Supplementary Information

Electrochemical Preparation of Pd Nanorods with high-index facets

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1. Shapes of the end of fivefold twinned nanorod bounded by different facets

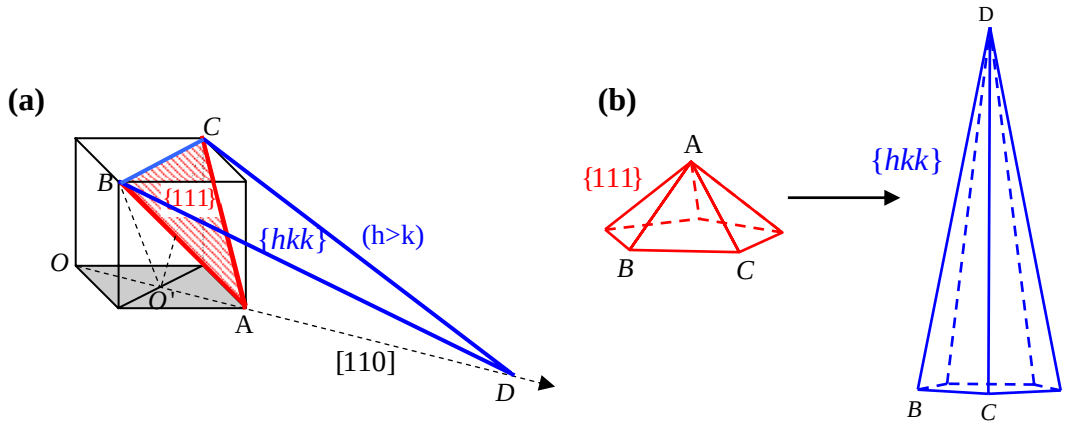


Fig. S1 (a) Relative positions of {111} facet (ΔABC) and {hkk} facet (ΔBCD) in cubic lattice; (b) Schematic illustration of the end of fivefold twinned nanorod changing from pentagonal pyramid into elongated pentagonal pyramid when its surfaces are transformed from {111} into {hkk}.

