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Transformation of thiolated chitosan-templated gold nanoparticles to huge microcubes

Yudie Sun [a,b], Honglin Liu [b,*], Liangbao Yang [b,*], Bai Sun [b], Jinhuai Liu [b]

[a] School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China
[b] Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, China

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ABSTRACT

The L-cysteine molecules were successfully grafted to the 2-amino group of chitosan by a reactive amine reduction, and the as-synthesized thiolated chitosan (TC) molecules were used as the templates to direct the self-assembly of gold nanoparticles and induce the transformation of these assemblies to gold microcubes through a deep-going dialysis. We found that the ratio of gold nanoparticles to TC molecules could greatly affect the shape of the assembled clusters. Different stages of these clusters and microstructures during the dialysis process were characterized by scanning electron microscope (SEM), and the microcubes with average side length of about 20 μm were successfully synthesized. According to the morphology evolution of the assembly, it could be concluded that the microcubes were formed from external to internal. The SERS area mapping images of microcubes and some clusters were also collected to study the formation mechanism of gold microcubes. Our work demonstrates a simple and highly effective way to assemble gold nanoparticles into microcubes with unique properties.

1. Introduction

Nano- and micro-gold structures have attracted tremendous interest because of their promising applications including optics [1], catalysis [2], electronics, biomedicine [3], and chemical sensing [4]. A variety of gold nanostructures and microcrystals, such as nanorods [5], nanotriangles, nanohexagons, nanocubes [6], nanowires [7], microhexagons [8] and microtriangles [9] have been synthesized. Several groups have experimentally and theoretically studied the optical properties of metal nanoparticles with different shapes and demonstrates the distinctive shape-dependent behaviors [10–13]. Sosa et al. found that the optical spectra were more complex as the particle had less symmetry or more vertexes. Since the intrinsic properties of metal particles change with both their shapes and sizes, the applications of gold structures strongly depend on their morphologies and sizes. Particularly, it is evident that gold microstructures have wide applications in many fields. For example, gold microtriangle is a high-quality and versatile substrate to generate nanoscale biochemical patterns for fundamental biophysical studies as well as practical biosensors [4]; gold microhexagons have been used to study the thermodynamically stable structure at high temperatures [14]; and gold microplates are also needed in many sensitive optical microscopic and spectroscopic techniques including surface plasmon resonance [15], surface enhanced Raman spectroscopy [16], and surface plasmon enhanced fluorescence [17]. What's more, gold microstructures are expected to have potentials in many other fields. However, among the various morphologies of gold microstructures that have been reported, there were few reports on the synthesis of gold microcubes (Au MCs). According to the excellent optical features of gold nanocubes, it is determined that the Au MCs should also possess many unique potentials and applications. As electric-field enhancement critically depends on particles' size and shape, edges and corners of Au MCs can act as hot sites for the electric-field enhancement. Hence, a single micro-particle with definite shape can be used to clearly profile the electric-field distribution and free the study of electromagnetic mechanism of surface enhanced Raman spectroscopy from conventions [18]. Moreover, catalytic reactions can directly occur on the surfaces of pure noble metals through photo-induced electron transfer, Au MCs may also be used to characteristic the unique photocatalytic property [19]. However, it is still a great challenge for scientists to control crystal growth for the formation of Au MCs.

* Corresponding author. Tel.: +86 551 65592385; fax: +86 551 5592420.
E-mail addresses: hlliu@iim.ac.cn (H. Liu), lbyang@iim.ac.cn (L. Yang).

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There are many physical techniques used for the fabrication of microstructures such as photolithography [20] and nano-imprinting [21], while these conventional methods are complex and cost-intensive, and often involve multiple steps. In addition, various chemical methods have been used to synthesize the gold microstructures. Gold microtubules have been synthesized through a citrate-directed assembly method [22]. Many nanometer-sized building blocks could readily assemble into macroscopic structures by DNA sequences with unique molecular recognition properties [23], and the resultant structures were ordered with a molecular-scale precision hard to achieve by other fabrication methods. Single-crystalline gold microplates with triangular or hexagonal shapes have also been synthesized by reducing $HAuCl_4$ in lyotropic liquid crystal (LLC) block copolymers and water after adding a small amount of capping agents [24]. Liquid–liquid interfacial reactions were simple and effective strategies for generating and assembling hierarchical micro/nanostructures of gold thorned roses without introducing any surfactant, seed or template [1]. However, the synthesis of high-dimensional assemblies is difficult using small molecules as mediators, and it is also difficult to control the structures of the assemblies using large biological molecules as templates. In principle, the synthetic functional polymers with well-defined monomer units could be used as ideal templates to direct nanoparticle assembly and control the properties of the assembled materials [25]. These polymers modified through some simple chemical reactions could be used as simple and highly effective templates to direct the nanoparticle assembly and to control the final structures of the assemblies. For example, chitosan molecules have been successfully used for the fabrication of nanoparticles and microstructures [26,27].

