Supplementary Information

Shape Effect of Ag-Ni Binary Nanoparticles on Catalytic Hydrogenation Aided by Surface Plasmon

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Experimental procedures

Synthesis of Ag-Ni snowman nanoparticles
Nickel acetylacetonate (81 mg; Sigma Aldrich, 90%) and silver acetylacetonate (40 mg; Sigma Aldrich, 98%) were dissolved in mesitylene (10 ml; Sigma Aldrich, 98%). Hexadecylamine (25 equivalents relative to the Ni precursor; Sigma Aldrich, 90%) was dissolved in mesitylene (10 ml). The hexadecylamine solution was mixed with the metal precursor solution and trioctylphosphine (0.7-1.8 equivalents relative to the Ni precursor; Sigma Aldrich, 90%) was injected under vigorous stirring. The resulting mixture was placed in a Teflon liner (30 ml) and sealed in the bomb of an autoclave that was pressurized to 10 bar with hydrogen gas. The autoclave was held at 140 °C for 24 hrs. The nanoparticle products were washed with toluene and gathered using magnetic force.

Synthesis of Ag@Ni core-shell nanoparticles
Ag@Ni core-shell nanoparticles were synthesized using a literature protocol. Briefly, nickel acetylacetonate (108 mg), silver nitrate (20 mg; Sigma Aldrich, 99+%), and triphenylphosphine (27 mg; Sigma Aldrich, 99%) were mixed with oleylamine (7 ml; Aldrich, 70%) under vigorous stirring in a round bottom flask. The mixture was degassed at 50 °C and heated to 200 °C under an argon atmosphere. The resultant nanoparticles were cooled to room temperature and centrifuged using acetone as an antisolvent. Ni spherical nanoparticles were synthesized using the same method except that 140 mg Ni precursor and no Ag precursor was used.

Characterization
The shape and composition of the Ag-Ni binary nanoparticles were investigated using HR-TEM and HAADF-STEM (TECNAI and JEOL). A powder X-ray diffractometer (SmartLab, RIGAKU) was used to investigate the crystalline structure of the nanoparticles. Optical properties of the Ag-Ni binary nanoparticles were evaluated using UV-Vis spectrometer (S-
3100, SCINCO) for absorption spectra and photoluminescence spectrometer (PC1, ISS) for emission spectra. XPS (K-alpha, Thermo U. K.) equipped with a monochromatic Al Kα X-ray source (energy resolution: 0.5eV FWHM) was used to measure the surface property of the nanoparticles. Binding energies were calculated using the maximum intensity of the advantageous C 1s signal at 285 eV as a reference. Elemental analysis was carried out using an inductively coupled plasma optical emission spectrometer (ICP-OES 720, Agilent).

**Catalytic activity test (4-nitrophenol hydrogenation)**

4-nitrophenol (Aldrich, 99%) was dissolved in isopropyl alcohol (Duksan) to a concentration of 2 mM. It should be noted that nonpolar solvents did not show distinct UV peaks when 4-nitrophenol was dissolved. NaBH₄ (Aldrich, 99%) was dissolved in ethanol (Duksan) to a concentration of 1 M. The binary Ag-Ni nanoparticles (0.5 mg of Ni) were dispersed in 5 ml of isopropyl alcohol. The NaBH₄ solution (5 ml) was mixed with the nanoparticle suspension for reduction of the nanoparticles. Then, 5 ml of the 4-nitrophenol solution was added to the mixture and stirred for 30 sec (t = 0). The reacting solution was sampled every 1 min (0.1 ml), diluted with 3 ml of isopropyl alcohol, and then monitored using UV-Vis spectroscopy. Light was irradiated using a 300 W Xe lamp and the distance from the light source to the reactor was 20 cm. A 5 cm thick liquid filter was located between the light source and the reactor to minimize the photothermal effect.

**FDTD calculations**

The simulation for the different shapes of the binary nanoparticles was performed by using the finite-difference-time-domain (FDTD) method. The software package of FDTD Solutions (Lumerical Solutions, Inc.) was used. The geometry shown in Fig. S2 was used for the simulation. Perfectly matched layers (PML) boundary conditions were used to obtain 3D FDTD simulation results, the mesh size was 0.25 nm, and the optical property of Ag and Ni were adopted from Palik data². Because the nanoparticles were dispersed in isopropyl alcohol for the hydrogenation, the refractive index of the medium was set as 1.3776.
**Scheme S1.** Scheme for a lattice strain-induced synthesis of Ag-Ni binary nanoparticles.
Fig. S1 TEM images with a low magnitude of typical (a) Ag-Ni snowman nanoparticles (Ag-Ni SM NPs) and (b) Ag@Ni core-sell nanoparticles (Ag@Ni CS NPs).
Fig. S2 (a-b) Schematic illustration of Ag-Ni binary nanoparticles with an average size. The size distribution was obtained from counting 225 snowman and 304 core-shell nanoparticles. (c-e) Size distribution of overall, each Ni and Ag part for the Ag-Ni SM NPs. (f-h) Size distribution of overall, Ni shell and Ag core for the Ag@Ni CS NPs. The size of the Ni thin shell and Ag core was measured from HR-TEM images, thus only 20 nanoparticles were measured.
**Fig. S3** (a) HR-TEM image of Ag-Ni SM NP. FFT patterns for (b) the Ag part noted with a blue square in (a), and (c) the Ni part noted with a green square in (a). Each pattern exhibits $<111>$ zone axis for (b) and $<120>$ zone axis for (c). (d) HR-TEM image of Ag@Ni CS NP. Powder XRD patterns for (e) Ag-Ni SM NPs and (f) Ag@Ni CS NPs with Rietveld refinements.
**Fig. S4** TEM images of Ag-Ni SM NPs synthesized with (a) 0.7, (b) 1.0, (c) 1.4 and (d) 1.8 equivalents of TOP relative to the amount of Ni precursor used. All of the nanoparticles were synthesized under the same conditions except for the amount of TOP.
**Fig. S5** XPS data of as-made Ag-Ni binary nanoparticles: Ni 2p peaks for (a) Ag-Ni SM NPs and (b) Ag@Ni CS NPs; Ag 4f peak for (c) Ag-Ni SM NPs and (d) Ag@Ni CS NPs.
Fig. S6 Effect of surface reduction on the optical properties of Ag-Ni binary nanoparticles upon the treatments by (a, b) H$_2$ bubbling or (c, d) NaBH$_4$. 
Fig. S7 XPS data of reduced Ag-Ni binary nanoparticles: Ni 2p peaks for (a) Ag-Ni SM NPs and (b) Ag@Ni CS NPs; Ag 4f peak for (c) Ag-Ni SM NPs and (d) Ag@Ni CS NPs. All samples were reduced by bubbling H₂ overnight while suspended in isopropyl alcohol.
Fig. S8 Spatial distribution of the SPR-induced enhancement of electric field intensity from FDTD calculations for (a) Ag-Ni snowman nanoparticle and (b) Ag@Ni core-shell nanoparticle. The white dotted line indicates the boundary of the nanoparticle.
Fig. S9 TEM image of Ni spherical nanoparticles used in the catalytic activity test. The average size of Ni NPs was 10.5±1.9 nm.

References