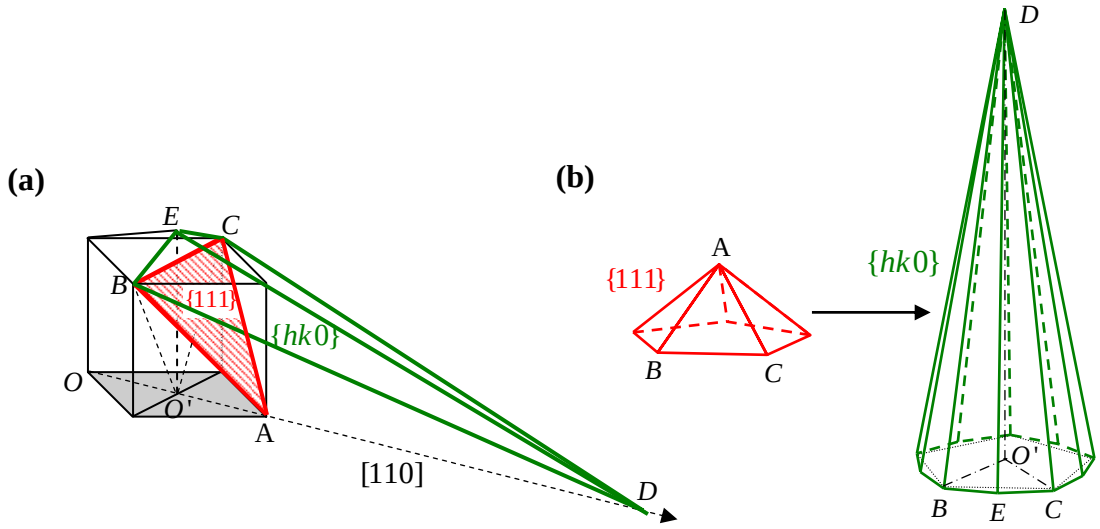


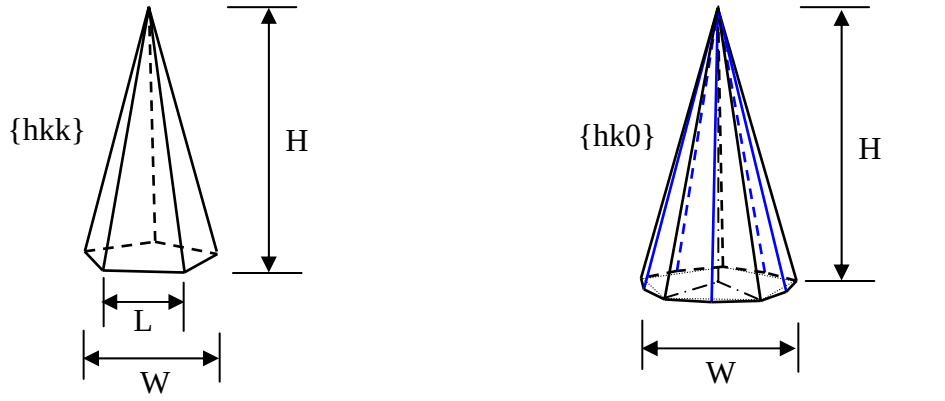
Fig. S2 (a) Relative positions of {111} facet (ΔABC) and {hk0} facets (ΔBDE and ΔCDE) in cubic lattice; (b) Schematic illustration of the end of fivefold twinned nanorod changing from pentagonal pyramid into decagonal pyramid when its surfaces are transformed from {111} into {hk0}.

2. Miller indices of the surfaces on fivefold twinned Pd nanorods

The Miller index of the end surfaces of fivefold twinned nanorod can be determined by measuring the geometric parameters of the end of nanorod. One is the ratio of height to edge length (H/L), and the other is the ratio of height to base width (H/W), as listed in Table 1. By measuring geometric parameters of tens of the synthesized Pd nanorods, we have determined that the surfaces of type-I Pd nanorods ranges from {10, 1, 1} to {15, 1, 1} facets (H/L: 5 ~ 7.4), and the surfaces of type-II Pd nanorods varies from {310} to {610} facets (H/W: 2.2 ~ 4.1). Fig. S3 shows the models of surface atomic arrangement of Pd(11, 1, 1) and Pd(410) surfaces. Atoms labeled with green and magenta colors are step atoms with a coordination number of 7 and 6, respectively.

Table S1 Relationship between geometric parameters and Miller indices of nanorod tip.

Shape	Pentagonal pyramid	Elongated pentagonal pyramid	Decagonal pyramid
Miller indices	{111}	{hkk}	{hk0}
H/W	$\frac{1}{4\sin 54°}$	$\frac{1}{4\sin 54°}\frac{h}{k}$	$(1+\frac{2h}{k})/(\sqrt{12}\cos 18°)$
H/L	$\frac{1}{2}$	$\frac{h}{2k}$	



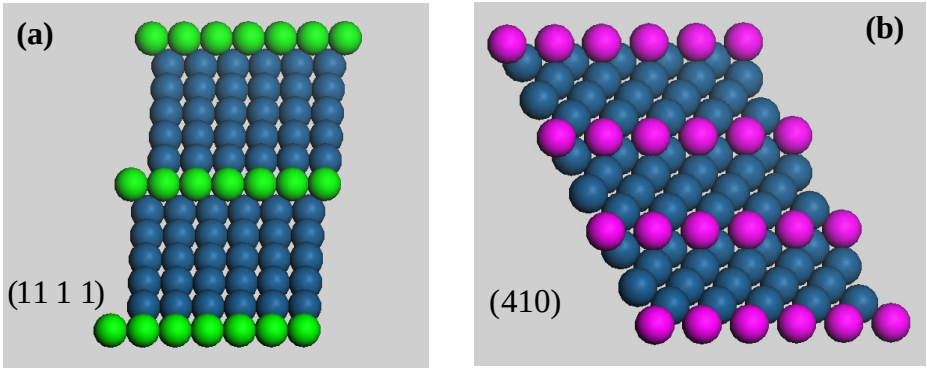


Fig. S3 Models of surface atomic arrangement of Pd(11, 1, 1) and Pd(410).

