



《电化學》期刊公益大讲坛系列

燃料电池低/非铂电催化剂 基础与应用研究

徐维林

中科院长春应用化学研究所

2020-05-30

研究背景

催化在能源高效利用与转化中发挥不可替代的作用

环境

绿水青山就是金山银山

——习近平



传统能源



燃料电池
洁净能源



传统能源

精准设计与制备高效催化剂

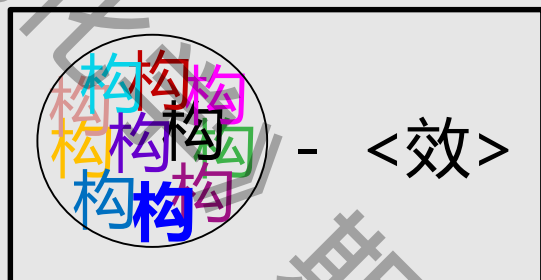
是当前洁净能源利用的重要基础

挑战性科学问题

如何实现精准设计高效催化剂？构—效

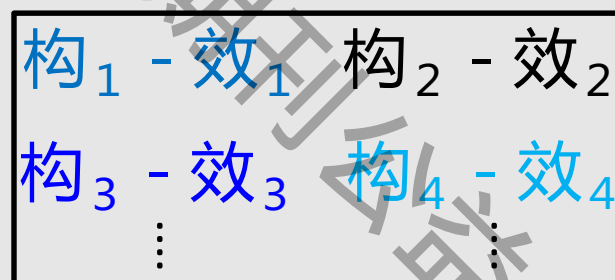
差之毫厘，谬以千里

传统催化研究手段不足



掩盖重要个性化信息
错失“最优结构”的发现

一个粒子一个粒子的研究



揭示众多精准“构—效”关系
找到最优“构—效”关系信息

单粒子催化

揭示单粒子个性化催化、催化信息原子/位点

The Main Research Topics

Basic research based on single molecule method:

- SM study for some practical reaction/catalytic process
electro-oxidation, O₂ reduction, photo/electrocatalysis,
photosynthesis;
- Developing new tools for SM study:
Integrated microscopy by combining TEM with optical microscopy;

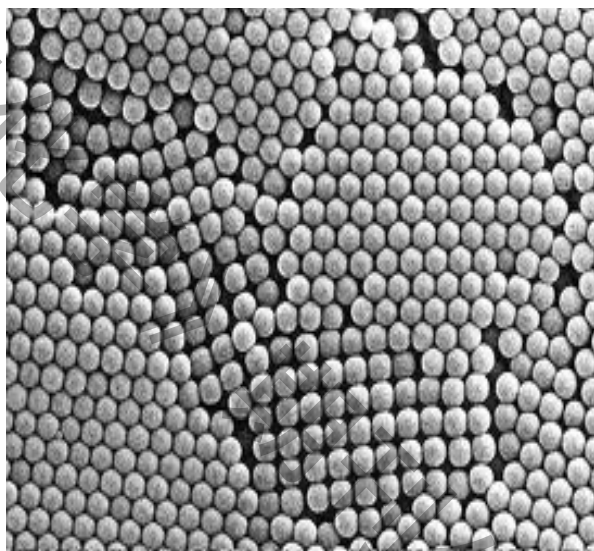
Practical research:

- New functional materials for energy process;
- New devices for energy harvesting.

Part A: Single molecule/single nanoparticle catalysis

Why need to study from single molecule level/Advantages?

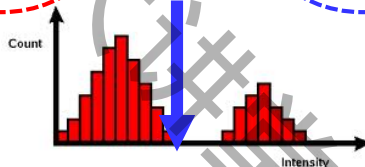
Traditional ensemble method



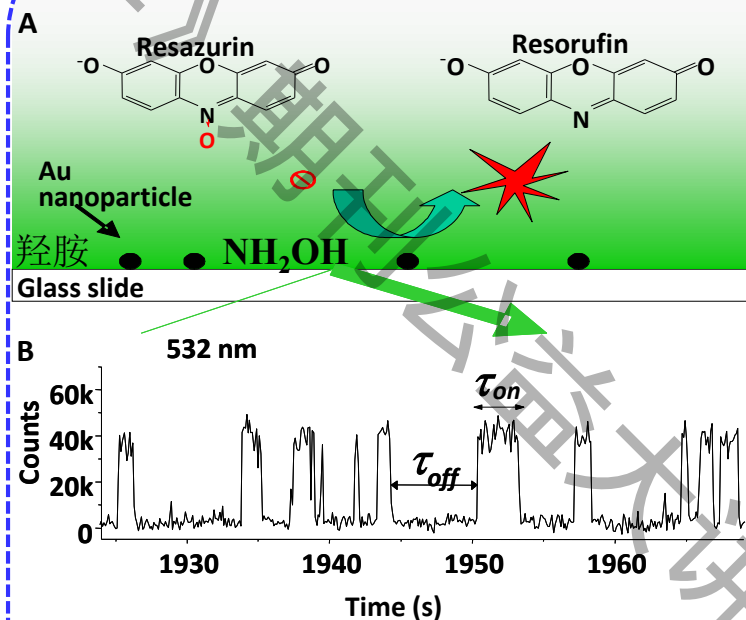
每个数据或现象都是来自无数个分子或纳米粒子的平均

整体平均

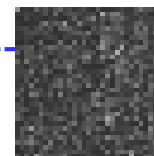
均值



Single Molecule Method



每个数据/现象都来自一个分子或纳米粒子



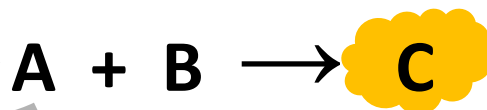
局限性！！

?

