Electronic Supplementary Information

Icosahedral Gold-Platinum Alloy Nanocrystals in Hollow Silica: A High Active and Stable Catalyst for Ullmann Reaction

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Experimental Section

Chemicals and Reagents. Tetraethoxysilane (TEOS), hydrofluoric acid (HF), potassium carbonate (K_2CO_3), ammonia solution ($NH_3 \bullet H_2O$), ethanol (C_2H_5OH), sodium formate (HCO_2Na) and poly (N-vinyl-2-pyrrolidone) (PVP, M_w=55,000) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. N-[3-(trimethoxysilyl) propyl] ethylenediamine (TSD) was purchased from Fluka. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$), Chloroplatinic acid (H_2PtCl_6), iodobenzene and pentamethylbenzene were purchased from Sigma-Aldrich. Pd/C (5% Pd loading) catalyst was purchased from Alfa Aesar. Pt/C (10% Pt loading) catalyst was purchased from Fluorochem. Deionized water was used for all experiments.

Preparation of Hybrid Silica Nanospheres. The hybrid silica nanospheres with an etchable and reductive middle layer structure were fabricated via a modified Stöber method according to our previous work. [1] In a typical reaction, solution A (2 mL TEOS in 18 mL ethanol), solution B (20 mL 28 % aqueous NH_3 and 60 mL ethanol) and solution C (250 μL TSD in 10 mL ethanol) were prepared. 3 mL of solution A was added into solution B and reacted for 10 min under vigorously stirring. Then, solution C and 10 mL of solution A were added into the reaction mixture. Lastly, remaining solution A was added. The reaction was kept for 3 h at 30 °C. The hybrid silica nanospheres were isolated by centrifugation and washed with ethanol and water repeatedly.

Synthesis of Icosahedral Au-Pt@SiO$_2$. The icosahedral Au-Pt@SiO$_2$ was prepared via a simultaneous etching and growth strategy. 30 mg of hybrid silica nanospheres were mixed into 10 mL of deionized water, and then 200 μL of $HAuCl_4$ (50 mM) and a bit of H_2PtCl_6 solution (15 μL, 50 mM) were added. After adjusting the pH value to 3.0 with HCl, the mixture was stirred for 1 h at room temperature then heated at 200°C for 3 h. After that the autoclave was cooled naturally to room temperature. The as-synthesized nanoparticles were collected, washed and dried. Then the icosahedral Au-Pt@SiO$_2$ with Au loading of 10.1% (wt %) was obtained, which was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Synthesis of Spherical Au@SiO$_2$. The synthetic procedure is silimar to the preparation of icosahedral Au-Pt@SiO$_2$ without adding H_2PtCl_6 solution. 30 mg of hybrid silica nanospheres were mixed into 10 mL of deionized water, and then 200 μL of $HAuCl_4$ (50 mM) was added. The mixture (pH 3.0) was stirred for 1 h at room temperature then heated at 140°C for 4 h. Then the spherical Au@SiO$_2$ with Au loading of 10.4% (wt %) was obtained.

General Protocol for Ullmann Homocoupling Reaction. 5 mg of catalyst, 1 mmol of K_2CO_3, 0.5 mmol of iodobenzene, and 0.5 mmol of pentamethylbenzene (as internal standard for HPLC analysis) were added to 10 mL of mixture of ethanol and water (v/v=4/1). The reaction was taken at 80 °C under stirring. A certain amount of the reaction mixture was collected at special time during reaction. The mixture was separated quickly by centrifugation, and the liquid was analyzed by high performance liquid chromatography (HPLC).

Material characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM 2010F electron microscope operating at 200 kV. X-ray Powder diffraction patterns were accumulated on a Japan Regaku D/max γA X-ray diffractometer using graphite monochromatized Cu K radiation (λ=1.5418 Å). The backscattered scanning electron microscopy (SEM) and the energy-dispersive X-ray (EDS) spectroscopic measurements were performed with a Hitachi S-4800 scanning electron field emission microscopy. The high-angle annular dark-field scanning TEM (HAADF-STEM) image and STEM-EDS scan were performed using a Tecnai G2 F20 U-TWIN transmission electron microscope. Nitrogen adsorption-desorption measurements were carried out on a Quadra-Sorb SI automated surface area and pore-size analyser by using the volumetric method.

