

Short Communication

A facile template synthesis of asymmetric gold silica heteronanoparticles



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ABSTRACT

Silica hemispheres containing gold nanoparticle cores have been synthesized via immobilization of gold nanoparticles on a substrate and site-selective growth of silica followed by removal of the hemispherical particles. The structure of these asymmetric heteronanoparticles allows selective etching or overgrowth of the core gold seeds, which results in the respective formation of hemispherical capsules or gold homodimers.

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Asymmetric nanoparticles consisting of metal nanoparticles connected with different constituents, such as polymers, organic molecules, and other inorganic materials, have become a subject of active research in recent years, because they exhibit unique optical properties and catalytic activity due to a synergetic effect between each component in the heterostructure [1]. These nanoparticles are also used to promote directed assembly into low-dimensional nanostructures for the realization of nanoscale optical, electrical and sensing materials. One of the most effective ways to achieve the desired nano-assemblies is mono-functionalization of the nanoparticles with protective molecules, by which several types of gold nanoparticle nano-assemblies could be synthesized, such as dimers [2–7], satellites [8,9], and chains [10]. Such low-dimensional gold nanoparticle structures have been reported to exhibit plasmon hybridization due to coupled dipole moments in individual nanoparticles [11], and to be effective catalysts for the guided growth of inorganic nanowire assemblies [12]. Since these properties depend on an interparticle separation as well as nanoparticle size, a facile and effective ways to control these nanostructures need to be developed. To date, several approaches toward the synthesis of mono-functionalized nanoparticles have been developed, including immobilization of nanoparticles onto planar substrates [3–5,13], polymerization of surface-bound protective molecules on nanoparticle surfaces [10], and synthesis of Janus-type nanoparticles with different protective molecules [14–17].

Partial surface coating of nanoparticles with other inorganic or organic materials also yields heteronanoparticles with asymmetrically exposed surfaces, which are then available for partial

functionalization. The heterodimer is one of the successful examples of such heterostructures, which include metal–metal [18,19], metal–polymer [20,21], metal–semiconductor [22–24], semiconductor–semiconductor [25,26], and metal–oxide heterodimers [27–29]. The surface coverage of the primary core of these nanoparticles with secondary materials is important for the construction of low-dimensional nanostructures. Many synthetic methods based on solution processes have been reported that yield such heterostructures, where almost half of the core nanoparticle surface is covered with different materials (these structures are thus referred to as “heterodimers”). However, the synthesis of quasi-core/shell heteronanoparticles where most of core nanoparticle surface is covered, but only a small portion of the surface is exposed, remains challenging [21]. These new types of structures are expected to be used as effective building blocks for low-dimensional nanostructures because directional assembly of the heteronanostructures is much more effectively possible due to the local functionality of the core nanoparticle surface. Here, we report a facile approach (Fig. 1) for the synthesis of asymmetric gold/silica heteronanoparticles through the immobilization of gold nanoparticles on silver-coated glass substrates followed by site-selective growth of silica shells. Desorption of the heteronanoparticles from the substrate yields silica hemispheres containing gold nanoparticle cores with partially exposed surfaces. We also demonstrate the synthesis of hollow silica hemispheres and gold dimers from these heteronanoparticles by the selective etching of the gold nanoparticle cores and by the catalytic growth of additional gold nanoparticles, respectively.

Gold nanoparticles (ca. 20 nm) are immobilized on thiol-terminated silver thin films deposited onto a glass substrate by immersion of the substrates into an aqueous solution of citrate-stabilized gold nanoparticles. The glass substrate with the gold

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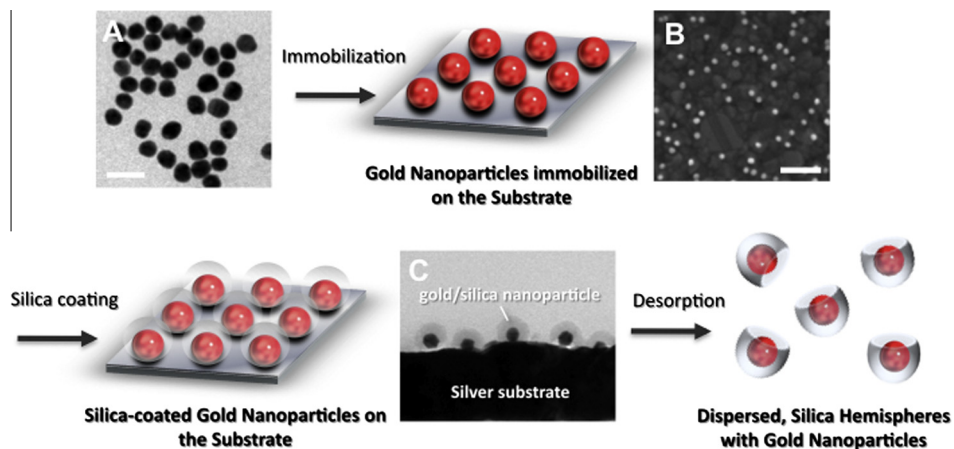


