Electronic supporting information for:

**Ru-assisted synthesis of \{111\}-faceted Pd truncated bipyramids: a highly reactive, stable and restorable catalyst for formic acid oxidation**

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**Experimental section**

*Chemicals and Reagents.* Ethylene glycol (EG) and polyvinylpyrrolidone (PVP K-30, Mw=58000) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ruthenium(III) chloride hydrate (RuCl₃·xH₂O) was purchased from Shanghai July Chemical Co., Ltd. Potassium tetrachloropalladate (II) (K₂PdCl₄) was obtained from Alfa Aesar. Pd-black and Nafion solution (5 wt. %) were obtained from Aldrich. All the chemicals were used as received. Ultrapure water is used during
experiments (Millpore, 18.2MΩ cm).

**Synthesis of (111)-faceted Pd truncated triangular bipyramids (TTBPs).** RuCl$_3$ aqueous solution (3M, 0.08 ml) and K$_2$PdCl$_4$ aqueous solution (0.08 M, 3 ml) was introduced into EG solution (15 ml) contained PVP (0.05 g), which had been heated at 373 K under magnetic stirring in a capped vial. The reaction was allowed to proceed for 1 h. After collection by centrifugation with acetone and washed three times with water, the collected black product was dispersed in ethanol.

**Characterization.** The morphologies of products were studied using JEOL-2010 and FEI Tecnai G20 transmission electron microscope (TEM). The sample for Inductively Coupled Plasma OES spectrometer (ICP) was performed on an Ultima 2 analyzer (Jobin Yvon). FTIR spectra are recorded with a spectral resolution of 2 cm$^{-1}$ on an ABB Bomen MB102 IR spectrometer in the range 4000-400 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microprobe. For testing if there is any metallic Ru(0) at the initial stage of the reaction (t = 40 s), we dropped several drops of the reaction mixture onto the polished single-crystal silicon-chip. Before drying in a vacuum oven at r.t., the silicon-chip was purged with high pure N$_2$ to clear the EG, soluble Ru-species and PVP. Finally, the residual species on the silicon-chip was tested for XPS. The TTB Pd NPs were dried in vacuum oven at r.t. to obtain powder. Binding energies were calibrated
by setting the measured BE of C 1s to 284.65 eV, and Si 1p to 101.09 eV for TTB Pd NPs and metallic Ru(0), respectively. Electrochemical measurements were conducted on Epsilon EC-2000 (BASi, America) analyzer.

Electrochemical measurement. Firstly, an ethanol dispersion of NPs colloid was mixed and stirred with carbon black for 48 h to give Pd/C catalysts. Based on the ICP analysis, the Pd loading was kept 10 wt. % of all samples. 3 μL of as-prepared catalysts aqueous suspension (1 mg<Pd> mL<sup>-1</sup>) was deposited on a modified glassy carbon electrode (3 mm in diameter). The solvent was allowed to evaporate at r.t. Then 4 μL dilute Nafion (0.02 wt. % in ethanol) was coated on the surface of catalysts and dried at r.t. Ag/AgCl electrode and Pt wire are used as a reference electrode and a counter electrode, respectively. Commercial Pd black (2 mg<Pd> mL<sup>-1</sup>, 3 μL) were employed as control group catalyst. All the electrolyte solutions were deaerated with high-purity nitrogen gas for 30 minutes. The Electrochemically active surface area (ECSA) calculated from the metal oxides reduction area was used to normalize the original CVs. All electrochemical experiments were performed at r.t. (22±1°).
**Fig. S1** size-distribution histogram of the TTBPs (obtained by counting at least 1000 nanoparticles).

**Fig. S2** TEM and HRTEM images of Pd decahedrons prepared under a
similar conditions with the standard process, except a) without the presence of RuCl$_3$, b) adding RuCl$_3$ after the nucleation of Pd.

**Fig. S3** Characterizations of sampled captured at $t = 40$ s. a) TEM images, inset is the corresponding HRTEM images. b) XPS curves shows Ru$_{3d}$ photoemission, c) the enlarged fitting spectrum of Ru$_{3d}$ photoemission in Fig. S2b.
**Fig. S4** Characterizations of sampled captured at t = 5 min. a) Large area TEM images, b) HRTEM images, the black arrows indicate the twinned boundaries, c) the HRTEM images and d) the corresponding Fast Fourier Transformation (FFT) pattern of an optional NPs in Fig. S4b, the red line suggests the presence of single-twinned plane, e) corresponding EDX spectra of the sample captured t = 5 min indicated that single-twinned Pd structures are coexist with Ru clusters.
**Fig. S5** TEM images of the TTBPs captured at a) 40 min, insets are a representative HRTEM image of an optional NPs and the corresponding FFT image; b) 3 h, respectively.

