Fabrication and Tuning of Gold Polyhedron Arrays

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Abstract

In this study, gold polyhedral arrays were successfully fabricated via a seed-mediated in-situ growth method. The effects of chloroauric acid ($HAuCl_4$) concentration and polyvinylpyrrolidone (PVP) concentration on the morphology of the arrays were systematically investigated. Periodically arranged two-dimensional gold nanosphere arrays were first prepared on silicon substrates as seed layers using a polystyrene colloidal sphere monolayer template combined with magnetron sputtering. Subsequently, well-defined and orderly arranged gold polyhedral arrays were constructed through the seed-mediated in-situ growth method, employing N, N-dimethylformamide (DMF) as the reducing agent, PVP as both the surfactant and capping agent, and $HAuCl_4$ as the gold precursor. The influence of reactant concentrations on the array morphology was also discussed. Scanning electron microscopy characterization reveals that the as-prepared gold polyhedral arrays exhibit uniform distribution and well-defined periodic features. This strategy provides a novel technical route for the morphology-controlled construction of two-dimensional noble metal nanostructure arrays.

Keywords

Nanomaterials, Gold polyhedral, Arrays, Seed-mediated growth

Introduction

In Nanotechnology, as an interdisciplinary frontier field, has permeated numerous research domains and facilitated the development of various novel nanomaterials [1]. Among these, gold polyhedral arrays exhibit significant application potential in fields such as concentration detection and medical therapy due to their unique structural characteristics. The structural units within these arrays possess abundant tips and edges, which can induce strong localized electromagnetic field enhancement. This results in the formation of “hot spots” that are essential for surface-enhanced Raman scattering, thus effectively improving the sensitivity of molecular detection [2]. Moreover, gold polyhedral particles typically expose high-index or high-surface-energy facets, which feature a high density of undercoordinated atoms, endowing the arrays with excellent catalytic activity and molecular adsorption capacity [3]. By tuning the size and morphology of the polyhedra, their plasmon resonance peaks can be extended from the visible to the near-infrared region, offering new possibilities for applications such as biosensing and photothermal therapy [4]. When these structural units are arranged into well-ordered arrays, not only can uniform and large-area detection signals be achieved, but the overall optical performance can also be further enhanced through coupling effects induced by the periodic structure [5]. Therefore, the controlled construction of gold polyhedra is of great significance to research.

Various methods exist for the preparation of gold polyhedral arrays. Conventional “top-down” etching techniques are often limited by high cost, low efficiency, and restricted structural and material diversity, resulting in high technical barriers and limited accessibility in laboratory settings. In contrast, “bottom-up” approaches, such as template-assisted assembly, offer simple operation and low cost, but face challenges in precisely controlling the position and orientation of individual nanoparticles, often compromising the stability of the periodic array structure. Template methods utilizing anodic aluminum oxide or polystyrene colloidal sphere monolayers provide advantages such as high structural controllability and good reproducibility. However, they also suffer from limitations, including potential damage to the product during template removal and the stoichiometric constraints of sacrificial template methods [6]. Thus, challenges remain in the controlled construction of gold polyhedral arrays.

In this study, a seed-mediated growth method is employed, integrating physical templating with seed-directed chemical growth to achieve controlled morphological evolution of structural units while maintaining array periodicity [7]. Gold nanosphere arrays were first deposited on substrates as seed layers using a colloidal sphere monolayer template combined with magnetron sputtering. Subsequently, gold polyhedral structural units were grown in situ on the seed surfaces using N, N-dimethylformamide (DMF) as the reducing agent, polyvinylpyrrolidone (PVP) as the surfactant, and chloroauric acid ($HAuCl_4$) as the gold precursor. This strategy ensures the periodicity of the arrays while enabling the controlled construction of gold polyhedral arrays, providing a novel technical route for the morphology-controlled fabrication and broad application of two-dimensional noble metal nanostructure arrays.

Experimental section

Preparation of gold seed arrays

Two-dimensional gold nanosphere arrays serving as seed layers were fabricated on substrates using a polystyrene colloidal sphere monolayer template method combined with magnetron sputtering technique. A Polystyrene colloidal sphere monolayer was first assembled via the gas-liquid interface self-assembly method and then transferred onto a silicon substrate. Subsequently, a gold thin film was deposited onto the substrate by magnetron sputtering. After high-temperature annealing treatment, periodically arranged gold nanosphere ordered arrays were obtained [8].

