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

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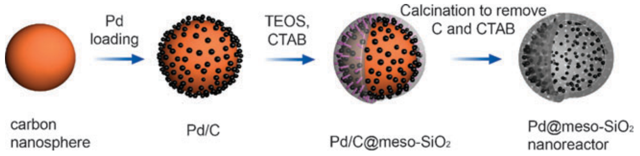
A true nanoreactor composed of mesoporous silica hollow spheres and Pd nanoparticles residing inside the spheres shows superior activity in Suzuki coupling reactions with 99.5% yield in 3 min.

All catalytic reactions occur in reactors, which accommodate the catalysts and reactants, and allow the chemicals to be transported in and out of the reactor. In conventional catalysis, reactor design is typically an independent craft, separate from catalyst design. However, some catalysts have uniform internal structures that resemble a reactor on the nano-/microscale. For example, the supercages inside Y zeolite particles can be considered as nanoreactors.[1] Another type of porous material, mesoporous silica, can draw the reactants into its pore channels, where the catalyst particles are located. Thus the mesopores within the silica can be considered as nanotubular reactors.[2,3]

Fully functional nanoreactors are realized using hollow spheres, especially mesoporous silica hollow spheres. Li *et al.* have encapsulated several chiral catalysts into mesoporous silica SBA-16 nanocages.[3] The resulting catalytic system shows remarkable activity for asymmetric synthesis. Most recently, Yamada *et al.* reported TiO_2 inside silica hollow spheres for photoreactions.[4] Lu *et al.* fabricated a series of yolk/shell structured materials with movable cores and porous shells, which have potential application in nanoreactors.[5–7]

Noble metal NPs tend to aggregate and sinter, leading to a rapid decay in catalytic abilities.[8,9] Restricting the noble metal NPs in isolated nanoreactors can effectively protect them against aggregation. Somorjai *et al.* designed a Pt@CoO composite for the hydrogenation of ethylene.[10] Song *et al.* fabricated a Au@SiO_2 yolk/shell structure for the catalytic reduction of *p*-nitrophenol.[11] Yin *et al.*'s multilayer core/shell structures also resemble nanoreactors, in which Pd nanoparticles are protected by a silica coating.[12]

In this study, we produced a true nanoreactor that is composed of mesoporous silica (*meso*-SiO_2) hollow spheres, and Pd nanoparticles residing inside the spheres. The fabrication process is a three step procedure, and each step is well-controlled (Scheme 1). The mesoporous walls of the silica hollow spheres prompt facile mass transportation. The Pd nanoparticles are all fully accessible. Both features enable the system to be very active in catalysis. In the Suzuki coupling reaction a 99.5% yield is obtained in 3 min.



Scheme 1 Synthesis route to the composite nanoreactor.

As illustrated in Scheme 1, we designed a three step procedure to produce the nanoreactor composite. Dividing the procedure into three separate steps allows precise control of the overall structure of the composite. Fig. 1 depicts the experimental realization of Scheme 1 (see ESI† for experimental details). Fig. 1a shows the smooth surfaces of the carbon nanospheres with abundant hydroxyl groups,[13] which help to anchor the Pd nanoparticles.[14] Fig. 1b is a TEM image of the Pd/C composite. The Pd nanoparticles with an average size of about 5 nm are uniformly distributed on the surfaces of the carbon nanospheres. Using TEOS as the silica source and CTAB as a soft template, a thin layer of mesoporous silica is coated onto the Pd/C spheres. Calcination of the precursor composite removes the carbon sphere and CTAB, leaving only Pd nanoparticles residing inside the hollow spheres.

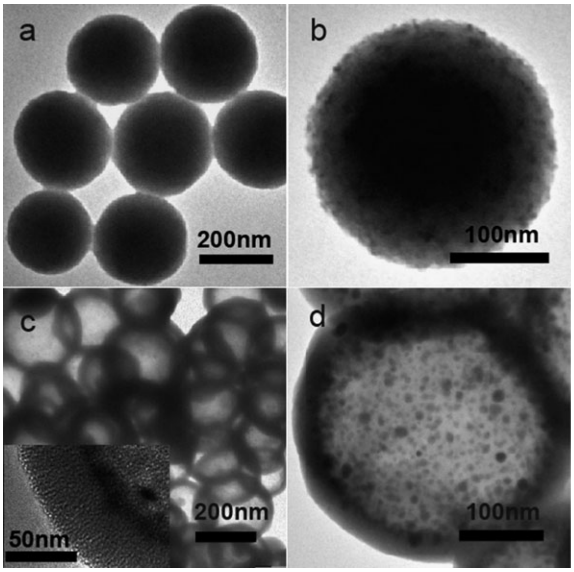


Fig. 1 (a) TEM of carbon nanospheres; (b) TEM of Pd/C nanosphere; (c) TEM of final composite nanoreactor in low magnification. The inset shows the mesopores of the SiO_2 wall; (d) TEM of composite nanoreactor in high magnification.

