## Branched Pd and Pd-based trimetallic nanocrystals with highly open structures for methanol electrooxidation

## Shengchang Jing, Xueli Guo, and Yiwei Tan\*

State Key Laboratory of Materials-Oriented Chemical Engineering, School of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, China, Email: <u>ytan@njtech.edu.cn</u>, Tel: +86-25-83172267

## **Experimental Section**

**Materials:** All reagents were commercially available and used as received. Palladium(II) chloride (PdCl<sub>2</sub>, Pd >59%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl<sub>4</sub> 3H<sub>2</sub>O, >99.9%), hydrogen hexachloroplatinate(IV) hydrate (H<sub>2</sub>PtCl<sub>6</sub> xH<sub>2</sub>O, >99.9%), copper(II) bromide (CuBr<sub>2</sub>, 99%), silver nitrate (99%), hydrochloric acid (36.5–38% HCl), ammonium hydroxide (25% NH<sub>3</sub>, 99%), sodium borohydride (>96%), and hexadecyltrimethylammonium bromide (CTAB, >99%) were commercially available from Sinopharm Chemical Reagent Co., Ltd.. L-Ascorbic acid (L-AA, >99%) was purchased from Alfa Aesar. An aqueous solution of 10 mM H<sub>2</sub>PdCl<sub>4</sub> was prepared by dissolving 0.089 g (0.5 mmol) of PdCl<sub>2</sub> in 50 mL of an aqueous solution of 0.02 M HCl at 60 °C under vigorous magnetic stirring and then used as the stock solution for the synthesis of branched Pd and Pd-based trimetallic NCs. Ultrapure water (18.2 MΩ) produced with a Milli-Q purification system was used in all syntheses and electrochemical measurements.

**Characterization:** A JEOL-1010 transmission electron microscope (TEM) operating at an accelerating voltage of 80 kV was used for taking traditional TEM micrographs. High resolution TEM (HRTEM) images were acquired using a FEI Tecnai G2 F20 S-Twin TEM operating at 200 kV. Scanning transmission electron microscopy (STEM) images, energydispersive X-ray spectroscopy (EDS), and elemental maps were obtained using the high-angle annular dark field (HAADF) mode on the same HRTEM. Specimens for TEM and HRTEM characterization were prepared by placing one drop of colloidal dispersions of purified branched NCs in water onto 300-mesh carbon-coated copper or nickel grids and drying under ambient conditions. Elemental analyses of the composition of the branched trimetallic NCs were carried out with EDS and inductively coupled plasma atomic emission spectrometry (ICP-AES, Teledyne-Leeman Laboratories Prodigy high dispersion ICP). X-ray photoelectron spectroscopy (XPS) measurements were conducted in an ion-pumped chamber (evacuated to  $6.7 \times 10^{-8}$  Pa) of a PHI5000 VersaProbe (Japan, ULVAC-PHI) spectrometer, employing a monochromatized microfocused Al- K $\alpha$  (hv = 1486.58 eV) X-ray source. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Smartlab diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) operating at 40 kV and 200 mA at a scanning rate of 6.0 °min<sup>-1</sup>.



**Figure S1.** (a–f) TEM images (top) and the corresponding models (down) of the branched Pd nanostructures with different shapes. (a) tripods with (i) a planar T-shape or (ii) the arms orthogonal to each other, (b) tetrapods with (iii) the arms being spaced obtuse angles apart from each other, (c) tetrapods with one arm perpendicularly bonding to other three pods with a planar (iv) T- or (v) Y-shape and a tetrapod with (vi) a cross-like shape, (d) pentapods with (vii) the arms orthogonal to each other or (viii) one arm perpendicularly bonding to a pyramid-like tetrapod, (e) hexapods with (ix) one arm perpendicularly bonding to a pyramid-like tetrapod, (e) hexapods with (ix) one arm perpendicularly bonding to a pyramid-like pentapod, and (f) hexapods with (x) the arms orthogonal to each other or (xi) multipods with the irregularly arrayed arms. (g) The morphology distribution histogram of the branched Pd nanostructures. Typically, the models at the bottom of panels a and c show the (i and iv) central cuboctahedral and (ii) multiple twinned nanoparticles for branching growth via oriented attachment process.



