Supporting Information

Rose-like Pd-Fe$_3$O$_4$ hybrid nanocomposite-supported Au nanocatalysts for tandem synthesis of 2-phenylindoles

Hyunje Woo, a Ji Chan Park, b Sungkyun Park c and Kang Hyun Park a*

a Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea. Phone: (+82)-51-510-2238; Fax: (+82)-51-980-5200; e-mail: chemistry@pusan.ac.kr

b Clean Fuel Laboratory, Korea Institute of Energy Research, Daejeon, 305-343, Korea.

c Department of Physics, Pusan National University, Busan 609-735, Korea.
Experimental Section

Instrumentation. High resolution transmission electron microscopy (TEM) analysis was performed at KAIST analysis center using a Tecnai TF30 ST and a Titan Double Cs corrected TEM (Titan cubed G2 60-300). Energy-dispersive x-ray spectroscopy (EDS) elemental mapping data were collected using a higher efficiency detection system (Super-X detector). FE-scanning electron microscopy (SEM) (Magellan400) was also used for analyses. The x-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB (12 kW) diffractometer. X-ray photoelectron spectroscopy (XPS) (Theta Probe, Thermo) was employed to measure the structural and chemical properties of the nanocomposites. The Pd, Fe and Au contents of the samples were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (iCAP 6300). The surface area and pore-size distribution of the samples were calculated by using the Brunauer-Emmett-Teller (BET) equation and the BJH method, respectively. Magnetization data were taken using a superconducting quantum interference device (SQUID) (MPMS-7, Quantum design). The tandem reaction products were analyzed by $^1$H nuclear magnetic resonance (NMR) spectroscopy using a Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants are given in Hz. Mass spectra were obtained on Shimadzu GC/MS QP-2010 SE (EI) (Pusan National University).

Synthesis of Pd-Fe$_3$O$_4$ nanocomposites. Pd(OAc)$_2$ (0.114 g) were added into a 50 ml three-neck flask that contained 10 ml of 1-octadecene (ODE) and 10 ml of oleylamine (OAm) under gentle Argon (Ar) gas flow. The flask was heated to 60 °C and further heated to 120 °C at a heating rate of 6 °C /min. Under a blanket of argon gas, 0.15 ml Fe(CO)$_5$ was added. Then the solution was further heated to 160 °C at a heating rate of 4 °C/min and kept at this temperature for 30 min. The heating source was removed, and the solution was cooled to room temperature. A black product was precipitated by adding ethanol and hexane, and separated by centrifugation. The dark-yellow supernatant was discarded. The black product was dispersed in 5 mL of hexane and precipitated by adding 45 ml of ethanol and centrifugation.

Synthesis of Au/Pd-Fe$_3$O$_4$ nanocomposites. Au precursor (HAuCl$_4$·3H$_2$O) are dissolved in OAm (12 ml) and hexane (3 ml) and heated at 80 °C. Pd-Fe$_3$O$_4$ solution was injected in to the above hot solution and stirred for 30 minutes. The temperature
was cooled down to room temperature. The sample was centrifuged in excess ethanol and hexane to achieve black precipitates.

**General procedure for one-pot synthesis of 2-arylindoles.** The catalyst (generally 0.1 mol% with respect to the Au content), 2-iodoaniline (0.11 g, 0.5 mmol, 1.0 equiv), phenylacetylene (0.061 ml, 0.55 mmol, 1.1 equiv), cesium acetate (0.19 g, 1.0 mmol, 2.0 equiv) and DMSO (2.5 mL) were mixed in a 10 ml vial glass. The mixture was vigorously stirred at 150 °C. After the reaction, catalyst was separated by external magnet and the reaction mixture was filtered with diethylether. Drying with MgSO₄, filtration, and solvent evaporation of the filtrate yielded the reaction products.

**Recyclability and Pd Leaching Tests.** After the reaction, the catalyst particles were separated by external magnet. The recovered particles were reused as a catalyst for the next reaction. For checking Pd leaching degree, poly(4-vinylpyridine) (PVPy) (150 equiv. with respect to the total Pd content) was employed prior to initiation of the reactions.
**Fig. S1** TEM images of the as-synthesized Pd-Fe₃O₄ nanocomposites with different amounts of Fe(CO)₅ (a,d) 0.15 ml, (b,e) 0.30 ml, and (c,f) 0.45 ml.
Fig. S2 TEM images of the Pd-Fe$_3$O$_4$ nanocomposites synthesized at (a,d) 160 °C, (b,e) 140 °C and (c,f) 120 °C.
**Fig. S3** SAED pattern of the Au/Pd-Fe$_3$O$_4$ nanocomposites.

**Fig. S4** SQUID graph of Pd-Fe$_3$O$_4$ and Au/Pd-Fe$_3$O$_4$ nanocomposites.
Fig. S5 The XPS spectra of Au/Pd-Fe$_3$O$_4$ nanocomposites.
Fig. S6 C1s peak (raw data) and its Lorentzian fitted result.
Fig. S7 EDS spectrum of Au/Pd-Fe₃O₄ nanocomposites.
Data for $^1$H and GC-MS spectra are reported as follows:
Chemical shift ($\delta$ ppm), multiplicity ($s =$ singlet, $d =$ doublet, $t =$ triplet, $m =$ multiplet),
coupling constant (Hz), and integration.

2-phenylindole$^1$ (Table 1): $^1$H-NMR (CDCl$_3$, 300 MHz): $\delta = 7.53$ (dd, $J = 2.4$ and 8.1
Hz, 2H), 7.38-7.39 (m, 1H), 7.35 (dd, $J = 2.4$ and 4.8 Hz, 3H) 7.15 (td, $J = 1.5$ and 7.8
Hz, 1H) 6.74 (d, 7.5 Hz, 2H) 4.28 (br, 1H). MS (EI) m/z: 193(100), 165(44), 89(20),
28(16).
