Flow Synthesis of Plasmonic Nanoshells using a Microreactor

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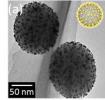
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Silica@gold core-shell nanoparticles consist of silica cores and gold nanoshells. Because of their plasmon resonance absorbance of near-infrared rays, they can find applications in a wide range of fields such as medical imaging and photothermal therapy. The absorption peak depends on the ratio of shell thickness to core size. Controlling the structure of silica@gold core-shell nanoparticles is of crucial importance. A widely-used preparation method of Au nanoshells is the seed-mediated growth, which is composed of three steps as follows: the surface modification of silica cores to increase affinity with Au, producing the formation of core-shell clusters (CSCs), in which silica cores are decorated with Au nanoparticle seeds, and the shell growth by reducing Au ions on the Au seeds. This method allows high coverage of gold seeds and good control in the shell thickness, although it is typically operated in a batch type process which takes about 1 week to complete the procedure. Hence, it is required to establish a facile and versatile method.

Here we developed a flow process using a microreactor to synthesize CSCs and silica@Au core-shell nanoparticles. The microreactor we applied is central collision type, which realizes quick and homogeneous mixing by intensively bombarding two inlet fluids. ^[2] In the process to synthesize CSCs, we mixed a surface-modified silica suspension containing Au ions with a strong reducing agent, NaBH₄, in the microreactor to in-situ reduce Au ions on core silica surfaces. Fig.1a shows a typical TEM image of resultant particles, in which core silica particles are uniformly decorated with monodispersed Au particles. Because a batch synthesis with the same procedure resulted in nonuniform decoration of polydispersed Au particles and also produced unattached Au nanoprticles, high mixing performance provided by the microreactor enabled one-step synthesis of CSCs. The microreactor is effective to produce

Au nanoshells as well. We successfully synthesized uniform Au nanoshells by mixing CSCs containing Au ions with a mild reducing agent, ascorbic acid, as shown in Fig.1b. By taking advantages of the microreactor, we established the flow process to synthesize CSCs and silica@Au core-shell nanoparticles, which dramatically shorten the synthetic period compared to batch processes.^[3]



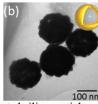


Fig. 1 (a) Gold-decorated silica particles (b) Gold nanoshells

As an application of this process, we examined silica@Pt core-shell nanoparticles. Because the wide use of Pt as a catalyst is prevented because of its preciousness, producing Pt nanoshells can reduce the cost and promote the utility. We applied the above-mentioned procedure and synthesized silica@Pt core-shell nanoparticles with the shell thickness of $15 \sim 20$ nm.

References

- 1. S.J. Oldenburg, R.D. Averitt, S.L. Westcott, and N.J. Halas, *Chem. Phys. Lett.*, **288**, 243 (1998)
- 2. H. Nagasawa, N. Aoki, and K. Mae, Chem. Eng. Technol., 28, 324 (2005)
- 3. S.Watanabe, T. Hiratsuka, Y. Asahi, A. Tanaka, K. Mae and Minoru T. Miyahara, *Part. Part. Syst. Charact.*, **32**, 234 (2015).