Electronic Supplementary Information

Facet-Dependent Optical Properties of Pd–Cu_2O Core–Shell Nanocubes and Octahedra

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Synthesis of 40-nm Pd nanocubes

For the growth of 40-nm Pd cubes, 9313.75 μL of deionized water were respectively introduced into sample vials. Subsequently 0.048 g of CTAC and 0.525 mL of 10 mM H_2PdCl_4 solution were added to each of the sample vials. The vials were kept in a water bath set at 35 °C throughout the particle synthesis. Then 37.5 μL of 1.0×10^{-3} M KBr solution was introduced. The vials were left undisturbed in the water bath for 15 min. Next, 3.75 μL of 1.0×10^{-3} M KI solution was introduced and the solution was left undisturbed for another 15 min. Finally, 120 μL of 0.05 M ascorbic acid was added with thorough mixing, and the mixture was kept in the water bath for another 30 min to form Pd nanocubes. The particles were collected by centrifugation at 5500 rpm for 10 min. The precipitate was centrifuged one more time with 10 mL of deionized water at 5500 rpm for 10 min to remove the surfactant and dispersed in 375 μl of deionized water.

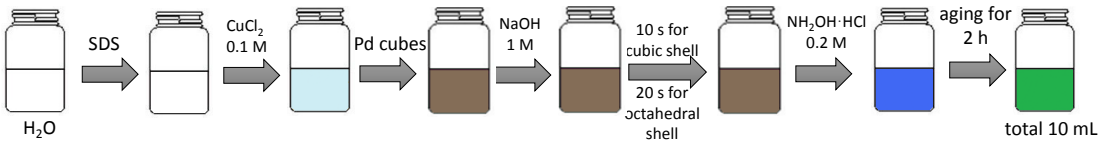

Fig. S1 Procedure for the preparation of Pd–Cu_2O nanocrystals. The observed solution colors are also shown.

Table S1 Amounts of reagents used in the synthesis of Pd–Cu_2O core–shell nanocubes and octahedra with shell thickness control. 29-nm Pd cubes were used

Shape	Size (nm)	SDS (g)	Water (ml)	0.1 M $CuCl_2$ (ml)	Pd cubes (ml)	1 M NaOH (ml)	0.2 M $NH_2OH.HCl$ (ml)
Cube	64	0.087	9.390	0.070	0.140	0.250	0.150
	70		9.410		0.120		
	82		9.430		0.100		
	93		9.450		0.080		
	107		9.470		0.060		
	124		9.490		0.040		
Octahedron	107	0.087	8.550	0.100	0.140	0.360	0.850
	115		8.570		0.120		
	121		8.590		0.100		
	136		8.610		0.080		
	142		8.630		0.060		
	183		8.650		0.040		