References.

1. D. Chen, L. Li, F. Tang and S. Qi, *Adv. Mater.*, 2009, **21**, 3804.

Figure S1. SEM image of Ih Au-Pt@SiO$_2$.

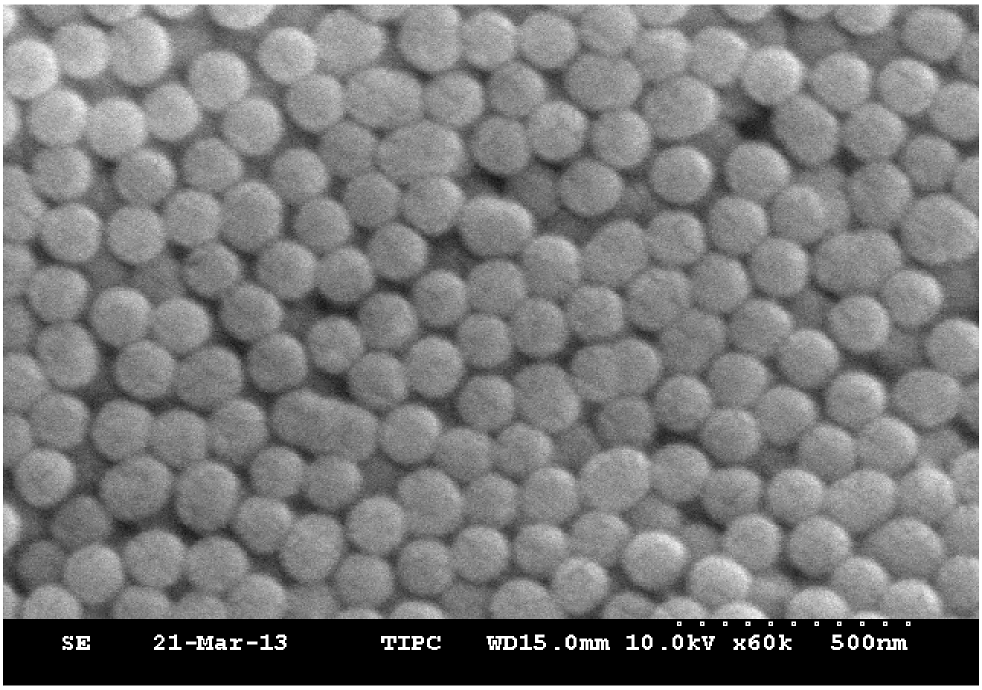

Figure S2. The nitrogen adsorption-desorption isotherm of Ih Au-Pt@SiO$_2$.

