

Supporting information

Shape-controlled synthesis of palladium nanocrystals by combination of oleylamine and alkylammonium alkylcarbamate and their catalytic activity

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1. Experimental

Reagents: Oleylamine, palladium (II) acetylacetonate, borane-tert-butylamine complex were purchased from Aldrich. Citral was provided by Fluka. All other chemicals (A. R. grade) used were provided by Sinopharm Chemical Reagent Co., Ltd.

Preparation of alkylammonium alkylcarbamate (AAAC) in toluene: 86.67 g of OAm/toluene solution with 23 wt% OAm was charged into 250 mL flask. The air in the flask was replaced by CO₂. Then a CO₂ balloon of 1 atm was connected to the flask, and the mixture was stirred for 30 minutes at room temperature. AAAC/toluene solution with 24.5 wt% AAAC was obtained. It was known from the masses of the mixture before and after absorption of CO₂ that the molar ratio of CO₂ and OAm was very close to 0.5, in agreement with the theoretical value (Scheme S1). The solution was diluted by toluene to obtain 23 wt% of AAAC solution.

Synthesis of Pd NCs: To prepare the spherical Pd NCs, 6.5 g of AAAC/toluene solution of 23 wt% AAAC was mixed with 6.5 g of OAm/toluene solution of 23 wt% OAm in a glass bottle of 25 mL to form a mixture with AAAC/OAm weight ratio of 5/5. Then 0.1 mmol of Pd(acac)₂ was dissolved in the solution by sonication to form a clear solution. The bottle was sealed after removing the air by nitrogen flow, and was heated at 60°C for 2 minutes with stirring before the addition of 0.3 mmol of BTB. The colour of the solution changed into brown in about 20 seconds and the system kept transparent all the time. The solution was cooled in water after 10 minutes. 10 mL of ethanol was added and the product was separated by centrifugation. Then, the product was dispersed in chloroform.

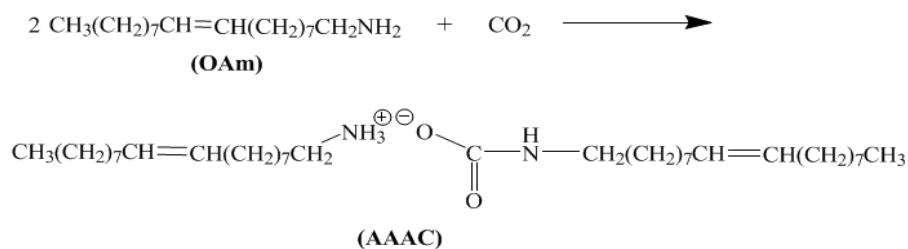
In the synthesis of the tetrahedral Pd NCs, 9.1 g of AAAC/toluene solution of 23 wt% AAAC and 3.9 g of OAm/toluene solution of 23 wt% OAm were mixed in the bottle to form a mixture with AAAC/OAm weight ratio of 7/3. The following procedures were the same as those to synthesize the spherical Pd NCs. 13 g of AAAC/toluene solution of 23 wt% AAAC was used to prepare the Pd multipods. Other procedures were also the same as those for the synthesis of the spherical Pd NCs.

Synthesis of Pd/SiO₂ catalysts: Pd/SiO₂ catalysts were prepared by commonly used impregnation method. Typically, the Pd NCs in chloroform prepared above were diluted to 40 mL by chloroform and then 4g of silica gel was added. This mixture was sonicated for about 30 seconds and stabilized for 2 hours. After evaporation of chloroform, 60 mL acetic acid was added to the Pd/SiO₂ dispersion and the mixture was maintained at 80°C for 4 hours. The Pd/SiO₂ was separated by centrifugation and was washed by 3×120 mL of ethanol. The solvent was evaporated and the resultant Pd/SiO₂ was used for the reaction. The contents of the Pd NCs in the Pd/SiO₂ composites were determined by inductively coupled plasma (ICP-AES, Vista-MPX).

