Experimental Details:

Synthesis of Ag nanocubes. The Ag nanocubes were prepared by following our well-established polyol protocol in which silver trifluoroacetate was used as an Ag precursor, and sodium hydrosulfide and hydrochloride acid served as a catalyst and an etchant, respectively.[S1] In a standard synthesis, 50-mL ethylene glycol (EG, Sigma-Aldrich) was added into a 250-mL round-bottom flask and heated under vigorous stirring in an oil bath preset to 150 ºC. When the temperature reached 150 ºC, NaHS (Sigma-Aldrich, 0.6 mL, 3 mM in EG) was quickly injected into the heated solution. After 4 min, a 3-mM HCl solution (5 mL) was injected into the mixture, followed by the addition of poly(vinyl pyrrolidone) (PVP, Sigma-Aldrich, 12.5 mL, 20 mg/mL in EG, M.W. = 55,000). The HCl solution was prepared by adding 4-μL HCl (AR, 38% by weight) into 12-mL EG just prior to the use. After another 2 min, silver trifluoroacetate (Aladdin, 4 mL, 282 mM in EG) was added into the mixture. The final solution was heated at 150 ºC in air for 1 h. Finally the reaction solution was quenched by quickly removing the heating source and moving the reactor into ice deionized (DI) water. Once cooled down, the samples were washed with acetone and then with water several times to remove most of the EG and PVP by centrifugation. The precipitate was redispersed in DI water in a bottle for synthesis of Pd nanocages.

Synthesis of Pd-Ag alloy nanocages. The Pd-Ag alloy nanocages were synthesized by modifying a protocol in literature,[S2] through galvanic replacement between Ag nanocubes and K_2PdCl_4 solution in the presence of stabilizer poly(vinyl pyrrolidone) (PVP). In a typical synthesis, 3.63-mg Ag nanocubes prepared above were added to a 250-mL round-bottom flask at a temperature of 90 ºC, followed by the addition of 50-mg PVP (M.W. = 55,000). Then DI water was added into the solution under vigorous stirring until the total volume of mixture reached 50 mL. After preheated for 20 minutes, different amounts of K_2PdCl_4 (Aladdin) solution (0.5 mM) (see Table

S1 for the specific amounts) was injected into the flask with a syringe pump at a rate of 0.25 mL/min. When the injection was completed, the reaction solution was quenched by quickly putting the reactor into cold water. Once cooled down, NaCl was added into the final solution until saturation, followed by centrifugation (10,000 rpm for 10 min). Finally the samples were washed with DI water three times by centrifugation (10,000 rpm, 10 min). The precipitate was redispersed in DI water in a bottle for further characterizations.

Synthesis of Pd nanocubes. The Pd nanocubes were synthesized by modifying a protocol in literature.[S3] In a typical synthesis, an 8.0-mL aqueous solution containing 105-mg PVP, 60-mg L-ascorbic acid (AA), and 1,200-mg KBr in a 50-mL three-neck flask was heated under magnetic stirring at 80 ºC for 10 min. Subsequently, a 3.0-mL aqueous solution of potassium palladium(II) chloride (K_2PdCl_4, Aladdin) (80 mg) was added with a pipette. The reaction was allowed to continue at 80 ºC for 3 h. The product was collected by centrifugation and washed three times with deionized water to remove excess PVP.

Synthesis of solid Pd-Ag alloy nanoparticles. The $Pd_{16}Ag_{84}$ alloy nanoparticles were synthesized by modifying a protocol in literature.[S4] Under a gentle nitrogen flow, 0.134 g of silver(I) acetate (Ag(Ac), 0.8 mmol) and 0.06 g of palladium(II) acetylacetonate ($Pd(acac)_2$, 0.2 mmol) were magnetically stirred in a mixture containing 4.5 mL of oleic acid (OAc), 0.5 mL of oleylamine (OAm), and 10 mL of 1-octadecene (ODE). The resulted mixture was heated to 85 ºC to form a homogeneous solution. Then the solution was then heated to 180 ºC at a rate of 3-5 ºC min^{-1} and kept at this temperature for 20 min. Once the reaction solution had been cooled down to room temperature, the nanoparticles were separated by adding 50 mL of isopropanol (IPA) and centrifugation (12,000 rpm, 10 min). To remove the organic impurities and precursor residues, the product was redispersed in 10 mL of hexane and then recollected by adding 40 mL of ethanol and centrifugation (12,000 rpm, 10 min).

