Supporting Information

Immobilization of Pd Nanocatalysts on Magnetic Rattles and Their Catalytic Property

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2. Experimental Section

Materials: Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), sodium acetate (NaOAc), sodium citrate (NaCit), ethylene glycol (EG), diethylene glycol (DEG), tetraethyl orthosilicate (TEOS), and urea were obtained from Sinopharm Chemical Reagent Co, Ltd. All chemicals are analytical grade and used as received without further purification.

Synthesis of MP Microspheres: Magnetic microspheres were synthesized according to a modified method [27]. Typically, $FeCl_3 \cdot 6H_2O$ (2 mmol), NaOAc (1.5 g), and NaCit (0.3 g) were dissolved in EG (20 mL) in a beaker. After vigorous stirring for an hour, the homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and then sealed to heat at 200 °C. After a 12 h reaction period, the autoclave was cooled to room temperature. The particles were washed with water and ethanol, and then vacuum dried at 60 °C for 12 h to obtain the MP microspheres.

Synthesis of MP@SiO_2 Core/shell Microspheres: The above synthesized Fe_3O_4 microspheres (10 mg) were dispersed in the mixture of water (3 mL) and ethanol (30 mL) by ultrasonication. Then, ammonia solution (1 mL) was added. After 30 min, a solution of TEOS in ethanol (0.2 mL/6 mL) was injected into the solution and the reaction was performed for 100 min. The product was collected by the help of a magnet and then washed with ethanol and water for several times. Finally, the product was dried in vacuum for 12 h to obtain the *MP*@SiO_2 with core/shell nanostructure.

Synthesis of MP@NiSiO Rattles: MP@SiO_2 core/shell particles (20 mg) were dispersed in 5 mL H_2O under sonication. 30 min later, 0.2 mmol $NiCl_2 \cdot 6H_2O$ was

added into the above solution and stirred vigorously. Then, a urea aqueous solution (2.25 M, 5 mL) was introduced. 20 min later, 5 mL ethanol was added under sonication. Then, the obtained solution was transferred to a Teflon-lined stainless-steel autoclave (25 mL volume) and sealed to heat at 190 °C. After a 6 h reaction period, the autoclave was cooled to room temperature. The products were washed with water and ethanol, and then dried in vacuum over night.

Synthesis of MP@NiSiO/Pd Nanocomposite: An aqueous solution (10 mL) containing MP@NiSiO rattles (10 mg) and K_2PdCl_4 (3 mg) was prepared in a vial under vigorously stirring. 6 h later, cold $NaBH_4$ solution (0.1 mL, 0.1 M) was added. The solution turned black from yellow immediately after the addition of $NaBH_4$, indicating the Pd nanoparticle formation. The MP@NiSiO/Pd products were magnetically separated from the solution after 2 h reaction. After washing several times with distilled water and ethanol, the magnetic nanocatalysts were dried under vacuum at 50 °C.

Heck Coupling Reaction: In a 10mL glass flask were placed aryl halide (1mmol), alkene (2mmol), Et_3N (2mmol), and MP@NiSiO/Pd (0.1mol %) in 3mL of N-methyl-2-pyrrolidone (NMP) at 120°C for the appropriate time. The reaction was monitored by thin-layer chromatography (TLC), and after completion of the reaction, the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure, and the mixture was then purified by column chromatography over silica gel to afford product with high purity.

Suzuki Cross-coupling Reaction: In a 10 mL glass flask were placed aryl halide (1mmol), boronic acid (1.2mmol), Na_2CO_3 (2mmol), and MP@NiSiO/Pd (0.1mol %) in Dimethyl Ether (DME)-H_2O (1.5mL/1.5mL) at 110°C for the appropriate time. The reaction was monitored by TLC, and after completion of the reaction, the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the mixture was then purified by column chromatography over silica gel to afford product with high purity.

The magnetic catalyst can be magnetically separated from the solution and reused in the next catalytic reaction.

Characterization: X-ray powder diffraction patterns (XRD) of the products were obtained on a Japan Rigaku DMax-γA rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ= 1.54Å). 78 Transmission electron microscopy (TEM) photographs were taken on a Model JEOL-2010 microscope and at an accelerating voltage of 120 kV and a high-resolution transmission electron microscope (HRTEM, Tecnai Model JEOL-2100) at an accelerating voltage of 200 kV.

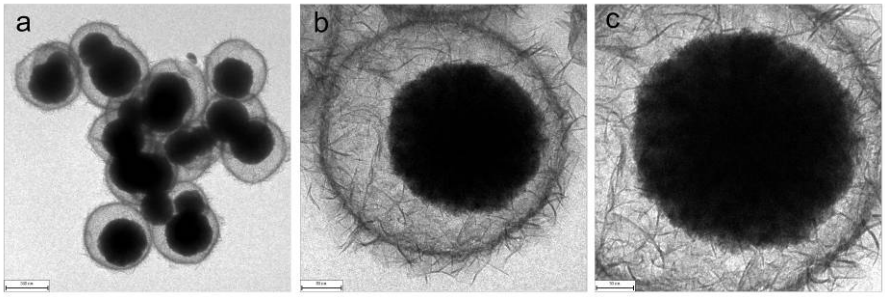

Figure SI1. TEM images of the MP@NiSiO rattles (a,b,c),

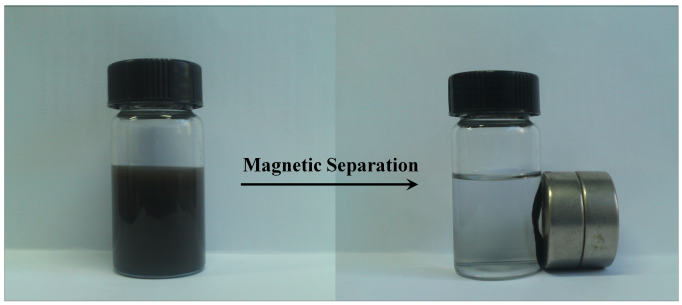

Figure SI2. photographs of the magnetic separation process.