Electronic Supplementary Information for

Construction of Au-Pd alloy shells for enhanced catalytic performance toward alkyne semihydrogenation reactions

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Experimental Section

Synthesis of Pd@Au-Pd Core/Alloy-Shell Nanocrystals. In a standard procedure, 5.5 mL of Pd nanocube solution prepared according to our reported work[1] was firstly washed with ethanol (5 mL) and re-dispersed in oleylamine (OAm, 5 mL) in a 20 ml vial. After the vial had been capped, the solution was transferred into an oil bath and heated at 200 ºC under magnetic stirring for 10 min. Then, 2 mg of $AuPPh_3Cl$, which was prepared according to the literature,[2] was dissolved in trioctylphosphine (TOP) (1.0 mL), and pumped into the above OAm solution of Pd nanocubes at the rate of 0.1 ml/min. The reaction was kept at 200 ºC for 6 hours. After the reaction, the solution was cooled down to room temperature. The final products were collected by centrifugation and washed with ethanol twice, then re-dispersed in hexane.

Preparation of EB-Bonded (or vinylbiphenyl) Pd@Au-Pd Nanocrystals. Pd@Au-Pd nanocubes (10 mg) were dissolved in 20 mL of toluene, to which 360 mg of EB-H (4-Ethynyl-1,1'-biphenyl) (or vinylbiphenyl) were then added. After the solution was stirred at 298 K overnight, toluene was removed by rotary evaporation. The remaining solids were washed with methanol for twenty times to remove the free EB-H (or vinylbiphenyl), and the final product was collected by centrifugation.

Pd@Au-Pd Catalyzed Semihydrogenation. In a typical semihydrogenation reaction, EB-H (90 mg, 0.5 mmol), Pd@Au-Pd nanocubes (0.5 mg), and 4 mL of toluene were added to a flask which was pre-purged twice by flushing with hydrogen. Then a balloon filled with H_2 was connected to this flask. The reaction was kept at room temperature for 30 min, and the final products were monitored by GC-MS. Similar procedure was carried out for other alkynes, except the reaction time due to the different semihydrogenation rate of the alkynes. The chemical yield was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard, and the ratio was determined with GC-MS and NMR analysis.

Sample Characterizations.

Powder XRD patterns were recorded using a diffractometer (X-ray Diffractometer SmartLab(3), Rigaku) operated at 3 kW. TEM images were performed at a Hitachi HT-7700 microscope equipped with a tungsten filament, operating at 100 kV. HRTEM, HAADF-STEM images and EDX elemental mapping were performed at Tecnai G^2 F20 STWIN operating at 200 kV. Infrared spectroscopy was collected on a VERTEX 70 spectrometer with samples prepared as KBr pellets. Absorption maxima (ν max) were reported in wave numbers (cm^{-1}). GC-MS analysis was carried out on an Agilent 7890A GC interfaced to an Agilent 5975C mass-selective detector (30 m × 0.250 mm capillary column, HP-5MS). NMR spectra were measured on a Bruker Avance-400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and chemical shift reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. XPS analyses were performed using a Kratos Ultra DLD spectrometer equipped with monochromatic Al K radiation. The binding energy scales were calibrated using the C1s peak at 284.6 eV from carbon contamination.

Calculation of turnover frequency (TOF)[3]

The Pd nanocube sample has an average edge length of d nm, the volume of each Pd nanocube is then

d^3 nm^3

The number of Pd atoms in a single Pd octahedron is

N (total) = $4*d^3\ nm^3 / 0.389^3\ nm^3$

A Pd octahedron is enclosed by 6 square facets. Its total surface area is

$d^2\ nm^2 *6$

Each unit cell on the {100} facet contains two Pd atom, distance of two {100} facet is 0.2 nm. So, its area is

$(0.2\ nm*2)^2 = 0.16\ nm^2$

The number of the surface Pd atoms on a single nanocube is

N (surface) = $d^2\ nm\ ^2*6*2/0.16nm^2$

D (dispersion) = N (surface)/N (total)

$$\text{TOF} = \frac{6.02\times10^{23} * \text{con.\%} * 0.5mmol}{\frac{2}{60} h * D * 6.02\times10^{23} * 0.5mmol * 1\%}$$

d(Au-Pd) = 20 nm, d (Lindlar) = 3.2 nm, d(Pd/C) = 4 nm, d (Au-Pd/C) = 4 nm.

