Tuning of size and shape of the gold nanoparticles by controlling the pH during seed mediated growth

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Gold-nanoparticles (GNPs) were found to have extraordinary electro-catalytic properties for potential applications in a number of fields. Two major parameters control the chemical, physical, and electro-catalytic properties of the GNPs, i.e., the particle size and shape (in other words, the crystallographic orientation) of the prepared nanometer scale gold (Au). Currently, shape-controlled synthesis of nanoparticles has been achieved either by using geometric templates or by using some additives, such as polymers or inorganic anions, to regulate the particle growth. A common approach of controlling the morphology of nanoparticles is the seed-mediated growth method. Hydroxylamine (NH_2OH) and ascorbic acid are common reducing agents used in the seed-mediated growth of gold nanoparticles. The particle size can be manipulated by varying the concentration ratio of $H[AuCl_4]$:seeds. In either one-step or step-by-step preparation of large-size spherical gold nanoparticles through the seed-mediated growth process, a certain percentage of non-spherical by-products such as nano-rods, triangles, and hexagonal nano-plates were frequently observed [1, 2].

In this work, we describe a way out for the preparation of GNPs with homogeneous shape resolving the problem of simultaneous formation of non-spherical by-products during the seed-mediated growth by controlling the pH of the growth solution. GNPs were first electrodeposited onto a clean glassy carbon (GC) electrode. Seed-mediated growth of the electrodeposited GNPs was performed in a solution of $H[AuCl_4]$ at various pHs (5.0 to 0.5) using NH_2OH as a reducing agent. The nucleation (i.e., formation of the new seeds) was found to dominate over growth process (i.e., enlargement of the seed particles) at higher pH during NH_2OH seeding, whereas only growth was recognized at low pH (0.5). Non-spherical by-products were noticed when the seed-mediated growth was performed at higher pHs, but interestingly, only spherical-shaped GNPs were evident from the SEM studies when the growth was performed at pH 0.5. The reductive desorption of a chemisorbed short-chain thiol, i.e., cysteine, from the GNPs prepared at different pHs revealed a high ratio of Au(111) facet (97%) for the GNPs prepared at pH 0.5. A probable mechanism for the seed-mediated growth at low pH was also proposed.

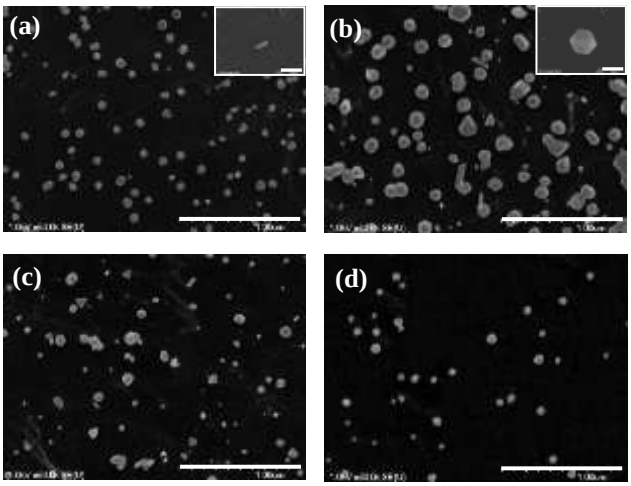

Figure 1. SEM images after growth of the GNPs at various pHs: (a) 3.6, (b) 2.6, (c) 1.4, and (d) 0.5.

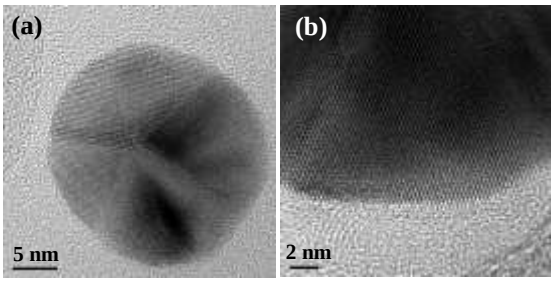

Figure 2. (a) HRTEM image of a single GNP. (b) represents the HRTEM image of an edge of a gold nano-decahedron.

References:

1. M. R. Rahman, F. S. Saleh, T. Okajima, T. Ohsaka, *Langmuir* **2011**, 27, 5126.
2. N. R. Jana, L. Gearheart, C. J. Murphy, *Langmuir* **2001**, 17, 6782.