Catalytic hydrogenation of styrene. The hydrogenation of styrene was carried out in an 18-cm tall quartz tube. 0.04-mg Pd-Ag alloy nanocages (based on the ICP-MS measurements) were added into the tube, followed by the addition of 0.2-mmol styrene. DI Water was added into the solution until the total volume of mixture reached 2 mL. A balloon filled with 100% H_2 was used to enclose the system and provide reaction gas H_2. After exhausting air with H_2, the catalytic reactions were carried out at different temperatures and/or under light illumination with different intensities. The light illumination was carried out using an Xe lamp (Solaredge 700, China) at varied power densities (0-50 mW cm^{-2}) with a 400-nm long-wave-pass cutoff filter (i.e., $\lambda > 400$ nm). The hydrogenation products of the catalytic reactions were analyzed using a gas chromatography-mass spectrometry (GC-MS, 7890A and 5975C, Agilent).

Characterizations: A drop of the aqueous suspension of particles was placed on a piece of carbon-coated copper grid and dried under ambient conditions. TEM, HRTEM and STEM images were taken on a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope or a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro Super diffractometer with Cu Kα radiation (λ=1.54178 Å). UV-vis extinction spectra were taken using an Agilent Varien Cary 60 spectrophotometer. The concentrations of silver nanoparticles were measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS) after dissolving them with a mixture of HCl and HNO_3 (3:1, volume ratio).

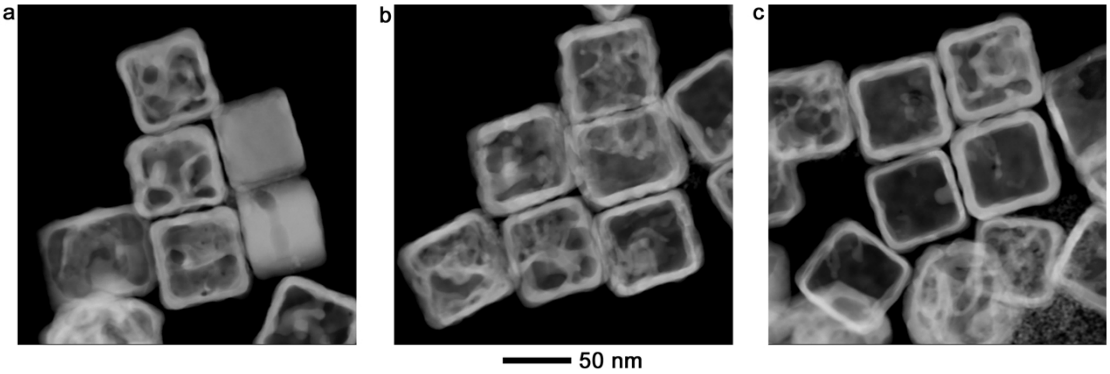

Fig. S1 STEM images of Pd-Ag alloy nanocages with different compositions (Pd wt.%): (a) 16.77%, (b) 25.84%, and (c) 44.08%.