TOF (Pd@Au-Pd nanocubes) = 11350 h^{-1}, (calculated with the content of both Au and Pd), calculated for 2 min hydrogenation reaction, 1 mol% catalyst.

TOF (Lindlar) = 467 h^{-1}, calculated for 2 min hydrogenation reaction, 1 mol% catalyst.

TOF (Au-Pd/C) = 4591 h^{-1}, calculated for 0.5 min hydrogenation reaction, 1 mol% catalyst.

TOF (Pd/C) = 1253 h^{-1}, calculated for 1 min hydrogenation reaction, 1 mol% catalyst.

References

[1] M. Jin, H. Liu, H. Zhang, Z. Xie, J. Liu and Y. Xia, *Nano Res.,* 2011, **4**, 83-91.

[2] Z. Jiang, Q. Zhang, C. Zong, B. J. Liu, B. Ren, Z. Xie and L. zheng, *J. Mater. Chem.* 2012, **22**, 18192-18197.

[3] Y. Wu, S. Cai, D. Wang, W. He a Y. Li, *J. Am. Chem. Soc*., 2012, **134**, 8975-8981.

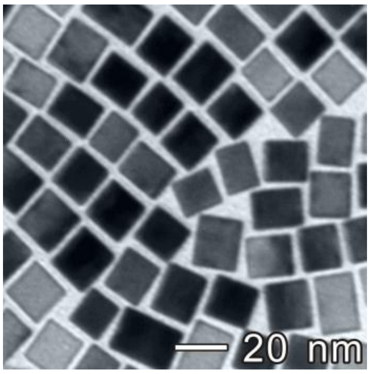


Figure S1. TEM image of the obtained Pd nanocubes after reacted with $AuPPh_3Cl$ in oleic acid for 12 h.

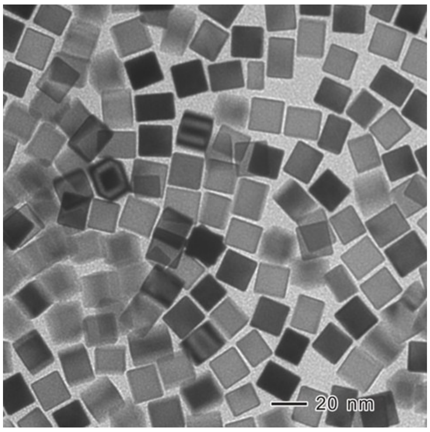


Figure S2. TEM image of the Pd nanocubes.

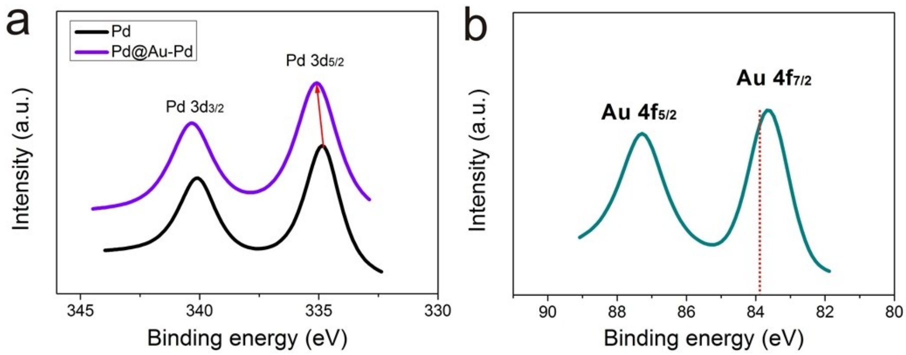


Figure S3. X-ray photoelectron spectroscopy (XPS) characterizations of the Pd@Au-Pd nanocubes. (a) XPS signals of Pd in Pd nanocubes and Pd@Au-Pd nanocubes. (b) XPS signals of Au in Pd@Au-Pd nanocubes.