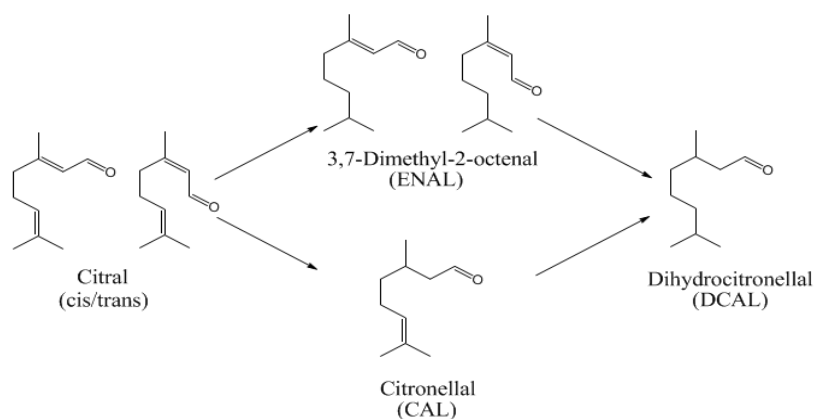
Characterization: Samples were dispersed in chloroform and dropped on amorphous carbon coated copper grids for TEM analysis. Images were obtained on a JEM 1011 (100kV). HRTEM image was obtained on a JEM 2011 (200kV). The scanning electron microscopy (SEM) observation was conducted on a Hitachi-s4800 electron microscope operated at 10 kV. FTIR spectra were recorded on Bruker Tensor 27 spectrometer. ¹³C NMR spectra (CDCl₃) were recorded on Bruker Avance (400MHz).

Hydrogenation reaction: The apparatus and procedures for the hydrogenation of citral and cyclohexene were similar to those reported previously,^{S1} and a stainless steel batch reactor of 6 mL was used. Typically, 5×10⁻⁵ mmol of catalyst and 0.67 mmol of citral or 2 mmol of cyclohexene were added into the reactor. The reactor was then sealed and heated up to desired temperature. H₂ was introduced into the reactor to 4 MPa firstly and then CO₂ (if used) was introduced into the reactor to the desired pressure with a high-pressure pump. At the end of the reaction, the reactor was cooled in ice water and the gases were released. The remaining residue was extracted with ethanol and analyzed by gas chromatography (GC, Agilent 6820) equipped with a flame ionization detector (FID) and a PEG-20M capillary column (0.25 mm in diameter, 30 m in length) and gas chromatography/mass spectrometry (GC-MS, SHIMADZU-QP2010).

2. Results



Scheme S1. Reaction of OAm and CO₂ to form AAAC.



Scheme S2. Reaction scheme for citral hydrogenation.

FTIR and ¹³C NMR spectra of OAm and AAAC: The FTIR and ¹³C-NMR spectra of fresh OAm and the AAAC are shown in Figures S1 and S2, respectively. The absorption bands at 1335 cm⁻¹, 1560 cm⁻¹, 3320 cm⁻¹ in the FTIR spectrum of AAAC result from C-N, C-O, and NH groups, respectively, indicating the formation of NHCOO⁻ group.^{S2} The new peak at 163 ppm appeared in the ¹³C-NMR spectrum of AAAC is carbonyl signal.^{S3}

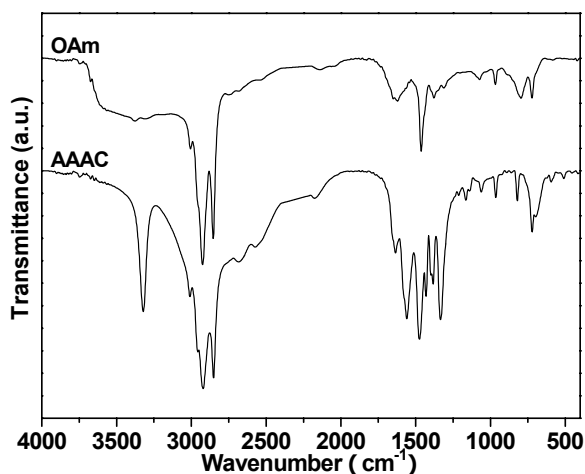


Figure S1. FTIR spectra of OAm and AAAC.

