Supporting Information

Organosilica nanotubes: large-scale synthesis and encapsulation of metal nanoparticles

Xiao Liu,[a,b] Xiaobo Li,[a,b] Zaihong Guan,[a,b] Jian Liu,[a] Jiao Zhao,[a,b] Yan Yang,[a,b] Qihua Yang[*,a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*

* To whom correspondence should be addressed.

E-mail: yangqh@dicp.ac.cn

Tel: 86-411-84379552. Fax: 86-411-84694447.

URL: http://www.hmm.dicp.ac.cn

† Dalian Institute of Chemical Physics, Chinese Academy of Sciences

‡ Graduate School of the Chinese Academy of Sciences

Chemicals and reagents

Triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Mw = 5800), 1,2-bis(trimethoxysilyl)ethane (BTME), and 1,4-bis(triethoxysilyl)benzene (BTEB) were purchased from Sigma-Aldrich Company Ltd. (U.S.A.). Tetramethoxysilane (99 %, TMOS), tetraethoxysilane (99 %, TEOS), and other reagents were obtained from Shanghai Chemical Reagent. Inc., of Chinese Medicine Group. All materials were analytical grade and used without any further purification.

Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation of 0.15406 nm wavelength over the 2θ range of 15 - 90^o with a scan speed of 5^o /min at room temperature. The nitrogen and water sorption experiment was performed at 77 K and 293 K on a Micromeritics ASAP 2020 system, respectively. Prior to the measurement, the samples were out gassed at 120 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) specific surface areas were calculated using adsorption data at the relative pressure range of P/P_0 = 0.05~0.25. Pore size distributions were calculated from adsorption branch using the Barrett-Joyner-Halenda (BJH) method. The total pore volumes were estimated from the amount adsorbed at a relative pressure (P/P_0) of 0.99. Field-emission scanning electron microscopy (FESEM) was undertaken on a HITACHI S-4800 microscope operating at an accelerating voltage of 1-30 kV. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G^2 Spirit at an acceleration voltage of 120 kV. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellet. ^{13}C (100.5 MHz) cross-polarization magic angle spinning (CP-MAS), and ^{29}Si (79.4 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity-plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. ^{13}C and ^{29}Si signals

were referenced to tetramethylsilane. The experimental parameters were 8-kHz spin rate, 3-s pulse delay, 4-min contact time, and 1500-3000 scans for ^{13}C CP-MAS NMR experiments; 4-kHz spin rate, 180-s pulse delay, 10-min contact time, and 116 scans for ^{29}Si MAS NMR experiments. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 ^{o}C/min by using a NETZSCH STA-449F3 thermogravimetric analyzer.

Synthesis of organosilica nanotubes and nanoparticles

In a typical synthesis of ethane-silica nanotubes, 0.55 g of P123 and 3.49 g of KCl were dissolved in different volume of 2 M HCl at 38 °C. After the copolymer was fully dissolved, 3.50 mmol of BTME was added under vigorous stirring. The resultant mixture was stirred for 6 minutes and remained quiescent for 24 h at the same temperature. After that, the mixture was aged at 100 °C under static conditions for an additional 24 h. The solid product was recovered by filtration and air-dried at room temperature overnight. Finally, the surfactant was extracted by refluxing 1.0 g of as-synthesized material in 200 mL of ethanol containing 1.5 g of concentrated aqueous HCl solution for 24 h. The surfactant-free samples were denoted as E-SNTs, where E denotes using1,2-bis(trimethoxysilyl)ethane (BTME) as silane precursor, SNTs refers to silica nanotubes. In order to investigate the formation mechanism, different weight concentration of P123 (0.74, 0.58, 0.30, 0.20, 0.15 and 0.12 wt%) were used by modulating the volume of 2 M HCl to 70, 90, 180, 270, 360, 450 mL respectively.

