Electronic Supplementary Information

Facile Synthesis of Au–Pd Core–Shell Nanocrystals with Systematic Shape Evolution and Tunable Size for Plasmonic Property Examination

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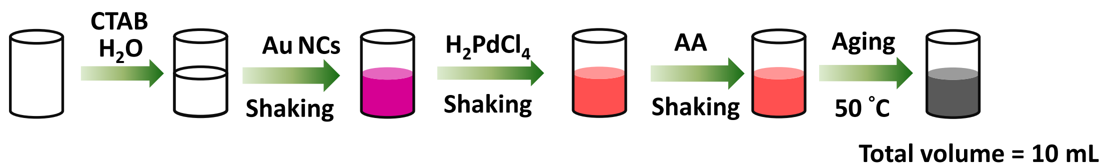
EXPERIMENTAL SECTION

Synthesis of Au Octahedra with Sizes of 35, 45, 74 and 92 nm. Octahedral gold nanocrytals were prepared following a hydrothermal synthesis method developed by our laboratory.[27] A total volume of 100 mL was prepared for each sample. First, 97, 97, 96, and 94.5 mL of deionized water were respectively used for preparing 35, 45, 74 and 92 nm gold octahedra. Next, 0.55 g of CTAB was mixed in a glass bottle. For the synthesis of gold octahedra with sizes of 35 and 45 nm, 2.5 mL of 0.01 M $HAuCl_4$ solution was added to the mixture. To make 74 and 92 nm gold octahedra, 3.5 and 5.0 mL of 0.01 M $HAuCl_4$ were respectively introduced. Finally, 0.5 mL of 0.1 M trisodium citrate was added. The glass bottle was sealed by a Teflon bolt with an O-ring and the bolt was wrapped with a polyimide tape to prevent the leakage of steam. The bottle was placed in an oven and the temperature was set at 110 °C. The reaction time was 12, 14, 18 and 19 hours for making 35, 45, 74 and 92 nm gold octahedra. After the reaction was finished, the glass bottle was removed from the oven and cooled to room temperature. To remove the residual CTAB, the solution was centrifuged at 6000 rpm for 10 min. The supernatant was removed and the precipitate was redispersed in deionized water for another cycle of centrifugation. The particles were finally dispersed in 5 mL of this solution.



Scheme S1 Schematic illustration of the procedure used to synthesize Au−Pd core−shell nanocrystals. The solution colors are also shown.

Table S1 Experimental conditions used for growing Au−Pd core−shell nanocrystals with various shapes and sizes. The size of octahedral gold cores is 45 nm.

Shape	**H_2O**	**CTAB**	**Au Octahedra (45 nm)**	**10 mM H_2PdCl_4**	**AA**	**Time**	**Size**
Cubes	8160µL	0.048 g	500 µL	1100 µL	0.1 M 240 µL	1 h	77 nm
	8910µL		500 µL	500µL	0.1 M 240 µL		53 nm
	8810µL		600 µL	500µL	0.1 M 240 µL		47 nm
Cuboctahedra	8780 µL	0.33 g	500 µL	500 µL	0.1 M 220 µL	2 h	56 nm
	9030 µL		500 µL	250 µL	0.1 M 220 µL		49 nm
	8830 µL		700 µL	250 µL	0.1 M 220 µL		46 nm
Truncated Octahedra	8500 µL	0.048 g	500 µL	700 µL	0.01 M 300 µL	2 h	54 nm
	8300 µL		700 µL	700 µL	0.01 M 300 µL		50 nm
	8100 µL		900 µL	700 µL	0.01 M 300 µL		47 nm
Octahedra	9000 µL	0.33 g	500 µL	300 µL	0.1 M 200 µL	2 h	71 nm
	8950 µL		500 µL	250 µL	0.1 M 200µL		60 nm

