Supporting Information

Rationally Selecting Halide Ion for Highly Active Au@Pd Nanobipyramids

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The preparation of Pd nanocubes (NCs)

45 nm Pd NCs were prepared with a previous method in our lab.[1] Briefly, 25 mL aqueous solution (0.1 M CTAB), 5 mL H_2PdCl_4 (0.01 M), 5 mL KI (0.04 M), 5 mL AA (0.02 M) and 10 mL deionized water were then successively added into a 100 mL beaker. The mixture was shaken slowly for 1 min to give a homogenous solution, and then put into a 90 °C water bath for promote the reduction of Pd(II) to Pd. Gradually, the solution changed from reddish brown to brown for Pd NCs formed. After 1 h, the solution was allowed to cool down to about 35 °C (**Low temperature causes the crystallization of CTAB**). The Pd NCs were precipitated via 7000 rpm centrifuging. Supernatant was discarded and the precipitation was dissolved in 5 mL water again. This purifying procedure was repeated twice to remove excess CTAB, KI and other byproducts. The resulting Pd NCs were dispersed in 10 mL water.

For the preparation of 30 nm Pd NCs, 98 °C oil bath and 10 mL AA (0.02M) were used (other conditions were unchanged).

The preparation of Pd octahedra

A seeded growth was used to prepare Pd octahedra. Briefly, 100 mg PVP (MW=5800), 50μL purified 30 nm Pd nanocubes were introduced into 10 mL diethylene glycol. After 5 min heating in 140 °C oil bath, PVP was dissolved completely. Subsequently, an aqueous Na_2PdCl_4 (0.01 M) was added (The molar ratio of Pd(II) and Pd seed was 2.5). After 2 h, the products were collected and purified using the similar procedure described in the above preparation of Pd NCs.
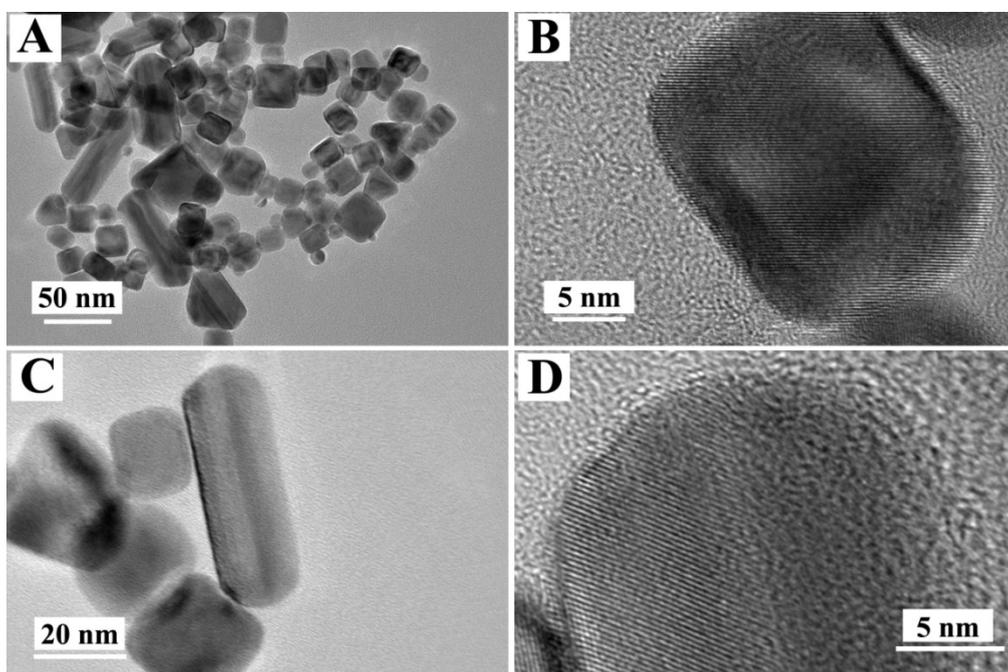
1. B. Jiang, L. Xu, W. Chen, C. Zou, Y. Yang, Y. Fu, S. Huang. Nano Res., 2017, doi:10.1007/s12274-017-1562-y.
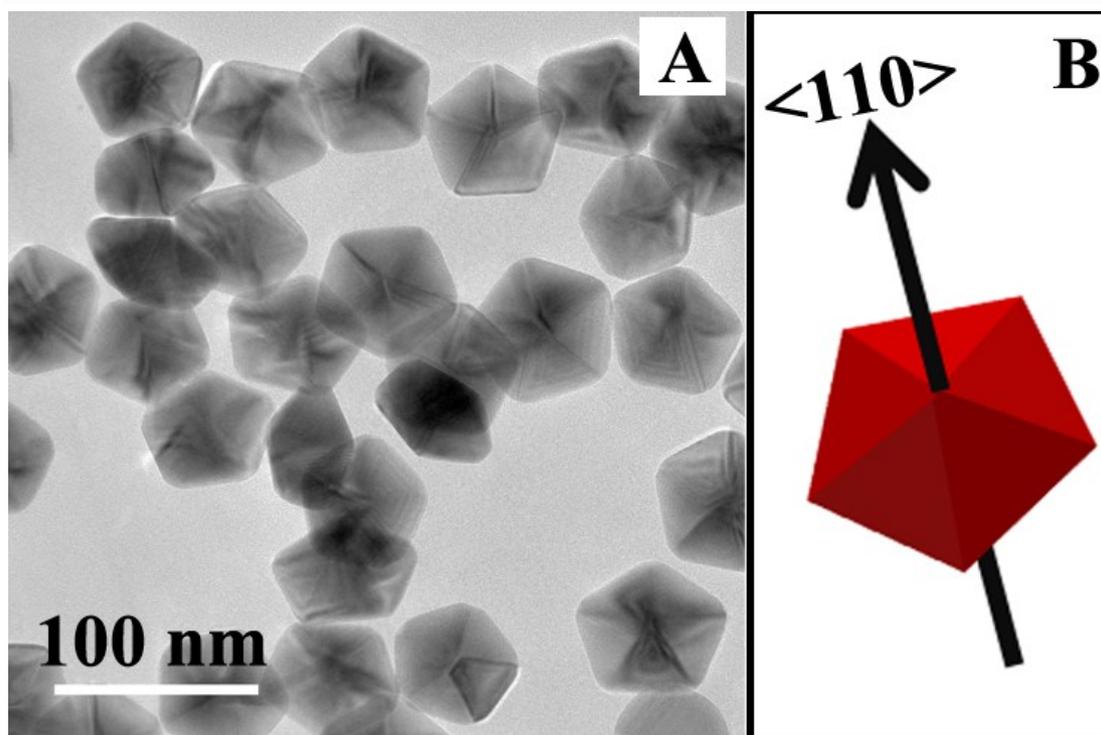
Fig. S1 (A) TEM images and (B) sketch of Au decahedral seeds.
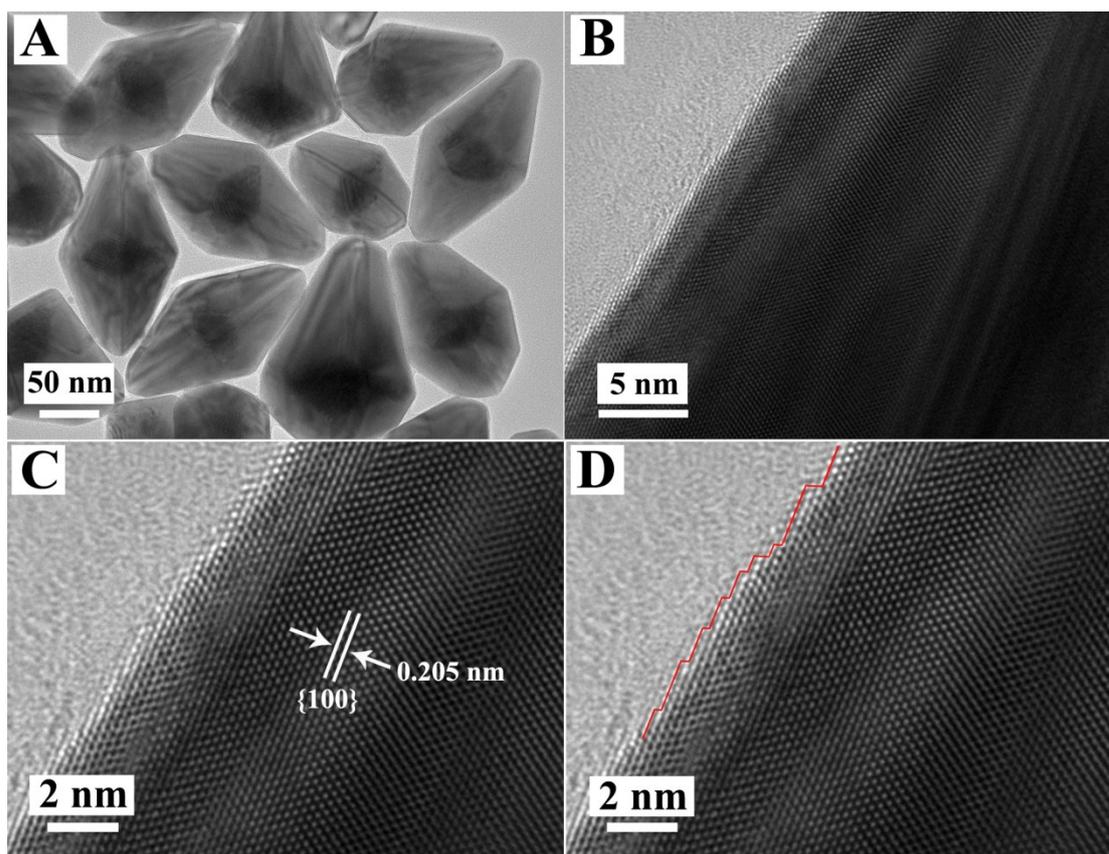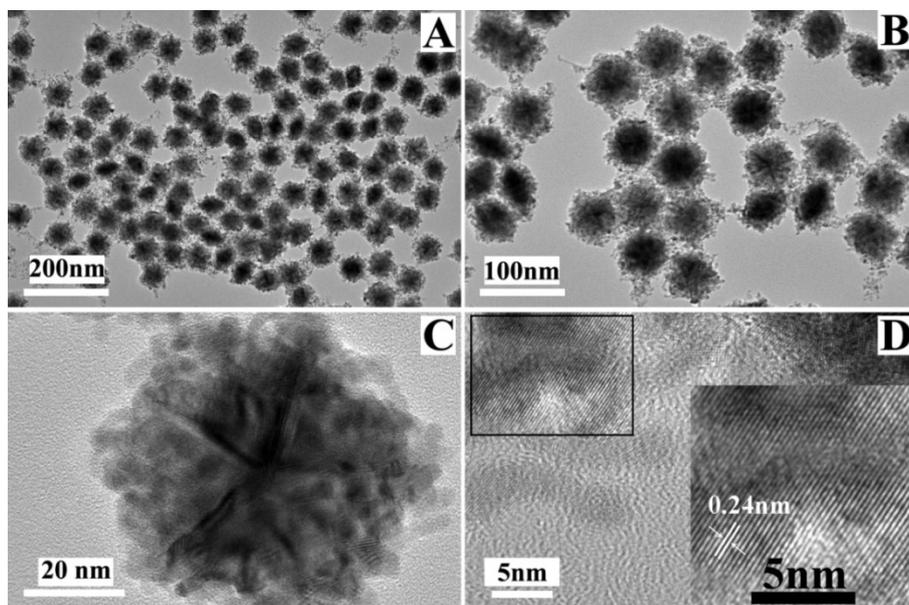
Fig. S2 (A-D) The HRTEM images of Au@Pdnanopyramids (Stepped {100} was marked with red line).


