Size-controllable ultrafine palladium nanoparticles immobilized on calcined chitin microspheres as efficient and recyclable catalysts for hydrogenation

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Supplementary Information

Materials

Chitin powders were purchased from Golden-Shell Biochemical Co., Ltd. (Zhejiang, China). Palladium acetate ($Pd(OAc)_2$, 99%, Beijing Bailing Wei Technology Co., Ltd), styrene (99.5%, Shanghai Hushi Laboratorial Equipment Co., Ltd) and benzaldehyde (98.5%, Shanghai Hushi Laboratorial Equipment Co., Ltd) were used as received. Commercial 5 wt% Pd/C, palladium oxide (PdO, 99.9%) powders were purchased from Aladdin. All the other reagents such as methanol, toluene, tetrahydrofuran etc. were gained from various merchant resources, which could be used without further purification.

Characterization

Infrared spectroscopy was recorded using a Fourier transform infrared (FT-IR) spectrometer (model 1600, PerkinElmer Co., U.S.A.). Surface area and pore size distribution were evaluated using nitrogen adsorption (Micromeritics, AsAp2020, U.S.A.). X-ray photoelectron spectroscopy (XPS) was collected on a VG Multi Lab 2000 system with a monochromatic A1 Kα X-ray source (Thermo VG Scientific). Scanning electron micrograph (SEM) images were recorded with a HITACHI 5-4800 microscope (Tokyo, Japan) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were observed on a JEM-2010 (HT) electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. The size distribution of PdNPs was determined by a Mastersizer 2000 laser particle size analyzer (Malvern, UK). The Pd loading contents were determined using an inductively coupled plasma-optical emission spectrum (ICP-OES), Prodigy 7 (Leeman Labs Inc., U. S. A.). GC yields were recorded with a Varian GC 3900 gas chromatography instrument with a FID detector. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded on beamline 01C1 at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, China. The electron storage ring was operated at 1.5 GeV with a current of 360 mA in top-up injection mode. The Si(111) double crystal monochromator was used with a resolution $\Delta E/E$ better than 1×10^{-4}. The Pd K-edge absorption spectra were recorded in fluorescence yield (FY) mode at room temperature using a Lytle detector. Standard Pd metal foil was used for energy calibration and also for comparing different valence states. The EXAFS data analysis was performed using the ATHENA and ARTEMIS programs in the Demeter computer package.[1, 2]

Determination of Pd loading

The obtained Pd@chitin were dissolved in 5 mL of aqua regia, and then diluted with water to 100 mL after the Pd@chitin was soluble. Subsequently, the resulting solution was performed on an ICP-OES. ICP-OES measurement showed that the Pd loading of these four catalysts were 0.37, 1.2, 3.5 and 6.6 wt%, respectively.