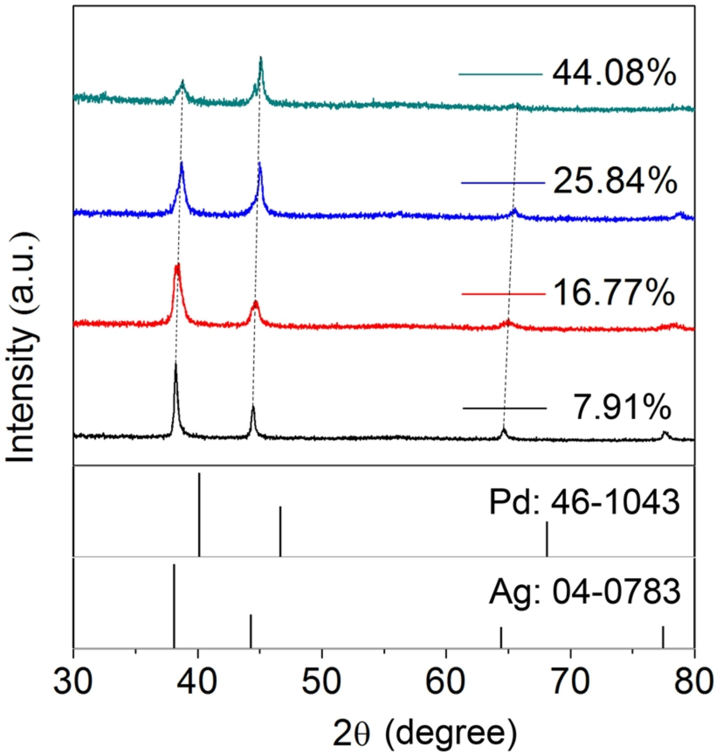

Fig. S2 XRD patterns of Pd-Ag alloy nanocages with different compositions (Pd wt.%: 7.91%, 16.77%, 25.84% and 44.08%). The standard XRD patterns of Pd and Ag with *fcc* structures are provided as references.