The synthesis conditions of benzene-silica nanotubes were almost the same as that for E-SNTs samples with the exception that BTEB was used as silane source. The volume of 2 M HCl solution is 180 mL. The samples were denoted as B-SNTs, where B refers to BTEB.

TMOS and TEOS were also used as silane precursors for the synthesis of materials in 180 mL of 2 M HCl solution. The samples were denoted as NP-M and NP-E, respectively using TMOS and TEOS as precursors.

Carbon/silica composite nanotubes synthesized through carbonization of ethane-silica nanotubes

The powders of E-SNTs (0.58 wt% of P123 weight concentration) were carbonized in nitrogen with a flow rate of 40 cm^3min^{-1} at 900 ^oC for 4h to obtain the C/SiO_2 composite nanotubes. It was denoted CS-NTs. Pure silica nanotubes were also obtained through calcination of E-SNTs in air at 900 ^oC for 4h, which were named SNTs.

Encapsulation of Pd particles in the nanotubes for the hydrogenation of alkenes

A series of 5% Pd/nanotubes were prepared as follows: 0.3 g nanotubes were immersed into the 10 mL ethanol solution containing $PdCl_2$ (0.026 g $PdCl_2$). After ultrasonic treatment for 1 h, the solution was stirred for 12 h at room temperature. The ethanol was removed by rotation evaporation at room temperature. The obtained solids were reduced at 150 °C in H_2 for 5 h. Besides, the 10% loading of Pd was encapsulated into B-SNTs as above method except using 0.052 g $PdCl_2$ as precursor, which was denoted Pd/B-SNTs'.

Hydrogenation of alkenes were performed at 50 °C and 1.0 MPa of hydrogen pressure in an 80-mL stainless-steel autoclave. Typically, 10 mg catalysts and acetone (30 mL) were put into the autocalve. Air in the autoclave was removed by sweeping the autoclave ten times with 1.0 MPa hydrogen. Then the catalysts were activated at 50 °C for 30 mins at 1.0 MPa hydrogen. Subsequently 5 mL alkenes were injected into the autoclave under the hydrogen. The mixture was stirred to start the reaction at 1.0 MPa hydrogen, a certain of solution was withdrew to monitor the reaction

progress during the experiment. Further hydrogen was added to the autoclave during the experiment to maintain the hydrogen pressure. Quantitative analysis of the reaction products was conducted with a GC (Agilent 6890) equipped with a FID detector and HP-5 capillary column.

Recycling test for the hydrogenation of alkenes is as follows: after the reaction finished, the solid catalyst was recovered by a centrifugation, and extracted repeatedly with acetone. The recovered catalyst was dried under vacuum and was directly used for the next reaction cycle. The reaction time for recycling test is two hours.

Table S1: Physicochemical properties of different nanostructured organosilicas materials

Sample	weight concentration of P123 (wt%)	HCl volume (mL)	BET Surface Area[a] (m^2 g^{-1})	Pore Diameter[b] (nm)	Total pore volume[c] (cm^3 g^{-1})
E-SNTs-1	0.73	70	860	6.2	1.13
E-SNTs-2	0.58	90	873	5.9	1.86
E-SNTs-3	0.30	180	844	5.9	2.52
E-SNTs-4	0.20	270	808	6.0	2.84
E-SNTs-5	0.15	360	787	6.4	2.66
E-SNTs-6	0.12	450	955	6.6	2.25
B-SNTs	0.30	180	672	6.5	1.68
NP-M	0.30	180	633	8.9	0.90
NP-E	0.30	180	657	8.4	0.92
CS-NTs	-	-	334	4.2	1.09
SNTs	-	-	443	3.9	1.43
Pd/E-SNTs	-	-	836	5.9	1.39
Pd/B-SNTs	-	-	690	6.1	1.07
Pd/B-SNTs’	-	-	587	6.1	0.87
Pd/CS-NTs	-	-	300	4.2	0.65
Pd/SNTs	-	-	375	3.9	1.21

[a] The Brunauer-Emmett-Teller (BET) surface areas were calculated using adsorption data at the relative pressure range of P/P_0 = 0.05~0.25; [b] Pore size distributions were calculated from adsorption branch using the Barrett-Joyner-Halenda (BJH) method; [c] The total pore volumes were estimated from the amount adsorbed at a relative pressure (P/P_0) of 0.99.