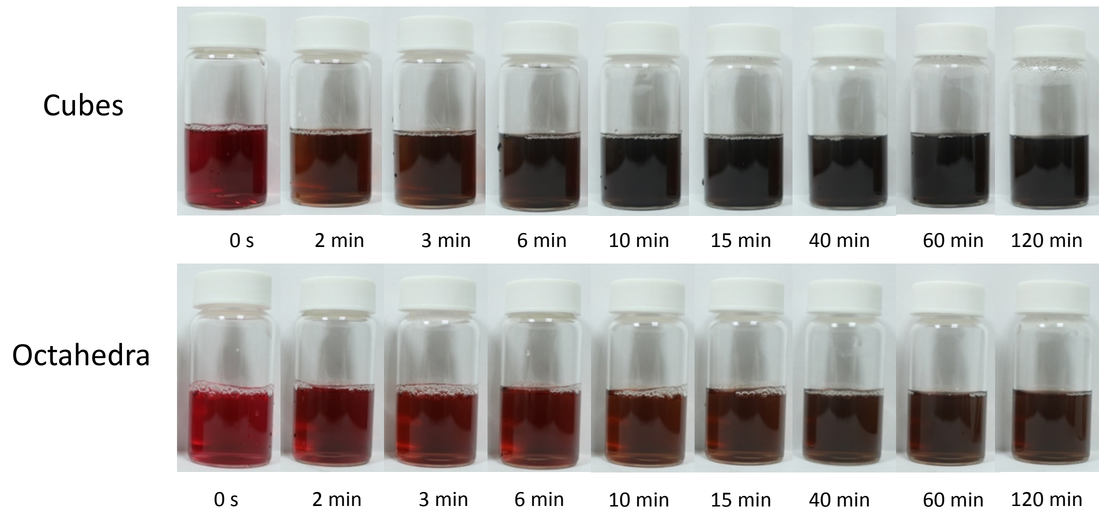


Fig. S1 Photographs showing the solution color evolution in the synthesis of Au–Pd core–shell cubes (47 nm) and octahedra (60 nm) using 45 nm octahedral gold cores. Evidently cubes become darker at a faster rate than octahedra with the formation of Pd shells. The solution for the formation of cubes appears somewhat darker than the solution for making octahedra at the beginning because more Au cores was added in the growth of Au–Pd cubes (see Table S1).

Table S2 A list of sizes of all synthesized Au–Pd core–shell nanocrystals. Average particle sizes and their size distributions are provided.

Sample	Particle size	Standard deviation
Cubes (Au core 35 nm)	50 ± 2 nm	4 %
	37 ± 2 nm	5.4 %
	36 ± 2 nm	5.6 %
Cuboctahedra (Au core 35 nm)	51 ± 2 nm	3.9 %
	46 ± 2 nm	4.3 %
	45 ± 2 nm	4.4 %
Trucated Octahedra (Au core 35 nm)	58 ± 3 nm	5.2 %
	49 ± 3 nm	6.1 %
Octahedra (Au core 35 nm)	54 ± 3 nm	5.6 %
	51 ± 4 nm	7.8 %
Cubes (Au core 45 nm)	77 ± 3 nm	3.9 %
	53 ± 3 nm	5.7 %
	47 ± 3 nm	6.4 %
Cuboctahedra (Au core 45 nm)	56 ± 3 nm	5.4 %
	49 ± 2 nm	4.1 %
	46 ± 2 nm	4.3 %
Trucated Octahedra (Au core 45 nm)	54 ± 2 nm	3.7 %
	50 ± 2 nm	4.0 %
	47 ± 2 nm	4.3 %
Octahedra (Au core 45 nm)	71 ± 4 nm	5.6 %
	60 ± 3 nm	5.0 %
Cuboctahedra (Au core 74 nm)	80 ± 3 nm	3.8 %
	77 ± 2 nm	2.6 %
	75 ± 2 nm	2.7 %
Trucated Octahedra (Au core 74 nm)	79 ± 2 nm	2.5 %
	77 ± 2 nm	2.6 %
	75 ± 3 nm	2.7 %
Octahedra (Au core 74 nm)	90 ± 3 nm	3.3 %
	87 ± 2 nm	2.0 %
Octahedra (Au core 92 nm)	98 ± 4 nm	4.3 %

