

Supporting Information for

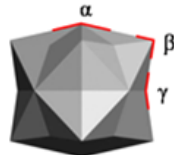
**One-Pot Synthesis of Au@Pd Core-Shell Nanocrystals with Multiple High-
and Low-Index Facets and Their High Electrocatalytic Performance**

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(a)

Projection directions				Equations for the relations between projection angles and Miller indices	
$\langle 1\ 0\ 0 \rangle$	$\langle 1\ 1\ 1 \rangle$	$\langle 1\ 1\ 0 \rangle$			
			 $\alpha = 2\arctan\left[\frac{\sqrt{2}h}{k-l}\right]$ $\beta = 90 - \left[\frac{\alpha}{2}\right] + \left[\frac{\gamma}{2}\right]$ $\gamma = 2\arctan\left[\frac{h+k}{\sqrt{2}l}\right]$		
Miller index	Calculated projection angles				
$\{hkl\}$	α	β	γ		
$\{3\ 2\ 1\}$	153.48°	87.41°	148.41°		
$\{4\ 2\ 1\}$	159.95°	86.76°	153.47°		
$\{5\ 3\ 2\}$	163.90°	78.58°	141.06°		
$\{12\ 5\ 3\}$	166.56°	82.71°	151.71°		
$\{13\ 6\ 2\}$	155.45°	93.81°	163.07°		

(b)

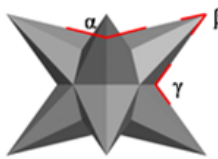
Projection directions				Equations for the relations between projection angles and Miller indices	
$\langle 1\ 0\ 0 \rangle$	$\langle 1\ 1\ 1 \rangle$	$\langle 1\ 1\ 0 \rangle$			
			 $\alpha = 2\arctan\left[\frac{\sqrt{2}h}{k-l}\right]$ $\beta = \left[\frac{\alpha}{2}\right] - \left[90 - \left[\frac{\gamma}{2}\right]\right]$ $\gamma = 2\arctan\left[\frac{h-l}{\sqrt{2}k}\right]$		
Miller index	Calculated projection angles				
$\{hkl\}$	α	β	γ		
$\{3\ 2\ 1\}$	153.48°	41.47°	109.47°		
$\{4\ 2\ 1\}$	159.95°	54.74°	121.01°		
$\{5\ 3\ 2\}$	163.90°	50.73°	117.56°		
$\{12\ 5\ 3\}$	166.56°	58.04°	129.52°		
$\{13\ 6\ 2\}$	155.45°	40.08°	104.71°		

Table S1. Geometric models, corresponding Miller indices, relations between the projection angles and Miller indices, and calculated projection angles of various (a) common HOH and (b) elongated HOH structures.

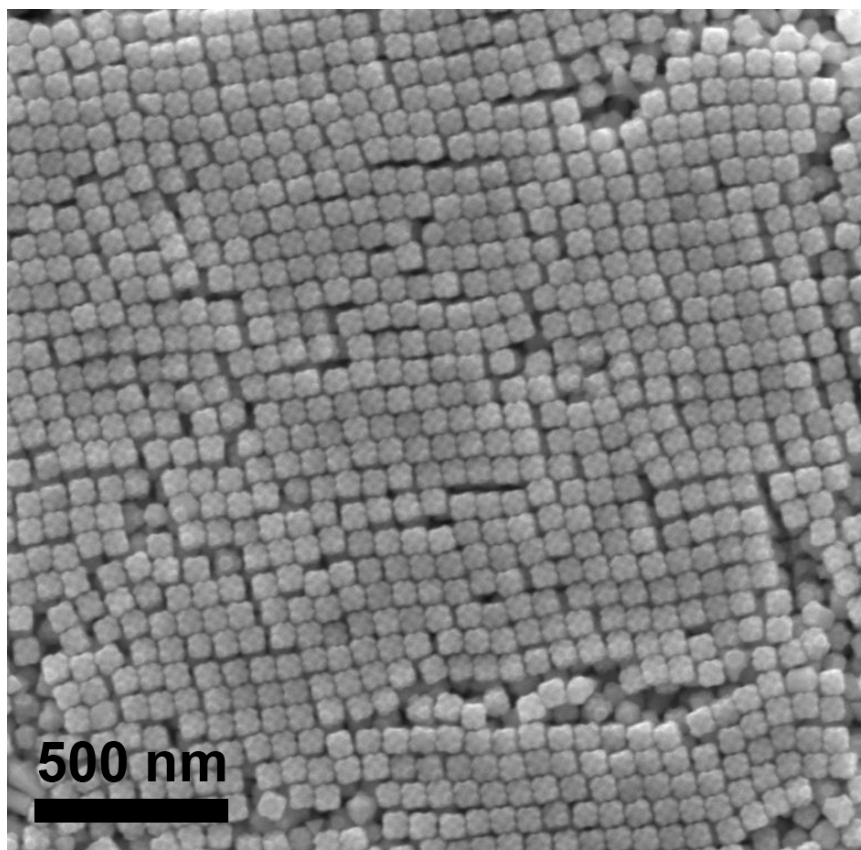


Fig. S1. Low-magnification SEM image of the THOH Au@Pd NCs.

