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Metallization of biologically inspired silica nanotubes

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ABSTRACT

The desire and need for various types of nanostructures have been met with challenges of feasibility, reproducibility, and long fabrication time. To work towards improved bottom-up methods of nanofabrication, we use bacterial flagella as bio-templates for fabricating silica-mineralized nanotubes, which are ideal for the formation of metal nanoparticles or metal oxide nanoparticles. In this study, we show that silica nanotubes formed from flagella templates can be coated with gold, palladium, and iron oxide nanoparticles under mild aqueous conditions. The process was accomplished through reactions including reductive metallization or oxidative hydrolysis. Morphology and chemical composition were analyzed by transmission electron microscopy and energy dispersive X-ray spectroscopy, respectively. The results from these studies provide evidence for the complete coating of silica nanotubes with metal nanoparticles using a simple and fast procedure.

1. Introduction

There is considerable interest in the synthesis of inorganic–organic nanotubes using bio-materials for the utilization of micro- or nanoscale devices. Biologically derived materials are claimed to be more advantageous over other artificial materials due to the reputed simplicity of chemically manipulating the synthesis and mass production of such materials. Recently, we demonstrated that bacterial flagella can be used as potential bio-templates because of their unique features such as small diameter (inner diameter is 2 nm and outer diameter is approximately 20 nm) and long length, their unique tubular structure, and their robustness in harsh conditions [1,2]. The flagella-template allowed the generation of silica-mineralized flagella nanotubes (SMFNs) in an efficient manner by a well-controlled hydrolysis and condensation reaction. Moreover, the synthesized silica on flagella templates successfully formed uniform layers with a controllable thickness in various sizes while maintaining the structure and function of the flagella [1].

Silica nanomaterials in particular are popular because, compared with carbon, production is cheaper and can be conveniently produced in large quantities and chemically functionalized [3]. Specifically, the ease of which one can functionalize silicon's surface makes it a very promising and useful scaffold for metallization with control over morphology and composition using metal nanoparticles or metal oxides [4,5]. Metallic nanoparticles possess unique optical and electrical properties making them extremely useful in broad range of fields. In particular, gold (Au) nanoparticles have attracted significant attention for the applications of photothermal therapy and optical systems because of their plasmonic property [6,7]. Palladium (Pd) nanoparticles are also of great interest in electronics and catalysis due to desirable electrical properties [8–10]. Another important example is iron oxide, which plays a vital role in imparting magnetic properties for the exploitation and manipulation of magnetic fluids [11,12].

Despite these significant uses of metal nanoparticles, their controllable synthesis is still challenging in aqueous reaction conditions. This challenge arises from unpredictable particle growth, aggregation and stability issues. Therefore, as an attempt to reduce those problems and limitations, employing the SMFNs as hard templates is a reasonable way to prepare novel metal nanomaterials incorporated with metal nanoparticles. Chemically functionalized silica surface enables metal atoms or molecules to become more reactive and stable [13,14]. For instance, the hydroxyl groups on the hydrophilic silica surface provide reactive sites that enable interaction with inorganic ions [15,16]. Alternatively, the utilization of crosslinking molecules has been extensively investigated to promote coatings of gold and palladium onto silica surfaces [4,5,17].

In this study, we applied several metal coatings onto the SMFN surface to incorporate multiple design variables and functionalities. The fabrication process of the multilayered structures is depicted in Fig. 1. We started with the synthesis of the silica mineralized nanotube with a flagella template following bottom-up approach. Subsequently, after metal deposition on the silica surface, nanotubes were characterized with transmission electron microscopy (TEM) to observe the distribution of the nanoparticles.

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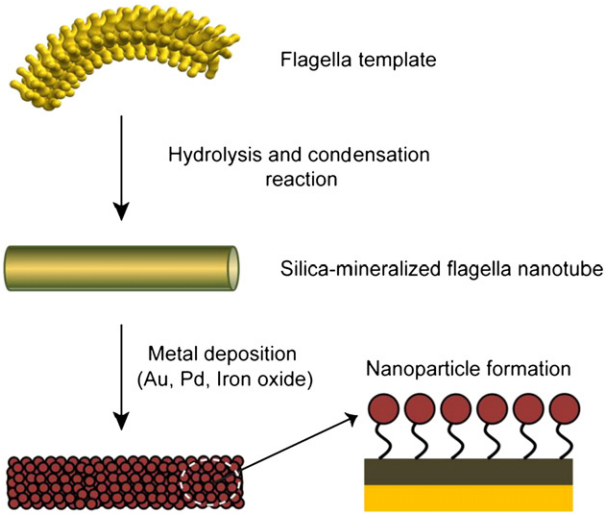

Fig. 1. Schematic illustration of the procedures for the fabrication of SMFNs and the deposition of metal nanoparticles on the surface of SMFNs.

2. Materials and methods

2.1. Materials

All chemicals were purchased from Sigma-Aldrich. 3-(Aminopropyl) triethoxysilane (APTES, #A3648) and tetraethoxysilane (TEOS, #333859) were prepared for silica formation. Gold(III) chloride hydrate ($HAuCl_4 \cdot 3H_2O$, #254169) and MES buffer (#M3671) were purchased for the deposition of Au nanoparticles, while sodium tetrachloropalladate(II) (Na_2PdCl_4, #379808) and hexamethylenetetramine (HMT, #33233) were purchased for the deposition of Pd nanoparticles. To synthesize iron oxide nanoparticles, ammonium iron(II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, #215406), iron(III) chloride hexahydrate ($FeCl_3$, #157740) and sodium hydroxide (NaOH, #221465) were used as received.

