

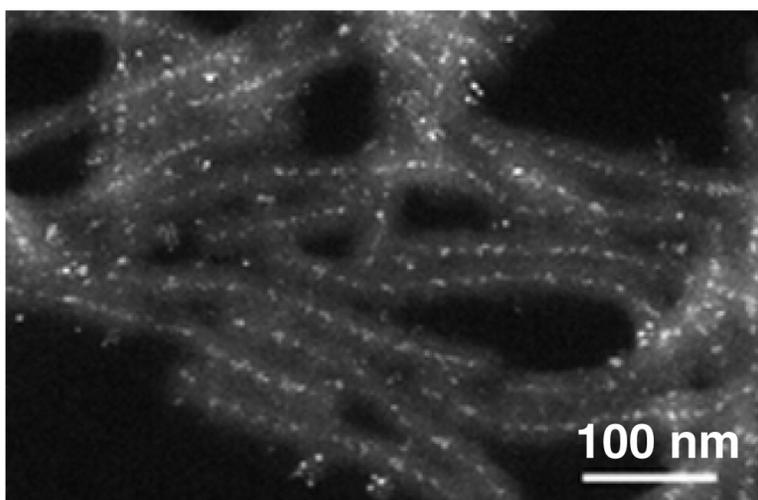
Communication

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Redox-Induced Synthesis and Encapsulation of Metal Nanoparticles in Shell-Cross-Linked Organometallic Nanotubes

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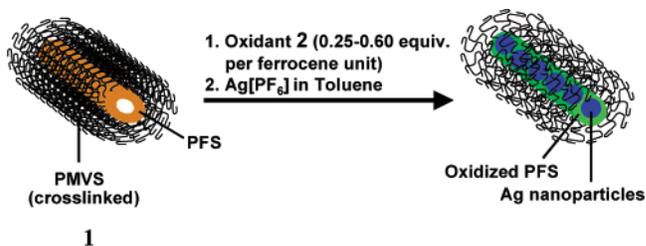
Nanosopic tubules have emerged as a group of novel materials since the discovery of carbon nanotubes in 1991.¹ Impregnation of hollow tubes with guest materials provides a potentially fascinating route to create functional nanomaterials for a variety of applications.^{2–4} In this regard, carbon nanotubes have been extensively investigated as templates to encapsulate foreign materials, such as ionic species,⁵ organic molecules,⁶ and metal nanoparticles.⁷ The mechanism of the encapsulation generally relies on the diffusion of guest materials. Consequently, there is usually a lack of control in the quantity of entrapped materials and their spatial organization. Furthermore, the diameter of carbon nanotubes is usually small (<5 nm), which prevents many useful materials from being incorporated. These drawbacks have stimulated recent developments in the synthesis of polymeric nanotubes,⁸ which can have relatively large cavities and tunable interior chemical functionality. These functional groups not only facilitate encapsulation through selective interactions with guest materials but also provide a possibility to organize encapsulated materials spatially along the tubes. For example, Liu and co-workers recently synthesized polymeric nanotubes with interior carboxylic acid groups and filled these tubes with Fe₂O₃ particles resulting in 1D magnetic nanostructures.^{8b} The process of the encapsulation involves two steps: binding of metal ions through their interaction with the carboxylic groups lined in the cavity of the tubes, followed by an oxidation reaction for the formation of magnetic nanoparticles.

In a recent communication,⁹ we reported the synthesis of shell-cross-linked¹⁰ organometallic nanotubes that contain a polyferrocenylsilane (PFS)^{11a} inner wall covered by a shell of a cross-linked network of polymethylvinylsiloxane (PMVS) chains (**1**). We prepared these intriguing structures through a solution self-assembly of PFS-*b*-PMVS block copolymers in hexane, a selective solvent for PMVS, followed by a Pt(0)-catalyzed hydrosilylation to cross-link the PMVS shell of the nanotubes. The resulting cross-linked nanotubes retain their structure in common solvents, such as THF and toluene. A special feature of these structures is that the PFS component makes them redox-active.^{11b} It is well-known that Fe(II) can easily reduce some metal ions, such as Ag⁺, to the corresponding metals. The nanotubes of **1** containing interior PFS with Fe(II) in each repeat unit represent an intriguing new type of reactive nanostructure. They have potential to induce chemical reactions within a confined area, which is of interest for the preparation of novel nanomaterials.

Herein, we report a conceptually new method to synthesize silver nanoparticles through a redox-induced encapsulation in **1**. In this approach, silver ions were reduced in situ by the PFS chains in the cavity of the tubes of **1** (see Scheme 1). Hence, the size and spatial position of resulting particles are regulated by confinement in the void of **1**.