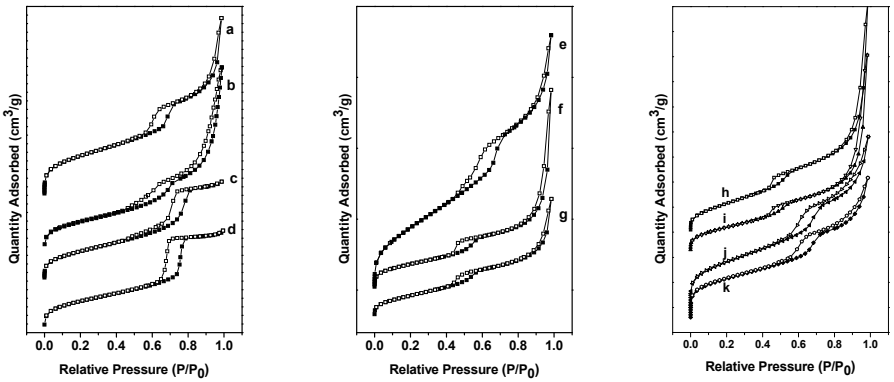

Fig. S1: Nitrogen adsorption and desorption isotherms of organosilicas samples: (a) E-SNTs (0.58 wt% of P123 weight concentration), (b) B-SNTs, (c) NP-M, (d) NP-E, (e) Pd/E-SNTs, (f) CS-NTs, (g) Pd/CS-NTs, (h) SNTs, (i) Pd/SNTs, (j) Pd/B-SNTs, (k) Pd/B-SNTs'

