

2014-08-28

## Electrochemical Fabrication of Two-Dimensional Flower-like Pt Nanostructures for Methanol Electrocatalytic Oxidation

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### Recommended Citation

Xia WANG, Jun HU, Yong-Jun LI. Electrochemical Fabrication of Two-Dimensional Flower-like Pt Nanostructures for Methanol Electrocatalytic Oxidation[J]. *Journal of Electrochemistry*, 2014 , 20(4): 365-369.

DOI: 10.13208/j.electrochem.131166

Available at: <https://jelectrochem.xmu.edu.cn/journal/vol20/iss4/11>

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DOI: 10.13208/j.electrochem.131166

Artical ID:1006-3471(2014)04-0365-05

Cite this: *J. Electrochem.* 2014, 20(4): 365-369

Http://electrochem.xmu.edu.cn

# 电化学制备二维“花状”Pt 纳米结构及其对甲醇的电催化氧化

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**摘要:** 采用恒电流电化学技术在玻碳基底上制得二维“花状”Pt 纳米结构(2D FPNs)样品, 所用的电解液为  $\text{HAuCl}_4 + \text{HClO}_4$  溶液, 无需添加任何表面结构诱导的有机试剂, Pt 纳米结构表面更“洁净”, 有较高的反应活性. 扫描电子显微镜测试显示, 2D FPNs 样品是由球状纳米花构成, 纳米叶子是构筑纳米花的最小单元. 通过控制电沉积时间可调控球状 Pt 纳米花数的密度. 高倍透射电子显微镜测试表明每个叶状纳米片沿着 Pt(111)晶面定向生长. 甲醇电催化氧化活性与电沉积时间有关. 2D FPNs 电极的甲醇的电催化活性稍高于商业 Pt/C 电极, 却有更好的抗毒化能力, 这可能归因于其特定的暴露晶面及表面的“洁净性”.

**关键词:** 铂; 甲醇; 纳米结构; 电沉积; 电催化氧化

中图分类号: O646

文献标识码: A

Pt 纳米粒子的甲醇氧化易产生中间体(如 CO)而毒化, 导致其电催化活性降低<sup>[1-2]</sup>. 目前, Pt 的复合金属或金属氧化物催化剂有 Pt-ZnO<sup>[3]</sup>、Au/Pt/Au<sup>[4]</sup>、PtRu<sup>[5]</sup>、PtPd<sup>[6]</sup>、PtTe<sup>[7]</sup>和 PtFeCo<sup>[8]</sup>等, 与纯 Pt 催化剂相比, 这些复合催化剂可能因其电子结构不同而有较高的电催化活性或抗毒化能力. 热分解  $\text{Fe}(\text{CO})_5$  和  $\text{Pt}(\text{acac})_2$  制备得  $\text{Fe}_{28}\text{Pt}_{38}\text{Pd}_{34}$ , 其甲醇电催化氧化活性较纯 Pt 纳米粒子提高了 2.4 倍<sup>[9]</sup>. Pt 电催化能力与其晶面有关, 尤其特定暴露晶面. Pt 纳米催化剂可呈不同形状, 进而有不同的电催化活性. 高指数晶面的 Pt 凹多面体, 其乙醇电催化活性分别是商业铂黑和 Pt/C 的 4.2 倍和 6 倍<sup>[10]</sup>. Pt 纳米形态主要有立方体<sup>[11]</sup>、纳米棒<sup>[12]</sup>、纳米线<sup>[13]</sup>及纳米叉<sup>[14]</sup>等. 这些纳米粒子的制备方法通常有溶液氧化还原法和电化学沉积法. 电沉积法简单、快捷<sup>[15]</sup>, 如采用方波技术制备 32 面体的 Pt 纳米晶<sup>[16]</sup>, 其高指数晶面的暴露, 在乙醇和甲酸中均呈现出优越的电催化活性<sup>[16]</sup>.

本文采用恒电流技术制备 2D“花状”Pt 纳米结构(2D FPNs), 表征其纳米结构形貌, 测试其甲醇的电催化氧化性能及其抗毒化能力.