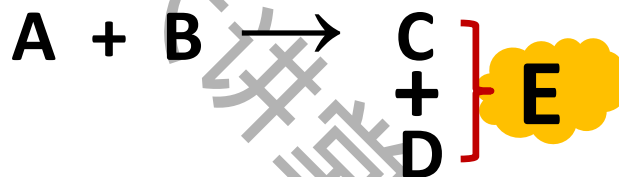
离不开荧光探针分子！

研究
方式

直接研究： 反应过程中的反应物或产物有荧光



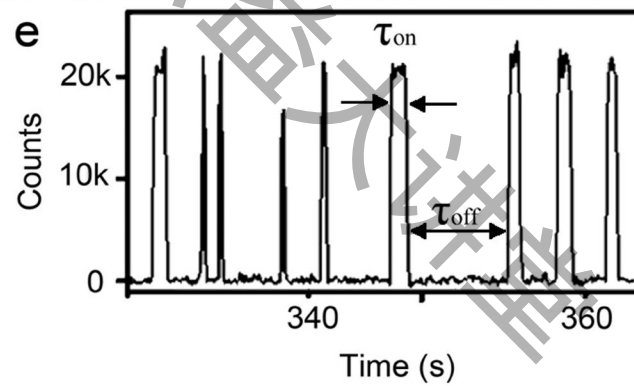
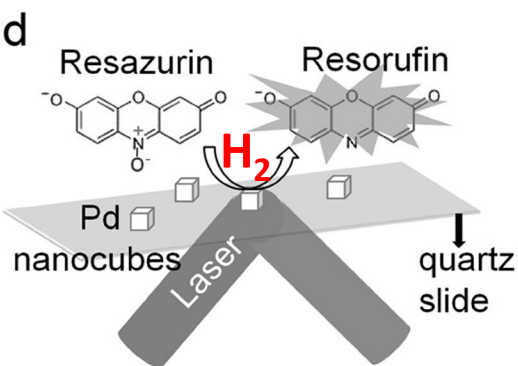
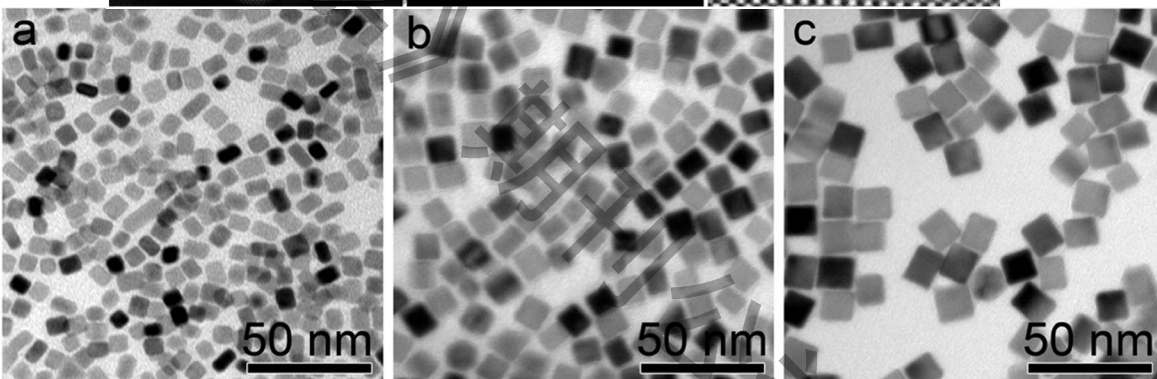
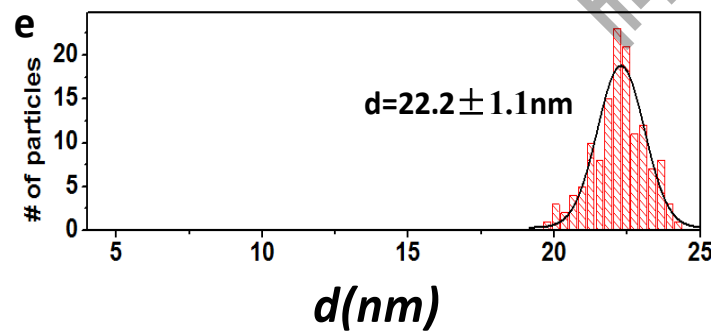
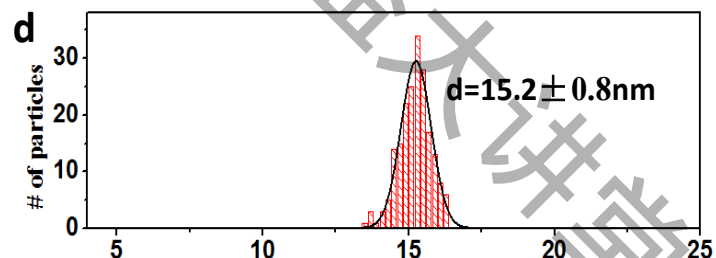
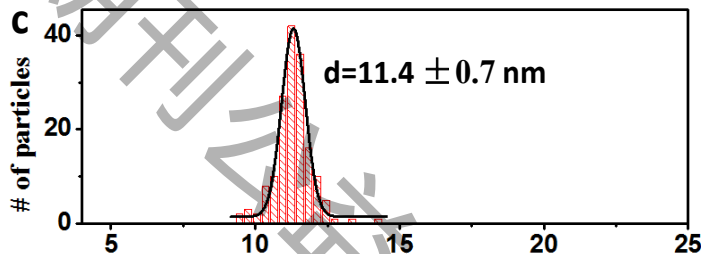
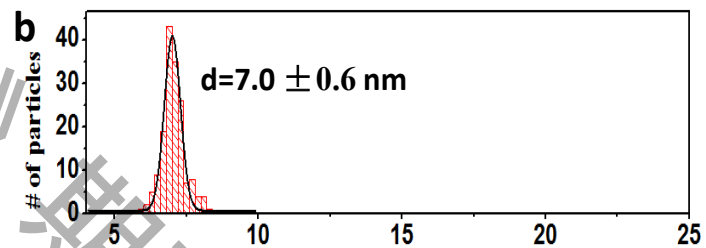
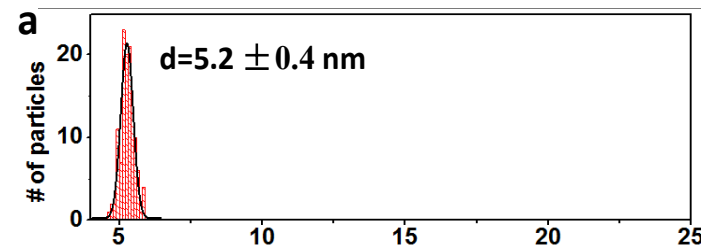
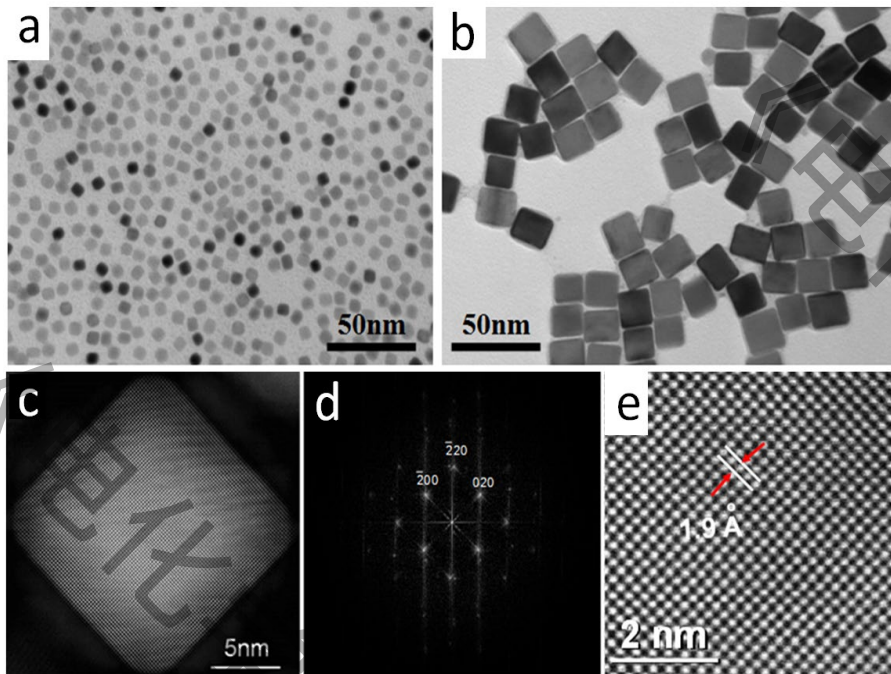
间接研究： 用某种荧光探针与所关注的反应过程结合上



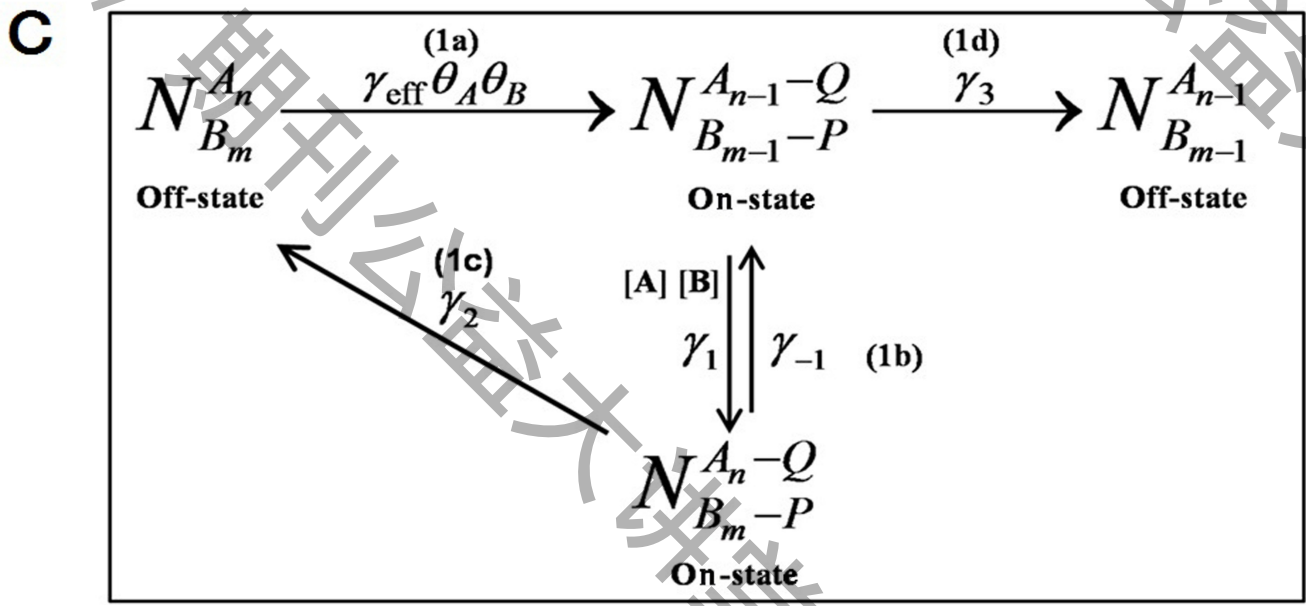
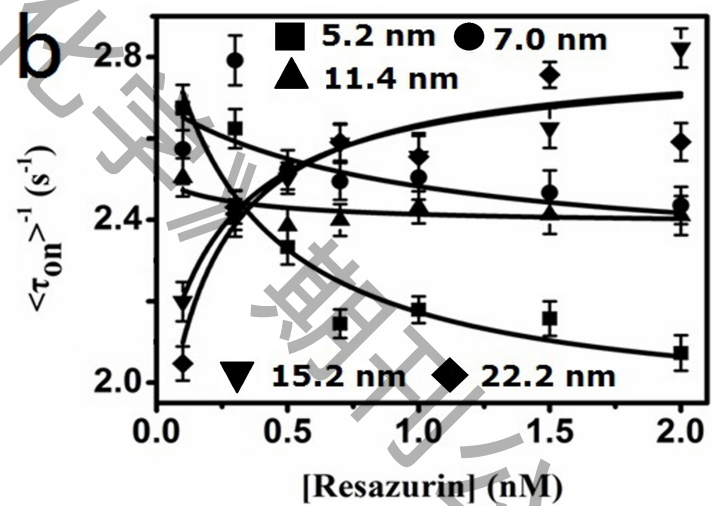
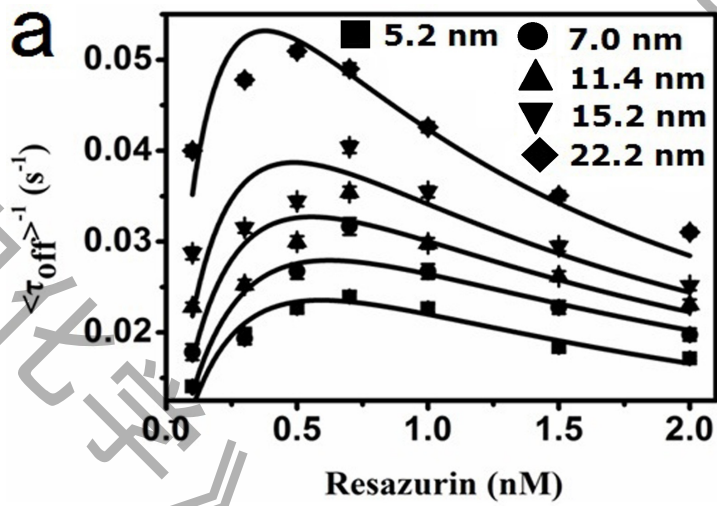
Example One:

