Supplementary Information

Anisotropic growth of palladium twinned nanostructures controlled by kinetics and their unusual activities in galvanic replacement

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Experimental Procedure:

Synthesis of palladium nanotapers: In a typical synthesis, 0.8000 g of poly(vinyl pyrrolidone) (PVP, M.W.≈55,000, Sigma-Aldrich, 856568-100g) was dissolved in 7.5 mL of deionized water. Meanwhile, 0.0486 g of sodium palladium(II) chloride (Na_2PdCl_4, Aldrich, 379808-1g) and 0.6000 g of potassium iodide (KI) were dissolved in another 7.5 mL of deionized water at room temperature. The two stock solutions were mixed together, and then transferred into a Teflon-lined stainless-steel autoclave with a capacity of 25 mL. The reaction mixture was heated at 150°C for 46 h, and then naturally cooled down to room temperature. The product was collected by centrifugation and washed with acetone once, with ethanol three times and with deionized water two times to remove excessive PVP. The as-obtained samples were then characterized by scanning and transmission electron microscopy (SEM and TEM).

Galvanic replacement: 10 mL of deionized water was placed in a 50-mL 3-neck flask (equipped with a reflux condenser and a magnetic Teflon-coated stirring bar) and heated in air at 90°C. When the temperature was balanced, 2 mL of palladium nanocrystals (416.32 mg/L) were added into the water. Then 8.695 mL of $HAuCl_4$ (0.6 mM) was added dropwise using a syringe pump at 30 mL/h. The reaction solution was maintained at 90°C for 30 min after the completion of adding $HAuCl_4$. The product was collected by centrifugation and washed with deionized water four times. The as-obtained samples were then characterized by SEM and TEM.

Instrumentation:

A drop of the aqueous suspension of particles was placed on a piece of carbon-coated copper grid or silicon wafer and dried under ambient conditions. TEM images were taken on a JEOL JEM-2010 LaB6 high-resolution transmission electron microscope or a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. HRTEM images and EDS spectra were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. SEM images were taken on a FEI Sirion 200 field emission scanning electron microscopy operated at 5 kV. UV-vis extinction spectra were taken using an Agilent Varien Cary 60 spectrophotometer. The concentration of nanoparticles was measured with a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS) after dissolving them with a mixture of HCl and HNO_3 (3:1, volume ratio).

Table S1. Projection angles between (100) and (h11) facets.

Facet 1	Facet 2	Projection Angle
(100)	(111)	55^{o}
	(211)	35^{o}
	(311)	25^{o}
	(411)	19^{o}
	(511)	15^{o}
	(611)	13^{o}
	(711)	11^{o}

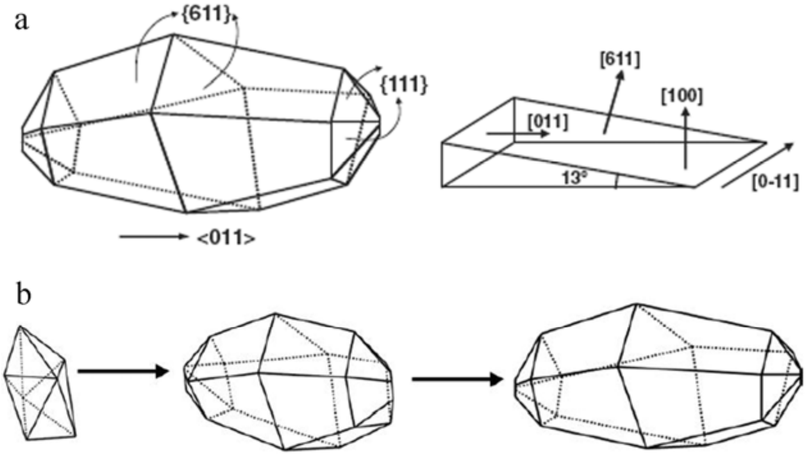

Fig. S1. (a) Models of a rice-like twinned structure of *fcc* metals. (b) Model image illustrating the shape evolution in lateral and longitudinal directions of rice-like structures. The figure is adapted from the reference (Y. Zheng, J. Tao, H. Liu, J. Zeng, T. Yu, Y. Ma, C. Moran, L. Wu, Y. Zhu, J. Liu and Y. Xia, *Small*, 2011, **16**, 2307).

