Electronic Supplementary Information for

PdC_x nanocrystals with tunable compositions for alkyne semihydrogenation

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Calculation of turnover frequency (TOF).[1,2]

The edge length of a Pd nanocube is d nm, its volume is d^3 nm^3. The unit cell of Pd nanocube is a face-centered-cubic structure with lattice constant of a nm, and the volume of a unit cell is a^3 nm^3. A unit cell contains 4 Pd atoms, so the number of Pd atoms in a single Pd nanocube is (d^3 nm^3) / (a^3 nm^3) × 4.

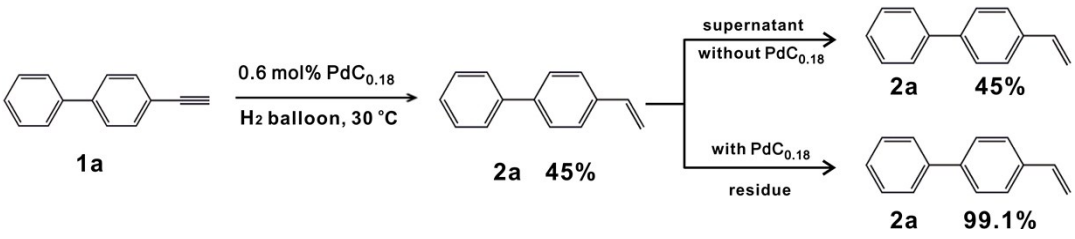
A total surface area in a single Pd nanocube is d^2 nm^2 × 6. Each unit cell on the {100} facet contains 2 Pd atoms, and the area of this unit cell is a^2 nm^2, so the total number of the surface Pd atoms on a single nanocube is (d^2 nm^2 × 6) / (a^2 nm^2) × 2.

The total number of Pd atoms in the catalyst is 0.2 mmol × 0.6 mol% × (6.02 × 10^{23} mol^{-1}) = 7.224 × 10^{17}. The number of Pd nanocubes involved in the catalytic reaction is (7.224 × 10^{17}) / (d^3 nm^3 / a^3 nm^3 × 4), so the total number of the Pd atoms on the surface of nanocubes involved in the catalytic reaction is (d^2 nm^2 × 6) / (a^2 nm^2) × 2 × (7.224 × 10^{17}) / (d^3 nm^3 / a^3 nm^3 × 4).

As for commercial Pd/C and Lindlar catalyst, d (commercial Pd/C) = 3.9 nm, d (Lindlar) = 3.4 nm, the dispersion of the commercial Pd/C and Lindlar were calculated followed by D (dispersion) = 1.13 / d (diameter, unit: nm), so the D (commercial Pd/C) = 0.290, D (Lindlar) = *0.332*, the total number of the Pd atoms in the catalyst surface is 7.224 × 10^{17} × D.

TOF for the Pd catalyst = (mole of the substrate conversion) / (mole of surface Pd atom in catalyst × reaction time). And for all measured of TOF, the conversion was controlled to be < 10%. TOFs per surface Pd atom for hydrogenation of EB-H was showed in Table S2.

Leaching experiments for the reaction using $PdC_{0.18}$ catalyst.



Scheme S1. Leaching experiments for the reaction using $PdC_{0.18}$ as catalyst.

EB-H (**1a**) was treated in the presence of $PdC_{0.18}$ catalyst in toluene at 30 °C, after 10 mins' reaction, a part of reaction solution was transferred to the other reaction vessel and **2a** was produced in 45% yield at this time. The supernatant was continuous reacted in the absence of the catalyst for another 170 mins, affording **2a** in 45% yield. In contrast, the residual reaction containing the

$PdC_{0.18}$ catalyst was completed in 180 mins, giving **2a** in 91% yield. In addition, ICP-MS analyses show that no Pd residual metal can be detected in the supernatant (Table S3).

Adsorption of vinylbiphenyl and EB-H on $PdC_{0.18}$ nanocubes.

