A key to the group's success has been the ability to isolate large amounts of very pure (6,5) SWNTs, based on a process developed by Huaping Liu and colleagues at the National Institute of Advanced Industrial Science and Technology and the Japan Science and Technology Agency. "We've shown that if you put in an impurity of (6,4) SWNTs, there's something about the junction between two dissimilar nanotubes that causes excitons to be irradiatively recombined, instead of separated and harvested for their current," said Strano. This happens even though (6,5) and (6,4) SWNTs have very similar bandgaps.

Strano acknowledges that this is a "humble advance" in photovoltaic research, because the efficiencies his group has measured to date for the nanocarbon devices are only about 0.1%. However, significant improvements can likely be made by combining the two nanocarbon materials in ways that maximize the surface area and produce continuous phases.

"We see this as a starting point—it expands the tools and the available technologies for the energy engineer to build new kinds of photovoltaic cells," Strano said. "It carves out a new space in photovoltaic technology."

Tim Palucka

Nano Focus

Vanadium oxide bronze nanowires show unprecedented metal–insulator transition

Researchers are working to identify materials that could one day replace silicon to make computing faster. Sambandamurthy Ganapathy, Sarbajit Banerjee, and their colleagues at the University of Buffalo have found a vanadium oxide bronze whose unusual electrical properties in nanowire form, including unprecedented metal–insulator transitions, could increase the speed at which information is transferred and stored.

In the August 17 online edition of *Advanced Functional Materials* (DOI: 10.1002/adfm.201201513), the researchers report that they have synthesized single-crystalline β-$Pb_xV_2O_5$ nanowires from vanadium oxide and lead. When exposed to an applied voltage near room temperature, the nanowires transform from insulators to metals that more readily conduct electricity. Each of these two states—insulator and metal—could stand for a 0 or 1 in the binary code that computers use to encode information, or for the "on" and "off" states that the machines use to make calculations.

"The ability to electrically switch these nanomaterials between the on and off state repeatedly and at faster speeds makes them useful for computing," said Ganapathy.

"Silicon computing technology is running up against some fundamental road blocks, including switching speeds," said Banerjee. "The voltage-induced phase transition in the material we created provides a way to make that switch at a higher speed."

As with other nanomaterials, the health and environmental impacts of the nanowires would have to be investigated before their widespread use, especially since they contain lead, Banerjee said.

One intriguing characteristic of the material they synthesized is that it only exhibits valuable electrical properties in nanoform. That is because nanomaterials often have fewer defects than their bulkier counterparts.

The distinctive structure in these nanowires is crucial to their ability to switch from an insulator to a metal. Specifically, in the insulator phase, the position of the lead in the nanowires' crystalline structure induces pools of electrons to gather at designated locations. Upon applying a voltage, these pools join together, allowing electricity to flow freely through them and transforming the material into a metal.

"When materials are grown in bulk, there's a lot of defects in the crystals, and you don't see these interesting properties," said Peter Marley who is lead author. "But when you grow them on a nanoscale, you're left with a more pristine material."

Cobalt-based nanomaterial catalyzes water splitting

Efficient storage technologies are required to exploit renewable energy sources such as wind and the sun. One strategy is the conversion of these energies into fuels such as hydrogen, which can be achieved by electrolysis of water—or water splitting—into H_2 and O_2. A range of approaches have been investigated to achieve this goal. Devices based on proton-exchange membranes have proven promising, but may ultimately not be viable because they rely on electrocatalysts made from scarce and expensive noble metals, such as Pt. Robust catalysts made from abundant elements such as Co, Ni, and Mn have also been developed for the evolution of oxygen gas from water (also called the oxygen evolution reaction, OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), but few catalysts have been developed for the hydrogen evolution reaction (HER: $4H^+ + 4e^- \rightarrow 2H_2$).

Addressing this problem, V. Artero and co-researchers from the French commission for Atomic Energy and Alternative Energies (CEA) centers in Grenoble and Saclay, and from the Free University Berlin, Germany, have recently developed a straightforward and practical approach to prepare a stable Co-based catalytic material for H_2 evolution.

As reported in the September issue of *Nature Materials* (DOI: 10.1038/NMAT3385; p. 802), Artero and co-researchers reduced $Co(NO_3)_2 \cdot 6H_2O$ from an aqueous phosphate buffer at a fluorine-doped tin oxide electrode. Electrolysis for 3 h at –1.0 V versus Ag/

AgCl resulted in a gray coating on the electrode, comprising nanoparticles of about 100 nm in diameter. This electrode, with a film thickness of catalytic material, termed H_2-CoCat, of about 2 μm, was then transferred to a Co-free electrolyte where its electrocatalytic properties for H_2 evolution were measured. The minimal overpotential required for H_2 evolution was 50 mV, which is significantly lower than the 500–700 mV overpotentials required by other recently reported molecular Co catalysts. A H_2-evolution turnover frequency of 80 h^{-1} per Co center at 385 mV overpotential was also demonstrated.

