surface to form nanowires at a very high growth rate."

MAXIM P. NIKIFOROV

Low-Temperature Diffusion of Water Clusters on Pd Surfaces Depend Critically on Cluster Size

Working with a scanning tunneling microscope (STM) that can be operated at extremely low temperatures, a research team at the Lawrence Berkeley National Laboratory, led by Miquel Salmeron, a physicist with the Materials Sciences Division, observed the movement of clusters of water molecules on a metal surface. The researchers reported in the September 13 issue of *Science* that the clusters moved across the surface more rapidly than did single molecules, which runs contrary to their previous understanding.

The research team cooled a single crystal of palladium, a good catalyst for reactions involving hydrogen and water, to a temperature of ~40 K in an ultrahigh vacuum. Water molecules were then introduced onto its (111) surface and their motion was tracked with the STM. As expected from previous studies, single molecules migrated across the surface to aggregate into clusters of two (dimers), three (trimers), four (tetramers), five (pentamers), and six (hexamers).

"Isolated water molecules moved by hopping from one lattice point [on the substrate crystal] to the nearest neighboring point whereupon if they collided with another water molecule they began to form clusters," said Salmeron. "The speed with which the molecules moved increased by four orders of magnitude when dimers were formed. The mobility of trimers and tetramers was also very high compared to the isolated molecules."

Salmeron and his colleagues observed that the hydrogen bonds which held two, three, or four water molecules together in a cluster forced the cluster into a geometric configuration that was mismatched with the lattice of the palladium surface. The individual water molecules within these clusters could no longer be bound to the palladium's lattice points with the same strength as when they were isolated. This allowed dimers, trimers, and tetramers to easily slide across the palladium's surface.

When clusters reached five water molecules in size, however, the combined strength of the water-substrate bonds prevailed and the movement of the pentamers slowed or stopped altogether. The addition of a sixth water molecule created highly stable hexamer rings, which spread out as a hexagonal honeycomb structure over the palladium substrate.

Salmeron said, "The hexagonal honeycomb of water molecules does not exactly match palladium's lattice and as a result honeycombs grow to a certain size and then stop, forming islands across the substrate's surface. As additional water molecules are introduced, they pile up on top of these islands. Slight heating will break these islands up into holes that form beautiful patterns, like nanoscale snowflakes."

The interaction of water with surfaces drives a wide variety of important phenomena that include wetting, corrosion, ice-melting, electrochemistry, dissolution, and solvation. Such interactions are equally important to many biological processes.

Salmeron said, "Numerous fundamental questions regarding the adsorption of water on surfaces and its evolution from isolated molecules to clusters, complete

Metallic Hydrogen Decoration Results from Hydrogen Adsorption on SWNT

Many carbon materials have excellent molecular adsorption and sieving properties. Because of their many unusual mechanical and electronic properties, single-walled carbon nanotubes (SWNTs) have been studied extensively for their potential in the fabrication of nanodevices and components in molecular-scale machines and electronics. Since structural deformation of SWNTs can give rise to significant physicochemical properties, researchers O. Gülseren at the University of Pennsylvania, T. Yildirim at the NIST Center for Neutron Research in Maryland, and S. Ciraci at Bilkent University in Turkey investigated structural and electronic properties of hydrogenated SWNTs (H-SWNTs) as a function of hydrogen coverage and decoration by extensive first-principles calculations. The team showed how changing the shape of tiny single-walled tubes of carbon may open a potential mother lode of technologically useful properties.

The new calculations by Yildirim and his colleagues, published in the September 15 issue of *Physical Review B*, indicated that strategically placing hydrogen on the exterior of carbon nanotubes leads to dramatic changes in their electronic and atomic structures. One of the most important results in this study was that upon hydrogenation at uniform half coverage, the zigzag (*n*,0) SWNTs are metallized with high density of states at the Fermi level. Surprisingly, the cross section of the nanotube—initially cylindrical—becomes rectangular, with a diamondlike carbon atom at each corner, as shown in the figure. These chemically passive carbon atoms isolate the four conducting faces of the H-SWNT, yielding a "four-wire nanocable," said Yildirim. Because of the high density of conduction electrons in this particular configuration, he said, it may be possible to chemically engineer nanotube wires that are ideal one-dimensional conductors or are even superconducting.

For other isomers at half coverage as well as exo- and endo-exohydrogenations at full coverage, the cross sections remain quasi-circular and electronic structures vary greatly among the resultant materials. For example, the chain pattern H-SWNTs exhibit a small bandgap of ~2 eV while the dimer pattern H-SWNTs exhibit a bandgap of ~4 eV. The team's calculations show that selective bonding of hydrogen to nanotubes can give rise to a number of potentially useful applications in the emerging field of molecular electronics.

