Trapping Pd(0) in nanoparticle-assembled microcapsules: an efficient and reusable catalyst†

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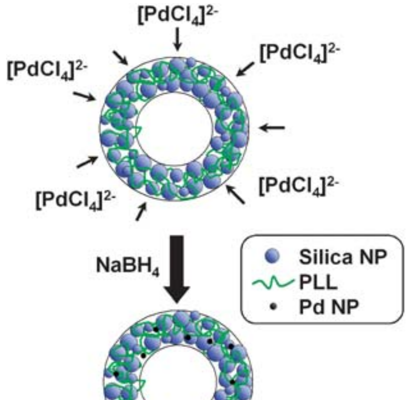
Pd nanoparticles dually encased by soft (polyamine) and hard (silica) materials in a microcapsule structure, obtained *via* a nanoparticle self-assembly method, exhibit excellent catalytic activity, with efficient catalyst recovery and reusability.

Palladium is among the most widely used transition metals in modern organic synthesis and synthetic transformations.[1] However, issues surrounding separation of the Pd from the desired product, stability to retain its activity and reusability often complicates its use. In this regard, there have been many efforts to immobilize Pd catalysts onto a support, such as charcoal, silica or alumina.[2] However, though this may result in high catalytic activities, the stability to metal leaching is not satisfactory.[3] Alternatively, encapsulation of the metal particles by polymers[4] or dendrimers[5] have been reported, but the catalysts further require mechanical stability against breakage of the host or leaching of the metallic particles. Recently, a number of reports have been published on the immobilization of Pd particles *via* ligand/polymer anchoring[6] and layer-by-layer assembly onto a solid support.[7] However, being a soft material, the ligand/polymer may not provide enough robustness against metal leaching, or for recyclability.[8] Therefore, our approach has been to uniquely combine the inorganic nanoparticles and polymeric components in such way that they intersperse with each other, so as to hold the Pd nanoparticles in a well-defined structure. While the polymer stabilizes the Pd nanoparticles in the structure, the inorganic particles provide the required mechanical stability.

In this report we demonstrate that microcapsules (MCs) formed by the self-assembly of nanoparticles and polyamines[9] can effectively be used to encapsulate Pd nanoparticles. MC formation by the polyamine-mediated self-assembly method involves ionic cross-linking of poly-L-lysine (PLL) chains with citrate to form spherical polymer aggregates.‡ These aggregates, because of their net positive charge, facilitate the assembly of negatively charged silica nanoparticles to form ordered MC structures. As a result, the shell wall acquires a composite structure, consisting of positively charged PLL chains interspersed with negatively charged SiO_2 nanoparticles. To immobilize the Pd particles, we firstly entrapped the negatively charged $[PdCl_4]^{2-}$ ions onto the polyamines present in the shell wall (Scheme 1). Then, in the second step, the entrapped Pd ions were reduced by adding sodium borohydride. The reduction of Pd(II) to Pd(0) in the Pd encapsulated MCs (Pd@MCs) was monitored by UV-vis absorption spectroscopy.† The disappearance of the absorption at 420 nm due to the Pd(II) ions indicated the reduction of the Pd ions present inside the MCs.

The optical microscopy, SEM and TEM images in Fig. 1(a)–(c) show the spherical morphology of the MCs of 2–5 μm diameter. As evident from the microscopic analyses, the Pd encapsulation did not cause any morphological change, indicating that the MCs are structurally robust under these experimental conditions. The TEM image in Fig. 1(c) clearly reveals the hollow nature of the MCs, with a shell thickness of 200–250 nm. The high resolution TEM (HRTEM) image in Fig. 1(d) illustrates the shell wall structure of the MCs, consisting of silica nanoparticles of ~15 nm diameter. In addition, a few darker spots, representing Pd nanoparticles of 2–3 nm diameter, are clearly seen embedded in the shell wall. The formation of well-dispersed, smaller-sized Pd nanoparticles may be a result of their stabilization by polyamines in a constrained porous medium, created by the assembly of silica nanoparticles. The porosity developed due to the assembly of silica nanoparticles in the MCs is evident in the HRTEM image (Fig. 1e).

The organic content of the Pd@MCs was characterized by FT-IR and TG-DTA analyses.† The IR bands at 3427 and 2925 cm^{-1}, assignable to N–H and C–H stretchings in the PLL, and 1647 cm^{-1}, due to carbonyl stretching in the citrate,



Scheme 1 Methodology to encapsulate Pd nanoparticles in nanoparticle-assembled MCs.

