Electronic Supplementary Information (ESI) for Chemical Communications

# Pd nanoparticles in silica hollow spheres with mesoporous walls: a nanoreactor with extremely high activity

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## 1. Experimental details

### 1.1 Materials and Reagents

Glucose, ethanol, sodium formate, tetraethyl orthosilicate (TEOS), ammonia solution (25 wt%), $PdCl_2$, $SnCl_2{\cdot}2H_2O$, $K_2CO_3$ and N,N-Dimethylformamide (DMF) were purchased from Beijing Chemical Reagent Co. Iodobenzene, phenylboronic acid, phenylacetylene, cetyltrimethylammonium bromide (CTAB) and pentamethylbeznene were bought from Alfa Aesar. All chemicals were used as received without further purification.

### 1.2 Synthesis of carbon nanospheres

Glucose (4.5g) was dissolved in 30mL water to form a clear solution and then transferred into a 40mL Teflon-sealed autoclave. The autoclave was maintained at 190 ºC for 4h. The products were separated by centrifugation, followed by washing three times using water and ethanol and finally oven-dried at 80 ºC for further use.

### 1.3 Loading Pd nanoparticals onto the carbon nanosphere to form Pd/C

In a typical process, 100 mg carbon nanosphere was dispersed in 50mL distilled water and stirred for 10 min as part A. 0.1 g $SnCl_2$ was dissolved in 20 mL 0.02 M HCl solution as part B. Parts A and B were mixed together under stirring for 10 min. Then the suspension was centrifuged. After washing with distilled water five times,

the precipitate was dispersed in 50 mL distilled water. Then 372 μL 0.0564 M $PdCl_2$ was added into it. Ten min later, 10 mL of 0.15 M sodium formate solution was added following stirring for 5 h. After centrifugation and washing with distilled water five times, the precipitate was dried at 60 ºC for 12 h.

**1.4 Production of Pd@mesoporous $SiO_2$ nanoreactor**

The Pd/C composite obtained from last step was first dispersed in the solution containing 40mL $H_2O$, 30mL ethanol, 0.15g CTAB and 568 μL $NH_3 \cdot H_2O$ with ultrasonic for 20min. Then 150 μL TEOS was added, and the mixture was vigorously stirred for 6h. The precipitate was harvested after centrifugation and washed with distilled water and with ethanol for three times, then dried at 60 ºC for 6 h. Then the product was calcined at 400 ºC in $N_2$ flow for 2 h then in air atmosphere for 6 h to remove carbon sphere, CTAB template and other organic species. The finally obtained Pd@mesoporous $SiO_2$ product was further employed as nanoreactor for Suzuki and Sonogashira cross-coupling reaction, respectively.

**1.5 Suzuki and Sonogashira cross-coupling reaction test**

For Suzuki cross-coupling reaction, 10 mg Pd@mesoporous $SiO_2$ nanoreactor catalyst, 0.5 mmol iodobenzene, 1mmol phenylboronic acid, 1 mmol $K_2CO_3$, and 0.5 mmol pentamethylbenzene (as internal standard for HPLC analysis) were added to 10mL ethanol under stirring. The reaction was carried out at reflux (ca.78 ºC) for definite time. Then the mixture was separated quickly by centrifugation, and the liquid was analyzed by High-performance liquid chromatography (HPLC). For Sonogashira cross-coupling reaction, 1 mmol iodobenzene, 1.5 mmol phenylacetylene (Alfa Aesar), 2 mmol $K_2CO_3$, 0.5 mmol pentamethylbeznene (internal standard) and 5 mL DMF was mixed together and stirred for definite time. Then the solid and liquid were separated by centrifugation and the liquid was analyzed by HPLC.