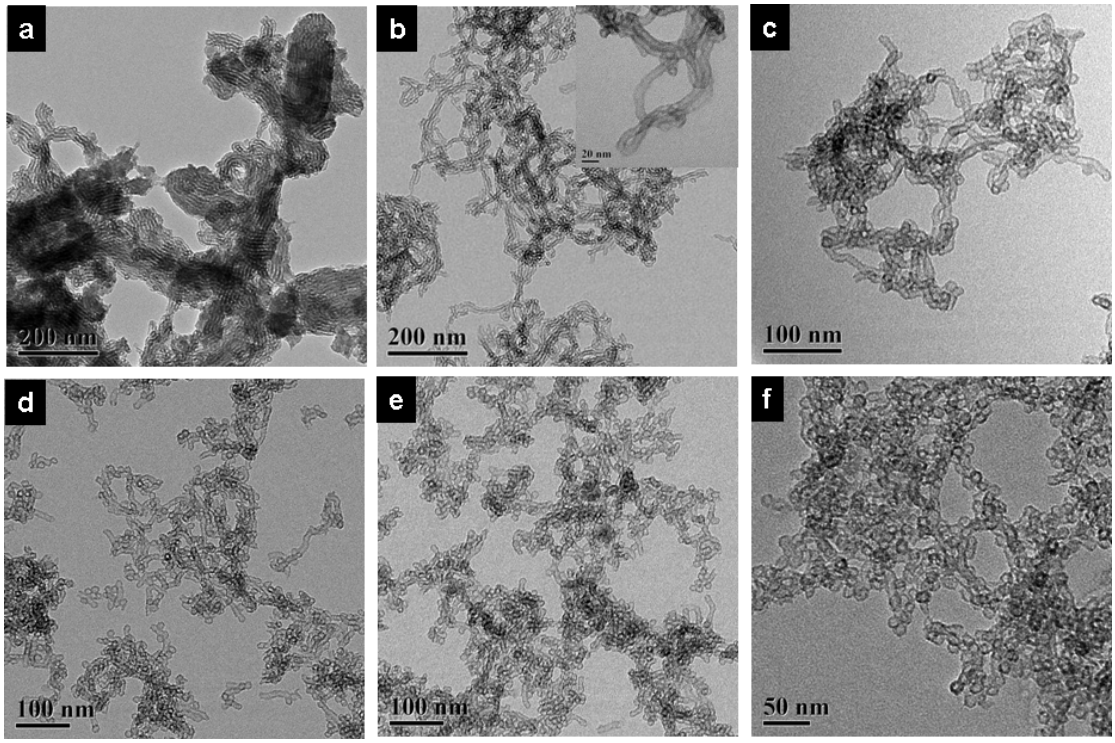

Fig. S2: TEM images of E-SNTs samples synthesized with different weight concentration of P123: (a) 0.73 wt%; (b) 0.58 wt%; (c) 0.30 wt%; (d) 0.20 wt%; (e) 0.15 wt% and (f) 0.12 wt%

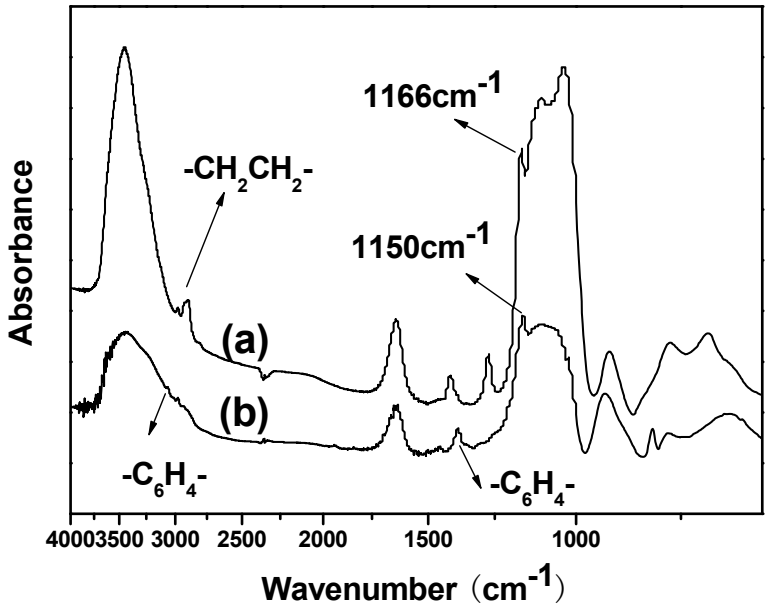

Fig. S3: FT-IR spectra of typical (a) E-SNTs and (b) B-SNTs samples

The FT-IR spectra of typical E-SNTs and B-SNTs samples are presented in Fig. S3. The C-H vibrations of –CH_2CH_2– and Si-C vibrations could be clearly observed in the range of 2986 ~ 2892 cm^{-1} and at 1166 cm^{-1} in the FT-IR spectrum of E-SNTs, respectively. The FT-IR spectrum of B-SNTs displays absorption bands attributed to the stretching modes of C–H species of aromatic moiety at 3035 cm^{-1} and the benzene ring vibrations at 1300 ~ 2000 cm^{-1}. The Si-C vibrations appeared at 1150 cm^{-1}, proving integrity of the bridging organic groups in the materials.

