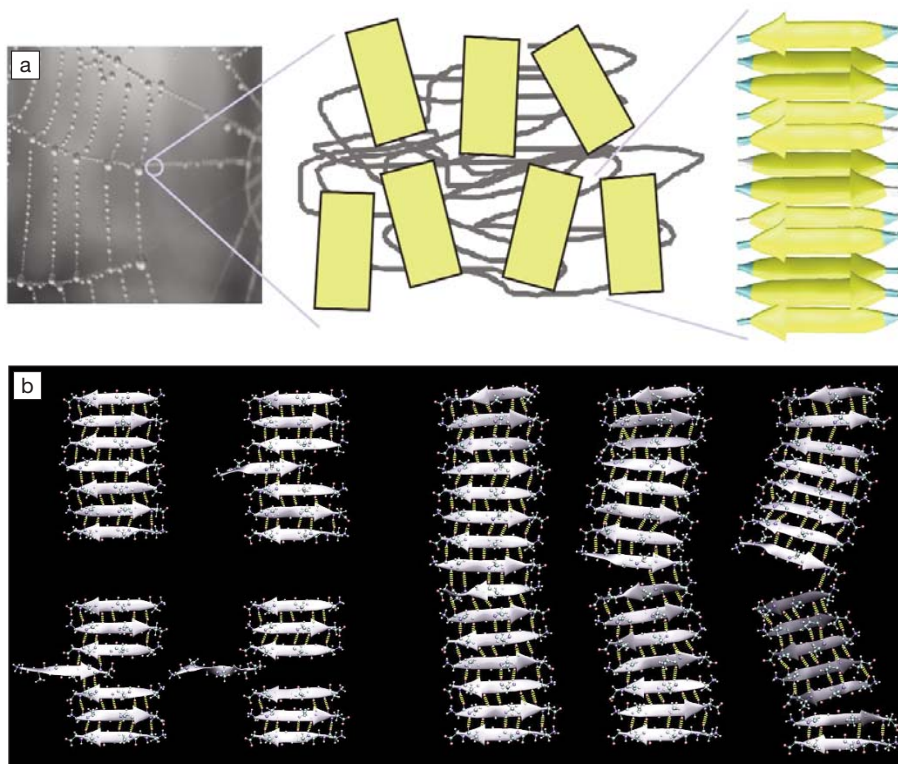


Figure 1. (a) Hierarchical structure of silk, which contains β -sheet nanocrystals. Hydrogen bonding occurs between the sheets, designated as arrows. (b) Breaking mechanisms of silk nanocrystals. The left part of the image shows a small crystal, which fails gracefully as a strand is being pulled out. The larger crystal on the right fails catastrophically as a crack forms at the left part. Figure courtesy M. Buehler (MIT). Reproduced with permission from *Nature Materials* 9 (4) (2010) 360; DOI: 10.1038/nmat2704. ©2010 Nature Publishing Group.

and allows nanocrystals below ~ 3 nm to achieve a much greater strength, toughness, and resilience.

This work shows that while hydrogen bonds are typically weak, confinement of these bonds to nanometer-sized domains can impart considerable mechanical strength, resolving a long-standing question that has puzzled materials researchers for

decades. In the case of silk, this strength can exceed that of steel. The results from this study may lead to the design of new, synthetic materials such as ultrahigh strength, light-weight composites, and may help to overcome the limitations of current engineered materials to achieve greater strength at greater toughness, simultaneously.

SCOTT COOPER

Gold Nanoparticle Arrays Display Plasmon-Induced Electrical Conduction

Fabrication at the nanoscale is fundamental to both molecular electronics and plasmonics, where optical interactions with nanoparticles induce surface plasmons (localized, collective oscillations of conduction electrons on the nanoparticle surface) creating locally intense electromagnetic fields. Applications that utilize surface plasmons include surface-enhanced Raman spectroscopy, targeted tumor treatment, and molecular recognition labeling. In addition, progress made

in several critical aspects of molecular electronics has resulted in useful devices. However, yet to be observed is the interaction of optically induced plasmons resulting in charge migration through single molecules. Recently, though, D.A. Bonnell of the University of Pennsylvania, P. Banerjee of the University of Maryland, M.J. Therien of Duke University, and their colleagues have demonstrated the ability of surface plasmons to alter the electrical properties of a molecular junction by coupling gold nanoparticle arrays with highly conjugated, chromophoric wires.

As reported in the February 23 issue of

ACS Nano (DOI: 10.1021/nn901148m; p. 1019), Bonnell and co-researchers chose a device platform consisting of an array of Au nanoparticles on an insulating glass substrate. These well-studied systems exhibit conduction that depends on nanoparticle spacing and occurs according to a percolation mechanism. The researchers controlled nanoparticle spacing by coating the Au nanoparticles with α,ω -dithiol-terminated meso-ethyne-bridged porphyrin supermolecules (dithiol-PZn₃), which serve as 4.6-nm bridges between Au nanoparticles (see Figure 1). In addition, dithiol-PZn₃ bridges possess optoelec-

tronic characteristics optimal for coupling Au surface plasmons. Scanning electron micrographs were used to compare array morphologies of uncoated 16-nm, 32-nm, and 46-nm Au nanoparticles, which displayed areal coverages of 52%, 54%, and 46%, respectively, and conductivities much lower than metal films because only a fraction of the nanoparticles provide conducting pathways. Dithiol-PZn₃ adsorption onto the 16-nm and 32-nm Au nanoparticles results in much higher conduction that displayed Arrhenius behavior. The researchers said that the 46-nm nanoparticle-array densities are below the critical point for percolation.

