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DNA-Templated Metallization for Formation of Porous and Hollow Silver-Shells

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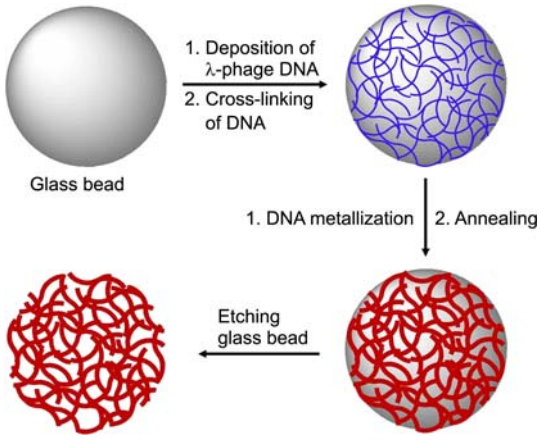
Formation of porous and hollow inorganic-structures with well-defined feature sizes and surface properties has been investigated in various areas because of fundamental interest in synthetically formed, novel inorganic-architectures and their properties as well as many technological applications, such as catalysis, filtration, (bio)sensing, drug delivery, Li-ion battery, and environmental engineering.[1-6] Porous silica shells are commonly found in nature, exemplified by the hierarchically organized, siliceous cell wall of diatoms, and the synthetic counterparts have been formed on the surface of yeast cells in the bioinspired fashion.[7-11] (Bio)template-based methods have generally been adopted for generation of hollow silica- or metal-structures with pores.[12] For example, porous and hollow composite-shells of metal (Au, Ag, or Cu) and silica were formed by using negatively charged polystyrene beads as a sacrificial template, where metallization and silicification were performed sequentially on the template.[13] Additionally, Suslick and coworkers successfully used micrometer-sized liquid droplets as a removable platform in the synthesis of porous and hollow metal oxide microspheres.[14,15]

DNA-assisted metallization would be an alternative but powerful strategy for formation of porous and hollow metal-shells. Transition metal ions (*e.g.*, Ag(I), Pd(II), Cu(II)) interact with DNA by electrostatic interaction and/or their intercalation into base pairs of DNA, which has been used for metal nanowire formation.[16-20] In addition, it is reported that 2-dimensional DNA nanomesh structures were formed at surfaces, and the pore sizes were further tuned by DNA self-assembly[21-24] and enzymatic amplifications.[25,26] These two unique characteristics of DNA, amenability to metallization and pore-size controllability, could be combined synergistically for generation of porous and hollow metal-shells. Furthermore, the semiflexible and highly negatively charged backbone of DNA makes it easy to be adsorbed onto various materials with high packing density *via* electrostatic interactions.[12,27-29] Recently, hollow, meshed CdS nano-shells were formed by a combination of DNA absorption onto amine-functionalized (positively charged) silica beads and mineralization of CdS.[12] In this paper, we report our first progress in the formation of porous and hollow silver shells by using λ-phage DNA. Silver was chosen as an inorganic material for DNA-metallization because of its good opto-electrical properties, and negatively charged bare glass beads were directly utilized as a spherical template for DNA adsorption without any further chemical modifications.

Scheme 1 shows a conceptual depiction for the construction of porous and hollow silver-shells employed in this work. As a proof-of-concept, we used λ-phage DNA as an initial model, because the DNA has a known base-pair sequence with no characteristic pattern and a contour length of up to 16 μm.[17] Clean glass beads (diameter: ≤ 106 μm) was immersed into a solution of λ-phage DNA (48.5 kbp, 1.7 ng/μL at pH 7.4) in the presence of 1 mM solution of $MgCl_2$. The Mg^{2+} ions have relatively high affinity for negatively charged SiO_2 surfaces but low affinity for transition metal-binding sites of DNA.[30,31] We, therefore, used the Mg^{2+} ions to promote tight adsorption of λ-phage DNA onto glass beads as well as minimizing nonspecific metallization of silver ions on the area of glass beads that was not covered with the DNA. After adsorption of λ-phage DNA, ultraviolet light (254 nm) was irradiated for 20 min to tighten the adsorbed DNA structures by interstrand cross-linking.[32] The resulting silica-DNA hybrid was washed thoroughly with Trizma-hydrochloride solution (0.5 M, pH 7.4) several times to remove free DNA molecules. The incorporation of Ag^{+} ions into the DNA stands was achieved by incubation in the



Scheme 1. A conceptual depiction of the synthesis of porous and hollow silver-shells through the DNA-assisted strategy.