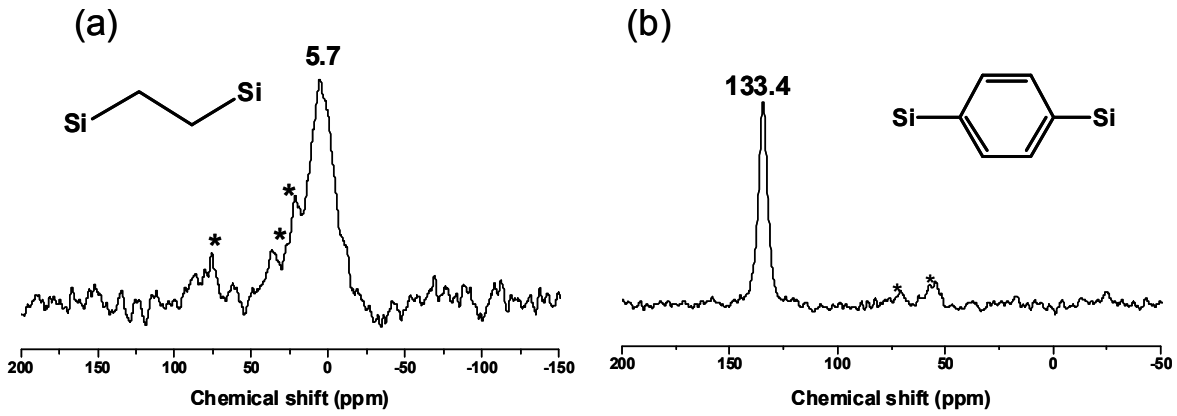

Fig. S4: Solid state ^{13}C CP MAS NMR spectra of typical (a) E-SNTs and (b) B-SNTs samples

The solid-state ^{13}C CP MAS NMR spectra of typical E-SNTs and B-SNTs samples are presented in Fig. S4. The chemical shift at 5.7 ppm of E-SNTs is due to the C species of ethane moiety. The ^{13}C NMR spectrum of B-SNTs displays the signal of benzene moiety at 133.4 ppm. The signals at 71.5, 55.6 and 18.8 ppm are due to the residue surfactants and the carbons of the ethoxy groups formed during the surfactant extraction process.

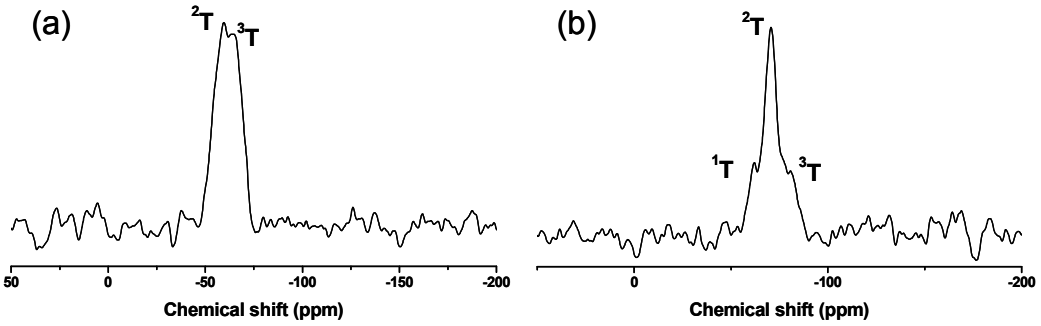

Fig. S5: Solid state ^{29}Si NMR spectra of typical (a) E-SNTs and (b) B-SNTs samples

The solid-state ^{29}Si NMR spectra of E-SNTs and B-SNTs show the existence of ^{n}T sites (Fig. S5). The signals at -59.2 and -65.0 ppm for E-SNTs are assigned to T^2 [$SiC(OH)(OSi)_2$] and T^3 [$SiC(OSi)_3$], and the signals at -60.7, -70.2 and -80.3 ppm for B-SNTs correspond to silicon species of T^1 [$SiC(OH)_2(OSi)$], T^2 [$SiC(OH)(OSi)_2$] and T^3 [$SiC(OSi)_3$], respectively, which confirm the full framework linkage of the organosilica nanotubes. The absence of SiO_4 species such as Q^3 [$Si(OH)(OSi)_3$] and Q^4 [$Si(OSi)_4$] in the range of -90 to -120 ppm confirms that no carbon–silicon bond cleavage occurred during the synthesis of organosilica nanotubes.

