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Short Communication

Synthesis and use of self-assembled rhamnolipid microtubules as templates for gold nanoparticles assembly to form gold microstructures

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ABSTRACT

Natural unmodified rhamnolipids are thermally self-assembled into soft microtubules, which can produce gold nanoparticles onto themselves due to the presence of rhamnose sugar moieties at their surface. The loading of gold nanoparticles on composite microtubules can be controlled by varying the concentration of gold salt to rhamnolipid and the reaction temperature. The composite rhamnolipid–gold nanoparticle microtubules are then heat treated to produce porous gold microwire-like structures with fairly controlled nanostructured features, which may have interesting applications in catalysis, biosensing and electronics.

1. Introduction

Metal nanoparticles have gained enormous scientific and commercial importance due to their size/shape-dependent, unique and tunable properties (e.g., quantum confinement, plasmon resonance, light scattering, etc.) [1–5], and their utility in a wide range of applications such as electronics, optics, catalysis and biotechnology [6–10]. The controlled assembly of nanoparticles allows the tuning of the properties of nanosystems, including surface area, optical and electrical properties, and the accessibility of the guest species. Therefore, various template-based and template-less strategies are now being explored to use metal nanoparticles as building blocks to develop nanostructured materials (e.g., superlattices [11–14], one-dimensional [15–22], two-dimensional [23–25] and three-dimensional assemblies [26–34]) with useful properties.

The use of biomolecular building blocks to assemble nanomaterials has the capability of integrating the structural and functional diversity of biosystems with the inherent properties of nanomaterials. A range of biomolecules have been used to assemble nanomaterials, including DNA [35–39], proteins [40,41] and peptides [42–45]. Biosurfactants provide pragmatically useful materials for nanomaterials self-assembly, given their ready accessibility, low cost, and structural diversity. Natural rhamnolipids, a subclass of glycolipids produced by bacteria, are particularly attractive building blocks, as they can easily be produced from bacteria grown on low-cost substrates such as food and agricultural waste.

Herein we report natural and unmodified rhamnolipids serve as both reducing and stabilizing agents to produce gold nanoparticles, and that these lipids self-assemble into soft microtubules providing scaffolds for nanoparticle assembly. These tubules can then be heat treated to produce porous nanostructured micro/macroscopic materials with fairly controlled nanoscale features. Fig. 1 describes the formation of such porous gold microwires using rhamnolipids as sacrificial biotemplates to self-assemble gold nanoparticles.

2. Material and methods

The rhamnolipids were produced by EBN-8, a gamma ray-induced mutant of *Pseudomonas aeruginosa*, grown on *n*-heptadecane as a sole carbon and energy source at 37 °C in a minimal salt medium [46,47]. The rhamnolipids were then extracted, separated from cell free culture broth (CFCB) and purified using standard procedures [46,47]. To produce gold discrete nanoparticles, an aqueous suspension of purified rhamnolipids (0.005 g/20 ml) was refluxed for 30 min with vigorous stirring under ambient atmosphere. One milliliter of pre-heated (~60 °C) aqueous solution (5 mM) of gold salt ($HAuCl_4{\cdot}3H_2O$) was then added to boiling suspension and reflux continued for another 60 min till the formation of red-coloured[2] gold nanoparticles (Fig. 1b′).

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[2] For interpretation of colors in Figs. 1 and 3, the reader is referred to the web version of this article.

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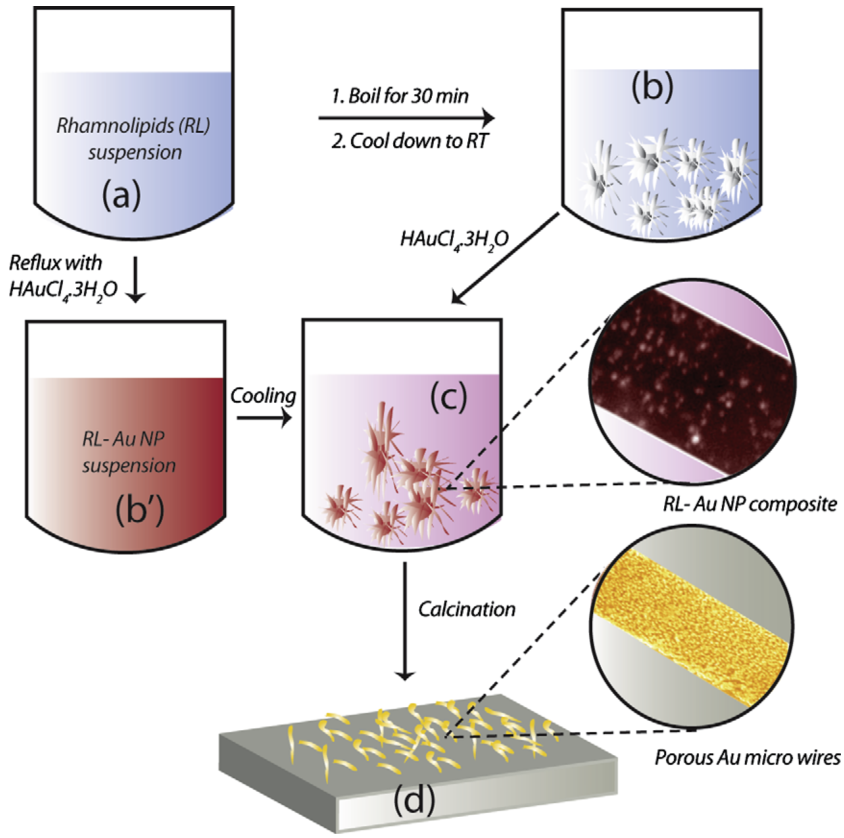

