Fabrication of Octahedral Gold Nanoparticle embedded Polymer Pattern based on Electron Irradiation and Thermal Treatment

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1. Introduction

Noble metal nanoparticles (NPs) such as gold (Au), silver, and copper have been a hot research issue due to their unique optical, electronic, and catalytic properties. On account of the size- and shape- dependent properties of the noble metal NPs, most researches are concentrated on tailoring sizes and shapes of the noble metal NPs. In particular, noble metal NPs with Platonic shapes such as tetrahedron, cube, octahedron, dodecahedron, and icosahedron have significant impact on a variety of applications including surface-enhancement spectroscopy, biochemical sensing, and nanodevice fabrication because sharp corners of the metals lead to high local electric-field enhancement.

In addition, patterning or controlled assembly of noble metal NPs is indispensible for biological sensors, micro-/nano-electronic devices, photonic and photovoltaic devices, and surface-enhanced Raman scattering (SERS)-active substrates. Although Platonic noble metal NPs with well defined sizes have been intensively studied, patterning of Platonic noble metal NPs has been rarely demonstrated.

Here, we present a strategy to fabricate patterned Au nano-octahedra embedded polymer films by selectively irradiating an electron beam onto $HAuCl_4$-loadaed poly(styrene-b-2-vinyl pyridine) (PS-b-P2VP) block copolymer (BCP) precursor films followed by thermal treatment. The BCP plays a important role for the patterning of the precursor film due to a cross-linking behavior under electron irradiation.

2. Methods

2.1 Chemicals

Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), PS-b-P2VP (M_n=PS(102000)-P2VP(97000) g·mol^{-1}), toluene were purchased and used without further purification.

2.2 Precursor film preparation

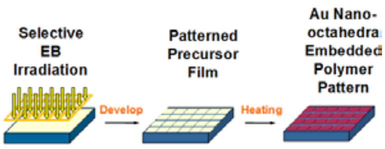
BCP solution was prepared by dissolving PS-b-P2VP in toluene at ~70 °C. And then $HAuCl_4 \cdot 3H_2O$ was added into the BCP solution. The precursor solution was drop-cast onto a Si substrate (1 × 1 cm^2) to form a precursor film.

2.3 Electron irradiation and thermal treatment

The as-prepared precursor films on Si substrates were irradiated with an electron beam using a metallic shadow mask. The beam energy was 30 keV and total electron fluence was $6.36 \times 10^{14} \sim 1.27 \times 10^{15}$ cm^{-2}. Due to the metallic shadow mask, only selected regions of a precursor film were electron-irradiated. After the electron irradiation, the samples were developed to remove unexposed regions of the film. Subsequently, the samples were heated in air at 270 °C for 30 min, through which Au NPs were created.

3. Results

The fabrication procedure of the patterned Au nano-octahedra embedded polymer films is illustrated in Scheme 1.



Scheme 1. Schematic Diagram of the Fabrication Process for the Patterned Au Nano-octahedra embedded polymer films

Figure 1 shows a field emission scanning electron microscope (FESEM) image of the patterned polymer film fabricated by the approach described in Scheme 1. Accordingly, a clear pattern of the precursor film was formed by a selective electron irradiation process using a Cu grid mask followed by developing with acetone.

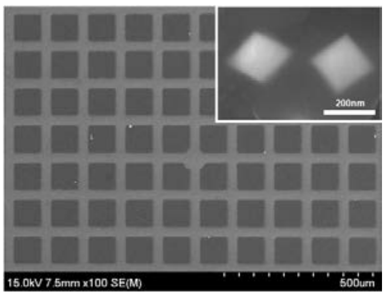


Figure 1. FESEM image of the sample thermally treated at 270 °C after selective electron irradiation using a 200 mesh Cu grid as a shadow mask. Inset is a magnified image of each pattern.

When the patterned precursor film was heated at 270 °C in air for 30 min, NPs were generated inside the BCP (Figure 1 and Figure 2). Since the NPs were embedded in the polymeric material, morphologies of the NPs cannot be clearly identified. However, the most particles had square or rhombus shapes as shown in Figure 1, which correspond to the top-views of an octahedral shape.