Herein, the huge gold microcubes with the side length of about tens of micrometers were synthesized using TC molecules as the templates. With active hydroxyl and amino groups, chitosan molecules with well-defined repeated units have a potent ability to mediate a chemical reaction. The shortage is that neither hydroxyl nor amino groups could bind stably to the surface of noble metal nanoparticles. It is known that thiol groups can bind strongly with Au nanoparticles (Au NPs) via S–Au bonds. Hence we here grafted thiol groups to chitosan molecules. L-Cysteine, a well-known amino acid, contains a thiol group and importantly provides a carboxylic acid group for additional chemical reactions at the unbound end of this molecule [28]. Hence, we grafted thiol groups to chitosan molecules by attaching cysteine molecules to the 2-amino group of chitosan. Finally, the thiolate-functionalized chitosan (TC) successfully directed the transformation of Au NPs to Au MCs. A schematic illustration of this transformation process was shown in Fig. 1. This work demonstrates a simple and highly effective way to synthesize the large Au MCs.

2. Experimental

2.1. Materials

Chitosan, Hydrogen tetrachloroaurate hydrate, L-cysteine hydrochloride, chloroauric acid and N,N′-dicyclohexylcarbodiimide (DCC) were obtained from Shanghai Chemical Regent Company (China). All chemical solvents and reagents were analytical grade and used without further purification. Deionized water (18 M) was used in all experiments.

2.2. Synthesis of the TC molecules

Chitosan (0.4 g, 2.5 mmol), DCC (5.0 mmol) and L-cysteine (5.0 mmol) were dissolved in 100 mL of 0.2% (v/v) hydrochloric acid aqueous solution. Then, the mixed solution was stirred for 72 h at room temperature to ensure the sufficient reaction. In this system, the DCC was used as the coupling agent. Besides, it can promote the dissolution of L-cysteine. The reaction solution was stewed to remove the precipitate in the solution, then the solution was filtered through a microporous membrane with apertures of ~0.22 mm, and the filtered solution was dialyzed (MWCO 10,000) against distilled water for 5 days and finally produced 180 ml of the colorless TC solution.

2.3. The assembly of Au NPs into microcubes

The Au NPs sols were synthesized by a simple sodium citrate reduction method, the ratio of $HAuCl_4$ to sodium citrate was 10:1. Before the preparation of Au NPs, all glasswares were cleaned in a bath of freshly prepared aqua regia (HCl/HNO_3 3:1) and then rinsed with deionized water prior to use. The TC solution was added to the prepared gold colloidal solution. The number ratios of gold nanoparticles to S atoms (P:S) were set to 1:1, 1:2, 1:3 and 1:4, respectively. The mixed solution was aged overnight and then dialyzed in 0.2% (v/v) HCl solution for different times.

2.4. Characterization

The scanning electron microscopy (SEM) images were taken by using a field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 10 kV). Raman spectra were taken on Lab-RAM HR800 confocal microscope Raman system (Horiba Jobin Yvon). The FTIR spectra were collected on a Shimadzu FTIR spectrophotometer (FTIR 8400) in the wavenumber range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1} in the transmission mode.

3. Results and discussion

TC molecules were prepared by a reactive amine reduction in the presence of L-cysteine, as described in the experimental section. The FTIR spectra of the as-synthesized product and the pure chitosan were collected to confirm the successful grafting of thiol groups on the side chain of chitosan molecule (Fig. 2). FTIR was a valuable tool for understanding the functional groups in organic molecules. From the chitosan spectrum (curve a in Fig. 2), it can be found that two distinctive absorption bands appearing at 1662 cm^{-1} (amide) and 1605 cm^{-1} ($-NH_2$ bending). Compared with the pure chitosan, a significant peak can be observed at 1632 cm^{-1} on the TC sample (curve b in Fig. 2) that is assigned to

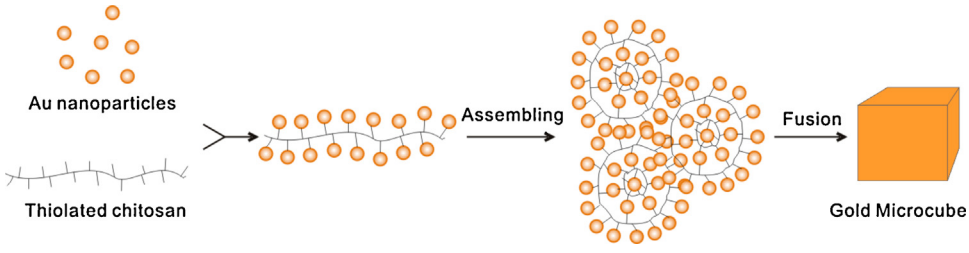

Fig. 1. Schematic illustration of the TC-directed transformation of Au NPs to Au MCs.