Electronic Supplementary Information

Laser-induced fabrication of $Ag@SiO_2@Ag$ sandwich nanostructures having enhanced catalytic performances

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Experimental section

Materials

Chemicals were used as received: $AgNO_3$ (99.9%), polyvinylpyrrolidone (PVP, Mw = 55,000), KBH_4 (99.9%), and tetraethyl orthosilicate (TEOS, >98%) from Sigma-Aldrich; 25% ammonia water from MERCK-Schuchardt; rhodamine B (RhB) from Wako Pure Chemical; ethanol (>99.0%) and ethylene glycol (EG, 99%) from Daejung Chemicals. Ultrapure deionized water (>17 MΩ cm) from a Millipore Milli-Q system was used throughout the experiments.

Preparation of silver nanoparticles

50 mg of $AgNO_3$ and 270 mg of PVP were added to the 20 mL of EG, which was then heated in an oil bath at 130 ℃ for 1 h under vigorous stirring. The mixture changed into the yellow-ochery color, indicating that silver nanoparticles were generated. The resultant product was then cooled to room temperature.[7]

Preparation of Ag@SiO_2@Ag-seed nanoparticles

9.4 mL of the above prepared colloidal solution of silver nanoparticles was added into a mixture containing 25 mL of ethanol, 4.0 mL of deionized water, 70 μL of TEOS, and 4.0 mL of ammonia water under vigorous stirring. After being stirred for 1 h at ambient temperature, the product was separated by centrifugation at 8000 rpm, washed with ethanol three times, then dispersed in 40 mL of ethanol to produce a ethanol colloidal solution of Ag@SiO_2@Ag-seed nanoparticles. Small silver nanoparticles tethered on the silica surfaces of Ag@SiO_2@Ag-seed nanospheres would be used as seeds for the growth of silver overlayers.

Laser-induced fabrication of Ag@SiO_2@Ag sandwich nanospheres and hollow SiO_2@Ag nanostructures

Nanosecond laser pulses of 355 nm having an average energy of 5.0 mJ from a Q-switched Quantel Brilliant Nd:YAG laser of 6 ns were irradiated at fluence of 5.3 mJ/cm^2 with a spot diameter of 11 mm to 3.0 mL of the above prepared but not-centrifuged ethanol colloidal solution of Ag@SiO_2@Ag-seed nanoparticles contained in a quartz cell having a path length of 10 mm and stirred vigorously for 30 min to produce Ag@SiO_2@Ag sandwich nanospheres and for 60 min to produce hollow SiO_2@Ag nanoparticles. Then, the resulting colloid was centrifuged, washed with ethanol several times, and dispersed in 3.0 mL of ethanol to produce the ethanol colloidal solution of Ag@SiO_2@Ag sandwich nanoparticles or hollow SiO_2@Ag nanostructures.

Catalytic performances

The catalytic activities of silver-based nanocatalysts were tested for the reduction reaction of rhodamine B in the presence of 1.1 mM KBH_4. In a typical experiment, 0.10 mL of an ethanol colloidal solution containing silver-based nanocatalysts was added into 2.0 mL of 20 μM RhB(aq) and 1.0 mL of deionized water contained in a polyphenyl cell having a path length of 10 mm, and then 0.40 mL of 10 mM KBH_4(aq) was added rapidly. The absorption spectral changes of RhB in the catalytic reaction mixture, where the concentration of precursor $AgNO_3$ was 0.10 mM, were measured at scheduled intervals; the color of the mixture vanished gradually, indicating the progressive reduction of rhodamine B. The catalytic activity of silver-based nanocatalysts was evaluated by monitoring the optical density of RhB at 554 nm.

Characterization

UV-visible absorption spectra were recorded by using of a Scinco S-3000 spectrophotometer, and TEM images were taken with a Hitach H-7600 microscope. While STEM mages and EDX elemental profiles were measured using a JEOL JEM-2100F microscope, HRTEM images were taken on a JEOL JEM-300F microscope.