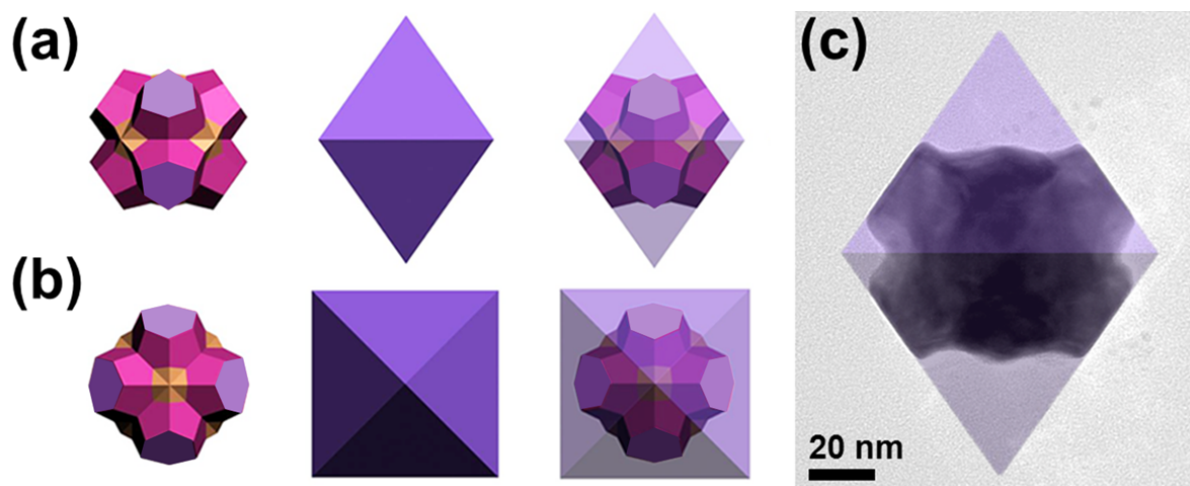


Fig. S2. Geometric models of typical THOH and octahedral NCs and their overlap viewed along the (a) $\langle 110 \rangle$ and (b) $\langle 100 \rangle$ directions. (c) Geometric model of octahedral NC with $\{111\}$ facets overlaid on the TEM image of a single THOH NC with the same orientation.

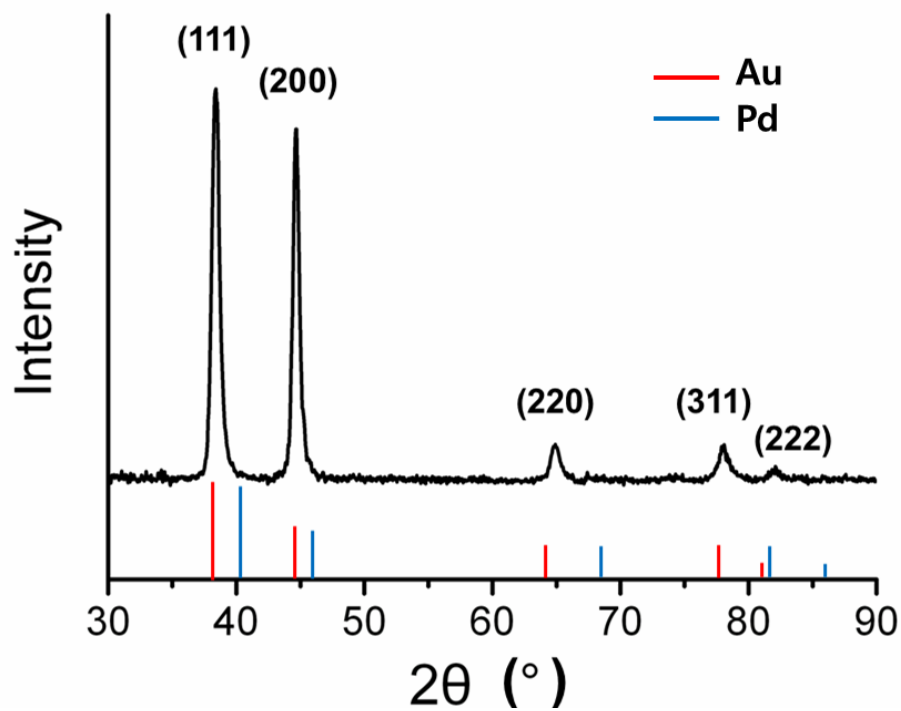


Fig. S3. XRD pattern of the THOH Au@Pd NCs. The positions and intensities of pure Au and Pd references were taken from the JCPDS database.

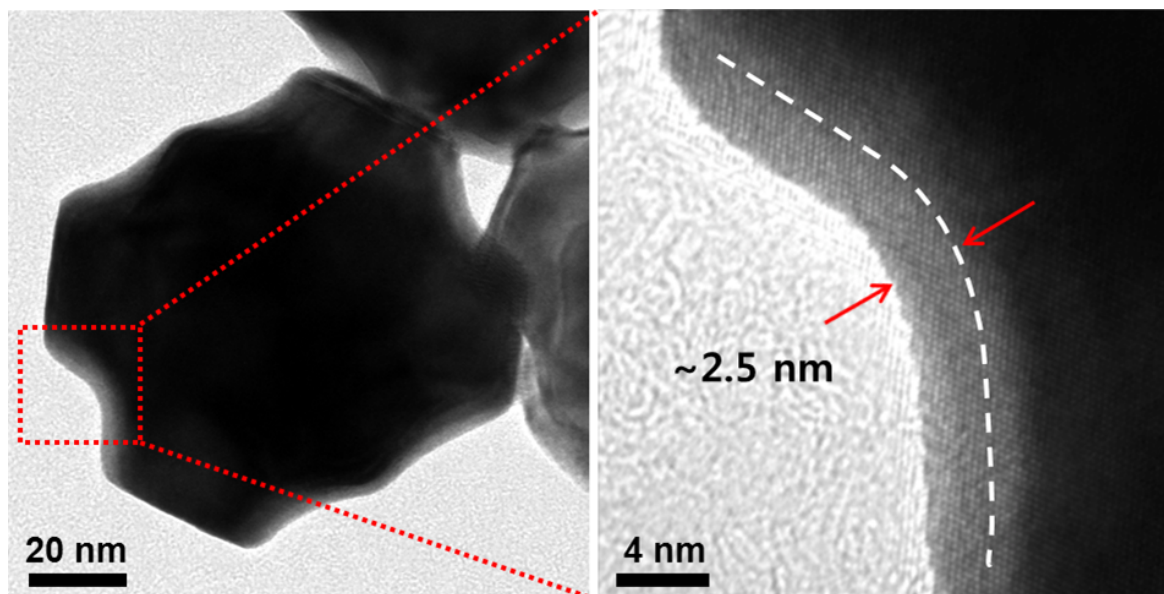


Fig. S4. High-resolution TEM (HRTEM) image of the THOH Au@Pd NC. Although the Pd shell thickness could not be clearly determined from the HRTEM image due to the unclear boundary between Au core and Pd shell, it should be in the range of 2-3 nm. The average Pd shell thickness could be calculated from the structural model and the Au:Pd atomic ratio of the prepared NCs. On the basis of the ICP-AES-determined Au:Pd atomic ratio of the THOH Au@Pd NCs (79.4:20.6) and the densities of Au and Pd metals (Au: 19.3 g cm⁻³, Pd: 12.02 g cm⁻³), the Au core:Pd shell volume ratio of the THOH Au@Pd NCs was calculated to be 81.6:18.4. By using the corresponding structural model, the average thickness of the Pd shell of the THOH Au@Pd NCs was then estimated to be 2.5 nm. This was consistent with the result of the HRTEM measurements. On the other hand, the Pd shell of the {321}- and {111}-faceted surfaces of NCs should be thicker than that of the {13 6 2}-faceted surfaces because the deposition of the reduced metal precursors onto the formed HOH Au cores occurred dominantly on the surface of the convex hexagonal pyramids of the cores with a preferential growth direction of <431> due to their high surface energy (see Fig. 5c).