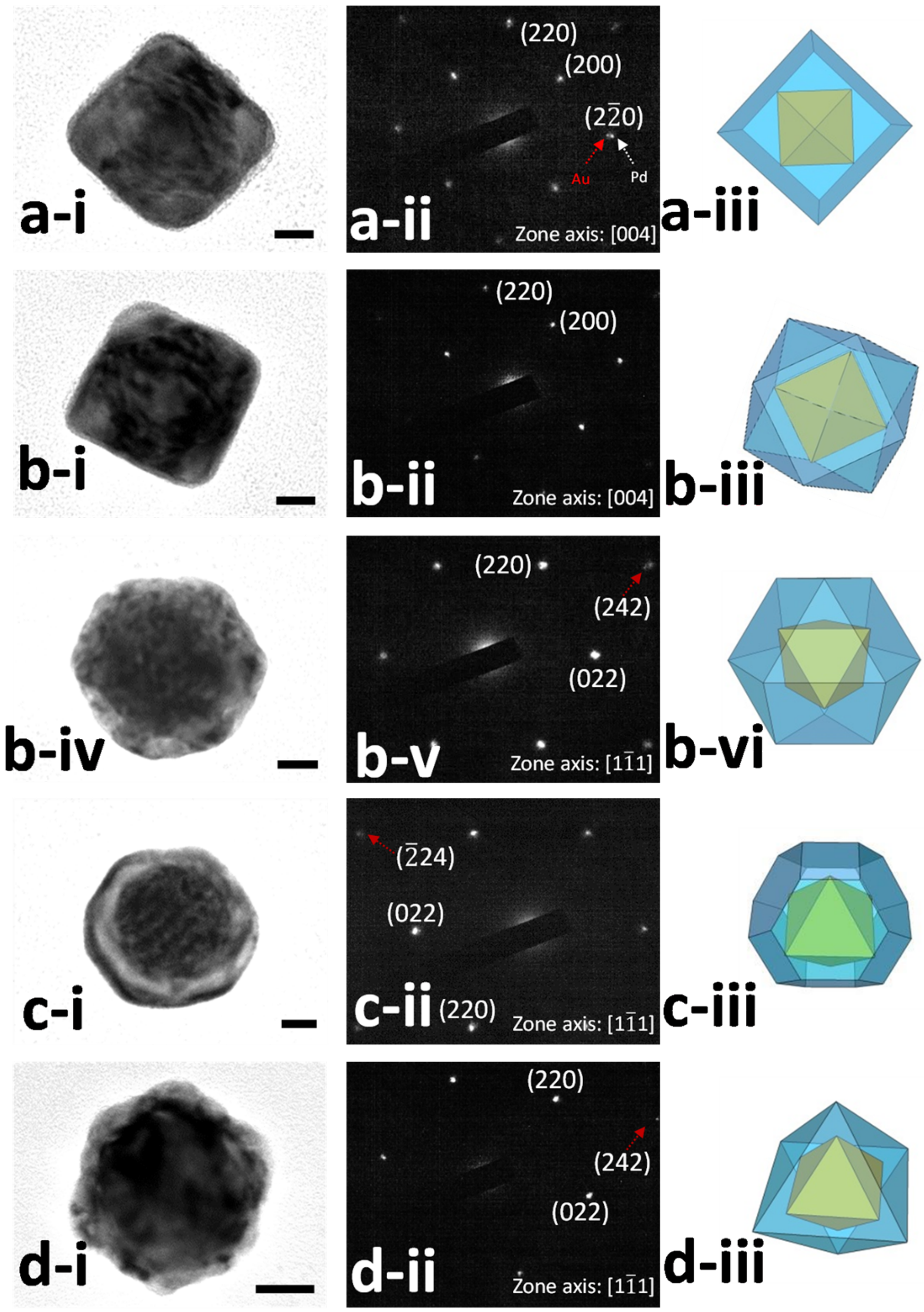


Fig. S2 TEM images, corresponding SAED patterns, and representative drawings of a single Au–Pd core–shell (a-i–a-iii) cube (size = 47 nm), (b-i–b-iii) cuboctahedron (size = 46 nm) viewed along the [100] direction, (b-iv–b-vi) cuboctahedron viewed along the [111] direction, (c-i–c-iii) truncated octahedron (size = 47 nm), and (d-i–d-iii) octahedron (size = 60 nm). Diffraction spots of Au are clearly visible in some SAED patterns. The octahedral gold cores have an average size of 45 nm. All scale bars are equal to 10 nm.

Table S3 Experimental conditions used for growing Au−Pd core−shell nanocrystals with various shapes and sizes. The size of octahedral gold cores is 35 nm.

