Construction of light-harvesting system for enhanced catalytic performance of Pd nanoframes toward Suzuki coupling reaction

Lini Yang, Qi Zhan, Zhenni Wang, Qiang Chen, Jing Tong, Dawei Fang, Lixin Xia* and Mingshang Jin*

College of Chemistry, Liaoning University, Shenyang, Liaoning 110036, People’s Republic of China. Email: lixinxia@lnu.edu.cn

Frontier Institute of Science and Technology and State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, People’s Republic of China. E-mail: jinm@mail.xjtu.edu.cn

†These two authors contribute equally to this work.
Experimental Section

Chemicals and Materials.
Hydrogen tetrachloroaurate trihydrate (HAuCl$_4$·3H$_2$O, 99.9%), sodium borohydride (NaBH$_4$, 98%), cetyltrimethylammonium bromide (CTAB, 98%), palladium (II) chloride (PdCl$_2$, 99%), L-ascorbic acid (AA, 99.7%), formaldehyde solution (HCHO, 37%), potassium iodide (KI), and N,N-dimethyl formamide (DMF) were all obtained from Sigma-Aldrich. H$_2$PdCl$_4$ solution (10 mM) was prepared by completely dissolving 0.089 g PdCl$_2$ in 50 mL of 20 mM HCl in a boil water bath. Deionized water with a resistivity of 18.2 MΩ·cm was used throughout the experiments.

Synthesis of Au octahedrons.
Firstly, 10 ml of an aqueous solution containing HAuCl$_4$ (0.25 mM) and CTAB (75 mM) was prepared in a vial. Then, 0.6 ml of ice-cold NaBH$_4$ (10 mM) was injected into this vial under magnetic stirring. The color of the solution turned brown immediately, indicating the formation of gold seed particles. The solution was kept stirring slowly for 3 hrs at room temperature to promote the decomposition of the remaining NaBH$_4$ in solution. Then, 1 ml of the prepared Au seed solution was diluted to 100 ml with water, serving as a seed solution in the later reactions. For the synthesis of Au octahedrons, 0.3 ml of the diluted Au seed solution, 0.1 ml of HAuCl$_4$ (10 mM), 2 ml of CTAB (0.2 M), and 1.5 ml of L-ascorbic acid (AA, 0.1 M) solution were introduced into a reaction vial and diluted to 25ml. The reaction mixture was shaken, and then left undisturbed at room temperature for 8 hrs. Finally, a typical light purple colloid was shown, indicating the formation of Au octahedrons. The colloid solution without other disposal was used as a seed solution for further synthesis of Au@Pd core-shell nanocubes.

Preparation of Au@Pd core-shell nanocubes.
For a typical synthesis, 0.5 ml of AA (0.1 M) and 1ml of H$_2$PdCl$_4$ (10 mM) were added to the Au octahedron solution. The mixture was shaken, and then left
undisturbed at room temperature for about 6 hrs and the color of the reaction solution changed from light purple to dark brown. After the reaction, the prepared Au@Pd core-shell nanocubes was centrifuged and washed with water twice to remove the excess CTAB, and finally re-dispersed in 3 ml of DMF for further synthesis of Au@Pd-frame nanocrystals.

**Preparation of Au@Pd-frame nanocrystals.**

In a standard procedure, 1.5 mL of DMF suspension containing 20 mg PVP, 1.5 mg KI, 1.0 mL of the as-obtained Au@Pd core-shell nanocubes, and 20 μl of aqueous HCHO (ten-fold dilution) was added into a vial. The reaction system was then evacuated, and 20 ml of O₂ was injected. The solution was then kept at 100 °C for 1 h. After that, the Au@Pd-frame nanocrystals can be obtained by centrifugation and washing. For the preparation of Pd nanoframes, Pd nanocubes, instead of Au@Pd core-shell nanocubes were used as the starting materials.

**Photocatalytic Suzuki coupling reaction.**

The Suzuki coupling reaction between Iodobenzene and acid were carried out in a vial, which contains DMF (1 ml), Iodobenzene (0.1 mmol), arylboronic acid (0.15 mmol), KOH (0.6 mmol), 0.3 ml of water, and the catalysts. ICP-OES measurements showed that all different catalysts contained 0.4 mg of palladium. The Suzuki coupling reaction was carried out under the irradiation of Xenon lamp (500 W) and cooled by a quartzose cryotrap. The reaction products were extracted with ethyl acetate twice and immediately analyzed by gas chromatography−mass spectrometry (GC-MS).

**Sample Characterizations.**

Powder XRD patterns were recorded using a diffractometer (X-ray Diffractometer SmartLab(3), Rigaku) operated at 3 kW. TEM images were performed at a Hitachi HT-7700 microscope equipped with a tungsten filament, operating at 100 kV. HRTEM, HAADF-STEM images and EDX elemental mapping were performed at
Tecnai G² F20 STWIN operating at 200 kV. GC-MS analysis was carried out on an Agilent 7890A GC interfaced to an Agilent 5975C mass-selective detector (30 m × 0.250 mm capillary column, HP-5MS).
Figure S1. TEM image of the obtained Au octahedrons.
Figure S2. TEM image of the Au@Pd core-shell nanocubes.
Figure S3. HRTEM images of the Au@Pd-frame nanocrystals.
Figure S4. The Suzuki coupling reaction between iodobenzene and phenylboronic acid used in the present work to evaluate the photo-enhanced catalytic activity of the catalysts.
Figure S5. TEM image of the Pd nanoframes.
Figure S6. TEM image of the Au@Pd-frame nanocrystals after Suzuki coupling reactions.