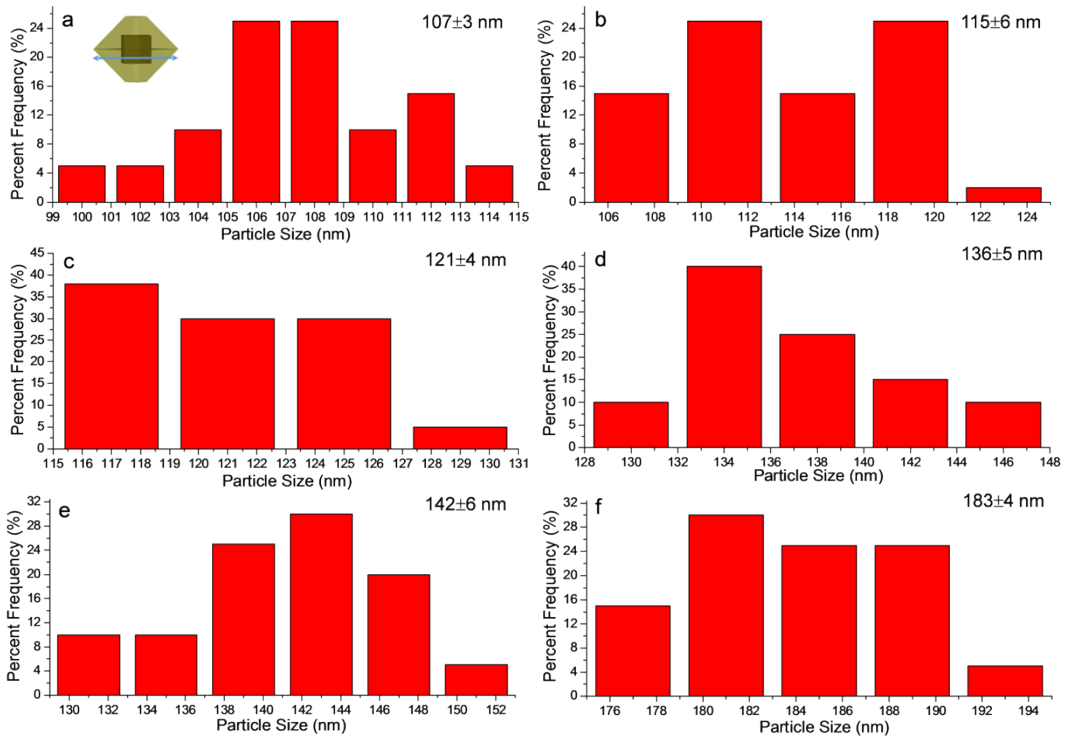

Fig. S2 Size distribution histograms of (a–f) Pd–Cu_2O octahedra. The drawing indicates the measured particle sizes. 29-nm Pd cubes were used.

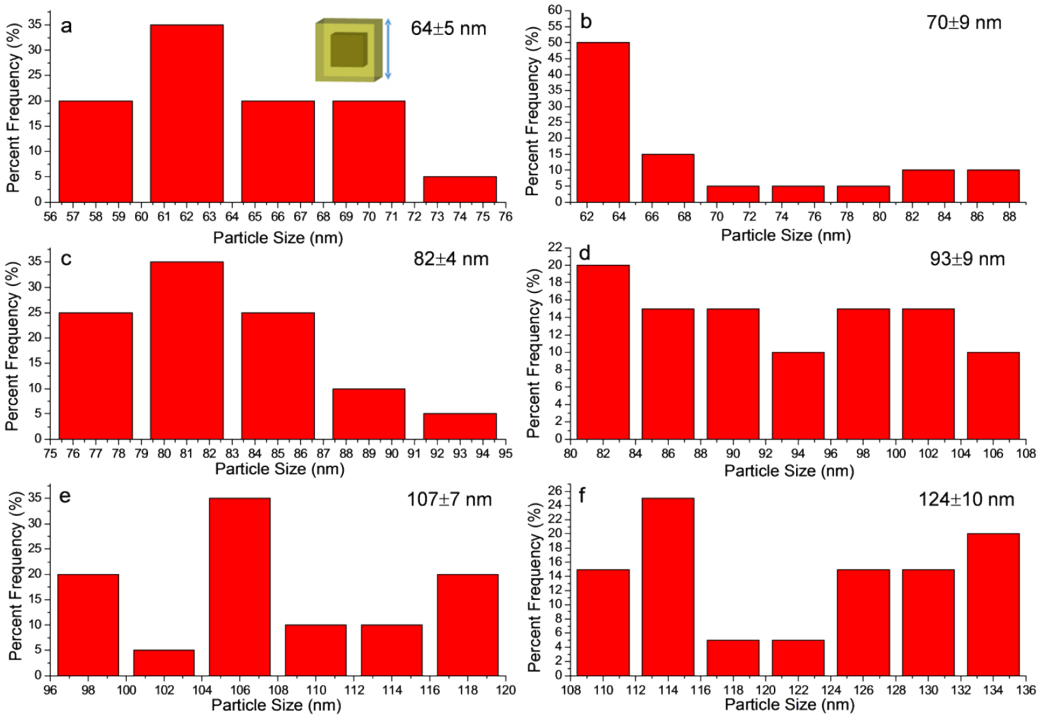

Fig. S3 Size distribution histograms of (a–f) Pd–Cu_2O octahedra. The drawing indicates the measured particle sizes. 29-nm Pd cubes were used.