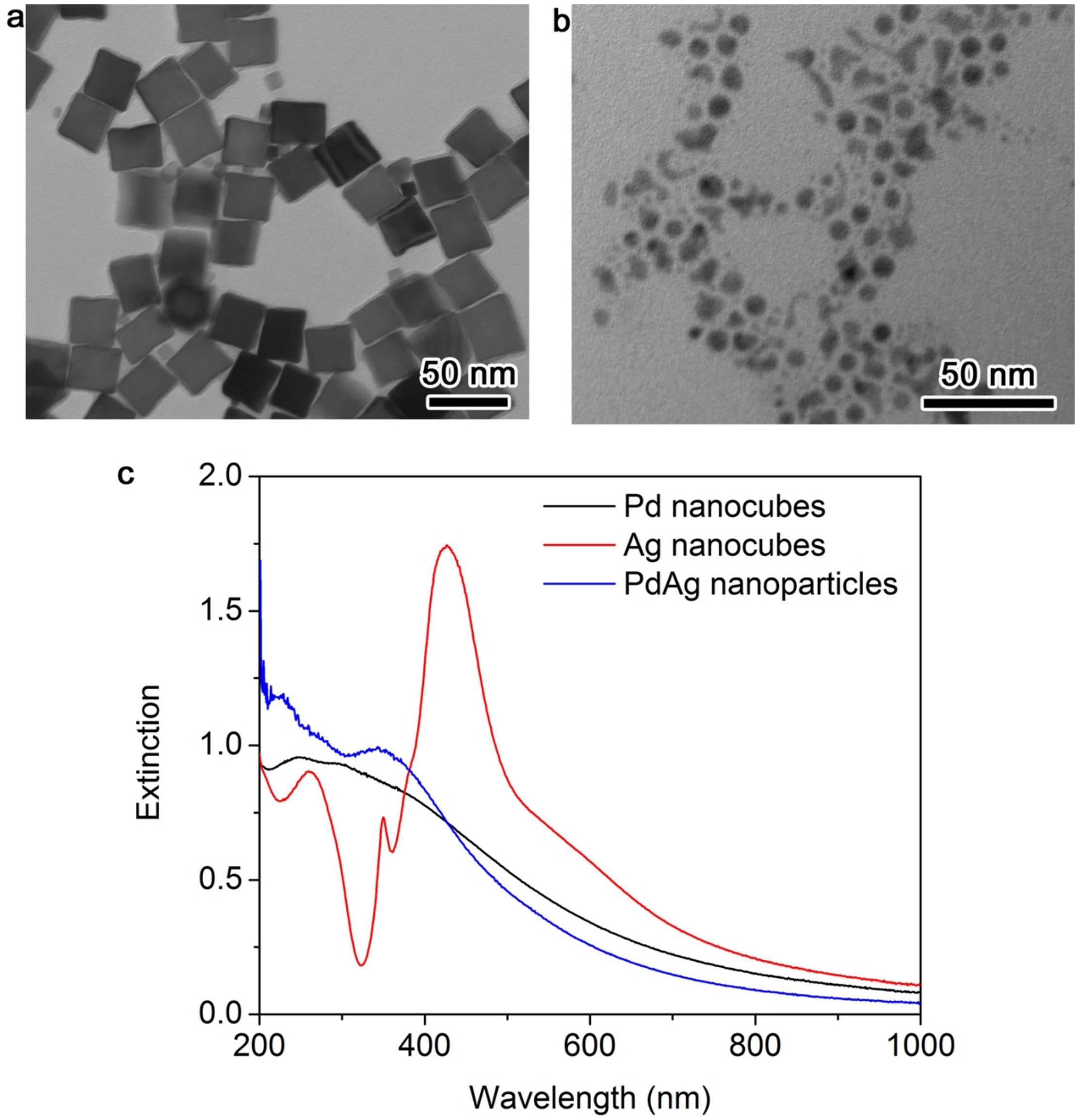

Fig. S3 TEM images of (a) 40-nm Pd nanocubes and (b) 5-nm solid $Pd_{16}Ag_{84}$ alloy nanoparticles. (c) UV-vis extinction spectra of 60-nm Ag nanocubes, 40-nm Pd nanocubes and 5-nm solid $Pd_{16}Ag_{84}$ alloy nanoparticles.

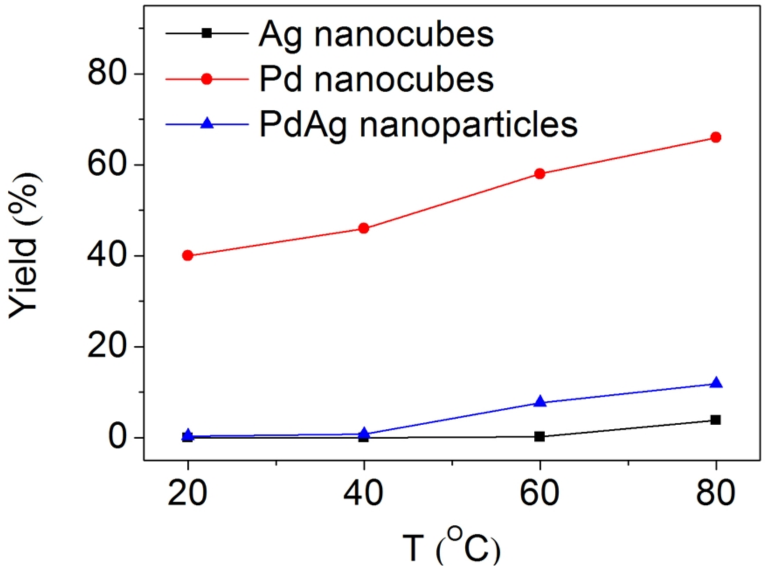

Fig. S4 Yield of ethylbenzene from the reaction catalyzed by 60-nm Ag nanocubes, 40-nm Pd nanocubes and 5-nm solid $Pd_{16}Ag_{84}$ alloy nanoparticles at 60 °C in dark. Reaction conditions: 0.2-mmol styrene, 0.04-mg Pd nanocubes, 0.09-mg Ag nanocubes (equivalent number of surface atoms) or 0.25-mg solid $Pd_{16}Ag_{84}$ alloy nanoparticles (equivalent mass of Pd), 2-mL H_2O, 1-atm 100% H_2, 1 h.

