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Photoinitiated Growth of Sub-7 nm Silver Nanowires within a Chemically Active Organic Nanotubular Template

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Silver nanowires have a huge potential for electronics, plasmonics, and sensing applications.[1,2] They have been obtained with a variety of methods[3] with thicknesses as low as ∼20 nm. Also thinner wires have been reported, albeit with a wide distribution of diameters[4] or within a three-dimensional array of nanotubes,[5] from which they cannot be readily removed. It remains a challenge to control the synthesis of precisely defined silver nanowires with diameters in the interesting range below 10 nm, where their electronic properties begin to deviate substantially from the bulk.

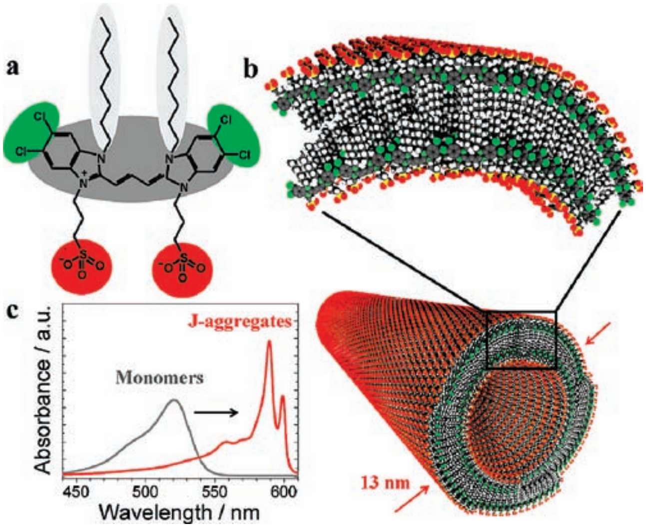

Figure 1. (a) Amphiphilic cyanine dye C8S3. (b) Schematic illustrating the dyes in water/methanol solution self-assembled into well-defined double-walled nanotubular J-aggregates with an outer diameter of (13 ± 1) nm.[7] (c) Absorbance spectra of the dye monomer's (gray) and the J-aggregate's (red) solution exhibiting the narrowed and red-shifted transitions typical for these tubular J-aggregates.

Herein, we report on the use of self-assembled nanotubular J-aggregates of amphiphilic cyanine dyes[6−9,11] as chemically active templates for the fabrication of silver nanowires with a diameter below 7 nm. As shown in Figure 1, the amphiphilic cyanine dye 3,3′-bis(2-sulfopropyl)-5,5′,6,6′-tetrachloro-1,1′-dioctylbenzimidacarbocyanine (C8S3) self-assembles in a water/methanol mixture (9:1 by volume) into double-walled nanotubular J-aggregates with an outer wall diameter of (13 ± 1) nm and lengths up to several tens of micrometers.[6,7] These nanotubes act as structure-directing agents and also as localized chemical reductants for silver ions and possess the following key features: (1) a small and well-defined diameter with a chemically homogeneous inner surface; (2) cyanine dye layers, which facilitate the photoinitiation of localized redox chemistry; and (3) reversible J-aggregate formation, which allows processing from solution, including the potential to remove the template after the reaction and to passivate or functionalize the surface of the product, e.g., by the subsequent adsorption of polycations.

Figure 2 displays the absorption spectrum of the neat solution of the nanotubular J-aggregates (red line) with the two strongest peaks at 589 and 599 nm attributed to the outer and inner wall of the nanotube, respectively.[8,9] Upon the addition of $AgNO_3$ (3×10^{-3}M) and storage for 4 h in the dark the spectrum changes only marginally (blue line), while upon exposure to white light dramatic changes are observed (black line). Particularly the absorption at 589 nm attributed to the outer wall disappears almost completely as a result of oxidation of the nanotube,[9] while a broad silver plasmon absorption peak around 420 nm grows, indicating light-enhanced growth of silver nanostructures.[10]

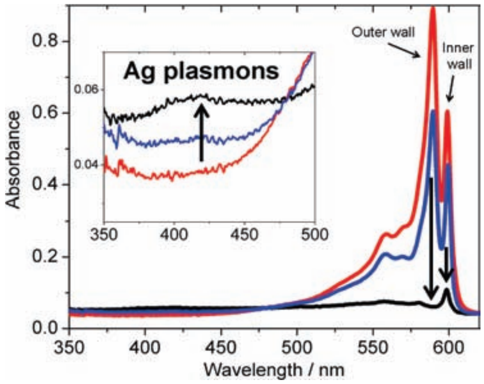

Figure 2. Absorption spectra of C8S3 solution. Red: Pure J-aggregate solution. Blue: 4 h after adding $AgNO_3$ (no light exposure). Black: 4 h after adding $AgNO_3$ and exposure to white light for 5 min. Inlet: Zoom on silver plasmon peak ∼420 nm.

