Comprehensive Microscopy Analysis of Au/Ag Nanoclusters on Silica Nanospheres

Hui Qian [1], Wei-zheng Shen [2], Kai Cui [1], Jae-Young Cho [1], Hicham Fenniri [1, 2, 3]

[1] National Institute for Nanotechnology, 11421 Saskatchewan Drive, Edmonton, Canada T6G 2M9
Phone: +1-780-641-1664, FAX: +1-780-641-1601, Hui.Qian@nrc-cnrc.gc.ca
[2] Department of Chemistry, University of Alberta, Edmonton, Canada
[3] Department of Biomedical Engineering, University of Alberta, Edmonton, Canada

ABSTRACT

Gold/silver (Au/Ag) bimetallic nanoclusters (shell) on silica (Au/Ag @ SiO_2) were synthesized by layer-by-layer technique. By adjusting the mole ratio of Au and Ag, the bimetallic alloy on the SiO_2 nanoshpere surface posseses tunable surface plasmon resonance. Several transmission electron microscopy (TEM) techniques have been applied to characterize the structure and morphology of the bimetallic nanoclusters, including scanning transmission electron microscopy (STEM) tomography, high angle angular dark field (HAADF) imaging, energy dispersive X-ray (EDX) spectoscopy, high resolution TEM (HRTEM) and electron diffraction (ED). The results revealed the Au/Ag alloy nanoclusters were interconnected on the surface of SiO_2 nanospheres with the nanoscale roughess varied with the mole ratio of Au and Ag.

Keywords: bimetallic nanoclusters, TEM, STEM, HAADF, EDX, HRTEM, ED

1 INTRODUCTION

Due to their optical, electronic, catalytic and physichemical properties, metal and bimetallic nanoparticles, such as Pt, Pd, Ag, Au and Fe etc., have been studied and found wide range of applications in biosensors, catalysis, in-vivo biomedical imaging etc. [1]. Au, Ag and their bimetallic nanoparticles have been also widely employed in surface enhanced Raman scattering (SERS) [2]. The Raman scattering is enhanced when a molecule makes contact with a metal nanoparticle covered surface.

The size, shape, material and surface to volume ratio are the main factors affecting the strength of enhancement. Therefore, a great deal of effort has been dedicated not only to the synthesis of metallic nanostructure to maximize the Raman enhancement, but also the proper characterization methods of the nanostructure and morphology.

TEM has been a powerful tool to characterize the morphology, crystallinity, electronic structure, chemical composition and even oxidate state of materials in nanoscale. In this paper, electron tomography and HAADF along with EDX, electron diffraction and HRTEM from lamellar sample prepared by focused ion beam (FIB) were applied to characterize the elemental distribution, the shape and the surface roughness, the molar ratio and the phase information of Au/Ag nanoclusters.

2 TEM ANALYSIS METHODS AND RESULTS

2.1 Sample Preparations and Instrumentation

The Au/Ag @ SiO_2 nanoparticles were fabricated via a three-step method. The silica colloids with better monodispersity were synthesized using well known Stöber procedure and the size of SiO_2 can be controlled ranging from nanometer to micrometer [3]. The Au nanoparticles (~ 5 nm) as seeds were attached to SiO_2 nanospheres. At last, Au/Ag nanocluseters were formed on the surface of SiO_2 by sequentially reducing the Au and Ag from aqueous solution of $HAuCl_4$ and $AgNO_3$. By adjusting the Au and Ag molar ratios, the nanoscale roughness of Au/Ag nanoclusters has been obtained and the tunable SERS signals are feasible. In this work, we mainly focus on the characterization and discussion of the sample with mole ratio of Au:Ag = 50:50 on SiO2 nanospheres.

To exam the nanoparticles in TEM, one drop of the Au/Ag @ SiO_2 aqueous solution was applied on holey carbon film supported TEM grids and the excess solution was blotted away using filter paper. A thin lamellar TEM sample was also prepared using a FIB instrument (Hitachi NB5500). To prepare the Au/Ag @ SiO_2 sample for lamellar, one drop of sample solution was placed on Si wafer and the excess solution was blotted away using filter paper. Then a thin layer of carbon was supttering coated on Au/Ag @ SiO_2 particles before milling by Ga^+ ion beam. The final lamellar was about 40 nm thick and was plugged out from the center of nanosphere.