## 1 实验

### 1.1 化学试剂

氯铂酸钾( $\geq 99.79\%$ )、高氯酸( $\geq 72.0\%$ )、甲醇(AR)、硫酸(AR)均购自上海国药集团化学试剂有限公司. Milli-Q 实验用水. Pt/C (20% Pt, by mass, 下同, 商业催化剂, Johnson Matthey).

### 1.2 二维“花状”Pt 纳米结构的制备

电沉积三电极电解池中如图 1 所示, 由饱和甘汞参比电极(SCE)、铂丝对电极(CE)以及玻碳基底(GC,  $\phi = 3 \text{ mm}$ )工作电极(WE)构成. 电沉积之前, GC 分别用  $1.0 \mu\text{m}$ 、 $0.3 \mu\text{m}$  和  $0.05 \mu\text{m}$  的氧化铝粉抛光, 依次用水和乙醇超声清洗至干净.  $50 \text{ mL K}_2\text{PtCl}_6(2.0 \text{ mmol} \cdot \text{L}^{-1}) + \text{HClO}_4(1.0 \text{ mol} \cdot \text{L}^{-1})$  为电解液. 采用  $3.5 \text{ mA} \cdot \text{cm}^{-2}$  的恒电流密度电沉积. 电沉积时间分别为 20 min、40 min 和 60 min. 电沉积后, 用水洗净所得即 Pt 纳米结构工作电极.

商业 Pt/C 电极: 将 5 mg Pt/C 超声分散于 1 mL Nafion 乙醇(0.05%)溶液中, 取  $3.0 \mu\text{L}$  滴加于 GC 基底, 室温下干燥即可.

### 1.3 甲醇电化学氧化

三电极电化学体系由饱和甘汞参比电极(SCE)、铂丝对电极和 Pt/GC 电极组成. 该电极先于  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ 、 $-0.25 \sim 1.2 \text{ V}$  电位下以  $50 \text{ mV} \cdot \text{s}^{-1}$

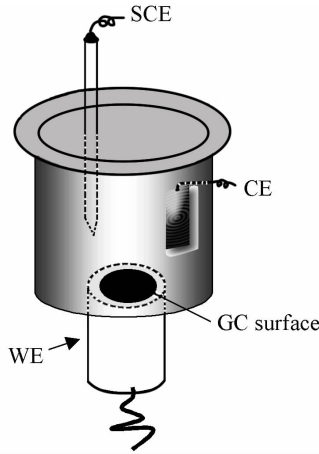


图 1 倒置三电极电解池示意图

Fig. 1 The schematic illustration of an inverted three-electrode cell

扫描速率循环伏安扫描, 清洁 Pt 纳米结构表面, 直到循环伏安曲线稳定. 随之再将电极插入到 50 mL  $H_2SO_4(0.5 \text{ mol} \cdot L^{-1}) + CH_3OH(1.0 \text{ mol} \cdot L^{-1})$  水溶液中, 通  $N_2$  20 min, 除溶解氧, 并维持  $N_2$  气氛保护下测试甲醇氧化曲线.

### 1.4 仪器与测量

使用 CHI660D 型电化学工作站(上海辰华)测试电极的电化学特性. 使用 Hitachi-S4800 扫描电子显微镜(日本, Hitachi)及附带 X 射线能量色散谱(EDS)的 T20 型的高倍透射电子显微镜(美国, FEI), 观察样品的形貌与结构, 其工作电压分别为 5 kV 与 200 kV.

## 2 结果与讨论

### 2.1 不同电沉积时间的样品形貌

图 2 是不同沉积时间 2D FPNs 样品的 SEM 照片. 从图 2A 中可以看到, 电极表面铺满了直径为 260 nm ~ 470 nm 花状 Pt 纳米球, 并相互连接形成 2D 纳米结构. 单个花状 Pt 纳米球(SEM 插图)由厚度大约为 10 nm 的纳米叶子构成. 电沉积时间增加至 40 min, 花状纳米球间的空隙减少并相互连接, 而大多数的纳米球形貌还可分辨(图 2B). 60 min 电沉积时间下, 单个花状纳米球形态已经不能分辨, 观察到由纳米叶子组成的 2D 致密结构(图 2C).

