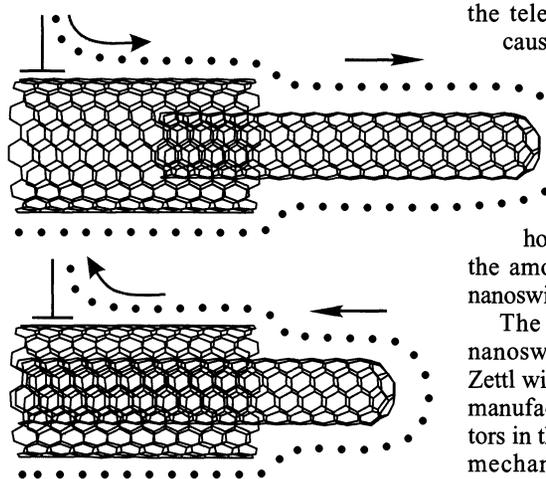


ma in the potential energy. The shaft will thus have certain preferred orientations. The advantage of an MWNT bearing is that each layer is likely to have a different chirality (depending on the way the graphene is rolled up in a cylinder) and that the barrier to rotation should therefore be very small, allowing the sleeve to rotate without difficulty. These properties may make the bearing fabricated by Cumings and Zettl a very efficient part of future molecular motors.

Another extremely interesting application of such a sharpened MWNT would be its use as a nanoswitch. The inner nanotube can be pulled out by a manipulator, and after release, it will "fly" back into the housing. In a simple analysis, Cumings and Zettl show that lowering the van der Waals energy by increasing the tube-tube contact area acts as a constant force on the extruded tube, and because the friction forces are very low, it is telescoped back within on the order of 10^{-9} seconds. Such a fast reaction switch offers the possibility of electronic control of back-and-forth movement. A simple trick would be to put charges on the nanoswitch. The electrons are located only on the surface of the housing and of



Electronic control of a tiny switch. A restoring van der Waals force acts on the extruded nanotube, which is opposite in sign to the electrostatic force exerted by electrons (blue dots) brought to the surface of the nanoswitch. The density of the charge can be changed through the electric contact (red) attached to the non-moving part of the nanotube, allowing the switch to be opened and closed. Blue arrows indicate the direction of the charge flow, and black arrows indicate the direction of the movement of the extruded tube.

the telescoped part of the nanotube because of the Faraday cage effect. The change in the electrostatic energy due to the increased surface charge density will be opposite in sign to the gain in van der Waals energy upon reinsertion of the inner tube into the housing (see the figure). By altering the amount of charge on the switch, the nanoswitch could be opened and closed.

The route toward nanobearings and nanoswitches reported by Cumings and Zettl will play a major role in our ability to manufacture nanomachines and nanomotors in the near future. The extremely light, mechanically and chemically resistant MWNTs represent the ideal starting material for these novel nanodevices.

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PERSPECTIVES: MATERIALS SCIENCE

Weird Gold Nanowires

E. Tosatti and S. Prestipino

When matter is reduced to just a few layers of atoms, very thin wires, or small clusters of atoms, the properties of solid matter do not remain quite the same, and there is room for surprises. In the realm of carbon alone, buckminster fullerenes and nanotubes display an amazing variety of unexpected behavior. A recent addition to the list of surprises is now reported on page 606 by Kondo and Takayanagi (*J*), who provide evidence that very thin gold wires form a helical structure, akin in some respects to carbon nanotubes.

Using transmission electron microscopy (TEM), the authors—whose group solved the structure of the famous Si(111) 7×7 surface in the 1980s—study atomically thin, several nanometers long, very regular gold nanowires formed by thinning down a narrow bridge between two oriented tips

(*J*). Shrunken to radii of 3 to 6 Å (roughly one or two times the bulk interatomic spacing of gold, 2.88 Å), these wires display "magic" preferred radii and geometries. This means that they only come in a few discrete sizes and shapes, a property long known for metal clusters. What is more striking is that the internal structure of these magic nanowires, which TEM is able to image and map despite their small size, is weirdly noncrystalline.

The structure consists of coaxial cylindrical tubes, or shells. A shell s contains a well-defined number n_s of strands, each strand a tiny monatomic gold necklace. The number of strands in the shell increases with the shell radius, and each magic wire is characterized by a well-defined n_s sequence. For example, if the outer shell contains seven strands and the inner shell consists of a central strand consisting of a single row of atoms, this is abbreviated as 7-1. Two other nanowires described by the authors are 11-4, or 14 7-1. For n_s larger than 1, the strands are wound up helically side by side, nearly but not exactly parallel to the wire axis, to form the tube. The pitch of the helix differs from one wire and another, but not between succes-

sive shells of the same wire: Atoms in successive shells appear to strain a bit to maintain perfect registry.