Cryo-Transmission Electron microscopy (Cryo-TEM) images of a vitrified aqueous solution reveal silver nanostructures formed within and on the nanotubular template. Figure 3a displays a Cryo-TEM micrograph of a partially filled nanotube, which allows visualization of both the silver nanowire and its template simultaneously. The image demonstrates that the template is filled rather than surrounded with silver. This is clearly seen in the cross-sectional line scan (Figure 3b), which shows the profile of both

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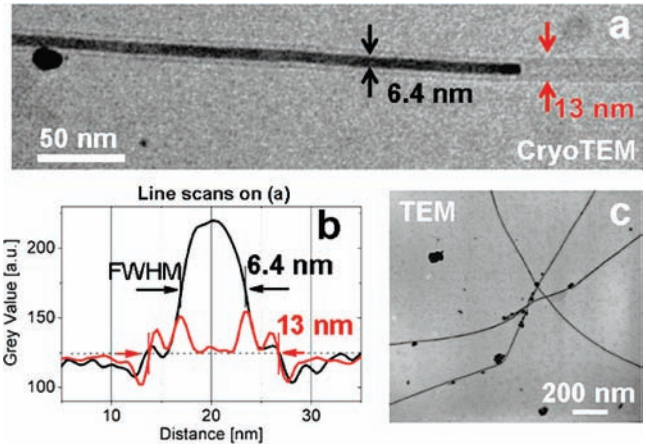

Figure 3. (a) Cryo-TEM image of a silver nanowire with a width of (6.4 ± 0.5) nm partially filling a supramolecular dye nanotube, and a silver nanoparticle on the nanotube's outside 15 min after adding AgNO$_3$ to the solution and exposure to white light for 20 s. (b) Line scans across the template filled with silver (black) and unfilled template (red). (c) TEM image of silver nanowires immobilized on a solid substrate 72 h after adding AgNO$_3$ and exposure of the solution to white light for 90 min.

the filled and unfilled portions of the nanotubular template. We note that the diameter of the template shows no significant changes upon formation of the silver nanowire and that the nanowire exhibits a remarkably homogeneous diameter of (6.4 ± 0.5) nm. In addition to nanowire structures, nanoparticles that decorate the J-aggregate's periphery are seen, similar to what has previously been reported for lower silver concentrations.[11] Figure 3c shows a representative TEM image at lower magnification, demonstrating that the nanowires can grow to lengths of more than a micrometer. High resolution TEM (HR-TEM) reveals crystalline nanowires, with a lattice structure that can be attributed to silver. Cryo-TEM images of nanowires rinsed in methanol after formation demonstrate that the templates can be partially removed (see Supporting Information for further electron microscopy images and analysis).

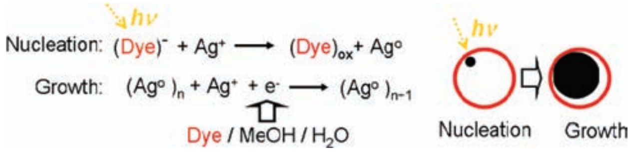

Figure 4. Proposed reaction mechanism for photoinduced formation of silver nanowires using a photochemically active nanotubular dye aggregate as a template.

In the absence of white light exposure only silver nanoparticles were observed. Hence the formation of the silver nanowires appears to be initiated by light, presumably controlled by the optical and the redox properties of the chemically active template.[9] The reduction of the silver ions was monitored by following the oxidation of the template's dye through the loss of its absorption, as investigated independently with spectroelectrochemistry.[9] The spectra show that the initial illumination step leads to only a small loss in absorption, while the oxidation then continues throughout the entire reaction time without the need for further illumination (Supporting Information). Based on this and the polycrystalline structure of the wire, we attribute the formation of the nanowires to a two-step process in which photoinitiated redox chemistry nucleates silver nanoparticle seeds on the interior of the nanotubular template followed by a subsequent light independent growth of the silver nanowires (Figure 4, Supporting Information). The preferential photoinitiated nucleation inside the nanotube may be explained by the transfer of excitation energy to the inner wall dye layer.[8] Silver growth at the interior of the template still leads to oxidation of the outer wall, presumably due to electron transfer from outer wall to inner wall dye, as previous electrochemistry experiments have shown that the outer wall is easier to oxidize.[9] However, even with a transfer of the two electrons per dye molecule needed for complete oxidation,[9] there is insufficient dye within the entire nanotube to account for all the silver formed on its interior. Previous reports have indicated that primary alcohols can act as sacrificial electron donors for the autocatalytic reduction of silver in the presence of an existing metal core.[12] We suggest that the reduction of silver ions during the growth phase involves methanol as the other electron source in addition to the dye once the silver seeds have been formed.

In conclusion, silver nanowires with a very small and highly homogeneous diameter of (6.4 ± 0.5) nm and lengths of more than a micrometer have been synthesized in solution using photochemically active templates, i.e. supramolecular nanotubes of J-aggregates from an amphiphilic cyanine dye. The template allows photoinitiation of the nanowire growth, defines the diameter, and provides solubility. Moreover, it provides the potential to control the growth further, e.g. by specifically exciting the inner and outer wall of the nanotubular template, since their different optical properties allow selective excitation. The nanowires may also be functionalized further, e.g. with optoelectronically active polycations, providing access to quasi one-dimensional hybrid structures with well-defined metallic nanowires as a core.

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Supporting Information Available: CryoTEM and HR-TEM, absorption spectra, materials and methods. The material is available free of charge via the Internet at http://pubs.acs.org.

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