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† Electronic supplementary information (ESI) available: FT-IR and TG-DTA of Pd@MCs, SEM images of Pd@MCs after the reaction, catalytic activity of Pd@MCs in the recycling reaction and reactivity of PLL–Pd(0). See DOI: 10.1039/b807736c

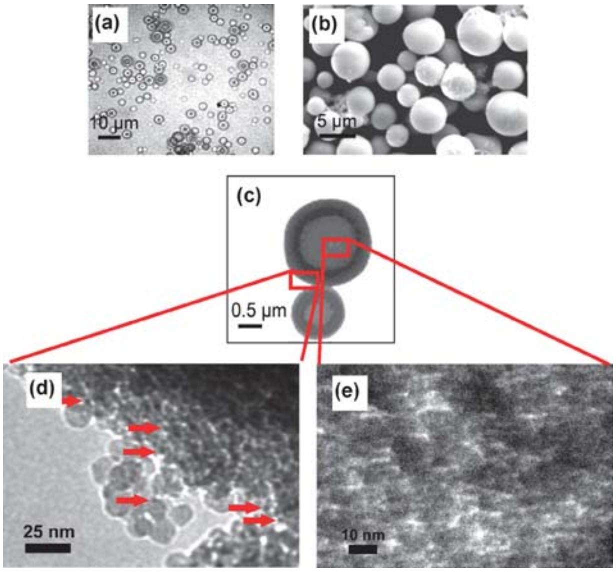


Fig. 1 (a) Optical microscopy, (b) SEM and (c) TEM images of Pd@MCs. (d) and (e) HRTEM images obtained from the indicated areas on the MC shown in Fig. 1(c). In Fig. 1(d), the Pd nanoparticles are indicated by arrows.

confirmed the presence of the respective organic molecules in the Pd@MCs. The total organic content was 20 wt%, as estimated by TGA. Atomic absorption spectroscopic (AAS) analysis showed that the Pd@MCs contain 4.31 wt% of Pd.

To ascertain the oxidation state of the Pd, X-ray photoelectron spectroscopy (XPS) studies were carried out. In Fig. 2, the XPS of a Pd@MC sample shows Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies (BE) at 336.4 and 342.1 eV, respectively. However, the literature value for pure metallic Pd is 335.1 eV (Pd $3d_{5/2}$).[10] As electron withdrawing groups are known to increase the BE of Pd,[11] the above peak shift is attributable to the presence of the surrounding positively charged ammonium groups of the PLL holding the metal nanoparticles inside the MC. The existence of Pd in a metallic state is a primary requirement for Pd-catalyzed hydrogenation reactions. It is also well recognized that amine groups can suppress the agglomeration of Pd nanoclusters, and hence enhance the catalytic efficiency of Pd nanoparticles.[12] It is therefore expected that the above criteria, along with the porous MC structure, should lead to enhanced activity and improved durability of the catalyst.

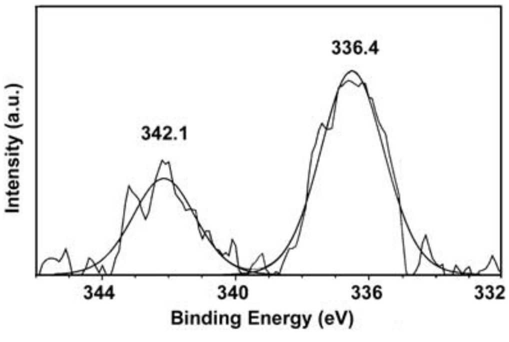
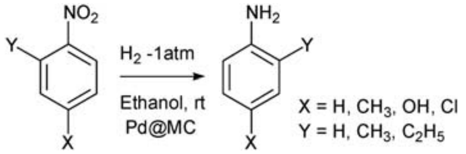


Fig. 2 XPS pattern of Pd@MCs showing Pd $3d_{5/2}$ and Pd $3d_{3/2}$ BE values.



Scheme 2 Pd@MC-catalyzed hydrogenation of nitroarenes.

The catalytic activity of the Pd@MCs was tested in hydrogenation of nitroarenes to anilines (Scheme 2).§ The Pd@MC particles are readily dispersable in the reaction mixture, and the conversion of unsubstituted nitrobenzene to aniline was excellent, with the reaction reaching completion within 1 h (Fig. 3(a)). In comparison, Pd/C takes ~10 h for only 65% conversion.[12] As expected for methyl- and ethyl- substituted nitrobenzene, the rate was relatively slow because of the positive inductive effect of the alkyl substituents (Fig. 3(a)). These results clearly prove that the Pd sites inside the MC are accessible by reactants of different molecular sizes and are also active in hydrogenation reactions. Furthermore, to test the effects of electron withdrawing groups as substituents, *para*-nitro phenol and *para*-chloro nitrobenzene were used as reactants. To our surprise, instead of enhancing the activity, both reactants exhibited either very low or no conversion. The same reactions were then carried out with Pd nanoparticles stabilized only by PLL (Pd–PLL), without the presence of silica.† On the contrary, the reduction of these substrates was possible with complete conversion. This indicates that the silica strongly interacts with the hydrophilic –Cl and –OH groups of the substrates, thereby not allowing them to access the Pd nanoparticles embedded inside the pores. More importantly however, the fact that the activity of Pd–PLL for other substrates was similar to that of Pd@MCs, clearly

