Short communication

Surface coverage and size effects on electrochemical oxidation of uniform gold nanoparticles

Donghyeop Han [a,1], Sung-Soo Kim [a,1], Yang-Rae Kim [a], Byeong-Hyeok Sohn [a,*], Taek Dong Chung [a,b,**]

[a] Department of Chemistry, Seoul National University, Seoul 151-747, Korea
[b] Advanced Institutes of Convergence Technology (AICT), Suwon-si, Gyeonggi-do 443-270, Korea

A B S T R A C T

We investigated the electrooxidative dissolution of uniformly distributed Au nanoparticles (NPs) without an extra adhesion layer or capping agent. Diblock copolymer micelles were exploited to fabricate the arrays of Au NPs where not only diameter of the particles but also inter-particle spacing, and thus coverage were finely controlled. The peak potential for electrochemical oxidation shifted greater as a function of coverage of NPs than the size.

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1. Introduction

Electrodes with nanostructured surfaces have been investigated for a variety of applications such as electrochemical catalysis, sensing, separations, plasmonics and nanoelectronics [1,2]. It is because the physical and chemical properties of 'nanoelectrodes' are distinct from those of flat electrodes composed of the same materials. While a great deal of efforts have been made to unravel the origin of the difference in due course, it is still far to reach complete understanding [3]. In particular, NPs on an electrode substrate tend to be dissolved as a consequence of electrochemical oxidation but the underlying mechanism responsible for that behavior is unclear yet.

Plieth theoretically predicted negative shift of redox potential with decreasing radius of NPs owing to surface free energy [4], which was followed by subsequent theoretical reports of similar results [5,6]. These inspired many researchers to experimentally tackle this issue by conventional electrochemical techniques such as voltammetry. It was ascertained that the electrochemical oxidation of Au [1,2,7], Ag [3,8–10], Pt [11,12], Pd [13] and Cu [14] NPs is significantly influenced by the radius of those. Compton and co-workers approached in another point of view, i.e. diffusion of metal ions dissolved from metal NPs

[9,15,16]. Recently, they derived the analytical expression of anodic stripping voltammetry of metal NPs under the consideration of mass transport as well as thermodynamic conditions, and the mass transport effects were experimentally investigated by the effect of surface coverage of NPs [3]. However, they could not experimentally corroborate their hypothesis due to clustering of Ag NPs.

To address this issue, it is an effective strategy to prepare arrays of NPs where size and spacing of those are controlled precisely. But it remains a challenging task due to the lack of appropriate technology and/or method to make it possible. In this work, we fabricated Au NP arrays without an adlayer on ITO/glass electrode using diblock copolymer micelles. From a monolayer of diblock copolymer micelles, we obtained well aligned Au NPs that are free from agglomeration throughout the experiment [17,18]. The diameter of the Au NPs and inter-particle spacing among them were sophisticatedly tuned in the range of 4–9 nm and 30–60 nm, respectively. With this novel array, we were able to examine voltammetric behavior that varied with diameter and coverage of pure Au NPs.

2. Experimental

2.1. Fabrication of array of Au nanoparticles

* Corresponding author. Tel.: +82 2 883 2154; fax: +82 2 889 1568.
** Correspondence to: T.D. Chung, Department of Chemistry, Seoul National University, Seoul 151-747, Korea. Tel.: +82 2 880 4362; fax: +82 2 887 4354.
E-mail addresses: bhsohn@snu.ac.kr (B.-H. Sohn), tdchung@snu.ac.kr (T.D. Chung).
[1] They made an equal contribution to this work.

toluene, a strongly selective solvent for PS blocks, to yield a 0.5 wt.% spherical micellar solution, which was stirred for 24 h at room temperature and for 3 h at 85 °C and then cooled at room temperature. $HAuCl_4$, a precursor of Au nanoparticles, was added to the micellar solution. The molar ratio of precursors to pyridine units in the P4VP block was 0.5 for all PS-P4VP micelles. Prior to spin-coating, indium tin oxide (ITO)-coated glass (15–20 Ω/sq) was cleaned by ultrasonication in isopropanol, acetone, and methanol, and was dried with nitrogen. Then a single-layered film of PS-P4VP micelles containing precursors of Au nanoparticles was spin-coated onto an ITO substrate for 60 s at 4000 rpm for PS-P4VP (25 k–7 k), PS-P4VP (32 k–13 k) and PS-P4VP (51 k–18 k), and at 2000 rpm for PS-P4VP (51 k–18 k) and PS-P4VP (48 k–21 k). To synthesize the nanoparticles along with the removal of the copolymer, substrates were treated with oxygen plasma etching for 5 min (100 W, 38 mTorr).
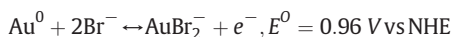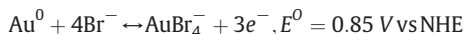
2.2. Electrochemical measurements

Linear sweep voltammograms were obtained with a CHI 604B electrochemical workstation (CH instruments). The electrochemical cell consisted of three electrodes. For working electrode, Au nanoparticle decorated ITO-coated glass electrode or no-decorated one was used. The geometric surface area was 0.28 cm^2. A platinum wire was used as a counter electrode and Ag/AgCl as a reference electrode. 0.1 M perchloric acid containing 0.01 M potassium bromide was used for electrochemical oxidation experiments. All plots were obtained after bubbling the solution with N_2 for 15 min. The results have been acquired for at least three repetitive measurements under respective conditions.