3. Onset potential of the formation of Pd surface oxide

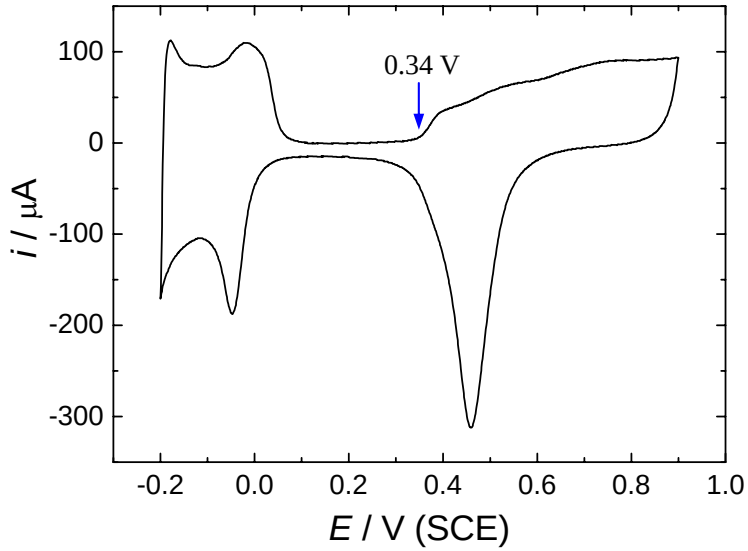


Fig. S4 Cyclic voltammograms of type-I Pd nanorods supported on GC substrate in 0.1 M $HClO_4$ solution. Scan rate: 50 mV s^{-1}.

The onset potential of the formation of Pd surface oxide is measured about 0.34 V.

4. Discussion of the formation of broken end on type-I Pd nanorods

The type I Pd nanorods had a broken end while the type-II Pd nanorods did not. This may be caused by crystal defects. During the preparation of Pd nanorods, at the lower potential (E_L), Pd nanocrystals can grow through the reduction of Pd^{2+} ions; at the upper potential (E_U), Pd surfaces can be oxidized and the slight dissolution of Pd may occur if potential is higher than ~ 0.70 V according to the results reported by Woods.[1] The E_L for growth of type-I nanorods is very low (-0.15 V) and Pd nanocrystals grow fast, which may introduce some crystal defects into the nanorods. These defects may lead to incompletely enclosed end for the five sub-crystals, and form the “broken end”. The E_L for type-II nanorods is relatively high (0.15 V), so the growth rate is relatively slow. More importantly, the E_U is as high as 0.85 V, where the dissolution of Pd is obvious. The crystal defects formed at E_L may be dissolved preferentially due to their high energy. So, the type-I nanorods prepared at E_L=-0.15 V, E_U=0.65 V had a broken end, while the type-II nanorods prepared at E_L=0.15 V, E_U=0.85 V were enclosed completely.

