Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pd Nanoparticle Concentration Dependent Self-assembly of Pd@SiO_2 Nanoparticles into Leaching Resistant Microcubes

Abheek Datta,† Anustup Sadhu,† Subhankar Santra,† S. M. Shivaprasad,‡ Swadhin K. Mandal† and Sayan Bhattacharyya†,*

†Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur - 741252, Nadia, W.B., India, and ‡International Centre for Materials Science & Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore – 560064, India.

* Email for correspondence: sayanb@iiserkol.ac.in

S1. Experimental Section

Materials: TEOS ($Si(OC_2H_5)_4$, Merck India, synthesis grade), DTAB (Sigma Aldrich, 98%), potassium tetrachloropalladate (K_2PdCl_4, Arora Matthey Limited), tri-sodium citrate dihydrtate ($Na_3C_6H_5O_7$, Merck India, 99%), polyvinylpyrrolidone (PVP, Loba Chemie, Mol. Wt. 40,000), SDS (Merck ≥90%), Triton®X-100 (Sigma-Aldrich, laboratory grade), hydrofluoric acid (HF, Merck, 40%), nitric acid (Suprapur, Merck, 65%), 4-bromo toluene (Sigma Aldrich, 98%), phenyl boric acid (Sigma Aldrich, 98%) and DMF (pro analysi N, N-dimethylformamide GR, Merck) were used without further purification.

Characterization: H_2 reduction of the Pd-SiO_2 composites were performed in a Carbolite wire-wound tube furnace - single zone, model MTF 12/38/400. The ICP-MS measurements were carried out in a Thermo Scientific X-series with Plasma lab software. 10 mg of the Pd-SiO_2 composites was mixed with 9 ml of distilled water and 1 ml HF followed by vigorous stirring for 2 h. The acidic solution was evaporated to dryness and the residue was kept in vacuum overnight. 5 ml of Suprapur HNO_3 was added to 2 mg of the dried residue and heated at 130^oC for 0.5 h. The solution was made up to 40 ml with H_2O and 200 μL was pipetted out to prepare 500 ppb aqueous solution, which was the required concentration for ICP-MS measurements. TEM images were obtained by UHR-FEG-TEM, JEOL, JEM 2100 F model using 200 kV electron source. The XRD measurements were carried out with a Rigaku (mini flex II, Japan) powder X-ray diffractometer having Cu Kα = 1.54059 Å radiation. FESEM images were recorded in Carl Zeiss SUPRA 55VP FESEM and the SEM images of the products from control experiments were recorded using the table-top Hitachi TM3000. EDAX studies were performed with the Oxford Instruments X-Max with INCA software coupled to the FESEM. The Fourier transform infrared (FTIR) measurements were carried out with a Perkin Elmer spectrum RX1 with KBr pellets. XPS measurements were performed on the samples mounted on copper stubs with silver paste, using Al Kα radiation (1486.6 eV) in a commercial photoelectron spectrometer from VSW Scientific Instruments. The base pressure of the chamber was maintained around 5×10^{-10} mbar during the experiments. The solid-state ^{1}H NMR measurements were performed on a Bruker Avance III 500 MHz spectrometer under magic angle spinning (MAS). The spectra were collected at the MAS speed of 10000 Hz with an error of ±1 Hz. Solution state NMR was recorded with JEOL-400 MHz at 278 K with $CDCl_3$ as the solvent. All chemical shift values are referenced to tetramethylsilane (TMS). The surface area and porosity measurements were carried out with a Micromeritics Gemini VII surface area analyzer. The nitrogen adsorption/desorption isotherms were recorded 2-3 times to obtain reproducible results and reported by BJH (Barret-Joyner-Halenda) surface/volume mesopore analysis. The micropore volume was calculated using the Frenkel-Halsey-Hill isotherm equation. Each sample was degassed at 300^{o}C for 2 h.

Materials Synthesis:

Pd NPs: Pd NPs were synthesized as reported by Šlouf *et al.*,[1] with slight modifications. 0.06 g of anhydrous K_2PdCl_4 was added to 4 mL of 1N HCl and the volume was made up to 200 mL with H_2O to prepare a 9.3×10^{-4} M solution of K_2PdCl_4. Aqueous solutions of 1% sodium citrate and 0.05 % NaOH was separately prepared. Thereafter, 30 mL of K_2PdCl_4 solution, 60 mL of citrate solution, and 210 mL of deionized water were mixed in a 500 mL round bottom flask and refluxed with intense stirring for 6 h. The pH of the solution was maintained at 10 with NaOH solution. At this step the Pd NP solution was synthesized.

Mesoporous SiO_2: Mesoporous SiO_2 was synthesized by acid hydrolysis of TEOS. 1.2 ml of TEOS and 0.05 g of DTAB were taken in a round bottom flask and 30 ml of distilled water was added to it. The pH of the solution was maintained at 2 by adding 1 (N) hydrochloric acid (HCl) and stirred overnight at 70°C. Upon completion of the reaction, the product was separated by centrifugation and washed three times with ethanol followed by drying at 150°C for 2 h. The above protocol was performed separately in air and N_2. A part of the AS samples was reduced under H_2 flow at 550°C for 2 h.

Pd-SiO_2 Core-shell Composites and Microcubes: After refluxing the Pd NP solution comprising 30 mL K_2PdCl_4, 60 mL sodium citrate, 210 mL H_2O and NaOH to maintain pH~10, 0.05 g of DTAB was added to the Pd NP solution and stirred for 0.5 h. 1N HCl was added to the solution to maintain an acidic pH~2 and stoichiometric quantity of TEOS was added to load the Pd NPs inside SiO_2.The mixture was stirred overnight at 70°C separately in air and N_2. The products were centrifuged and washed three times with ethanol. The AS products were dried at 150°C for 2 h and reduced under H_2 flow at 550°C for 2 h.

Pd NPs immobilized on Mesoporous SiO_2 Surface: H-550 pristine SiO_2 (prepared in air) and colloidal Pd NP solution were prepared as described previously. An aqueous solution of PVP was prepared by dissolving 0.067 g of PVP in 50 ml distilled water. 0.01 g of SiO_2 was mixed with the PVP solution and stirred for 1 h followed by addition of required amount of Pd NP colloidal solution to obtain Pd NPs attached to the surface of porous SiO_2. The final solution was stirred for 6 h followed by separation of the products by centrifugation. The products were washed three times with ethanol and dried at 150°C for 2 h.

Suzuki Miyaura Coupling Reactions and Recyclability Tests: Suzuki Miyaura cross-coupling reactions were performed with 0.41 wt% Pd@SiO_2 microcubes and 0.37 wt% Pd NPs immbolized on mesoporous SiO_2. For optimized reaction conditions, the catalysis reactions were performed in a 25 ml schlenk flask. A mixture of 4-bromotoluene (1 mmol), phenylboronic acid (1.5 mmol, 0.182 g), K_2CO_3 (2 mmol, 0.27g), Pd-SiO_2 catalyst (5-6 mg) and DMF:H_2O (1:3; 5 ml) was heated at 100°C with constant stirring for 6 h under N_2 atmosphere. After the completion of reaction the product was separated by column chromatography and characterized by NMR studies. For the recyclability tests, the product mixture was filtered and the solid catalyst obtained was washed with distilled water and ethanol followed by drying in vacuum for 2h. Then the recovered catalyst was used for further reactions.