New method to study the catalytic kinetics of sub-particles

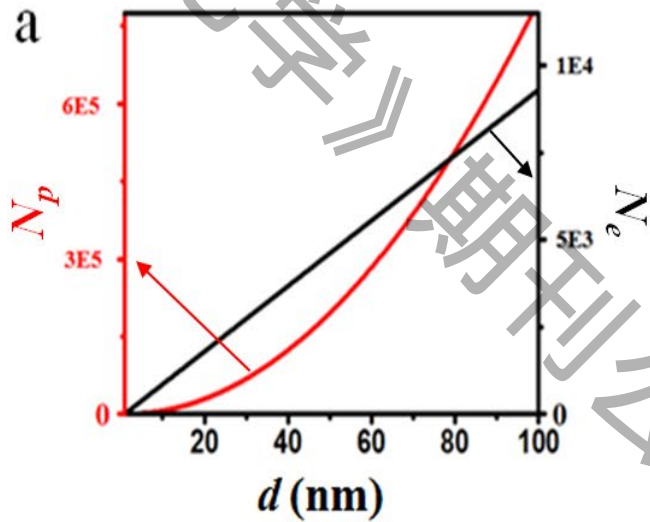
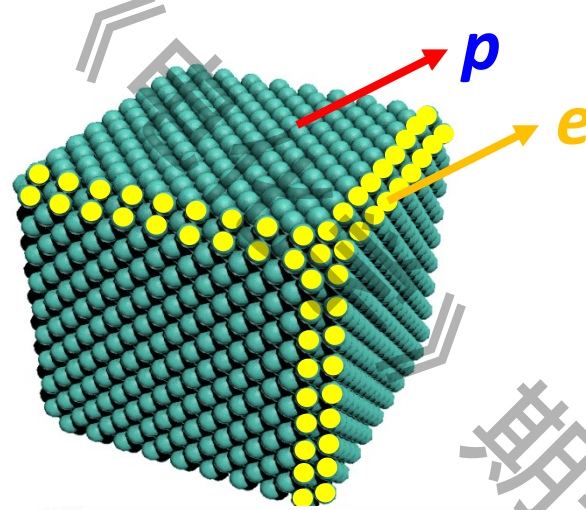
Catalytic Kinetics of Different Types of Surface Atoms on Shaped Pd Nanocrystals