It worth noting that at the initial stage, the EG, PVP and RuCl₃ mixture went through a sequence of colour change within 40 s, which was from reddish brown to pale light green and then almost colourless. TEM image along with XPS analysis (Fig. S3, ESI†) shows the formation of ultra-small Ru(0) branched cluster at t = 40 s. With the addition of K₂PdCl₄ aqueous, the mixture colour changed slowly into light brown within 5 min. In sharp contrast with the burst nucleation in control groups (Fig. S2, ESI†), such a slow nucleation suggests a different nucleation pathway. Large-area TEM image and the corresponding EDS analysis at t= 5 min indicate that Pd structures coexist with Ru clusters (Fig. S4a and e, ESI†). These Pd structures are uniformly dispersed, characterized of rougher boundary and surface, and of about 5 nm in size. The representative HRTEM images and the corresponding 2-fold streaking FFT pattern further indicate the single-twinned nature (Fig. S4b-d, ESI†). As the reaction continues, the Ru clusters gradually disappear and the anisotropic and epitaxial growth of single-twinned Pd structures continues. The morphology of Pd NPs at t = 40 min (Fig. S5a, ESI†) shows well-faceted TTBPs with smooth surfaces, distinct single-twinned planes and increased particle size. Beyond 1 h, neither the size nor structure has significant change up to 3 h (Fig. S5b, ESI†).
Fig. S6 TEM images of samples obtained at a varied concentration of RuCl$_3$ aqueous solution, a) 0.03 M, b) 0.3 M, c) 0.6 M, d) 1.5 M, e) 6 M, f) 15 M; g) the corresponding EDS analysis of the sample in Fig S6f. The volume of the aforementioned RuCl$_3$ aqueous solution added into the reaction was fixed at 0.08 ml with the standard synthetic procedure.

It is clearly that the amount of RuCl$_3$ in the reaction solution played a critical role in the formation of TTBPs. Figure S6a shows TEM image of the as-prepared sample
when a 100 times reduced amount of RuCl$_3$ (0.03 M, 0.08 ml) was added to the reaction solution. In this case, irregular shaped Pd NPs were obtained with a rare exception of a few single-twinned NPs and with a large size distribution varying in the range of 3-50 nm. This can be explained by the insufficient Ru(0) formation in the early stage of the reaction. With increasing amount of RuCl$_3$ to 0.3 M, the number of TTBPs gradually increase with about 70% purity along with a narrower size distribution (Fig. S6b). When the concentration of RuCl$_3$ is in the range of 0.6 M-6 M, we obtained TTBPs with almost 90% purity (Fig. S6c-e). It worth noting that the average size of the as-obtained NPs are decreasing from 16.5 nm, 13.8 nm to 9.9 nm, respectively, with the increasing amount of RuCl$_3$. It can be attributed to the increasing amount of Ru(0) clusters can lead to increasing amount of single-twinned Pd structures. The amount of K$_2$PdCl$_4$ used to epitaxial growth, however, are decreasing when the dosing of added K$_2$PdCl$_4$ precursor is fixed for all cases, and thus leading to a smaller size of Pd NPs in the end. When the amount of RuCl$_3$ added into the reaction was increased to 15 M, Pd NPs are co-existed with the branched Ru NPs as shown in Fig. S6f. Such result also can be testified by the corresponding EDS analysis in Fig. S6g. This might be due to the amount of Ru(0) clusters is a lot excess over the stoichiometric ratio of the GRR. Therefore, the optimal amount of RuCl$_3$ for producing TTBPs should be in the range of 0.3-6 M.

![Fig. S7 a) TEM and b) HRTEM images of commercial Pd black catalysts fresh from Sigma-Aldrich company, c) TEM images of commercial Pd black catalysts after degradation test.](image)
Fig. S8 CVs of TTBPs and Pd black in N$_2$-purged 0.5 M H$_2$SO$_4$. Scan rate: 50 mV s$^{-1}$. 
**Fig. S9** degradation curves, ECSA% of commercial Pd black after each 200 potential cycles in N₂-saturated 0.5 M H₂SO₄. After the 1ˢᵗ, 2ⁿᵈ, ... and 5ᵗʰ 200 potential cycles, the DC potential amperometry (DCPA) technique was conducted for formic acid oxidation at 0.2 V in 0.5 M H₂SO₄ + 0.25 M HCOOH solution for 2000 s, respectively. The ECSAs were calculated with respect to that of the 1ˢᵗ 200 potential cycles, respectively. Scan rate: 50 mV s⁻¹.