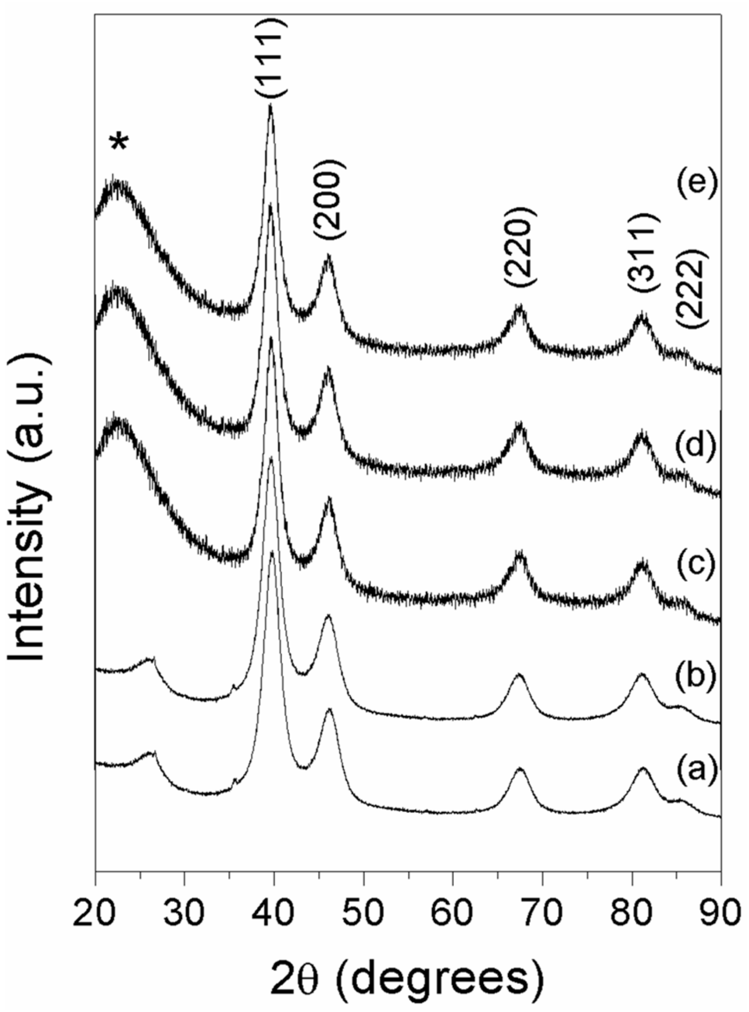


Figure S2: XRD patterns of H-550 Pd-SiO$_2$ composites with Pd wt% of (a) 0.14 (air), (b) 0.09 (N$_2$), (c) 0.41 (air), (d) 0.34 (N$_2$) and (e) 0.37 (deposited outside SiO$_2$). The Pd^0 reflections are indicated and the asterick (*) shows the peaks of amorphous SiO$_2$.

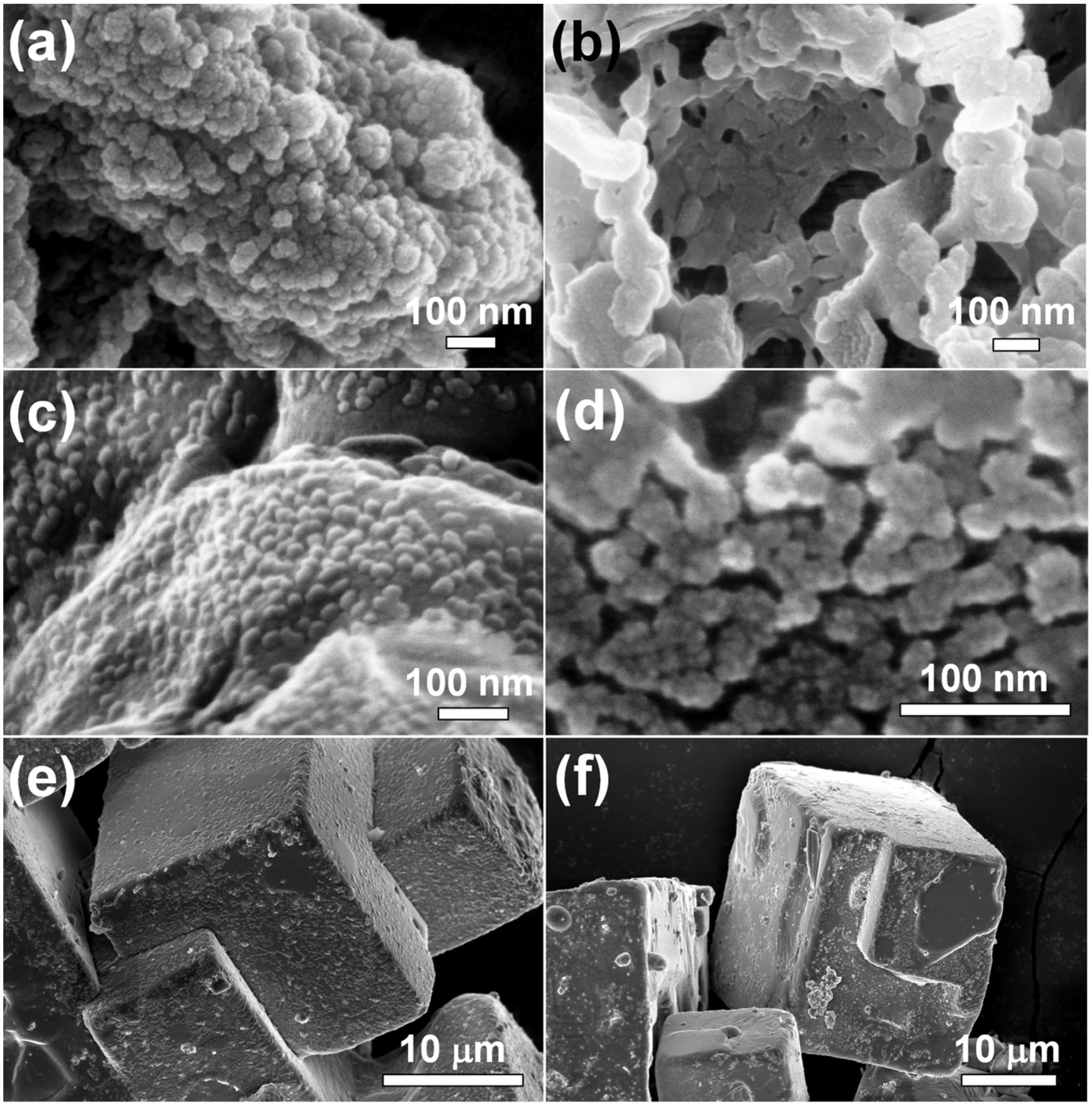


Figure S3: FESEM images of the as-synthesized Pd-SiO$_2$ composites with Pd wt% of (a) 0 (air), (b) 0 (N$_2$), (c) 0.14 (air), (d) 0.09 (N$_2$), (e) 0.41 (air) and (f) 0.34 (N$_2$).