JEOL 2200FS TEM equipped with a Schottky electron emitter combined with a cryo polepiece for cryo-tomography with large tilting angles and an in-column

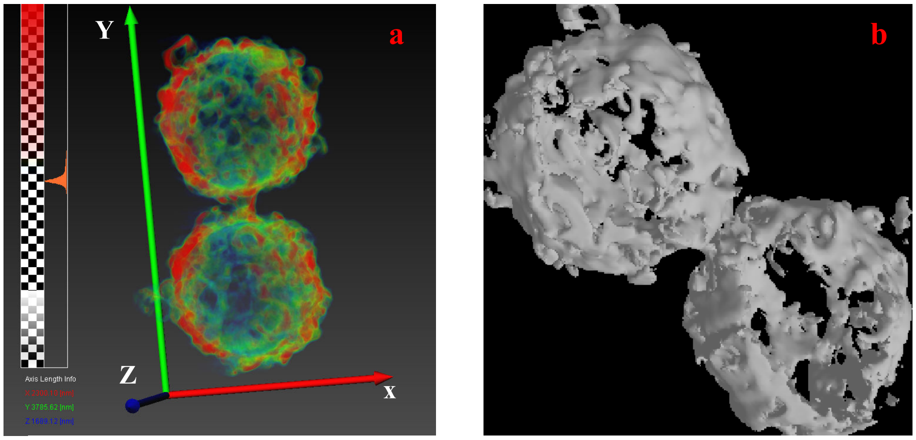

Figure 1: a) A 3D reconstructed volume view of Ag/Au nanoclusters on SiO_2 nanospheres; b) Isosurface display of 3D reconstructed Ag/Au nanoclusters.

energy filter was applied for all electron microscopy analysis. TEMography™ software package was used for recording, reconstructing and visualizing the tomography data. EDX spectra was collected and analyzed using INCAEnergy software from Oxford Instrument.

2.2 Electron Tomography (ET)

The well dispersed Au/Ag @ SiO_2 nanoparticles on a carbon film with a large tilting angle range were used for electron tomography. The tilt-series of STEM bright field images of nanopartilces was obtained by tilting the sample

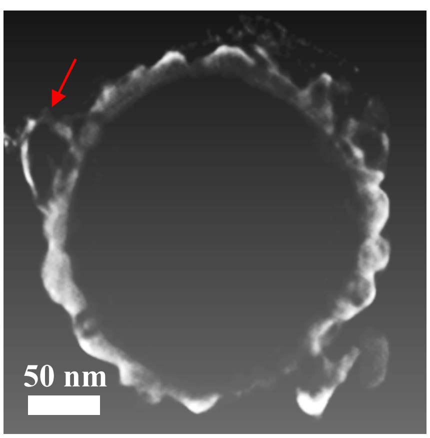

Figure 2: The slice view of the 3D reconstructed data along Z direction of Au/Ag nanoclusters on SiO_2.

holder from + 75° to - 75° with 2° increments. The beam probe was 1 nm and the image size was 512 × 512 pixels with dwelling time for each pixel of 100 µs. The raw tilt – series data was fine aligned before reconstruction. The filtered backprojection (FBP) method was used for reconstruction. Figure 1a shows that the reconstructed 3D volume tomography data. Movies of the reconstructed 3D data will be presented at the meeting session. Figure 1b shows the isosurface display of Au/Ag nanoclusters where the roughness was demostrated. Through slicing view along Z direction, the Au/Ag nanoclusters were found to be interconnected and formed the islands close to the SiO_2 core surface; also onion - like shape clusters (arrow 1) were shown on the surface of the shell, as shown in Figure 2.

2.3 STEM HAADF Imaging and EDX

The signal recorded in HAADF-STEM image is proportional to Z^n (Z is the atomic number and n~1.6 considering the screening effects from electrons in the atom) when the inner collection angle is greater than 50 mrads [4]. Figure 3a, a typical HAADF image of Au/Ag @ SiO_2 lamellar prepared by FIB, shows four typical regions as marked and numbered. Based on the atomic number contrast, the central region marked as number 3 is the SiO_2 core. The nanoclusters, marked as number with a bright contrast, were interconnected on the surface of SiO_2. While the nanoclusters marked as number 2 which has a weaker contrast were on the outside of nanoclusters in region 1. And there were some onion – like shape region marked as region 4.