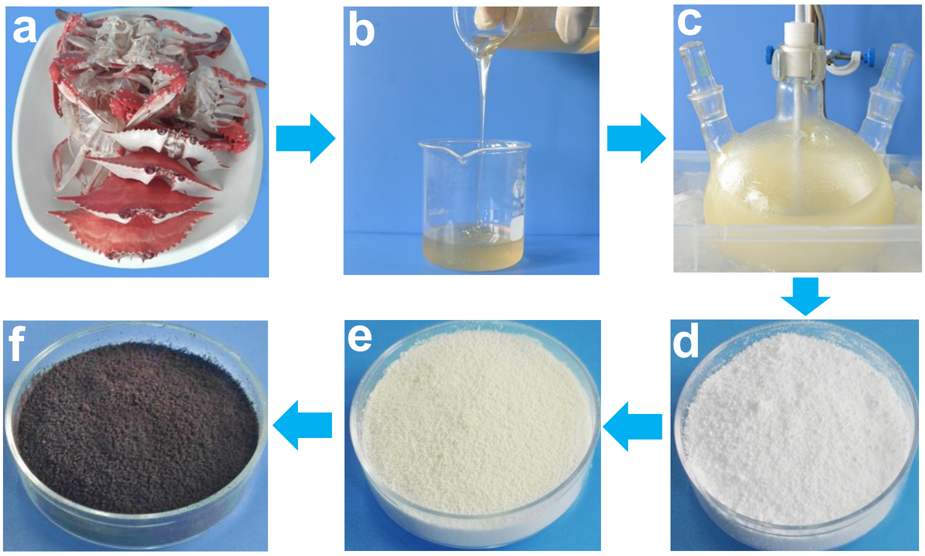

Figure S1. The preparation process of the Pd@chitin composite microspheres: crab shell (a), chitin solution (b), chitin solution in isooctane/Span85 (c), chitin microspheres (d), $Pd(OAc)_2$@chitin composite microspheres (e), Pd@chitin composite microspheres (f).

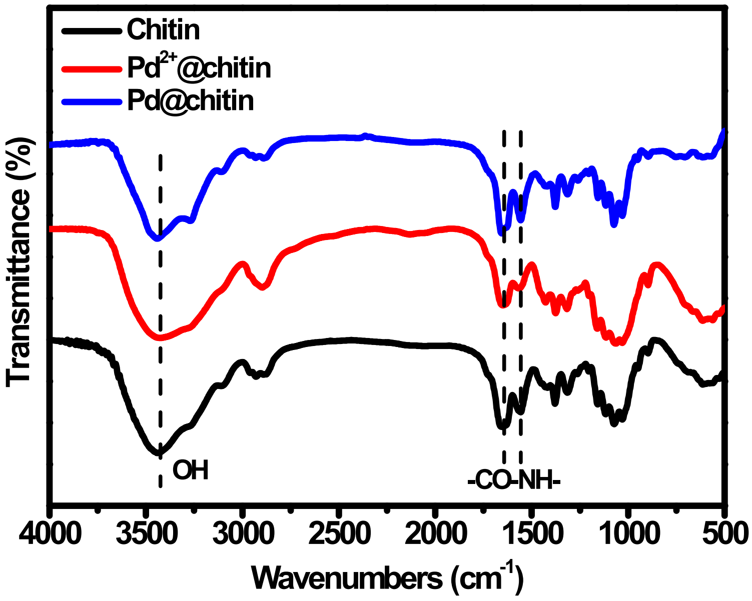

Figure S2. FT-IR spectra of the chitin, Pd^{2+}@chitin, and Pd@chitin.

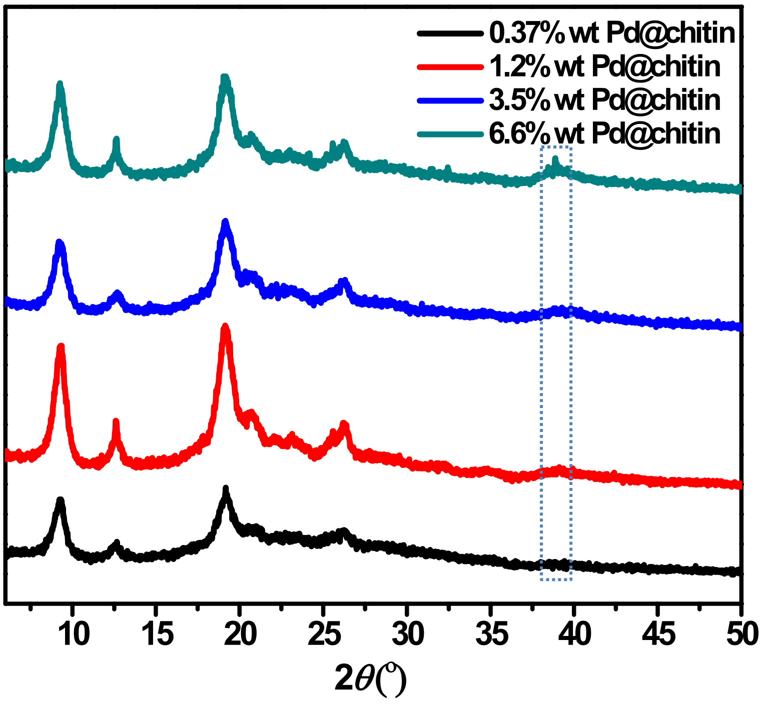

Figure S3. XRD patterns of the 0.37 wt%-Pd@chitin catalyst, 1.2-wt% Pd@chitin catalyst, 3.5 wt%-Pd@chitin catalyst, and 6.6 wt%-Pd@chitin catalyst, respectively.

