Electronic Supplementary Information

Dual Roles of Underpotential Deposition in the Synthesis of Tetrahexahedral Pd-Ag Alloy Nanocrystals

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EXPERIMENTAL DETAILS

1 Materials. Palladium(II) chloride ($PdCl_2$) and L-ascorbic acid (AA) were obtained from Sigma-Aldrich. Silver nitrate ($AgNO_3$) was obtained from Sinopharm Chemical Reagent Co., Ltd. Cetyltrimethylammonium bromide (CTAB) was obtained from Acros Organics. Hydrochloric acid (HCl, 37.5%) was obtained from Beijing Chemical Works. Commercial Pd/C (10 wt. %) was purchased from Alfa Aesar. Ultrapure de-ionized water was used throughout the experiments.

2 Synthesis of Pd Cubic Seeds. The cubic seeds were synthesized according to previously reported protocols. To prepare a 10 mM H_2PdCl_4 solution, 0.1773 g $PdCl_2$ was added in 10 mL of 0.2 M HCl solution and the mixture was heated at 60 ˚C until all the solids were dissolved, then the solution was further diluted to 100 mL with water. To synthesize Pd cubic seeds, a vial containing 45.6 mg CTAB and 10 mL of water were heated at 95 ˚C with constant electromagnetic stirring for 5 min. Then 0.5 mL of 10 mM H_2PdCl_4 solution was added. After another 5 min, 80 μL of 0.1 M ascorbic acid solution was quickly injected. The mixture was further stirred for 10 min at 95 ˚C and finally stored at 30 ˚C for future use.

3 Growth of Pd-based NCs in the presence of silver nitrate. In a typical synthesis, 50 mL of 0.1 M CTAB solution was preheated in a 60 ºC water bath for 10 min. Then, 0.25 mL 1 M HCl solution, 1.25 mL of 10 mM H_2PdCl_4 solution, different amounts of 10 mM $AgNO_3$ solution, and 0.4 mL of the as-synthesized Pd cubic seed solution were added and gently mixed, followed by the addition of 0.5 mL of 0.1 M ascorbic acid solution. The resulting solution was placed in a water bath at 60 ºC without disturbance. After 12 h, the products were collected by centrifugation (12000 rpm, 5 min) and washed by water. The centrifugation was performed again, and the precipitates were re-dispersed in water for further characterization.

4 Instrumentation. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images were acquired using a JEOL JEM-2100F TEM

operating at 200 kV. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Discover with GADDS and Cu Kα radiation. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-6700F microscope operating at 20 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Hsi spectrometer using monochromatic Al Kα X-ray source (1486.6 eV). C 1s at 284.5 eV was used as the charge reference to determine core level binding energies. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) data were obtained with a JEM-2010 apparatus operating at 200 kV. The element mole ratio of NCs was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo Scientific iCAP6300 instrument (Thermo Fisher Scientific, USA).

5 Electrochemical measurements. All the electrochemical measurements were conducted in a three-electrode system with CHI760E electrochemical workstation (CH Instruments, Instrument Corporation, China). Glassy carbon electrodes (GCE, 3.0 mm diameter) were used as the working electrode. Ag/AgCl electrode (saturated KCl) and Pt wire were used as the reference and counter electrodes, respectively. 1 mg of as-synthesized Pd NCs were dispersed in 0.5 mL of 20 vol.% isopropyl alcohol solution containing 0.1 wt.% Nafion. The mixture was then sonicated vigorously for 30 min to form a homogeneous suspension. Subsequently, 5 μL of the above suspension was dropped on the GCE and used for electrochemical measurements after solvent evaporation. Accelerated durability test (ADT) was performed in N_2-saturated 1.0 M KOH + 1.0 M CH_3OH by continuous potentiodynamic swept between -0.8 and 0.2 V for 500 cycles at a scan rate of 50 mV s^{-1}.

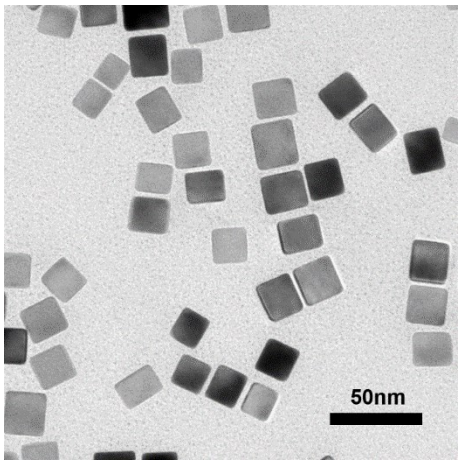


Fig.S1. TEM image of Pd cubic seeds (size ~22nm) for synthesis of Pd-based nanocrystals.