Table S2 Average particle sizes, standard deviations, and coefficients of variation of the Pd–Cu_2O particles synthesized from 29-nm Pd cubes.

Shape	Pd cubic core used (ml)	Mean (nm)	Standard deviation (nm)	Coefficient of variation (%)
Cube	0.140	64	5	7
	0.120	70	9	12
	0.100	82	4	4
	0.080	93	9	9
	0.060	107	7	6
	0.040	124	10	8
Octahedron	0.140	107	3	2
	0.120	115	6	5
	0.100	121	4	3
	0.080	136	5	3
	0.060	142	6	4
	0.040	183	4	2

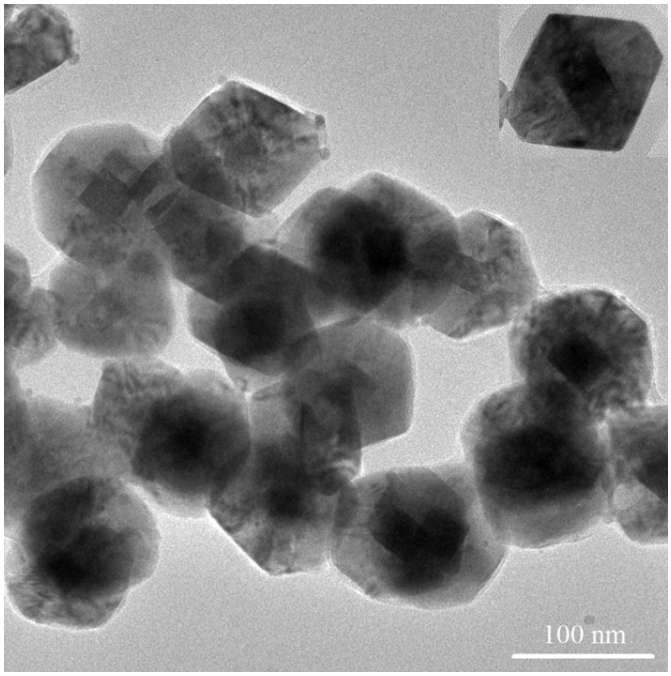

Fig. S4 TEM image of the 107-nm Pd–Cu_2O truncated octahedra synthesized using 29-nm Pd cubes. Inset shows another TEM image of the sample.

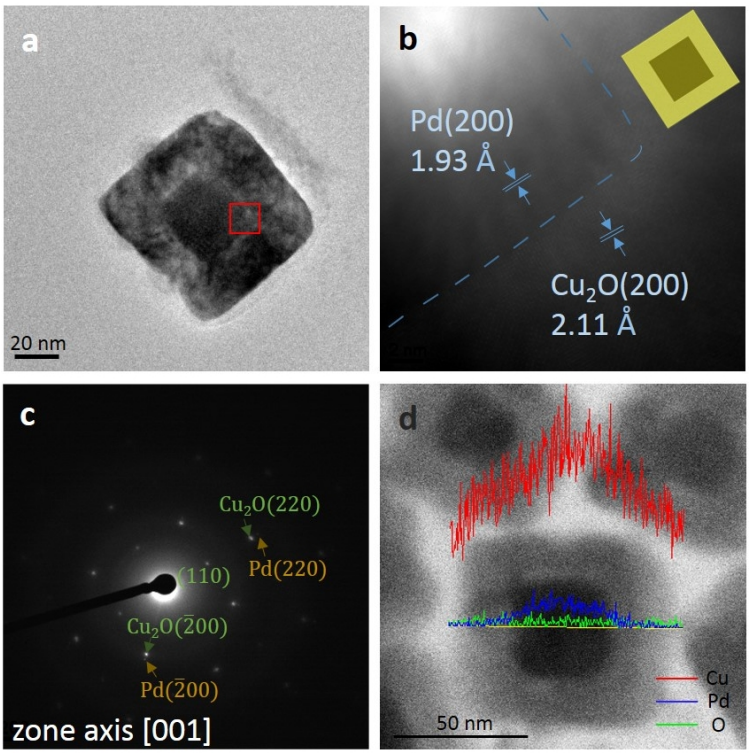

Fig. S5 (a) TEM image, (b) HR-TEM image and drawing of a Pd–Cu_2O cube, (c) SAED pattern, and d) EDS line scans of a Pd–Cu_2O cube. The dashed line in panel b indicates the interface between Pd and Cu_2O. The particle may be rotated while taking its SAED pattern, or a different cube was used for the SAED pattern, so that the SAED pattern does not match the particle orientation in the TEM image.