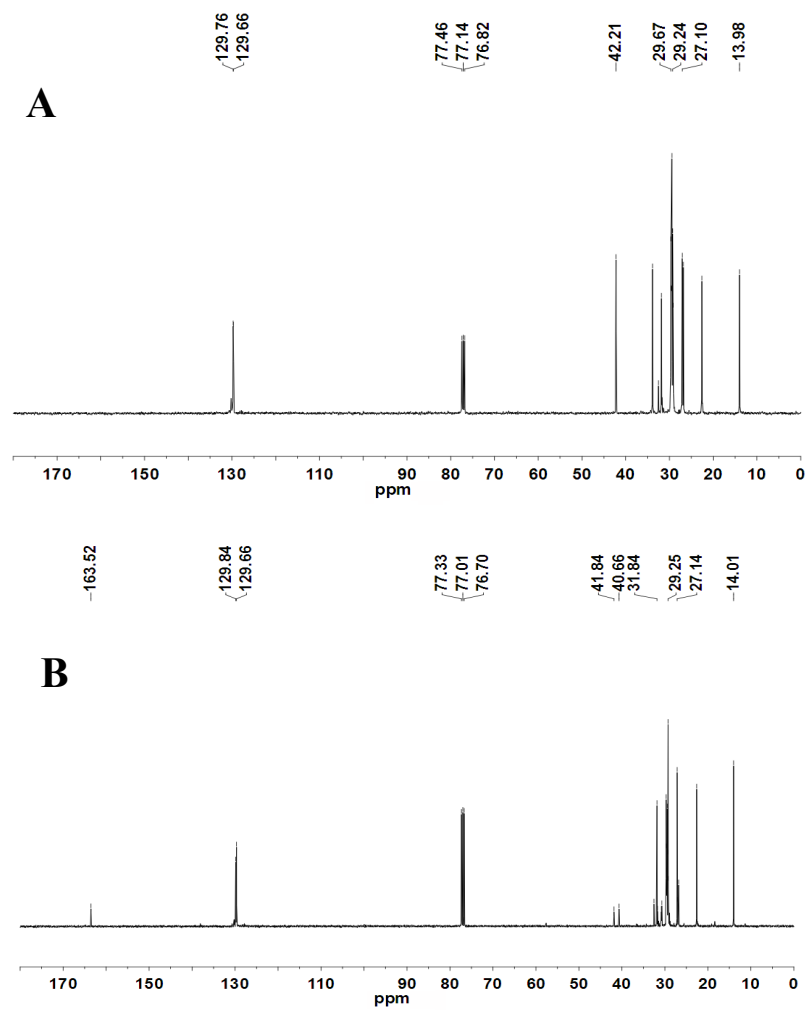
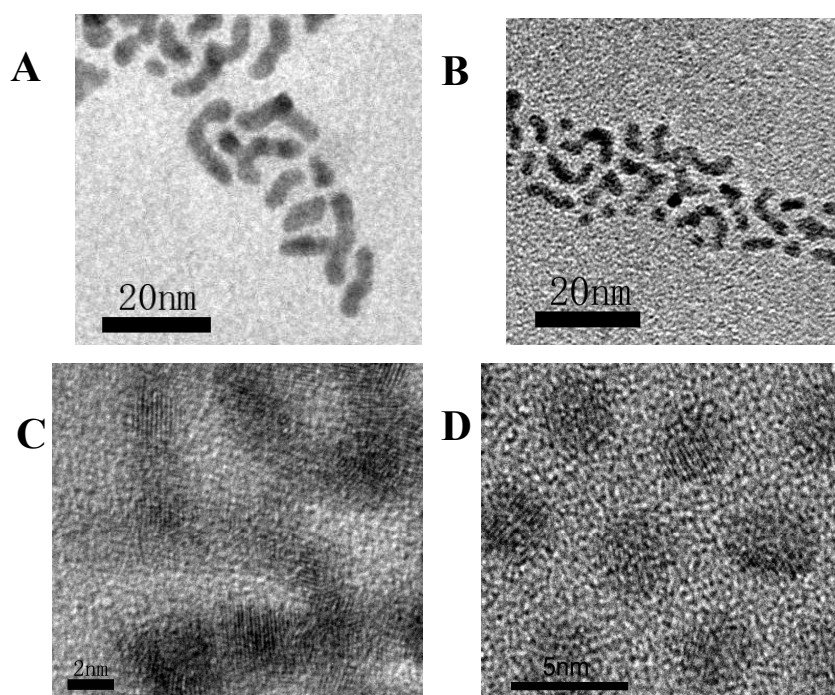