Table S1 XANES and EXAFS parameters of references and samples

Sample	Edge Energy (eV)	OS[a]	Coordination Atom	CN[b] (avg.)	*d*[c] (Å)
Pd foil[d]	24350.0	0	Pd	12[i]	2.74
1.2 wt% Pd@chitin[e]	24351.4	0, +2	O(C)	1.7	1.99
			Pd	4.5	2.77
3.5 wt% Pd@chitin[f]	24351.6	0, +2	O(C)	1.1	1.98
			Pd	5.6	2.77
6.6 wt% Pd@chitin[g]	24351.5	0, +2	O(C)	1.0	1.96
			Pd	7.0	2.75
PdO powder[h]	24353.3	+ 2	O	4	2.02

[a] OS: oxidation state; [b] CN: coordination number; [c] *d*: bond distance. [d] FT range: 2.31 Å^{-1} ~ 12.92 Å^{-1}; fitting range: 1.85 Å ~ 2.89 Å. [e] FT range: 3.14 Å^{-1} ~ 11.74 Å^{-1}; fitting range: 1.28 Å ~ 2.97 Å. [f] FT range: 3.18 Å^{-1} ~ 11.62 Å^{-1}; fitting range: 1.24 Å ~ 2.93 Å. [g] FT range: 3.07 Å^{-1} ~ 12.72 Å^{-1}; fitting range: 1.18 Å ~ 2.87 Å. [h] FT range: 2.82 Å^{-1} ~ 11.78 Å^{-1}; fitting range: 1.00 Å ~ 1.96 Å. [i] These values were fixed during EXAFS fitting, based on the known structure of Pd foil. The detail fitting spectra were displayed in Figure S4-7.

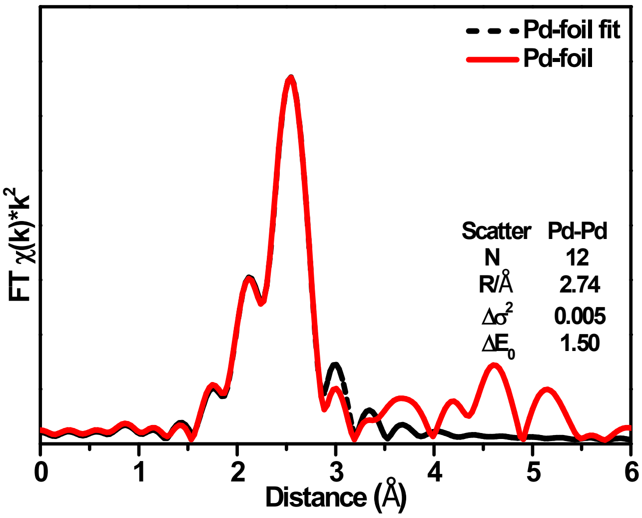

Figure S4 k^2-weighted R-space EXAFS spectra of Pd foil (FT range: 2.31< k < 12.92 Å^{-1} and fitting range: 1.85 < R < 2.89 Å).