$PdC_{0.18}$ catalyst (0.6 mmol) were dispersed in 10 mL of toluene, to which substrates (1 mmol of pure EB-H, 1 mmol of pure vinylbiphenyl, or a mixture of 0.5-mmol EB-H and 0.5-mmol vinylbiphenyl) were then added. After the solution was stirred at 30 °C for 3 h, the remaining solids were collected by centrifugation and washed with ethanol for ten times to remove the free substrates.

Reference

1 M. Jin, H. Zhang, Z. Xie and Y. Xia. *Angew. Chem. Int. Ed.*, 2011, **123**, 7996-8000.

2 A. J. Plomp, H. Vuori, A. O. I. Krause, K. P. de Jong and J. H. Bitter, *Appl. Catal. A: General*, 2008, **351**, 9-15.

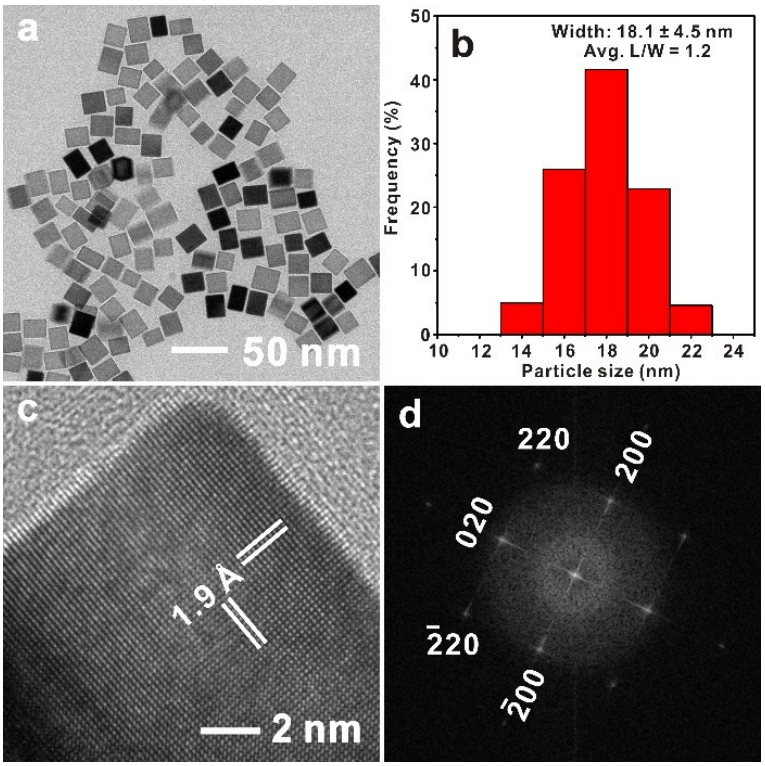


Fig. S1. (a) TEM image of the obtained Pd seeds and (b) corresponding histogram of size distribution. (c) HRTEM image of an individual Pd nanocube and (d) FFT pattern of Pd nanocube shown in (c) recorded along the <001> zone axis.

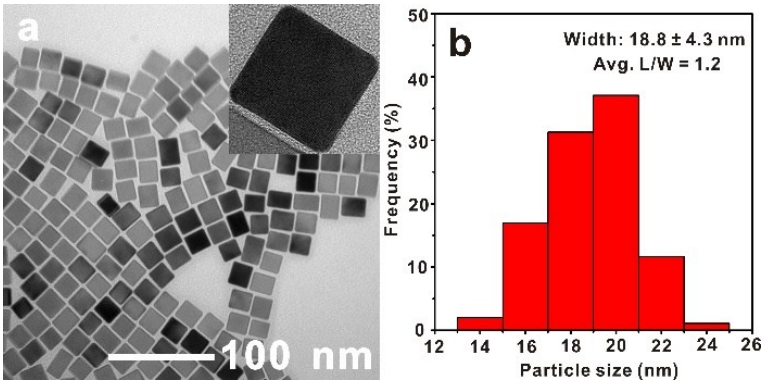


Fig. S2. (a) TEM images of the obtained $PdC_{0.18}$ nanocubes and (b) corresponding histogram of size distribution.