5. Measurement of electroactive surface area of Pd catalysts

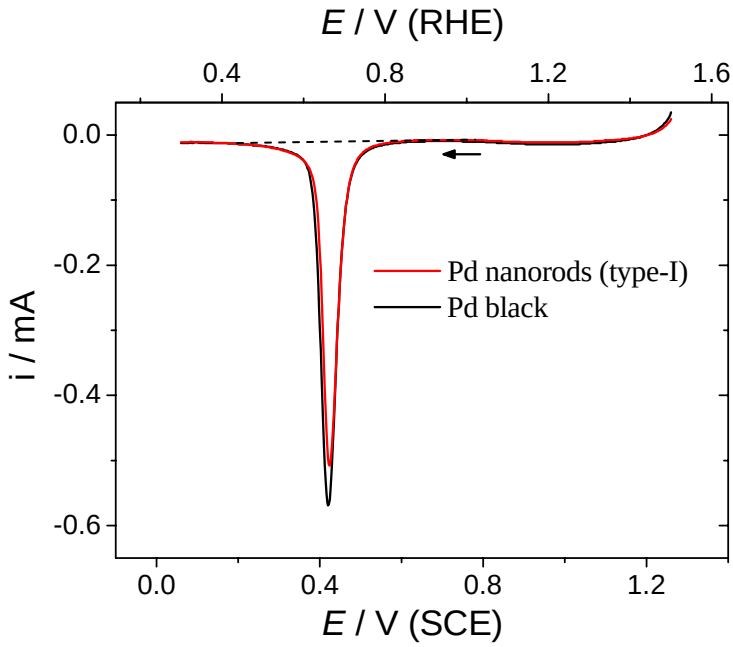


Fig. S5 Cathodic voltammograms of type-I Pd nanorods (red line) and commercial Pd black catalysts (black line) after holding at 1.26 V *vs.* SCE (or 1.50 V *vs.* RHE) for 10 s. The cathodic peak at about 0.42 V (SCE) is the reduction of Pd surface oxide. 1 M H_2SO_4 solution; scan rate: 20 mV s^{-1}.

The electroactive surface area of Pd was calculated according to the method proposed by Woods. [2] At the potential about 1.50 V (RHE), monolayer Pd oxide would form on the Pd surfaces. With the assumption of 424 μC cm^{-2} for the reduction of this Pd oxide, the electroactive surface area of Pd can be calculated. In Fig. S5, the reduction charge of Pd surface oxide is integrated to be 1368 μC and 1572 μC for Pd nanorods and commercial Pd black, respectively. So the corresponding electroactive surface area is 3.23 cm^2 and 3.71 cm^2, respectively. Note that to avoid disturbing the surface structure of Pd nanorods, the measurement of electroactive surface area was carried out after the measurement of ethanol electrooxidation.

6. Catalytic activity of type-II Pd nanorods and nanoparticles

As can be seen in the Fig. 2, the type-II Pd nanorods and irregular faceted nanoparticles coexist on the GC surface. It is difficult to evaluate the intrinsic catalytic activity of type-II Pd nanorods, since their distribution density is very low and the contribution of nanoparticles can not be neglected. We have tested the catalytic activity of the sample with type-II Pd nanorods and nanoparticles (red line), which is 3~5 times higher than that of commercial Pd black catalyst (black line), as illustrated in Fig. S6. Therefore, the preparation of Pd catalysts with {hk0} facets is a promising method to improve the catalytic activity.

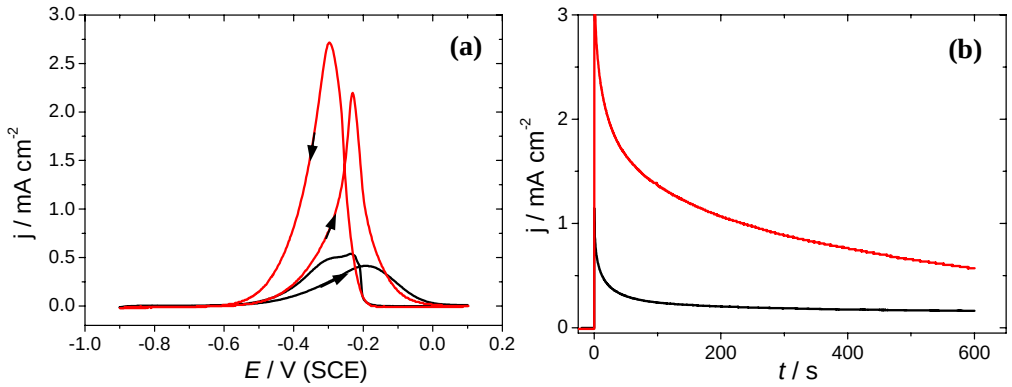


Fig. S6 (a) Cyclic voltammograms (10 mV s^{-1}) and (b) Current ~ time (E = -0.30 V) curves of ethanol oxidation on type-II Pd nanorods + nanoparticles (red line) and commercial Pd black catalyst (black line) in 0.1 M ethanol + 0.1 M NaOH solution.

1 D. A. J. Rand, R. Woods, *J. Electroanal. Chem.* 1972, **35**, 209.

2 D. A. J. Rand, R. Woods, *J. Electroanal. Chem.*, 1971, **31**: 29.