**Figure S2.** (a–c) HRTEM images of different branched Pd nanocrystals show zoom-in views of the central core domains with (a) multiple twinned or (b and c) single-crystalline structures. (d–f) The HRTEM images show the corresponding entire branched Pd nanocrystals. (g) Low- and (h) high-magnification HRTEM images show the single-crystalline features of a T-shaped tripod. The insets are the corresponding fast Fourier transform (FFT) patterns.



**Figure S3.** (a–e) TEM images showing the temporal structural evolution of the branched Pd nanocrystals prepared in the presence of  $NH_4OH$ : (a) 5 min, (b) 10 min, (c) 30 min, (d) 60 min, and (e) 90 min. The inset in panel a shows an enlarged view of the tiny Pd nanoparticles. (f) TEM image of the Pd nanocrystals prepared in the absence of  $CuBr_2$  while keeping other experimental parameters the same as in the preparation of branched Pd nanocrystals.



**Figure S4.** HRTEM images showing the oriented attachment of the Pd nanocrystals obtained after 10 min of reaction. (a) Attachment of multiple Pd nanocrystals. (b) A zoom-in view of the marked area shows the attachment of a Pd nanocrystal and a branch along the <200> crystallographic direction. (c) Two branches attached along the <200> crystallographic direction.



Figure S5. (a and b) High-magnification TEM images of the branched  $Pd@Pt_{72}Cu_{28}$  nanocrystals.



Figure S6. (a, c, and e) TEM and (b, d, and f) HRTEM images of the branched (a and b)  $Pd@Pt_{65}Cu_{35}$ , (c and d)  $Pd@Pt_{84}Cu_{16}$ , and (e and f) Pd@Pt nanocrystals synthesized with (a) 0.20, (b) 0.30, and (c) 0.10 mM H<sub>2</sub>PtCl<sub>6</sub> by

vigorously stirring the reaction solution for an additional time of (a) 30, (b) 45, or (c) 60 min upon completion of the addition of  $H_2PtCl_6$ . The insets show the corresponding FFT patterns.



 $\label{eq:Figure S7.EDS} Figure S7. EDS \ spectra \ of \ the \ branched \ (a) \ Pd@Pt_{65}Cu_{35}, \ (b) \ Pd@Pt_{84}Cu_{16}, \ and \ (c) \ Pd@Pt \ nanocrystals.$ 



**Figure S8.** HAADF-STEM images of the branched (a)  $Pd@Pt_{65}Cu_{35}$ , (b)  $Pd@Pt_{84}Cu_{16}$ , and (c) Pd@Pt nanocrystals. The aggregation of various branched nanocrystals is invoked by thoroughly washing the samples prior to depositing them onto carbon-coated nickel grids for HAADF-STEM characterization.





**Figure S9.** XPS spectra collected from the branched  $Pd@Pt_{65}Cu_{35}$ ,  $Pd@Pt_{72}Cu_{28}$ ,  $Pd@Pt_{84}Cu_{16}$ , Pd@Pt, Pd@AuCu, and Pd nanocrystals. (a) XPS survey spectra, (b) Pd 3d, (c) Pt 4f, (d) Au 4f, (e and f) Cu 2p, and (g and h) O 1s detail spectra.