Fig. S3 (A-D) TEM and HRTEM images of products prepared using a standard procedure without Au decahedral seeds. Fig. S3B and Fig. S3D are the HRTEM images of one single crystalline Pd nanoparticle and one penta-fold twinned Pd nanorod,

respectively.

Fig. S4 (A-D) TEM images of Au@Pd nanoparticles prepared using Pd(NO$_3$)$_2$ as metal precursor and polyvinylpyrrolidone as capping agent (Inset in Fig. S4C is the enlarged view of area marked by the black box). The molar ratio of Pd(NO$_3$)$_2$ and Au was 2.
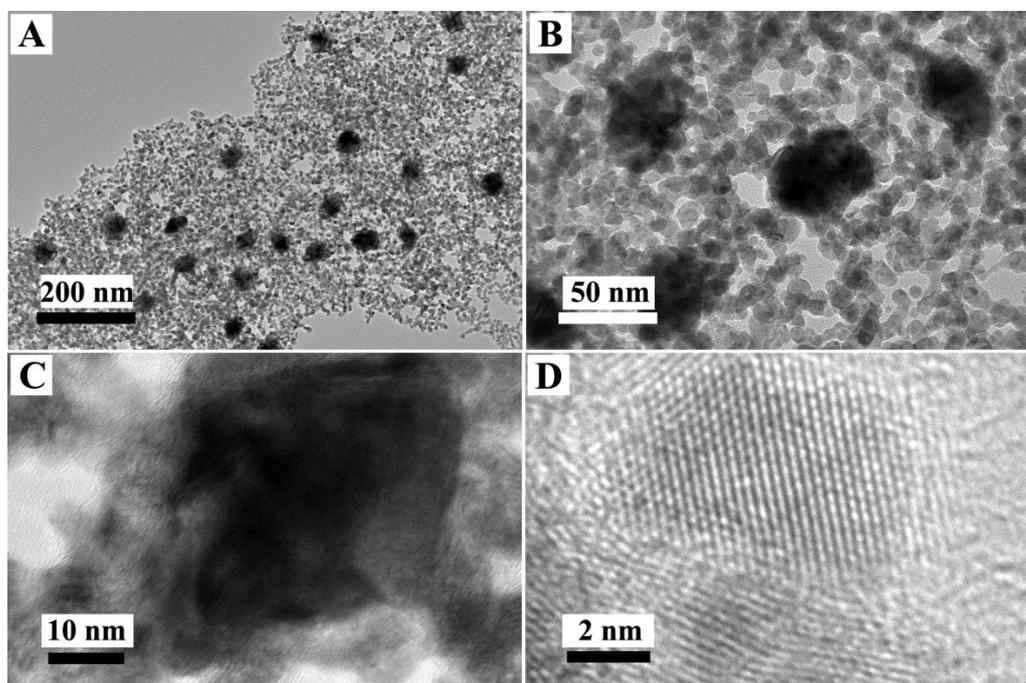

Fig. S5 (A-D) TEM images of Au@Pd nanoparticles prepared using Pd(NO$_3$)$_2$ as metal precursor and polyvinylpyrrolidone as capping agent. The molar ratio of Pd(NO$_3$)$_2$ and Au was 8.