Figure S2. ^{13}C NMR spectra of (A) OAm and (B) AAAC.



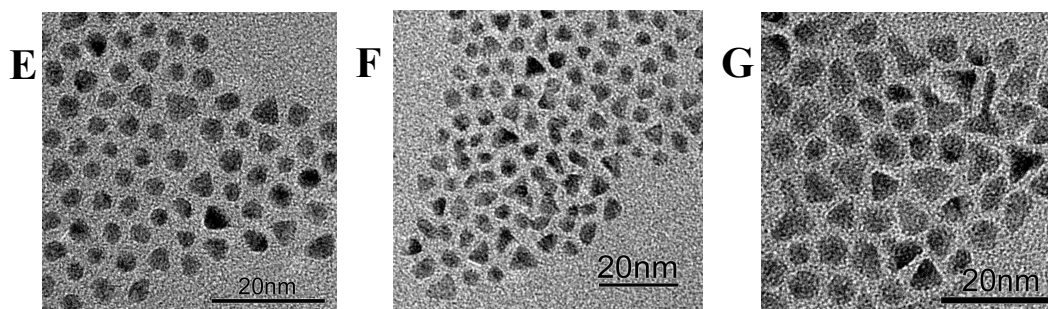


Figure S3. (A) TEM image of Pd NCs synthesized in OAm/toluene system at 60°C for 10 minutes. (B) TEM image of the Pd NCs synthesized at 60°C for 10 minutes with AAAC/OAm weight ratio of 3/7. (C) HRTEM image of (A). (D) HRTEM of the spherical Pd NCs in Fig. 1A. TEM image of the Pd NCs synthesized at 60°C for 10 minutes with AAAC/OAm weight ratio of 6/4 (E), 8/2 (F), 9/1 (G).

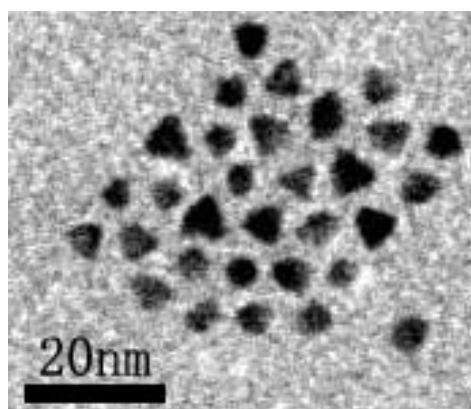


Figure S4. TEM image of Pd NCs synthesized in AAAC/OAm (7/3) system at 60°C for 2 minutes.