For the branched Pd@AuCu or various Pd@PtCu nanocrystals, strong Au or Pt signals along with the moderate Pd and Cu signals are found besides O peaks. The chemical state of the surface species is analyzed according to binding energy (BE) data. The Pd 3d signals can be fitted into two pairs of doublets by deconvolution, one pair of peaks centered at 334.8 ( $3d_{52}$ ) and 339.9 eV  $(3d_{32})$  and the other pair of peaks at 337.2  $(3d_{52})$  and 342.6 eV  $(3d_{32})$  (Figure S9b), which can be indexed to the metallic Pd(0) and ionic Pd(II) species that are adsorbed or reoxidized, respectively.<sup>1</sup> Note that the peaks of ionic Pd(II) species from the branched Pd NCs have much higher intensities than those measured from the Pd@AuCu and various Pd@PtCu nanocrystals, presumably due to the significant etching of Pd nanocrystal surface in the presence of NH<sub>4</sub>OH. In contrast to the branched Pd@AuCu and various Pd@PtCu nanocrystals, the very weak Cu 2p signal from the branched Pd nanocrystals indicates trace Cu species adsorbed on their surface (Figure S9f). No Cu signal can be observed from the branched Pd@Pt nanocrystals, further confirming the composition of exclusive elements Pd and Pt. The Cu 2p and Pd 3d regions are integrated to quantify the surface composition of the branched Pd nanocrystals, which gives the atomic ratio of Cu to Pd close to 3.5/100. However, the Cu content is too low on the bulk level to be reliably discernible by XRD, EDS, and ICP-AES quantitative analyses. The Cu 2p signals from the branched Pd@AuCu and various Pd@PtCu nanocrystals can be fitted into two sets of peaks (see Figures S9e and S9f), which can be assigned to the species related to Cu(I) and Cu(II), respectively.<sup>23</sup> As compared to the Pd@Pt72Cu28 and Pd@Pt84Cu16 nanocrystals, the Cu signal of the Pd@Pt65Cu35 nanocrystals shows a higher relative intensity, indicating a higher ratio of Cu species at the nanocrystal surface (Figure S9a). In addition, the XPS spectra of the Cu 2p region show the shake-up satellites associated with CuO or CuO H<sub>2</sub>O,<sup>24</sup> originating from the reaction between Cu(I) and O<sub>2</sub>.<sup>5</sup> Figure S9g and S9h show that the O 1s main line and its satellite line are associated with the Cu or Pd atoms on the surface and the adsorbed OH species, respectively.



**Figure S10.** CV curves recorded in a N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution for determination of the ECSAs of (a) the branched Pd, Pd@Pt, and Pd@AuCu, and (b) different branched Pd@PtCu catalysts. The CV curve recorded from the commercial Pt/C control is also shown in panel (b) for comparison. All the measurements were carried out at a sweep rate of 50 mV s<sup>-1</sup> at room temperature. The inset in panel (a) shows the corresponding CV curves on an expanded Y-axis scale for clarity.

As shown in Figure S10a and S10b, CVs curves are used to determine the ECSAs of the branched Pd and the commercial Pt/C catalysts. The CV curve of each catalyst is recorded after the potential is continuously cycled between 0 and 1.2 V until a stable CV is obtained. The ECSA value of the Pt/C catalyst is obtained by measuring the total charge of hydrogen adsorption/desorption (Q) after deduction of the double-layer region on the corresponding CV curve and using 210  $\mu$ C cm<sup>-2</sup> as the value corresponding to the adsorption of a hydrogen monolayer (see Table 1 in the text). The Q value is determined by integrating the corresponding CV curve between 0 and 0.37 V. In the case of the branched Pd NCs, the ECSA value is estimated by taking into account the charge associated with the cathodic reduction of a PdO monolayer and by taking advantage of the formula of ECSA<sub>Pd</sub> = Q/S, where Q and S are coulombic charge and the charge required for reducing the PdO monolayer (424  $\mu$ C cm<sup>-2</sup>), respectively.<sup>6-8</sup> For the commercial PtRu/C catalyst, considering the Ru oxidation potential (ca. 0.25 V vs NHE) being within the range of the hydrogen oxidation potentials (0–0.3 V), the formula of ECSA<sub>PtRu</sub> = Q<sub>CO</sub>/420 is used to estimate the ECSA value. Q<sub>CO</sub> is the oxidation charge of CO stripping and can be calculated by integrating the area under CO stripping curve (see Figure 4 in the text). The oxidation charge for removing one monolayer of CO was assumed to be 420  $\mu$ C cm<sup>-2</sup> on PtRu surfaces.



**Figure S11.** (a) Mass activity normalized to the loading amount of noble metal and (b) specific activity CV curves of various catalysts for the MOR in a N<sub>2</sub>-purged solution of 0.5 M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub>. The CVs are recorded at a scan rate of 20 mV s<sup>-1</sup>. (c) Chronoamperometry (CA) and (d) the normalized current density–time curves of different catalysts. The CA measurements are carried out at an applied potential of 0.865 V<sub>RHE</sub> in a N<sub>2</sub>-purged solution of 0.5 M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Table S1. The parameters for the electrocatalytic performance of various catalysts toward the MOR in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