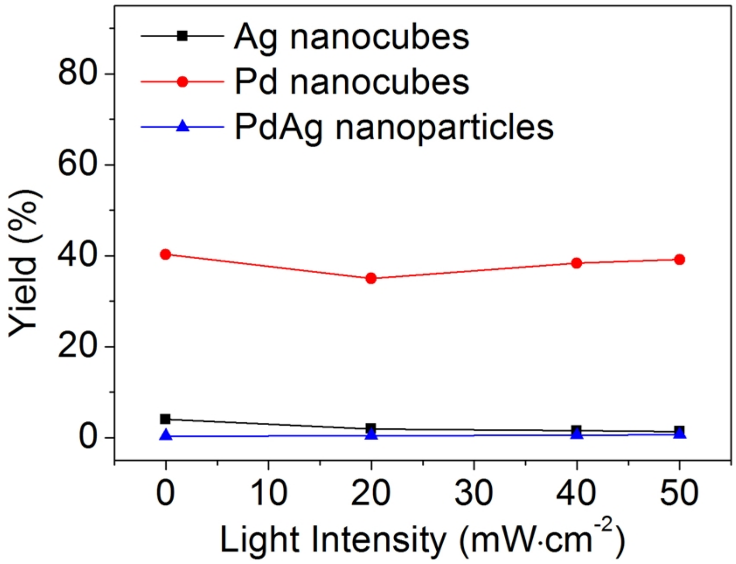

Fig. S5 Yield of ethylbenzene from the reaction catalyzed by 60-nm Ag nanocubes, 40-nm Pd nanocubes and 5-nm solid $Pd_{16}Ag_{84}$ alloy nanoparticles at room temperature under light illumination ($\lambda > 400$ nm) with different intensities (0-50 mW cm^{-2}). Reaction conditions: 0.2-mmol styrene, 0.04-mg Pd nanocubes, 0.09-mg Ag nanocubes (equivalent number of surface atoms) or 0.25-mg solid $Pd_{16}Ag_{84}$ alloy nanoparticles (equivalent mass of Pd), 2-mL H_2O, 1-atm 100% H_2, 1 h.

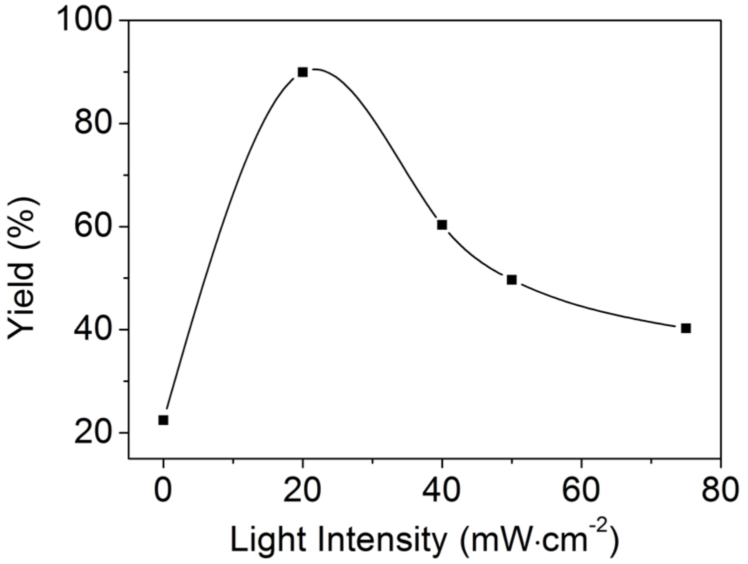

Fig. S6 Yield of ethylbenzene from the reaction catalyzed by Pd-Ag nanocages with 25.84% Pd content at room temperature under light illumination (λ > 400 nm) with different intensities (0-75 mW cm^{-2}). Reaction conditions: 0.2-mmol styrene, Pd-Ag nanocages containing 0.04-mg Pd, 2-mL H_2O, 1-atm 100% H_2, 1 h.

Table S1. The amounts of K_2PdCl_4 added into the synthesis of Pd-Ag alloy nanocages (see “Synthesis of Pd-Ag alloy nanocages” in the SI Experimental Details for other experimental parameters), and the contents of Pd in the resulted products (wt. %).

K_2PdCl_4 (μmol)	2.5	5.0	7.5	9.5	10.0	12.5
Contents of Pd (wt.%)	7.91	16.77	25.84	44.08	49.89	62.67

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