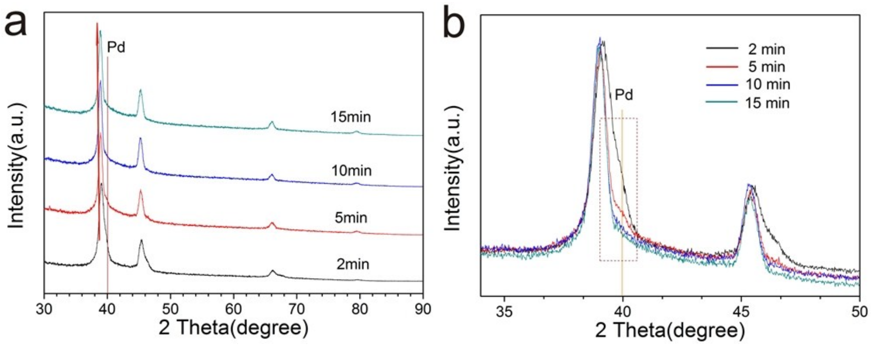


Figure S4. XRD patterns of the Pd@Pd-Au alloy surface nanocubes obtained at different reaction times.

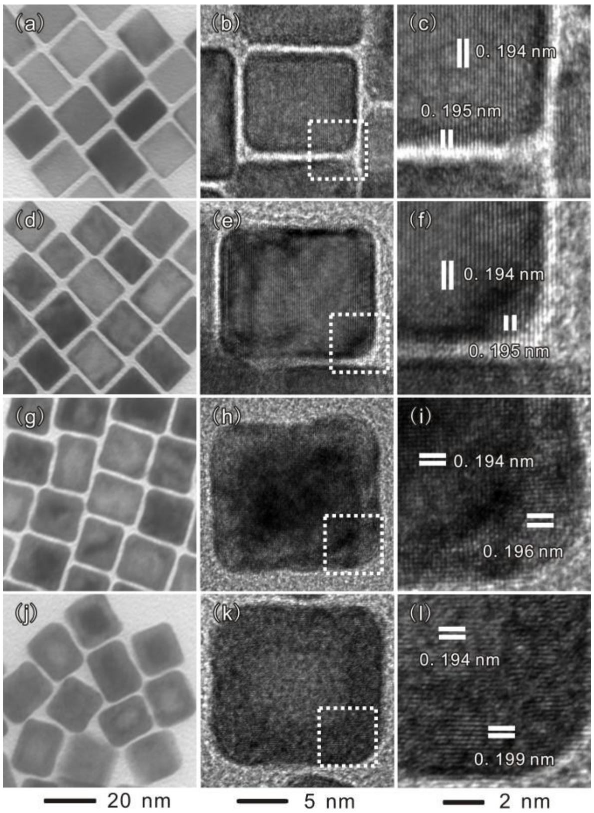
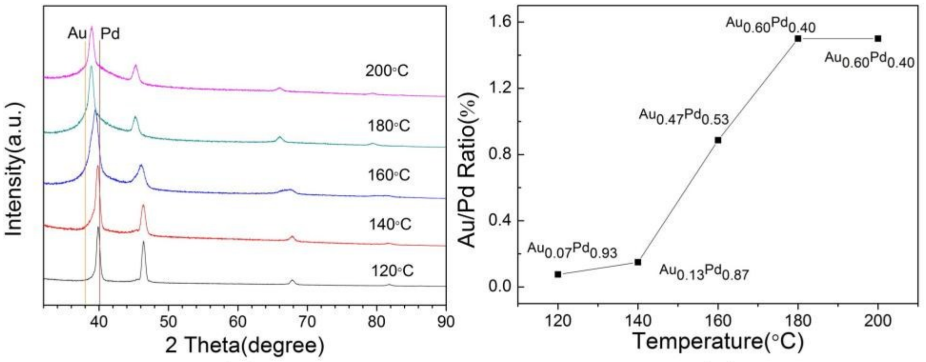


Figure S5. TEM and HRTEM images of the Pd@Au-Pd nanocubes formed at different temperatures: (a-c) 120 °C, (d-f) 140 °C, (g-i) 160 °C, (j-l) 180 °C.