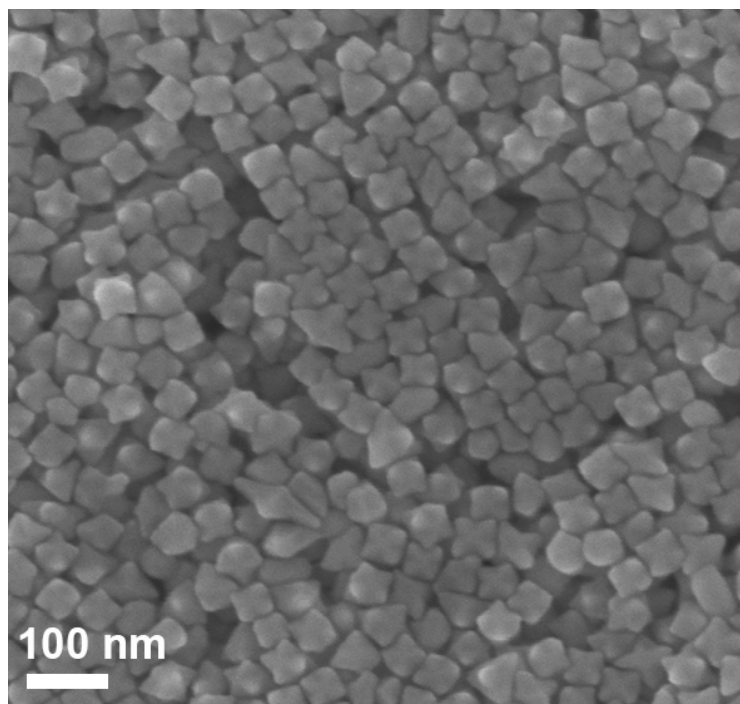


Fig. S5. SEM image of HOH NCs obtained after 3 min of reaction.

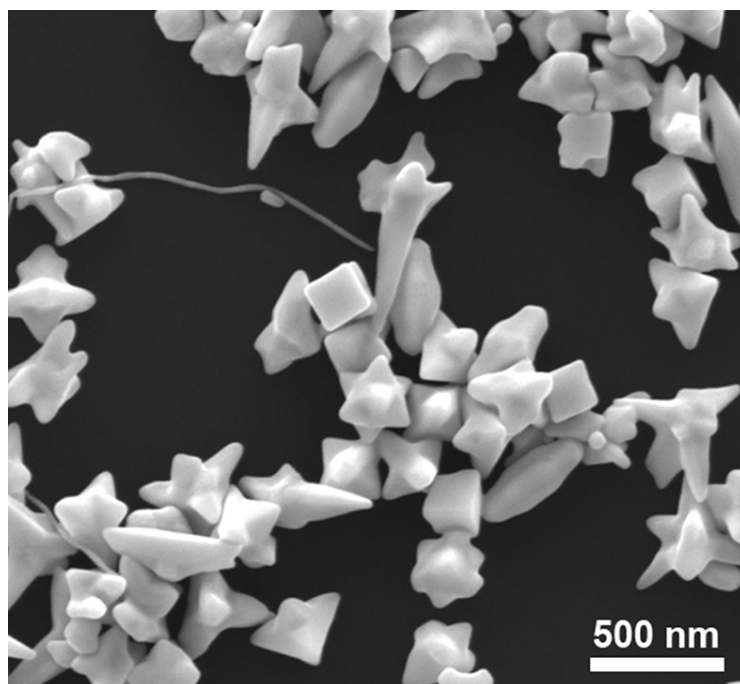


Fig. S6. SEM image of NCs prepared in the absence of a Pd precursor.

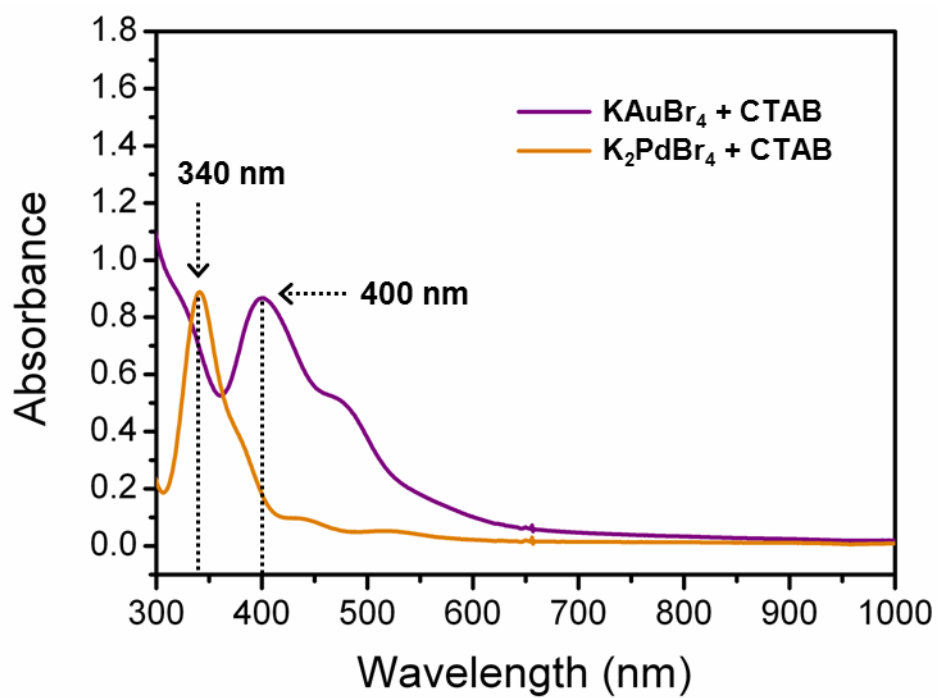


Fig. S7. UV-vis absorption spectra of the aqueous solutions of metal precursors in the presence of CTAB.