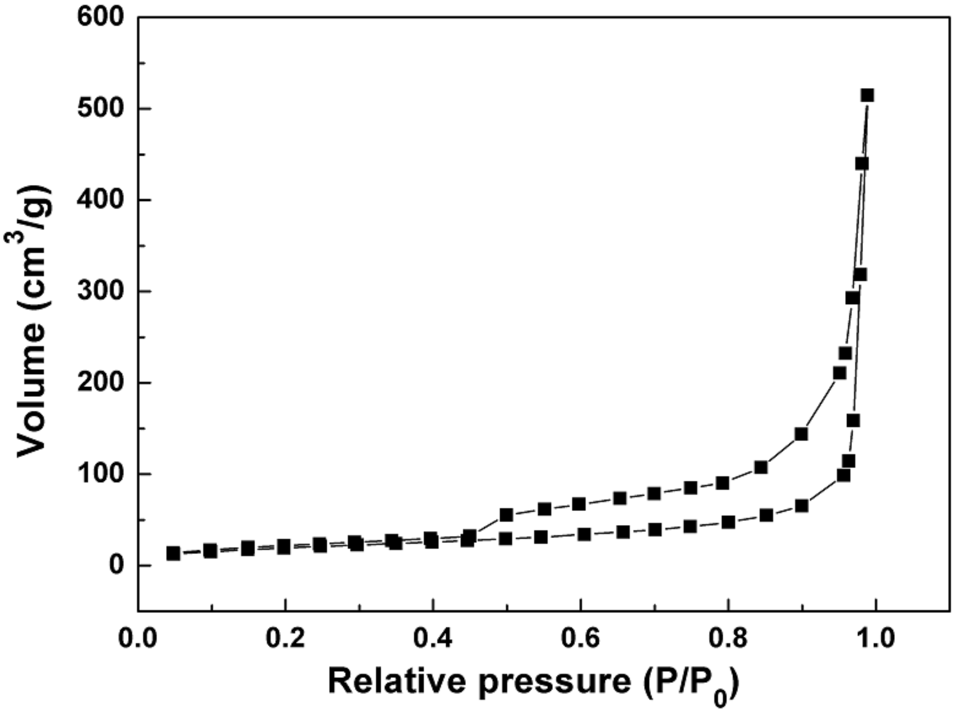

Figure S3. The UV−vis spectra of Sr Au@SiO_2 and Ih Au-Pt@SiO_2. The peak of Sr Au@SiO_2 and Ih Au-Pt@SiO_2 is 524nm and 519nm, respectively.

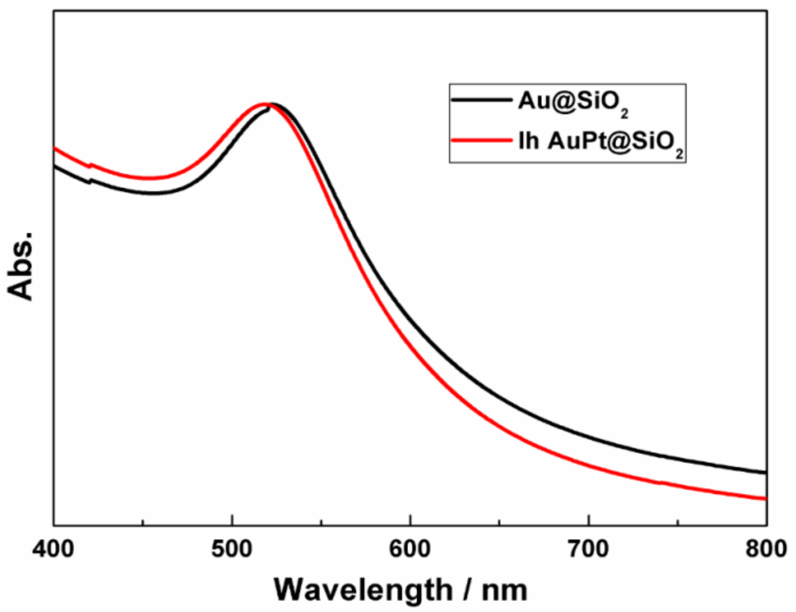

Figure S4. Wide-angle XRD pattern of Ih Au-Pt@SiO_2.