（a）　　（b）

Figure S6. (a) XRD of Pd@Au-Pd core-shell nanocubes prepared at different temperatures. (b) Plots of the changes of Au/Pd ratio as a function of the reaction temperature.

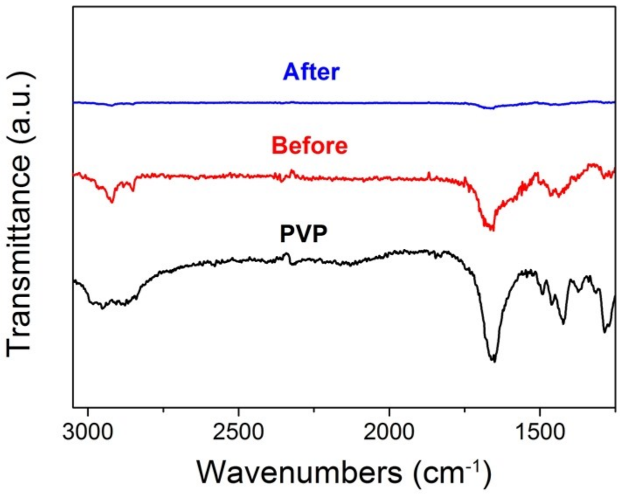


Figure S7. Transmittance IR spectra of the cubic Pd seeds before and after removing the capping agents.

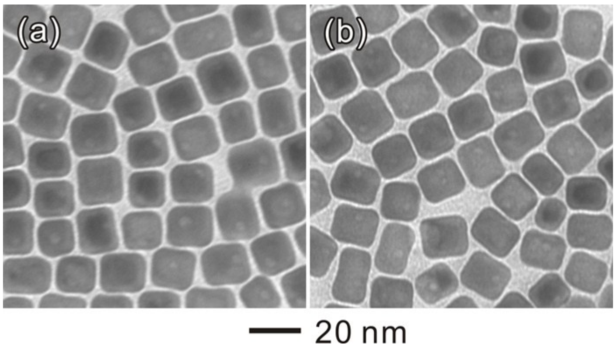


Figure S8. TEM images of the Pd@Au-Pd alloy surface nanocubes prepared with cubic Pd seeds before (a) and after (b) removing the capping agents (PVP and Br^- ions).