We carried out our initial reaction by simply titrating a toluene solution of **1** (ca. 1 mg/mL) with a saturated solution of Ag[PF₆]

Scheme 1



in toluene.¹² The color of the reaction mixture gradually changed from pale amber to dark brown, and a precipitate formed. Upon centrifugation, we separated the precipitate and obtained a clear green supernatant. An aliquot of the supernatant was collected and characterized by UV–vis spectroscopy, which showed an absorbance band at 630 nm attributed to ferrocenium centers, suggesting that oxidation had occurred.^{11b} TEM samples were prepared from the supernatant by drying a drop of an aliquot on carbon-coated copper grids. From both bright field and dark field TEM images,¹³ we observed nanoparticles with a diameter of ca. 7 nm dispersed randomly within the center of the tubes, consistent with redox-induced synthesis and encapsulation of Ag nanoparticles in **1**. However, the majority product of the reaction was in a form of a precipitate. TEM characterization of the precipitate revealed that the precipitate is a network of nanoparticles and **1**.¹³ It appeared that the particles adhered to the outer surface of the PFS domains rather than were formed and encapsulated inside the cavity. We also noticed that the particles with diameters of around 30 nm are much larger than the cavity of **1** (ca. 8 nm). On close inspection, one can identify some particles as being able to bind more than one nanotube, thereby promoting network formation.¹³ Therefore, preventing nanoparticles from forming outside the cavity of **1** is essential to avoid precipitation and to improve encapsulation.

We rationalized that a more controlled reaction might occur if the PFS domains were partially preoxidized before Ag[PF₆] addition. We imagined that two factors might impair the encapsulation. First, in diffusing toward the nanotubes, silver ions initially encounter the outer surface of the PFS inner wall and react with exterior Fe²⁺, creating nanoparticles outside the tubes; second, a high local concentration of Fe²⁺ in the nanotubes might render the redox reaction less controllable. Accordingly, before adding silver ions, we pretreated **1** with the organic oxidant tris(4-bromophenyl)aminium hexachloroantimonate (**2**). The degree of the oxidation of **1** can be detected by UV–vis, in which ferrocenium units give rise to an absorption at 630 nm, while a peak at 450 nm represents unoxidized ferrocene groups.

The pretreatment was carried out by adding a dichloromethane solution of **2** (0.25 equiv with respect to total ferrocene units) to a toluene solution of **1**, followed by dialysis against toluene to isolate the resulting nanotubes from other small molecule products, such

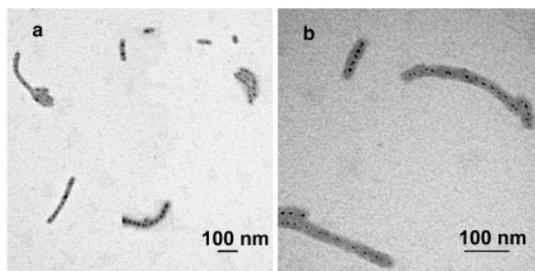


Figure 1. TEM images for a sample prepared from an aliquot of reaction mixture of Ag[PF₆] and **1** pretreated with **2**: (a) lower magnification, (b) higher magnification.

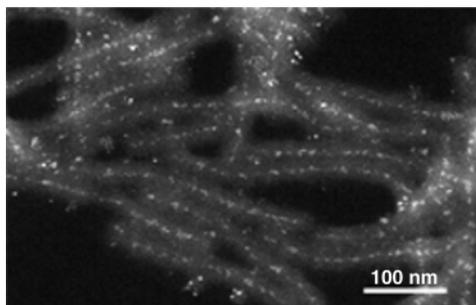


Figure 2. STEM image in dark field mode for a sample prepared from an aliquot of reaction mixture of Ag[PF₆] and **1** pretreated with **2**.

as tri(bromophenyl)amine. The purified nanotubes were characterized by UV–vis spectroscopy, indicating that PFS chains were partially oxidized.¹³ To these pretreated nanotubes we slowly added Ag[PF₆] to induce the encapsulation reaction. During the titration, we did not observe any precipitation, which contrasts sharply with the reaction of pristine **1** with Ag[PF₆]. This improvement in the reaction suggests that **2** played an essential role in the passivation of the outer surface of the PFS domains.

TEM analysis of the samples prepared from the clear reaction mixture was carried out, from which we discerned the encapsulation of nanoparticles inside **1**. Figure 1 presents representative images with either low or relatively high magnification. As shown in the images, the silver particles with diameters in an approximate range from 4 to 8 nm are spaced along the center line of the tubes.

We also verified this structure by using scanning TEM (STEM) in the dark field mode, in which the electrons elastically scattered by the sample were recorded to give an image. Figure 2 shows a STEM image from another experiment, where we see the presence of particles with high electron density (white) in the midst of the relatively less electron-rich PFS domains (gray). From EDX analysis, we confirmed that the encapsulated particles are silver metal.¹³

It is striking that the in situ redox chemistry of the reactive PFS nanotubes provides promising control and regulation of silver nanoparticle formation and complements other approaches, such as encapsulation through a mechanism involving electrostatic interactions or coordination.^{8,14} In this context, we note that Shelnutt and co-workers have recently reported the use of an in situ

photocatalytic redox reaction to fabricate metal nanowires inside the cavity of porphyrin nanotubes.¹⁵

In summary, we have developed a new conceptual approach to synthesize one-dimensional arrays of silver nanoparticles within block copolymer nanotubes. We found that pretreatment of **1** with organic oxidants, such as **2**, is a key step to obtain silver particles within the tubes in high yield. The exact mechanism of the encapsulation and further synthesis of silver nanowires¹⁶ are currently under investigation. The resulting soluble peapod-like hybrid nanostructures may ultimately be useful for the fabrication of nanodevices.¹⁷

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Supporting Information Available: Experimental details for the synthetic work. TEM images for the sample prepared from pristine **1** and Ag[PF₆] and UV–vis and EDX spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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