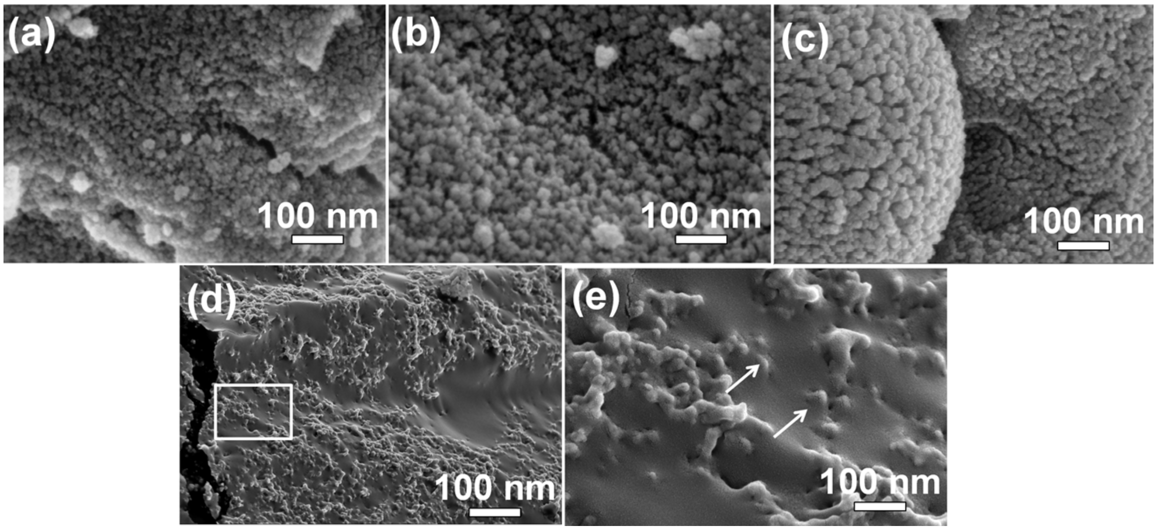
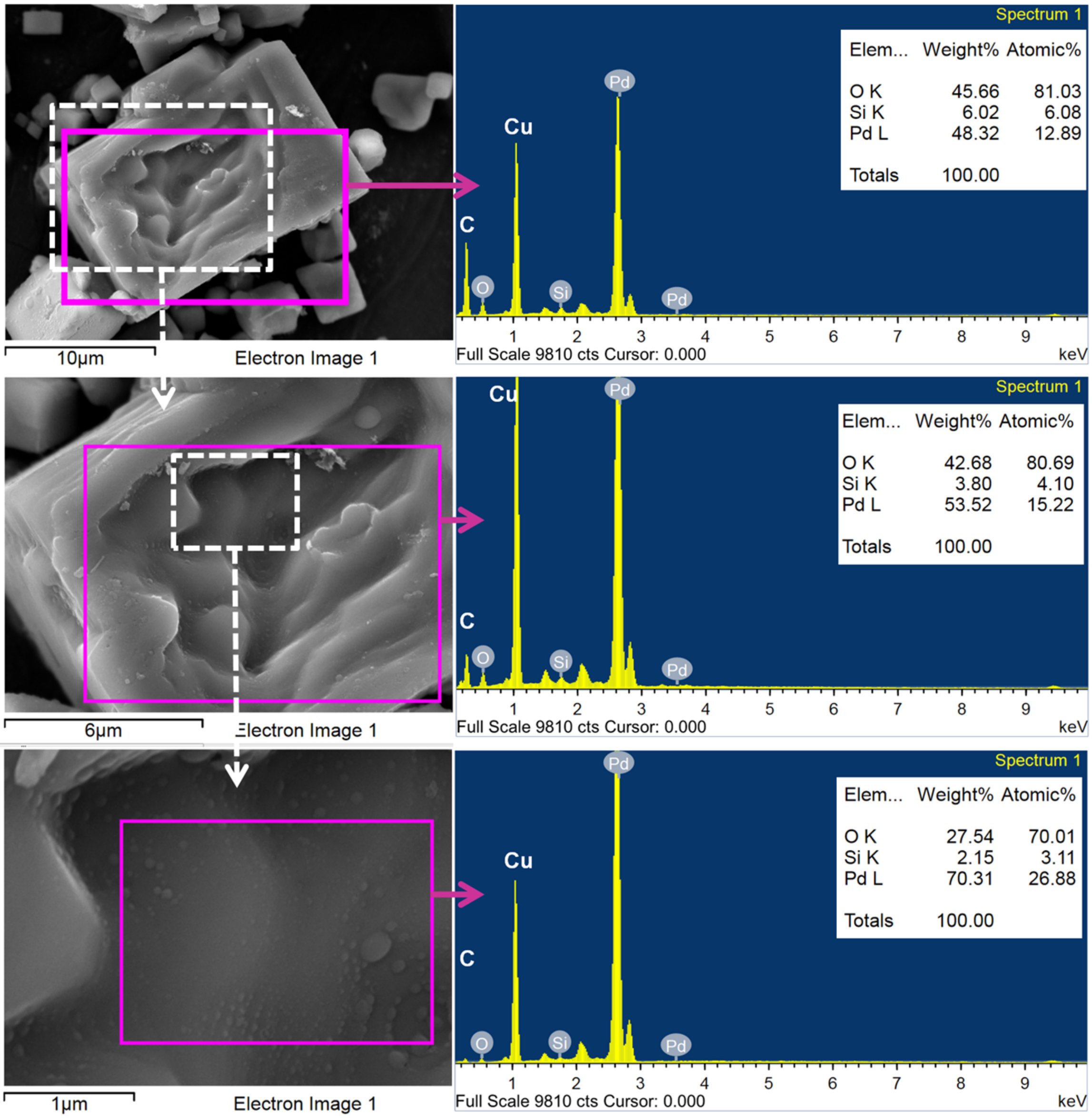


Figure S4: FESEM images of H-550 Pd-SiO_2 composites with Pd wt% of (a) 0 (air), (b) 0 (N_2), (c) 0.09 (N_2). (d) 0.37 wt% Pd deposited outside mesoporous SiO_2 and (e) enlarged view of the marked area in *(d)* with arrows showing the PVP capped Pd NPs.



Elem...	Weight%	Atomic%
O K	45.66	81.03
Si K	6.02	6.08
Pd L	48.32	12.89
Totals	100.00	

Elem...	Weight%	Atomic%
O K	42.68	80.69
Si K	3.80	4.10
Pd L	53.52	15.22
Totals	100.00	

Elem...	Weight%	Atomic%
O K	27.54	70.01
Si K	2.15	3.11
Pd L	70.31	26.88
Totals	100.00	

Figure S5: EDAX spectra of a 0.34 wt% Pd-SiO_2 microcube synthesized in N_2, showing the relative increase of Pd concentration from the surface to the core of the microcube groove.

