

Facile synthesis of Pt@Ir zigzag bimetallic nanocomplexes for the hydrogenation application

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Experimental Section

Materials

Oleylamine (OAm, technical grade, 70%) and sodium oleate (NaOA, technical grade, 97%) were obtained from TCI. Platinum (II) pentanedionate (Pt(acac)₂, Pt 48%) and iridium (III) 2,4-pentanedionate (Ir(acac)₃, Ir 37.5%) were purchased from Alfa Aesar. Nitrobenzene and its derivatives, toluene, ethanol and chloroform were supplied by Sinopharm Chemical Reagent Co., Ltd (SCRC). All chemicals were directly used as received without further purification.

Preparation of Pt nanorods

Pt(acac)₂ (200 mg), sodium oleate (150 mg) were added to oleylamine (OAm) (20 mL) under Ar and stirring for about 5 minutes. The mixture was then heated to 120 °C for 15 min. As the solution turned clear yellow, a drop of Fe(CO)₅ (~0.005mL) was quickly injected into the hot solution. The solution turned dark in color quickly. The temperature was further heated to 250 °C and kept at this temperature for 30 min before it was cooled down to room temperature. The sample was centrifuged in excess isopropanol to separate the nanorods. The nanorods were dispersed in 10 mL toluene and precipitated out by adding ethanol. The process was repeated one more time to purify the nanorods. The final product was dispersed in 10 mL of ethanol for further use.

Preparation of Pt@Ir zigzag bimetallic nanocomplexes

Pt nanorods (12.5 mg) dispersed in 1 mL toluene, Ir(III) acetylacetonate (122.5 mg) were added to oleylamine (OAm) (10 mL) under Ar and stirring for about 5 minutes. The mixture was then heated to 80 °C for 10 min and then 120 °C for 10 min. The temperature was further heated to 280 °C and kept at this temperature for 30 min before it was cooled down to room temperature. Pt@Ir nanocomplexes were precipitated by ethanol and collected by centrifugation. The black precipitate was thoroughly washed with ethanol, and redispersed in hexane for further use.

Typical catalytic hydrogenation procedure

To a reaction tube equipped with a magnetic stirrer an appropriate amount of catalyst (2 mg), nitrobenzene (102 μL, 1 mmol), and ethanol (2 mL) were added. The air in the tube was then exchanged 3 times with 1 atm of H₂. Finally, the tube was immersed in an oil bath at 70 °C in a sealed H₂ system. After stirring for 3 h at 70 °C, the mixture was cooled to room temperature. A sample of the mixture was immediately analyzed by GC and GC-MS.

Material characterization

The nanostructure morphologies were characterized by SEM, TEM and high-resolution TEM (HRTEM). SEM was performed on a Hitachi S-4700 cold field emission scanning electron microscope operated at 30 kV, TEM (Tecnai G220, FEI, USA) was performed using a Gatan CCD794 camera

operated at 200 kV and HRTEM was carried out on a Tecnai G2 F20 S-TWIN microscope with an accelerating voltage of 200 kV. XPS data were obtained using a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with monochromatic Mg K α X-ray (1283.3 eV).

Catalytic products characterization

The product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m \times 0.25 mm) and an FID detector.

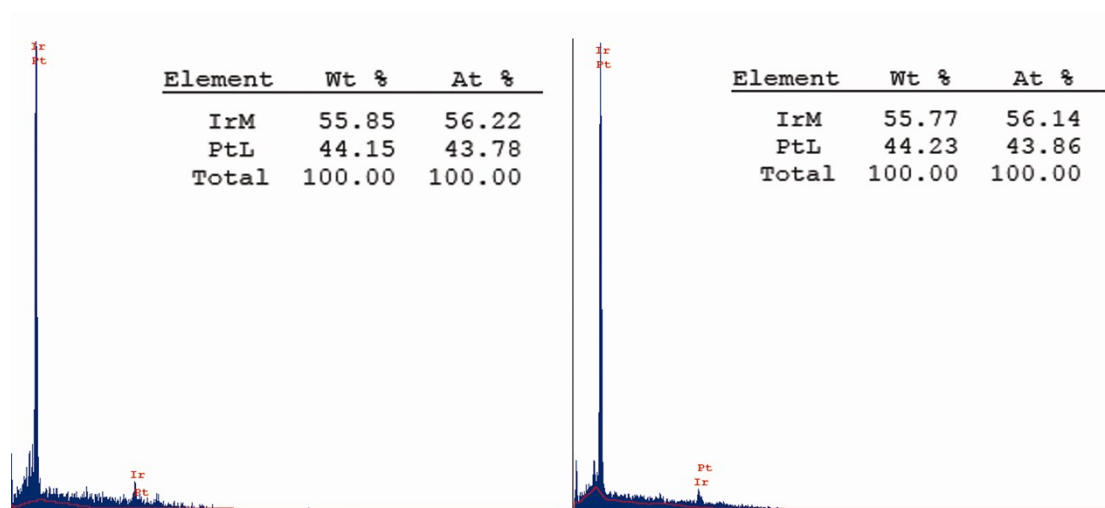


Fig. S1 Large area (A) and selected area (B) Energy dispersive spectrum (EDS) analysis of Pt@Ir nanocomplexes.

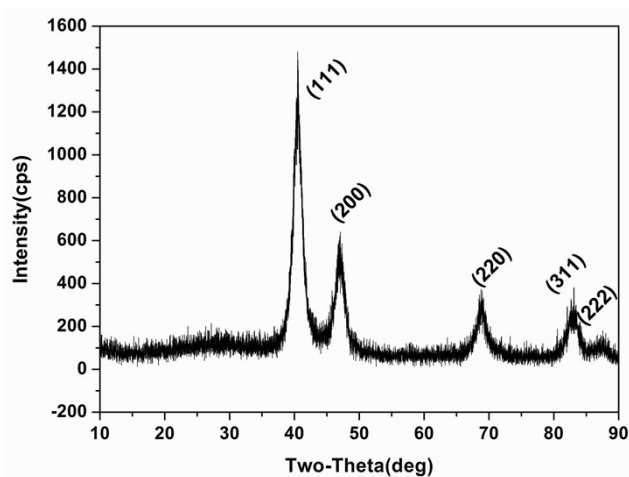


Fig. S2 X-ray diffraction (XRD) analysis of Pt@Ir nanocomplexes.

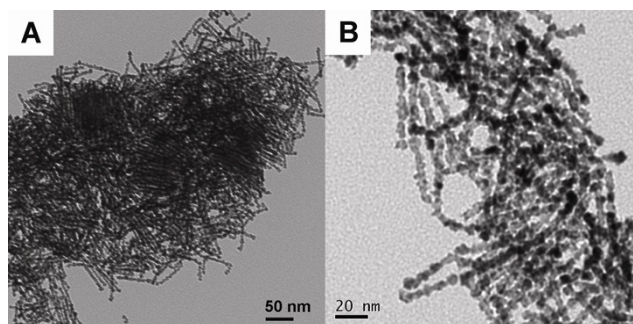


Fig. S3 TEM images of the nanocatalyst after catalytic reactions