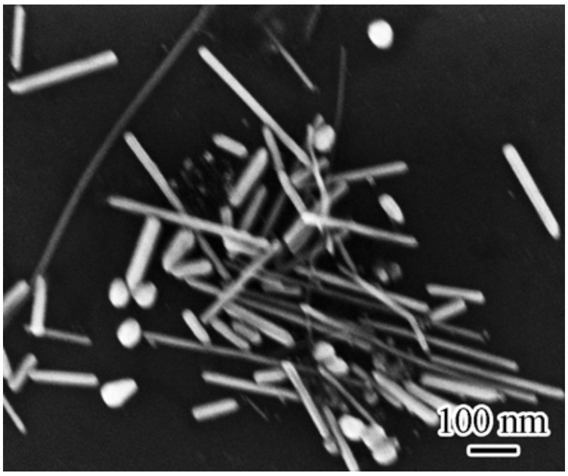

Fig. S2. SEM images of Pd nanostructures prepared under the same condition as that in Fig. 1, except the use of PVP (M.W. ≈29,000) instead of PVP (M.W. ≈55,000). This change results in a larger number of PVP chains in the reaction, when the total weight of PVP is kept constant. As the end hydroxyl groups of PVP are the only functional parts for reduction, it actually increases the amount of reducing agents in the synthesis and makes the reaction faster. As a result, the twinned structures grow into five-fold twinned nanowires. It confirms that the reaction kinetics is the key to uneven atomic addition to nanocrystal surface during crystal growth.

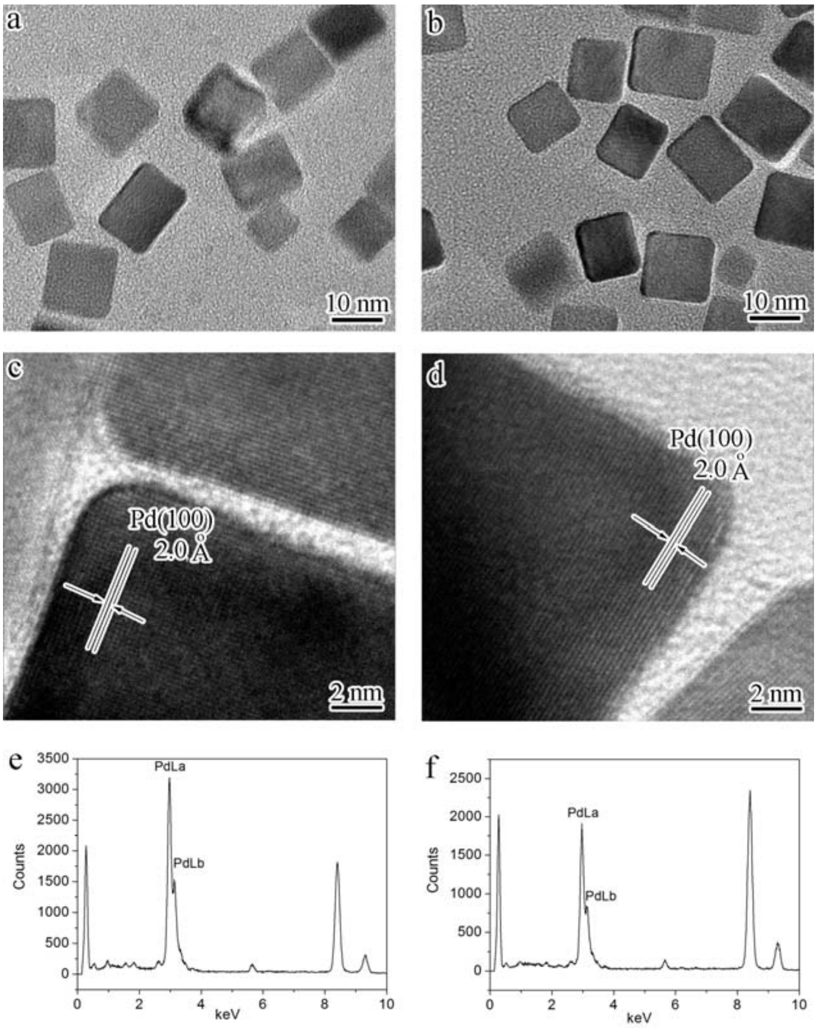

Fig. S3. TEM images of the sample of palladium nanocubes before (a) and after (b) mixed with $HAuCl_4$ solution under the same condition as that in Fig. 3. HRTEM images of the samples in (a) and (b) are shown in Panels c and d, respectively. EDS spectra of the samples were also collected as shown in Panels e and f, respectively. TEM images show that there is no morphological change after treated with $HAuCl_4$ solution at 90ºC. More careful observation based on HRTEM images confirms that both the edges and truncation of the nanocubes were maintained the same after $HAuCl_4$ treatment, indicating that no morphological change occurs on the nanocubes. Moreover, EDS spectrum of the nanocubes does not detect any signal from Au. The results clearly show that palladium nanocubes cannot react with $HAuCl_4$ solution through galvanic replacement.