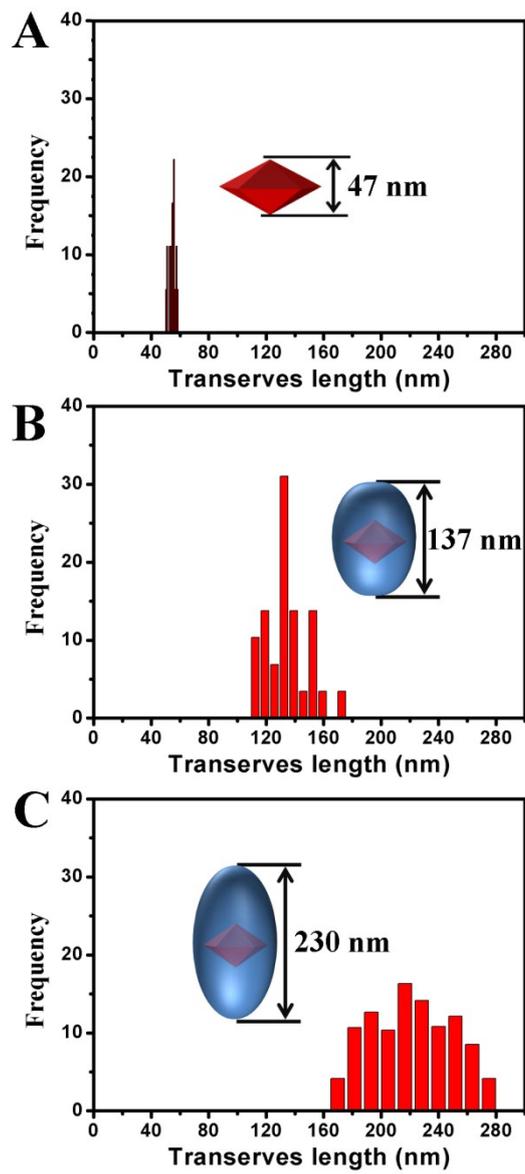**Table S1** Redox potential of various half reactions.