2.2. Silica coating on flagella templates

For synthesis of SMFNs, we used hydrolysis and condensation method as previously described in Jo et al.'s paper [1]. Briefly, 1 μl APTES solution was added into 500 μl of flagella solution and thoroughly mixed. The reaction tube was placed in ice-water for 5 min. 2 μl of TEOS was then added to the APTES/flagella solution gently stirring to carry out the silica growth reaction. The mixture was transferred to ice-water bath and placed over a period of 20 min again. Finally, the solution was allowed to proceed at room temperature without any stirring to promote silica formation. Within 10 min, the solution turned turbid indicating the formation of silica on flagella templates.

2.3. Metal coating on the flagella-templated silica nanotubes

2.3.1. Gold (Au) nanoparticle coating

The SMFNs were functionalized again by 2 μl of APTES overnight. The functionalized silica nanotubes were then centrifuged at 5000 rpm for 5 min and resuspended in 500 μl of 0.1 M MES buffer. To achieve gold metallization, 10 μl of 0.05 M $HAuCl_4 \cdot 3H_2O$ was added and incubated for 10 min, followed by reduction with 10 μl of 0.5 M HMT. After 10 min, purple precipitates were obtained indicating that gold nanoparticles were coated on the silica nanotube surface.

2.3.2. Palladium (Pd) nanoparticle coating

The as-prepared 200 μl of SMFNs was mixed with 5 μl of 0.05 M Na_2PdCl_4 for 20 min. Then, 5 μl of 0.5 M HMT was well-dispersed in the mixture and placed for the same time period, producing brownish yellow precipitate indicating successful coating of the nanotubes. The solution containing Pd coated SMFNs was centrifuged at 8000 rpm for 15 min to pelletize the Pd-SMFNs. The supernatant was discarded and the pellet was resuspended in distilled water.

2.3.3. Iron oxide nanoparticle coating

The process for the fabrication of iron oxide nanoparticles was partially modified from Shenton et al.'s method [18]. First, acidic solution containing 1 mM $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 2 mM $FeCl_3$ was prepared. For deposition processing, the freshly synthesized SMFNs were mixed with 7 μl of acidic solution and left to stand for 2 min. Next, 2 μl of 1 M NaOH was added dropwise to give a final pH of 9. After addition of NaOH, a small amount of brown precipitate was observed, and iron oxide nanoparticles were produced in the solution.

2.4. Characterization

The surface morphologies of the metal nanoparticles coated on SMFNs were examined using a field emission scanning electron microscope (FE-SEM, Zeiss Supra 50VP) operated at 2 kV. A small volume of diluted samples was dropped on a silicon wafer without staining and coated with platinum. The flagella structure in the silica nanotube was imaged with transmission electron microscopy (TEM, JEOL JEM 2100) at 200 kV by evaporating the solution on a carbon grid. Energy dispersive X-ray (EDX) spectroscopy was used to analyze the chemical composition of the metal nanoparticles and nanotubes.

3. Results and discussion

Among the biologically-inspired machinery used by microorganisms, bacteria flagella are particularly an attractive template due to the structure's surface chemical groups which have ion-binding capability. Taking advantage of hydrogen bonding or electrostatic interaction between the amino groups in the APTES and the peptide compound on the flagella surface, the absorption of APTES on flagella surface was accomplished. By forming complexes with functional groups of the amino acids in the presence of APTES, the exterior surface of flagella was activated and a silica shell was formed via hydrolysis and successive condensation of TEOS. As shown in Fig. 2, silica shells were formed on the surface of flagella bio-templates. The regular flagella with uniform diameter were recognized at the center of all the resulting silica nanotubes. As clearly evidenced in this figure, the SMFNs demonstrated dimensions of over ~100 nm in thickness (Fig. 2b). Due to the silica layer deposition, the thicknesses of nanotubes were increased in a controllable manner.

The resulting SMFNs were further developed for a uniform array of metal nanoparticles including Au, Pd and iron oxide to make multifunctionalized nanotubes. First of all, to induce attachment of Au nanoparticles onto silica surface, the well fabricated SMFNs were functionalized with APTES overnight. It has been reported that the $Au(OH)_3$ seeds on the bare surface of the untreated silica cores were generally larger and less uniform in size and shape. Furthermore, surface coverage was lower on the untreated silica compared to the amine treated silica cores. This result clearly shows the influence of the amine terminated surface functionalization on the metal deposition process of Au nanoparticles in terms of particle size, uniformity and surface coverage [19]. The APTES-treated SMFNs were then dispersed in MES buffer acting as a crosslinking reagent. The reactive ends containing in the crosslinkers chemically attached to specific functional groups on other molecules. Among many types of crosslinking reagents, a carbodiimide is a complete crosslinker that facilitates the direct conjugation of carboxyls to primary amines [20]. Since MEM buffer is a suitable carbodiimide reaction buffer, silane or amine is able to interact with the silica surface. Then the sulfur group is easily able to interact with Au metal ions in aqueous solution. The process of Au nanoparticle formation is explained by the following steps: (1) binding of Au(I) ions by sulfur groups of the MES-APTES treated