Fig. 1. A scheme for the formation of porous gold microwires using rhamnolipids (RL) as sacrificial biotemplates for the synthesis and self-assembly of gold nanoparticles. RL suspension (a) is boiled to produce microtubules (b), which reduce ionic gold to gold nanoparticles (GNPs) to form RL–GNP composites (c). RL–GNPs composites may also be produced by boiling RL suspension with gold salt to produce suspended gold nanoparticles (b′) followed by cooling. Heat treatment of RL–GNP composites lead to the formation of porous gold microwires (d).

For self-assembled tubules, the precursor rhamnolipid microfibers (Fig. 1b) were produced by boiling an aqueous suspension of rhamnolipid (0.001 g/20 ml) for 30 min and then allowing the obtained transparent dispersion to cool down slowly to room temperature. Self-assembled biomass started appearing after about 48 h and white fluffy cotton-like biomass became clearly visible after about 72 h. Self-assembled microfibers of rhamnolipids were then incubated with 0.2 mM aqueous solution of gold chloride at room temperature and the appearance of reddish colour of rhamnolipids biomass after 48 h indicated the formation of gold nanoparticles onto the lipid template (Fig. 1c). Less structured rhamnolipid–gold nanoparticle composite microtubules were also formed when rhamnolipid stabilized gold nanoparticles were allowed to cool due to the lesser concentration of rhamnolipids.

The gold nanoparticles and the rhamnolipid composite microtubules before and after gold deposition were characterized by field emission scanning electron microscope (FESEM, JSM 7500F) equipped with a transmission electron (TE) detector, and energy dispersive X-ray (EDX) detector.

3. Results and discussion

The gold nanoparticles formed by an aqueous suspension of rhamnolipids were fairly uniform with an average size of ca. 20 nm, and a characteristic plasmon resonance band at 526 nm. Fig. 2 shows representative TEM micrographs and UV–visible spectrum (inset) of these nanoparticles, respectively.

Fig. 3a and b shows the representative scanning electron micrographs of several micrometers long rhamnolipid microtubules without and with gold nanoparticles at their surface, respectively.

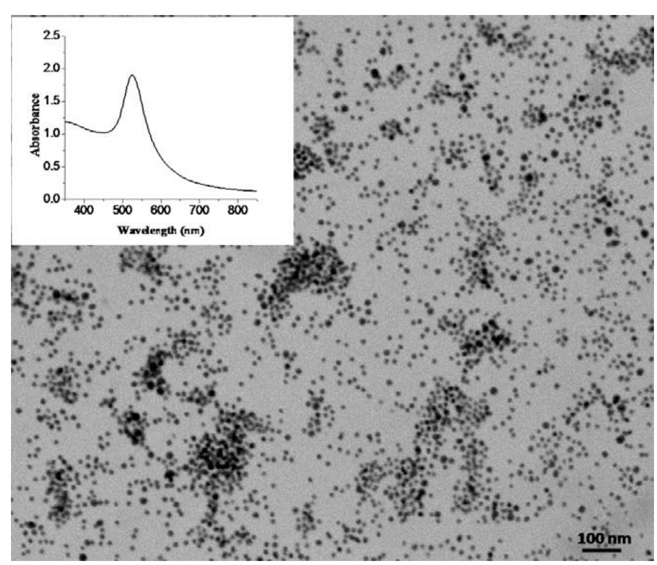

Fig. 2. A representative transmission electron micrograph of gold nanoparticles formed using rhamnolipids as reducing and stabilizing agents. The inset shows UV–visible scanning spectrum of gold nanoparticles.

The presence of gold nanoparticles at the surface of rhamnolipid micro/nanotubules was confirmed by scanning and transmission electron microscopy as shown in inset of Fig. 3b and c, respectively. Both the scanning and transmission electron micrographs showed that the surface of rhamnolipid microtubules was uniformly coated