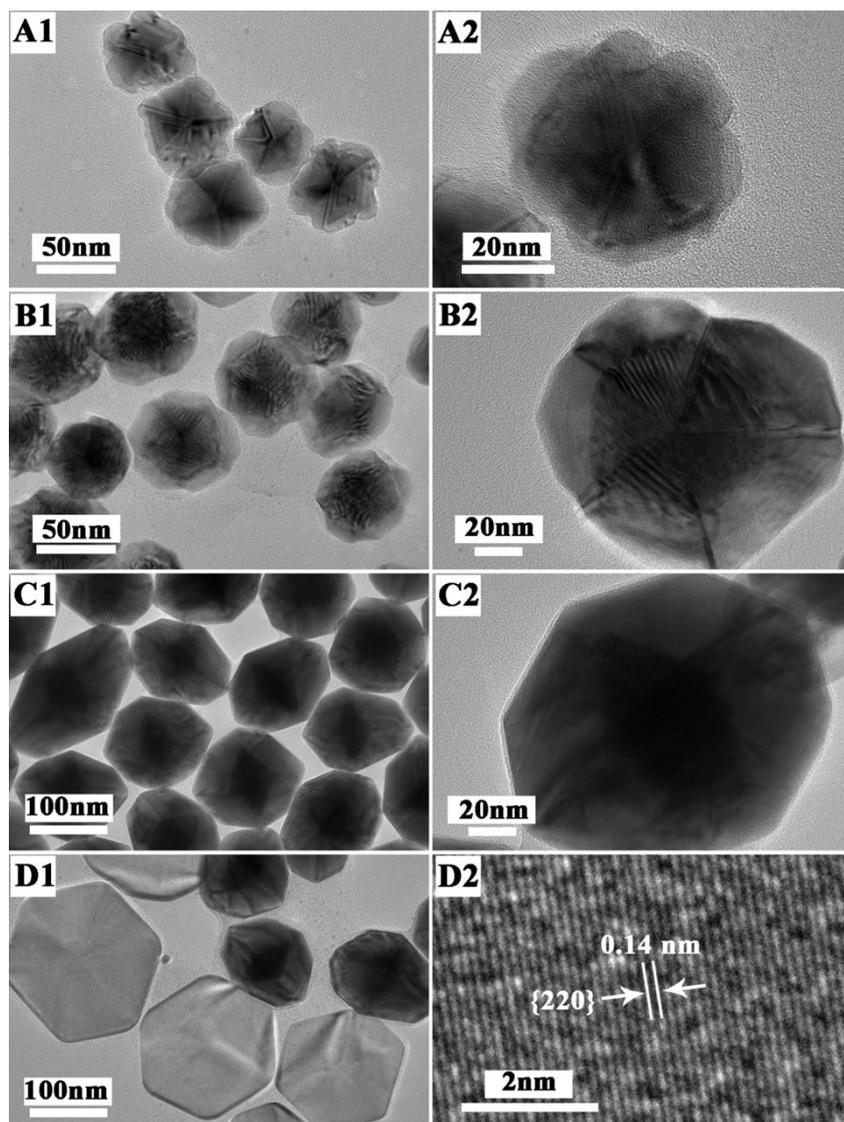| Half Reaction	Redox Potential
$Pd^{2+} + 2e^- \rightarrow Pd$	$E^\theta = 0.985\ V\ vs.\ NHE$
$PdCl_4^{2-} + 2e^- \rightarrow Pd + 4Cl^-$	$E^\theta = 0.59\ V\ vs.\ NHE$
$PdBr_4^{2-} + 2e^- \rightarrow Pd + 4Br^-$	$E^\theta = 0.49\ V\ vs.\ NHE$
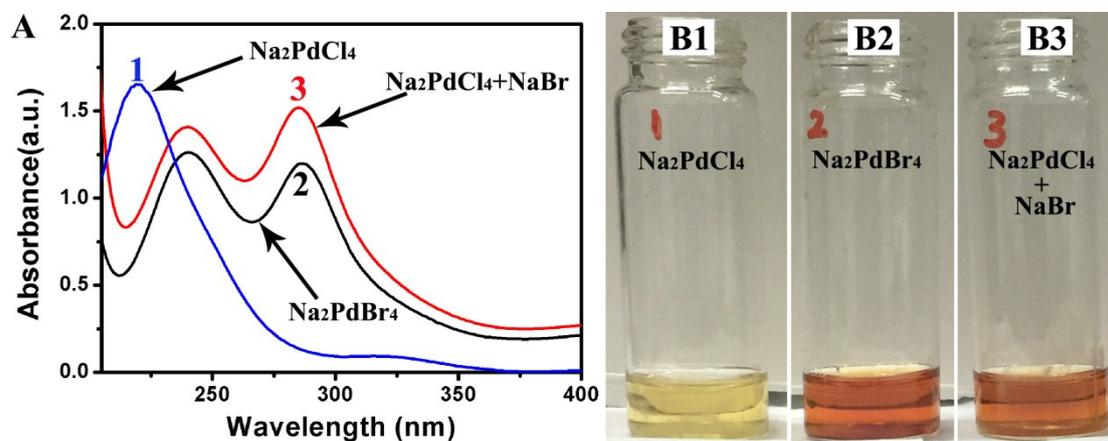
Fig. S6 (A) Spectra and (B1-B3) optical photographs of different solutions.
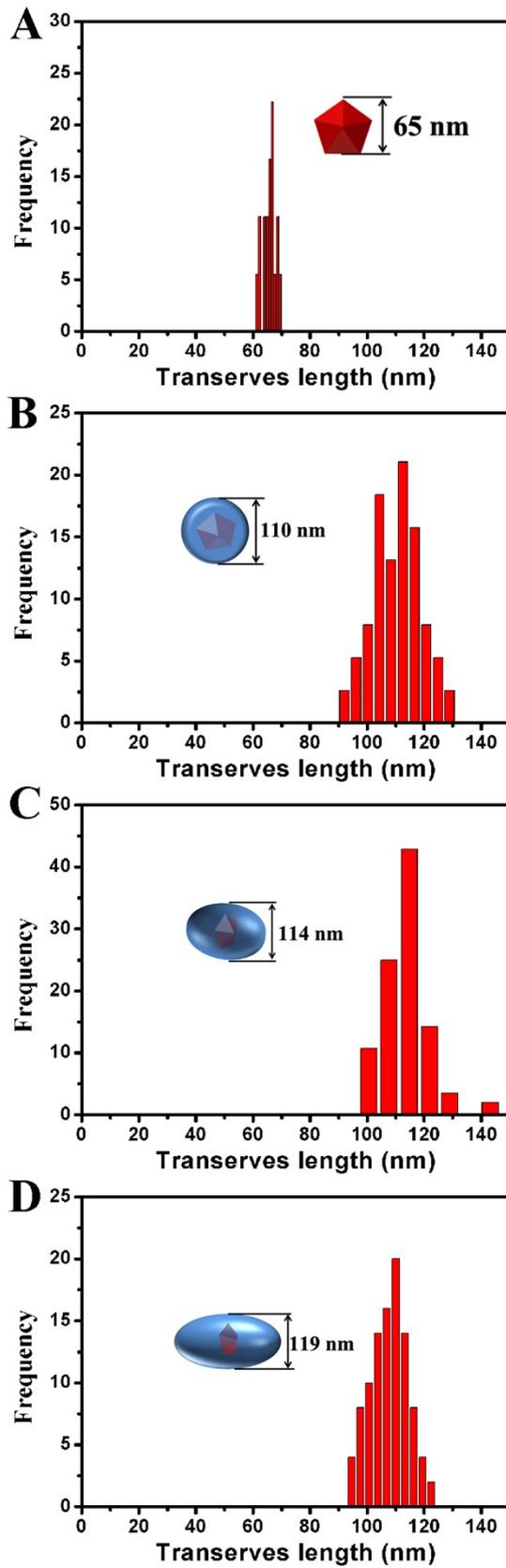
Fig. S7 Evolution of transverse length with time: (A) 0 min; (B) 1.5 h; (C) 3 h; (D) 5 h.

Fig. S8 Evolution of longitudinal length with time: (A) 0 min; (B) 3 h; (C) 5 h.
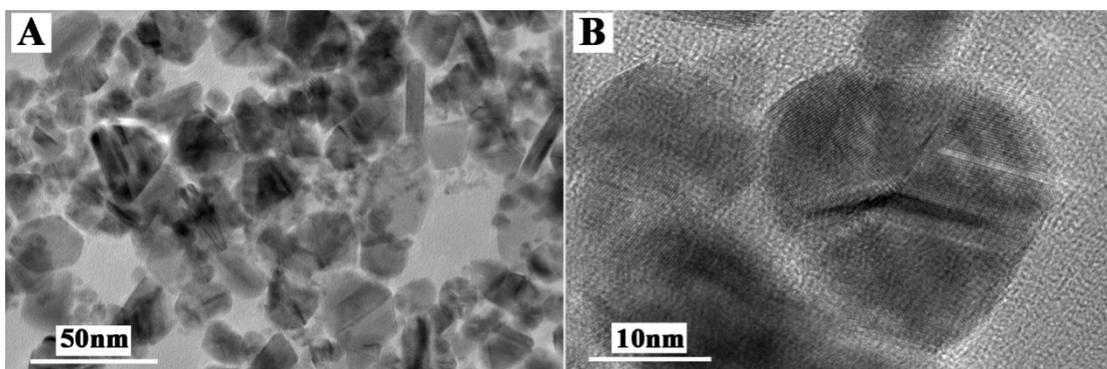
Fig. S9 TEM images of products prepared at different temperatures: (A1-A2) 90 °C; (B1-B2) 120 °C; (C1-C2)150 °C; (D1-D2) 180 °C. Reaction times in all cases were 5 h.