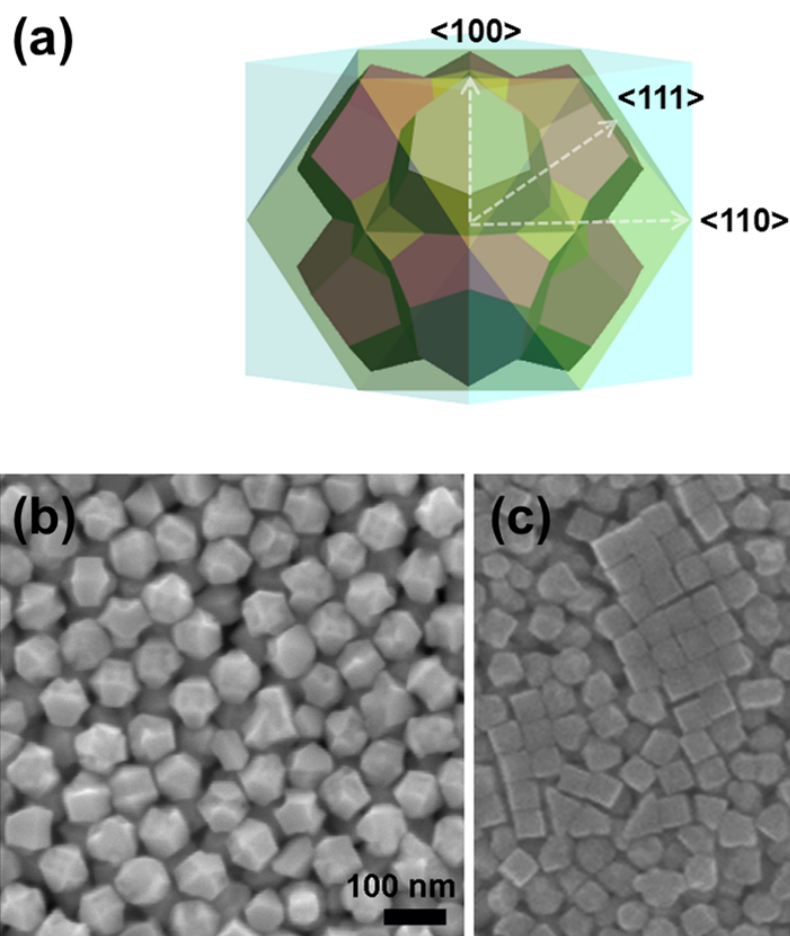


Fig. S8. (a) Overlay of three geometric models for cuboctahedral, cubic, and THOH NCs. SEM images of NCs prepared with the (b) 3:2 and (c) 2:3 molar ratios of $\text{KAuBr}_4/\text{K}_2\text{PdBr}_4$.

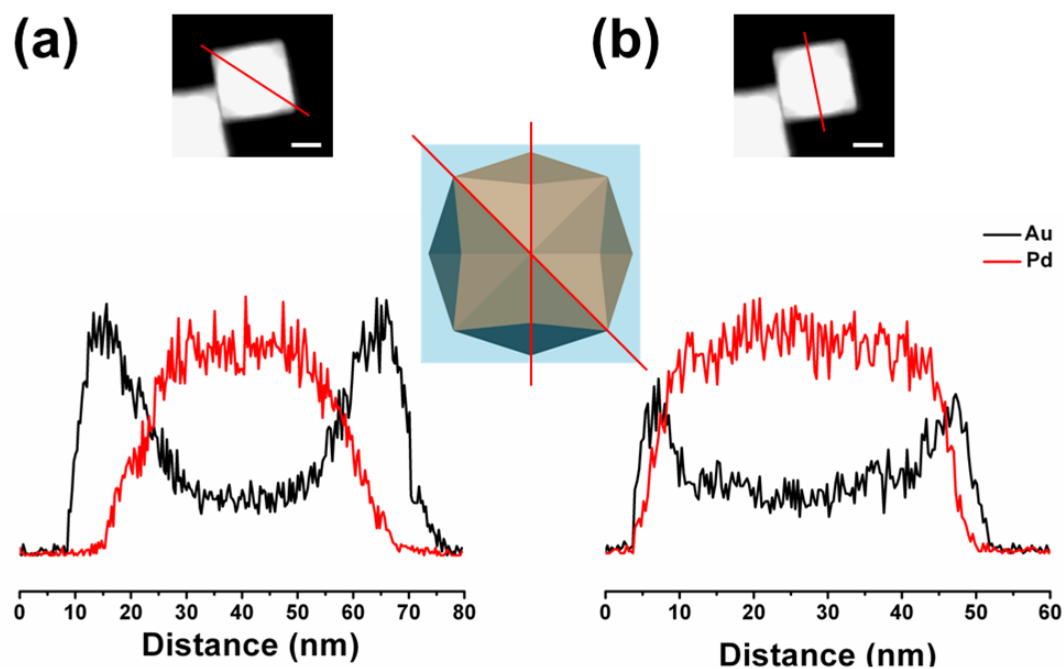


Fig. S9. HAADF-STEM-EDS cross-sectional compositional line profiles of a cube-like Au@Pd NC, which was obtained using the precursor mixture with the Au:Pd molar ratio of 2:3, along different directions, which is denoted in the geometric model of cubic NC grown from HOH NC. HAADF-STEM image of a cube-like Au@Pd NC is shown in each inset. Scale bars indicate 20 nm.