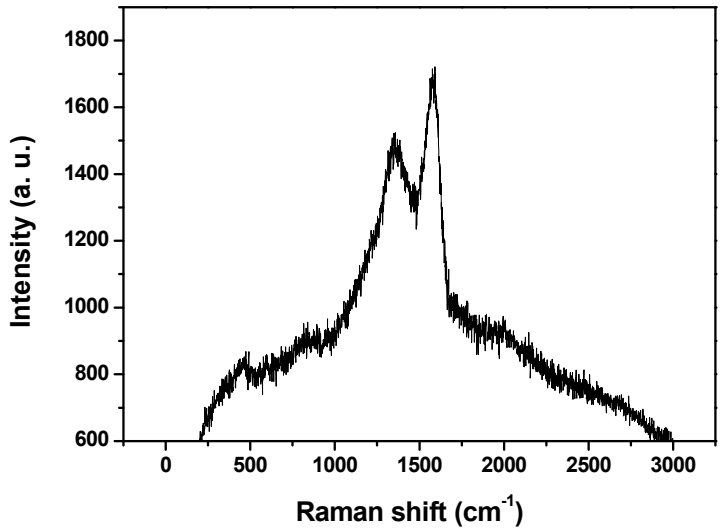

Fig. S6: Raman spectrum of CS-NTs

The Raman spectrum of the material obtained by carbonization of E-SNTs at 900 °C under N_2 atomospheres showes D and G bands at 1355 cm^{-1} and 1581 cm^{-1}, respectively. The intensity ratio of the D and G bands demonstrates the existence of disordered carbon in the nanocomposite.