Discussion about results presented in Fig. S9. With the reaction temperature increasing, the reaction rate became fast (**Fig. S9A-8C**). However, 180 °C caused self-nucleation and pure Pd nanoplates formed (**Fig. S9D**). If reaction temperature was increased to 210 °C, self-nucleation became much significant and lots of small sized Pd nanoparticles formed (**Fig. S10**).
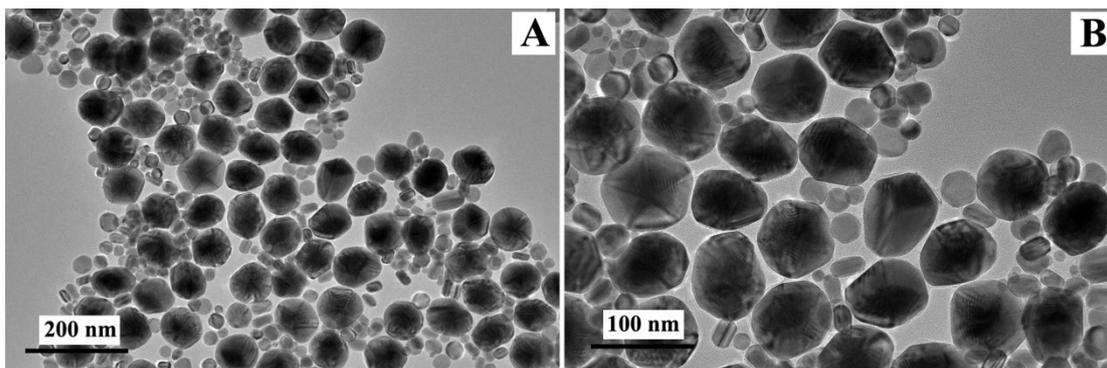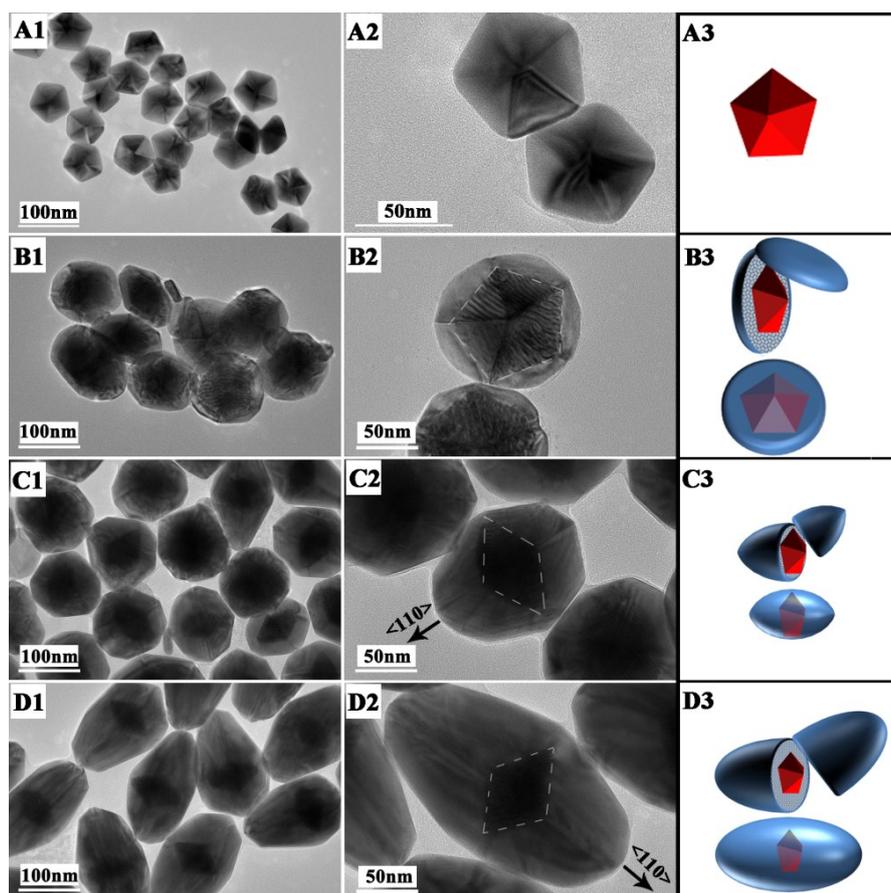
Fig. S10 (A-B) TEM images of products prepared at 210 °C.

Fig. S11 (A-B) TEM and HRTEM images of products prepared without N_2.