To further exam the composition in different regions, EDX spectra were collected by positioning the beam probe (1nm) at the specified regions. The EDX spectra as shown in Figure 3b and c indicated the nanoclusters both in region 1 and 2 were made up of metallic Au and Ag but with different ratio of Au and Ag. Other elements shown on the spectra were from the FIB ion source, protection coating and TEM grid, such as Ga, W and Cu. In average, the presence of about 65 % Au and 35 % Ag for nanoclusters was indicated in region 1, called Au-rich region; while about 40 % Au and 60 % Ag in region 2, called Ag-rich region. From the EDX data, it indicates that the Au/Ag bimetallic nanostructure is formed on the shell with the layered structure.

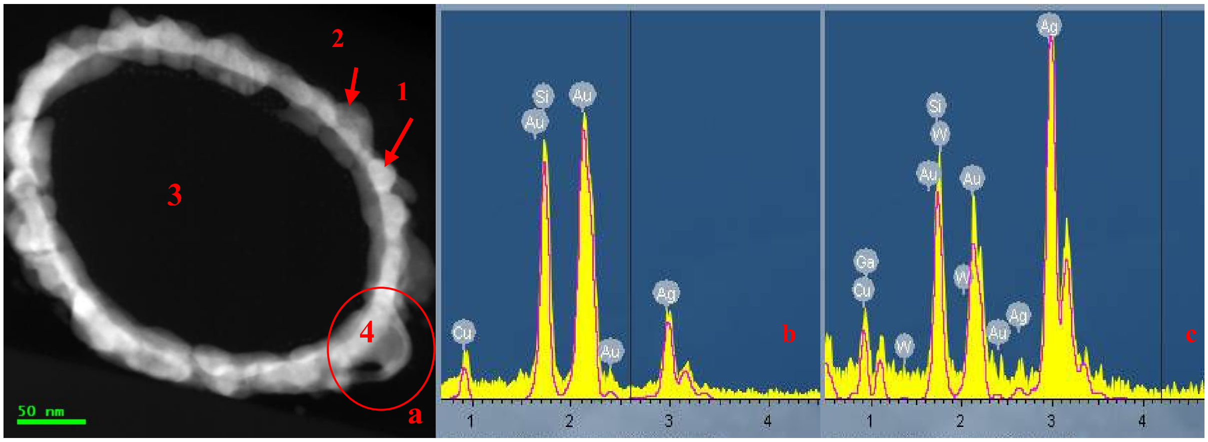

Figure 3: a) A typical HAADF image of the lamellar from one Au/Ag @ SiO_2 particle prepared by FIB. Arrow 1 – Au enriched, arrow 2 – Ag enriched region, region 3 – SiO_2 and region 4 – onion -like shape; b) one typical EDX spectrum from region 1; c) one typical EDX spectrum from region 2.

2.4 Electron Diffraction

As indicated in HAADF images, in terms of composition, the Au/Ag nanoclusters on the shell form two layered regions: Au-rich and Ag-rich region. To investigate the crystal structure in different regions, selected area diffraction (SAD) and nano beam diffraction (NBD) were performed. The SAD was obtained from a whole Au/Ag @ SiO_2 particle, while the NBD was acquired from about 5 nm region where the beam was positioned on single Au/Ag nanocluster. Figure 4a shows a typical SAD pattern and the calculated d–spacings along with the plane indices (hkl) corresponding to the rings from center to periphery in the pattern are summarized in Table 1. Compared to the crystallography database, the Au/Ag nanoclusters are still in a FCC structure which is same as Au or Ag. There were also extra diffraction spots (as arrow) in SAD pattern with a d-spacing of 2.9 ± 0.1 Å and 2.7 ± 0.1 Å, respectively. These interplanar distances are significantly larger than the largest interplanar distance of FCC Au or Ag. And it may come from Ag_2O [5]. Figure 4b shows the HRTEM image of Au/Ag nanoclusters in region 4 which includes the nanoclusters interconnected on the SiO_2 surface and the onion-like shape clusters. The lattice images indicates the nanoclusters are crystalline. A typical NBD pattern as shown in figure 4c was collected from the region in red circle marked in figure 4b. The largest d – spacing is 2.4 Å. Also, no d – spacing larger than 2.4 Å was observed from the freshly made samples. Therefore, the extra diffraction spots may come from the Ag oxides which is on the surface of shell exposed to the atmosphere for a long time before the TEM examination [6, 7].