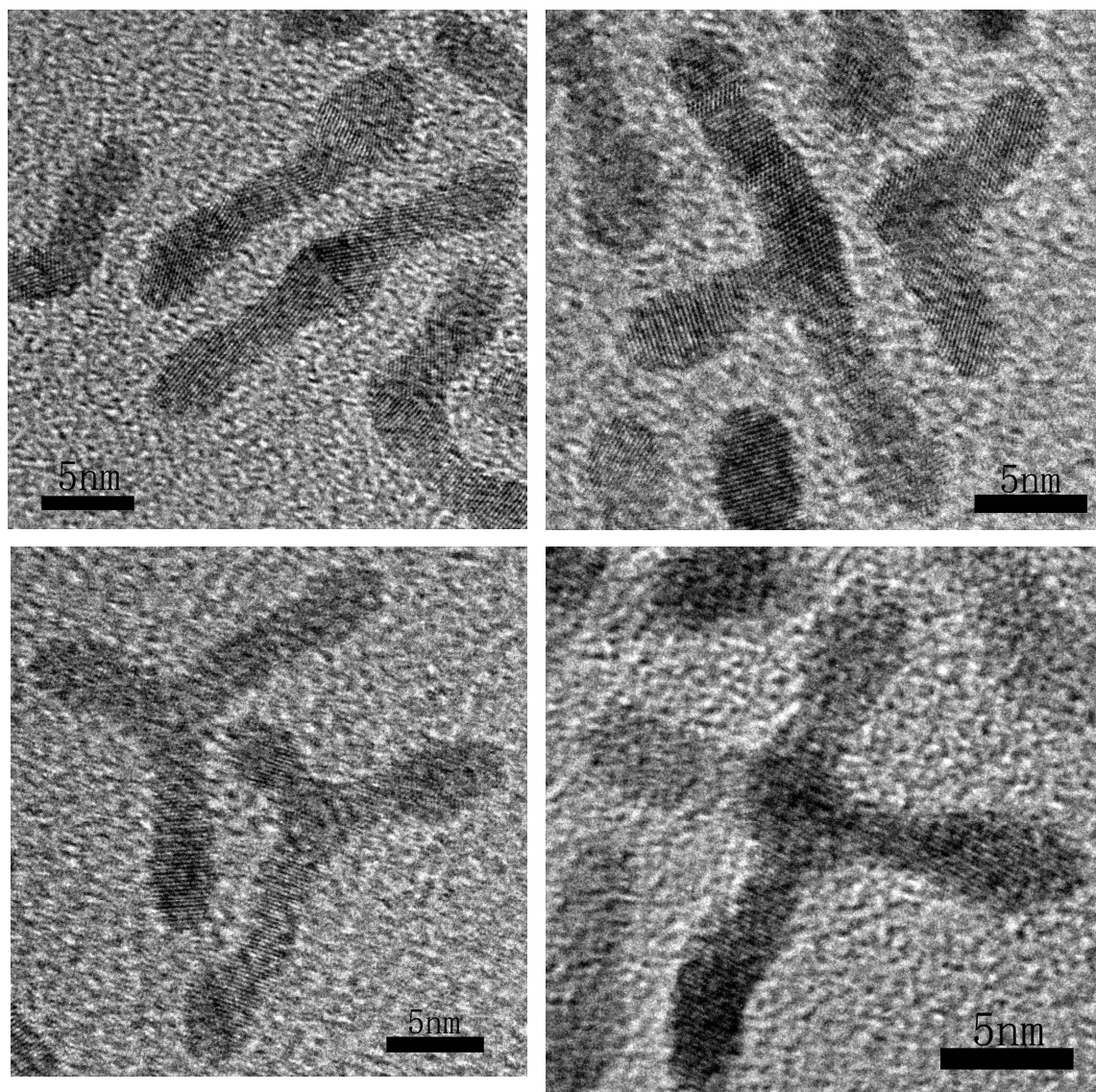


Figure S5. HRTEM images of typical Pd multipods showed in Figure 1F.