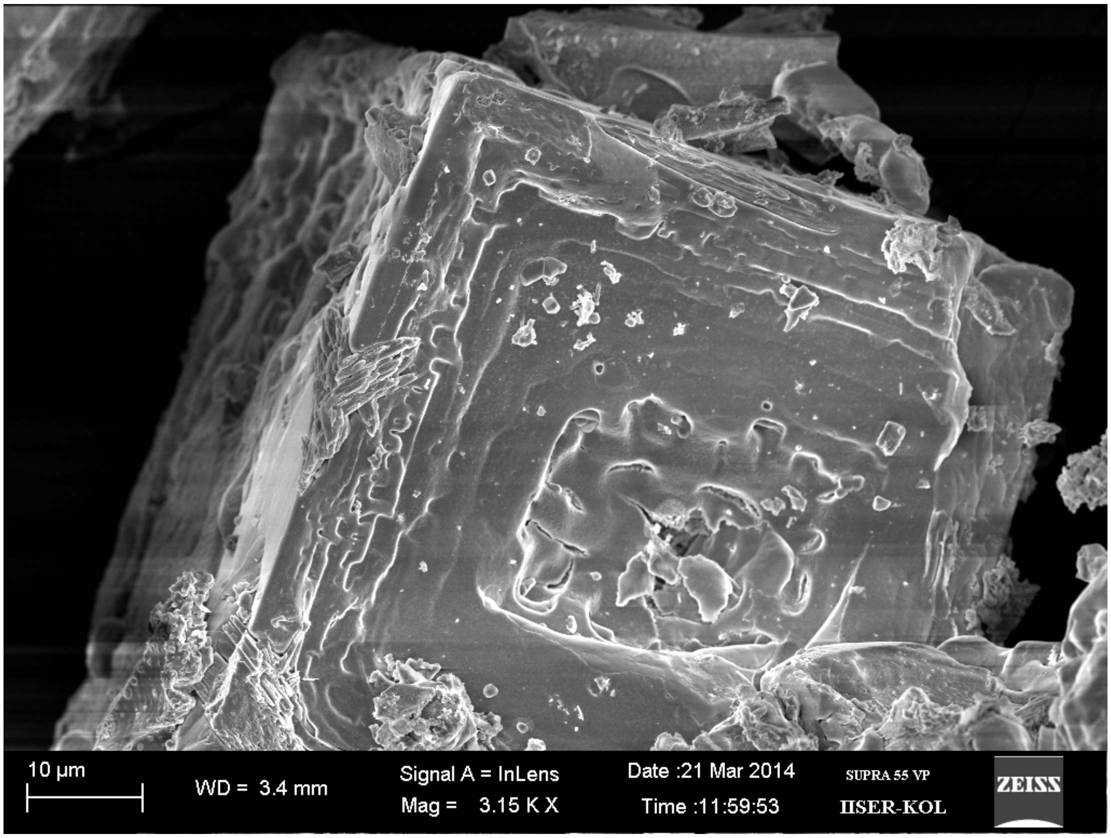


Figure S6: FESEM image of ~1 wt% Pd-SiO_2 microcube synthesized in air.

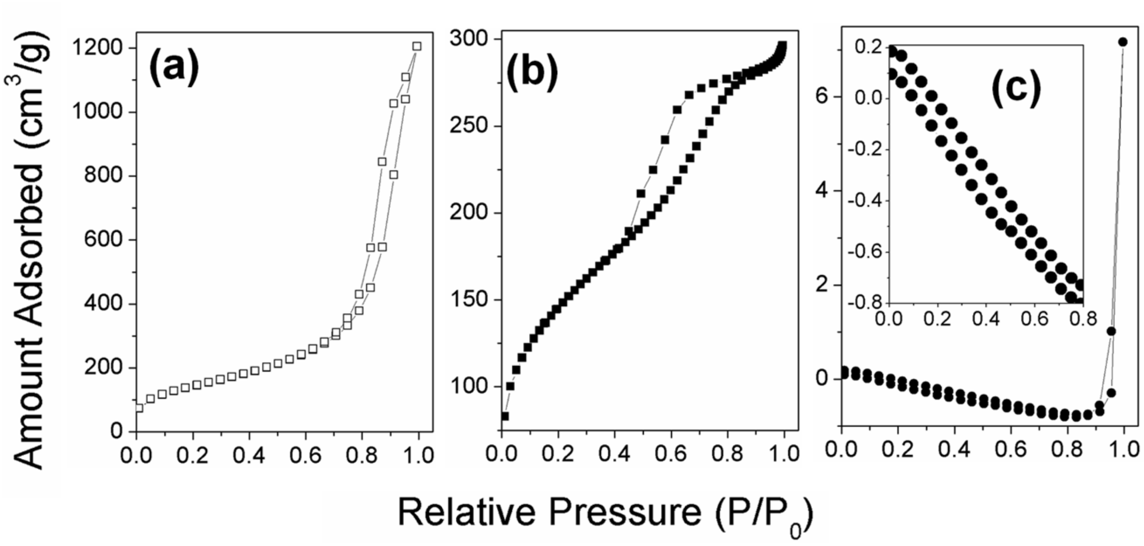


Figure S7: Nitrogen adsorption/desorption isotherms of H-550 Pd-SiO_2 composites with Pd wt% of (a) 0 (air), (b) 0 (N_2) and (c) 0.09 (N_2). Inset (d) show the enlarged view of the low pressure hysteresis.

Table S8: Surface area (SA), pore diameter (D) and pore volume (V) of the AS and H-550 samples.

Sample	Pd NP (weight %)	Air			N_2		
		SA (m^2/g)	D (nm)	V (cm^3/g)	SA (m^2/g)	D (nm)	V (cm^3/g)
AS	0	573.5	3.2 (sharp), 6.6 (strong), 9.2 (broad)	0.9	580.5	3.8	0.49
	0.14, 0.09	8.2	---	---	11.0	---	0.14
	0.41, 0.34	0.17	---	---	0.15	---	---
H-550	0	512.0	13.8	1.8	510.9	3.8 (sharp), 5.0 (broad)	0.38
	0.14, 0.09	49.0	---	0.04	0.03	---	---
	0.41, 0.34	1.4	---	0.03	1.0	---	---

