Porphyrin-Based Nanostructures for Electronic Applications

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Motivation—Nanostructures composed of porphyrin molecules were recently discovered at Sandia and their application to important catalytic reactions such as light-assisted water splitting to make hydrogen fuel is being actively investigated. Another unexplored realm of potential use of these multi-functional nanostructures is in nanoelectronics and nanophotonics, as previous research on porphyrin crystals and aggregates have demonstrated conducting and semiconducting properties. Photoconductivity and non-linear optical properties with visible light have also been demonstrated in porphyrinic materials. Now, with the advent of our well-defined porphyrin nanostructures like tubes, spheres, wires, rods, and structures with more complex morphologies, an opportunity presents itself for integration of these functional porphyrin-based nanostructures into electronic and optoelectronic devices.

Accomplishment—A variety of porphyrin nanostructures with different morphologies has been synthesized by ionic self-assembly of oppositely charged porphyrin tectons and by metal-coordination-induced self-assembly of functionalized porphyrins. We have extensively investigated the catalytic properties of these porphyrin nanostructures in the photocatalytic reduction of metal complexes to deposit zero-valent metals. In many cases, the metal deposits onto the porphyrin nanostructure to form a metal composite with the porphyrin nanostructure thus leading to functional nanodevices. For example, we have used porphyrin nanospheres that are platinized to reduce water to hydrogen using visible light as an energy source. Similarly, a porphyrin nanotube containing a gold nanowire and platinum particles on the outer tube surface is being investigated for water splitting to produce hydrogen and oxygen using solar energy. Figure 1 illustrates the water-splitting nanodevice base on the porphyrin nanotube and a transmission electron microscopy (TEM) image of the gold nanowire that has been grown in the nanotube. The photocatalytic activity that allows the nanowires to be grown in the tubes suggests that nanotubes and other porphyrin nanostructures will likely have interesting electronic and optoelectronic properties.

We are now actively investigating the electronic properties of porphyrin nanosheets and nanowires. For example, porphyrin nanosheets (see Fig. 2a) were synthesized and characterized by TEM. Atomic force microscopy (AFM) on conducting surfaces (with HP Palo Alto, CA) was used to determine the conductivity through the 10-nm thick nanosheets. In addition, nanowires composed of porphyrin nanofiber bundles (Fig. 2b) have been successfully deposited electrophoretically onto interdigitated electrodes for conductivity measurements and to determine their surface charge.

Significance—The integration of micro-electronics with unconventional nanomaterials such as self-assembled soft nanostructures is an important processing goal. The porphyrin-based nanostructures offer a unique opportunity for exploring bioinspired functional nanostructures and nanodevices and for discovering the means to incorporate them into conventional electronic and photonic devices.

Sponsors for various phases of this work include: DOE Office of Basic Energy Sciences Core Program and Center for Integrated Nanotechnologies (CINT), and Laboratory Directed Research & Development

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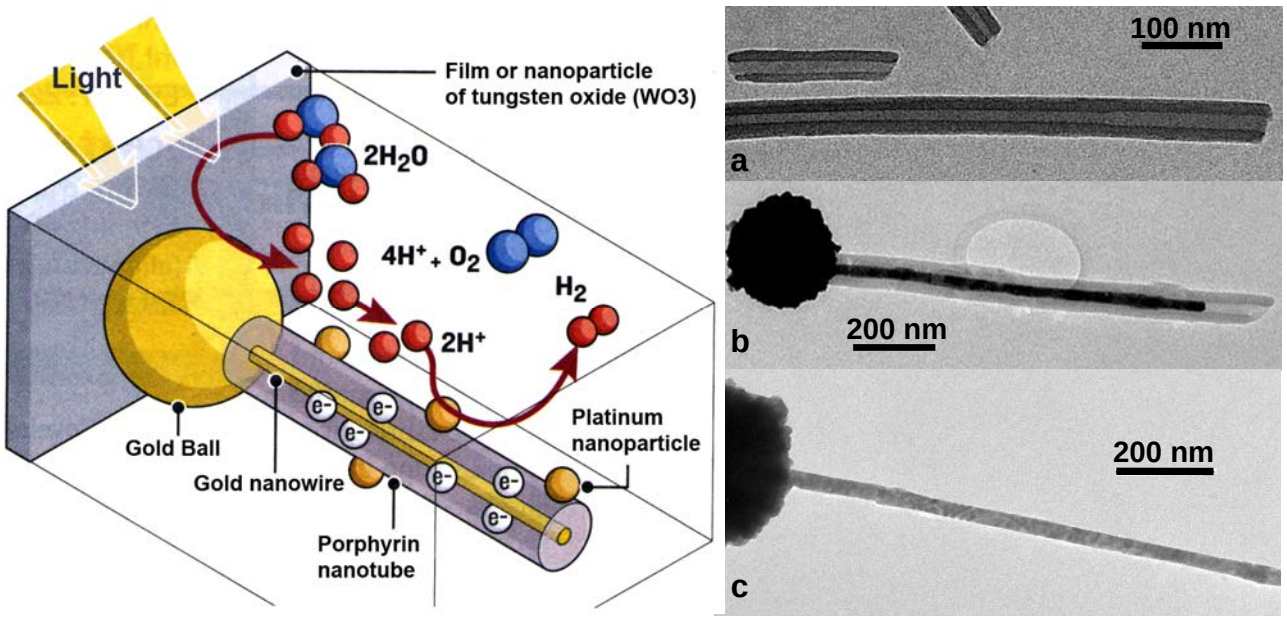