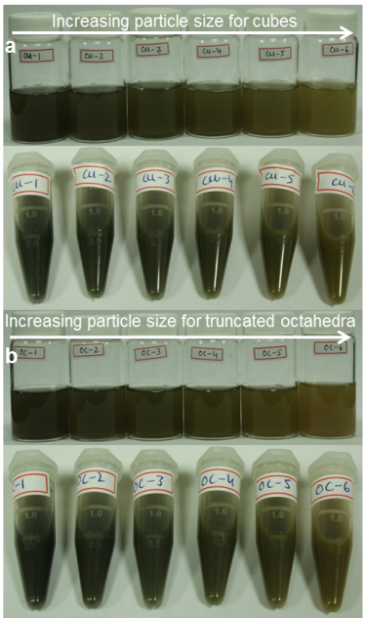

Fig. S6 Optical photographs of Pd–Cu_2O (a)cubes and (b) truncated octahedra with increasing particle size. The solution color changes from dark greenish to brown with increasing particle size. 29-nm Pd cubes were used.

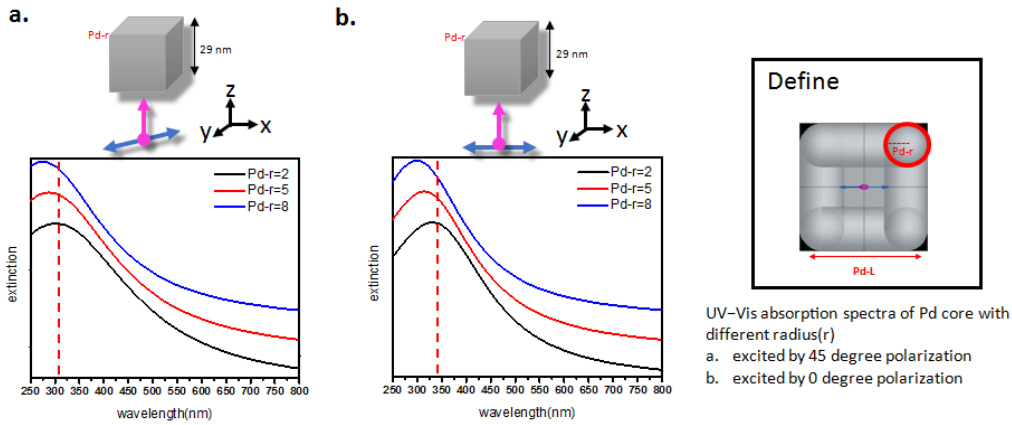

Fig. S7 Simulation spectra of the 29-nm cubic Pd cores. The dash line indicates the band positions if radius of the corner red circle was selected to be 2 nm.

Table S3 Amounts of reagents used in the synthesis of Pd–Cu_2O core–shell nanocubes and octahedra with shell thickness control using 40-nm Pd cubic cores.

Shape	Size (nm)	SDS (g)	Water (ml)	0.1 M $CuCl_2$ (ml)	Pd cubes (ml)	1 M NaOH (ml)	0.2 M $NH_2OH.HCl$ (ml)
Cube	76	0.087	9.230	0.070	0.300	0.250	0.150
	82		9.290		0.240		
	93		9.330		0.200		
	100		9.370		0.160		
	109		9.410		0.120		
	120		9.450		0.080		
Octahedron	102	0.087	8.390	0.100	0.300	0.360	0.850
	116		8.450		0.240		
	123		8.490		0.200		
	136		8.530		0.160		
	145		8.570		0.120		
	178		8.610		0.080		