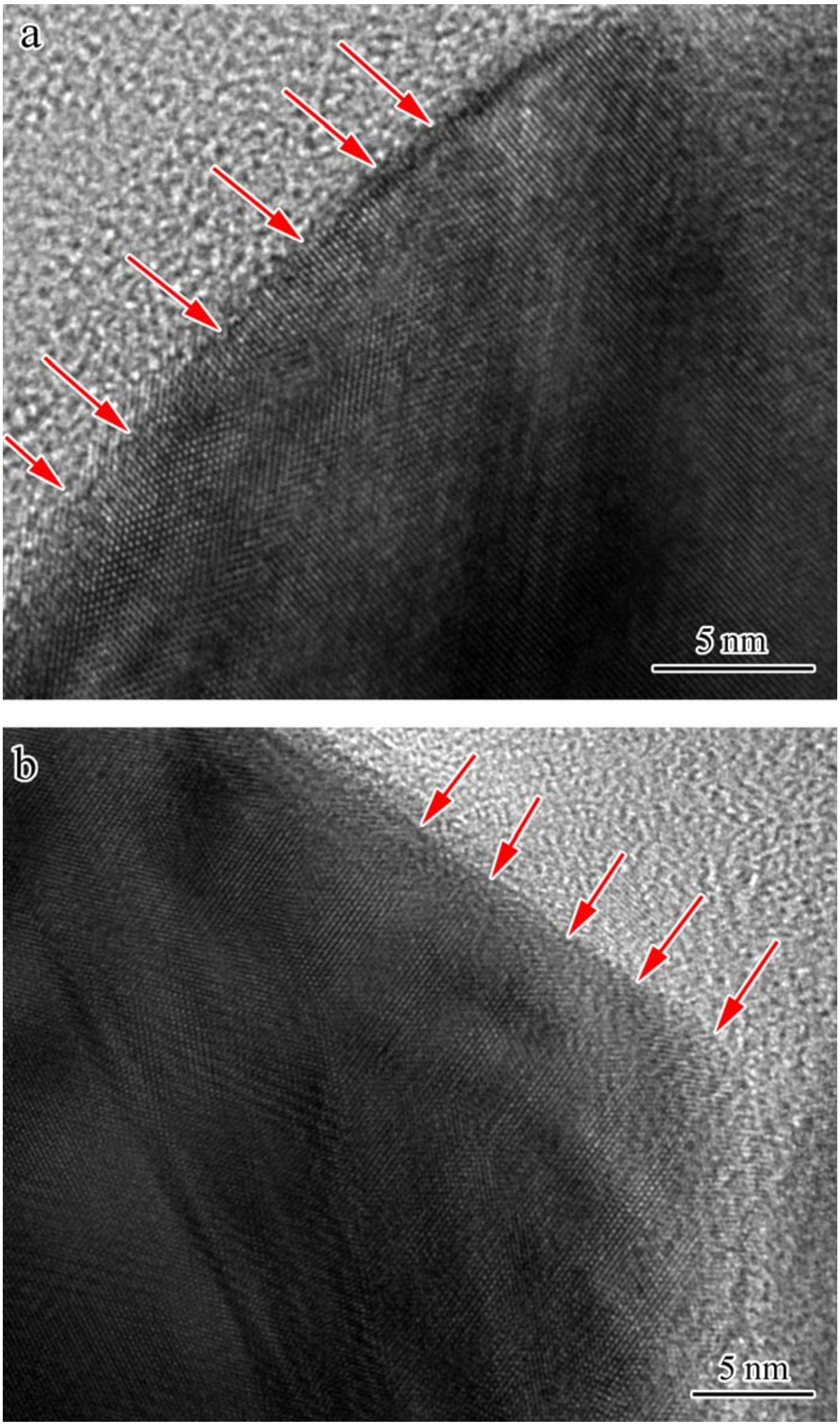

Fig. S4. High-resolution TEM images of nanotapers showing the presence of terraces and steps on surface. The locations of terraces and steps are marked by red arrows.