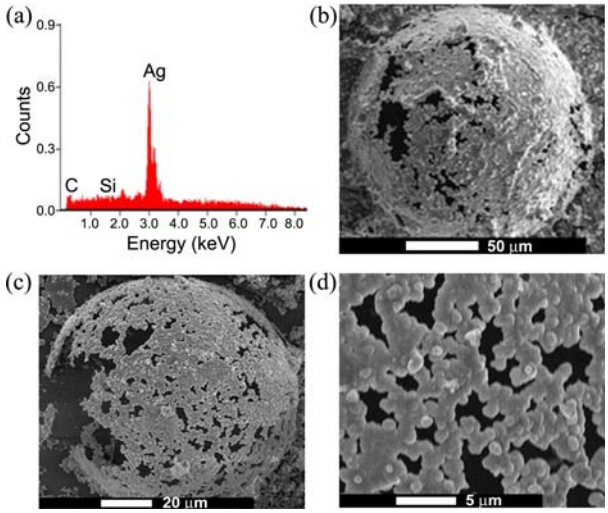


Figure 1. Characterizations of porous and hollow silver-shells. (a) Spectrum of EDX-elemental analysis. (b and c) FE-SEM micrographs. (d) Magnified FE-SEM image.

20 mM solution of $AgNO_3$ for 15 min, and $NaBH_4$ was used as a reducing agent for DNA metallization. Finally, the glass beads were etched with the diluted solution of hydrofluoric acid, after thermal annealing.

We characterized the resulting structures by field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray (EDX) microanalysis. The spectrum of EDX-elemental analysis clearly showed silver (Ag) peaks around 3 keV, indicative of successful silver-metallization (Figure 1(a)).[20] Furthermore, the FE-SEM micrographs confirmed the formation of porous and hollow silver-shells (Figure 1(b)-(d)). Figure 1(b) and 1(c) indicated that the Mg^{2+}-treated glass beads were covered with the λ-phage DNA, which was successfully used for Ag^+ incorporation and reduction at the surface. Open areas with various sizes were observed in the samples, and we cannot draw the clear-cut reasons at this moment; it could be hypothesized that the collapse occurred at silica-dissolution or sample-preparation step.[33] The porous structures were verified by the magnified FE-SEM image (Figure 1(d)). Taken together, the characterizations confirmed that the porous and hollow silver-shell was formed the DNA-assisted method.

In summary, we demonstrated a DNA-based methodology for formation of porous and hollow silver-shells with λ-phage DNA. The synthetic steps are simple, because of the use of bare silica beads, and can be extended to other metals. The development of porous and hollow metal-structures would facilitate the construction of functional nanomaterials, such as nanocarriers for drug delivery, and the improvement of optoelectrical properties of electronic devices. We believe that the advances in structural DNA nanotechnology, including the size-controlled DNA nanomeshes,[19,21,23,24] will be efficiently applied to the method demonstrated in this paper.

Experimental

Formation of Porous and Hollow Silver-Shells. The glass beads were washed with absolute ethanol under sonication and then cleaned with an oxygen-plasma cleaner (Herrick PDC-002) for 1 min. The cleaned glass beads were immersed in the reaction solution consisting of λ-phage DNA (5 ng/μL), Trizma-hydrochloride solution (0.5 M, pH 7.4 adjusted by 1.5 M Trizma-base solution), and 3 mM aqueous solution of $MgCl_2$ (volume ratio: 1/1/1) at room temperature for 15 min. After deposition of λ-phage DNA onto the glass beads, the substrates were rinsed with Trizma-buffer solution several times and dried under a stream of argon. The resulting substrates were evenly irradiated by UV light (254 nm) for 20 min, and then the sample was thoroughly washed with the buffer solution. The glass beads coated with the cross-linked λ-phage DNA were incubated in the 6.5 mM solution of $AgNO_3$, which had been dissolved in the Trizma-buffer solution, for 15 min at room temperature in a dark room. The resulting substrates were treated with 100 mM solution of $NaBH_4$ for 15 min at room temperature in a dark room and carefully washed with Trizma-buffer solution several times. The metallized glass beads were annealed in the range of 50-60 °C for 10 min. Finally, the resulting glass beads were etched with the diluted solution of hydrofluoric acid for 20 min at room temperature in a fume hood.

Characterizations. Field-emission scanning electron microscopy (FE-SEM) micrographs were obtained with Philips XL30SFEG and Hitachi S-4800 equipped with a thermally assisted filed-emission gun. Energy-dispersive X-ray (EDX) microanalysis was performed on FE-SEM by using INCA X-Sight (Oxford Instruments).

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