## Concave and Duck Web-like Platinum Nanopentagons with Enhanced Electrocatalytic Properties for Formic Acid Oxidation

Jianping Lai,<sup>a,b</sup> Wenxin Niu,<sup>a</sup> Suping Li,<sup>a</sup> Fengxia Wu,<sup>a,b</sup> Rafael Luque,\*,<sup>a,c</sup> and Guobao Xu\*,<sup>a</sup>

<sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, PR China;

<sup>b</sup> University of the Chinese Academy of Sciences, Chinese Academy of Sciences, No. 19A Yuquanlu, Beijing 100049, PR China.

<sup>c</sup> Departamento de Química Orgánica, Universidad de Córdoba Campus de Rabanales, Edificio Marie Curie (C-3), Ctra Nnal IV, Km 396, Córdoba (Spain), E-14014.

**Table S1.** Specific peak current density  $(J_s)$ , mass peak current density  $(J_m)$ , the residual current densities  $(J_{2000s})$ , and Normalized  $J_s$  (%) during the 2000s test for FOR on Pt black, Pt/C, Pd/C and Pt CWPNP in 0.5M H<sub>2</sub>SO<sub>4</sub> and 0.5M formic acid.

|          | J <sub>s</sub> /mAcm <sup>-2</sup> | $J_m/mAmg^{-1}$ | $J_{2000s}/mA \ cm^{-2}$ | Normalized $J_s$ (%) |
|----------|------------------------------------|-----------------|--------------------------|----------------------|
| Pt black | 0.21                               | 32              | 0.02                     | 11                   |
| Pt/C     | 0.66                               | 108             | 0.14                     | 27                   |
| Pd/C     | 2.52                               | 432             | 0.12                     | 5                    |
| Pt CWPNP | 5.63                               | 739             | 1.62                     | 32                   |

Table S2. Specific activity of novel Pt CWPNP catalyst compared with others

| Catalysts                   | J <sub>s</sub> /mAcm <sup>-2</sup> | references       |  |
|-----------------------------|------------------------------------|------------------|--|
| Pt CWPNP                    | 5.63                               | This work $\Box$ |  |
|                             |                                    |                  |  |
| Ordered Pt <sub>3</sub> Ti  | 0.61                               | 1                |  |
| Pt-Cu nanocube              | 2.29                               | 2                |  |
| Pd/GO                       | 5.2                                | 3                |  |
| Branched Pt                 | 1.5                                | 4                |  |
| Sb/Pt <sub>octahedral</sub> | 2.8                                | 5                |  |
| Pd-Ni <sub>2</sub> P/C      | 2.2                                | 6                |  |
| ERD PtCu <sub>3</sub>       | 3.15                               | 7                |  |
| $Pt_7Ru_{1.5}Fe_{1.5}NW$    | 2.15                               | 8                |  |
| PtCu HTBNFs                 | 3.77                               | 9                |  |
|                             |                                    |                  |  |



**Figure S1.** Image of solutions before and after the solvothermal reaction. Synthetic solution: 4 mL of oleylamine and 4 mL of tri-*n*-propylamine containing 5 mg of platinum (II) acetylacetonate.



**Figure S2.** Large-area FESEM image of Pt CWPNP. Synthetic solution: 4 mL of oleylamine and 4 mL of tri-*n*-propylamine containing 5 mg of platinum (II) acetylacetonate.



**Figure S3.** FESEM image of Pt CWPNP. Synthetic solution: 4 mL of oleylamine and 4 mL of tri-*n*-propylamine containing 5 mg of platinum (II) acetylacetonate.



Figure S4. (A) TEM image of Pt CWPNP and (B) corresponding SAED pattern of Pt CWPNP.



Figure S5. HRTEM images of Pt duck-web like edges. Inset: corresponding FFT pattern.



Figure S6. EDX spectrum of Pt CWPNP.



Figure S7. XRD pattern of Pt CWPNP.