3. Results and discussion

PS-P4VP diblock copolymer micelles containing $HAuCl_4$ in core region were spin-coated onto ITO/glass substrates at various rotational speeds (v) to form a monolayered micellar film (Fig. 1(b)), which can act as a nanotemplate to yield arrays of NPs (Fig. 1(c)). TEM image in Fig. 1(d) shows a single-layered film of PS-P4VP micelles spin-coated on the substrate after selective I_2 staining of P4VP core blocks. From this micellar film, we synthesized arrays of Au NPs along with the removal of copolymers by the treatment of oxygen plasma as shown in Fig. 1(e). We confirmed that hexagonally-ordered Au NPs

were successfully prepared without aggregation among individual NPs. Moreover, we were able to precisely control the diameter and spacing in nanoscale by molecular weights of copolymers as well as rotational speed for spin-coating (See Table 1).

We acquired linear sweep voltammograms (LSVs) to investigate electrochemical oxidation of Au NPs on ITO as prepared. Fig. 2 shows the LSVs of Au NP arrays from five different conditions in Table 1. For the sake of convenience, Au NPs, which were prepared from PS-P4VP (molecular weight of PS – molecular weight of P4VP-modulated speed of spin-coating), were denoted as Au(molecular weight of PS – molecular weight of P4VP – v). Different conditions led to different particle diameters and surface coverages as listed in Table 1. There are two pathways that electrochemical oxidation of the Au in the solution of halide ions can follow [2,19].

$$Au^0 + 4Br^- \leftrightarrow AuBr_4^- + 3e^-, E^O = 0.85\ V\ vs\ NHE$$

$$Au^0 + 2Br^- \leftrightarrow AuBr_2^- + e^-, E^O = 0.96\ V\ vs\ NHE$$

Upper reaction pathway is known to be thermodynamically preferred [19–21] so that we can assume the faradaic oxidation of three electron transfer process in the presence of sufficient bromide ions. While there was a report of 1.9 and 1.5 electron processes for this reaction, it could have come from combination of two pathways [1,19]. By scanning potential slowly at 5 mVs^{-1}, sufficiently long time was given to make the Au NPs oxidized and dissolved. As seen from the current decay back to the background current, Au NPs were completely dissolved as a consequence of electrochemical oxidation and the charge that flowed during potential scan can be regarded as that for total amount of Au NPs [1]. The amount of charge for faradaic reaction can be calculated by integrating the current under the peak of LSV and was used as surface coverage in this work.

Looking into three conditions from the top in Table 1, not only coverage but also diameter of Au NPs is varied to a similar extent with the molecular weight of copolymers, while E_p still shifts. So, the effects of diameter and coverage of Au NPs to the electrochemical reaction are hardly discriminated from each other. Plieth equation allows us to see the influences of diameter to peak potential [4]:
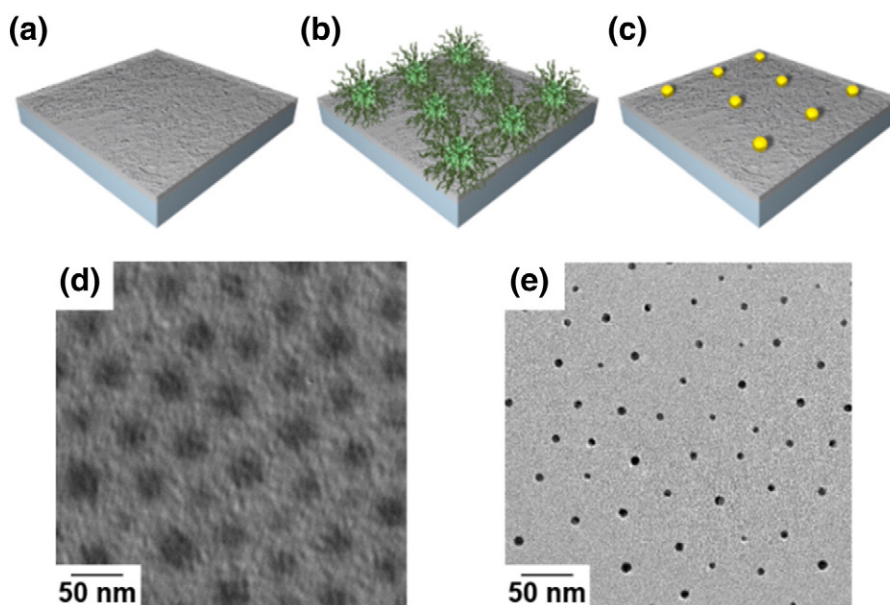
$$E_{NPs} = E_{bulk} - (4\gamma V_m/zFd)$$

Fig. 1. Schematic diagram for fabrication of an array of Au NPs. (a) an ITO/glass substrate; (b) a single-layered film of PS-P4VP micelles that enclose $HAuCl_4$ in core region; (c) an array of Au NPs; (d) TEM image of a single-layered film of PS-P4VP (51 k–18 k) micelles; (e) TEM image of Au NP arrays fabricated from PS-P4VP (51 k–18 k).