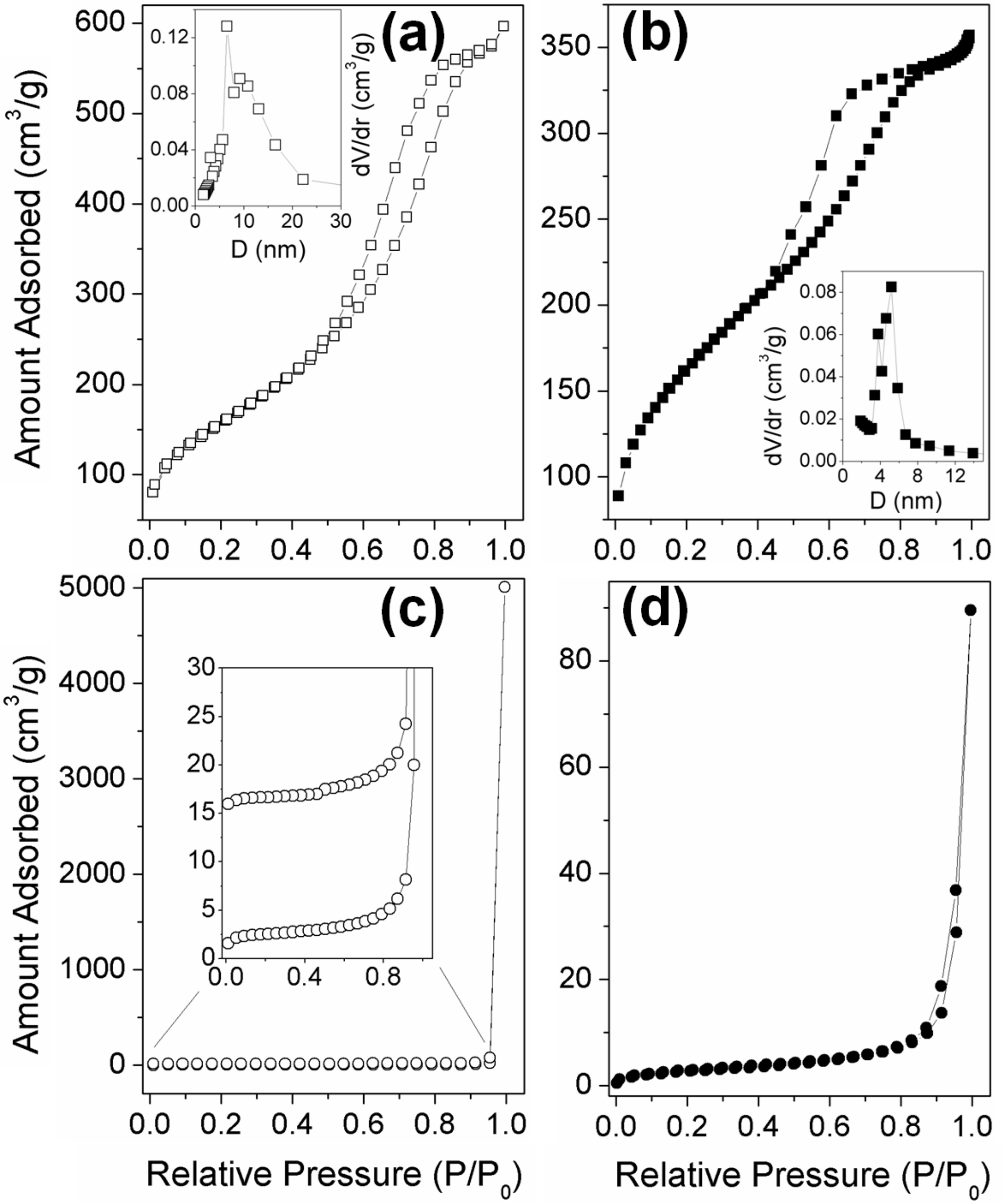


Figure S9: Nitrogen adsorption/desorption isotherms of as-synthesized Pd-SiO_2 composites with Pd wt% of (a) 0 (air), (b) 0 (N_2), (c) 0.14 (air) and (d) 0.09 (N_2). Insets (a, b) show the corresponding pore size distribution and inset (c) shows the enlarged view of the low pressure hysteresis.

S10. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of AS 0.41 wt% Pd-SiO_2 microcubes in air showed that at 246, 550 and 950°C, the corresponding weight losses were 6, 20 and 30 wt%, respectively. At ≤ 246°C, the weight loss corresponds to the melting of citrate and DTAB and also the loss of adsorbed H_2O. At 550°C, the hydrogenation temperature, the remaining loss of 14 wt% was primarily due to the loss of DTAB close to the surface of the microcubes. The additional DTAB trapped within the microcube grooves contributed in stabilizing the cube structure. When the microcubes were heated at higher temperatures in air, the trapped DTAB and silanol groups were also lost, which amounts to ~10 wt% at 950°C. TGA analysis of the H-550 microcubes showed ~6 wt% loss at 950°C. Thus ~14 wt% DTAB contributed in the morphological transformation and ~6 wt% DTAB helped in stabilizing the microcube structure.

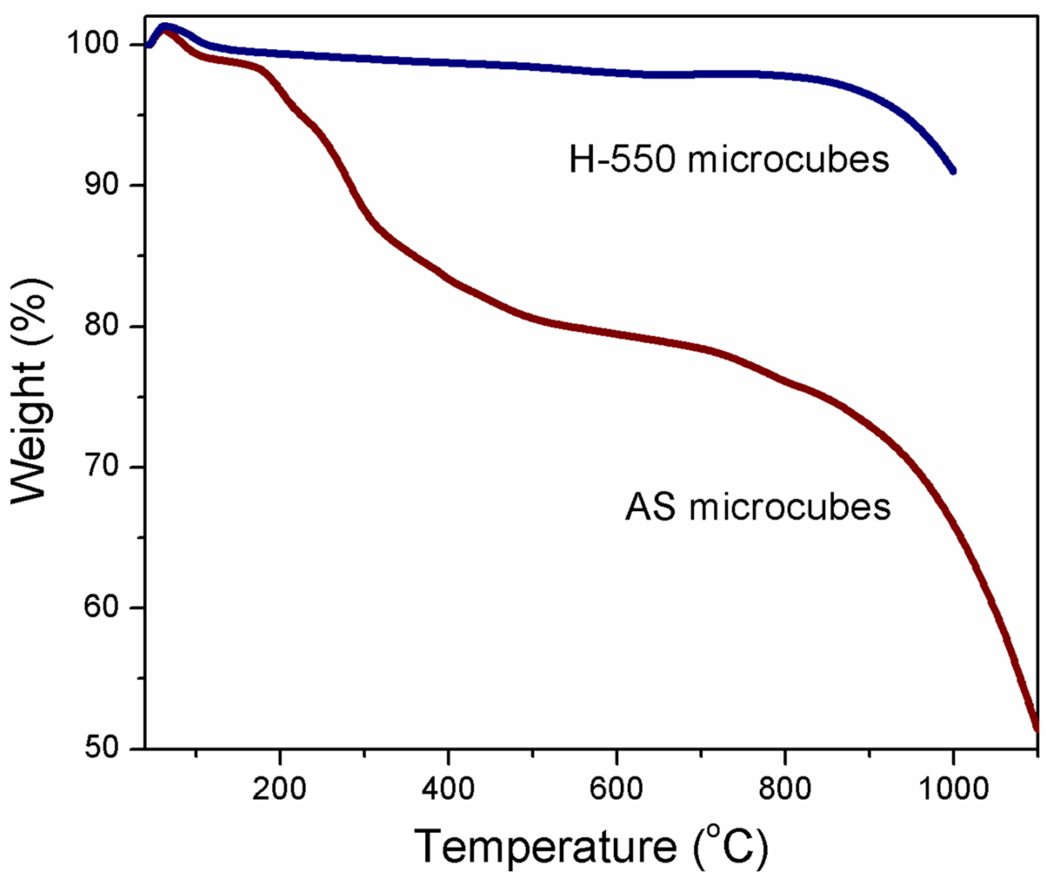


Figure S10: TGA plots of AS and H-550 0.41 wt% Pd-SiO_2 microcubes in air.