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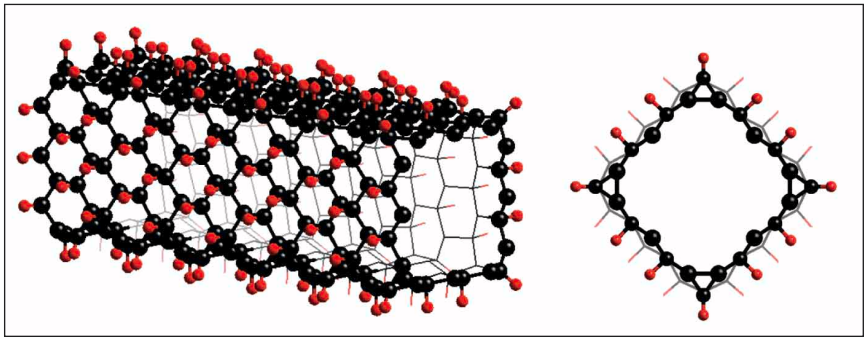

Figure. A side and top view of a hydrogenated (8,0) single-walled carbon nanotube at half coverage. Red and black represent H and C atoms, respectively.

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layers, and beyond, remain unanswered. Structural probes that analyze cluster formation do not address the important issue of the movement of water on surfaces."

Copper Found in Bloodworm May Serve as Paradigm for New Materials

Researchers report in the October 11 issue of *Science* their detection of a copper-based biomineral in the jaw tip of *Glycera dibranchiata*, better known as the marine bloodworm, the bait of choice for certain kinds of fish. This is in contrast to the much more commonly observed Ca-, Si-, or Fe-based minerals. Herbert Waite of the University of California—Santa Barbara (UCSB) and colleagues determined that copper also occurs in non-mineral form in the bloodworm jaw where it may act as a structural element in cross-linking long chains of fibrous proteins. The researchers reported, "The marriage of protein with copper mineral as well as with bound copper ions is an intriguing concept per se but may also serve as a design prototype for new materials that need to be hard, lightweight, and durable."

In addition, the research team found the non-mineral form of copper on the surface of the jaw canal through which venom is injected. That copper may be acting as a catalyst that activates venom being discharged by the worm into its prey, they said.

The researchers found that the jaw tip exhibits the ordered crystalline structure of the copper-based biomineral atacamite [$Cu_2(OH)_3Cl$]. They found that the bloodworm's unmineralized copper as well as the copper biomineral is concentrated in the first half millimeter of the jaw, and that the copper biomineral is organized in nanostructured fibers (~50 nm in diameter) within a protein matrix. They reported that the "fiber orientation within the tip is roughly parallel to its outer shape."

Through nanoindentation, performed by Thomas Schöberl of the Erich Schmid Institute for Materials Science, Leoben, Austria, the researchers mapped hardness (H) and stiffness (E) with composition in the bloodworm jaw. They then determined that both hardness and stiffness increased with increasing mineral content. The hardness-to-stiffness ratio in bloodworm jaws was higher than in other known mineralized tissue. According to the research team, this was indicative of a high abrasion resistance, commonly understood as equal to hardness to the three halves power divided by stiffness [$H^{3/2}/E$].

"With the worm," said Waite, "it is that quotient that is revealing rather than individual hardness and stiffness measurements. So when you look at that quotient, the wear resistance value is very close to the best materials we can make."

But high values for H and E also correlate with the presence of copper, even where the copper is not in mineral form. First author Helga Lichtenegger's analysis of the distribution of copper in the bloodworm jaw suggested that about half the copper was in a biomineral form and half in the form of copper aggregates.

Waite said, "I know from my research that the proteins in invertebrate jaws and particularly in the jaw tips are not complicated. They have generally just two types of amino acids, glycine and histidine. These two amino acids probably repeat in a precise chainlike sequence. In this respect it is one of nature's closest analogues to synthetic polymer molecules. I expect that the copper cation in the bloodworm jaw plays a role in the cross-linking of these amino acid chains."

"Storing venom in nontoxic form that is being catalytically activated as it passes through this syringe may," suggested Waite, "afford us a model for delivering an unstable chemical by activating a stable form of it as part of the parting shot." Among the applications he envisions is a system for delivery of unstable drugs—those with a short shelf life. "We may be able to synthesize the drug in a precursor form and have that last important step done as part of delivery." □

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