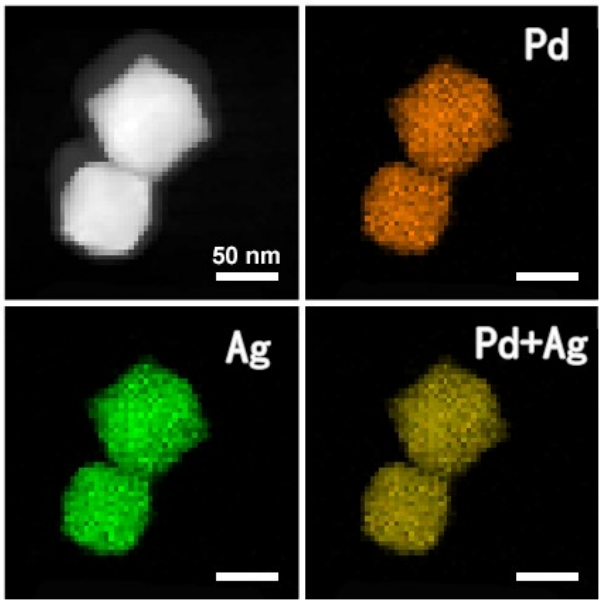


Fig.S2. STEM and EDX mapping images of Pd-Ag THH nanocrystals. (Ag(I)/Pd(II) precursor ratio of 0.32).

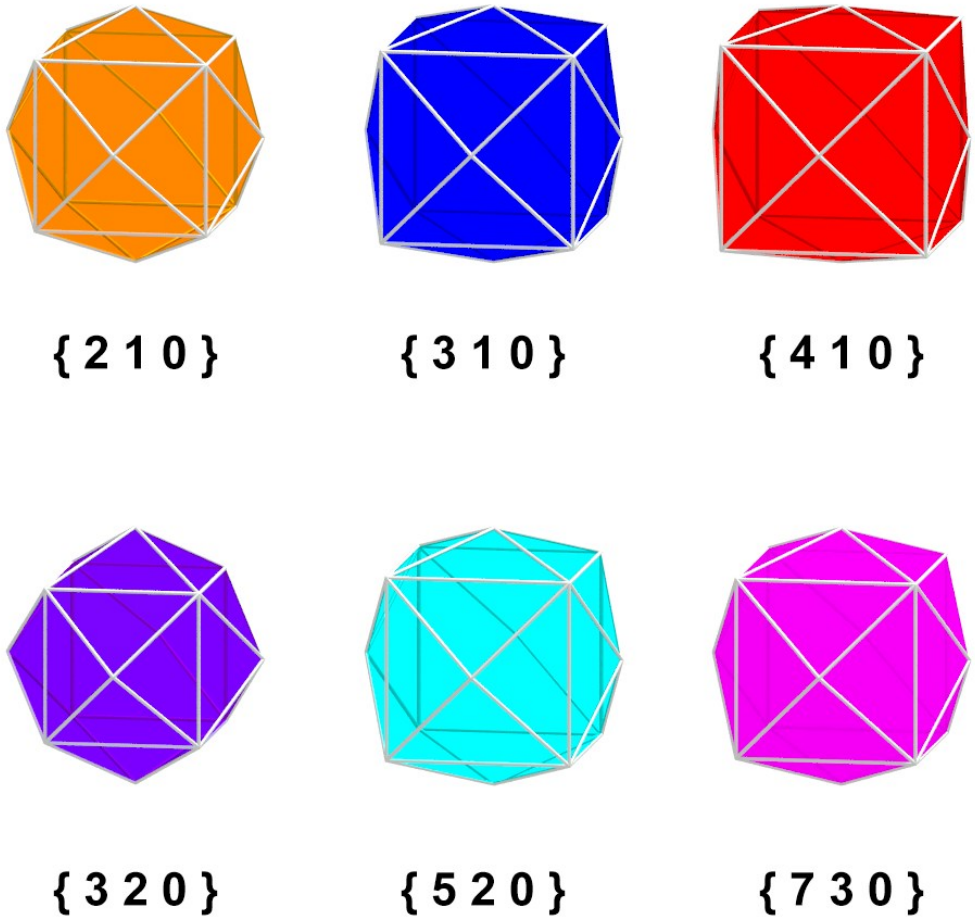


Fig.S3. Models of THH NCs enclosed by different {hk0} high-index facets (h>k>0).

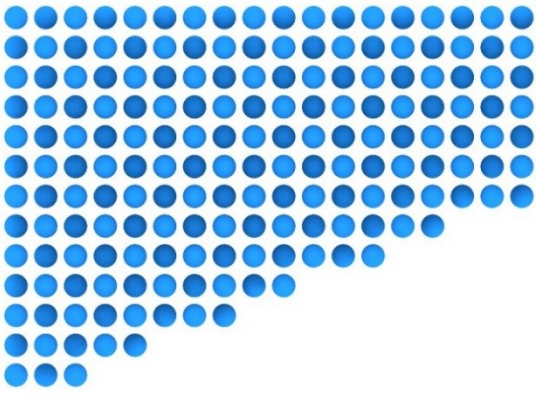


Fig.S4. Theoretical step configuration of {520} facets made of {310} and {210} sub-steps.