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† Electronic supplementary information (ESI) available: Preparation of the composite nanoreactor; experimental details of Suzuki reaction; characterization and measurement methods of catalyst; TEM of catalyst post-use. See DOI: 10.1039/c0cc01786h

Apparently, the Pd nanoparticles are located at the inside pore mouths of the mesopores. No Pd nanoparticles were observed within the mesopore pores (inset of Fig. 1c). The wormhole-like mesopores can be seen in the inset of Fig. 1c. The thickness of the *meso*-SiO_2 walls is about 40 nm, and can be readily controlled by adjusting the concentration of TEOS. Fig. 1d shows a TEM image of the composite in high magnification, showing well-dispersed Pd nanoparticles on the inside surface of the hollow spheres. EDX analysis (see ESI† Fig. S1b) and elemental analysis results indicate 4.0 wt% of Pd loading. We also produced composites with 20 wt% and 0.8 wt% Pd loadings. In these materials, the Sn content was below 0.05 wt%, and the presence of Sn was not considered as significant in the catalytic performance of the composites.

The small-angle XRD pattern depicted in Fig. 2a shows a broad peak at 2.6°, indicating a worm-like mesopore with a uniform pore size. This is consistent with Fig. 1c and similar mesoporous materials. Fig. 2b shows the nitrogen adsorption–desorption isotherm of the composite with a narrow hysteresis loop; both of which indicate the presence of mesopores. The BET surface area of the composite is 1123 $m^2\ g^{-1}$, similar to normal mesoporous silica. The inset of Fig. 2b shows the BJH pore size distribution, showing a sharp peak at 2.1 nm.

Each of the composite spheres is a true nanoreactor with outstanding features. The mesoporous channels on the sphere walls provide entrances for the reactants and exits for the products. The large surface of the composite enriches the reactants around the composite. The 2.1 nm pore size also keeps the Pd nanoparticles within the inner space of the hollow space, as the Pd nanoparticle diameter is about 5 nm on average. In addition, the hydrophilic nature of the mesoporous silica can induce a wettability control over the catalytic reactions in liquid media. Hydrophilic liquids may be preferentially adsorbed into the composite nanoreactor.

This synthesis route can also be applied for loading other noble metal nanoparticles such as Au, Ag, and their bimetallic alloy nanoparticles into the composite nanoreactors. As shown in Fig. 3, Au NPs with a diameter of sub-10 nm are dispersed uniformly inside silica. The system supplied a platform to fabricate nanoreactors which can be used in a broad range of noble metal catalyzed reactions.

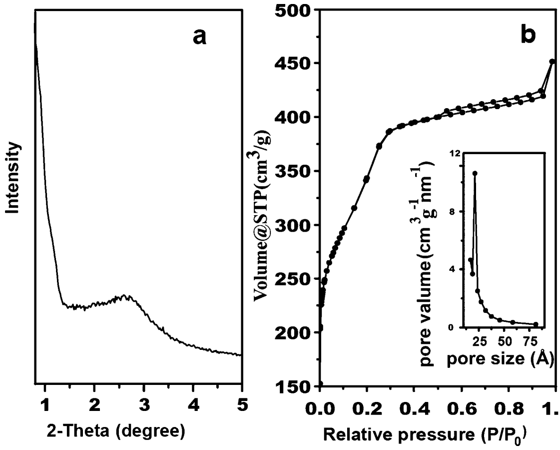


Fig. 2 (a) Small-angle XRD pattern of the composite nanoreactor. (b) Nitrogen adsorption–desorption isotherms of the composite. Inset is the BJH pore size distribution.

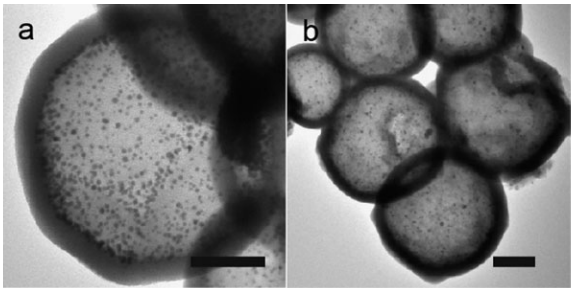
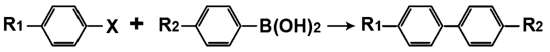
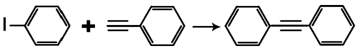


Fig. 3 (a, b) Au NPs residing in *meso*-silica at different magnifications. All bars are 100 nm.

We carried out Suzuki cross-coupling reactions (1) and a Sonogashira reaction (2) as model reactions to evaluate the catalytic ability of the composite nanoreactors. The Suzuki cross-coupling reaction provides a simple yet versatile route to form C–C and C–N bonds under relatively mild conditions.[15] The results of Suzuki reactions using different reagents are listed in Table 1. The R_1 and R_2 side groups on either iodobenzene or phenylboronic acid are intentionally changed to test the effects of side group substitution. The composite catalyst showed outstanding activity in all these reactions.