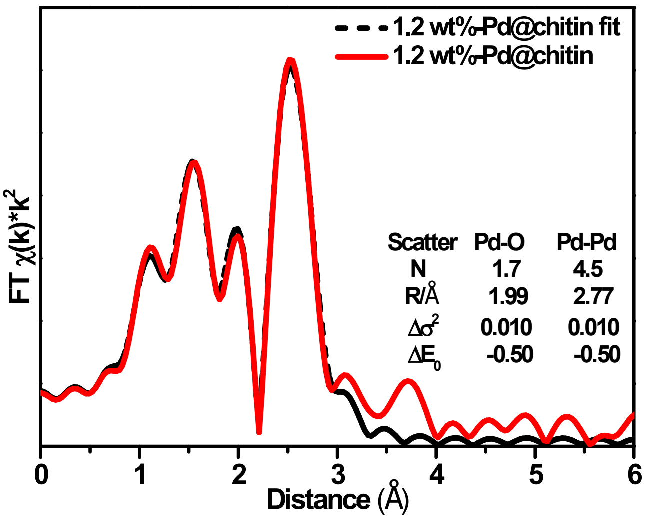

Figure S5 k^2-weighted R-space EXAFS spectra of 1.2 wt%-Pd@chitin (FT range: $3.14 < k < 11.74$ Å^{-1} and fitting range: $1.28 < R < 2.97$ Å).

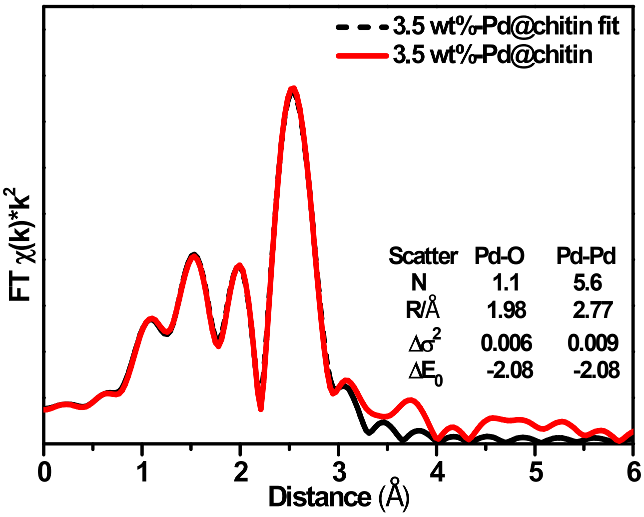

Figure S6 k^2-weighted R-space EXAFS spectra of 3.5 wt%-Pd@chitin (FT range: $3.18 < k < 11.62$ Å^{-1} and fitting range: $1.24 < R < 2.93$ Å).

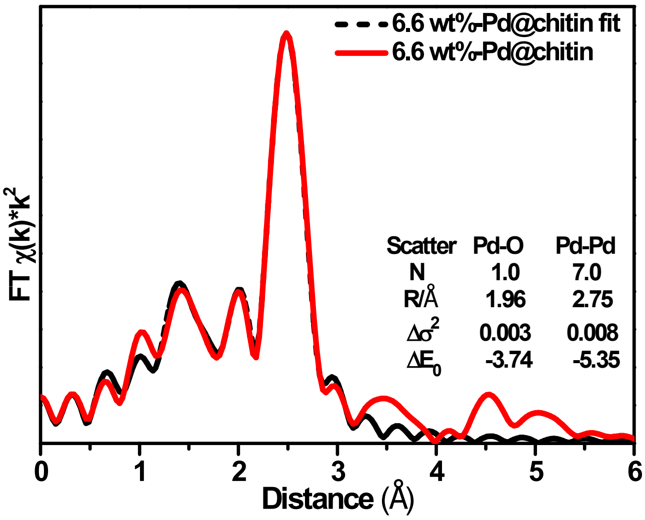

Figure S7 k^2-weighted R-space EXAFS spectra of 6.6 wt%-Pd@chitin (FT range: $3.07 < k < 12.72$ Å^{-1} and fitting range: $1.18 < R < 2.87$ Å).