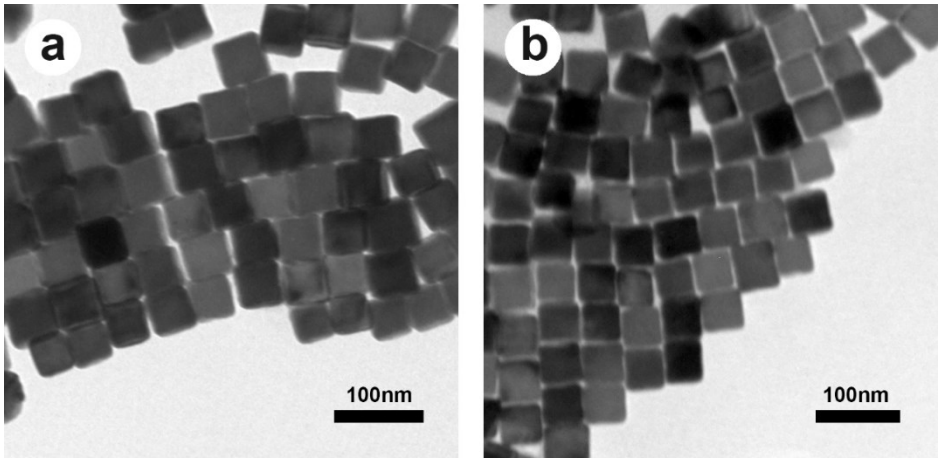


Fig.S5. TEM images of Pd-based nanocrystals before (a) and after (b) reaction in the absence of H_2PdCl_4 precursor, other conditions are the same as the growth of the THH NCs. Pd nanocubes of ~50 nm in size were used as seeds.

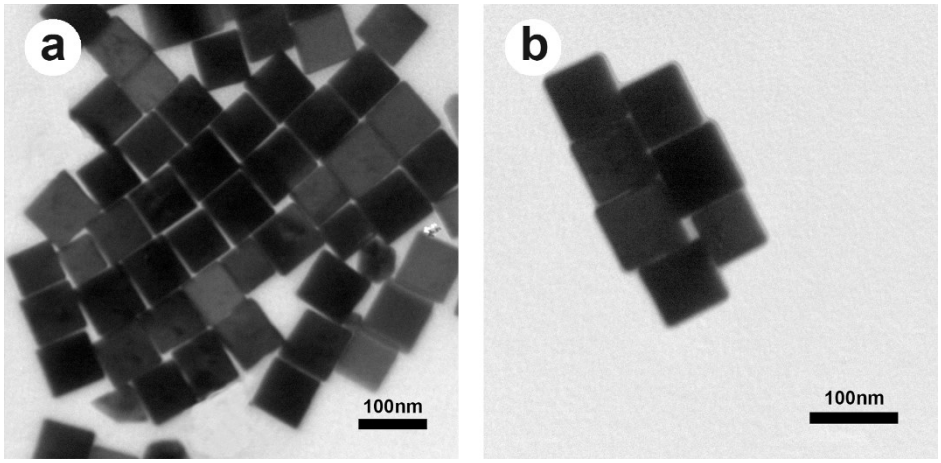


Fig.S6. Pd nanocubes with exposed {100} facets (size ~76nm) for electrochemistry measurements.

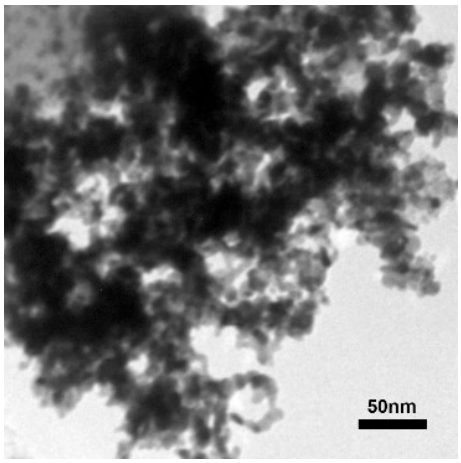


Fig.S7. TEM image of commercial Pd/C (10 wt.%) catalysts.