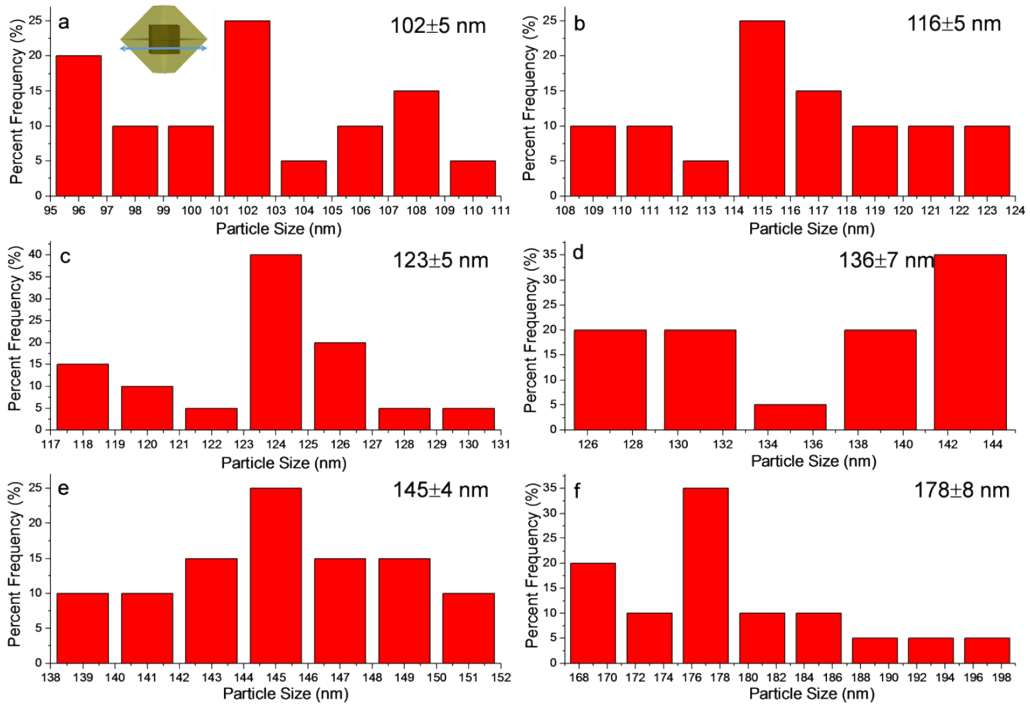

Fig. S8 Size distribution histograms of Pd–Cu_2O octahedra synthesized from 40-nm Pd cubes.