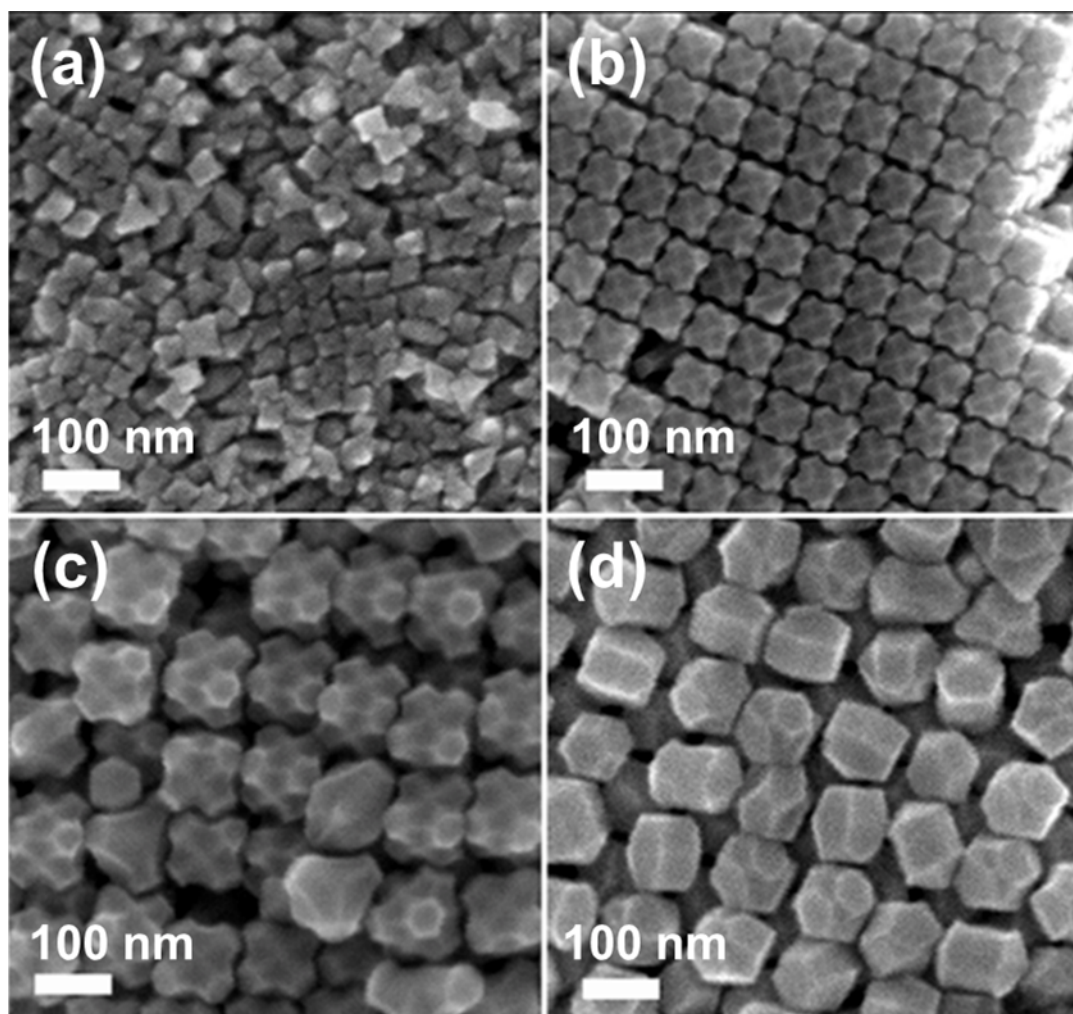


Fig. S10. SEM images of NCs prepared by using CTAC (30 mM, 5 mL) as a surfactant instead of CTAB in the presence of different amounts of KBr. A 0.2 mL of KBr solution with different concentrations was added to the reaction solution: (a) 0.25, (b) 0.50, (c) 0.75, and (d) 1.00 M. The amount of Br⁻ ions in the case of (c) was identical to that used in the original experiment.

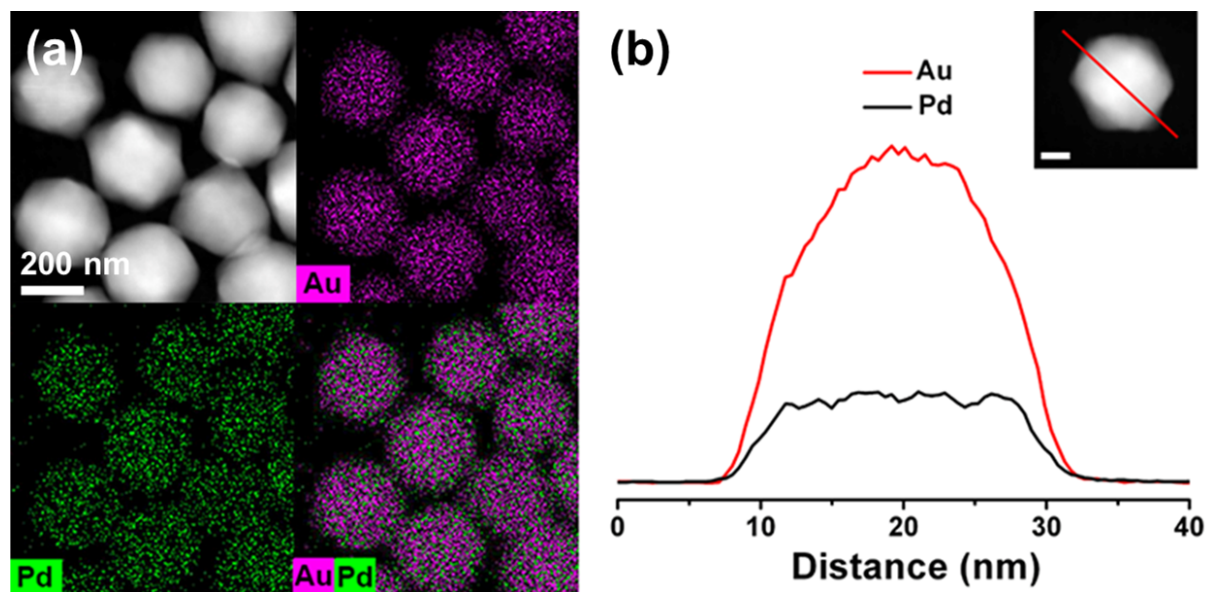


Fig. S11. (a) HAADF-STEM-EDS elemental mapping images and (b) cross-sectional compositional line profiles of NCs prepared by using $\text{AuCl}_4^-/\text{PdCl}_4^{2-}$ mixture and CTAC as metal precursors and surfactant, respectively. Scale bar in the inset of (b) indicates 10 nm.