Shape	H_2O	CTAB	Au Octahedra (35 nm)	10 mM H_2PdCl_4	AA	Time	Size
Cubes	8560μL	0.048 g	500 μL	700 μL	0.1 M 240 μL	1 h	50 nm
	9090 μL		500 μL	250 μL	0.1 M 160 μL		37 nm
	9140μL		500 μL	200 μL	0.1 M 160 μL		36 nm
Cuboctahedra	8580 μL	0.33 g	500 μL	700 μL	0.1 M 220 μL	2 h	51 nm
	8200 μL		500 μL	700 μL	0.01 M 600 μL		46 nm
	9000 μL		500 μL	200 μL	0.1 M 220 μL		43 nm
Truncated Octahedra	8460 μL	0.048 g	500 μL	700 μL	0.01 M 340 μL	2 h	58 nm
	9070 μL	0.055 g	500 μL	300 μL	0.01 M 130 μL		49 nm
Octahedra	8600 μL	0.048 g	500 μL	700 μL	0.01 M 200 μL	2 h	54 nm
	8900 μL	0.33 g	500 μL	300 μL	0.1 M 300 μL		51 nm

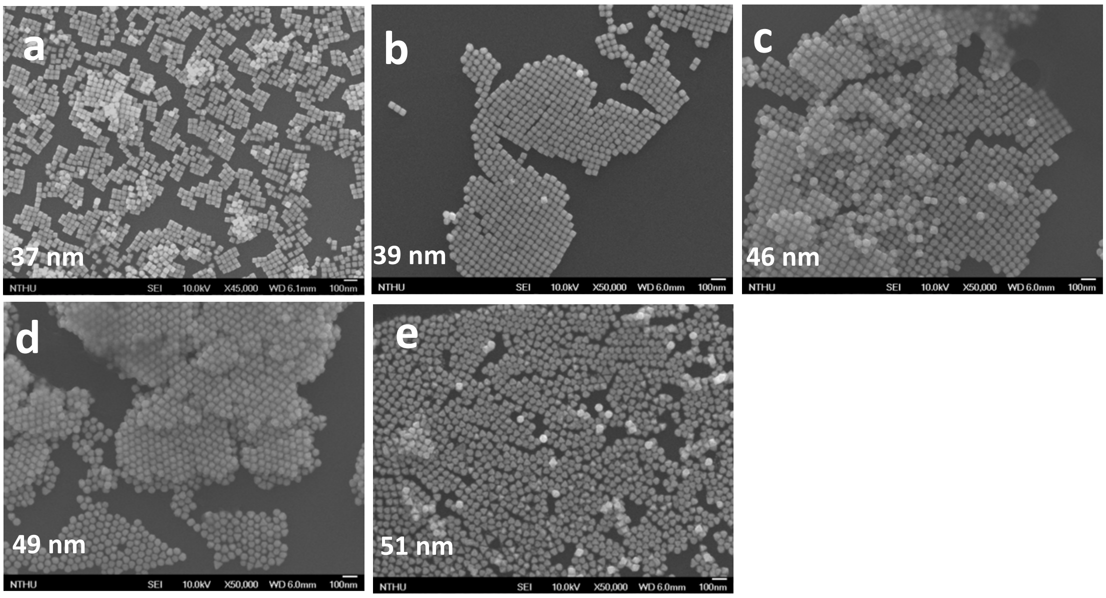


Fig. S3 Large-area SEM images of Au−Pd core−shell nanocrystals having 35 nm octahedral gold cores. These are the same samples as those shown in Fig. 4 (panels a-ii to e-ii).

Table S4 Experimental conditions used for growing Au−Pd core−shell nanocrystals with various shapes and sizes. The size of octahedral gold cores is 74 nm. Condition used to make Au−Pd octahedra from 92 nm octahedral Au cores is also listed.

Shape	H_2O	CTAB	Au	10 mM	AA	Time	Size

			Octahedra (74 nm)	H_2PdCl_4			
Trucated Cubes	8300 μL	0.33 g	500 μL	400 μL	0.1 M 800 μL	1 h	75 nm
Cuboctahedra	8500 μL	0.33 g	500 μL	600 μL	0.1 M 400 μL	1 h	80 nm
	8600 μL		500 μL	500 μL	0.1 M 400 μL		77 nm
	8700 μL		500 μL	400 μL	0.1 M 400 μL		75 nm
Truncated Octahedra	8650 μL	0.048 g	500 μL	250 μL	0.01 M 600 μL	1 h	79 nm
	8550 μL		600 μL	250 μL	0.01 M 600 μL		77 nm
	8530 μL		800 μL	250 μL	0.01 M 600 μL		75 nm
Octahedra	9150 μL	0.33 g	500 μL	250 μL	0.1 M 100 μL	2 h	90 nm
	9200 μL	0.33 g	500 μL	200 μL	0.1 M 100 μL	2 h	87 nm
Octahedra	8300 μL	0.33 g	500 μL (92 nm core)	400 μL	0.01 M 800 μL	2 h	98 nm