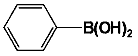
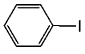
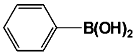
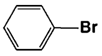
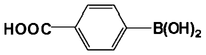
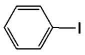
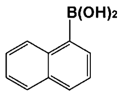
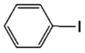
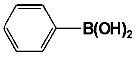
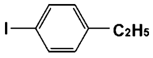
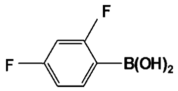
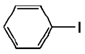
(1)



(2)

In a typical Suzuki reaction in which neither iodobenzene nor phenylboronic acid has side groups, the conversion of iodobenzene reaches 99.5% within 3 min of reaction at 80 °C under reflux conditions. The turn-over frequency (TOF) is 0.74 s^{-1}. Bromobenzene shows 32% conversion in 3 min, with

Table 1 Suzuki reactions catalyzed by composite reactors[a]

Run	Reagent	Reagent	Time/min	Yield (%)
1			3	99.5
2			3	32.4
3			3	67.2
4			3	86.3
5			10	80.0
6			3	50.6

[a] Reaction conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1 mmol), K_2CO_3 (2 mmol), catalyst (10 mg, with Pd loading 4 wt%).

a TOF 0.24 s^{-1}. Even at room temperature, the conversion of iodobenzene reaches 52% at 10 min. The composite nanoreactor is also very active for substituted iodobenzene and phenylboronic acids, as shown in Table 1. In addition, the conversion of iodobenzene reaches 55% in 30 min for the Sonogashira reaction (reaction 2). These results prove that the composite nanoreactors are extremely active for Pd-catalysed C–C coupling reactions. For comparison, a reported Pd/TiO_2 composite catalyst converts only 15% of iodobenzene in 3 min at 80 °C, and the iodobenzene conversion is nearly zero at room temperature.

The catalyst can be easily recovered from the reaction solution by centrifugation. The conversions of iodobenzene reached 99.0% in 3 min in 4 consecutive runs, showing no sign of deactivation. A TEM image of the used composite catalyst (see ESI† Fig. S1c.d) shows no apparent change from the fresh catalyst.

The superior catalytic performance of this nanoreactor composite is due to the structural features of the composite nanoreactor. The reagents (iodobenzene, phenylboronic acid and K_2CO_3) can be adsorbed by high surface area *meso*-SiO_2, then diffuse through the mesoporous pores, being enriched within the pore mouth. The concentration of reagents around the Pd nanoparticles is relatively higher than that in the bulk solution. The thin layer of mesoporous silica is only 40 nm, indicating a very short diffusion course for both reactants and products. Such a short diffusion course is beneficial for heterogeneous catalysis.[16] The 2 nm-pores may also pose a certain space confinement effect to the reactants, leading to a higher reaction rate.

Improving the activity and stability of a catalyst is the core of heterogeneous catalysis.[17,18] In Pd and other noble metal catalyzed reactions, leaching of the noble metal is a major cause of catalyst deterioration. In this regard, the nanoreactor feature of this composite prevents Pd nanoparticles from leaching. In a series of controlled experiments, a composite with Pd nanoparticles loaded on carbon nanospheres (as shown in Fig. 1b, with no mesoporous SiO_2 coating) was used as catalyst. After the reactions, the catalyst was recovered, and the Pd content in the mother liquor as well as the Pd content on the catalyst was analyzed by ICP elemental analysis. After removal of the solid catalyst by centrifugation, the mother liquor was treated with fresh Suzuki reaction mixture to test the activity of the molecular Pd species that remained in the mother liquor.[19]

As shown in Table 2, the catalyst with Pd in the composite nanoreactor has a much higher activity than the catalyst with Pd on carbon nanospheres, showing again the superior catalytic activity of the composite nanoreactor. More significantly, the Pd leaching from the Pd on carbon spheres composite is about 8 times that of the Pd in hollow *meso*-SiO_2 composite. Note that both catalysts have the same initial Pd loading of 4.0 wt%. This proves that the nanoreactor feature of the composite indeed reduces Pd leaching. As a result, the iodobenzene conversion using the mother liquor from the composite nanoreactor as a catalyst is also much lower.

Table 2 Catalytic activity and Pd leaching of different catalysts

Catalyst	Catalysis activity[a] (%)	Pd in mother liquid (ppb)	Mother liquor activity[b] (%)
Composite nanoreactor	99.5	43	4.0
Pd@Carbon sphere	25.4	321	30

[a] In iodobenzene conversion at 3 min. [b] In iodobenzene conversion at 30 min. Conditions: 80 °C, ethanol (10 mL), iodobenzene (0.5 mmol), phenylboronic acid (1 mmol), K_2CO_3 (2 mmol), catalyst (10 mg, with Pd loading 4 wt%).

In summary, we have produced a composite nanoreactor with mesoporous silica hollow spheres and Pd nanoparticles inside. A multi-step and well-controlled route was developed to synthesize this composite material. The nanoreactor-like composite shows extremely high activity for Suzuki cross-coupling reactions: near complete conversion was reached in 3 min. Pd leaching is substantially reduced on the composite, which enables stable catalytic performance.

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