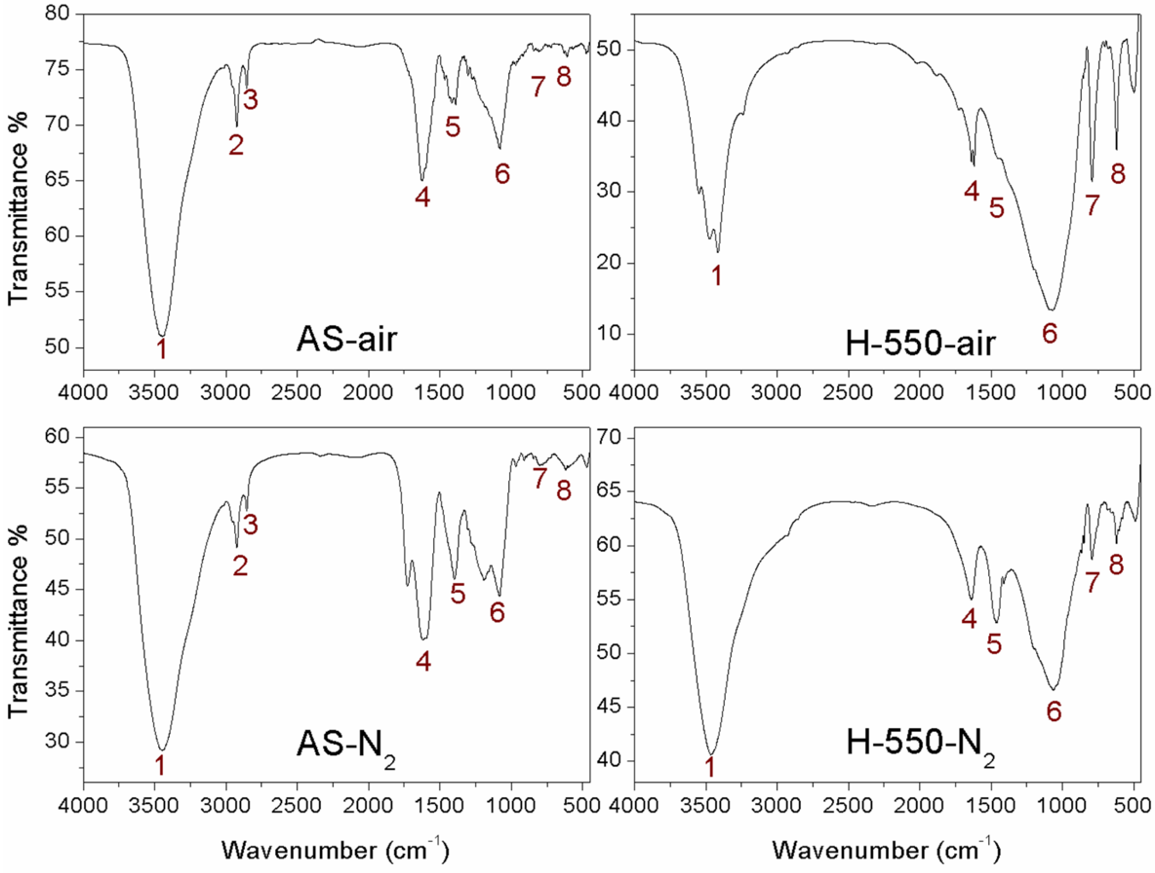


Figure S11: FTIR spectra of the AS and H-550 0.34-0.41 wt% Pd-SiO_2 microcubes prepared in air and N_2. The bands: (1) O-H stretching, (2, 3) C-CH_2 stretching (from DTAB),[2, 3] (4, 5) N-CH_3 stretching (from DTAB),[2] (6) Si-O-Si stretching (TO_3 mode),[3, 4] (7) Si-O-Si stretching (TO_2 mode)[3] and (8) Si-O-Si stretching (TO_1 mode).[3]

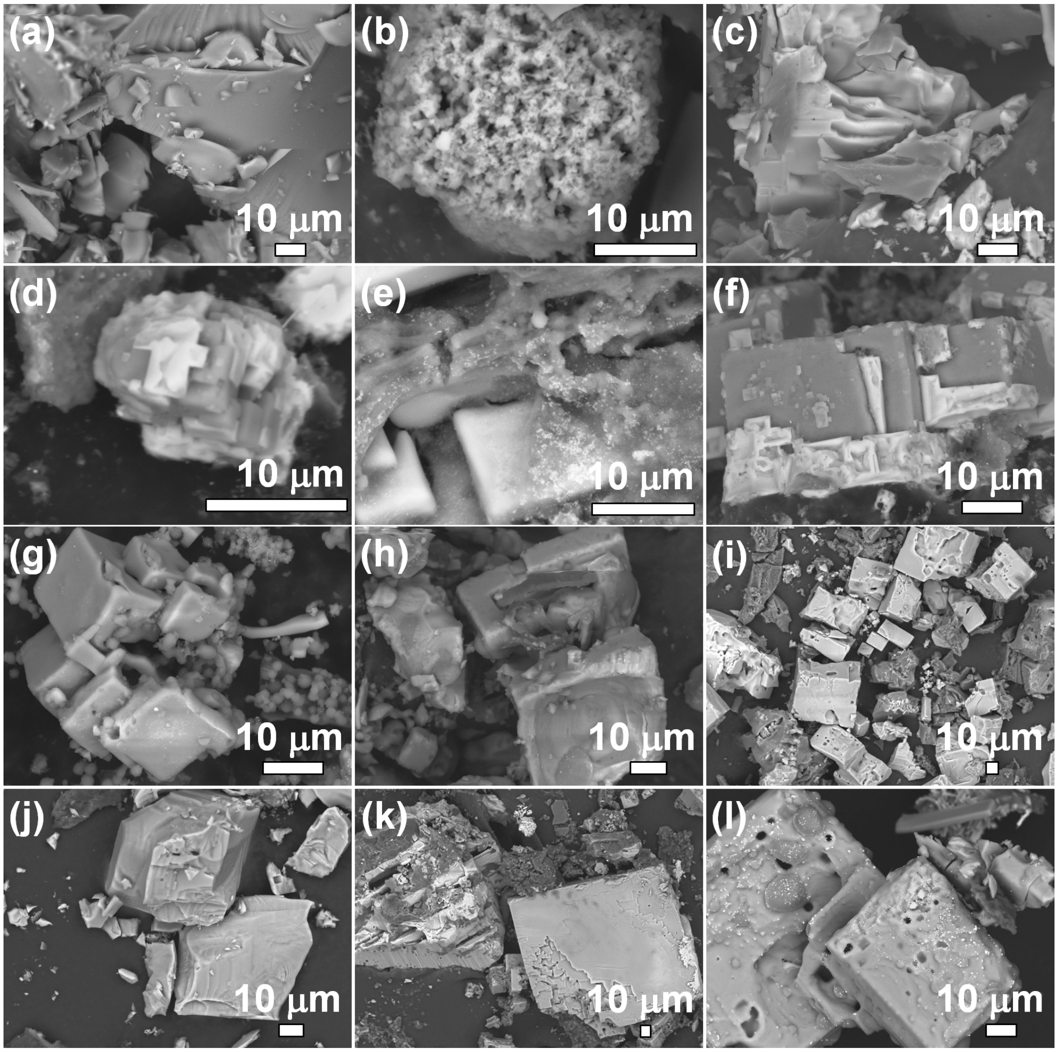


Figure S12: SEM images of the ~0.35 wt% Pd-SiO_2 composites obtained from control experiments performed in air. (a) as-synthesized SiO_2 without Pd NPs and DTAB, (b) hydrogenated *(a)*, (c) as-synthesized Pd-SiO_2 without DTAB, (d) hydrogenated *(c)*, (e) as-synthesized Pd-SiO_2 with 0.025 g DTAB, (f) hydrogenated *(e)*, (g) as-synthesized Pd-SiO_2 with 0.1 g DTAB, (h) hydrogenated *(g)*, (i) as-synthesized Pd-SiO_2 with 0.05 g SDS, (j) hydrogenated *(i)*, (k) as-synthesized Pd-SiO_2 with 0.05 g Triton X-100, (l) hydrogenated *(k)*.

DTAB plays a key role in stabilizing the porous structure of pristine SiO_2 and without DTAB random shapes were obtained. The same holds true for the Pd-SiO_2 composites without DTAB, where after hydrogenation, the Pd-SiO_2 stacks did not assemble into microcubes. During the formation of the microcubes, 0.05 g DTAB was optimized. Half the amount of DTAB resulted in a mixture of a gluey mass over the plate-like structures and grooved microcubes were not observed after hydrogenation. With 0.1 g of DTAB, broken microcubes were obtained, showing that 0.05 g DTAB is the optimum concentration in making the microcubes. Control experiments were also performed with an anionic surfactant, sodium dodecyl sulfate (SDS) and a neutral surfactant Triton®X-100. Both formed irregular to cube-like shapes.