No. of ring	d-spacing [Å]	h k l
1	2.3 ± 0.1	111
2	2.0 ± 0.1	200
3	1.4 ± 0.1	220
4	1.2 ± 0.1	311

Table 1: The d-spacing of Au/Ag nanoclusters calculated from SAD.

3 SUMMARY AND DISCUSSIONS

In summary, several TEM techniques have been applied to comprehensively and successfully analyze the Au/Ag nanoclusters. ET results demonstrated that the degree of the coverage and roughness of nanoclusters on the SiO_2 nanospheres. Other samples with the ratio of Ag : Au = 5 : 95 were also characterized and the surface was smoother than the sample with the ratio of Ag : Au = 50 : 50. Also the surface to volume ratio can be measured from the 3D reconstruction data using a certain segregation method. Through the slice view of 3D reconstructed data, the internal nanostructure has been also revealed, for example, the nanoclusters were interconnected in both solid form close to the SiO_2 core as well as the onion-like shape on the surface of the shell. While the composition distribution of Au and Ag can not be localized by ET in this case.

The benefit of FIB prepared lamellar sample is that the localized chemical composition and nanostructure can be revealed when the STEM HAADF imaging, HRTEM , NBD and EDX techniques are incorporated. Thus it helps to understand the growth mechanism and control the growth of alloy. Through the comprehensive analysis, the Au/Ag nanoclusters has been proved as alloy but not homogeneous. The Au-rich alloy is formed around the Au seeds and interconnected as islands. Then the Ag-rich alloy grow between the islands to fill the gap. When the ratio of Au and Ag is lower, the surface of Au/Ag @ SiO2 is more rough and the surface to volume ratio increases. Also more

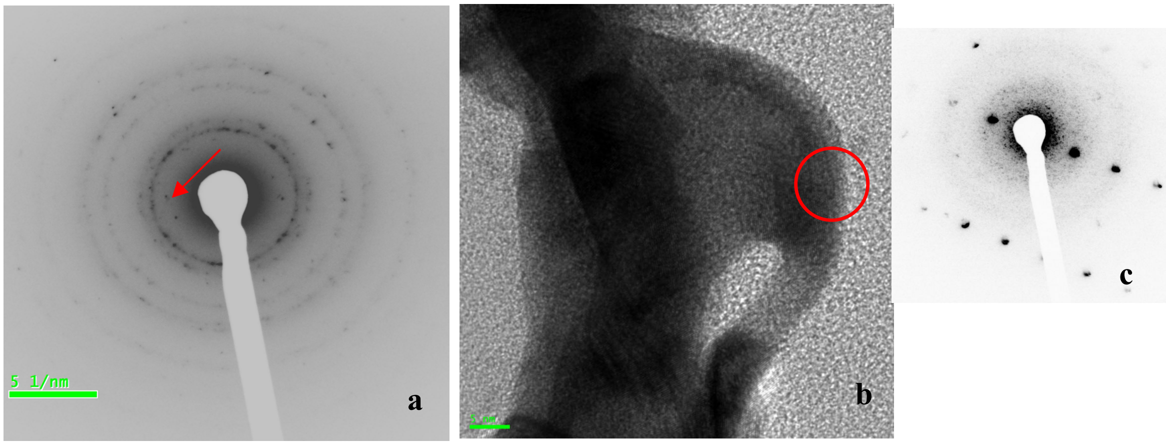

Figure 4: a) A selected area diffraction pattern of Au/Ag @ SiO_2; b) A HRTEM image of Au/Ag nanocluster with onion-like shape; c) A NBD pattern obtained from the area marked as red circle in b.

Ag grows on the surface; which is consistent with the optical measurement of surface plasma absorption. Hence, the SERS signal is enhanced which might be due to the increase of surface to volume ratio and the percentage of Ag.

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