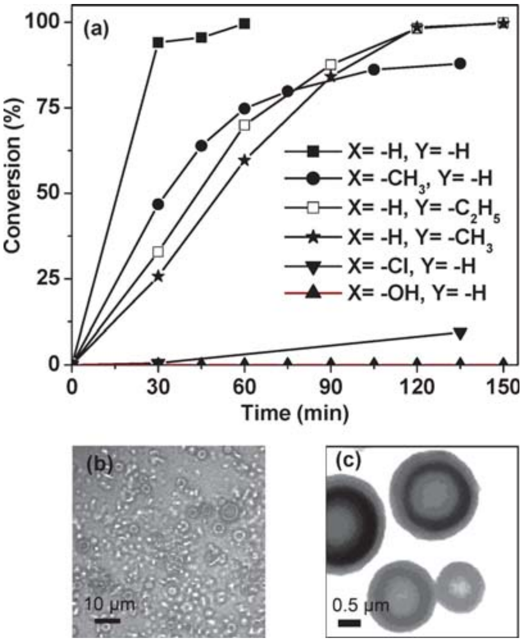


Fig. 3 (a) Plots of conversion *vs.* time when using the Pd@MC catalyst; (b) optical and (c) TEM images of the Pd@MCs after the 3rd reaction.

proves that the activity of the Pd nanoparticles is retained in the MCs.

After the reaction, the Pd@MC catalyst was separated from the reaction mixture by centrifugation (4000 rpm, 2 min). It should be noted that in the case of Pd–PLL, catalyst recovery was not possible at the same centrifugal speed. In Fig. 3(b)–(c), the optical and TEM images of the used catalysts reveal the intact hollow structure of the MCs. The reusability of the separated catalyst was checked in the hydrogenation of nitrobenzene to aniline, and it was found to be as active as in the 1st cycle.† The activity was consistently similar, even up to the 5th cycle. An AAS analysis of the MCs after the 5th cycle showed a Pd content of 4.28 wt%, indicating no apparent reduction in metal content. Since the MCs' structures remain mostly unaltered, it is believed that the active Pd sites also remain unchanged, and hence the catalytic activity is not affected.

The combination of nanoparticles, polyamines and porous MC structure probably give rise to synergistic effects that enhance the activity and durability of the catalyst. Thus, the above unique approach of encapsulating nanoparticles in a MC structure may find wide application in other transition metal-catalyzed reactions. Moreover, this method can also be modified to create different pore sizes or architectures in the MC, depending upon the size of the silica particles and the way they are assembled, thereby leading to shape selective catalysis.

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Notes and references

‡ *Synthesis of Pd@MCs:* To encapsulate Pd inside the MCs, PLL was used as the structure-directing agent. In a typical process, 1.3 mL of PLL (2 mg mL^{-1}, 150 kDa) was gently vortex-mixed for 10 s with 7.8 mL of trisodium citrate solution (5.36 mM), keeping the ratio, *R*, of the total negative charge on the citrate to the total positive charge on the PLL at 10 : 1. The slightly turbid solution was aged for 30 min and then vortex-mixed with 7.8 mL of silica sol (Snowtex-O, particle diameter 13 ± 3 nm; 20 wt% SiO_2) for 20 s to form the MCs. The cloudy suspension was allowed to age for 2 h, then centrifuged (4000 rpm, 2 min) to remove the unreacted reagents. The colourless precipitate was redispersed in 2.5 mL of trisodium citrate (5.36 mM) and aged for another 12 h. To this suspension was added 1.25 mL of sodium tetrachloropalladate (0.01 M), and this was stirred for 30 min to allow the binding of $[PdCl_4]^{2-}$ with the positively charged polyamines present inside the MC. The solution was then centrifuged to remove the unbound $[PdCl_4]^{2-}$ ions, and the yellow precipitate was redispersed in 2 mL of trisodium citrate (5.36 mM). To reduce the entrapped Pd ions, 100 μL of sodium borohydride (0.01 M) was added and the vessel kept closed for 30 min, during which time the colour of the precipitate changed to greyish-black. The Pd@MCs that formed were centrifuged (4000 rpm, 2 min), washed with de-ionized water, dried at room temperature and stored for further studies.

§ *Pd@MCs as a catalyst for hydrogenation reactions:*To demonstrate the catalytic activity of the Pd@MCs, the hydrogenation of nitroarenes to anilines was used as a model reaction. In a typical reaction, 2 mmol of nitroarene was dissolved in 5 mL of ethanol with 0.005 g of catalyst under 1 atmosphere of hydrogen. The reaction progress was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After the reaction, the hollow silica Pd@MCs were separated from the reaction mixture by centrifugation (4000 rpm, 2 min). Thereafter, the catalyst was washed with ethyl acetate and used in the next reaction.

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