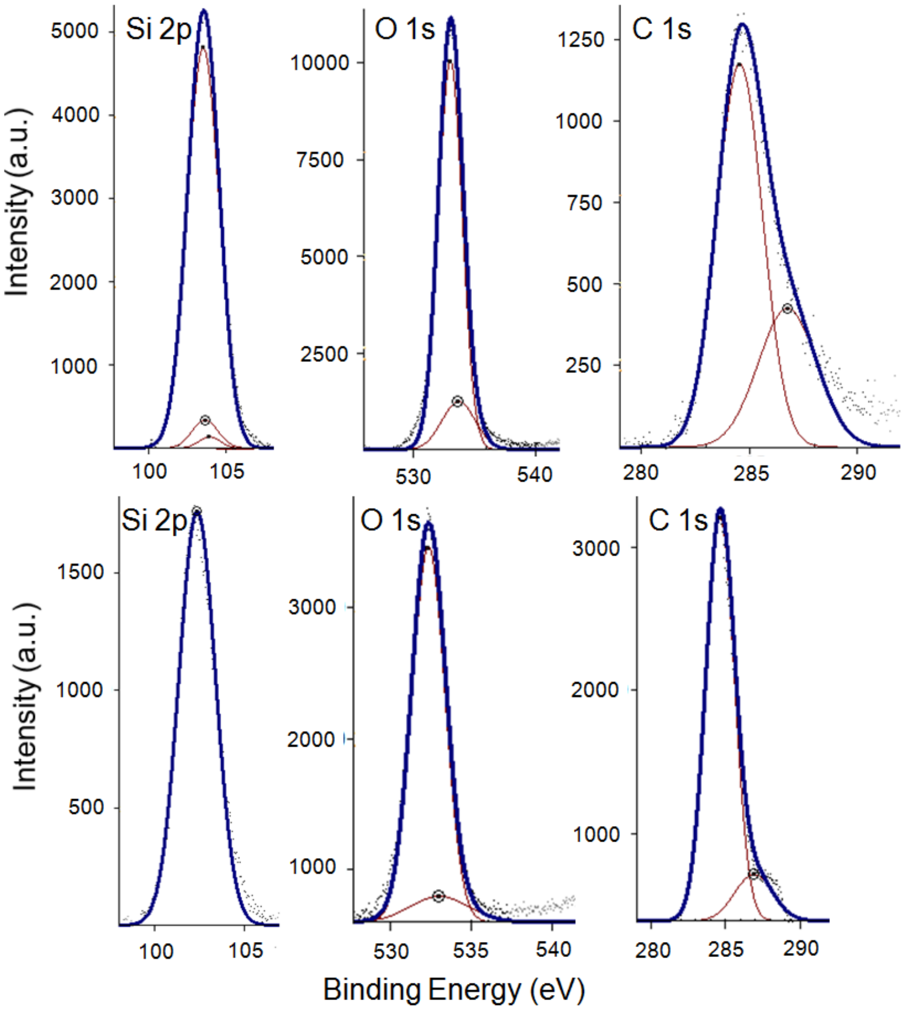


Figure S13: XPS spectra. (Top panel) H-550 0.41 wt% Pd-SiO_2 microcubes synthesized in air and (bottom panel) 0.37 wt% Pd NPs deposited outside mesoporous SiO_2. The fitted spectral positions of the deconvoluted Si *2p*,[5-8] O *1s*,[9-11] and C *1s* levels,[12] match well with the literature reports.

Table S14: Deconvoluted XPS peaks at different binding energies (B.E.), their full width at half maximum (FWHM) and corresponding assignment.

Sample	Element	B.E. (eV)	FWHM	State	Relative area %
0.41 wt% Pd-SiO_2 (air) H-550	Pd $d_{5/2}$	335.1	1.63	Pd^0	64
		336.8	2.92	Pd^{2+}	36
	Pd $d_{3/2}$	340.2	2.22	Pd^0	63
		342.4	2.58	Pd^{2+}	37
	Si *2p*	103.3	2.40	SiO_2	93
		103.6	1.9	Si-OH	05
		103.9	1.6	Si-OH	02
	C *1s*	284.2	3.34	C=C	69
		284.6	2.60	C-OH	31
	O *1s*	532.9	2.50	SiO_2	79
		533.4	1.50	Pd-O	21
0.37 wt% Pd deposited outside SiO_2	Pd $d_{5/2}$	335.4	1.65	Pd^0	57
		337.1	3.00	Pd^{2+}	43
	Pd $d_{3/2}$	340.6	1.43	Pd^0	51
		342.1	2.58	Pd^{2+}	49
	Si *2p*	102.4	2.40	SiO_2	100
	C *1s*	284.6	2.24	C=C	85
		286.8	3.00	C-OH	15
	O *1s*	532.4	2.40	SiO_2	89
		533.0	4.00	Pd-O	11

Table S15: Suzuki-Miyaura cross-coupling of phenylboronic acid and 4-bromotoluene, catalyzed by 0.41 weight% Pd-SiO_2 microcubes using various bases and solvents. All reactions were performed at 100°C for 6 h.

Base	Solvent	Yield (%)
K_2CO_3	DMF: H_2O (1:3)	~99
K_3PO_4	DMF:H_2O (1:1)	~86
K_3PO_4	Iso-propanol	~79
Cs_2CO_3	DMF	~75
K_2CO_3	DMF	~74
Cs_2CO_3	Dioxane	~69
NaOMe	Dioxane	~55

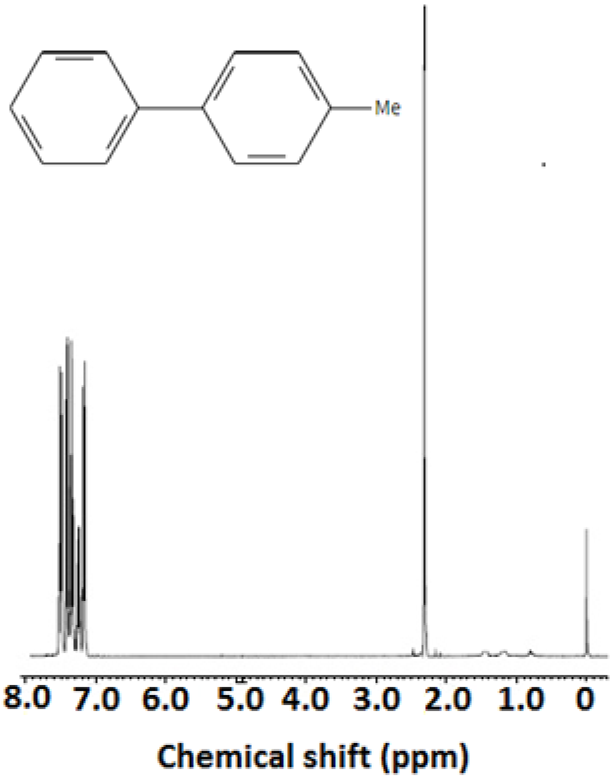


Figure S15: ^{1}H NMR spectrum of the product.

S16: Turnover number (TON) and Turnover frequency (TOF)