### 1.6 Characterization and measurements

Scanning electron microscopy (SEM) images were obtained on JEOL-6701F scanning electron microscope at 10.0 kV. Transmission electron microscopy (TEM) was carried out on a JEOL 1011F electron microscope running at 100 kV while high resolution (HR) TEM image and energy dispersive absorption X-ray (EDAX) spectroscopy were acquired from JEOL 2010F electron microscope with an energy dispersive X-ray system operated at 200 kV. Nitrogen adsorption–desorption isotherms was obtained on Quantachrome Autosorb AS-1. The XRD measurements were carried out in Rigaku D/max-2400 diffractometer equipped with a secondary graphite monochromator with CuKα radiation (wavelengths $\lambda = 0.154$ nm). Data were collected in a step-scan mode in the range of 0.6-8 degree with step-width of 0.02 and speed of 1 degree /min. The conversions of reagent were measured using HPLC (Shimadzu LC-10 AVP Plus). Leaching of Pd was characterized by ICPE (Shimadzu ICPE-9000).

## 2. Supplemental figures

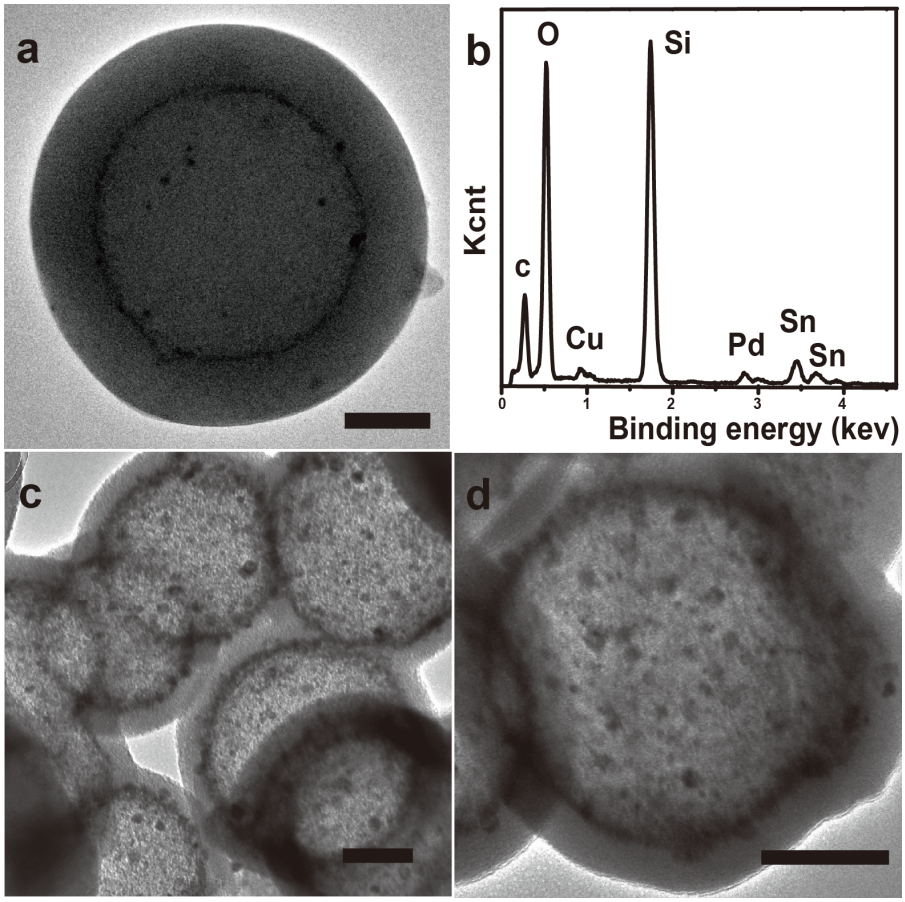


Fig. S1 (a) Pd/C@mesoporous $SiO_2$ composite before calcinations. (b) Energy-dispersive X-ray absorption spectroscopy (EDAX) of the Pd@mesoporous $SiO_2$ nanoreactor. Sn was raised from residual $SnCl_2$ used in the synthesis procedure, while C and Cu were attributed to the sample grid film. The Sn contents were below 0.05 wt%, and the Sn presence was not considered as significant in the catalytic performance of the composites. (c-d) TEM of catalyst has been used for 5 times in different magnification. All bars are 100nm.