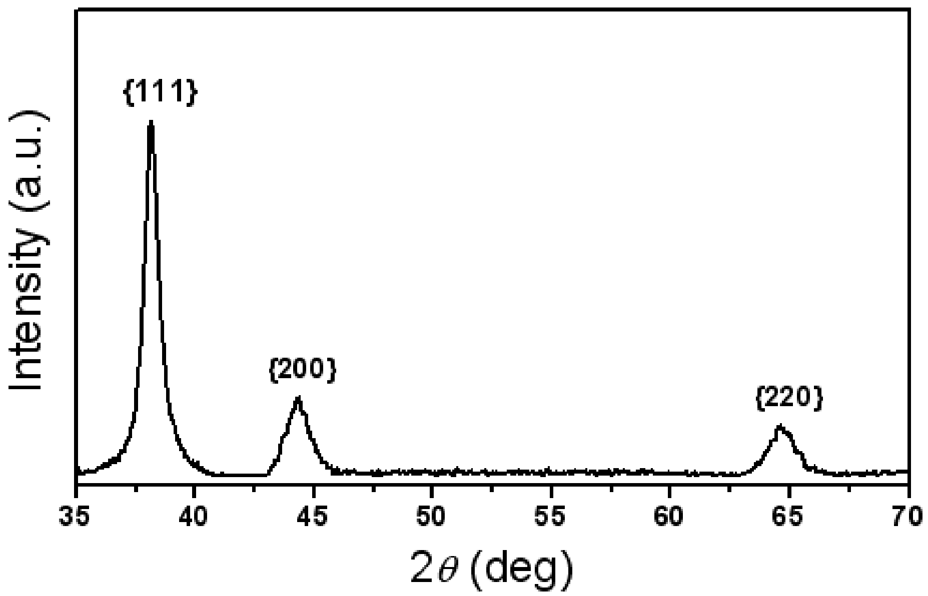

Figure S5. SEM-EDX spectrum of Ih Au-Pt@SiO_2.

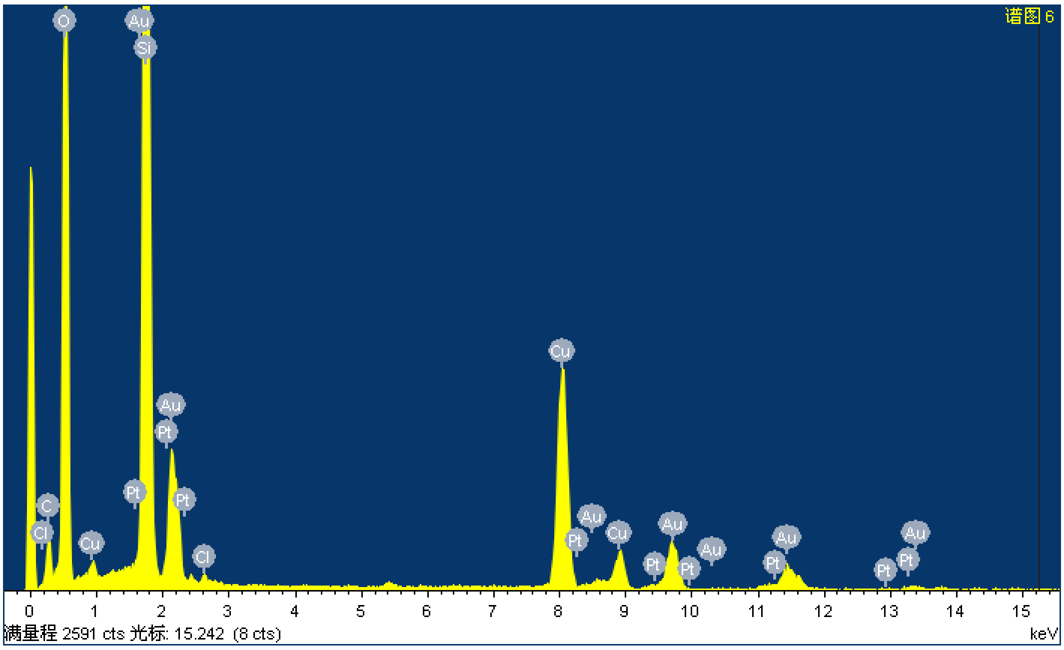

Figure S6. The illustration of Ullmann reaction catalyzed by Ih Au-Pt@SiO_2.