Characterization of the H_2-CoCat material using methods including x-ray diffraction, x-ray photoelectron spectroscopy, energy-dispersive x-ray spectroscopy and x-ray absorption spectroscopy, suggested that H_2-CoCat is amorphous, and that it is composed of nanoparticles with a cobalt oxo/hydroxo phosphate component that is principally located at the particle surface, with metallic cobalt in the bulk.

Remarkably, anodic equilibration of the H_2-CoCat resulted in its conversion to the OER catalyst O_2–CoCat, which catalyzes O_2 evolution. The switch between these two forms was fully reversible, and corresponded to a progressive and local transformation between two morphologies on the surface of the electrode. The coating therefore demonstrates a Janus-like activity, behaving as a switchable catalyst.

The researchers said that their approach could be applied to the fabrication of "an artificial-leaf device" for light-driven water splitting "even in the absence of a proton-conducting membrane separating (photo)anode and (photo)cathode," as well as to "photoelectrodeposition [of catalysts] on heterogeneous semiconductor nanoparticles."

Steven Trohalaki

Energy Focus

Li-ion batteries fabricated by spray painting

Li-ion batteries have high energy and power density, although their design, wherein sandwiched battery components are "jelly-rolled" into metal canisters (see Figure), puts constraints on the ultimate form factors of the devices they power. Flexible batteries, stretchable textile energy storage, and paper batteries are some of the unconventional battery designs that were devised for devices without form-factor constraints, although their seamless integration remains a challenge. Self-powered electronics with integrated energy storage also require batteries that can be directly incorporated into the device design.

Moving toward these goals, P.M. Ajayan and a team of researchers from Rice University have fabricated multilayer Li-ion batteries by sequentially coating their components onto commonly encountered materials by spray painting, as reported in the June 28 issue of *Scientific Reports* (DOI: 10.1038/srep00481). Component materials were formulated into liquid dispersions (paints), and the researchers chose lithium cobalt oxide (LCO, $LiCoO_2$) as the cathode and lithium titanium oxide (LTO, $Li_4Ti_5O_{12}$) as the anode, for which the effective cell voltage is about 2.5 V. While a commercially available conduc-
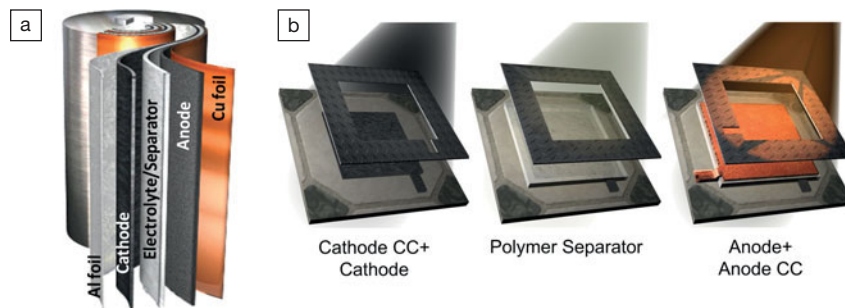
(a) A jellyroll assembly of the layered components of a conventional Li-ion battery; and (b) direct fabrication of a multilayer battery achieved by sequential spraying of component paints, using stencil masks tailored for a desired geometry and surface.

tive Cu paint was used for the negative current collector (analogous to Cu foil in Li-ion batteries), Al paint could not be employed for the positive current collector because Al micro-powders form explosive aerosols. In its place, the researchers made a viscous, highly consistent ink containing high concentrations (0.5–1% w/v) of single-walled carbon nanotubes (SWNTs) that was suitable for spray painting. Using commercial polymers, the researchers were also able to make a spray-paintable separator with a morphology that allowed optimal electrolyte uptake and formation of a microporous gel electrolyte with sufficient adhesion to adjacent layers to ensure mechanical stability.

After preheating nonconducting substrates (glass, ceramics, and polymer sheets) to 120°C, the researchers spray-painted the component paints layer by layer, starting with the SWNT (cathode charge collector) paint, then the LCO (cathode) paint. After drying and preheating to 105°C, the polymer separator was sprayed on in several light coats up to a final thickness (~200 μm) that prevented internal shorting from solvent penetration from the LTO (anode) layer, which was deposited after preheating to 95°C. The Cu (anode current collector) paint was then deposited. After drying the cell in vacuum, it was transferred to an Argon-filled glove box, soaked in electrolyte, and then packaged with laminated poly(ethylene)-aluminum-poly(ethylene terephthalate) sheets.

For a typical cell, the SWNT layer is ~25 μm, the LCO layer ~120 μm, the polymer separator ~180 μm, the LTO layer ~90 μm, and Cu layer ~5 μm. Pla-