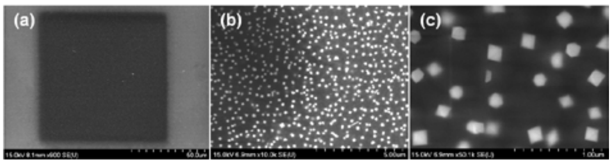


Figure 2. FESEM images of Au nano-octahedra within the polymer film.

X-ray diffraction (XRD) patterns in Figure 3 are useful to understand the formation process of the Au NP from the precursor material comprising $HAuCl_4$-loadaed PS-b-P2VP BCP. No Au peaks were observed in the XRD pattern of the pristine film (Figure 3a) and the electron-irradiated film (Figure 3b), suggesting that Au NPs were not created by the electron irradiation process. Au XRD peaks did not still appear for the sample that was electron-irradiated followed by thermal treatment at 170 °C (Figure 3c). Au peaks started to appear when the temperature was increased to higher than 180 °C (Figure 3d, e). The XRD pattern of the produced nano-octahedra displays peaks at 38.2°, 44.4°, 64.6°, 77.6°, and 81.7° (Figure 3e), which correspond to (111), (200), (220), (311), and (222) planes of face-centered cubic (fcc) Au, respectively. Therefore, Figures 1, 2, 3e confirm that a patterned film of octahedral Au NP embedded polymer can be produced by electron irradiation combined with thermal treatment.

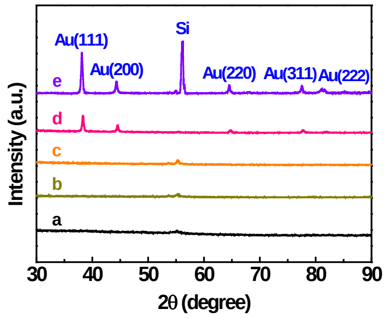


Figure 3. XRD patterns corresponding to the samples of (a) the pristine, (b) the electron-irradiated, the post-thermally treated at (c) 170 °C and (d) 190 °C, respectively. (e) XRD pattern of the sample after electron irradiation and post-thermal treatment at 270 °C.

In addition, differential scanning calorimetry (DSC) data of the electron-irradiated precursor films show that crystallization occurs at ~177 °C (Figure 4a). Since neat PS-b-P2VP BCP without $HAuCl_4$ does not show any crystallization behavior by heating (Figure 4a), these results indicate that Au crystals are produced at the temperature above ~177 °C due to the thermal reduction of $HAuCl_4$ in the precursor film. The DSC data also show that the glass transition temperature (T_g) of the electron-irradiated precursor film is ~87 °C and the melting temperature (T_m) of the film is ~284 °C. In our study, the irradiated films were heated at 270 °C that is much higher than T_g. At this temperature, the film becomes viscous and the mobility or the molecular motion of the precursor material is increased. Higher temperature is better to increase the molecular motion of the precursor material, facilitating the formation of Au crystals inside the film. However, heating the patterned precursor film above T_m can break the patterned shape of the film. This is the reason why we chose 270 °C as the heating temperature.

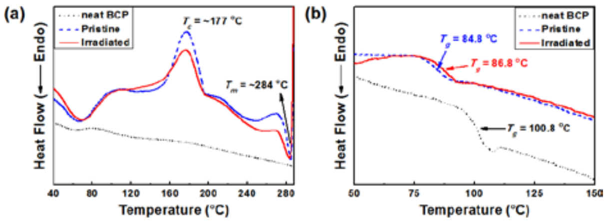


Figure 4. DSC data of the neat BCP, the pristine precursor and the electron-irradiated precursor. (a) 1st heating cycle of DSC was carried out to measure the crystallization temperature (T_c) and T_m, and (b) quenching followed by 2nd heating cycle of DSC was carried out to measure T_g.

4. Conclusions

We report for the first time that patterned Au nano-octahedra embedded polymer films can be fabricated by electron irradiation followed by thermal treatment of a solid precursor material, which is composed of $HAuCl_4$ and PS-b-P2VP BCP. Due to the cross-linking behavior of the BCP, the precursor material could be easily patterned by selective electron irradiation using a shadow mask. The thermal treatment of the as-prepared films leads to the formation of Au nano-octahedra inside the polymer pattern. The patterned metal-polymer composite films might be useful for the applications to solar cells, photonic band-gap materials, and catalysts.

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