Preparation of gold polyhedral arrays

Using the as-prepared two-dimensional gold nanosphere arrays as seed layers, gold polyhedral arrays were fabricated via a seed-mediated in-situ growth method. Typically, 0.0888 g of PVP (molecular weight: 10,000) was placed into a 5 mL glass vial, followed by the addition of 4 mL of N, DMF to achieve a PVP concentration of 0.2 M. The mixture was ultrasonicated for 15 min. Subsequently, $HAuCl_4$ was added to the homogeneous solution to a final concentration of 0.15 mM, and the solution was stirred for 5 min. The mixed solution together with the two-dimensional gold seed arrays was transferred into an autoclave liner and heated at 120 °C for 6 h. After the reaction, gold polyhedral arrays with uniform morphology and well-ordered arrangement were successfully obtained.

Characterization of gold polyhedra

The surface morphology and structural features of the as-prepared gold polyhedral arrays were characterized by scanning electron microscopy (SEM). Figure 1 presents the SEM images of the closely packed gold polyhedral arrays at different magnifications, where panels (a), (b), and (c) correspond to 10×, 20×, and 50× magnifications, respectively.

The low-magnification image (Figure 1a) provides an overview of the large-scale distribution of the arrays, demonstrating that the gold polyhedral structures are uniformly distributed across the substrate surface without significant defects or agglomeration, indicating good large-area uniformity. The medium-magnification image (Figure 1b) reveals the detailed arrangement of individual polyhedral units, clearly showing that these structural elements are organized in a regular and well-ordered pattern with consistent interparticle spacing.

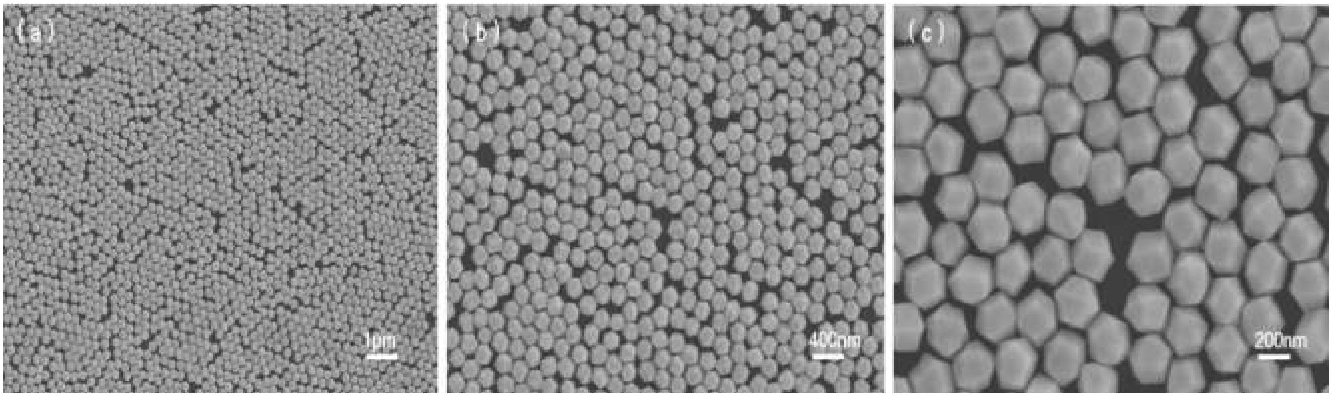

Figure 1. SEM images of gold polyhedra: (a) 10×, (b) 20×, (c) 50×.

The high-magnification image (Figure 1c) offers a closer view of the morphological characteristics of individual gold polyhedra, revealing that these structures exhibit relatively consistent shapes, well-defined edges, and clear geometric features. The SEM characterization results collectively demonstrate that the as-prepared gold polyhedral arrays possess uniform distribution, distinct periodic arrangement, and good morphological consistency across the entire substrate surface, reflecting a high degree of structural uniformity and controllability.