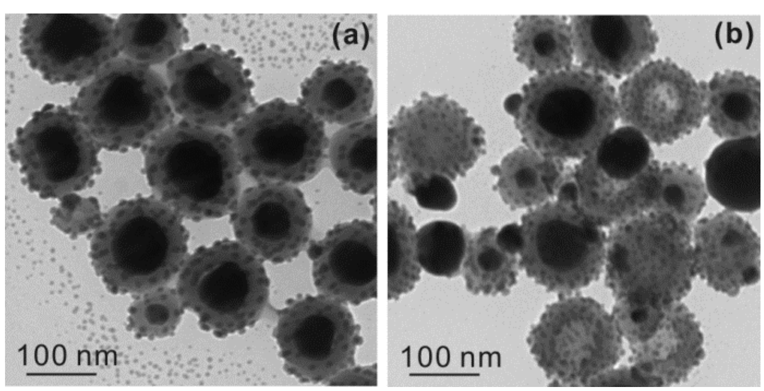

Fig. S1 TEM images of Ag@SiO_2@Ag-seed nanoparticles irradiated with 355 nm laser pulses for 15 (a) and 45 min (b).

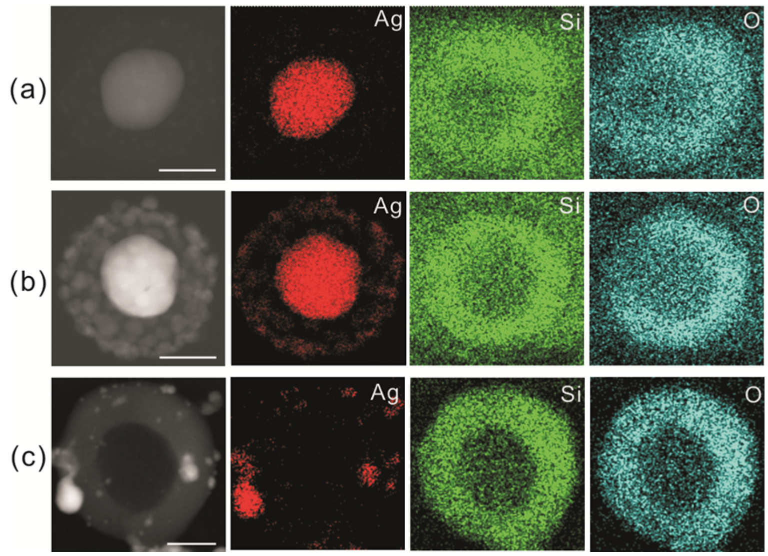

Fig. S2 STEM images (left) and EDX elemental maps (right) of a Ag@SiO$_2$@Ag-seed nanoparticle after irradiation with 355 nm laser pulses for 0 (a), 30 (b), and 60 min (c). Note that each scale bar indicates 50 nm and that the original particle transformed into the particle of (b) or (c) is different from the particle of (a).

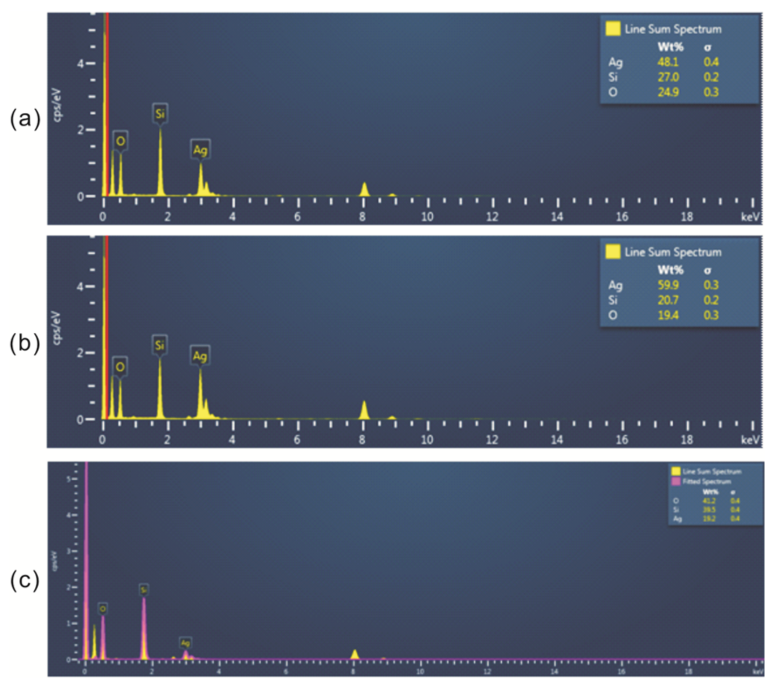

Fig. S3 EDX analysis spectra of Ag@SiO$_2$@Ag-seed (a), Ag@SiO$_2$@Ag (b), and hollow SiO$_2$@Ag (c), scanned along the indicated lines of the insetted STEM images of Fig. 3, whose molar percentages of silver have been observed to be 48.1%, 59.9%, and 19.2% respectively.