For a whole single nanoparticle

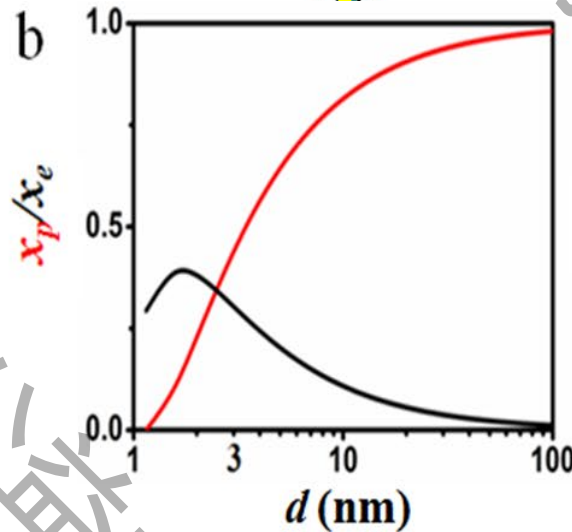


Deconvolution into the contributions from plane and edge atoms



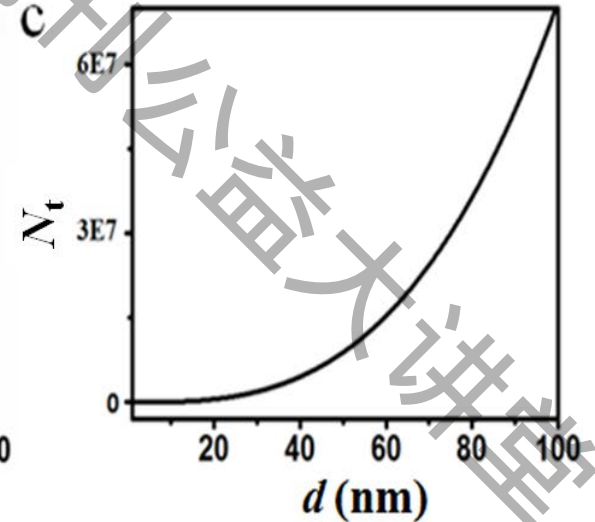
$$m = d/2^{1/2}L_{Pd-Pd} + 1$$

$$N_s = 12m^2 - 12m - 4$$



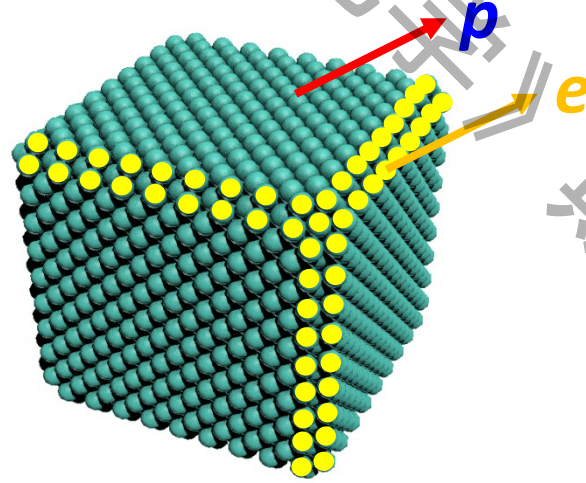
$$N_e = 20 + 36(m-3)$$

$$N_p = 12(m-3)^2$$



$$N_t = 4m^3 - 9m + 6$$

Deconvolution into the contributions from plane and edge atoms

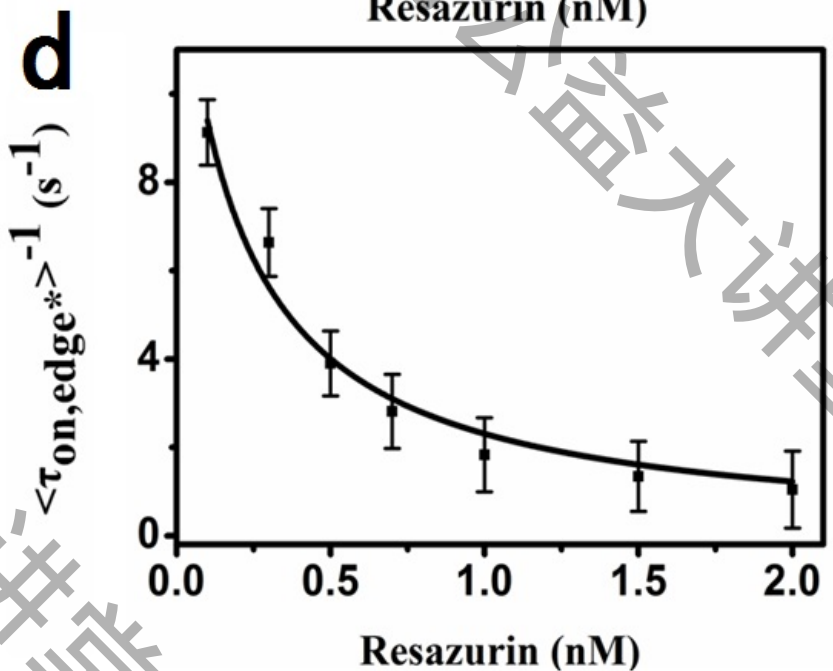
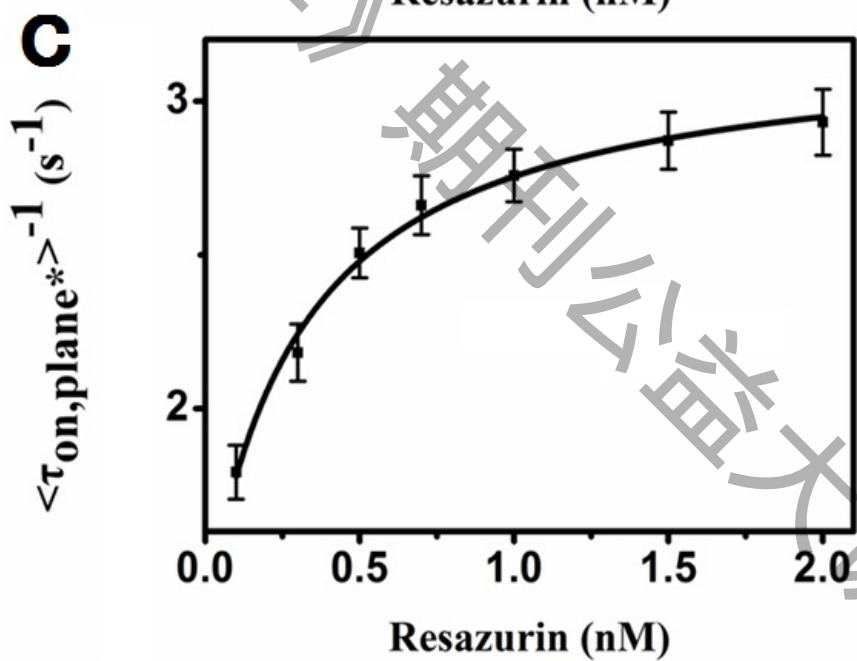
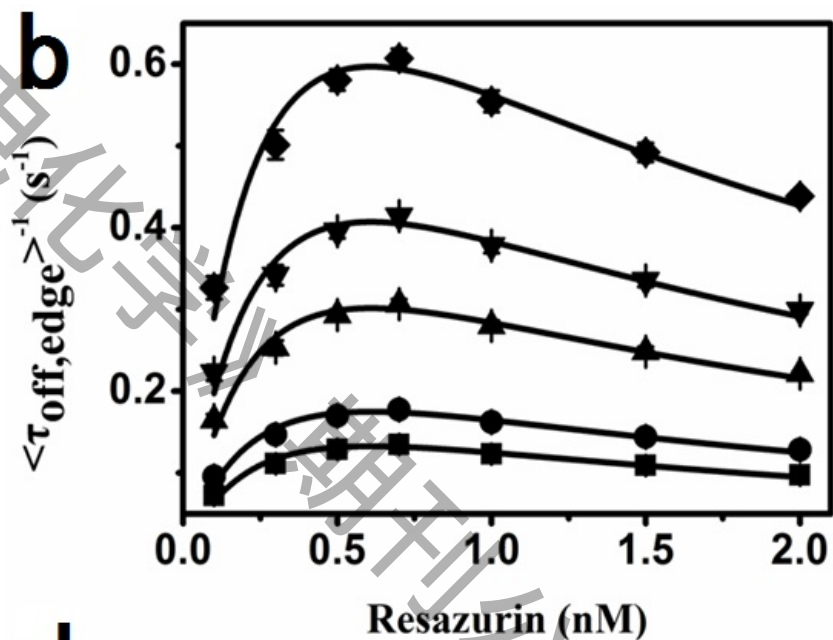
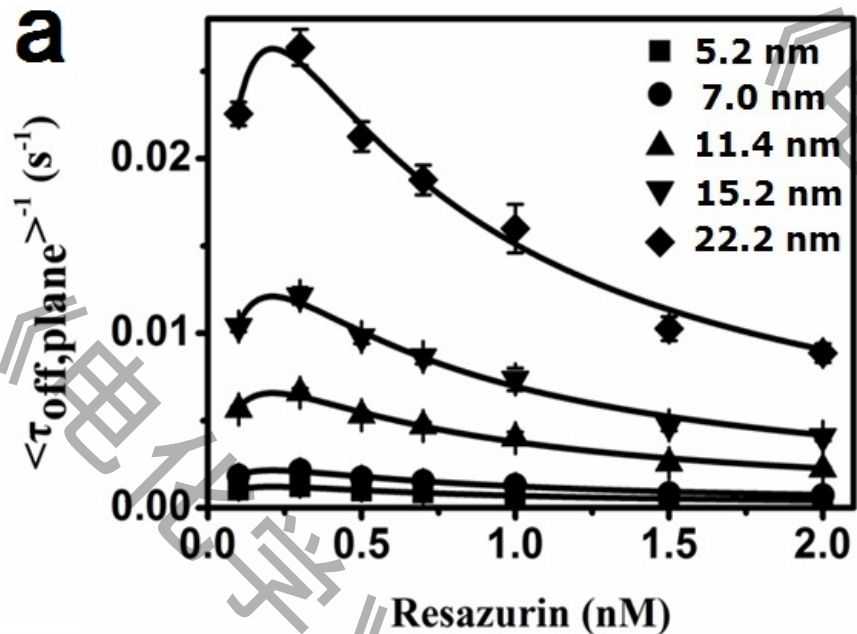


Model Off:

$$\langle \tau_{off} \rangle^{-1} = \langle \tau_{off,plane*} \rangle^{-1} \cdot N_{plane} \cdot x_p + \langle \tau_{off,edge*} \rangle^{-1} \cdot N_{edge} \cdot x_e$$

Model On:

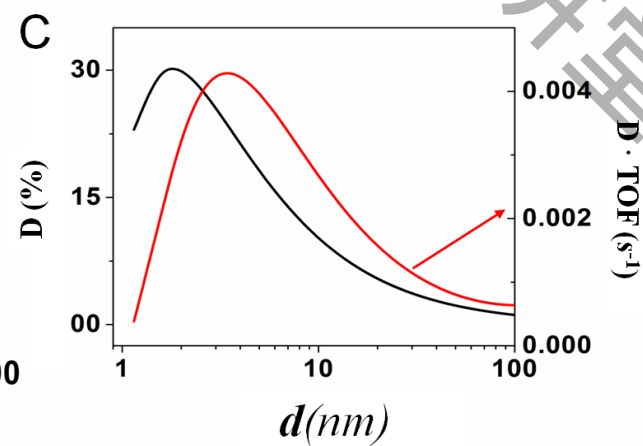
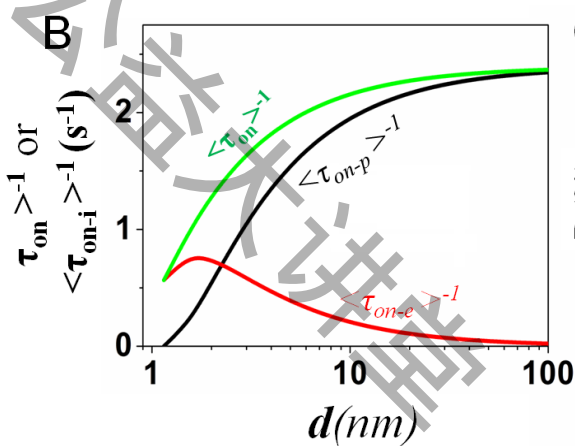
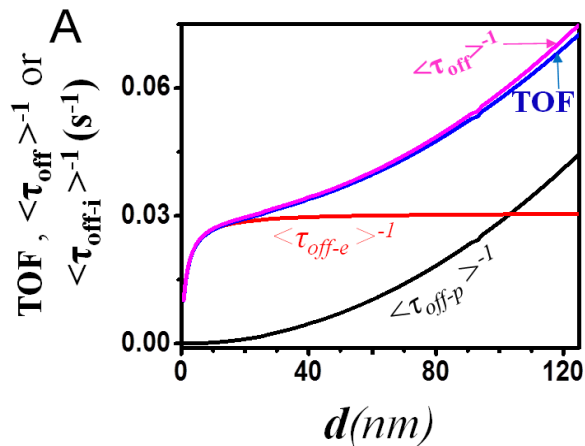
$$\langle \tau_{on} \rangle^{-1} = \langle \tau_{on,plane*} \rangle^{-1} \cdot x_p + \langle \tau_{on,edge*} \rangle^{-1} \cdot x_e$$