Had the nanowires retained instead the main features of the regular face-centered cubic (fcc) crystal structure of bulk gold, they would look very different indeed: no tubes, no curly strands, no helicity. Even when regular crystallinity is abandoned and a close-packed nanowire made of tubes centered about a central straight strand is built from hard spheres, a non-helical shell structure with 6-1, 12-6-1, etc., results, quite different from what is observed.

Cluster physics suggests at least two conceptually different sources for magic wire sizes. The first could be electronic shell closing. A small metal cluster may behave as a giant atom, with the most stable cluster sizes corresponding to closed electronic shells, very much as rare gas atoms are the most stable ones in the periodic table. This kind of shell-closing is observed in clusters of alkali metals such as sodium. The second source of magic sizes, although also electronic, is best explained in terms of packing. Imagine modeling atoms roughly as balls, endowed with some hard core repulsion as well as a soft mutual attraction (representing the electronic cohesive forces) that glue and pack the atoms together in the most effective way. This attraction has a

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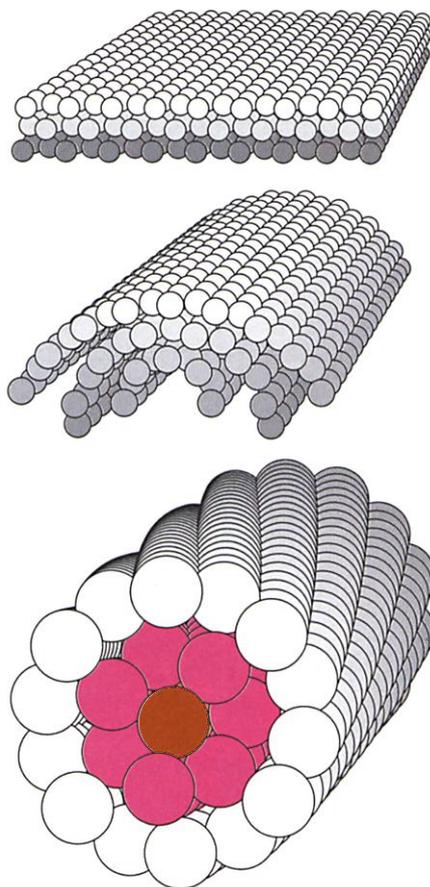
major influence, particularly at the surface. This is important because in a nano-object, such as a cluster or a nanowire, surface atoms outnumber those in the interior (the “bulk”). The natural tendency of the bulk atoms is to arrange themselves in an fcc crystal lattice, whereas the surface atoms prefer some smooth, well-packed low-surface energy structure that optimizes the attraction. The two tendencies are in conflict, because a crystalline bulk implies surface facets and edges of high energetic cost, but a smooth, facet- and edge-free surface is in turn only possible by modifying the bulk-like crystalline packing underneath (2).

By all available evidence, the weird gold nanowire structures appear to originate from the second mechanism. Although their detailed electronic structure is not yet known, it seems unlikely that simple electronic shell closing can explain the magic radii. Calculations for an ideal monatomic gold wire (3) suggest that the electronic d states in the nanowires should be totally filled, as in bulk gold. Thus, a possible electronic shell closing could affect at most the s electrons alone and not the other all-important player, the d electrons. A second argument in favor of the packing explanation is that very similar noncrystalline wire structures, nicknamed “weird wires,” have been predicted on the basis of computer simulations of packing-dominated metal nanowire optimal structures (2). In that study, crystalline or noncrystalline structures formed, depending on whether the wire radius was larger or smaller than a critical value in the subnanometer range. Experimental evidence now appears to demonstrate such a size-driven crystalline-noncrystalline structural transition for gold nanowires, with the thicker wires internally crystalline (4) and the thinner ones noncrystalline and weird (1).

What determines the magic noncrystalline nanowire shapes and sizes? Kondo and Takayanagi point out that each coaxial tube forms a bent and strained triangular lattice. This is reminiscent of carbon nanotubes, which are made up of bent graphite planes. In analogy with that case, we could view the nanowire shells as sheafs of gold crystal planes [here, triangular (111) fcc lattice planes] that are bent into tubes, inserted telescopically into one another, and then strained to get into registry with one another (see the figure). The registry between successive shells represents a curved equivalent of epitaxy, the exact registry that permits the growth of a regular surface crystalline layer onto a strong periodic substrate. It is absent in the carbon nanotubes, where the interaction between successive shells is much weaker.