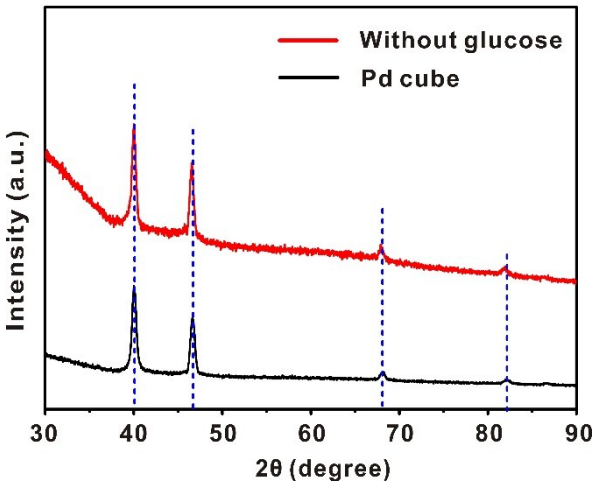


Fig. S3. XRD patterns of the original Pd nanocubes and the obtained nanocrystals without the addition of α-D-glucose.

Table S1. Lattice parameters for PdC_x nanocrystals, corresponding XRD showed in Figure 2.

Reaction time (min)	{111} peak position in 2θ (°)	Corresponding lattice parameter (Å)	Approximate composition
0	40.11	3.890	Pd
2	39.83	3.917	$PdC_{0.04}$
3	39.59	3.939	$PdC_{0.07}$
5	39.31	3.966	$PdC_{0.11}$
8	39.13	3.983	$PdC_{0.13}$
10	38.85	3.994	$PdC_{0.15}$
20	38.72	4.018	$PdC_{0.18}$

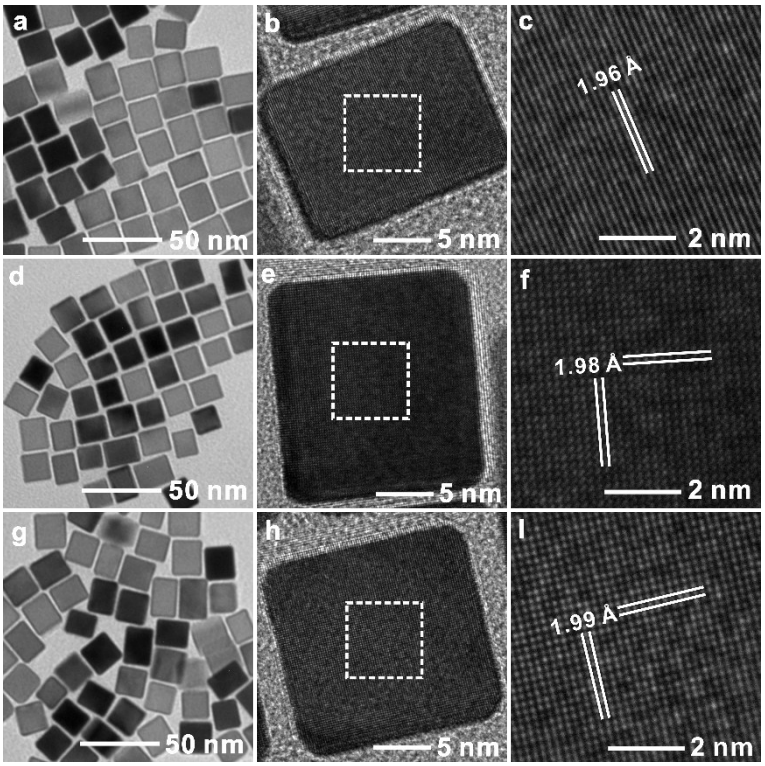


Fig. S4. TEM and HRTEM images of as-prepared (a-c) $PdC_{0.07}$, (d-f) $PdC_{0.13}$, and (g-i) $PdC_{0.15}$ nanocrystals.