Since 6 μg of commercial Pd black cannot withstand the first 200 potential cycling, catalyst loading on the GC electrode is 16 μg in this case. The ECSA only preserve 33.2% of the initial value at the 2ⁿᵈ point. At the 3ʳᵈ point, there is only 0.7% left. From the 4ᵗʰ point, the ECSA value decrease by three and four orders of magnitude. In sharp contrast, the TTBPs still preserves its initial ECSA at the 6ᵗʰ point as shown in the main text.
Fig. S10 (a) TEM images of TTBP5 after degradation test. (b) The corresponding HRTEM image of the TTBP marked by a white circle, from which the twin boundary can be seen clearly as indicated by the white dash line.

Fig. S11 a) CVs of 5-fold twinned Pd decahedrons obtained in 0.5 M H₂SO₄ + 0.25 M HCOOH solution. b) Degradation curves, ECSA% of 5-fold twinned Pd decahedrons after each 200 potential cycles in N₂-saturated 0.5 M H₂SO₄. The 5-fold twinned Pd decahedrons were obtained in
control group, which was manipulated under the condition without the addition of RuCl₃ as shown in Fig. S2a and b.

![Fig. S12](image)

**Fig. S12** a) TEM and b) HRTEM images of the 5-fold twinned Pd decahedrons after degradation test. Compared with their original TEM and HRTEM images as shown in Fig. S2a and b, it is obvious that the 5-fold multiply-twinned boundaries almost disappear after degradation test.
Fig. S13 FTIR spectra of the a) pure PVP. b) 5-fold twinned Pd decahedrons. c) the as-prepared TTBPs.

Fig. S14 XPS curves of O$_{1s}$ photoemission in a) 5-fold twinned Pd decahedrons, b) TTBPs

As shown in Fig. S11a, the forward peak current density of 5-fold twinned Pd decahedrons is 1.36 mA cm$^{-2}$, which is only one-half of that of TTBPs. After the degradation test, their initial ECSA only has 36% left as shown in Fig. S11b. TEM and HRTEM images in Fig. S12 further demonstrate that the twinned planes have
disappeared after the degadation test. The weaker antioxidant capacity of multiply-twinned structures than that of single-twinned structures may be one reason leading to such bad durability of decahedrons.

In view of catalytic activity, however, the multiply-twinned morphology of these decahedrons should be more active towards formic acid oxidation than TTBPs because they expose more corner and edge atoms than single-twinned NPs. But the fact that the 5-fold twinned decahedrons are not actually like that. Similar to TTBPs, 5-fold twinned Pd decahedrons are also {111}-faceted nanoparticles apart from the surface-adsorbed Ru(II) species. Therefore, it can speculate that the surface-adsorbed Ru(II) species may lead to an enhancement on the catalytic activity of the TTBPs.

FTIR spectra and XPS curves were used to give further information about the surface-adsorbed Ru(II) species. As shown in Fig. S13, for pure PVP molecules, a typical transmitted peak at $\nu_{\text{max}}/\text{cm}^{-1}$ 1661 is clearly observed, arising from the stretching vibration of C=O. A slight red shift around 3 cm$^{-1}$ is observed in the corresponding band for 5-fold twinned Pd decahedrons (1658 cm$^{-1}$), indicating an interaction of the PVP carbonyl group to the surface Pd atom. In a sharp comparison, the C=O of the TTBPs sample has a strong red shift of 9 cm$^{-1}$, suggesting that a interaction between Ru(II) and the C=O of PVP and the C=O is becoming softer in the TTBPs assembly. This effect can be attributed the electron-donation from the electron-rich carbonyl portal to Ru(II), weakening the C=O bond. In consistent with the FTIR analysis, the XPS curves of O$_{1S}$ photoemission also indicate that in TTBPs the surface-adsorbed Ru(II) has a interaction with C=O from PVP molecules. As shown in Fig. S14, for 5-fold twinned Pd decahedrons, the $\nu_{\text{max}}$ in C=O has a peak at 531.3 eV, which is similar to pure PVP molecules. As a comparison, the corresponding energy in the TTBPs shifts to 532.3 eV (Fig. 2b), indicating an electron transfer from C=O to Ru(II). The atomic percentage of Ru(II) is 0.6% revealed by ICP. In contrast, the semi-quantitative result of XPS analysis shows that the percentage of Ru can reach 30 %. Such results suggest that Ru(II) are enriched on the surface of the formed TTBPs by interacting with with the surfactant PVP.

In theory, the surface-adsorbed Ru(II) can provide more favorite items for TTBPs’ application in electrocatalysis. First, the interaction between Ru(II) and PVP weakens the protecting ability of PVP to expose more active sites on Pd surface and consequently enhances the activity. Second, the Ru(II)-PVP species can act as a unique capsule protecting the Pd atoms from migrating and aggregating. And thus, the TTBPs demonstrate much more enhanced catalytic performance than 5-fold twinned Pd decahedrons.

References

1. K. Chan, L. E. Kostun, W. E. Tenhaeff and K. K. Gleason,