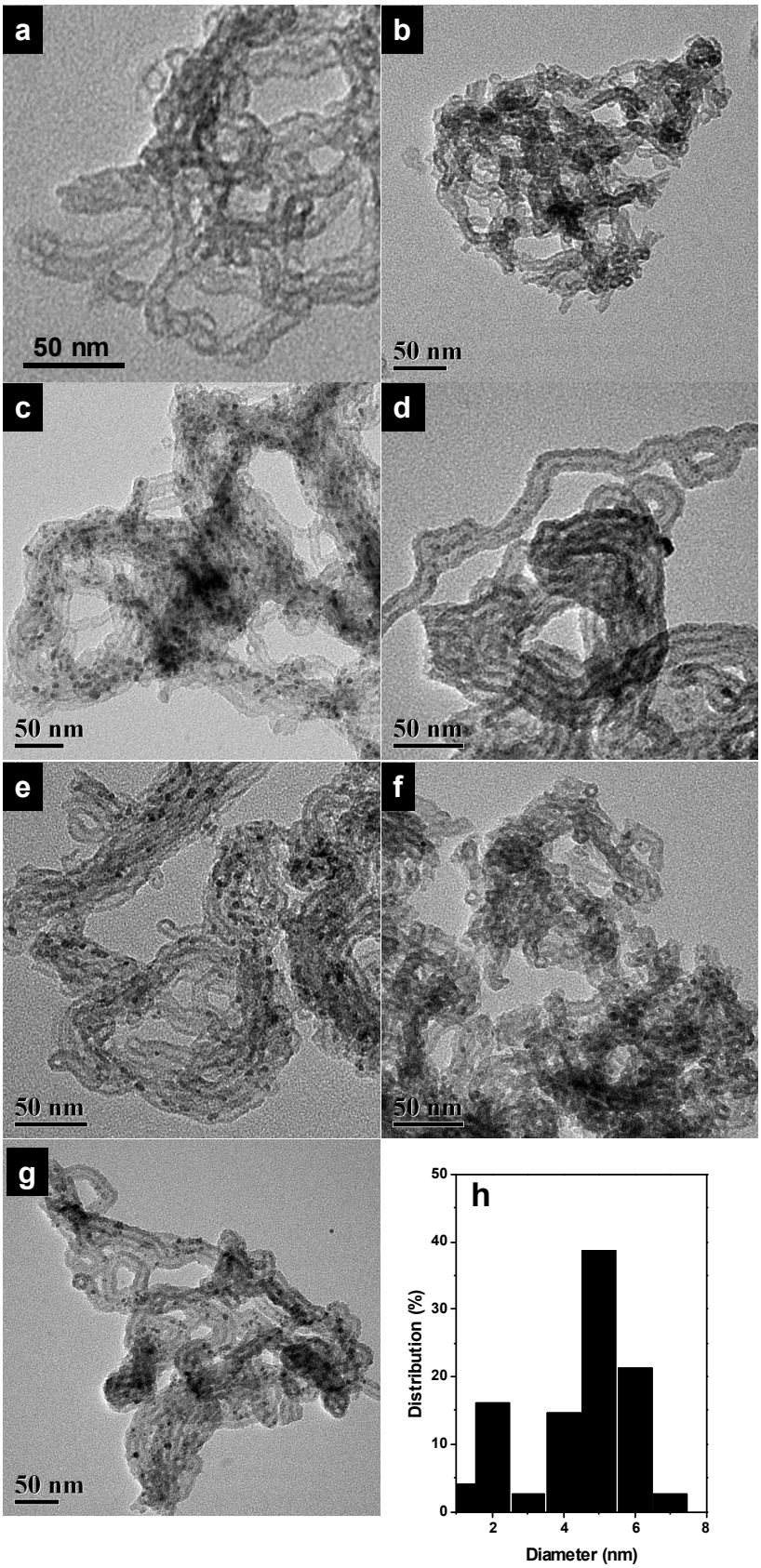

Fig. S7: TEM images of (a) CS-NTs, (b) SNTs, (c) Pd/E-SNTs, (d) Pd/B-SNTs, (e) Pd/CS-NTs, (f) Pd/SNTs, (g) Pd/B-SNTs' and (h) size distribution of Pd/B-SNTs'

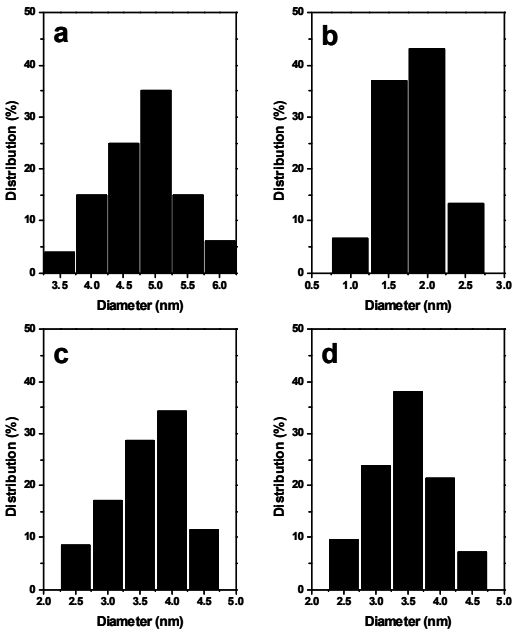

Fig. S8: Size distribution of (a) Pd/E-SNTs, (b) Pd/B-SNTs, (c) Pd/CS-NTs and (d) Pd/SNTs

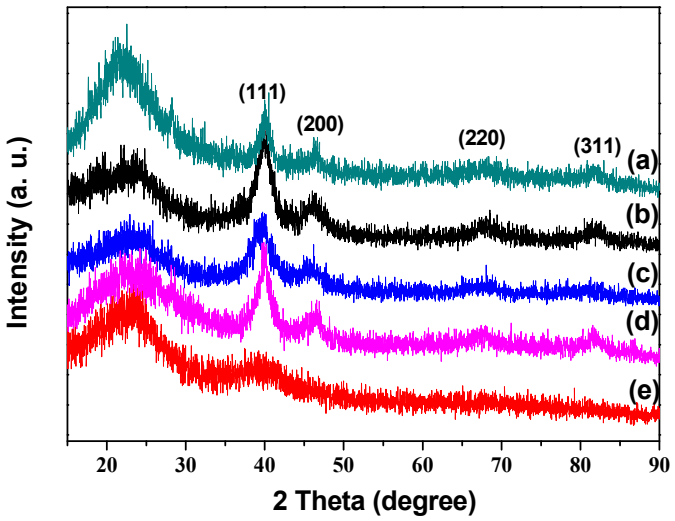

Fig. S9: Wide-angle XRD of (a) Pd/E-SNTs, (b) Pd/CS-SNTs, (c) Pd/SNTs, (d) Pd/B-SNTs' and (e) Pd/B-SNTs

