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Shape evolution of 3D flower-like gold microstructures from gold nanosheets via oriented attachment

Supeera Nootchanat[a], Chutiparn Lertvachirapaiboon[b], Vittaya Amornkitbamrung[c], Pikaned Uppachai[d], Sanong Ekgasit[a], Kanet Wongravee[a,*]

[a] Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, 254 Phyathai Road, Patumwan, Bangkok 10330, Thailand
[b] Graduate School of Science and Technology, Niigata University, 8050, Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan
[c] Integrated Nanotechnology Research Center, Khon Kaen University, Khon Kaen 40000, Thailand
[d] Department of Applied Physics, Faculty of Engineering, Rajamangala University of Technology Isan, Khon Kaen Campus, Khon Kaen 40000, Thailand

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ABSTRACT

Herein, we present a shape evolution of 3D flower-like gold microstructures (3D-FLGMSs) from gold nanosheets induced by H_2O_2 with the presence of starch. A systematic investigation of the influence of the parameters on the size, morphology and structural evolution of 3D-FLGMSs was presented. Under the starch-stabilized environment, H_2O_2 plays a key role on the formation of 3D-FLGMSs as it promotes a rapid generation of small nanosheets with starch-bound {111} facet at the very early stage. At a high concentration of H_2O_2, the nanosheets undergo oriented attachment and transform into a large primary gold nanosheets with imperfect facet-binding. The oriented attachment (OA) and subsequent epitaxial growth of nanopetals from the imperfects turns the primary nanosheets into 3D-FLGMSs with lateral size as large as 30 μm within 120 min. Without starch, quasi-microspheres of gold with diameters of 5–7 μm are the sole product. In addition, the 3D-FLGMSs can be employed as SERS substrates which allow the detection limit of Rhodamine 6G (R6G) at the concentration as low as 0.1 μM. The developed green synthetic method utilizes non-toxic reducing and stabilizing agents while limiting the discharge of harmful chemical wastes.

1. Introduction

In the past decade, synthesis and fabrication of structural-controlled metal nanostructures have been extensively studied [1,2] due to their potential applications as catalysts [3], sensors [4], and photovoltaic devices [5]. The applications take advantages of the unique size- and shape-dependent properties of the nanostructures which are not existing in the bulk materials or spherical nanostructures [6].

Gold nanostructures have continuously been the centre of attention as it can be engineered into various morphologies, such as spheres [7,8], rods [9,10], wires [11], sheets [12,13], polyhedrons [14], stars [15], and dendrites [16], with distinctively high chemical stability. Among numerous gold nanostructures, flower-like gold structures (FLGSs) with sub-micrometre size consist of various sub-structures such as nanogrooves, sharp edges and tips. The sub-structures provide not only high surface area, but also numbers of nanometre-scale junctions and interconnections, which can serve as hotspots for surface-enhanced Raman spectroscopy (SERS) [17]. The FLGSs have been used as substrates for SERS [18–20] and electrochemical catalysts [21,22]. Furthermore, FLGSs exhibited potential usages as nanocarriers of DNA for cellular uptake, drug or gene delivers and contrasting agents as they provide acceptable cytotoxicity toward cells in toxicological investigations [23,24].

Various techniques for the fabrication of FLGSs have been developed, particularly electrochemical [20,21,25] and wet chemical procedures [18,19,23,24,26,27]. The wet chemical approaches seem to be the most practical choice as the complicated instruments are not required and the process can be easily scaled up. A development of simple, effective, fast and green protocol using environmentally benign method and low cost chemicals is still a challenge. In general, additives (i.e., capping agents, shape-directing agents, and stabilizers) play a pivotal role as it directs the formation of anisotropic nanostructures. The specific absorption of the additive molecules on the particular crystal facets of nanoparticles leads to the modification of the surface energy and consequently alters their growth rate [17] to generate particles with shape selectivity. Various additives (i.e., 2-[4-(2-hydroxyethly)-1-piperazinyl] ethanesulfonic acid (HEPES) [28], dopamine [19], poly(vinyl pyrrolidone) (PVP), sodium dodecyl sulfate (SDS) [27],

* Corresponding author.
E-mail address: kanet.w@chula.ac.th (K. Wongravee).

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and gum Arabic [24]) have been employed. Although there were several successful techniques for FLGSs fabrications, only a few demonstrated a basic understanding on the growth mechanism of the FLGSs structure. As discussed in our previous work on the synthesis of gold nanosheets using H_2O_2 as a reducing agent and starch as a green stabilizer [12], a very low concentration of H_2O_2 leads to a selective preservation and growth of high anisotropic gold nanosheets as starch preferentially adsorbed and then prevented the growth on the {111} basal planes. Tridib Kumar Sarma et al. [29]. reported the change in shape from spherical to triangular and to hexagonal particles by increasing initial concentration of $HAuCl_4$ in the presence of H_2O_2 and starch with assisted ultrasonic waves. From the work, it suggested that the ratio of $[H_2O_2]/[HAuCl_4]$ might be an important factor for the shape selectivity. Decreasing of the ratio by increasing concentration of $HAuCl_4$ induced the formation of plate shapes. Interestingly, we found that a complex structure (flower-like structure) could be generated instead of the nanosheets when high concentration H_2O_2 was involved. This indicates that the concentration of H_2O_2 and the high ratio of $[H_2O_2]/[HAuCl_4]$ plays a pivotal role in the complex structure formation. However, in this system, the shape evolution roles of this complex structure are still unclear.