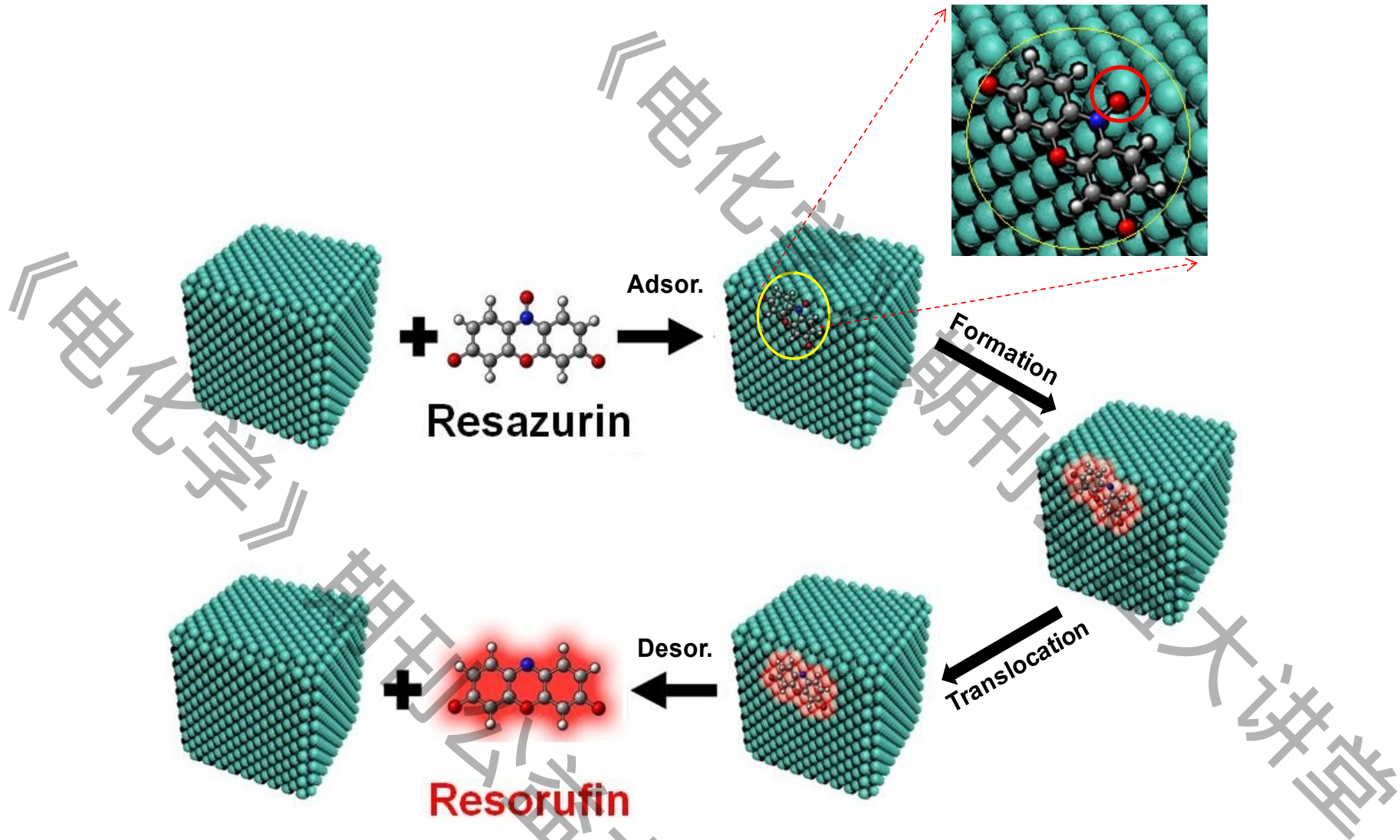


Size -dependence

τ_{off}	Plane			Edge		
	$\gamma_{\text{eff},p}$ (s^{-1})	$a_{A,p}$ (mM^{-1})	$a_{B,p}$ (nM^{-1})	$\gamma_{\text{eff},e}$ (s^{-1})	$a_{A,e}$ (mM^{-1})	$a_{B,e}$ (nM^{-1})
5.2(A)	0.013 ± 0.003	1.68 ± 0.18	9.33 ± 0.39	1.19 ± 0.21	1.66 ± 0.21	2.93 ± 0.14
7.0(B)	0.035 ± 0.004	1.69 ± 0.17	9.32 ± 0.39	1.57 ± 0.41	1.66 ± 0.21	2.94 ± 0.13
11.4(C)	0.058 ± 0.002	1.68 ± 0.18	9.30 ± 0.38	2.72 ± 0.33	1.67 ± 0.20	2.94 ± 0.14
15.2(D)	0.11 ± 0.02	1.67 ± 0.17	9.32 ± 0.39	3.67 ± 0.24	1.67 ± 0.21	2.93 ± 0.13
22.2(E)	0.23 ± 0.01	1.69 ± 0.18	9.32 ± 0.40	5.38 ± 0.38	1.66 ± 0.21	2.94 ± 0.13

τ_{on}	On-state			
	$i=p,e$	$\gamma_{2,i}$ (s^{-1})	G_i (nM^{-1})	$\gamma_{3,i}$ (s^{-1})
plane(p)		3.20 ± 0.06	3.19 ± 0.68	1.32 ± 0.12
edge(e)		-0.08 ± 0.33	4.92 ± 1.32	14.06 ± 1.70