图 3A 是 Pt 纳米叶子样品的高分辨 TEM 照片. 从图中可以清楚地看到样品晶格条纹, 其晶格间距 0.21 nm, 属于(111)晶面(JCPDF04-0802). 这些晶格条纹呈平行状, 整个 Pt 纳米叶子沿着 Pt(111)晶面

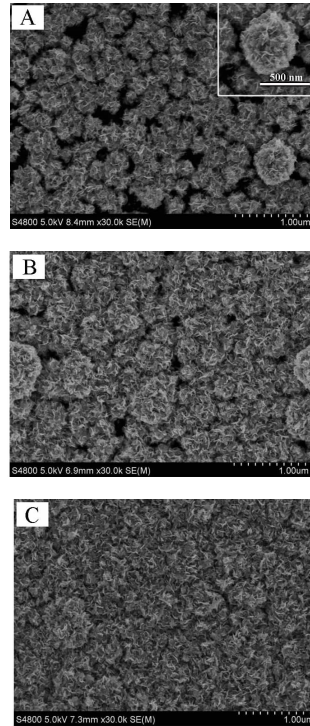


图 2 不同电沉积时间 2D FPNs 样品的 SEM 照片: A. 20 min; B. 40 min; C. 60 min (插图为高倍 SEM 照片)

Fig. 2 SEM images of 2D FPNs with different electrodeposition time: A. 20 min (inset shows higher magnification); B. 40 min; C. 60 min

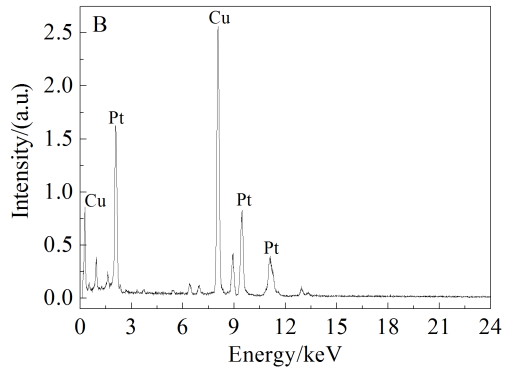
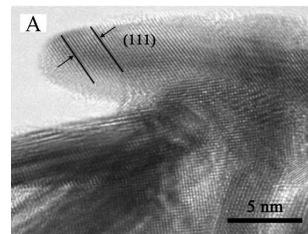


图 3 40 min 电沉积的 2D FPN 样品的 HRTEM 照片(A) 和 EDS 谱图(B)

Fig. 3 HRTEM image (A) and EDS pattern (B) of 2D FPN after electrodepositing for 40 min

方向生长. EDS 谱图中除了来自基底 (Cu 网)Cu 外,只存在 Pt 的特征峰(图 3B),属纳米结构纯 Pt.

## 2.2 Pt/GC 电极的电化学活性面积

图 4 是不同电沉积时间 2D FPNs 电极在  $\text{H}_2\text{SO}_4$  溶液的循环伏安曲线. 从图看出,各电极在  $-0.25 \sim 0.05 \text{ V}$  电位区间均出现了氢特征吸脱附峰.  $\sim 0.5 \text{ V}$  处为 Pt 氧化物的特征还原峰. 电沉积时间从 20 min 增加至 40 min,不论氢的吸脱附峰或 Pt 的还原峰,其电流均增加. 电沉积时间增加至 60 min, Pt 还原峰电流增加,而其氢吸脱附峰电流变化不大,这可能归因于氢吸脱附能力受晶面影响,而 Pt 氧化还原只取决于电位. 尽管如此,其电催

化活性面积 (ESAs) 仍可用传统氢吸脱附峰电量估算<sup>[17]</sup>(图 4B). 随电沉积时间增加,ESAs 逐渐增加,40 min 后其增加趋于缓慢,沉积时间过长,底层大量的 Pt 却不能有效利用.