Hence, the spectacular telescopic motions seen in nanotubes (5) are not expected in the gold nanowires (see pages 602 and 560).

This picture, however, does not tell us what periodicities to expect. The number seven seems to be ubiquitous in the nanowire structures. The thinnest wire is a 7 1; in all other wires, two successive neigh-



How to make a weird gold wire, conceptually. (Top) Structure of three stacked (111) gold crystal planes. (Middle) To form the nanowires, the layers are first bent. (Bottom) In the final 14–7–1 nanotube, each triangular layer is joined onto itself, yielding a generally helical structure. The layers, now tubes, are strained so that they fall in registry with each other. A helical structure results.

boring shells always appear to differ by seven strands. Assuming perfect triangular lattices, geometry permits this difference to range from 7.35 (1) for parallel strands on neighboring shells to 5.44 for strands at 30°. Strands in successive shells are indeed nearly parallel to each other and to the wire axis, justifying the difference of seven (the closest integer to 7.35). But it remains unclear why they are not at 30° instead, which would have led to a difference of five or six (the closest integers to 5.44).

A closer look at the seven strands of the thinnest 7 1 nanowire may provide some

insights. The outer shell of this wire is very smooth, with no facets or edges. Moreover, because of the jamming caused by one extra strand, it is denser than the hypothetical 6 1 wire that one can make with hard spheres. Such a smooth, triangular surface structure of enhanced lateral density is well known in gold. It characterizes all of the spectacular “surface reconstructions” typical of bulk gold (6). A connection between the gold nanowire structure and the surface reconstruction of gold therefore seems likely.

The helical structure of the gold strands causes the nanowires to be generally chiral; that is, they are endowed with handedness. Once a given orientation with respect to the suspending tips is fixed, the nanowire will be either right or left handed. The data do not yet show whether the two chiralities are, as one would expect, equally likely. Chirality of metal nanowires was also predicted by simulations (7) and arises naturally when a triangular lattice is wrapped around a cylinder, quite similar to the wrapping of a graphene sheet in chiral carbon nanotubes. For an alternative viewpoint, imagine filling the hollow space between two concentric cylindrical walls with hard spheres, with the hollow width exactly equal to the sphere diameter. As one can see after some simple algebra, perfectly tight packing of the spheres inside the hollow space is possible, albeit only at special cylinder radii, yielding a structure that is generally chiral (7).

It is perhaps too early to say what kind of properties the weird gold nanowires might possess. Ballistic conductance measurements should reveal whether the number of conductivity channels is consistent with the electronic structure derived from the proposed structural model. The nanowires may also act as microcoils, an idea previously put forward for nanotubes (8). The evolution of the wire structure and properties under external agents, including temperature, stress, and fields, is also potentially interesting.

What about nanowires made of other metals besides gold? It is not clear whether similarly equilibrated, regular nanowires (as opposed to nonequilibrated, irregular “neck” contacts) can be made from metals lacking gold’s unique atomic mobility. If it is possible, we might anticipate, for example, that platinum—a noble metal with surface reconstructions quite similar to those of gold—might yield nanowires with similarly crowded cylindrical shells as gold. By contrast, nanowires made of a metal with surfaces that do not reconstruct may not exhibit surface crowding. In simple metals, one could even observe an opposite, “anti-

crowding" effect, resulting in pentagonal wires, as previously predicted by theorists (2, 9). Finally, nanowires of magnetic metals like nickel could exhibit an interesting interplay between structure, magnetism, and conductance. All in all, there could be, hanging impalpably between two fine needle tips, a whole new nanoworld to be explored.

PERSPECTIVES: BIOCHEMISTRY

All in the Ubiquitin Family

Mark Hochstrasser

The function of a protein can be altered by changing its conformation, localization, or interaction with other molecules. An efficient way to do this is to modify the protein after it has been synthesized (posttranslational modification) through the addition of other molecules. For example, the addition of a ubiquitin molecule to a protein (called ubiquitination) often tags that protein for degradation.

In the case of ubiquitination, the modifying group, ubiquitin, is itself a protein. Recently, a surprisingly diverse set of additional ubiquitin-like modifier proteins (Ubls) have come to light. These Ubls all resemble ubiquitin in their amino acid sequences and often have similar means of attachment to their target proteins, but they also have unique and unanticipated functions (1, 2). In addition, there are ubiquitin-related proteins in which a ubiquitin domain (Ubd) is built into a larger polypeptide and is not excised or attached to other proteins. Such UbdS may impart properties to a protein similar to those conferred by a transferable Ubl, but the Ubd is irreversibly tied to a single protein.