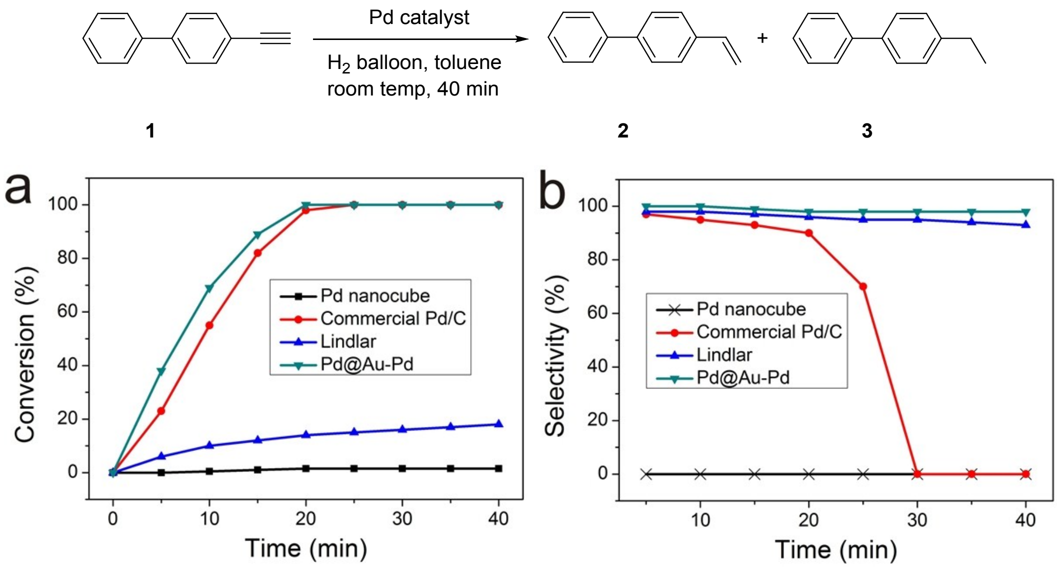


Figure S9. Semihydrogenation of EB-H catalysed by different Pd catalysts: (a) Conversion of alkyne, (b) Selectivity of alkene. Reaction condition: 0.5 mmol EB-H, 1 mol % Pd catalyst, 4 mL of toluene, room temperature. The results were determined by GC-MS analysis and ^{1}H NMR spectroscope using CH_2Br_2 as internal standard.

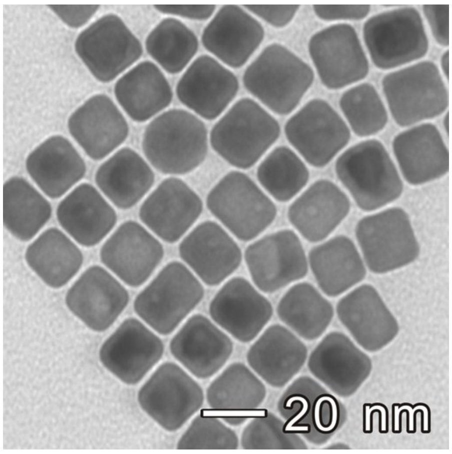


Figure S10. TEM images of the Pd@Au-Pd nanocubes after four cycles of semihydrogenation reaction.

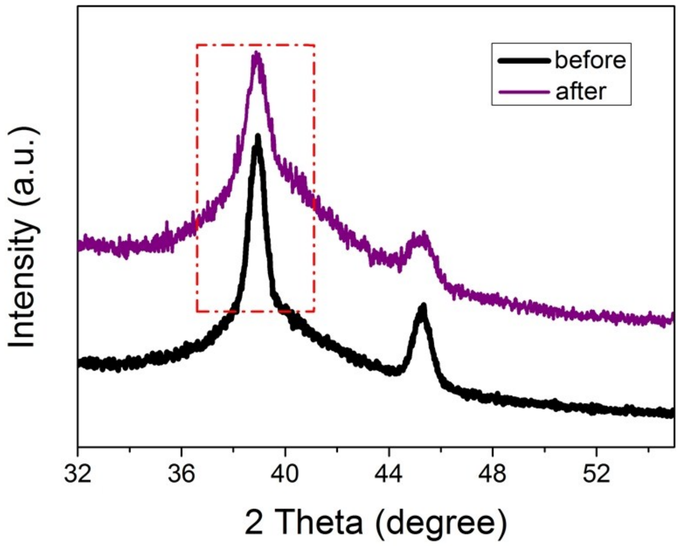


Figure S11. X-ray diffraction patterns of the Pd@Au-Pd nanocubes before and after four cycles of the semihydrogenation reaction.