## 2.3 甲醇氧化电催化活性

图 5A 给出不同电沉积时间 2D FPNs 电极在  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$  水溶液中的循环伏安曲线 (图中为归一化电流密度). 正向扫描,在  $\sim 0.65 \text{ V}$  处的氧化峰归因于甲醇的直接氧化;负向扫描  $0.43 \sim 0.48 \text{ V}$  范围出现了另一氧化峰,即为该电极表面正向扫描甲醇氧化产生的中间体进一步氧化<sup>[18-19]</sup>. 40 min 电沉积时间 2D FPN

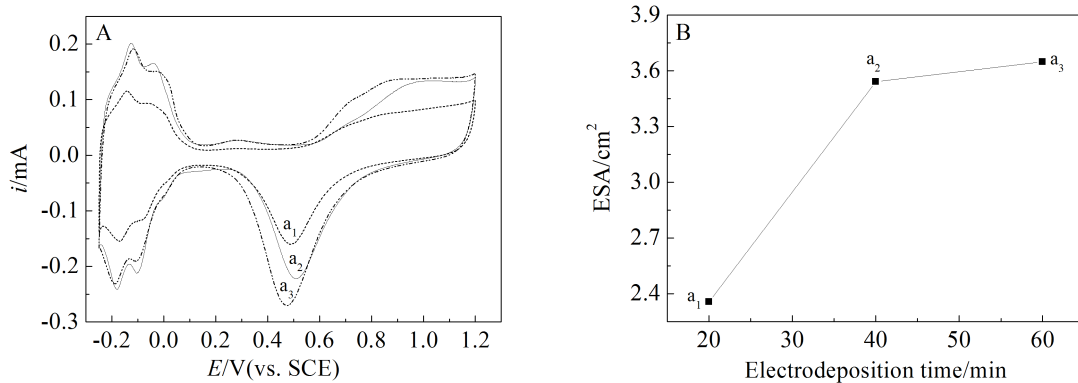


图 4 A. 不同电沉积时间下的 2D FPNs 在  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$  溶液中的循环伏安曲线:  $a_1$ , 20 min;  $a_2$ , 40 min;  $a_3$ , 60 min. 扫描速率为  $50 \text{ mV} \cdot \text{s}^{-1}$ . B. 电化学活性面积 (ESAs) 与电沉积时间曲线

Fig. 4 A. Cyclic voltammograms of 2D FPNs with different electrodeposition time in  $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$  solution:  $a_1$ , 20 min;  $a_2$ , 40 min;  $a_3$ , 60 min. The scan rate is  $50 \text{ mV} \cdot \text{s}^{-1}$ . B. Correlation between ESAs of 2D FPNs and electrodeposition time