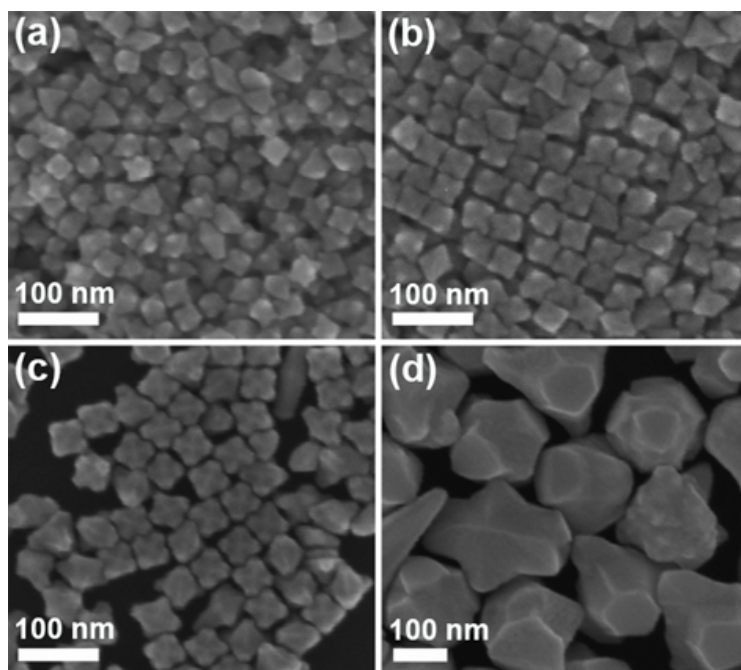


Fig. S12. SEM images of NCs prepared with different concentrations of AA: (a) 300, (b) 200, (c) 100, and (d) 20 mM. The concentration of NaOH was adjusted to the same value with that of AA for each case. 50 mM of AA was used in the standard synthesis.

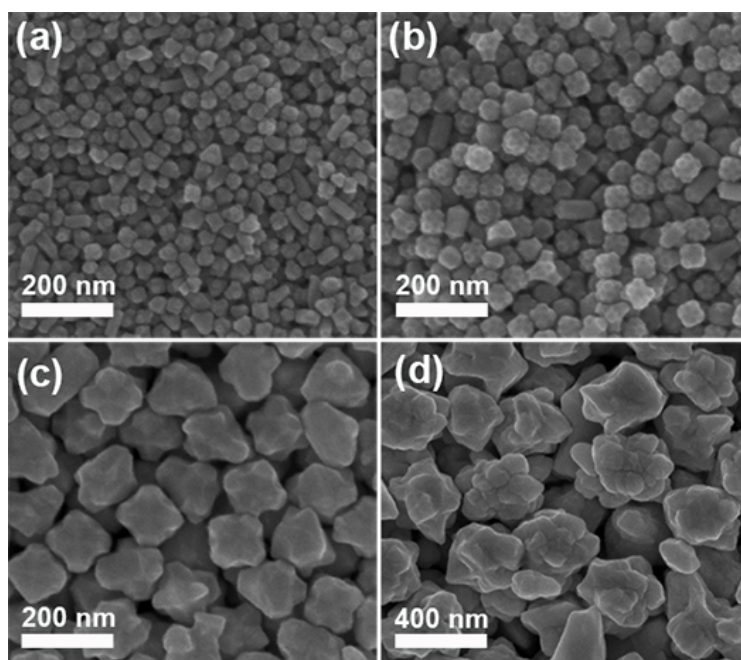


Fig. S13. SEM images of NCs prepared with different concentrations of CTAB: (a) 10, (b) 20, (c) 50, and (d) 100 mM. 30 mM of CTAB was used in the standard synthesis.

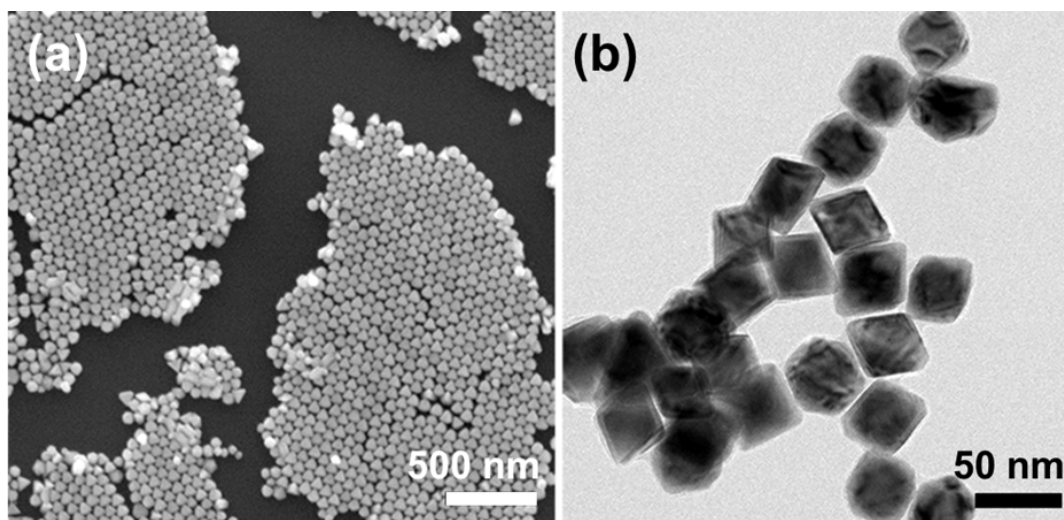


Fig. S14. (a) SEM and (b) TEM images of the octahedral Au@Pd NCs.

