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Nicotinamide adenine dinucleotide assisted shape-controlled synthesis of catalytically active raspberry-like gold nanostructures

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ABSTRACT

We describe the shape-controlled growth of raspberry-like gold (Au) nanostructures and their application in the electrochemical oxidation of methanol and reduction of oxygen. Nicotinamide adenine dinucleotide (NAD^+) plays a vital role in the growth of raspberry-like Au nanostructures. The preferential adsorption of NAD^+ onto the (011) facets of Au favors the growth of raspberry-like morphology. In the absence of NAD^+, icosahedral Au nanostructures were obtained. The raspberry-like Au nanostructures have been characterized by UV-visible spectroscopy, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and electrochemical measurements. The FESEM image shows that the raspberry-like morphology has an average size of 170 nm. The spectral profile shows a broad band between 650 and 795 nm. Compared to Au nanoseeds and icosahedral Au nanostructures that were grown in the absence of NAD^+, the raspberry-like morphology has excellent catalytic activity towards the electrochemical oxidation of methanol and reduction of oxygen. On the raspberry-like nanoparticle-based electrode, the oxidation of methanol was observed at 0.35 V in alkaline pH, and the reduction of oxygen was observed at -0.06 and -0.4 V in 0.1 M PBS. The electrochemical reduction of oxygen occurs in two steps: (i) reduction of oxygen to H_2O_2 and (ii) further reduction of electrogenerated H_2O_2 to water. The electrochemical performance of the raspberry-like nanostructure-based electrode is highly stable.

1. Introduction

Synthesis of inorganic nanomaterials with tailored shapes and sizes have drawn much attention because of their possible application in various fields of science and technology. In particular, due to their fascinating shape-dependent optical and catalytic properties, much attention has been given to the synthesis of gold (Au) nanostructures [1]. Au nanostructures show excellent physiochemical properties compared to their bulk counterpart. Therefore, shape-controlled synthesis of Au nanostructures has become an emerging area in nanoscience and nanotechnology. Wet-chemical approaches have been predominantly adopted for the synthesis of Au nanostructures with diverse shapes [2–8]. For many practical applications, these nanostructures must be integrated onto the solid supports, which is very challenging job. He, Goyal and Oyama's groups have demonstrated several methods for the integration of Au nanostructures onto different conducting supports [9–15]. However, by electrochemical approach simultaneous nanostructure synthesis and immobilization can be done easily without using any toxic reagents or costly instruments. For instance, Duan et al. have demonstrated the electrochemical growth of flower-like Au nanocrystals by adding polyvinylpyrrolidone to the electrolyte [16]. Li and Shi have electrochemically synthesized Au nanocrystals with dendritic rod, sheet, flower-like and pinecone-like shapes by regulating the electrodeposition conditions and have also demonstrated that the flower-like Au nanocrystal has higher electrocatalytic activity [17]. Praig et al. have synthesized two-dimensional Au nanostructures on amine terminated ITO surface by electrochemical seed-mediated growth approach [18]. Guo et al. have electrochemically synthesized hierarchical flower-like Au microstructures with clean surfaces [19]. Electrochemical approach has also been employed to synthesize Au nanoplates, Au nanothorns, and Au nanowires [20]. Wang et al. have electrochemically synthesized a hierarchically micro/nanostructured array of Au and demonstrated that by

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controlling the electrodeposition time, it is possible to transform quasi-spherical shaped structures into quasi rod-shaped structures [21]. Chen et al. have demonstrated one-step growth of mono-dispersed three-dimensional branched Au nanostructures at room temperature [22]. Huang et al. have synthesized Au nanocubes using electrochemical technique [23]. Yu et al. have demonstrated the electrochemical growth of Au nanorods [24]. Abdelmoti and Zamborini have demonstrated the potential controlled electrochemical seed-mediated growth of Au nanostructures [25]. Following electrochemical approach, Das and Raj have synthesized Au nanostructures of different shapes on a conducting surface [26,27]. Electrochemical synthesis of Au nanostructures in the absence [28,29] and presence of additives such as iodide ions [30], $Pb(CH_3COO)_2 \cdot 3H_2O$ [31], cysteine [32], ethylenediamine [33], N-methylimdazole [34], cytosine [35], and $FeCl_3$ [36] is well known, where the additives present in the electrolyte solution plays an important role during the electrochemical growth of the Au nanostructure. Though the effect of these additives on the morphology of Au nanostructure is well established, yet, the shape and morphology dependent optical and electrochemical properties of the Au nanostructures further demands the exploration of other potential additives which could be used in the shape tailoring of Au nanostructures. Considering this fact, we have explored another shape regulating agent which can be used in the shape-controlled synthesis of raspberry-like Au and other metal nanostructures. Though the synthesis of raspberry-like Au nanostructures [37,38] using different methods and reagents has been reported, to the best of our knowledge, there is no report on the NAD^+ assisted seed mediated growth of raspberry-like Au nanostructures.

