SHAPE CONTROLLED SYNTHESIS OF AU NANOPARTICLES

Sung Ik Yang, Seon Ho Kim, S un Young Park
College of Environment and Applied Chemistry, Materials Research Center for Information Display, Kyung Hee University, Yongin, 449-701, Republic of Korea
siyang@khu.ac.kr

Inorganic nanoparticles have attracted great attention to the scientific community due to their potential applications in nanoelectrons, nanophotonics, chemical sensing, and biological imaging [1-3]. In particular, noble metal nanoparticles have been of considerable interest since chemical and physical properties of metal nanoparticles are strongly influenced by the size and shape due to surface and quantum size effect [4,5]. For example, the absorption wavelength of the surface plasmon band of spherical Au nanoparticles is 530 nm, whereas that of the rod shape of Au nanoparticles with aspect ratio 4 is 780 nm.
Xia *et al*. have prepared single crystal cubes and tetrahedrons through selective etching and dissolution processes [6,7]. Murphy and El-Sayed group have synthesized various aspect ratio of Au nanorods via seed-mediated growth method [8-10].
We have synthesized Au nanoparticles with controllable shape via seed-mediated growth method with modification and characterized their optical properties as a function of shape. We examine the nucleation and growth conditions to understand the growth mechanism and reaction parameters that determine the shape of nanoparticles. To synthesize various shapes of Au nanoparticles, we prepared Au seed particles by reducing gold chloride with $NaBH_4$ in the presence of cetyltrimethylammonium bromide (CTAB). We prepared aqueous growth solution with $HAuCl_4$, ascorbic acid (AA), $AgNO_3$ and CTAB. Tehn we added an appropriate quantity of Au seed to the aqueous growth solution. The shapes of Au nanoparticles strongly depend on the ratio of the concentration of seed solution, AA and CTAB and could be controlled from sphere to square to star by varying the ratio of seed over AA and CTAB.
The synthesized Au nanostructures were observed by TEM. The bright-field plan-view images for Au nanoparticels with sphere, cube, and multipod are shown in Fig. 2. In Fig. 2 (B), the particles synthesized at room temperature are round and have an average diameter of around 13 nm. By controlling the additional AA quantity, Au particles with various shapes were observed; adding 0.6 ml AA resulted in mono-dispersed cube nanoparticles with 17 nm in diameter. As we increased the concentration of $AgNO_3$, we could obtain multipod with 21 nm in diameter.
Fig. 1 shows the electronic absorption spectra of Au nanoparticles in hexane solutions as a function of shape, which is consistent with previously reported results. According to the Mie theory [11], the decrease in the size gives rise to intense surface plasmon absorption around 530 nm due to the coherent oscillation of the free electrons from the surface of the silver nanoparticles. Plasmon absorption maximum slightly shifted to red at 550 and 560 nm upon forming cube and multi-pod, respectively. In particular, the absorption spectrum of star shaped has two strong plasmon absorption bands at 560 and 850 nm which is related with the transverse and longitudinal plasmon absorption, respectively of Au nanoparticles.
In conclusion, we have synthesized various shape of Au nanoparticles via seed-mediated growth and characterized their optical properties.

References:

[1] Y. Huang, X. Duan and C. M. Lieber, Science **291** (2001) 630.
[2] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requichia and H. A. Atwater, Adv. Mater. **13** (2001) 1501.
[3] R. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, Science **294** (2001) 1901.
[4] M. A. El-Sayed, Acc. Chem. Res. **34** (2001) 257.
[5] N. Toshima, M. Kuriyama, Y. Yamada and H. Hirai, Chem. Lett . **10** (1981) 793.

[6] B. Wiley, T. Herricks, Y. Sun and Y. Xia, Nano Lett. **4** (2004) 1733.
[7] S. H. Im, Y. T. Lee, B. Wiley and Y. Xia, Angew. Chem. Int. Ed. **44** (2005) 2154.
[8] G. Linfeng, C. J. Murphy, Chem. Mater. **17** (2005) 3668.
[9] Nikoobakht, B.; El-Sayed, M. A. Chem. Mater. **15** (2003) 1957.
[10] T. K. Sau, C. J. Murphy, C. J. Langmuir 20 (2004) 6414.
[11] G. Mie, Ann. Phys. **25** (1908) 329.

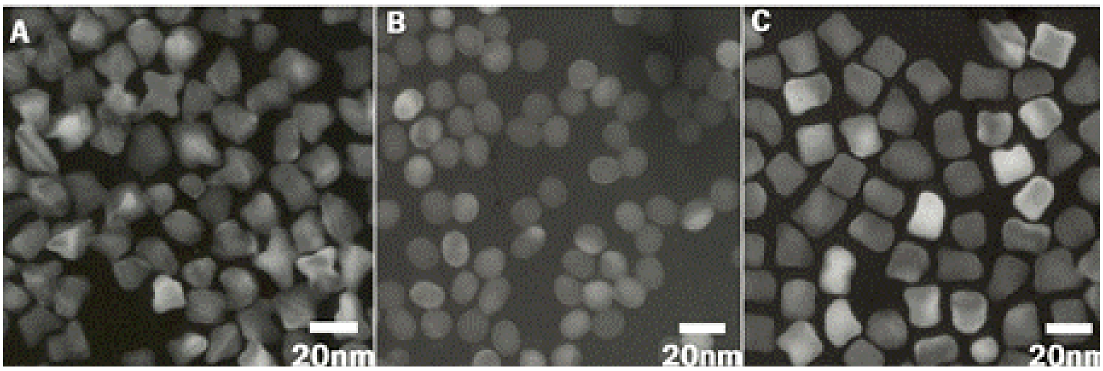

Figure 1. TEM images of (A) mulipod, (B) sphere, and (C) cube Au nanoparticles

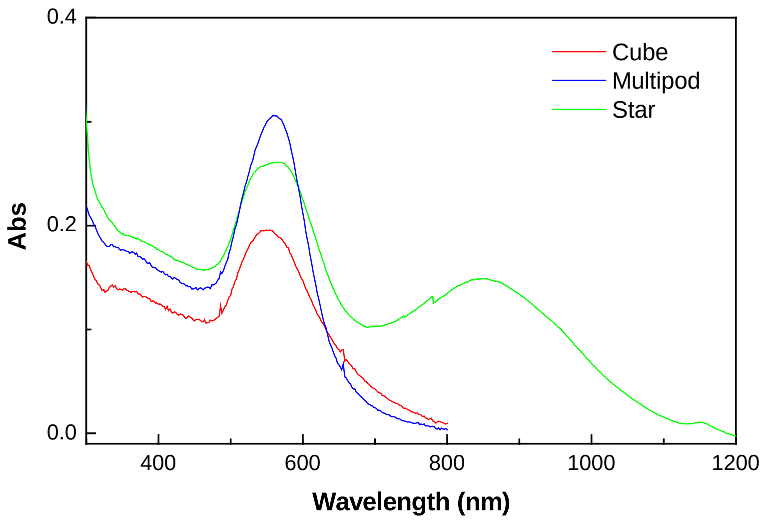

Figure 2. Absorption spectra of cube, multipod, and star shaped Au nanoparticles.