A series of enzymes are responsible for attaching ubiquitin and its cousins to other proteins (see the figure) (1). For all Ubls, the carboxyl group of the last amino acid of the Ubl (ubiquitin and most Ubls terminate in a glycine-glycine dipeptide) is first activated by adenylation. A thiol group in the activating enzyme (E1), which initiates the ubiquitination enzyme cascade, then attacks the Ubl-carboxyl-adenosine 5'-monophosphate to yield an E1-Ubl thiolester. Then, E1 transfers its activated Ubl to a cysteine on another protein (the conjugating enzyme, E2). From E2, the Ubl is transferred to a lysine residue in the target protein with the help of an E3 ligase.

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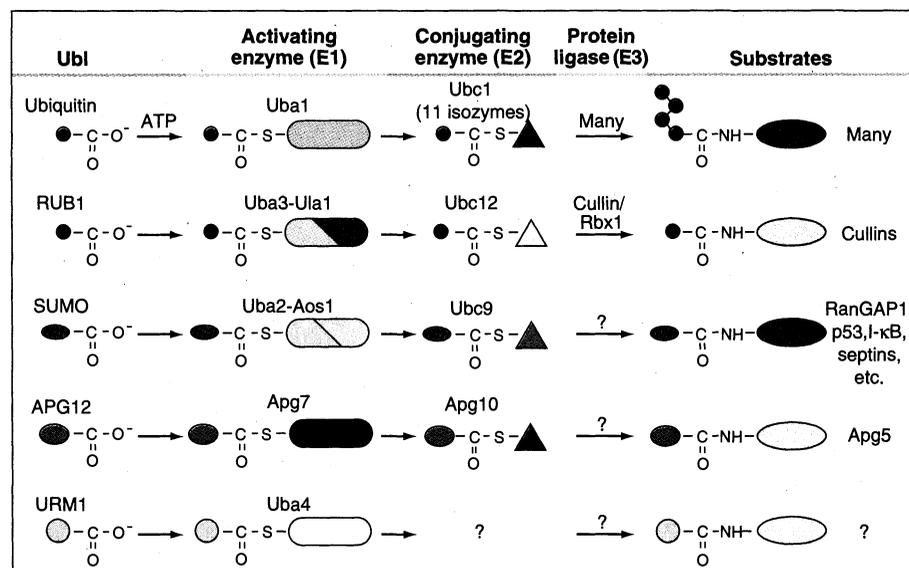
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PML nuclear bodies) also depends on their sumoylation (3).

Recent genetic data support the view that protein sumoylation is required for the import of at least some proteins into the nucleus. In *Drosophila* embryos, most of the morphogen called Bicoid is imported into the nucleus, where it regulates transcription. This import requires an operational SUMO-conjugation system (4). Potentially, sumoylation of RanGAP1 (or another transport machinery component) is required for Bicoid import. Alternatively, a SUMO-conjugated form of Bicoid may be more efficiently imported (or less efficiently exported). Whether Bicoid is directly modified by SUMO is not yet known, but the *Drosophila* Dorsal protein (a member of the NF- κ B rel family of transcription factors) is sumoylated in vivo, and elevated levels of SUMO pathway components stimulate its nuclear import (5). In some situations, different sumoylation events may have opposite functional effects in the same system. The mammalian I- κ B protein—

From direct biochemical analysis or, more tentatively, from sequence comparisons, we now know of at least a dozen distinct Ubl-ligation pathways. Two of the most intensively studied Ubls are SUMO (small ubiquitin-related modifier) and RUB1 (related-to-ubiquitin 1). Several of SUMO's target proteins have been identified, and more can be anticipated. In at least some instances, addition of SUMO to a target protein (sumoylation) changes the localization of this protein or its interactions with other proteins. Indeed, the first identified target of SUMO, the trafficking protein RanGAP1 (which helps to shuttle proteins from the cytoplasm to the nucleus) requires the addition of SUMO before it can be localized to the nuclear pores. Localization of several proteins to discrete sites within the nucleus (called



Wrestling with target proteins. The pathways for conjugation of ubiquitin or members of the related ubiquitin-like modifier family (such as SUMO and RUB1) to their target proteins. Three steps are involved: activation of ubiquitin or a related modifier molecule by the E1 activating enzyme, transfer of the activated moiety to the E2 conjugating enzyme, and transfer of the modifier to its protein target through the activity of an E3 ligase. SUMO refers to a family of Ubls that has three known members in vertebrates, the founding member being SUMO-1 (ortholog of yeast Smt3). In mammalian cells, RUB1 is called NEDD8.