Fig. 1. Schematic of the synthesis of silica hemispheres containing gold nanoparticles. (A) TEM image of citrate-stabilized 20 nm gold nanoparticles. Scale bar: 50 nm. (B) SEM image of gold nanoparticles immobilized on 1,10-dodecanedithiol-functionalized silver thin film on a glass substrate. The sample was obtained after immersion of the substrate into a solution of gold nanoparticles for 10 min. Scale bar: 200 nm. (C) Cross-sectional TEM image of gold nanoparticles coated with silica shells after hydrolysis reaction with TEOS for 15 min. Scale bar: 50 nm.

nanoparticle monolayer is then immersed into an ethanol solution of aminopropyltrimethoxysilane (APTMS) for surface modification of the immobilized gold nanoparticles. The nanoparticles on the substrate are then subjected to the selective growth of silica shells by ammonia-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS). Subsequent ultrasonication of the substrates in ethanol yields heteronanoparticles dispersed into solution.

The formation of gold nanoparticle monolayers on the substrate was confirmed using scanning electron microscopy (SEM), and it was found that the amount of immobilized gold nanoparticles increased almost proportionally with the reaction duration up to 15 min (Fig. S1). For example, the substrate with an average coverage of gold nanoparticles at 135 ± 20 particle/ μm^2 was achieved after reaction for 10 min (Fig. 1B). The gold nanoparticles were then subjected to silica coating because the average

interparticle distance between adjacent gold nanoparticles (65 nm, calculated by assuming simple square arrangement for 20 nm gold nanoparticles) was appropriate for the growth of silica shells. The evolution of silica shell growth on the gold nanoparticles was monitored by taking samples at 10, 15, 20 min after immersion of the substrate with immobilized gold nanoparticles. An SEM image of the sample during the early growth stage (10 min) reveals the growth of silica on the immobilized gold nanoparticles (Fig. 2A), which is promoted by modification of the gold nanoparticle surface with APTMS. A cross-sectional TEM image of the sample directly reveals the selective growth of shells only on the exposed surface of the immobilized gold nanoparticles (Fig. 1C). As the reaction proceeds, the thickness of the silica shells increases, and some interconnected structures are observed (Fig. 2B and C).

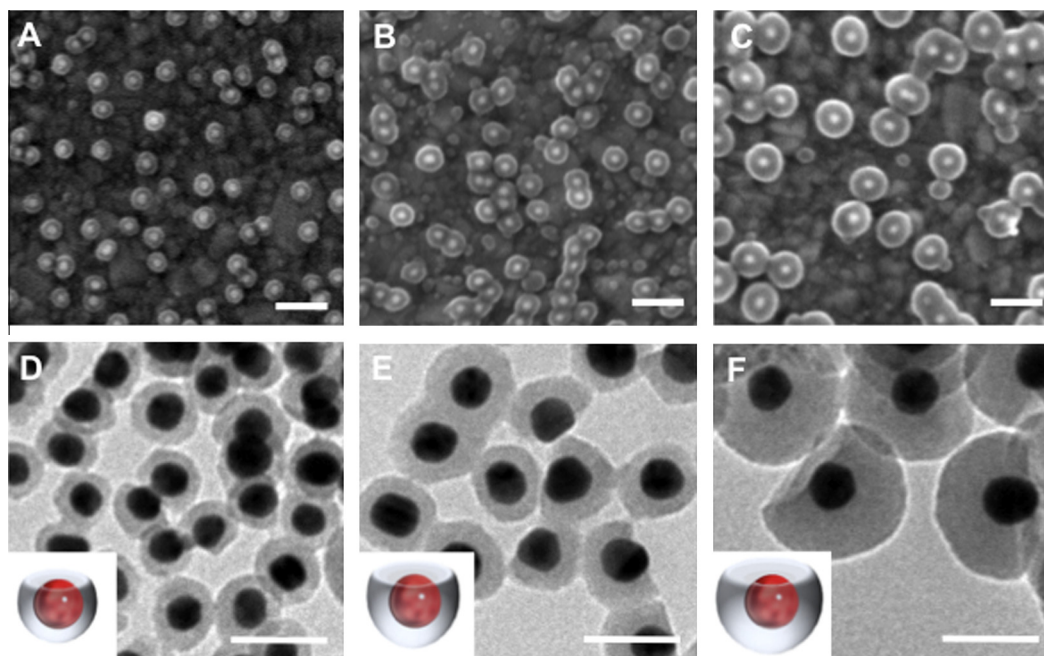


Fig. 2. (A)–(C) SEM images of immobilized gold nanoparticles obtained after silica coating for 10, 15, and 20 min, respectively. (D)–(F) Corresponding TEM images of the gold nanoparticles covered with silica hemispheres shown in (A)–(C) after desorption by ultrasonication and purification using density-gradient centrifugation. Insets in (D)–(F): schematics of the gold nanoparticles coated with different thickness silica hemispheres.

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