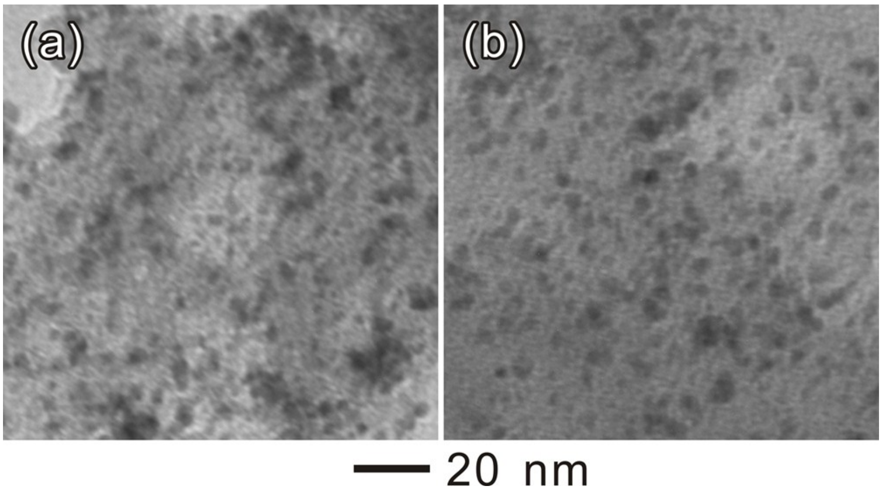


Figure S12. TEM images of (a) the original Pd/C and (b) surface alloyed Pd@Au-Pd/C.

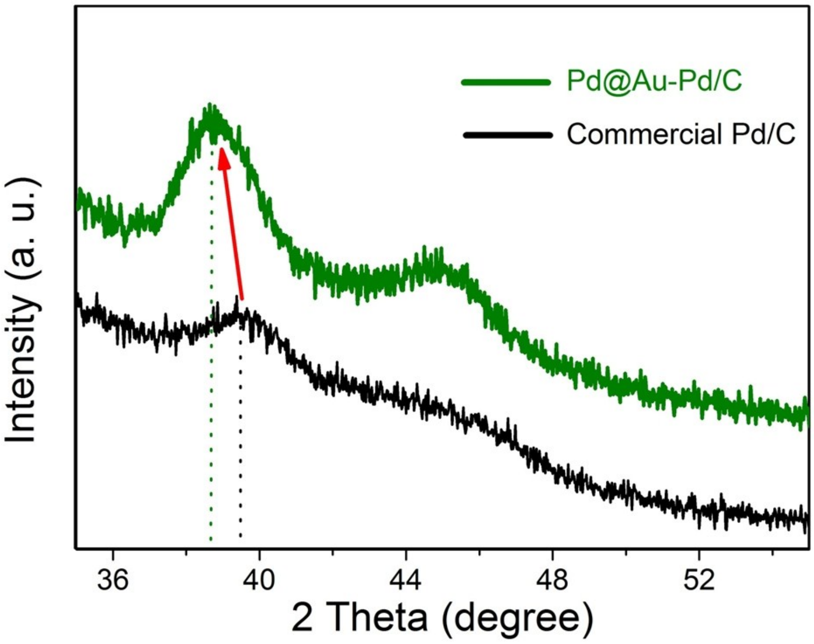


Figure S13. XRD patterns of the commercial Pd/C and surface alloyed Pd@Au-Pd/C nanocatalysts.

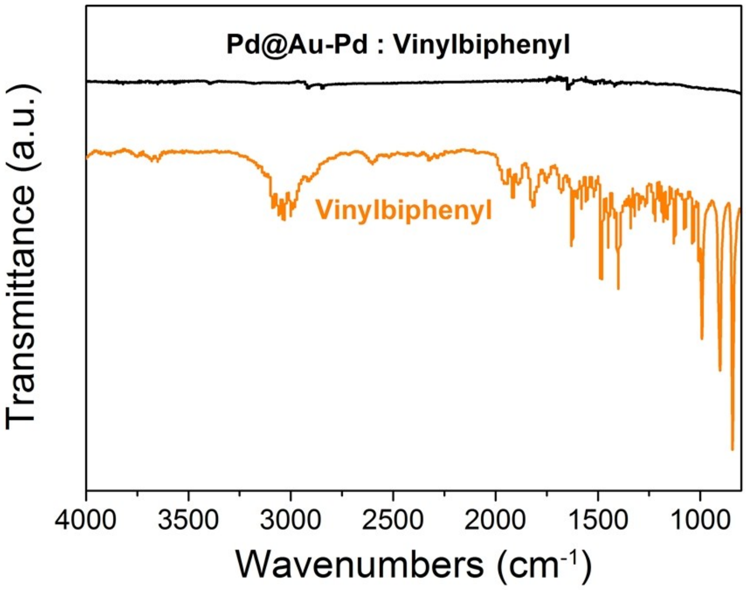


Figure S14. Transmittance IR spectra of pure vinylbiphenyl and vinylbiphenyl adsorbed on the Pd@Au-Pd nanocubes.