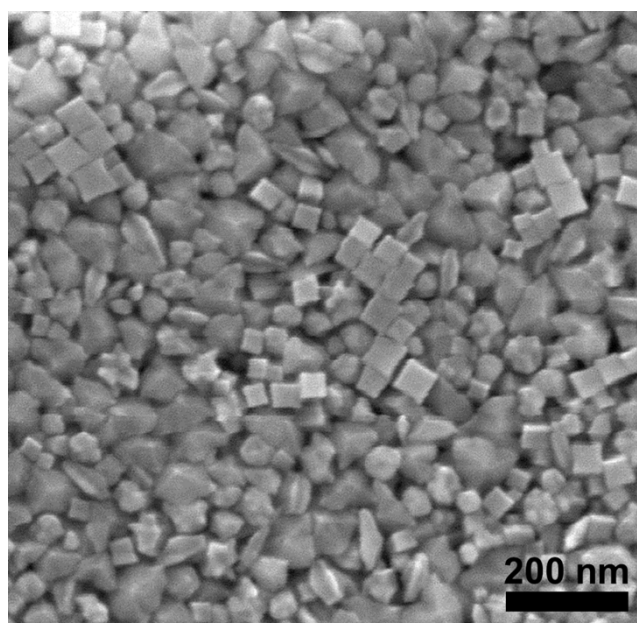


Fig. S15. SEM image of Pd NCs prepared in the absence of an Au precursor under same experimental conditions with those employed in the preparation of the THOH Au@Pd NCs.

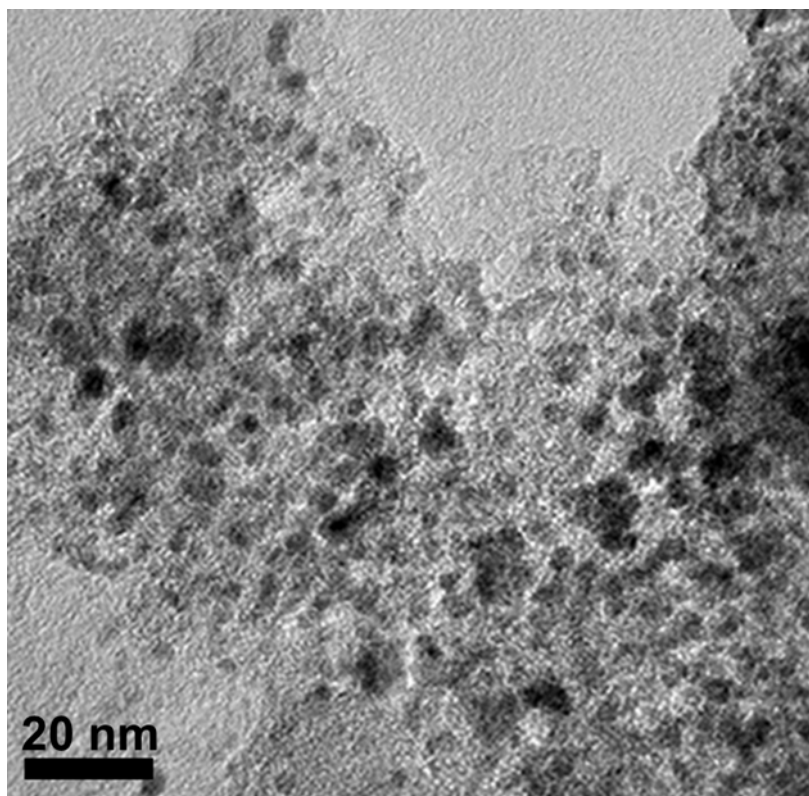


Fig. S16. TEM image of the commercial Pd/C catalyst.

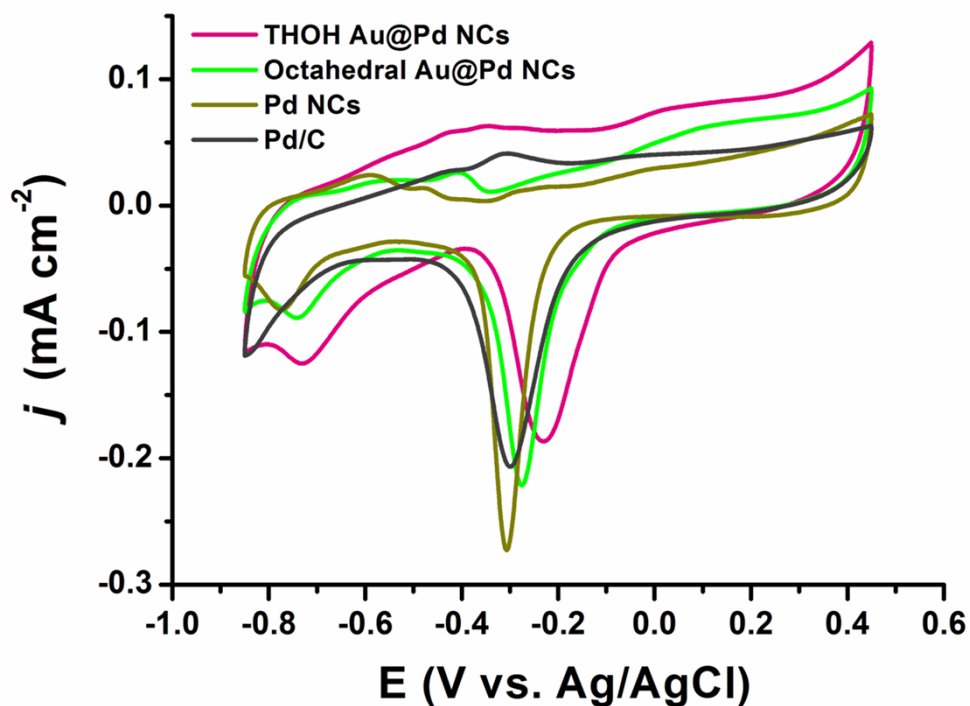


Fig. S17. CVs of the THOH Au@Pd NCs, octahedral Au@Pd NCs, Pd NCs, and commercial Pd/C catalyst in 0.1 M KOH. Scan rate = 50 mV s⁻¹. Current values were normalized with respect to the ECSA. The ECSA was estimated as $ECSA = Q_o/q_o$, where Q_o is the surface charge obtained from the area under the CV trace for the reduction of Pd oxide, and q_o the charge required for desorption of monolayer of oxygen on the Pd surface (424 $\mu\text{C cm}^{-2}$, ref.: Woods, R. In *Electroanalytical Chemistry: A Series of Advances (vol.9)*; Bard, A. J., Ed.; Marcel Dekker: New York, 1974; pp 1-162).