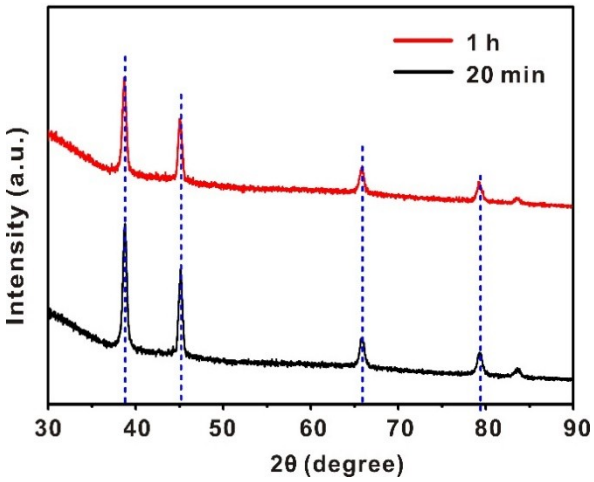


Fig. S5. XRD patterns of the samples with the reaction time extended from 20 min to 1 h under the standard synthetic condition.

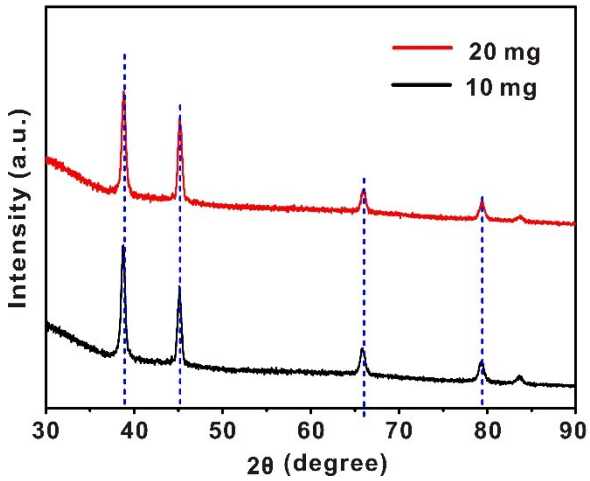


Fig. S6. XRD patterns of the samples with α-D-glucose content increased from 10 to 20 mg under the standard synthetic condition.

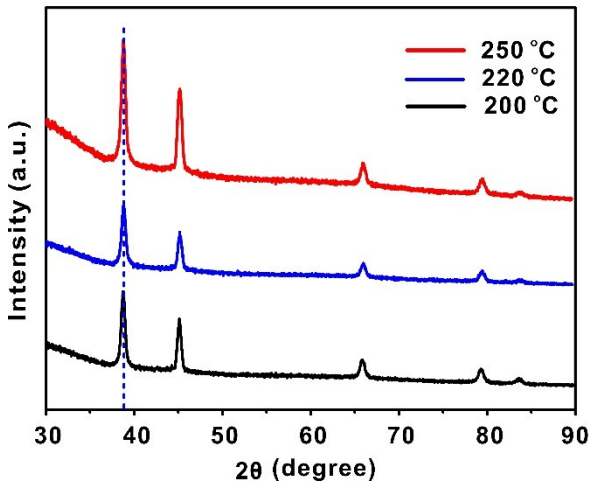


Fig. S7. XRD patterns of the samples with reaction temperatures raised from 200 °C to 220 °C and 250 °C under the standard synthetic condition.