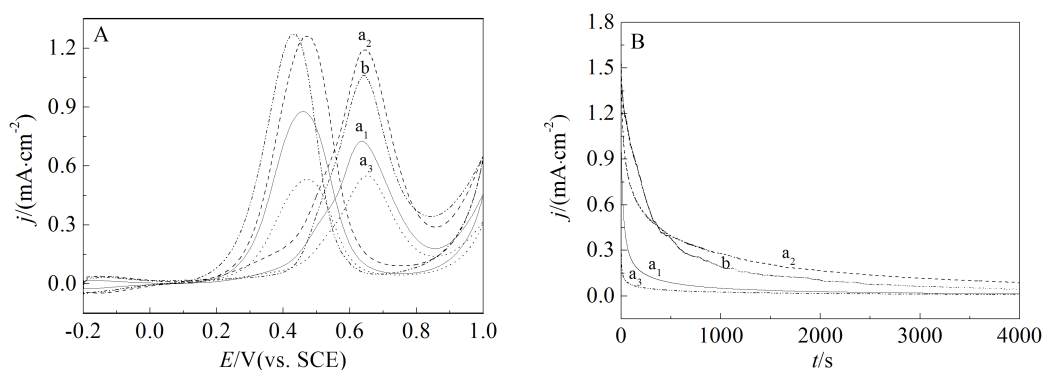


图 5 不同电沉积时间 2D FPNs 电极在  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$  溶液的循环伏安曲线 (A) 及其电流-时间曲线 (B):  $a_1$ , 20 min;  $a_2$ , 40 min;  $a_3$ , 60 min; b. 商业 Pt/C 电极. 循环伏安的扫描速率为  $50 \text{ mV} \cdot \text{s}^{-1}$ , 电流-时间曲线的极化电位为  $0.6 \text{ V}$

Fig. 5 Cyclic voltammograms (A) and  $j-t$  polarization curves (B) of as-prepared 2D FPNs with different electrodeposition time in  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{ CH}_3\text{OH} + 0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ :  $a_1$ , 20 min;  $a_2$ , 40 min;  $a_3$ , 60 min; b. commercial Pt/C. The scan rate of cycle voltammograms was  $50 \text{ mV} \cdot \text{s}^{-1}$ . The potential of  $j-t$  curve was  $0.6 \text{ V}$ .

电极的甲醇电催化氧化电流密度最大, 电极的活性最佳; 60 min 电沉积 2D FPN 电极的电催化活性最差; 20 min 电沉积 2D FPN 电极的电催化活性居中. 20 min 和 60 min 电沉积时间 2D FPN 电极的电催化活性均不如商业 Pt/C 电极, 而 40 min 电沉积 2D FPN 电极的电催化活性为商业 Pt/C 电极的 1.1 倍, 二者活性基本相当. 图 5B 给出了不同电沉积 2D FPNs 电极的电流-时间曲线. 从图中可以看到, 4000 s 时, 40 min 电沉积 2D FPN 电极的电催化活性为商业 Pt/C 电极的 2 倍. 而 20 min 和 60 min 电沉积下 2D FPNs 的稳定性均较商业 Pt/C 电极差. 这些样品的唯一差异就是电极表面纳米花状叶子数的密度, 从而导致电极电催化活性如此变化. 可以推测, 催化剂粒子之间的空间排布有可能影响着表面催化动力学.

### 3 结 论

恒电流电沉积技术制得 2D “花状”Pt 纳米结构(2D FPNs)样品, 其由纳米叶子构成. 花状 Pt 纳米花, 结构层次分明, Pt 纳米叶子可沿着 Pt(111)晶面定向生长形成. 与 Pt/C 电极相比, 2D FPN 电极(40 min 电沉积)的甲醇初期电催化活性稍优于商业 Pt/C 催化剂, 而 4000 s 后有 2 倍的电催化活性, 抗毒化性能更好.

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## Electrochemical Fabrication of Two-Dimensional Flower-like Pt Nanostructures for Methanol Electrocatalytic Oxidation

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**Abstract:** Two-dimensional flower-like Pt nanostructures (2D FPNs) were fabricated on glassy carbon substrates by galvanostatical electrochemical technique. The electrolyte was the  $\text{HAuCl}_4 + \text{HClO}_4$  aqueous solution without addition of any structure-directing organic reagent, which made as-prepared Pt nanostructures cleaner, exhibiting much higher reactivity. Scanning electron microscopic images revealed that 2D FPNs were spherical Pt nano-flowers constructed by the smallest building blocks, nano-leaves. The number density of spherical Pt nano-flowers can be tuned by controlling the electrodeposition time. High resolution transmission electron microscopic images indicated that each nano-leaf was formed by growing along Pt(111) direction. Electrocatalytic activities of as-prepared 2D FPNs were closely linked with the electrodeposition time. The electrocatalytic activity of 2D FPNs under the optimized electrodeposition time was slightly higher than that of the commercial Pt/C catalyst with much better tolerance to CO-like poisoning molecules. It may be attributed to the exposure of specified facets and the cleanness of surface.

**Key words:** platinum; methanol; nanostructure; electrodeposition; electrocatalytic; oxidation