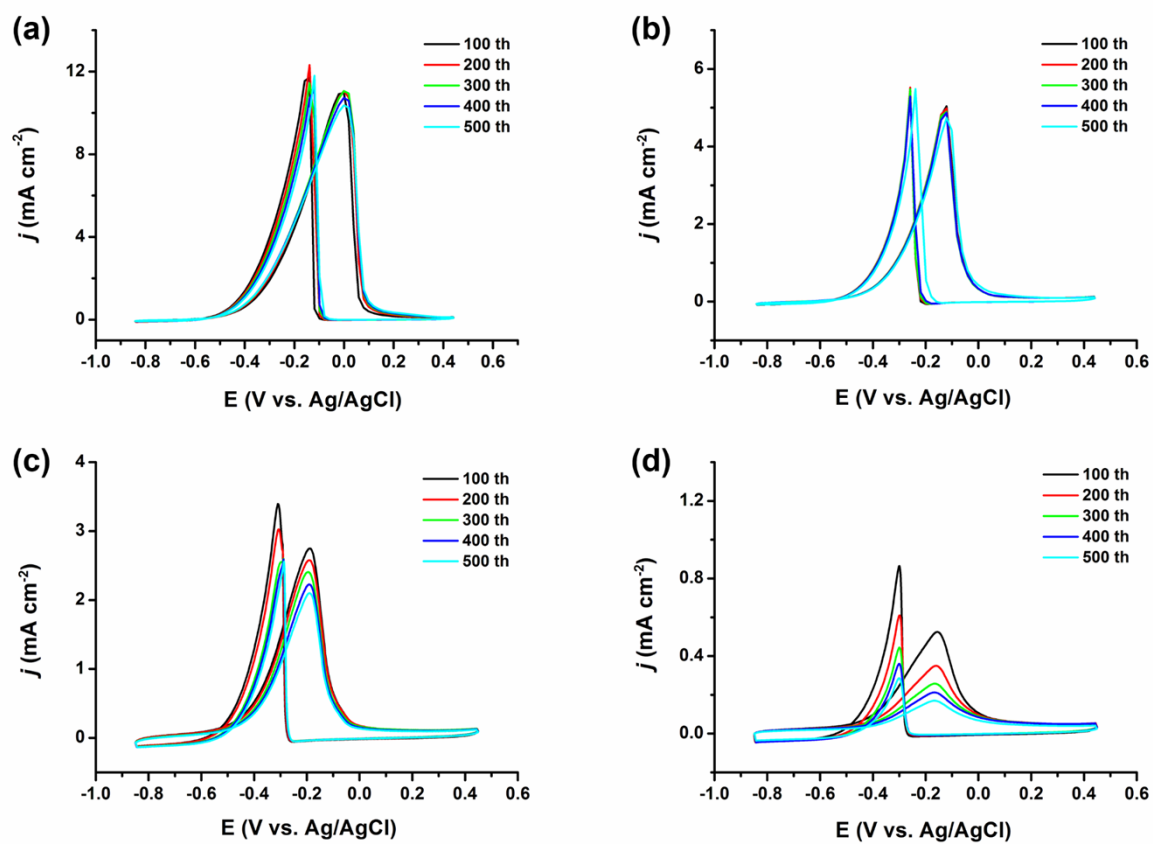


Fig. S18. CVs of ADT for the (a) THOH Au@Pd NCs, (b) octahedral Au@Pd NCs, (c) Pd NCs, and (d) commercial Pd/C catalyst in 0.1 M KOH + 0.5 M ethanol. Scan rate = 50 mV s⁻¹. Current values were normalized with respect to the ECSA.

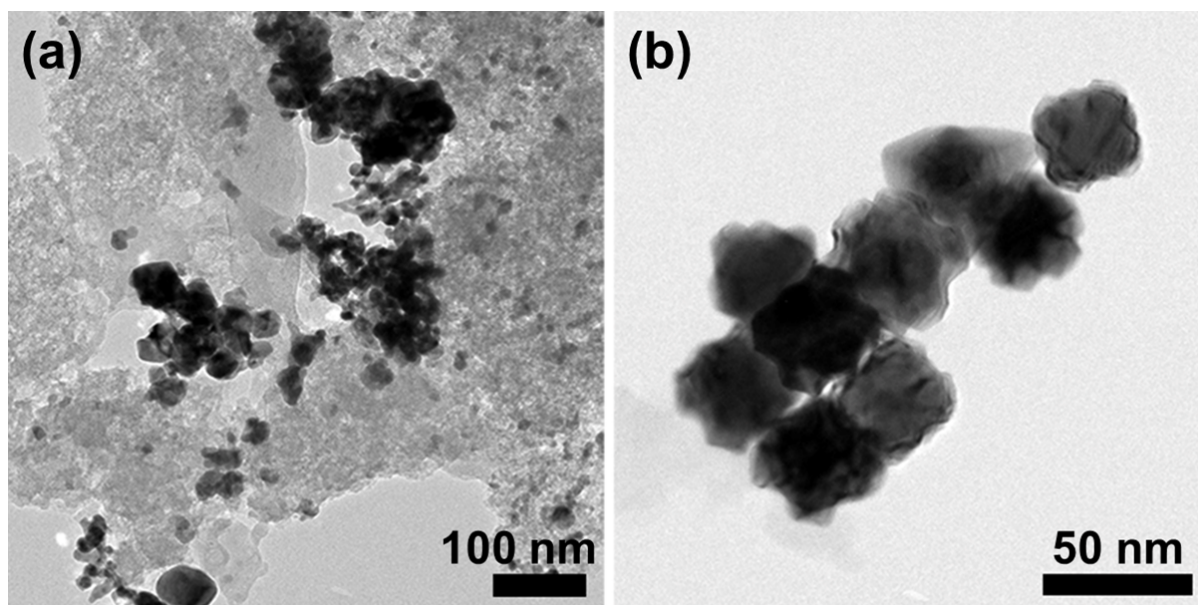


Fig. S19. TEM images of the (a) Pd/C catalyst and (b) THOH Au@Pd NCs after 500 ADT cycles.