All samples except for Pd/B-SNTs exhibit four distinct peaks in the XRD spectra at $2\theta = 40.0^{o}$, 46.3^{o}, 68.2^{o} and 82.0^{o} corresponding to the (111), (200), (220) and (311) reflections of Pd metal, respectively. Using Scherrer's equation with a spherical model for approximation, the average Pd particle sizes are estimated to be 5.1 nm, 3.8 nm, 3.7 nm, 2.0 nm and 4.9 nm for Pd/E-SNTs, Pd/CS-NTs, Pd/SNTs, Pd/B-SNTs and Pd/B-SNTs', respectively, which are consistent with results of TEM characterizations.

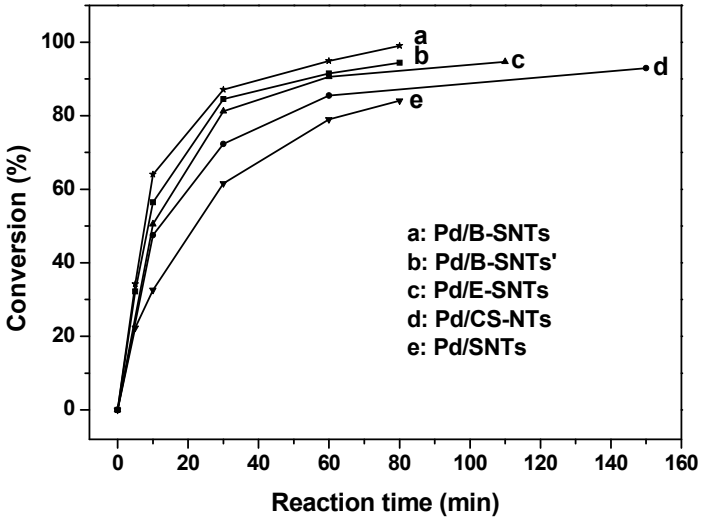

Fig. S10: The time profiles of the hydrogenation of cyclohexene catalyzed by different Pd catalysts

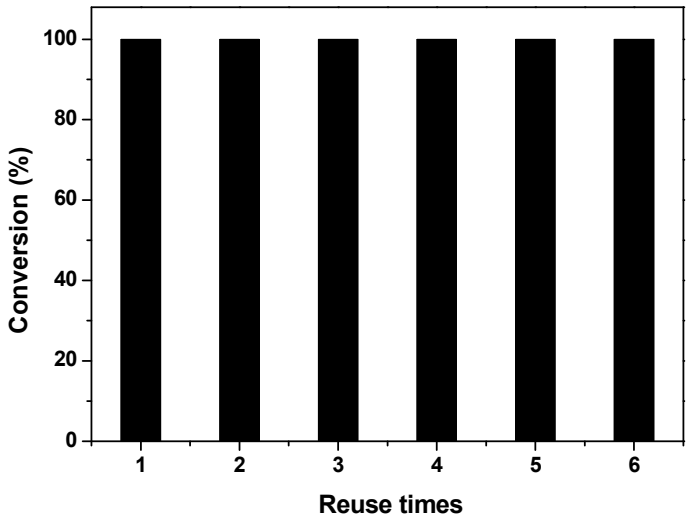

Fig. S11: The recyclability test of Pd/B-SNTs for the hydrogenation of cyclohexene to cyclohexane.