In this study, we report the shape evolution pathways of 3D flower-like gold microstructures (3D-FLGMSs) from the nanosheets. The influences of the concentration of H_2O_2, starch and molar ratio of $[H_2O_2]/[HAuCl_4]$ were systematically investigated in detail. The developed method for the fabrication of 3D-FLGMSs is simple, effective, fast, green and efficient with industrial-scale production capability. To our knowledge, this is the first for the preparation of such a complex microstructure of 3D-FLGMSs using H_2O_2 as a green reducing agent and starch as stabilizer. It could serve as a challenge for the fabrication of microstructures using a simple chemical approach. Furthermore, a potential application of 3D-FLGMSs as SERS substrate was demonstrated.

2. Experimental

2.1. Chemicals

Nitric acid (HNO_3, 65% w/v), hydrochloric acid (HCl, 37% w/v), sodium hydroxide (NaOH), soluble starch and hydrogen peroxide (H_2O_2, 30% w/w) were purchased from Merck (Thailand). All chemicals were analytical grade and were used as received. A solution of tetrachloroauric (III) acid ($HAuCl_4$, 0.5 M) employed as gold metal precursors, was prepared from a stock solution of concentrated $HAuCl_4$ solution. The stock solution was prepared using a method described elsewhere [12]. Prior to use, all glassware and magnetic bars were carefully rinsed with aqua regia in order to get rid of any metallic residuals before cleaning with liquid detergent and rinsing with deionized (DI) water.

2.2. Preparation of 3D-FLGMSs

The 3D-FLGMSs were synthesized by a simple wet chemical method using H_2O_2 as a reducing agent and starch as a stabilizer. Briefly, starch solution (25 mL, 2% w/v) and $HAuCl_4$ (1.25 mL, 0.5 M) were mixed under vigorous stirring for 30 min. The volume of the mixture was adjusted to 33.3 mL using deionized water and stirred for another 30 min before an instantly addition of H_2O_2 (16.7 mL, 30% w/w). The solution was stirred for another 5 min and kept in ambient condition without disturbance. Within 20 min, the golden yellow solution turned colorless with a concomitant formation of dark-brown solid 3D-FLGMSs together with a formation of many oxygen bubbles according to the following redox reaction [12,13].

$$2AuCl_4^-(aq) + 3H_2O_2(aq) \rightarrow 2Au(s) + 3O_2(g) + 8Cl^-(aq) + 6H^+(aq)$$
$$\Delta E^\circ_{cell} = +0.307\ \text{V}. \quad (1)$$

The mixture was kept undisturbed for another 100 min before the separation of 3D-FLGMSs by centrifugation. The 3D-FLGMSs were thoroughly washed with hot DI water before keeping as an aqueous suspension for further characterizations.

2.3. Characterizations

The morphologies of 3D-FLGMSs were observed by a scanning electron microscope (SEM) model JEOL JSM-6510A with accelerating voltage of 20 kV under high vacuum mode. The crystallographic information and the X-ray diffraction (XRD) pattern of 3D-FLGMSs were analysed using an XRD diffractometer model Rigaku D/MAX-2200 (Cu K_α radiation) operated at 40 kV and 30 mA. The diffraction angle was in range of 20–90° with the step size of 0.2°. High-resolution transmission electron micrographs and selected area electron diffraction (SAED) patterns of nanocrystals were monitored by a high-resolution transmission electron microscope (HRTEM) model FEI Tecnai G2 20 using LaB_6 filament with operating of 200 kV.

3. Results and discussion

3.1. H_2O_2 induced 3D-FLGMS formation

H_2O_2 is well known as a strong oxidizing agent. However, its mild reducing capability is suitable for the formation of anisotropic nanostructures, particularly silver nanoplates [30,31] and gold nanosheets [12,13]. The utilization of low concentration H_2O_2 is the key parameter as it enables a slow reduction allowing the nucleation and growth of gold nanosheets under a kinetically controlled environment [12]. This phenomenon provides the formation of plate-like seeds that will further grow into nanoplates [32,33]. The liberated oxidizing species (e.g. O_2/Cl^-) act as strong oxidative etchant which selectively dissolves the unstable seeds and preserves the plate-like seeds [12].

When a low concentration of H_2O_2 (3.2 mM) was employed, within 10 h, large gold nanosheets with an average lateral size of 9.2 ± 5.2 μm (thickness of 20–50 nm) were produced as the major product (Fig. 1A). The reaction time was determined by the fading of yellow colour of $HAuCl_4$ solution with the disappearance of O_2 bubbles. The clear solution implied that the $AuCl_4^-$ ions were completely consumed. Increasing H_2O_2 concentration from 3.2 to 32 mM decreases the reaction time to 8 h while small gold nanosheets with an average lateral size of 2.2 ± 1.2 μm were created (Fig. 1B). These observations on the generated gold nanosheets are in a good agreement with our previous work [12]. As a high concentration of reducing agent was employed, the metal ions were rapidly reduced into Au nuclei in the early stage of the reaction. Therefore, the decrease of the particle size can be attributed to the insufficient of metal ions for the growth of gold nanosheets.

Interestingly, when the concentration of H_2O_2 was further increased to 320, 970, 1600, and 3200 mM, the complex structures defined as 3D-FLGMSs were produced within only 1 h (Fig. 1C–F). According to the SEM images, morphology of 3D-FLGMSs is mainly stacking assembly of gold nanosheets (thickness of 40–110 nm, similar to petals of flowers). The morphological evolutions from nanosheets to 3D-FLGMSs were occurred when the concentration of H_2O_2 was over 320 mM. This observation suggests that high concentration of H_2O_2 is the key parameter that triggers the formation of 3D-FLGMSs. An adequate concentration of H_2O_2 is crucial for a rapid reduction that generates a large number of gold nanosheets. The nanosheets later undergo though aggregation and self-organization to 3D-FLGMSs. It should be noted that the surfaces of nanosheets were rough when the H_2O_2 concentration was higher than 1600 mM. These rough surfaces can normally occur in the system with fast growth rate [34].