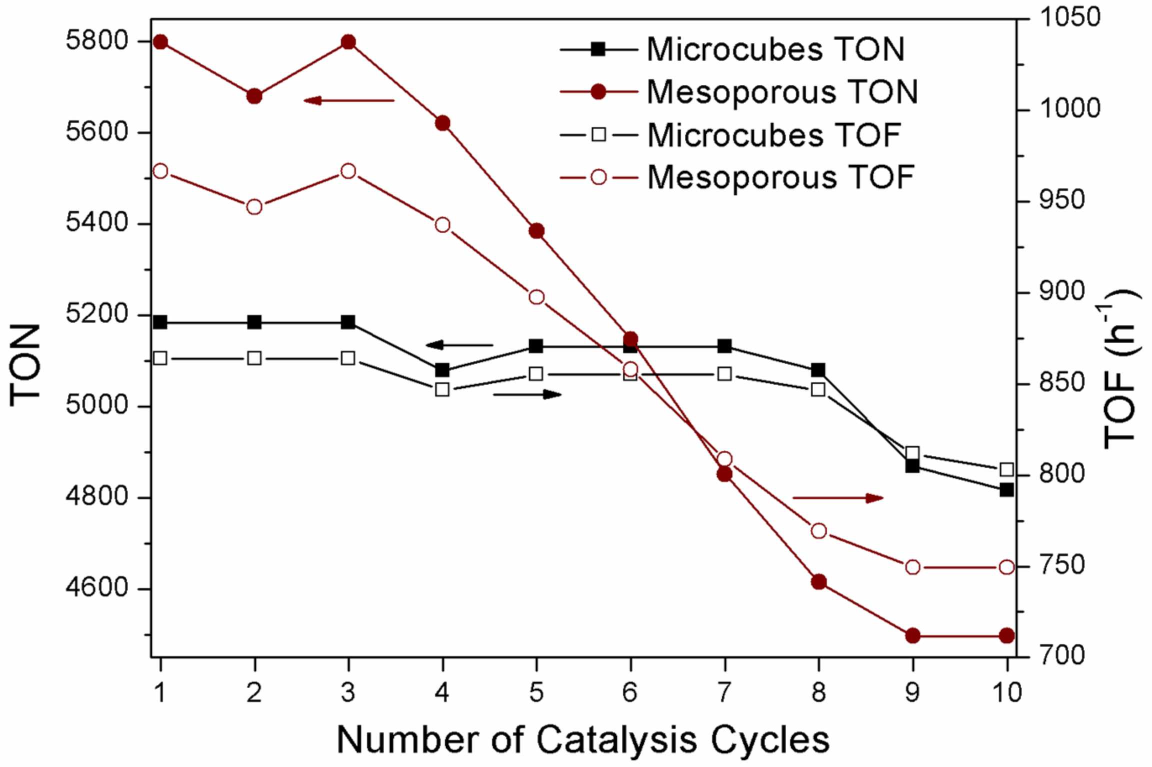


Figure S16: Catalytic activity of H-550 0.41 wt% Pd-SiO_2 microcubes and 0.37 wt% Pd NPs deposited outside mesoporous SiO_2.

Note: When the initial concentration of DTAB was lowered, the Pd NPs were exposed outside leading to higher chances of leaching. With higher concentration of DTAB than the threshold amount of 0.05 g, DTAB formed a thick coating around the microcubes providing limited access to the reactants. With 0.025g and 0.1 g DTAB the Pd-SiO_2 microcubes showed isolated yields of 27 and 15%, respectively.

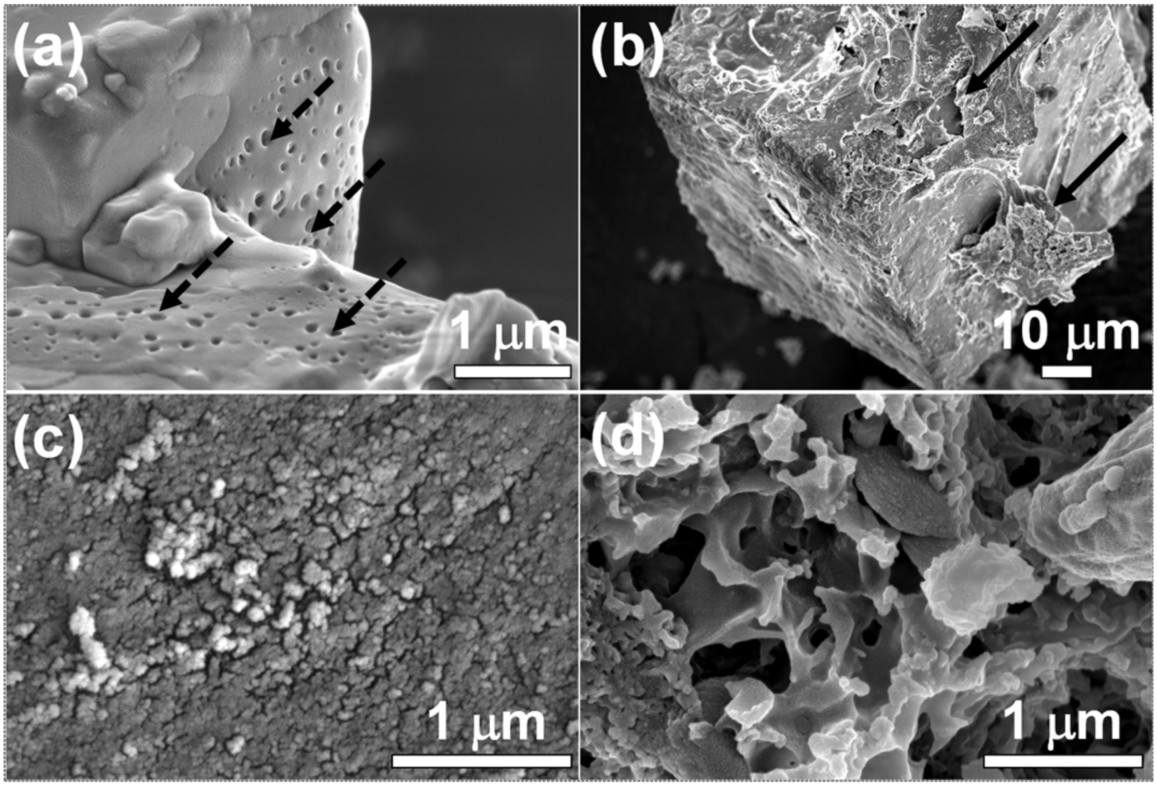


Figure S17: FESEM images of the Pd@SiO_2 microcube catalyst after (a) 5th and (b) 10th cycle and Pd NP - mesoporous SiO_2 catalyst after (c) 5th and (d) 10th cycle. The dotted arrows in (a) show the holes created by leaching of the surface unprotected Pd NPs and the solid arrows in (b) show the exfoliation of the outer layer of the microcube.

In comparison, commercial silica supported Pd catalyst systems undergo fast deactivation due to leaching of the nanoparticles and Pd nanoparticles anchored on conventional silica show diminished catalytic activity due to excessive leaching.[13, 14]

References

1 M. Šlouf, E. Pavlova, M. Bhardwaj, J. Plĕstil, H. Onderková, A. A. Philimonenko and P. Hozák, *Mater. Lett.,* 2011, **65**, 1197-1200.

2 R. B. Viana, A. B. F. da Silva and A. S. Pimentel, *Adv. Phys. Chem.,* 2012, **903272**-(1-14).

3 P. Innocenzi, P. Falcaro, D. Grosso and F. Babonneau, *J. Phys. Chem. B,* **2003**, **107**, 4711-4717.

4 J. Osswald and K. T. Fehr, *J. Mater. Sci.,* 2006, *41,* 1335-1339.

5 G. Kumar, G. R. Blackburn, R. G. Albridge, W. E. Moddeman and M. M. Jones,. *Inorg. Chem.,* 1972, **11**, 296-300.

6 A. Tressaud, S. Khairoun, H. Tohara and N. Watanabe, *Anorg. Allg. Chem.,* **1986, 540**, 291-299.

7 M. C. Militello and S. J. Simko, *Surf. Sci. Spectra.*, ***1994***, 3, 387-392.

8 T. H. Fleisch, G. W. Zajac, J. O. Schreiner and G. Mains, *Appl. Surf. Sci.,* 1986, **26**, 488-497.

9 S. Salimian and M. Delfino, *J. Appl. Phys.,* 1991, **70***,* 3970-3972.

10 S. L. Andersson and T. M. S. Scurrell, *J. Catal.*, **1979**, 59, 340-356.

11 D. Sprenger, H. Bach, W. Meisel and P. Gütlich, *J. Non-cryst. Solids,* 1990, **126***,* 111-129.

12 S. Santra, P. Ranjan, P. Bera, P. Ghosh and S. K. Mandal, *RSC Adv*., 2012, **2**, 7523–7533.

13 Y. Ji, S. Jain and R. J. Davis, *J. Phys. Chem. B,* 2005, **109,** 17232-17238.

14 V. Polshettiwar, C. Len, A. Fihri, *Coord. Chem. Rev.,* 2009, **253**, 2599-2626.