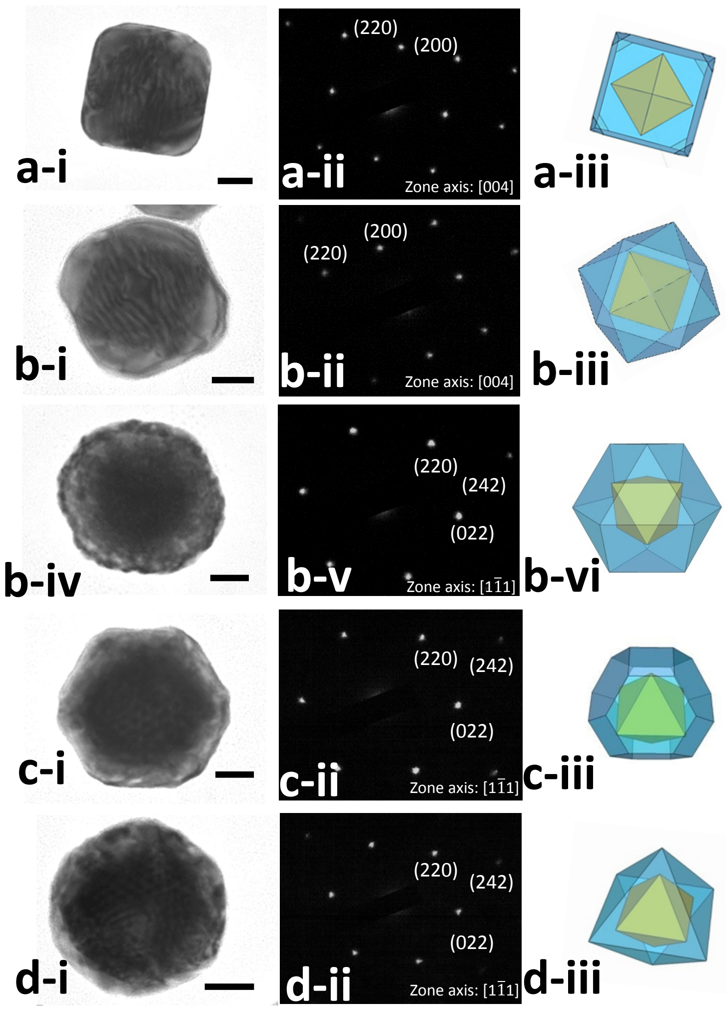


Fig. S3 TEM images, corresponding SAED patterns, and representative drawings of a single Au–Pd core–shell (a-i–a-iii) truncated cube, (b-i–b-iii) cuboctahedron viewed along the [100] direction, (b-iv–b-vi) cuboctahedron viewed along the [111] direction, (c-i–c-iii) truncated octahedron, and (d-i–d-iii) octahedron. The recorded SAED patterns match the orientations of the viewing particles. Triangular diffraction spots can be seen in some SAED patterns, possibly due to the core–shell nature of these nanocrystals causing double diffractions and the particle geometry. The octahedral gold cores have an average size of 74 nm. All scale bars are equal to 20 nm.

