Flow Synthesis of Silica@Au Core-Shell Particles by Using Microreactor

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[Introduction]

Silica@Au core-shell type particles are quite attractive because of their unique optical properties and potential biomedical applications including imaging, sensing, photothermal therapy, and gene-silencing technology. A widely-used preparation technique of Au nanoshells is the seed-mediated growth, which is composed of three steps: surface modification of core silica particles, Au seeds decoration of the modified silica surface, and the shell growth by reduction of Au ions on the Au seeds. Although this technique allows good control in the shell thickness, it takes a long time on the order of days to complete the preparation process [1]. In the present study, we develop a flow synthetic process by applying a microreactor separately to the Au seeds decoration and the shell growth processes [2].

[Results and Discussion]

In the decoration process, we mixed a reducing agent ($NaBH_4$) and a silica suspension containing $HAuCl_4$ with a microreactor to promote the reduction of Au ions. Silica particles were modified with 3-amino-propyltrimethoxysilcane (APTS) before the decoration process. The microreactor we used is a central collision type in which two inlet fluids intensively collide with each other into small segments to realize quick and homogeneous mixing [3]. As a typical example, Figure 1a shows resultant gold-decorated silica particles prepared with the microreactor. Monodispersed gold nanoparticles uniformly cover silica particles, and unattached gold nanoparticles were not observed through TEM observation, which would be due to preferential nucleation on silica particle surface enabled by the homogeneous mixing of the microreactor. In contrast, batch type synthesis resulted in polydispersed gold nanoparticles randomly attached on silica particles (Fig.1b).

In the shell growth process, we mixed a reducing agent ($NaBH_4$) and a gold-decorated silica particle suspension containing $[Au(OH)_4]^-$ with the microreactor. However, complete shells on core silica particles did not form although gold nanoparticles grew larger and approximately 80 % of silica surface was covered (Fig.2a). A higher gold ion concentration resulted in the self-nucleation of gold nanoparticles in the bulk phase, suggesting that $NaBH_4$ is too strong a reducing agent to form shells. We accordingly used a milder reducing agent ($NH_2OH \cdot HCl$) instead of $NaBH_4$ and successfully obtained complete gold nanoshells with the thickness of 17 nm (Fig.2b). In this manner, the microreactor is demonstrated to enable one-step fabrication of gold decorated silica particles and gold nanoshells by directly reducing Au ions in the presence of core particles, without any self-nucleation of gold nanoparticles in the bulk phase, which remarkably shortens the preparation period.

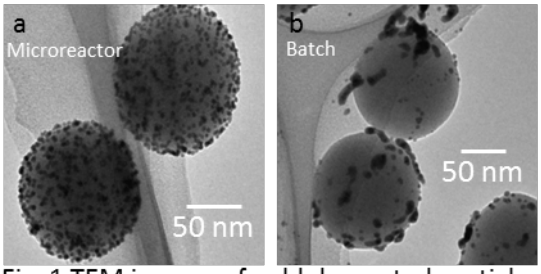

Fig. 1 TEM images of gold decorated particles

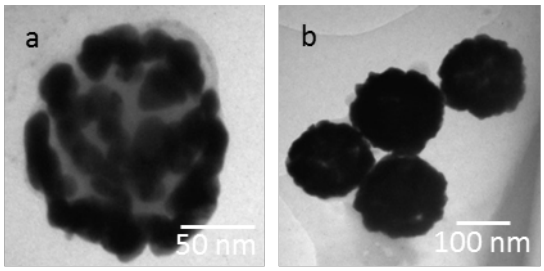

Fig. 2 SiO_2@Au particles (a) $NaBH_4$ (b) NH_2OH

[References]

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