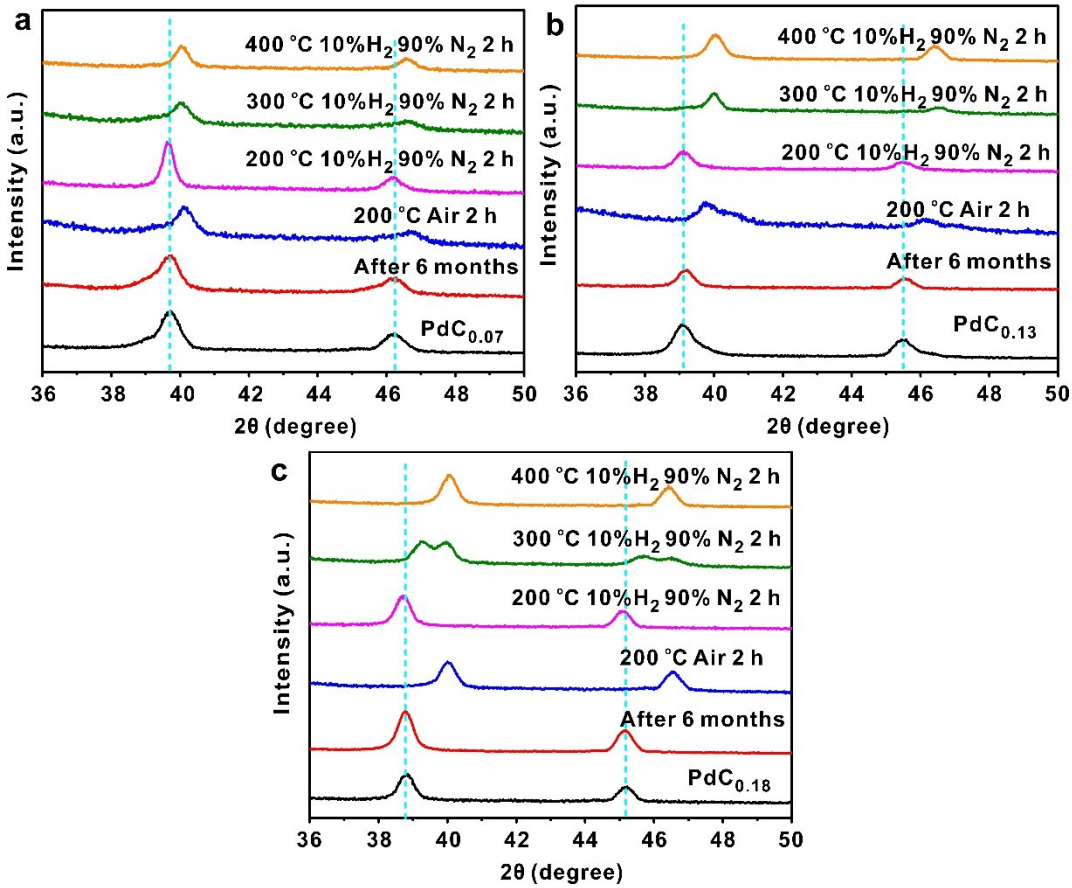


Fig. S8. XRD patterns comparison of (a) $PdC_{0.07}$, (b) $PdC_{0.13}$, and (c) $PdC_{0.18}$ nanocrystals that were kept at room temperature before and after 6 months, annealing tests under air at 200°C, 10% H_2 90% N_2 at 200 °C, 300 °C and 400 °C for 2 h, respectively.

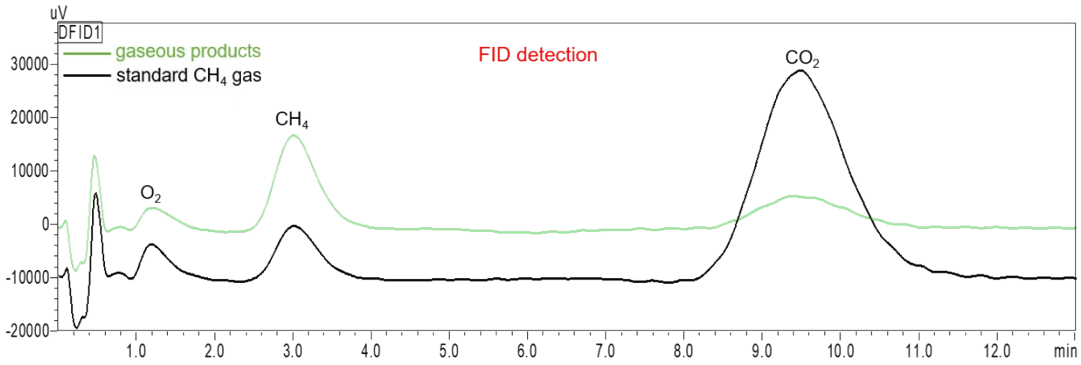


Fig. S9. GC spectra of the gaseous products after annealing $PdC_{0.18}$ nanocrystals under H_2 at 400 °C.