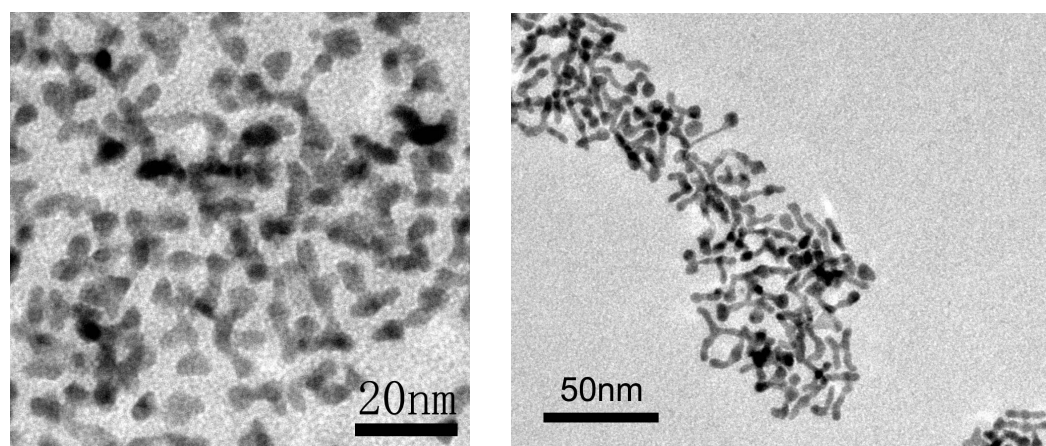


Figure S6. TEM image of Pd multipod structures formed in AAAC/toluene system at 60°C for 5 seconds (left) and 40 seconds (right).