catalysts	specific activity $(mA cm^{-2})^{a}$	mass activity $(A m g_{NM}^{-1})^{a}$	peak potential (V vs RHE)	onset potential (V vs RHE) <sup>b</sup>
Pd				
Pd@AuCu	0.69	0.36	0.892	0.517
Pd@Pt <sub>65</sub> Cu <sub>35</sub>	1.74	0.72	0.874	0.483
Pd@Pt <sub>72</sub> Cu <sub>28</sub>	2.42	0.88	0.865	0.465
Pd@Pt84Cu16	1.62	0.62	0.895	0.500
Pd@Pt	0.80	0.33	0.895	0.504
PtRu/C	0.32	0.21	0.910	0.459 <sup>c</sup>
Pt/C	0.35	0.20	0.890	0.527

<sup>a</sup> The specific and mass activities are calculated at the corresponding peak potential of each catalyst. <sup>b</sup> The onset potential is determined at the potential when the specific current is  $10 \,\mu A \,\mathrm{cm}^{-2}$ . <sup>c</sup> While the commercial PtRu/C shows a lower onset potential for the MOR in acid solution than our prepared catalysts, it has a much lower peak current, higher peak potential, and poorer durability in comparison with various branched catalysts.







**Figure S12.** (a, c, e, g, i, and k) CV curves and (b, d, f, h, j, and l) TEM images recorded from (a and b) the branched  $Pd@Pt_{72}Cu_{28}$ , (c and d)  $Pd@Pt_{65}Cu_{35}$ , (e and f)  $Pd@Pt_{84}Cu_{16}$ , (g and h) Pd@AuCu, (i and j) Pd@Pt, and (k and l) Pd catalysts for the MOR in a N<sub>2</sub>-purged solution of 0.5 M methanol and 1 M NaOH. The CV curves for each catalyst were recorded after 1 and 10 000 potential cycles of the durability test. The TEM image of each catalyst is obtained after 10 000 potential cycles of CV measurements for the MOR.

catalysts	surface atomic ratio (in NaOH) Pd : Cu : Pt (Au)	surface atomic ratio (in H <sub>2</sub> SO <sub>4</sub> ) Pd : Cu : Pt (Au)
Pd@Pt <sub>65</sub> Cu <sub>35</sub>	15.6 : 34.3 : 50.1	15.2 : 33.1 : 51.7
Pd@Pt <sub>72</sub> Cu <sub>28</sub>	17.5 : 19.2 : 63.3	18.9 : 22.6 : 58.5
Pd@Pt <sub>84</sub> Cu <sub>16</sub>	14.8 : 19.7 : 65.5	15.7 : 17.9 : 66.4
Pd@AuCu	30.7 : 18.6 : 50.7	28.4 : 20.2 : 51.4

**Table S2.** The XPS surface chemical compositions of various Pd core–alloy shell catalysts after 10 000 potential cycles of CV measurements in 1 M NaOH or CA measurements for 5000 s in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

## **REFERENCES AND NOTES**

- 1. Y. Xiong, H. Cai, B. J. Wiley, J. Wang, M. J. Kim and Y. Xia, J. Am. Chem. Soc., 2007, 129, 3665–3675.
- M. Yin, C.-K. Wu, Y. Lou, C. Burda, J. T. Koberstein, Y. Zhu and S. O'Brien, J. Am. Chem. Soc., 2005, 127, 9506– 9511.
- 3. C. D. Wagner, W. M. Riggs, L. E. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelectron spectroscopy*, Perkin-Elmer Corporation Physical Electronics Division, U.S.A., 1979.
- 4. Q. Yu, X. Ma, Z. Lan, M. Wang and C. Yu, J. Phys. Chem. C, 2009, 113, 6969–6975.
- 5. T. S. Sreeprasad, A. K. Samal and T. Pradeep, *Langmuir*, 2007, **23**, 9463–9471.
- 6. P. Kannan, T. Maiyalagan and M. Opallo, *Nano Energy*, 2013, 2, 677–687.
- 7. M. T. Gorzkowski and A. Lewera, J. Phys. Chem. C, 2015, 119, 18389–18395.
- 8. L. Xiao, L. Zhuang, Y. Liu, J. Lu, H. D. Abruña, J. Am. Chem. Soc., 2009, 131, 602–608.