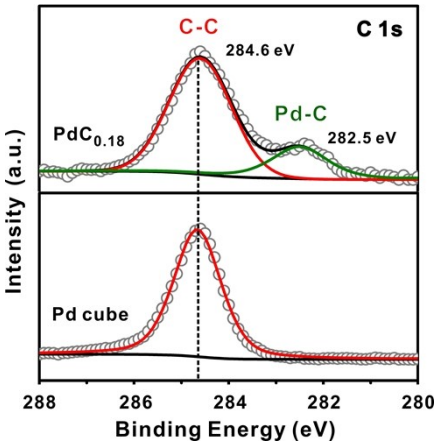


Fig. S10. XPS spectra of C 1s in the Pd and $PdC_{0.18}$ nanocubes.

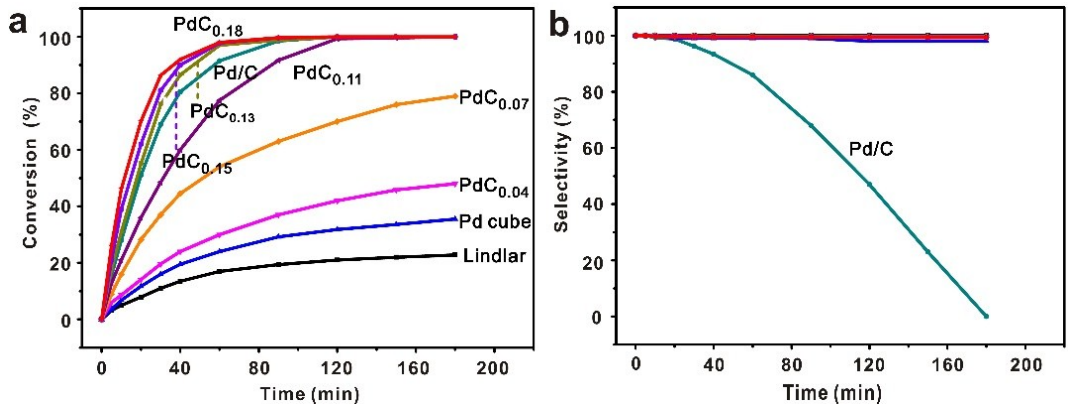


Fig. S11. (a) Conversion and (b) selectivity as a function of reaction time for catalytic hydrogenation of EB-H over different catalysts. Reaction condition: 0.2 mmol of EB-H, 0.6 mol% of Pd catalysts, 2 ml of toluene, H_2 balloon, 30 °C, 180 min. The results were determined by GC-MS analysis.

Table S2. Turnover frequencies (TOFs) per surface Pd atom for hydrogenation of EB-H.

Catalyst	Total number of Pd atoms in the catalyst surface	Conversion (%)	TOF (h^{-1})
Pd cube	4.685×10^{16}	0.78	1203
$PdC_{0.04}$	4.686×10^{16}	1.24	1912
$PdC_{0.07}$	4.684×10^{16}	1.84	2838
$PdC_{0.11}$	4.687×10^{16}	2.53	3899
$PdC_{0.13}$	4.686×10^{16}	3.56	5488
$PdC_{0.15}$	4.685×10^{16}	4.14	6384
$PdC_{0.18}$	4.684×10^{16}	5.12	7896
Commercial Pd/C	2.095×10^{17}	3.01	1038
Lindlar	2.401×10^{17}	0.69	208

Table S3. Metal content in the supernatant of reaction solvent after centrifugation.

Element	Concentration in supernatant
Pd	0 ppb

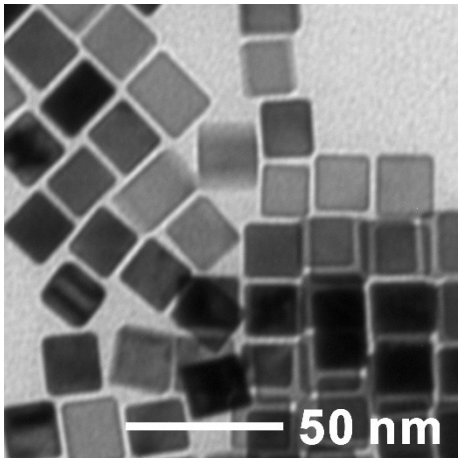


Fig. S12. TEM images of $PdC_{0.18}$ catalysts after four cycles of semihydrogenation.