Photocatalytic Nanotubes

by Zhongchun Wang, Craig J. Medforth, and John A Shelnutt

Motivation—Photocatalytic processes in nature are efficient means for generating energy sources and controlling chemical reactions. A biological example is the generation of energy-rich sugar molecules through photosynthesis. The goal of this research is to understand the energy- and electron-transfer processes that function within porphyrin nanotubes. We recently discovered these nanotubes, which may mimic the photosynthetic function of the chlorosomes of green sulfur bacteria, and can be used to create functional composite nanotube devices such as a nanodevice that splits water to produce hydrogen.

Accomplishment—The porphyrin nanotubes were discovered while attempting to make photocatalytic porphyrin fibers as templates for metal growth. The nanotubes are formed by ionic self-assembly of two types of porphyrin molecules of opposite charge. The tubes were imaged by electron microscopy and found to be hollow with a uniform average outside diameter of 60 nm and inside diameter of 20 nm; the lengths are variable and typically micrometers long. Smaller diameter nanotubes can be made by altering the molecular structure of one of the porphyrins. Transmission electron microscope (TEM) images of the porphyrin nanotubes are shown in Fig. 1.

The aggregated porphyrins forming the walls of the tubes are *J*-type aggregates, leading to intense resonance light scattering from the *J*-aggregate absorption bands in the green and red region of the UV-visible spectrum. The coherent coupling of porphyrin molecules indicated by the resonance light scattering suggests that energy and electron transport in the porphyrin nanotubes is facile and further suggests that the nanotubes may be conductive, photoconductive, and might serve light-harvesting and electron-transport functions in nanodevices. We have also found the nanotubes to be mechanically responsive to light; that is, they become soft when exposed to bright light and heal when they are returned to the dark. Since the nanotubes are composed of a porphyrin that is a known photocatalyst, we have investigated the possibility of growing novel metal composite structures by using the nanotubes as templates. Reduction of metal is found to take place only on the tubes and in a surface-selective manner. Figure 2 shows TEM images of nanotubes upon which either platinum or gold has been grown by photocatalytic reduction of metal ions from aqueous solution. In the case of gold, metal is deposited only in the cores of the tubes in the form of continuous polycrystalline wires, which grow a gold ball at one end of the nanotube. In contrast, platinum metal appears as 3-nm particles attached to the outer surfaces of the tubes, dense columns of platinum particles inside the tube cores, or as nanodentrites attached to the outer surface of the tubes.

We are continuing our efforts to gain synthetic control over these metal-nanotube composites. We are also attempting to build nanodevices for chemical sensing and other applications. For example, we have designed a nanodevice for water-splitting to produce hydrogen based on the use of the gold nanowire as a conductor linking an inorganic photocatalyst for oxygen evolution to our hydrogen-evolving platinized nanotubes.

Significance—The photocatalytic nanotubes are capable of serving as functional elements in many types of self-assembled nanodevices, including chemical sensors, mechanical sensors, and artificial photosynthetic systems. The photocatalytic properties of the nanotubes themselves can be employed for the assembly of the nanodevice. The porphyrin tubes may also serve as nanoscale functional elements of other photonic and electronic devices that utilize their novel conductivity and light scattering properties.

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Contact: John A. Shelnutt; Biomolecular Materials & Interfaces, Dept. 1116
Phone: (505) 272-7160, Fax: (505) 272-7077, E-mail: jasheln@unm.edu

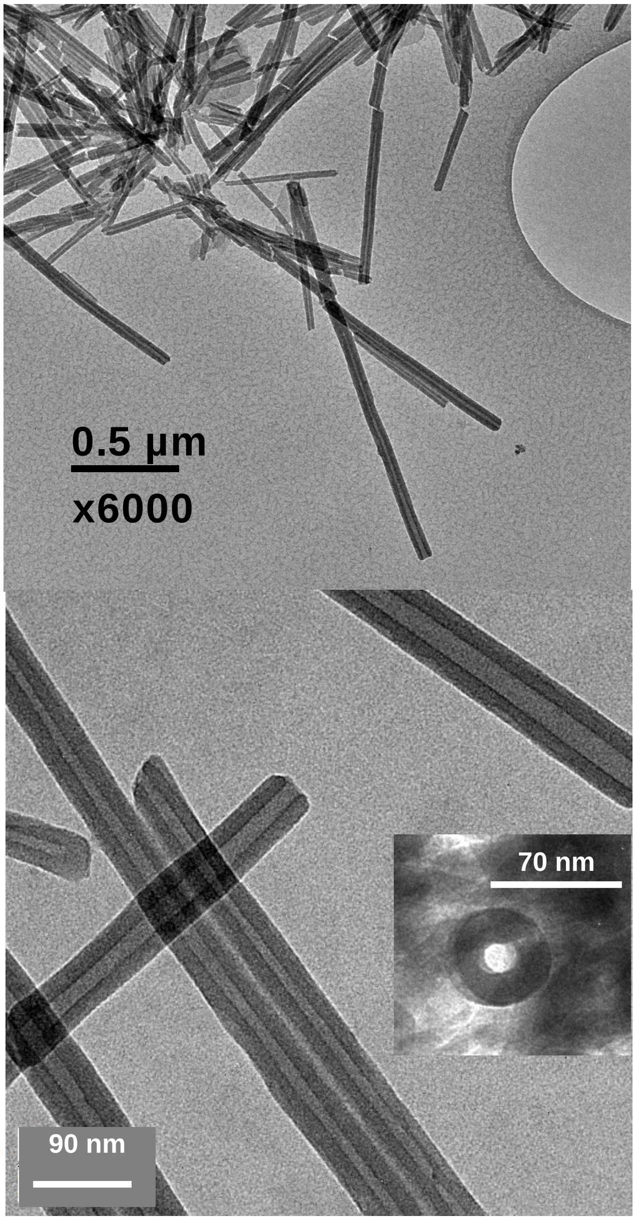

Figure 1. TEM images of porphyrin nanotubes at low (top) and high (bottom) magnification. Inset: a tube caught in a vertical orientation.

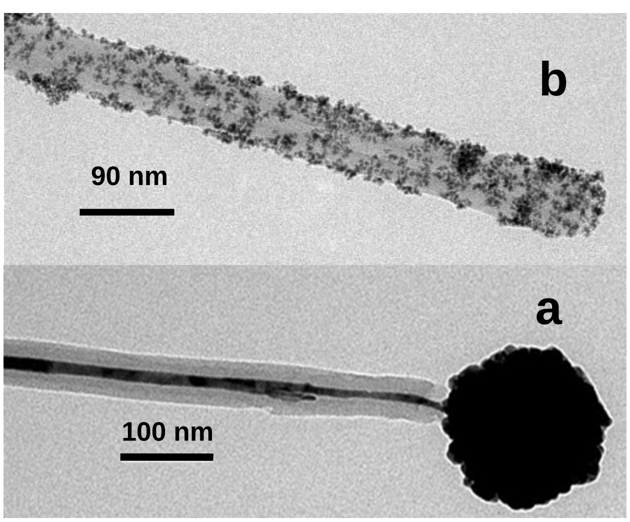

Figure 2. TEM images of a gilded porphyrin nanotube (a) and a platinized porphyrin nanotube (b).