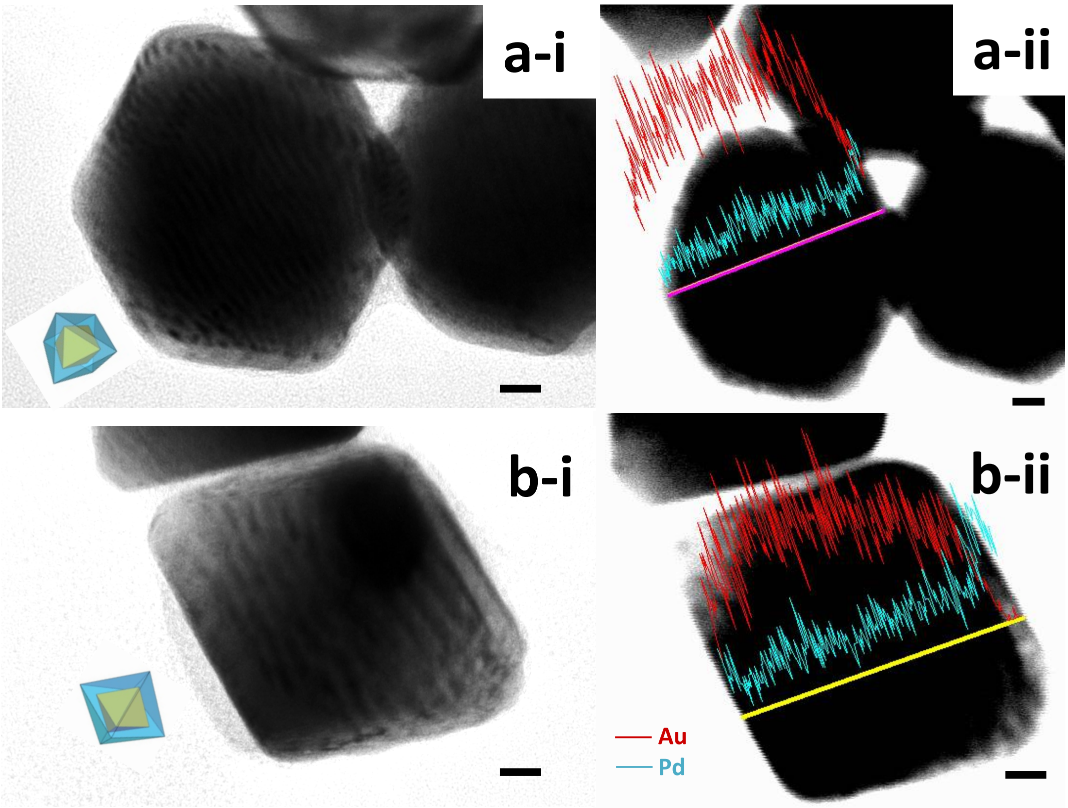


Fig. S4 (a-i, b-i)TEM images, (a-ii, b-ii) STEM images, and (a-i, b-ii) EDS line-scan profiles of Au–Pd core–shell octahedron (size = 98 nm, Au core = 92 nm) viewed along the (a-i–a-ii) [111] direction and (b-i–b-ii) [110] direction. All scale bars are equal to 10 nm. Pd intensity increases appreciably at the edges of the particle, while Au intensity drops rapidly at the edges, proving the core–shell nature of these nanocrystals.