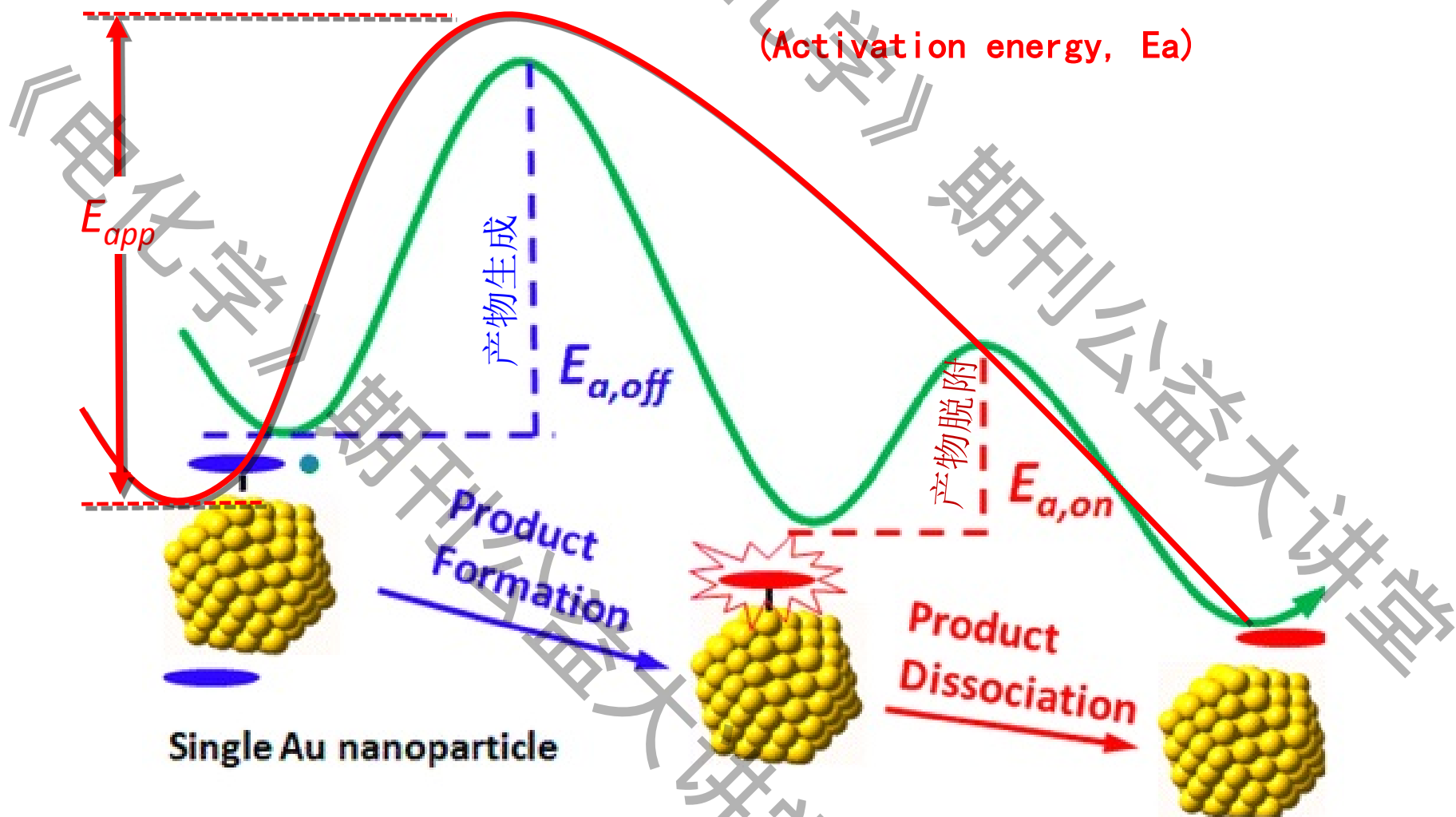
纳米催化研究拓展到了亚单纳米粒子的水平

把纳米催化研究从单粒子水平拓展
到了亚单粒子水平

在单分子单纳米粒子水平上发现产
物分子新的脱附方式

揭示单个纳米粒子催化热力学信息

测量单个纳米粒子催化产物生成和脱附过程的活化能

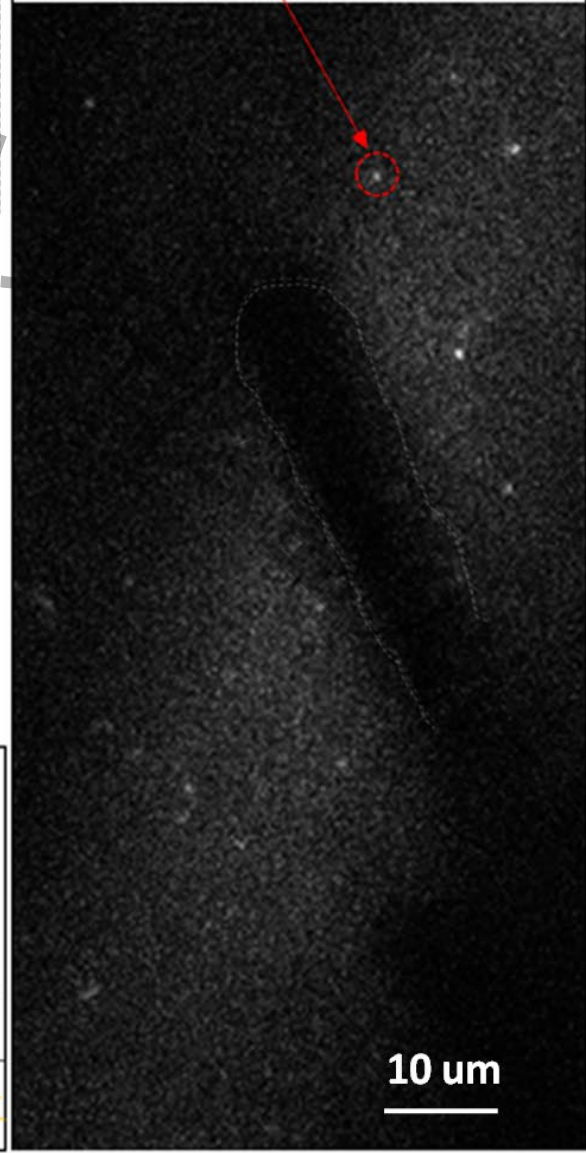
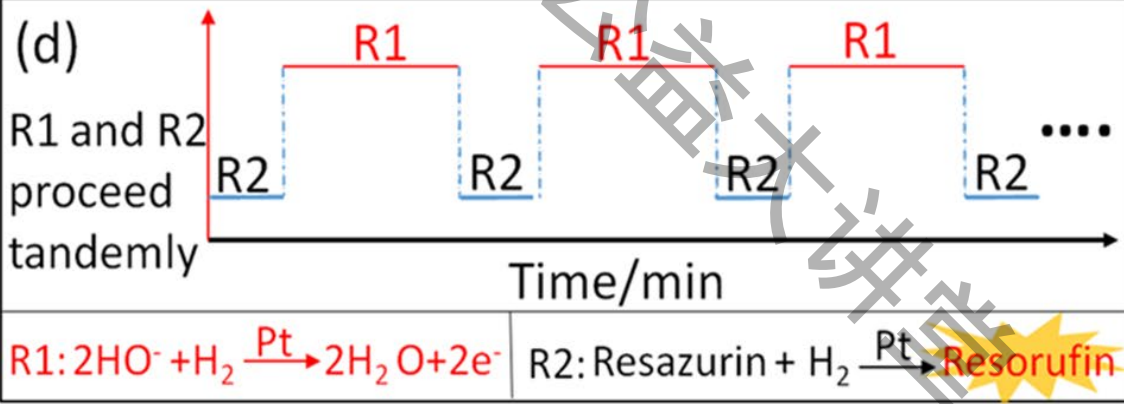
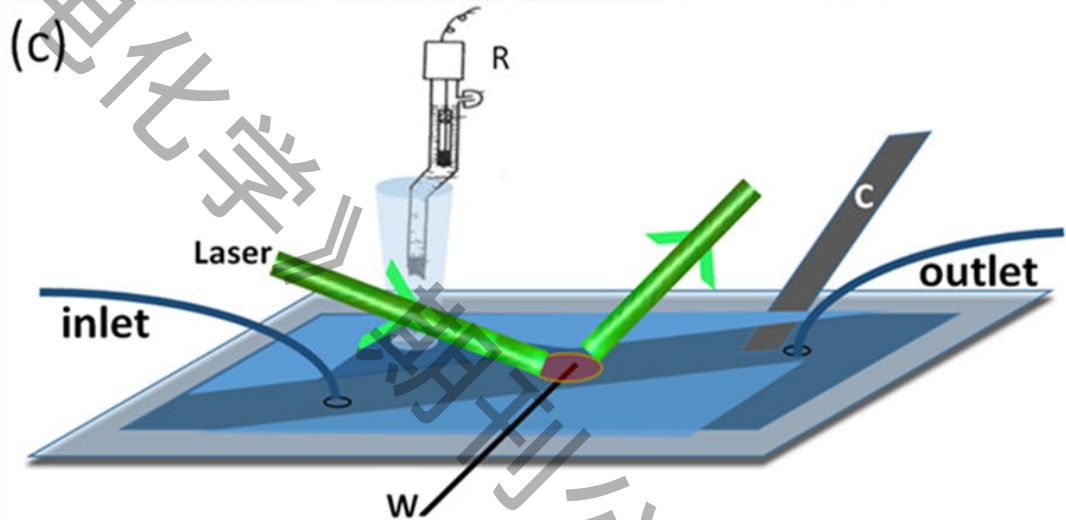
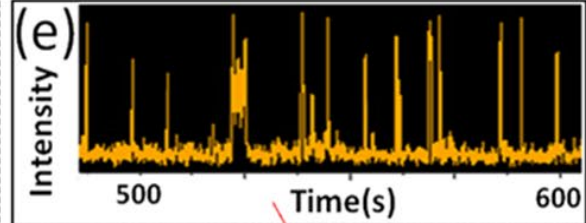
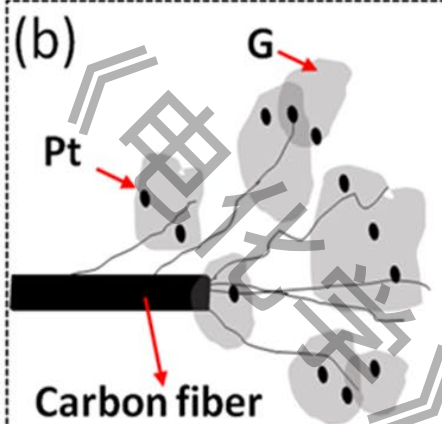
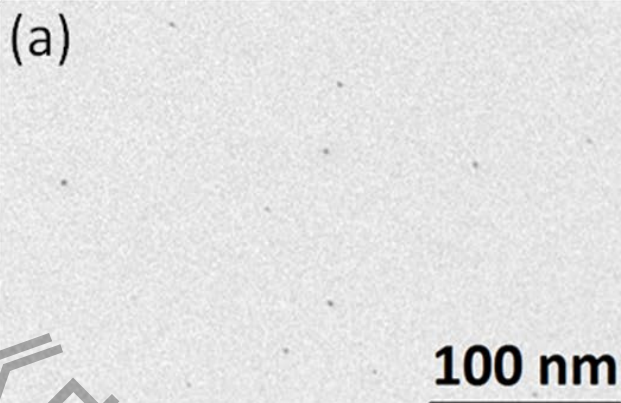


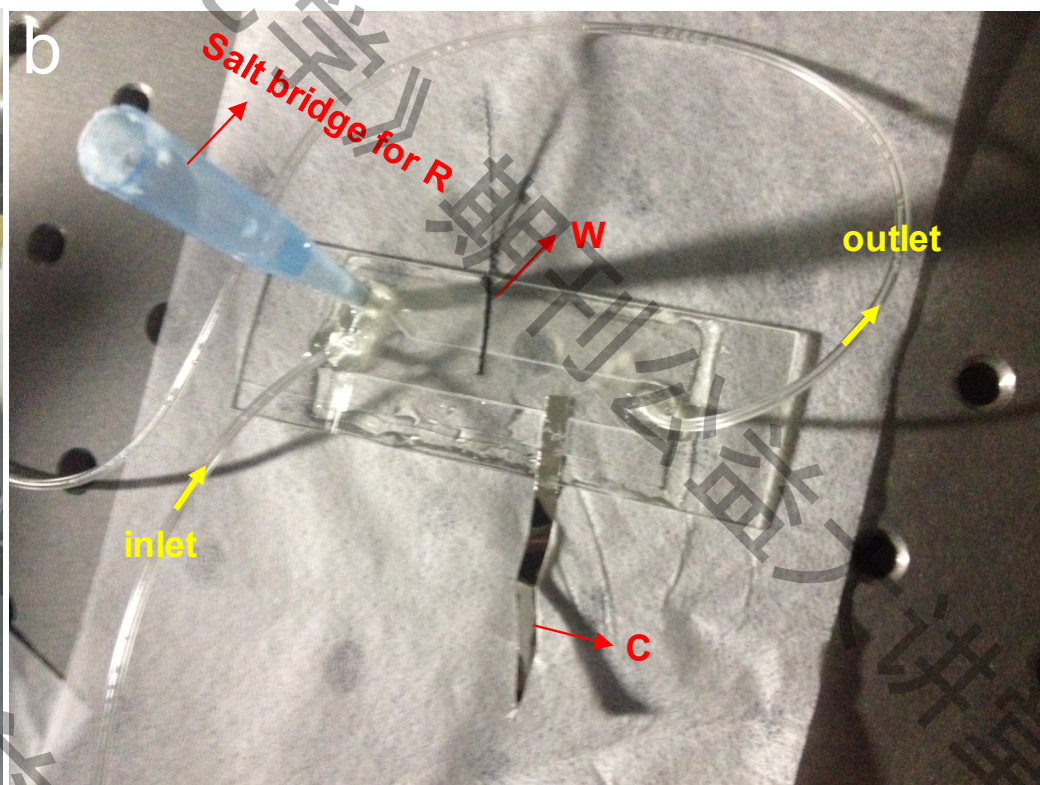
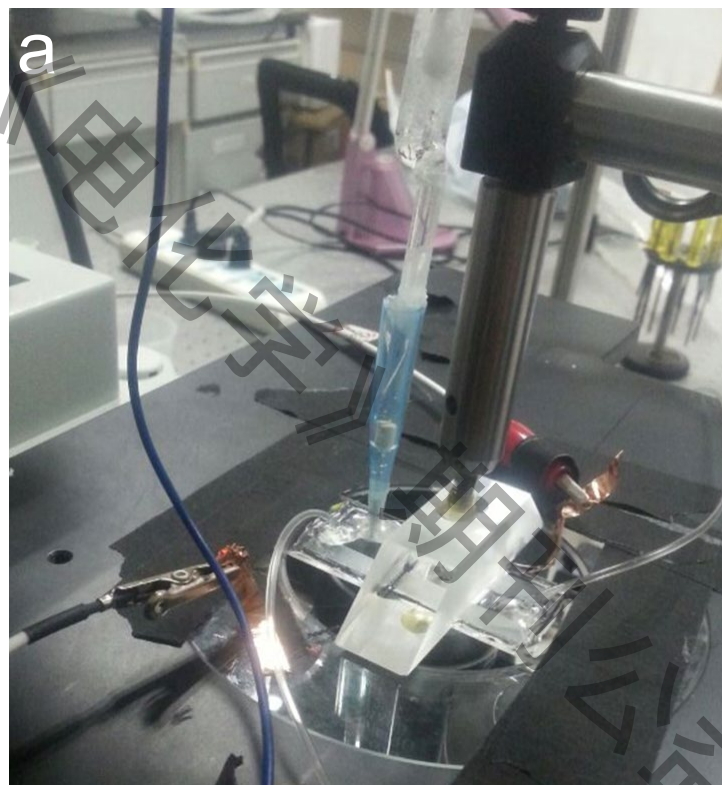
用单分子方法研究能源电化 过程相关的关键电化过程