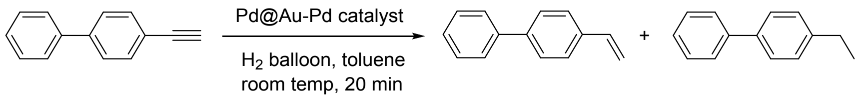
Table S1. Br content for the original Pd seeds before and after removing the capping agent.

Sample	**Concentration of Br**
Before	636 ppb
After	< 1 ppb

Table S2: Turnover frequency (TOFs) per surface Pd atom for Semihydrogenation of EB-H. For all calculations of the TOF, the conversion of EB-H was controlled to be < 10%.

Catalyst	Number of surface atoms	TOF $[h^{-1}]$
Pd@Au-Pd nanocubes	1.23×10^{17}	4540
Au-Pd/C	8.18×10^{17}	4591
Pd/C	8.18×10^{17}	1253
Lindlar catalyst	9.21×10^{17}	467

Table S3. Semihydrogenation of EB-H using Pd@Au-Pd nanocubes with different alloy thicknesses as the catalyst. Reaction condition: 0.5 mmol EB-H, 1 mol% catalyst, 4 mL of toluene, room temperature, 20 min.



1 **2** **3**

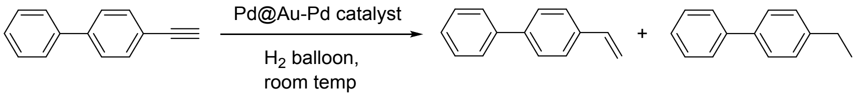
The thickness of AuPd alloy	Conv. (%)[a]	Yield of 2 (%)[a]	2 : 3[a]
0.3	10	7	76 : 24
0.7	80	73	91 : 9
1.2	>99	93	94 : 6
1.8	>99	95	96 : 4
2.8	>99	98	98 : 2
3.3	>99	98	98 : 2

[a] Conversion and product distribution were determined by GC-MS analysis and ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard.

Solvent Effect of the Semihydrogenation Reaction

The solvent effect of semihydrogenation of EB-H using Pd@Au-Pd nanocubes as the catalyst was shown in Table S4. In our reaction system, the reaction rate and selectivity were affected by the choice of solvents. The use of EtOAc as solvent can lead to a similar catalytic activity and selectivity toward semihydrogenation of EB-H with toluene. Other solvents, like DMF, CH_3CN and MeOH would result in slightly lower catalytic activities and selectivity. In contrast, the use of water as the solvent will cause the lowest reaction rate and the worst selectivity of 4-vinylbiphenyl due to the limited solubility and large difference in polarity with EB-H.

Table S4. Semihydrogenation of EB-H in different solvents while using Pd@Au-Pd nanocubes as the catalyst. Reaction condition: 0.5 mmol EB-H, 1 mol% catalyst, 4 mL of solvent, room temperature, 20 min.

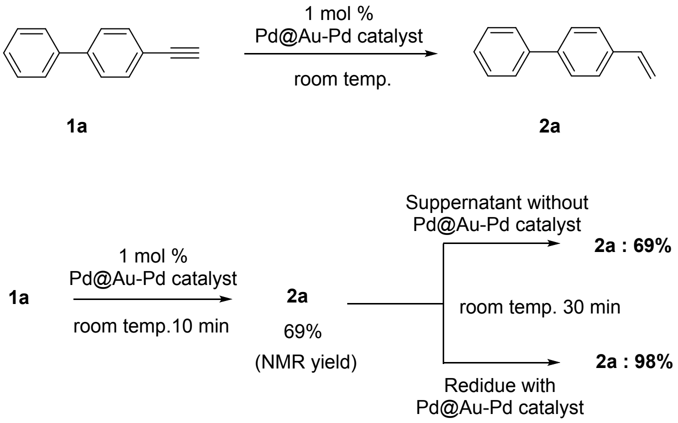


1 2 3

solvents	Conv. (%)[a]	Yield of 2 (%)[a]	2 : 3[a]
Toluene	>99	98	98 : 2
AcOEt	>99	98	98 : 2
DMF	>99	98	98 : 2
CH_3CN	>99	92	93 : 7
MeOH	>99	90	91 : 9
H_2O	14	5	37 : 63

[a] Conversion and product distribution were determined by GC-MS analysis and ^1H NMR spectroscopy using CH_2Br_2 as internal standard.