Table S2 Comparison of hydrogenation activity of styrene

Catalyst	T (°C)	P_{H2}	Yield (%)	TOF (h^{-1})	Ref
Pd/PAM	25	1 atm	99	1250	3
Pd/PEG	rt	balloon	100	660	4
Pd/polymeric	35	1 atm	100	1449	5
Polymer/palladium(II)	25	1 atm	98	765.6	6
Pd/Dendrimers	25	1 atm	100	1620	7
Pd-EPS	30	1 atm	81.8	1636	8
Polymer/Pd	25	1 atm	92	850	9
HMMS–NH_2–Pd	rt	1 atm	99	198	10
SiliaCat Pd	rt	balloon	94	1880	11
Pd-G_1	rt	balloon	90	19.4	12
Pd/NH_2-PIL-Br	rt	1 MPa	90	3600	13
1.2 wt%-Pd@chitin	30	balloon	96%	7200	in this work
1.2 wt%-Pd@chitin	30	5 Mpa	100%	50000	in this work

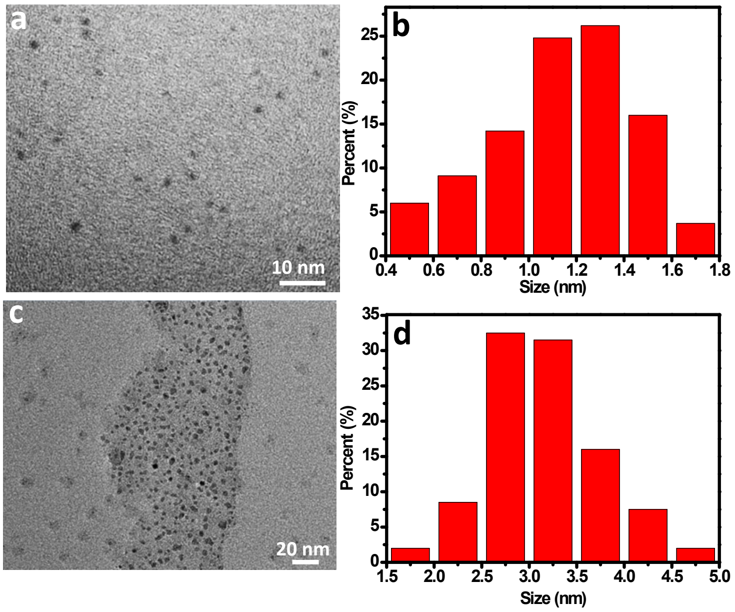

Figure S8. TEM image and size distribution of the Pd-$NaBH_4$ (a, b). TEM image and size distribution of the Pd-$NaBH_4$ after 10 reaction runs (c, d).

Control experiments: The Pd loading for catalyst of Red-Pd@$NaBH_4$ was 1.2 wt%, and the catalyst run 10 cycles of styrene hydrogenation. The cycling reaction conditions were performed the same as catalyst of 1.2 wt%-Pd@chitin.

Table S3. Benzaldehyde hydrogenations in various catalysts and solvents[a]

Entry	Catalyst	Solvent	Catalyst (mol%)	T (°C)	T (h)	Yield[c] (%)
1	1.2 wt%-Pd@chitin	MeOH	0.06	30	6.5	6
2	1.2 wt%-Pd@chitin	MeOH	0.06	50	6.5	61
3	1.2 wt%-Pd@chitin	THF	0.06	50	6.5	58
4	1.2 wt%-Pd@chitin	Toluene	0.06	50	6.5	41
5	1.2 wt%-Pd@chitin	H_2O	0.06	50	6.5	76
6	1.2 wt%-Pd@chitin	MeOH/H_2O[b]	0.06	50	6.5	97
7	1.2 wt%-Pd@chitin	MeOH/H_2O	0.2	50	1	99
8	3.5 wt%-Pd@chitin	MeOH/H_2O	0.2	50	1	80
9	6.6 wt%-Pd@chitin	MeOH/H_2O	0.2	50	1	67
10	Pd/C	MeOH/H_2O	0.2	50	1	35
11	$Pd(OAc)_2$	MeOH/H_2O	0.2	50	1	30
12	Blank	MeOH/H_2O	0.2	50	1	0

[a] Reaction conditions: 1.88 mmol substrate, 0.06 mol%/0.2 mol% [Pd], 5 mL solvents, H_2 balloon.
[b] MeOH/H_2O=4:1.
[c]Yield of benzyl alcohol were determined by GC and GC-MS.

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