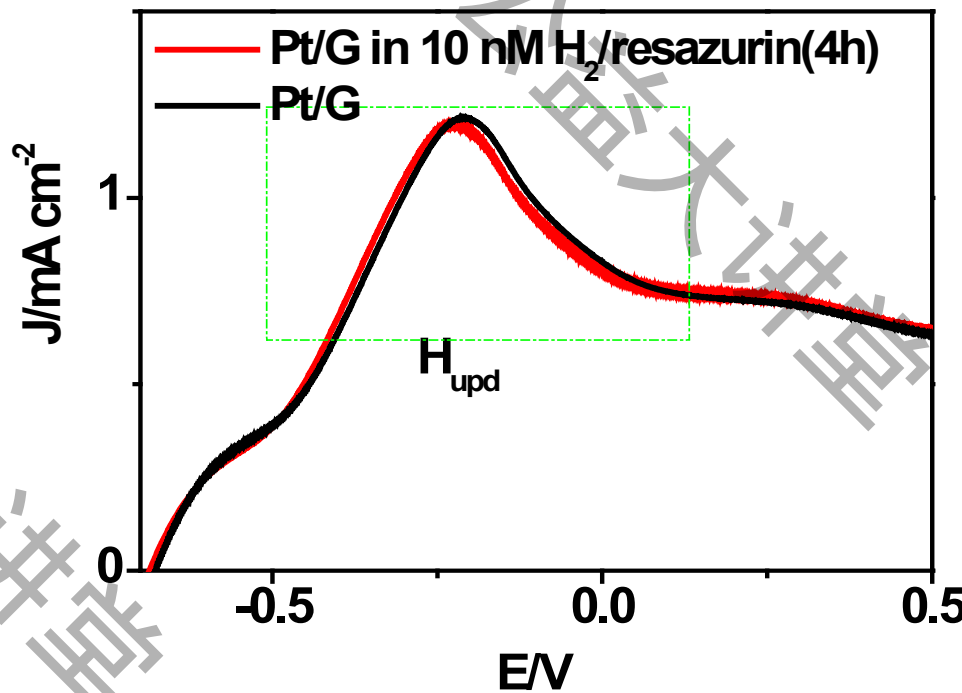
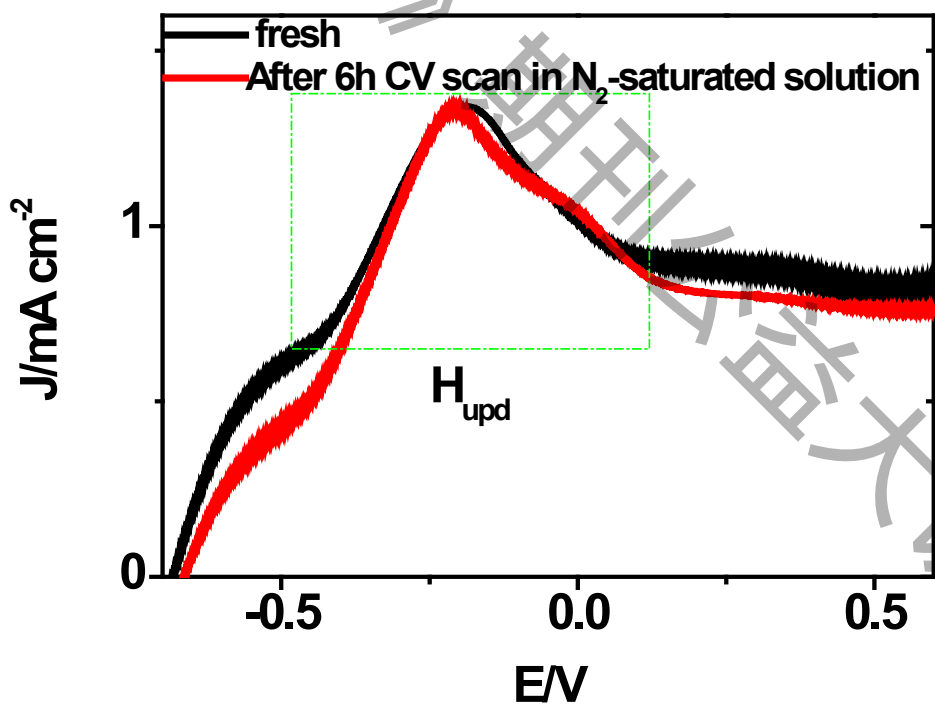
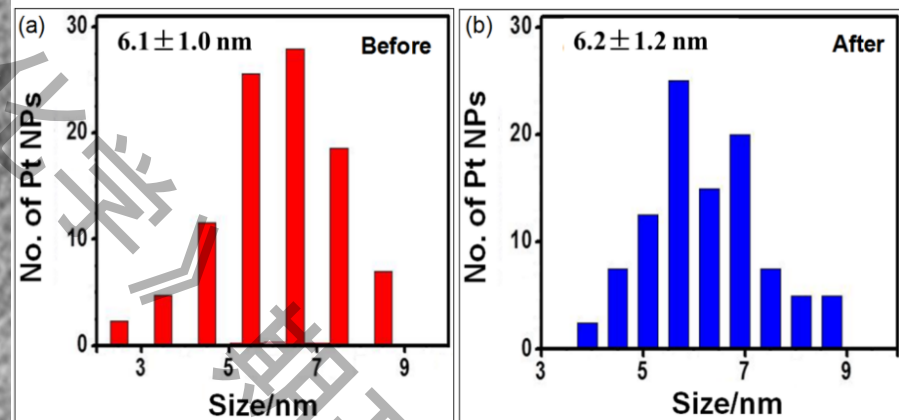
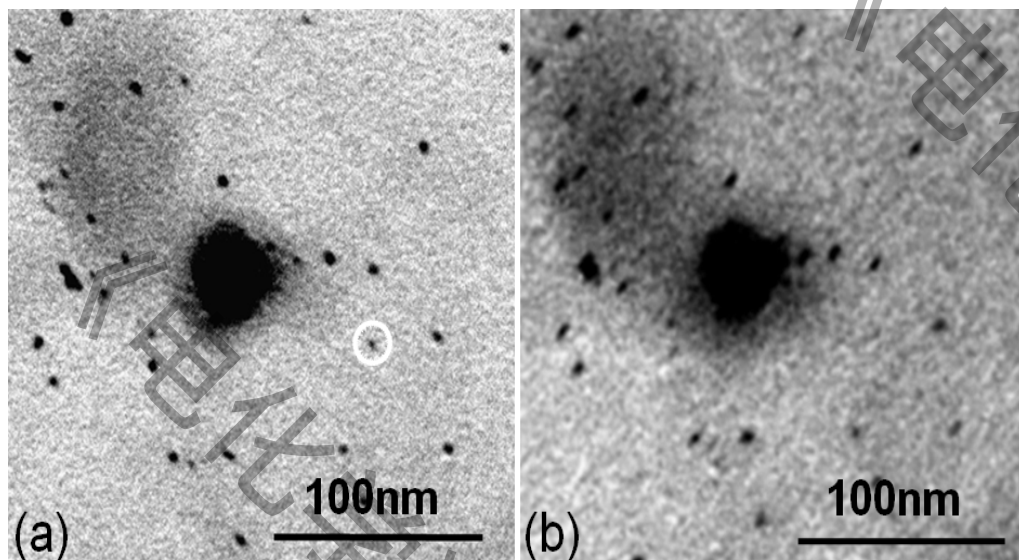
ORR, OER, HER, MOR, CO₂RR, NRR....