**Figure S8.** FESEM image of Pt nanostructures obtained in 4 mL of oleylamine and 4 mL of tri-*n*-propylamine containing 6.6 mg  $H_2$ PtCl<sub>6</sub>•6H<sub>2</sub>O.



**Figure S9.** Large-area FESEM image (Upper) and enlarged FESEM image (Low) of Pt nanoparticles obtained in the absence of tri-*n*-propylamine (8 mL oleylamine containing 5 mg platinum (II) acetylacetonate).



**Figure S10.** Large-area FESEM images (Left) and enlarged FESEM images (right) of Pt nanoparticles obtained at different tri-*n*-propylamine/oleylamine volume fractions. A) 2 mL: 6 mL, B) 6 mL: 2 mL, C) 8 mL: 0 mL.



**Figure S11.** Large-area FESEM images (Left) and enlarged FESEM images (right) of Pt nanostructures obtained in 4 mL of oleylamine and 4 mL of A) ethylenediamine; B) *n*-Butylamine and C) tributylamine; all containing 5 mg platinum (II) acetylacetonate.



**Figure S12.** Fourier transforms infrared (FT-IR) spectra of pure oleylamine, tri-*n*-propylamine and the purified Pt CWPNP (product). It can be seen that some weak peaks, corresponding to  $v_{-NH2}$ ,  $\delta_{=CH}$ ,  $v_{-CH2}$ ,  $v_{-CH3}$ ,  $\delta_{-NH2}$ ,  $\delta_{-CH2}$ , and some strong peaks, corresponding to  $\delta_{-CH3}$  and  $\delta_{-C-N}$  appeared in the FT-IR spectra of the purified Pt CWPNP, suggesting the small amount of residual adsorption of oleylamine and tri-n-propylamine on the surface of Pt CWPNP.



**Figure S13.** Cyclic voltammograms of Pt black, Pt/C, Pd/C and Pt CWPNP -modified glassy carbon electrodes in  $0.5 \text{ M H}_2\text{SO}_4$  solution (scan rate: 50 mV/s).



**Figure S14.** Normalized specific peak current density (100%)-cycling numbers curve of 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.5 M formic acid for Pt black (square), Pt/C (dot), Pd/C (triangle) and Pt CWPNP (inverted triangle)-modified glassy carbon electrode.



Figure S15. SEM images of Pt CWPNP after stability tests.

## References

1. H. Abe, F. Matsumoto, L. R. Alden, S. C. Warren, H. D. Abruña and F. J. DiSalvo, *J. Am. Chem. Soc.*, 2008, **130**, 5452-5458.

2. D. Xu, S. Bliznakov, Z. Liu, J. Fang and N. Dimitrov, *Angew. Chem. Int. Ed.*, 2010, **49**, 1282-1285.

3. X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie and X. Wang, J. Am. Chem. Soc., 2011, 133, 3693-3695.

4. L. Ma, C. Wang, M. Gong, L. Liao, R. Long, J. Wang, D. Wu, W. Zhong, M. J. Kim, Y. Chen, Y. Xie and Y. Xiong, *ACS Nano*, 2012, **6**, 9797-9806.

5. F. J. Vidal-Iglesias, A. López-Cudero, J. Solla-Gullón and J. M. Feliu, *Angew. Chem. Int. Ed.*, 2013, **52**, 964-967.

6. J. Chang, L. Feng, C. Liu, W. Xing and X. Hu, Angew. Chem. Int. Ed., 2014, 53, 122-126.

7. Y. Jia, Y. Jiang, J. Zhang, L. Zhang, Q. Chen, Z. Xie and L. Zheng, J. Am. Chem. Soc., 2014, **136**, 3748-3751.

8. M. E. Scofield, C. Koenigsmann, L. Wang, H. Liu and S. S. Wong, *Energy Environ*. *Sci.*, 2015, **8**, 350-363.

9. S. Chen, H. Su, Y. Wang, W. Wu and J. Zeng, *Angew. Chem. Int. Ed.*, 2014, **54**, 108-113.