Factors influencing the morphology of gold polyhedral arrays

Effect of $HAuCl_4$ concentration

During the seed-mediated growth process, the concentration of $HAuCl_4$ plays a crucial role in determining both the generation rate of Au atoms and their subsequent deposition kinetics on the seed surface, thereby governing the morphological characteristics and periodic arrangement of the resulting polyhedral arrays. Under otherwise identical reaction conditions, with the concentration of PVP fixed at 0.2 M, it can be clearly observed from Figure 2 that the morphology of the nanoparticles undergoes significant and systematic evolution as the $HAuCl_4$ concentration increases. At relatively low $HAuCl_4$ concentrations, the number of Au atoms generated via reduction is limited, resulting in a mild deposition process on the seed surface and the predominant formation of quasi-spherical nanoparticles [9]. Under these conditions, the growth is mainly governed by kinetic factors, where the insufficient supply of Au atoms restricts their diffusion and incorporation onto specific crystallographic facets. Consequently, the resulting structures exhibit smooth surfaces, weak anisotropy, and relatively low morphological complexity. As the $HAuCl_4$ concentration increases to an appropriate range, the generation and deposition rates of Au atoms become moderate, providing favorable conditions for controlled growth. In this regime, Au atoms can effectively diffuse and redistribute across the seed surface, preferentially accumulating at high-energy sites such as edges and vertices. This process facilitates the formation of well-defined polyhedral nanostructures with sharp tips and clear geometric features. Meanwhile, the presence of PVP helps maintain good dispersion by preventing nanoparticle aggregation, thereby preserving the uniformity and ordering of the array. When the $HAuCl_4$ concentration continues to increase, the generation rate of Au atoms is further accelerated, leading to a significant increase in the deposition rate on the seed surface.

Figure 2 presents the scanning electron microscopy (SEM) images of gold polyhedral arrays prepared at different $HAuCl_4$ concentrations. It can be clearly observed that as the concentration of $HAuCl_4$ increases, the size of the structural units gradually increases, while the sharpness of the vertices first improves and then decreases. Notably, when the $HAuCl_4$ concentration is optimized at 0.15 mM, gold polyhedral arrays with well-defined morphology and highly ordered arrangement can be successfully obtained. Therefore, selecting an appropriate $HAuCl_4$ concentration is one of the key factors for achieving the controllable and reproducible fabrication of gold polyhedral arrays.

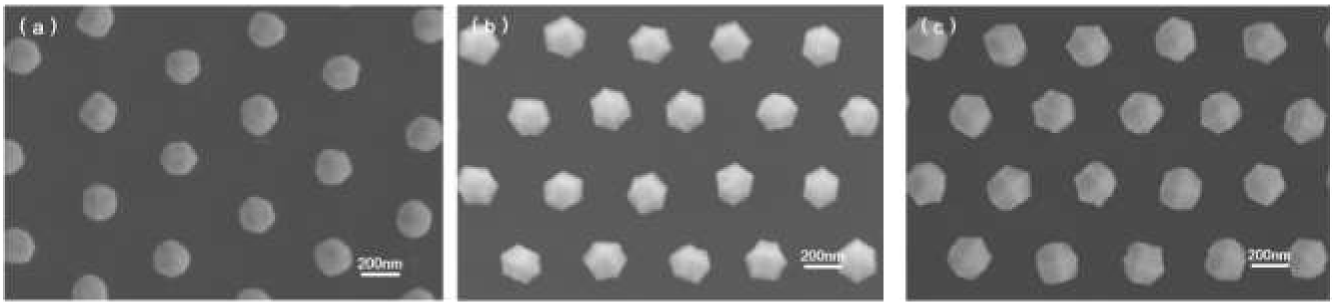

Figure 2. SEM images of gold polyhedral arrays prepared with different $HAuCl_4$ concentrations: (a) 0.05 mM, (b) 0.15 mM, (c) 0.25 mM.