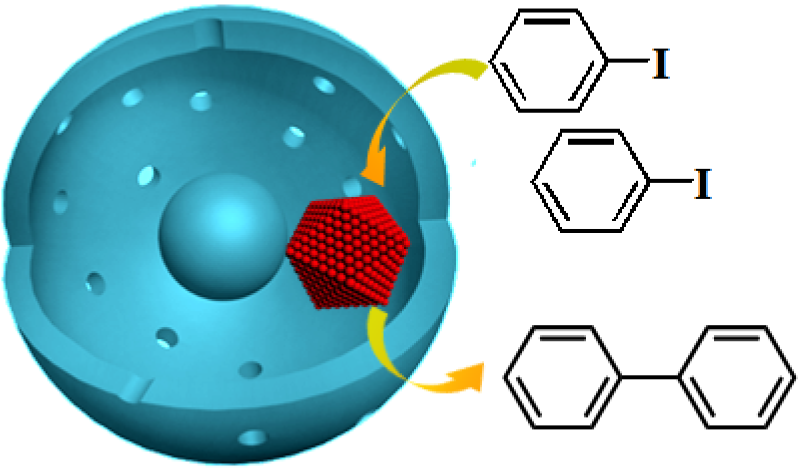

Figure S7. TEM image of Ih Au-Pt@SiO_2 after calcination in air at 500℃ for 1 hour.

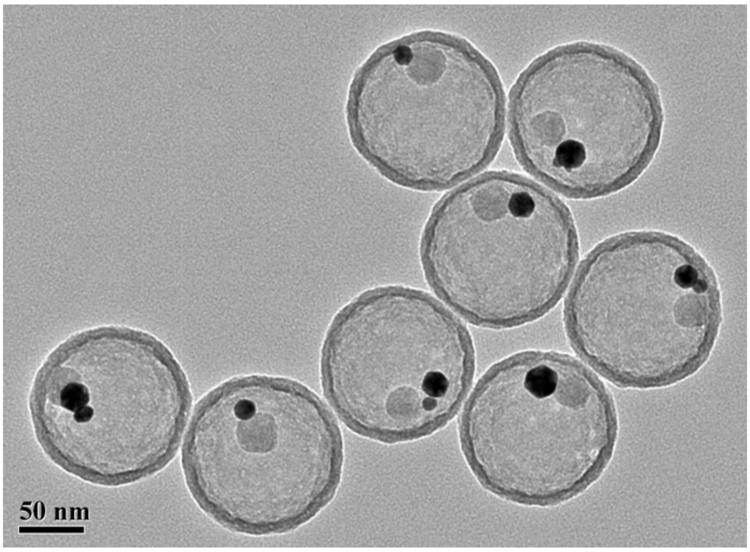

Figure S8. TEM image of Sr Au@SiO_2 after calcination in air at 500℃ for 1 hour.

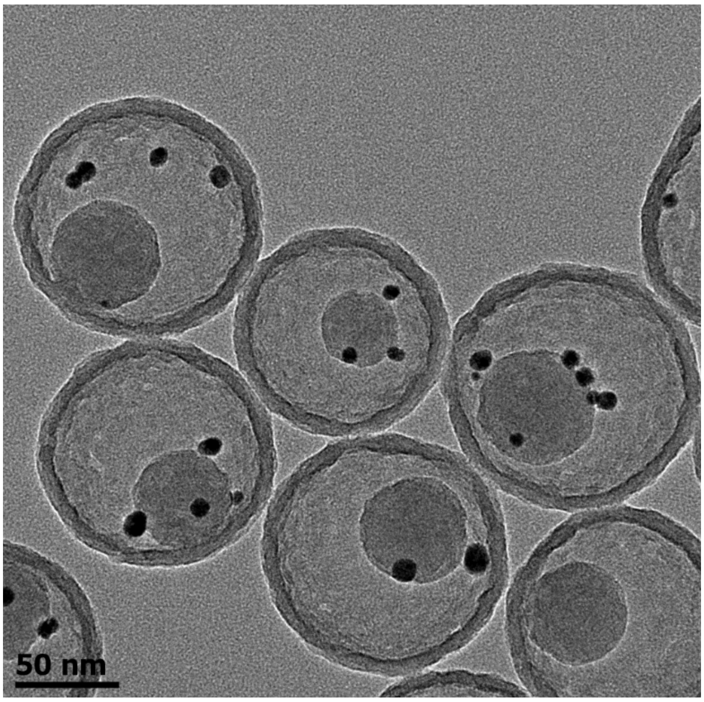

Figure S9. Yields of biphenyl versus the recycle number using Ih Au-Pt@SiO_2 nanoparticles and unsupported Ih Au-Pt nanoparticles as catalysts.