The discussion about the effect of N_2.

N_2 environment is very important to the growth of Au@Pd NBs. NPs are unstable because size effect increases their activity of surface atom, so they are oxidized by Br^-/O_2 in air,[1] especially at high temperature. For penta-fold twinned NPs, high energy is present in their twinned interfaces and they are etched more easily than other nanostructures. In our system, the preparation was carried out at 180 °C and products are typically penta-fold twinned. Therefore, N_2 protection was necessary. The synthesis in air also proceeded and result shows that no any Au@Pd NBs formed (**Fig. S11**). Products had irregular shapes and small sized fragment formed, indicating that etching occurred. Therefore, in the whole growth of Au@Pd NBs, a N_2 environment should be used to avoid etching.

1. Y. Zheng, J. Zeng, A. Ruditskiy, M. Liu and Y. Xia, *Chem. Mater.*, 2013, **26**, 22–33.

Fig. S12 TEM images and schematic sketches of products prepared using different molar ratios of Pd precursor and Au: (A1-A3) 0; (B1-B3) 1; (C1-C3) 3; (D1-D3) 8.

**The discussion about the effect of the ratio between Pd precursor and Au.**

The amount of precursor is an essential factor which affects the growth kinetics of nanostructures and in turn product morphology. Here, the effect of precursor amount was investigated and results are shown in **Fig. S12**. When the molar ratio of Na_2PdBr_4 and Au was 1, the growth of Pd on Au decahedral NPs clearly occurred along <100> (**Fig. S12B**). Besides, the growth along <110> was also observed. However, the growth along <110> was not dominant over along <100>. HRTEM image shows that the growth surrounding seed is