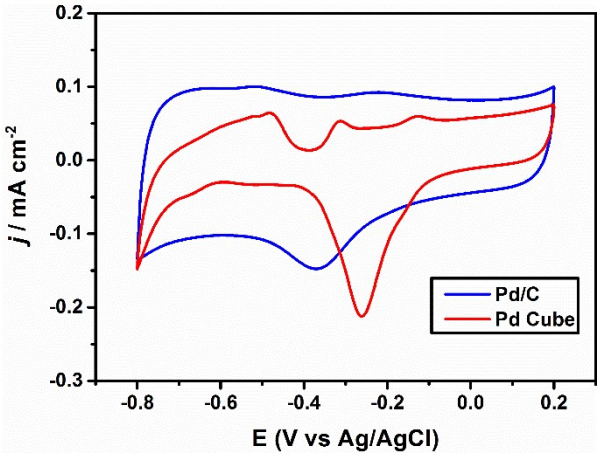


Fig.S8. CV curves of Pd nanocubes and Pd/C catalysts in 1.0 M KOH solution with a scan rate of 50 mV s^{-1}.

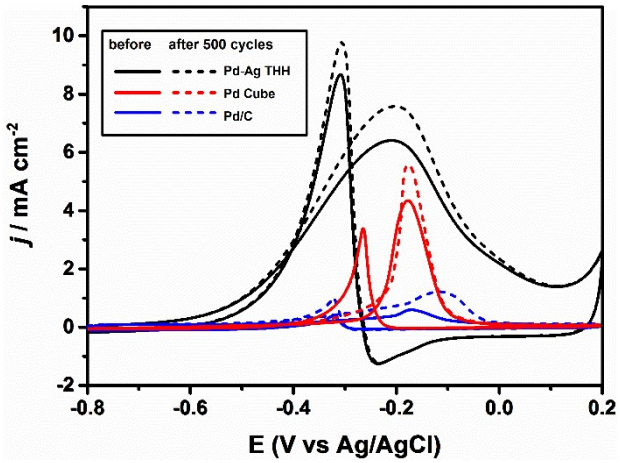


Fig.S9. CV curves of different samples before and after 500 cycles ADT in 1.0 M KOH+1.0 M CH_3OH solution with a scan rate of 50 mV s^{-1}.

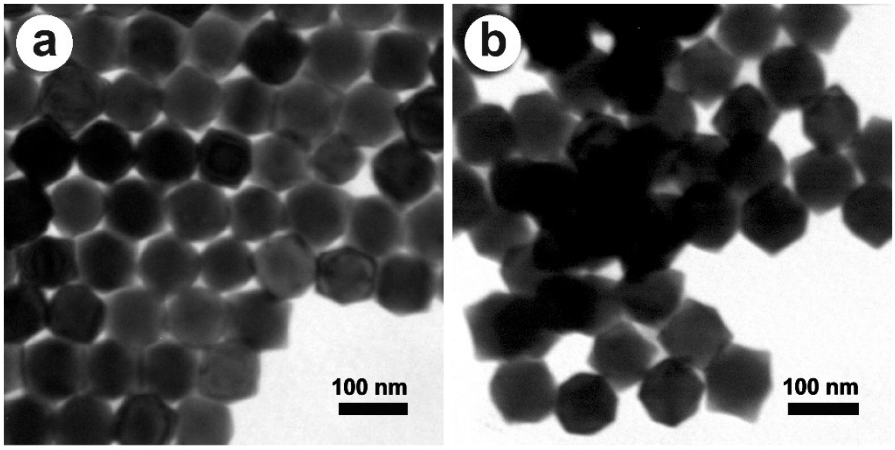
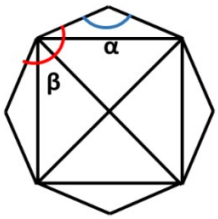


Fig.S10. TEM images of Pd-Ag THH NCs before (a) and after 500 cycles ADT (b) in 1.0 M KOH+1.0 M CH_3OH solution.

Table S1. ICP results of Pd-based NCs synthesized with different ratios of Ag(I)/Pd(II) precursors.

Ag(I)/Pd(II) precursor ratio	Mass percentage of Ag (%)	Molar percentage of Ag (%)	Corresponding morphology
0	0	0	Cube
0.04	2.56	2.53	Truncated cube
0.08	4.63	4.57	Truncated THH
0.16	5.48	5.42	Slightly truncated THH
0.32	6.96	6.88	THH
0.64	8.26	8.15	THH
0.96	9.76	9.64	THH
1.28	11.75	11.61	THH

Table S2. Projections from [001] direction and corresponding geometrical parameters of THH NCs bounded by {hk0} facets (h>k>0).

Projection image	Surface facets	Projection degree	
		α	β
	{3 2 0}	112.62	157.38
	{2 1 0}	126.87	143.13
	{7 3 0}	133.60	136.40
	{5 2 0}	**136.40**	**133.60**
	{3 1 0}	143.13	126.87
	{4 1 0}	151.93	118.07
	{h k 0}	2*arc tan(h/k)	270-α