Herein, we demonstrate the shape-controlled synthesis of catalytically active raspberry-like Au nanostructures and their application in the electrochemical oxidation of methanol and reduction of oxygen. The prior immersion of the surface-confined Au nanoseeds in a fixed concentration of NAD^+ for a fix time period is the key for the growth of raspberry-like Au nanostructure. Exclusion of this step results in the growth of icosahedral Au nanostructures. To the best of our knowledge, this is the first report which describes the utility of NAD^+ as an additive and its role in the synthesis of catalytically active raspberry-like Au nanostructures. The raspberry-like Au nanostructure has excellent electrocatalytic activity towards the electrochemical oxidation of methanol and reduction of oxygen. The surface morphology of the Au nanostructure plays an important role in the electrochemical process.

2. Experimental section

2.1. Materials

$HAuCl_4$, hydroxylamine, $Pb(NO_3)_2$, and NAD^+ were purchased from Sigma–Aldrich and were used as received. Methanol, KOH, H_2SO_4, Na_2HPO_4, NaH_2PO_4, and all other chemicals were of analytical grade and used as received. ITO plates were obtained from HS technologies, Korea. All the solutions used in this investigation were prepared using Millipore water.

2.2. Instrumentation

UV–visible spectra of Au dendrites were recorded using a UVS-2100 SCINCO spectrophotometer. X-ray diffraction (XRD) patterns were recorded with a Max 2500 V/PC (Rigaku Corporation, Tokyo, Japan). The spectra were recorded at a scan rate of 1°/min with Cu-Kα targets (λ = 0.15406 nm) operated at a voltage of 40 kV and a current of 100 mA. The surface morphologies of the Au nanostructures were investigated with field emission scanning electron microscopy (FE-SEM) via a JSM-6701F (JEOL, Japan). Electrochemical investigations were carried out with a computer-controlled CHI660D electrochemical analyzer attached to a Faraday cage/picoampere booster (CH Instruments, Austin, USA). The measurements were performed with a two-compartment three-electrode cell using ITO plates as working electrode, a Pt wire as the auxiliary electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. Except for the oxygen reduction measurement, all other electrochemical measurements were conducted in an argon atmosphere. Current density was obtained by dividing the current by real surface area (measured in H_2SO_4).

2.3. Synthesis of raspberry-like Au nanostructures

The raspberry-like Au nanostructures were synthesized by a seed-mediated growth approach. Typically, following the chronoamperometric technique, Au nanoseeds were first electrodeposited on the ITO surface by stepping the potential from 1.1 to 0 V for 100 s from a supporting electrolyte solution containing 1 mM $HAuCl_4$ in 0.5 M H_2SO_4. The Au nanoseed electrodeposited ITO surface was then washed properly and immersed in an aqueous solution of 1 mM NAD^+ for 2 h. The electrode was then removed from the NAD^+ solution and washed repeatedly with water. After careful cleaning the electrode was immersed in a solution of hydroxylamine and $HAuCl_4$ (0.9 mM each) for 12 h without any disturbance. Finally, the electrode was carefully washed with water and used in the other experiments.

3. Results and Discussion

3.1. Characterization of raspberry-like Au nanostructures

3.1.1. UV-visible spectra

The Au nanostructures were characterized by UV-visible spectral measurement. Fig. 1 shows the spectral profile obtained for the as-deposited Au nanoseeds and the nanostructures synthesized in the absence and presence of NAD^+. The as-deposited Au nanoseeds show a weak spectral band at 545 nm and a broad band in the NIR region. The Au nanostructure synthesized by seed-mediated growth in the absence of NAD^+ shows a sharp band at 628 nm. Alternatively, the nanostructure synthesized in the presence of NAD^+ shows a broad band between 650 and 795 nm. This difference in the spectral profile indicates that Au nanostructures with different morphologies have been grown. NAD^+ is known adsorb onto Au facets; in principle, its use during

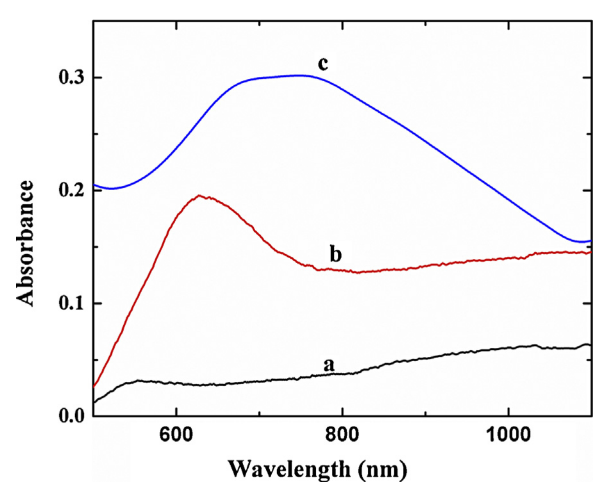

Fig. 1. UV-Vis spectra for (a) Au nanoseed, (b) icosahedral Au nanostructure and (c) raspberry-like Au nanostructure.