Leaching experiment of Pd@Au-Pd catalyst.



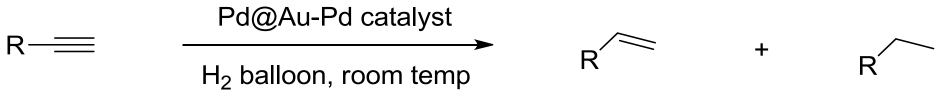
Scheme S1. Leaching experiments for the reaction using Pd@Au-Pd as catalyst.

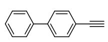
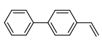
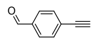
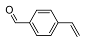
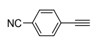
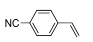
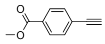
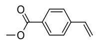
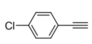
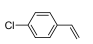
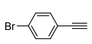
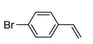
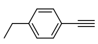
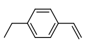
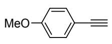
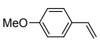
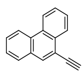
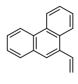
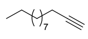
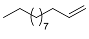
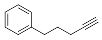
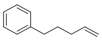
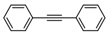
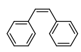
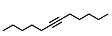
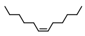
The toluene solution of EB-H (**1a**) in the presence of Pd@Au-Pd catalyst (1 mol%) was stirred at room temperature for 10 min. At this time the yield of **2a** was 69% which determined by ^{1}H NMR using CH_2Br_2 as internal standard. Then, 2 mL of the reaction solution was removed from the reaction solution, and centrifuged at 11000 rpm for 10 min. After centrifugation, the supernatant was transferred to the other reaction vessel. The supernatant without Pd@Au-Pd catalyst was continuously stirred at room temperature for 30 min, affording the corresponding product **2a** in 69% ^{1}H NMR yield, implying that no further reaction has taken place in the supernatant. In comparison, the yield of **2a** in the other 2 ml solution reached 98% after 30 mins′ reaction. In addition, ICP-MS analyses (Table S5) show that no Au, Pd elements and other residual metal can be detected in the supernatant, indicating no metal leaching during the catalytic reaction and the reaction was catalyzed by the Pd@Au-Pd catalyst and not by the residual metal which sometimes comes from the used glassware or chemicals.

Table S5. Metal content in the supernatant of reaction solvent after centrifugation.

Sample	Concentration in supernatant
Au	0 ppb
Pd	0 ppb
Pt	0 ppb
Rh	0 ppb

Table S6. Semihydrogenation of alkynes using Pd@Au-Pd alloy surface nanocubes as the catalysts. Reaction condition: 0.5 mmol alkynes, 3 mol% Pd catalyst, 4 mL of toluene, room temperature. Due to reaction rate differences, different alkynes may need different reaction times to achieve 100% conversions.



Substrate	Product	t (min)	Conv. (%)[a]	Yield of Alkene	Alkene: Alkanea
		12	100	98	98:2
		12	100	95	95:5
		12	100	94	94:6
		10	100	96	96:4
		14	100	96	96:4
		10	100	97	97:3
		13	100	97	97:3
		12	100	96	96:4
		12	100	99	99:1
		12	100	90	91:9
		12	100	97	97:3
		13	100	90[b]	91:9
		12	100	99[c]	99:1

[a] Conversion and product distribution were determined by GC-MS analysis and ^{1}H NMR spectroscope using CH_2Br_2 as internal standard. [b] Z : E = 100 : 0. [c] Z : E = 97 : 3.