Effect of PVP concentration

PVP, serving as both a surfactant and a stabilizing agent, plays a vital role in regulating the morphology and structural evolution of gold polyhedral arrays. The concentration of PVP has a pronounced influence on both the size and shape of the resulting gold nanoparticles. As the PVP concentration increases, the average particle size gradually decreases, indicating a more effective suppression of particle growth. This behavior can be attributed to the enhanced ability of PVP molecules at higher concentrations to encapsulate and passivate the surface of gold nuclei, thereby limiting further atomic deposition and growth. In addition, the amide functional groups in PVP chains exhibit strong affinity toward the gold surface, forming adsorption layers that introduce steric hindrance, which effectively prevents nanoparticle aggregation and improves colloidal stability [10]. Furthermore, PVP may selectively adsorb onto specific crystallographic facets, thereby modulating their relative growth rates and contributing to anisotropic shape evolution. Beyond its influence on particle size, PVP concentration also plays a decisive role in governing the morphological evolution and structural integrity of nanoparticle arrays. At a fixed $HAuCl_4$ concentration of 0.15 mM, when the reaction system contains a relatively low concentration of PVP, the protective and stabilizing effects are insufficient. Under such conditions, gold seeds are unable to uniformly capture and incorporate the reduced Au atoms, leading to nanoparticles with broad size distributions and poor uniformity. In some cases, particles may undergo surface diffusion, migration, or even coalescence with neighboring particles, thereby disrupting the initial periodic arrangement of the seed array and reducing overall structural order. When a modest amount of PVP is introduced, the system exhibits improved control over particle growth. The gold polyhedra begins to display relatively uniform sizes, and the ordering within the array is significantly enhanced. This improvement arises from the formation of a more effective adsorption layer on the particle surface, which balances atomic deposition and surface diffusion. As the PVP concentration further increases to an optimal level of approximately 0.20 M, the growth process becomes highly controlled. Under these conditions, gold polyhedra undergoes uniform in-situ growth on the seed surfaces, maintaining consistent dimensions while faithfully preserving the periodic and ordered structure of the original seed array.

This indicates that an optimal PVP concentration enables a delicate balance between surface passivation and atomic supply, which is essential for achieving high-quality anisotropic nanostructures.

Figure 3 presents scanning electron microscopy (SEM) images of gold polyhedral arrays synthesized at different PVP concentrations. It can be clearly observed that PVP concentration serves as a key parameter in regulating both the periodicity of the array and the uniformity of particle morphology. An appropriate concentration of PVP effectively stabilizes the gold seed surfaces, promotes anisotropic growth pathways, and suppresses undesirable particle displacement and aggregation. As a result, gold polyhedral arrays with well-defined morphology, high uniformity, and highly ordered arrangement can be successfully obtained.

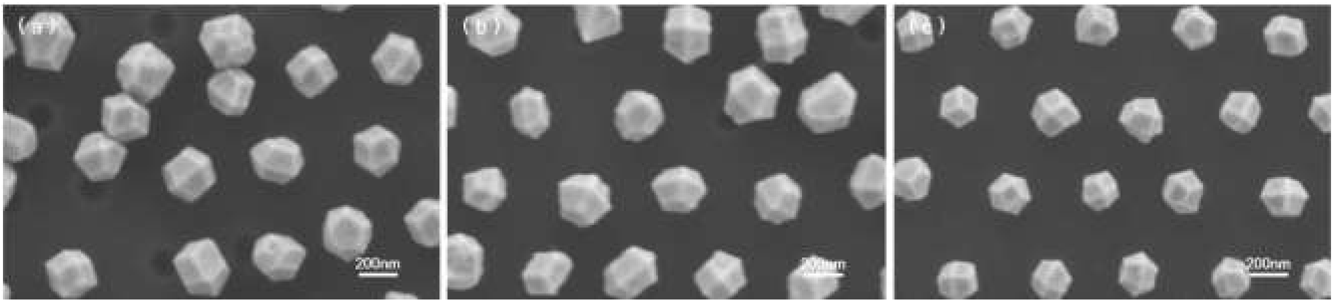

Figure 3. SEM images of gold polyhedral arrays prepared with different PVP concentrations: (a) 0.10M, (b) 0.20M, (c) 0.30M.

Conclusion

In this study, gold polyhedral arrays are successfully fabricated via a seed-mediated in-situ growth method. Two-dimensional gold nanosphere arrays are first prepared on substrates as seed layers using a polystyrene colloidal sphere monolayer template combined with magnetron sputtering technique. Subsequently, well-defined gold polyhedral structural units are grown in situ on the seed surfaces by regulating reaction parameters, employing DMF as a mild reducing agent and PVP as a surfactant.

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Conflicts of Interest

The authors declare no conflict of interest.

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