inhomogeneous (**Fig. S12B2**). When the molar ratio was increased to 3, TEM images show that the products are short NBs (**Fig. S12C**), indicating that the growth rate along <110> is faster than that along <100>. With the molar ratio raised to 6, the growth along <110> further increased, resulting in the formation of Au@Pd NBs (**Fig. S12D**). Above results show that the growth of Au@Pd was also governed by the kinetics.
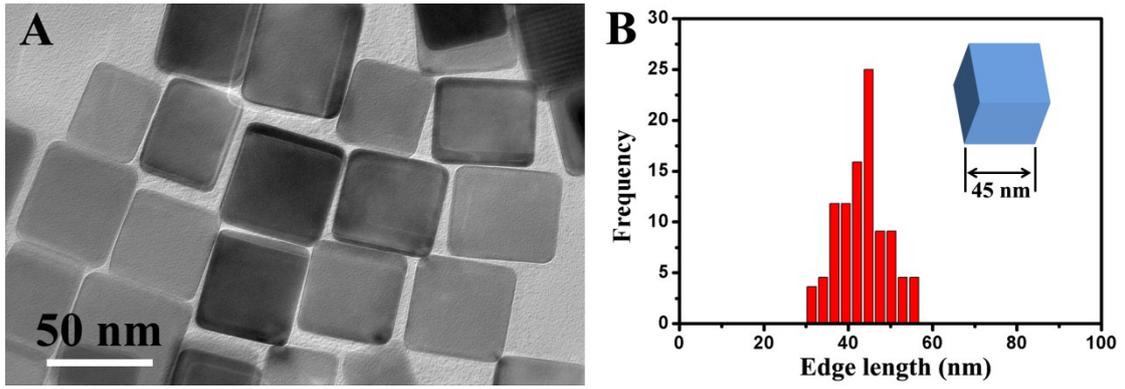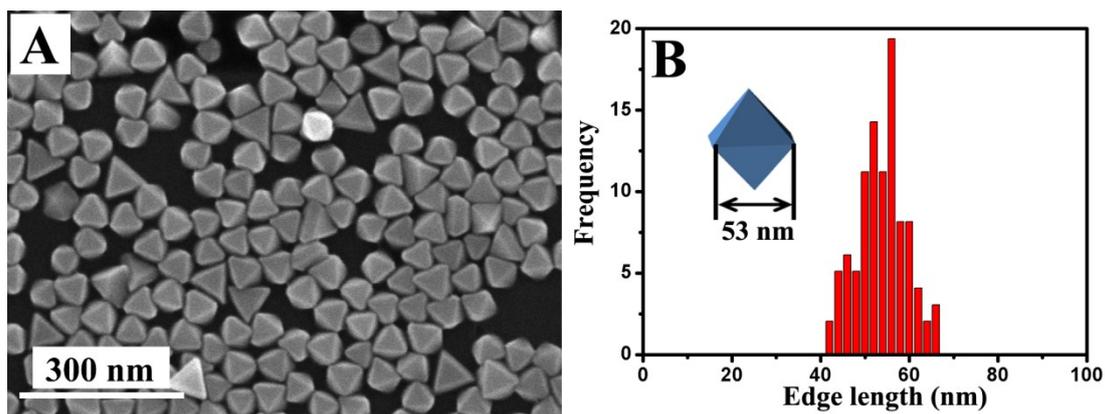
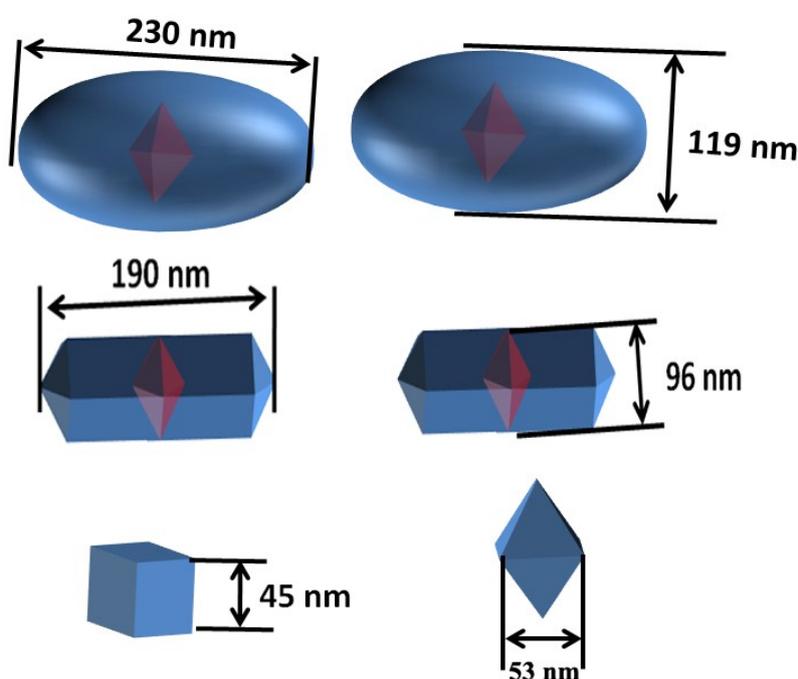**Fig. S13** (A) TEM images and (B) size distribution of Pd nanocubes.
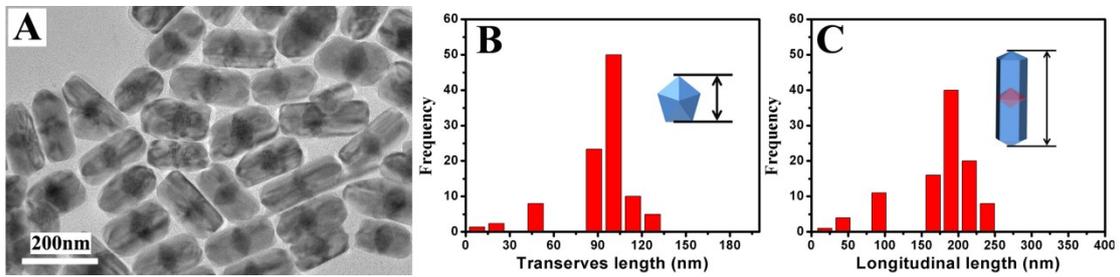
Fig. S14 (A) TEM images, (B) transverses length distribution and (C) longitudinal length distribution of Pd-Au-Pd segmental nanorods.
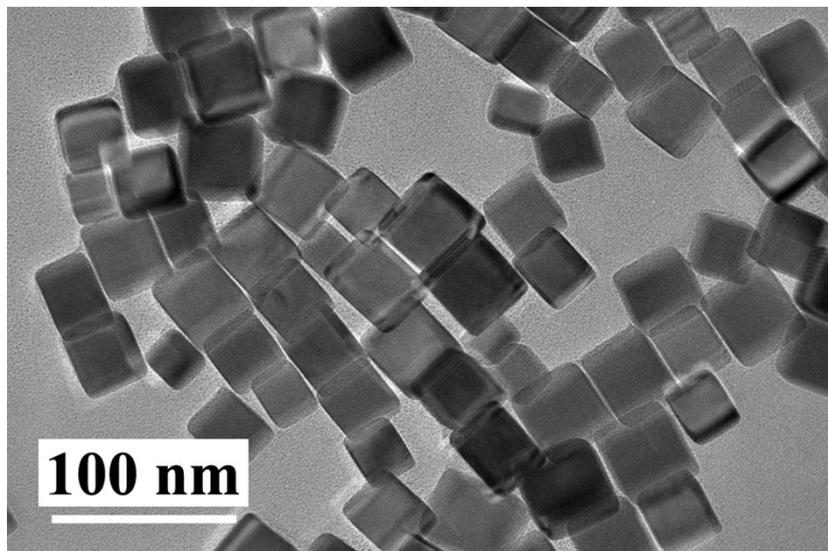
Fig. S15 SEM image of Pd nanooctahedra with 30 nm mean edge

Fig. S16 SEM image of Pd octahedral nanoparticles with 55 nm mean edge

Fig. S17 Scheme of various nanostructures

For the cubic and octahedral Pd NPs, it is easy to know the ratio of surface area because they are regular polyhedron. The total surface area of 53 nm octahedra is 1.1 time of that of 45 nm cubes. Because the transverses and longitudinal lengths of Au@Pd NB and Pd-Au-Pd nanorod are much bigger than these of Pd octahedron and Pd nanocube, so the total surface areas of Au@Pd NB and Pd-Au-Pd nanorod are smaller than that of Pd octahedron and Pd nanocube, when the mass of metal is constant. Similarly, through analyzing the transverse and longitudinal length difference of Au@Pd NB and Pd-Au-Pd nanorod, we can know the total surface area of Au@Pd NB is smaller than that of Pd-Au-Pd nanorod.