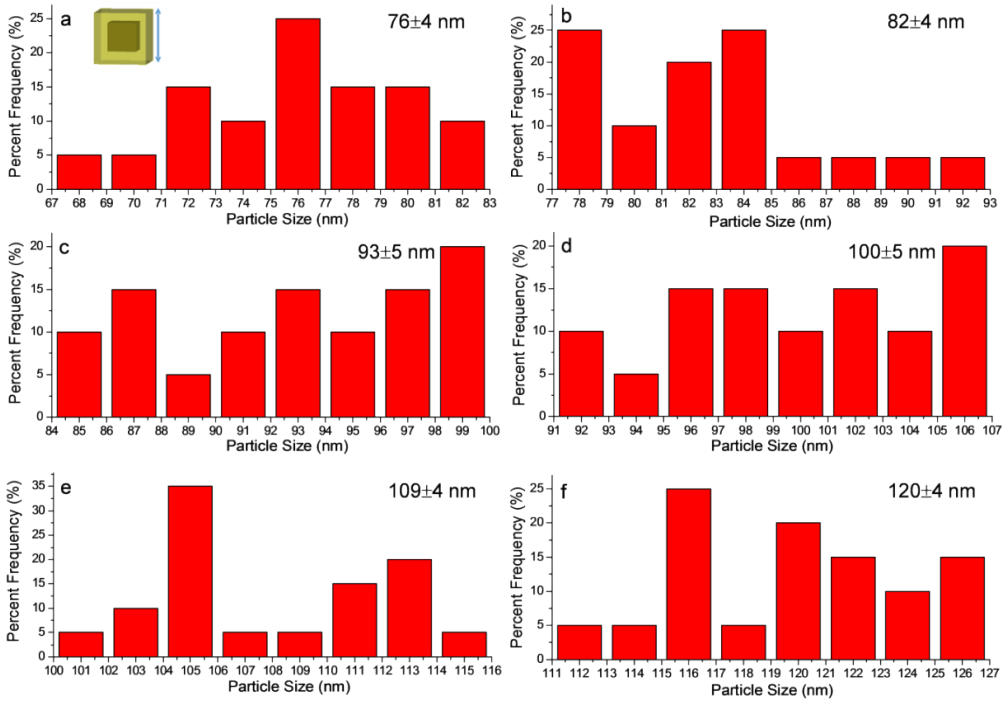

Fig. S9 Size distribution histograms of Pd–Cu_2O cubes synthesized from 40-nm Pd cubes.

Table S4 Average particle sizes, standard deviations, and coefficients of variation of the Pd–Cu_2O particles synthesized from 40-nm Pd cubes.

Shape	Pd cubic core used (ml)	Mean (nm)	Standard deviation (nm)	Coefficient of variation (%)
Cube	0.300	76	4	5
	0.240	82	4	4
	0.200	93	5	5
	0.160	100	5	5
	0.120	109	4	3
	0.080	120	4	3
Octahedron	0.300	102	5	4
	0.240	116	5	4
	0.200	123	5	4
	0.160	136	7	5
	0.120	145	4	2
	0.080	178	8	4

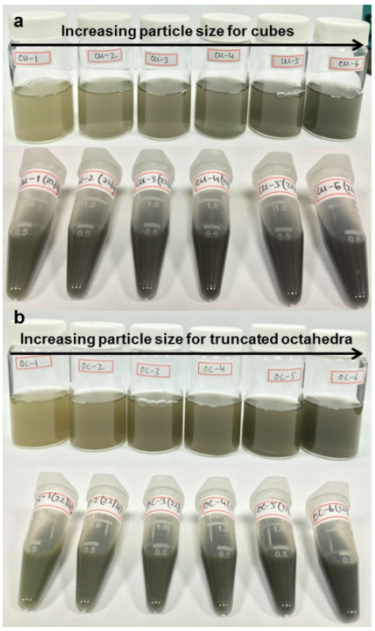

Fig. S10 Photographs of the (a) Pd–Cu_2O core–shell cubes and (b) truncated octahedra with different average particle sizes synthesized from 40-nm Pd cubes. The solution color changes from yellowish green to black with increasing particle size. Cubes appear darker than octahedra when particles size decreases.

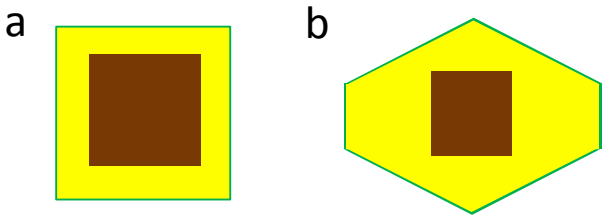

Fig. S11 Schematic drawings of (a) a Pd–Cu_2O cube and (b) a Pd–Cu_2O truncated octahedron highlighting the presence of a thin surface layer (shown in green color) having different degrees of band bending.

Numerical methods

We employed finite-difference time-domain method (FDTD solutions, Lumerical, Canada) to simulate the extinction spectra of our Pd–Cu_2O nanoparticles. Refractive indices of Pd and Cu_2O are obtained from literature data.[34] Refractive index of surrounding medium is set to be 1.36 in order to mimic the aqueous solution environment. Boundaries of the simulation area are set to be at least 2000 nm away from the outer surface of the shell such that spurious absorption of optical near fields is avoided. Uniform mesh size with discretization of $1 \times 1 \times 1$ nm^3 was used to cover the whole core–shell particles. To simulate the real structures, the edges and corners of the octahedral cores are rounded with cylinders or spheres with radius of 10 nm. About 3 femtosecond broadband plane wave source centered at 800 nm was

used as a source, and the polarization was aligned to the diagonal direction of the octahedral core. All particle dimensions are obtained from the SEM images.