

## Self-Metallization of Photocatalytic Porphyrin Nanotubes

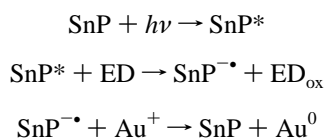
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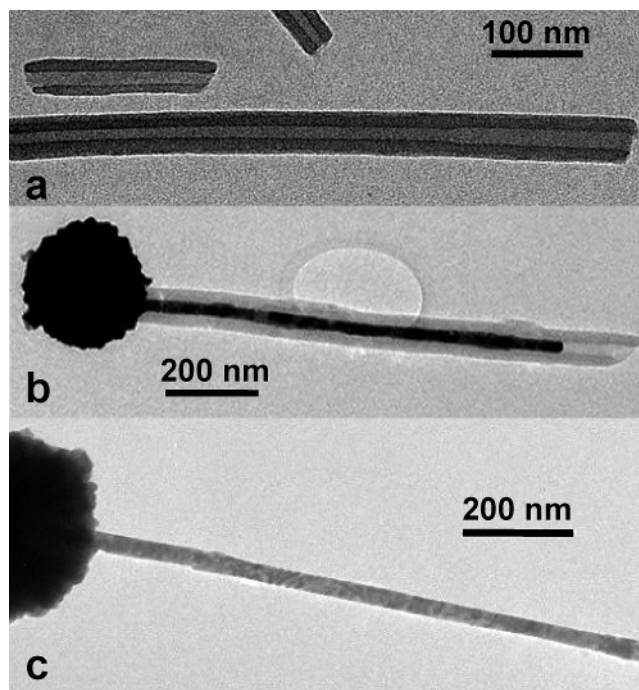
Functional self-assembled nanostructures with well-defined shapes and dimensions are of great current interest<sup>1–3</sup> for applications in electronics, photonics, light-energy conversion, and catalysis. Porphyrins are attractive building blocks for these nanostructures because of their electronic, optical, and catalytic properties. Recently, we showed that porphyrin nanotubes can be prepared by ionic self-assembly of two oppositely charged porphyrins in aqueous solution.<sup>4</sup> These sturdy nanotubes represent a new class of porphyrin nanostructures for which the molecular building blocks can be altered to control their structural and functional properties. Here, we show that the nanotubes containing a Sn porphyrin are photocatalytic and can reduce metal ions from aqueous solution. The metal is selectively deposited onto the tube surfaces, producing novel composite metal nanostructures (Figures 1 and 2). These composites are themselves photocatalytically active and have potential applications as nanodevices.

Sn porphyrins are known to be good photocatalysts in homogeneous solutions,<sup>5,6</sup> so we investigated whether the Sn porphyrins in the nanotubes make the tubes photocatalytic. To demonstrate photocatalytic activity of the tubes, we examined the reduction of aqueous metal complexes, for example, Au(I) and Pt(II) complexes. The photocatalytic reduction reaction mediated by Sn(IV) porphyrins in homogeneous solutions is described for reduction of a Au(I) complex by the following simplified cyclic reactions:



Au(I)-thiourea or -thiosulfate complexes were used with ascorbic acid as the electron donor (ED). These reductions are predominately photocatalytic, unlike those for many other gold complexes that may also involve chemical and photochemical reduction. The photochemical reduction is prevented by the higher stability of the Au(I) complexes relative to Au(III) complexes and their transparency to visible light. Autocatalytic growth of gold was found to be negligible.

The Sn-porphyrin-containing nanotubes used in the metallization reactions were prepared in aqueous solutions by ionic self-assembly of *meso*-tetrakis(4-sulfonatophenyl)porphyrin diacid ( $\text{H}_4\text{TPPS}_4^{2-}$ ) and Sn(OH)(H<sub>2</sub>O/OH) tetrakis(4-pyridinium)porphyrin ( $\text{SnTPyP}^{5+/4+}$ ) as described previously.<sup>4</sup> A transmission electron microscope (TEM) image of the porphyrin nanotubes before metal deposition is shown in Figure 1a. The tubes can be micrometers in length and have diameters typically in the range of 50–70 nm with approximately 20-nm thick walls. Images of the nanotubes caught in vertical



**Figure 1.** Transmission electron microscopy images of (a) the porphyrin nanotubes, (b) a gilded nanotube obtained using the Au(I)-thiourea complex, and (c) a gold wire obtained after the porphyrin tube has been dissolved away at pH 10 by adding 0.05 M NaOH. The latter demonstrates the structural integrity of the free-standing nanowires. Concentrations of the Au(I) complex and ascorbic acid were 1 and 10 mM, respectively; the light exposure time was 8 min at 800 nmol cm<sup>2</sup> s<sup>-1</sup>.

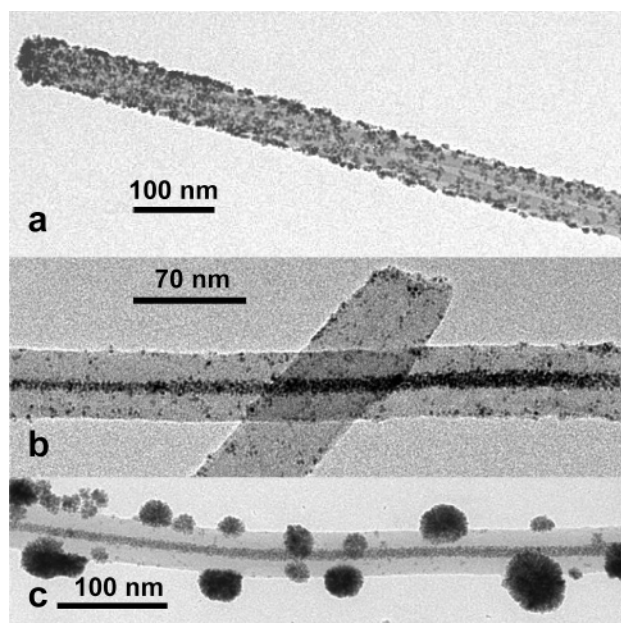
orientations confirm a hollow tubular structure with open ends rather than a solid cylindrical symmetric structure.