Figure 1. A proposed water-splitting nanodevice based on our photocatalytic porphyrin nanotube, TEM images of a nanotube (a), a gold nanowire grown inside the hollow core of a porphyrin nanotube (b), and a free standing gold nanowire after dissolving the porphyrin nanotube (c).

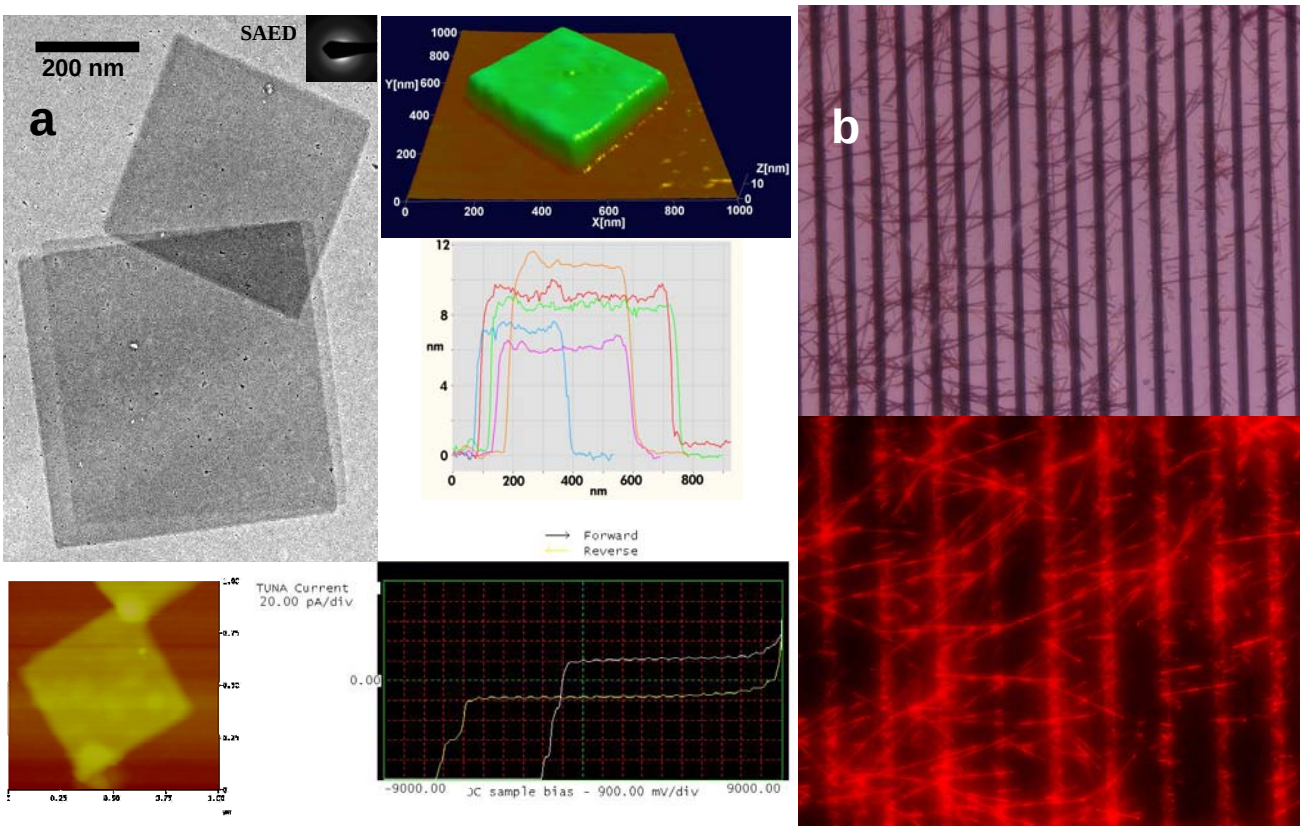

Figure 2. (a) TEM and AFM images of porphyrin nanosheets, AFM thickness profiles, and their current-voltages traces from AFM on silicon. (b) Optical (top) and fluorescence (bottom) microscope images of porphyrin nanofiber bundles electrophoretically deposited onto gold interdigitated electrodes.