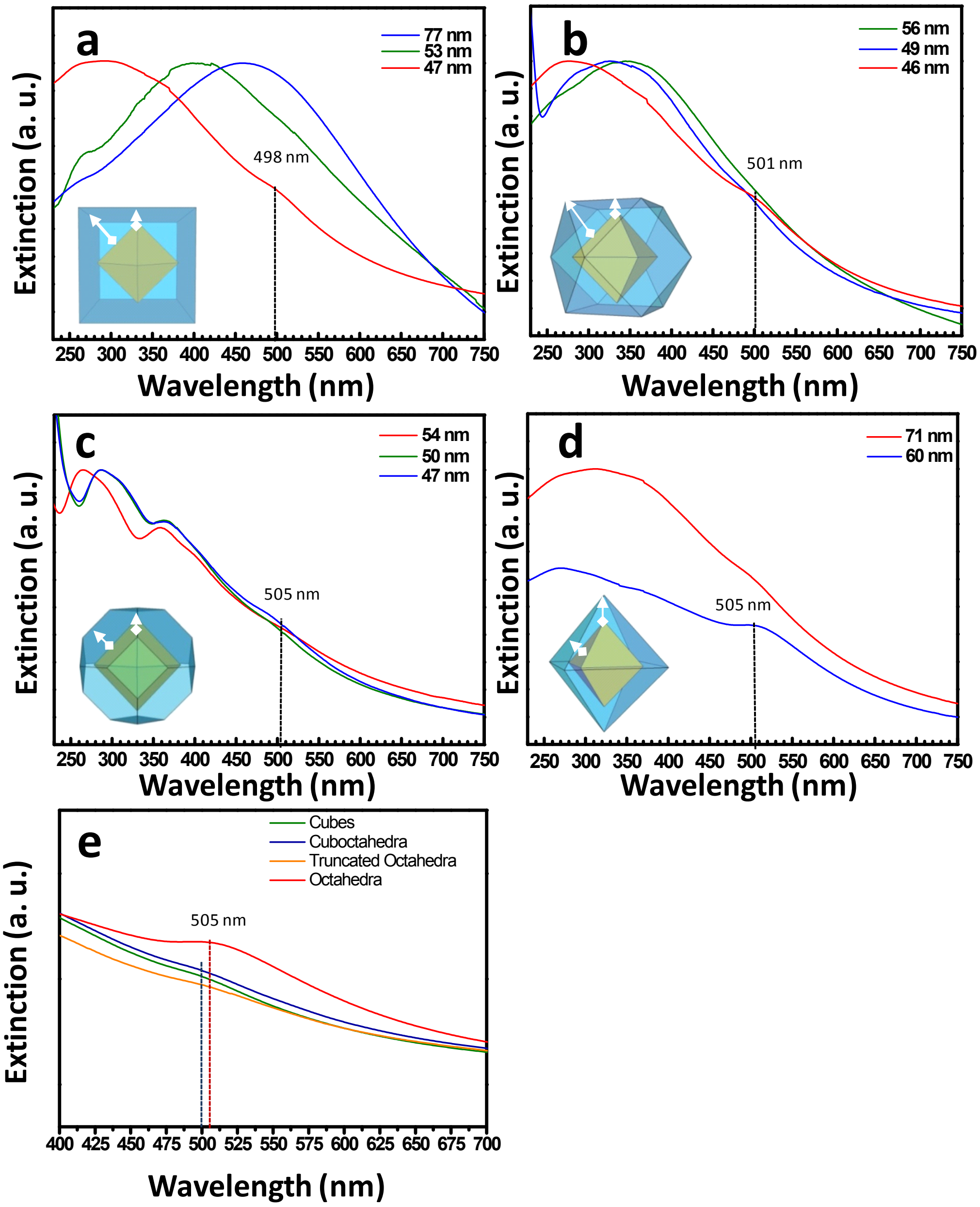
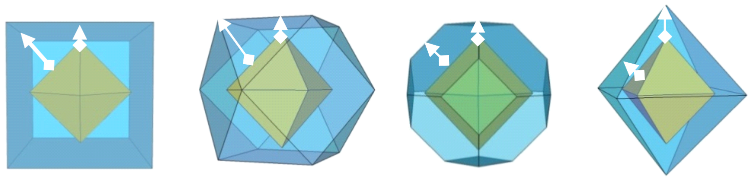


Fig. S5 UV−vis absorption spectra of the Au–Pd core−shell (a) cubes, (b) cuboctahedra, (c) truncated octahedra, and (d) octahedra of different sizes. The Au core size is 45 nm. (e) Combined UV−vis absorption spectra of Au–Pd nanocrystals with thinnest shell thicknesses.

Table S5 A list of thinnest and thickest Pd shell thicknesses for the smallest Au–Pd core–shell polyhedra of various shapes. Size and edge length of the octahedral Au cores used are 45 and 32.1 nm, respectively. Their absorption band positions are also provided.



Shape	Size	Thinnest Shell thickness	Thickest Shell thickness	Au LSPR
Cubes	47 nm	1 nm	27.6 nm	498 nm
Cuboctahedra	46 nm	0.5 nm	16.5 nm	501 nm
Truncated Octahedra	47 nm	1 nm	8.4 nm	505 nm
Octahedra	60 nm	5.5 nm	7.5 nm	505 nm

Table S6 A list of thinnest and thickest Pd shell thicknesses for all the Au–Pd core–shell polyhedra synthesized using 74 nm octahedral Au cores with an edge length of 52.9 nm. The shell thicknesses of 98 nm Au–Pd octahedra with an edge length of 65.3 nm are also listed.

Shape	Size	Thinnest Shell thickness	Thickest Shell thickness
Cuboctahedra	80 nm	3 nm	30.1 nm
	77 nm	1.5 nm	28 nm
	75 nm	0.5 nm	26.6 nm
Truncated Octahedra	79nm	2.5 nm	10.6 nm
	77 nm	1.5 nm	9.6 nm
	75 nm	0.5 nm	8.6 nm
Octahedra	90 nm	5.5 nm	8 nm
	87 nm	5.3 nm	6.5 nm
Octahedra (92 nm core)	98 nm	1.7 nm	3 nm