When the nanotubes are used to photoreduce the positively charged Au(I)-thiourea complex, the metal is deposited exclusively within the hollow interior of the nanotubes, forming a continuous polycrystalline gold nanowire that is of the same diameter as the tube core (Figure 1b). For those tubes that contain nanowires, only continuous gold wires are found, that is, multiple short segments of wire are not observed in the same nanotube. In addition, the nanowires are typically terminated at one end of the nanotube with a gold ball of larger diameter than the tube. When the porphyrin nanotubes are dissolved by raising the pH, the gold wire and ball remain intact, as shown in Figure 1c. In contrast with the thiourea complex, reduction of the *negatively* charged Au(I)-thiosulfate complex produces gold particles mainly on the outer surfaces of the tubes (data not shown). These results suggest that the electrostatic and other interactions between the complex and the tube surfaces determine where the metal is deposited for the two oppositely charged complexes. Directional electron/energy transport within the tube walls might also play a role. (Experimental details

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**Figure 2.** Transmission electron microscopy images of (a) a platinumized porphyrin nanotube with Pt nanoparticles distributed mainly on the outside surface, (b) a long Pt dendrite in the core of the tube obtained at a higher concentration of Pt complex, and (c) at a later stage in the development, a Pt dendrite in the core and globular Pt dendrites on the outer surface of the nanotube. The concentrations of the Pt complex and ascorbic acid were 0.1 and 1 mM, respectively (for a), and 1 and 10 mM, respectively (for b and c). Exposure times were 15 min (for a and b) and 35 min (for c). The concentration of the nanotubes was the same for all reactions.

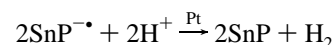
of the conditions and methods used to metallize the nanotubes are given in the Supporting Information.)

The continuous nature of the nanowire and the formation of the ball at the end of the tube suggest a novel mechanism for its formation by the nanotube. The continuity of the wire implies a single nucleation site on the inner surface with mobile electrons generated in the tube flowing into the wire at that site. Thus, under illumination, the tube acts as a photoelectrochemical cell, charging up the growing nanowire at a potential negative enough to reduce the gold complex at gold surfaces accessible to the complex. When the wire reaches the end of the tube, it expands into the ball where most of the electrons will collect. The J-aggregate composition of the tube walls indicates strong electronic coupling of multiple porphyrin subunits,<sup>4</sup> which might be expected to facilitate the electron transport necessary to grow the nanowire. Photoconductivity is also found in nanorods composed of the  $H_4TPPS_4^{2-}$  J-aggregates.<sup>7</sup> In addition, photoinduced electron transfer between porphyrins would explain why some of the unmetallized tubes appear as rodlike structures (collapsed tubes) in TEM images.<sup>4</sup> That is to say, photoinduced electron transfer disrupts the charge balance between the porphyrin subunits and hence the structure of the ionic solid.

Nanotube composites can also be made using other metals. We have previously used Sn porphyrins as photocatalysts to control the growth of dendritic platinum on surfactant templates using ascorbic acid as the electron donor.<sup>8</sup> The platinum metal grows as dendritic 2-nm thick sheets or as spherical dendrites, depending on the nature of the surfactant assembly (liposomes or micelles) upon which the growth is templated. Similarly, platinum metal can be grown onto the nanotube surfaces, as illustrated in Figure 2a. Photocatalytic initiation<sup>8</sup> of growth by photoreduction of the platinum salt ( $K_2PtCl_4$ ) occurs with the nanotubes to produce small

Pt seed nanoparticles. These seed particles decorate mainly the outer surfaces of the porphyrin nanotubes (Figure 2a). Normally, fast autocatalytic reduction of Pt occurs after the seed particle reaches a certain size, producing a Pt dendrite, and some nascent Pt dendrites are visible in high magnification TEM images. At higher Pt concentrations, we have also successfully grown long Pt dendrites within the cores of the nanotubes (Figure 2b). Composites with both filled cores and large platinum dendrites on the outer surface can also be produced at high Pt concentration and longer light exposure times (Figure 2c).

Interestingly, the platinum nanoparticles combined with the porphyrin nanotube act as a catalytic device for photocatalytic water reduction. In the presence of visible light and an electron donor, such as ascorbic acid, the platinumized nanotubes evolve hydrogen by the reaction



$H_2$  production by platinumized porphyrin nanotubes of the type shown in Figure 2a was found to increase with increasing exposure to light (data not shown). The colloidal nature of the platinumized nanotube suspension and the intense resonance light scattering of the porphyrin nanotubes make accurately measuring the quantum yield for the formation of hydrogen problematical. However, on the basis of the photocatalytic reaction of Sn porphyrins in homogeneous solutions, one might expect quantum yields to approach unity once the platinum coverage and the concentration of the nanotubes have been optimized.

Additional studies are underway to further characterize the functional properties of these unique photocatalytic nanotube-metal composite structures. We expect that variation of the porphyrin subunits in the nanotubes and of the metals deposited onto the tubes will ultimately produce a range of useful nanodevices. For example, the gold wire and the ball at the end of the tube might be used as an electrical connector between components of a nanoscale photoelectrochemical device, such as one that would carry out photocatalytic water splitting.

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**Supporting Information Available:** Experimental details of the nanotube metallization reactions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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