The researchers observed much larger photocurrents (which are absent in arrays of uncoated Au nanoparticles) in a device consisting of 32-nm, dithiol-PZn₃-coated Au nanoparticles when illuminated with red light (655 nm) than when illuminated with blue (405 nm) or green (532 nm) light. The photocurrents are not simply proportional to the extinction coefficients at red, blue, and green wavelengths. The researchers attribute the anomalously large photocurrent observed at 655 nm to optical focusing and increased photon flux resulting from coupled surface plasmons. The researchers said, "Since molecular compounds exhibit a wide range of optical and electrical properties, the strategies for fabri-

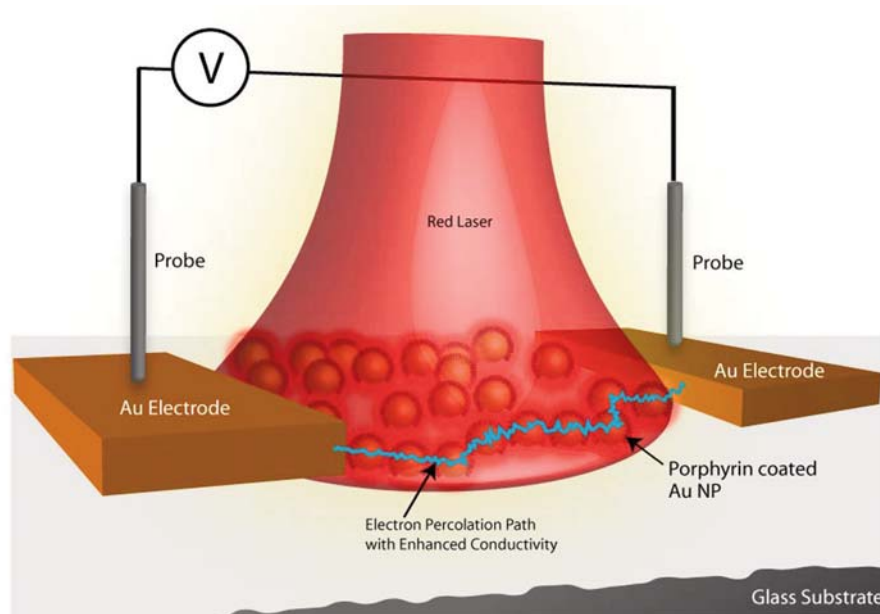


Figure 1. A schematic of a hybrid molecular device shows metal electrodes connected by a percolation pathway composed of dithiol-PZn₃-coated Au nanoparticles.

cation, testing and analysis elucidated in this paper can form the basis of a new set of devices in which plasmon-controlled electrical properties of single molecules

could be designed with wide implications to plasmonic circuits and optoelectronic and energy harvesting devices."

STEVEN TROHALAKI

News of MRS Members/Materials Researchers



John Joseph Gilman, Adjunct Professor of Materials Science and Engineering at the University of California—Los Angeles, died on September 10, 2009. Jack's persona is gone but all MRS members should know that

Jack and his record of accomplishments in Materials Science and Engineering will be remembered. The many accomplishments, both in academia and industry, have been very positively commented-on already in a number of reports: M.A. Meyers and S.M. Walley, "In Memory of TMS Fellow John Gilman, 1925–2009," *JOM*, p. 8 (November 2009); and, a tribute prepared for the National Academy of Engineering by Jack's colleague, J.D. Mackenzie, "Professor John J. Gilman," also delivered at a Memorial Lecture organized by Jenn-Ming Yang, at the Department of Materials Science and Engineering, UCLA, January 22, 2010.

Among our shared reminiscences about Jack is the recurring thought that many conference speakers, including past

MRS Symposium ones and new ones to come, will not be kept "higher on their toes" because of Jack being absent from languishing comfortably in a front row seat until rising and pursuing a probing posture during the ensuing question period! John Mackenzie reports that the UCLA students lauded such educationally-benefitted questioning at their own departmental seminars. And then there is the wider research coverage of Jack Gilman's own multiple research articles and conference presentations, spanning the topics of his book titles: *Micromechanics of Flow in Solids* (1963); *Inventivity: The Art and Science of Research Management* (1992); *Electronic Basis of the Strength of Materials* (2003); and, most recently, *Chemistry and Physics of Mechanical Hardness* (2009). The latter book brings to mind Jack's pioneering article "Hardness: A Strength Microprobe" in *The Science of Hardness Testing and Its Research Applications*, edited by J.H. Westbrook and H. Conrad (ASM, Metals Park, OH, 1973) pp. 51–74. MRS *Bulletin* and the *Journal of Materials Research* readers will note the foresighted connection with modern capabilities

being reported on methods of nano-indentation hardness testing.

The National Academy of Engineering cited Jack Gilman's "contributions to dislocation behavior of ceramics, disclination behavior of polymers, and leadership in development and production of metallic glasses." The longevity of his work is already indicated, for example, through use made in university course instructions of measurement techniques reported for cleavage surface energy determinations and dislocation velocity estimations. As indicated in the 2003 book title, a particular interest of Jack's was to make quantitative connection between electronic forces at the atomic or molecular level and the macroscopic plasticity and fracturing properties of materials—a goal unquestionably nearer in this 21st century because of his persistent research endeavors.

RON ARMSTRONG
University of Maryland

JAMES LI
University of Rochester

MARC MEYERS
University of California, San Diego