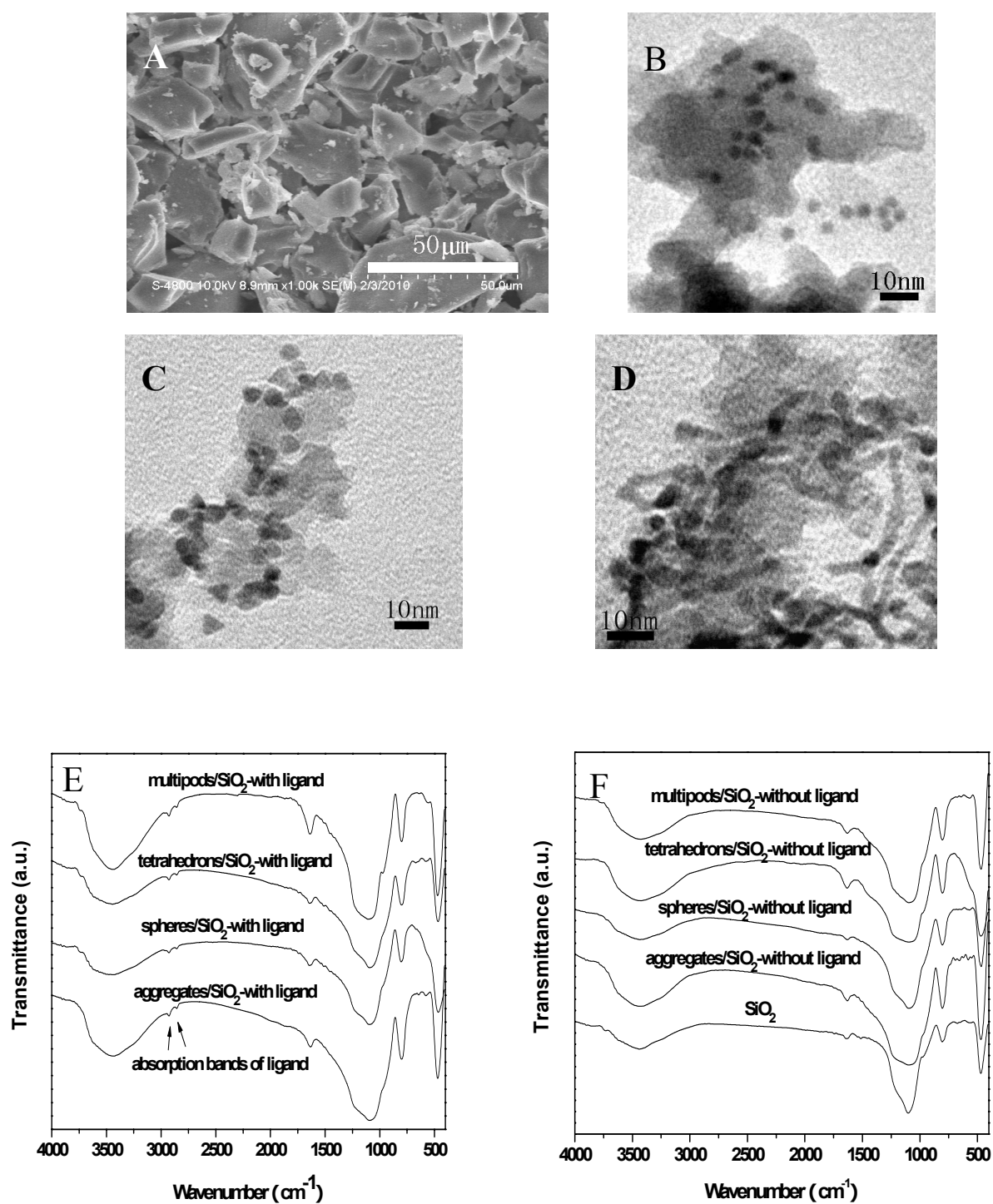


Figure S7. SEM image of Silica support (A) and TEM image of supported Pd NCs synthesized at AAAC/OAm weight ratios of 5/5 (B), 7/3 (C), 10/0 (D). FTIR spectra of supported Pd NCs before (E) and after (F) washing using acetic and ethanol. The bands in the range of 2850 to 2950 cm⁻¹ in spectra of (E) are attributed to the vibration of C-H bonds. These bands can not be observed in the spectra of (F), indicating that the AAAC and OAm were removed after washing.

Table S1. Results of citral hydrogenation by Pd NCs with different morphologies

Catalysts	CO ₂ pressure /MPa	Reaction time/h	Conversion /%	Selectivity/%				TOF/h ⁻¹ ^a	TOF /mol·m ⁻² ·h ⁻¹ ^b
				CAL	DCAL	ENAL	Others		
Pd-aggregates /SiO ₂	—	2	5	62	10	27	1	333	
Pd-spheres/SiO ₂	—	2	18	47	6	41	6	1197	0.67
Pd-tetrahedrons/SiO ₂	—	2	43	57	18	24	1	2860	1.30
Pd-multipods/SiO ₂	—	2	68	46	36	17	1	4522	3.77
	8	2	95	56	36	6	2	6318	5.27
	10	0.5	27	58	6	35	1	7182	5.99
	10	0.75	44	54	11	34	1	7803	6.50
	10	1.25	77	45	42	12	1	8193	6.83
	10	1.5	91	42	48	9	1	8069	6.72
	10	2	100	24	71	3	2	6650	5.54
	12	2	64	46	17	35	2	4256	3.55
Pd/C	—	2	6	59	4	35	2	399	

Reaction conditions: citral, 0.67 mmol; Pd, 5×10^{-5} mmol; mole ratio of citral/Pd, 1.33×10^4 ; temperature, 323 K; H₂, 4 MPa. The Pd-aggregates, Pd-spheres, Pd-tetrahedra, Pd-multipods correspond to those in Figure S3, Figure 1A, Figure 1D, and Figure 1F;

a. Moles of citral converted in 1 h on 1 mole of Pd atom.

b. Moles of citral converted in 1 h on 1 square meter surface of Pd NCs; The Pd surface areas were calculated by assuming these NCs to be ideal spheres with diameter of 3 nm, tetrahedra with the edge length of 6 nm, and cylinders with diameter of 3 nm.

References

- (S1) Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. *Angew. Chem. Int. Ed.* **2004**, *43*, 1397.
- (S2) Masuda, K.; Ito, Y.; Horiguchi, M.; Fujita, H. *Tetrahedron* **2005**, *61*, 213.
- (S3) George, M.; Weiss, R. G. *Langmuir* **2003**, *19*, 8168.