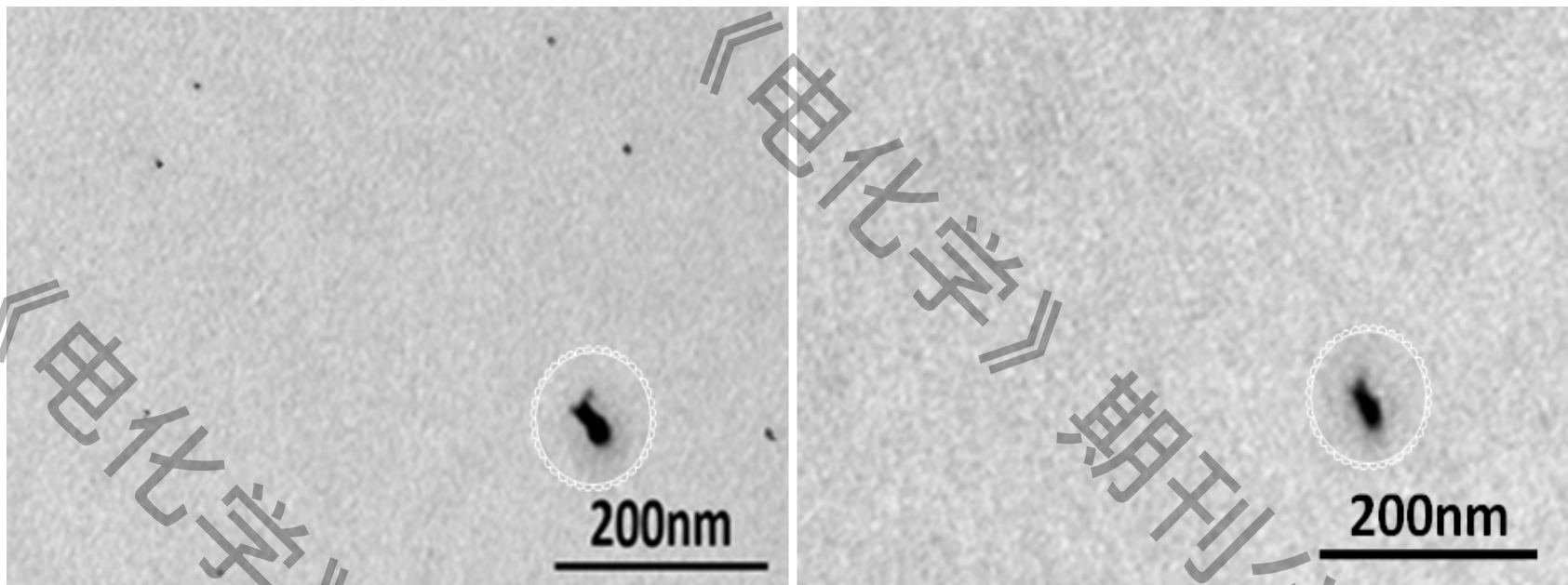
Example Two

电化学单分子荧光显微法揭示催
化剂纳米粒子失活机理

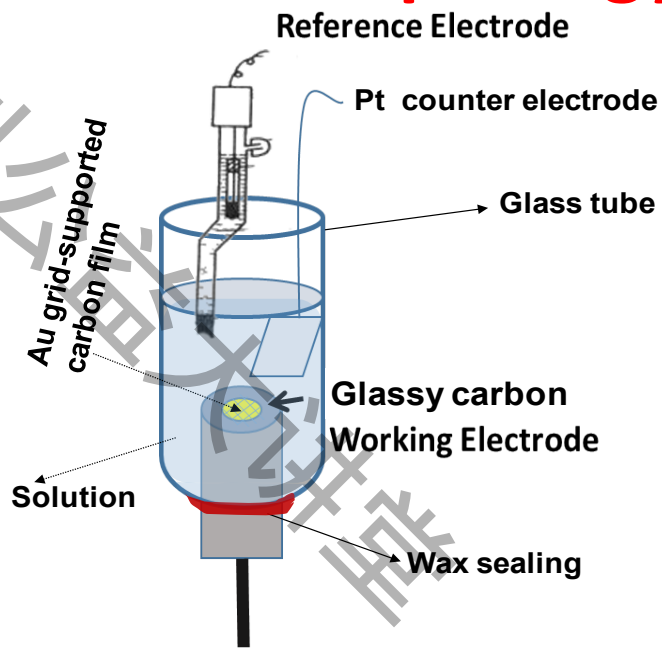


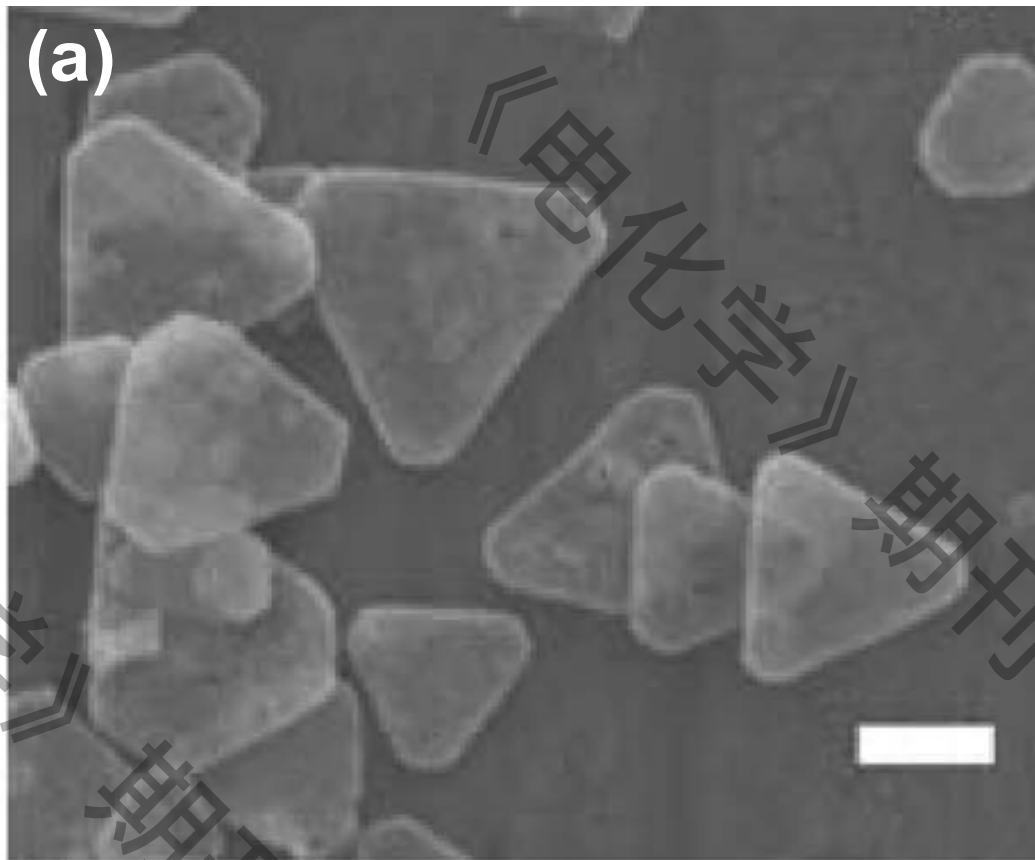




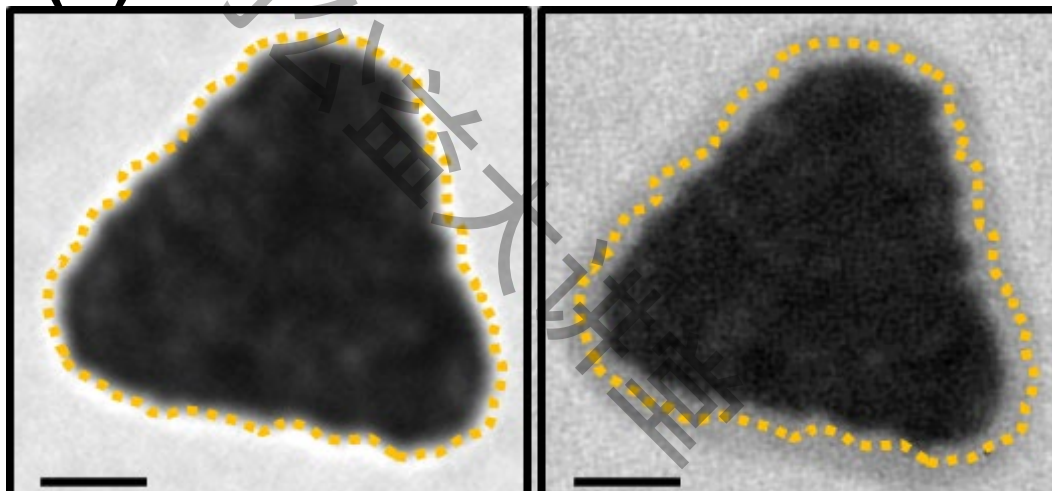


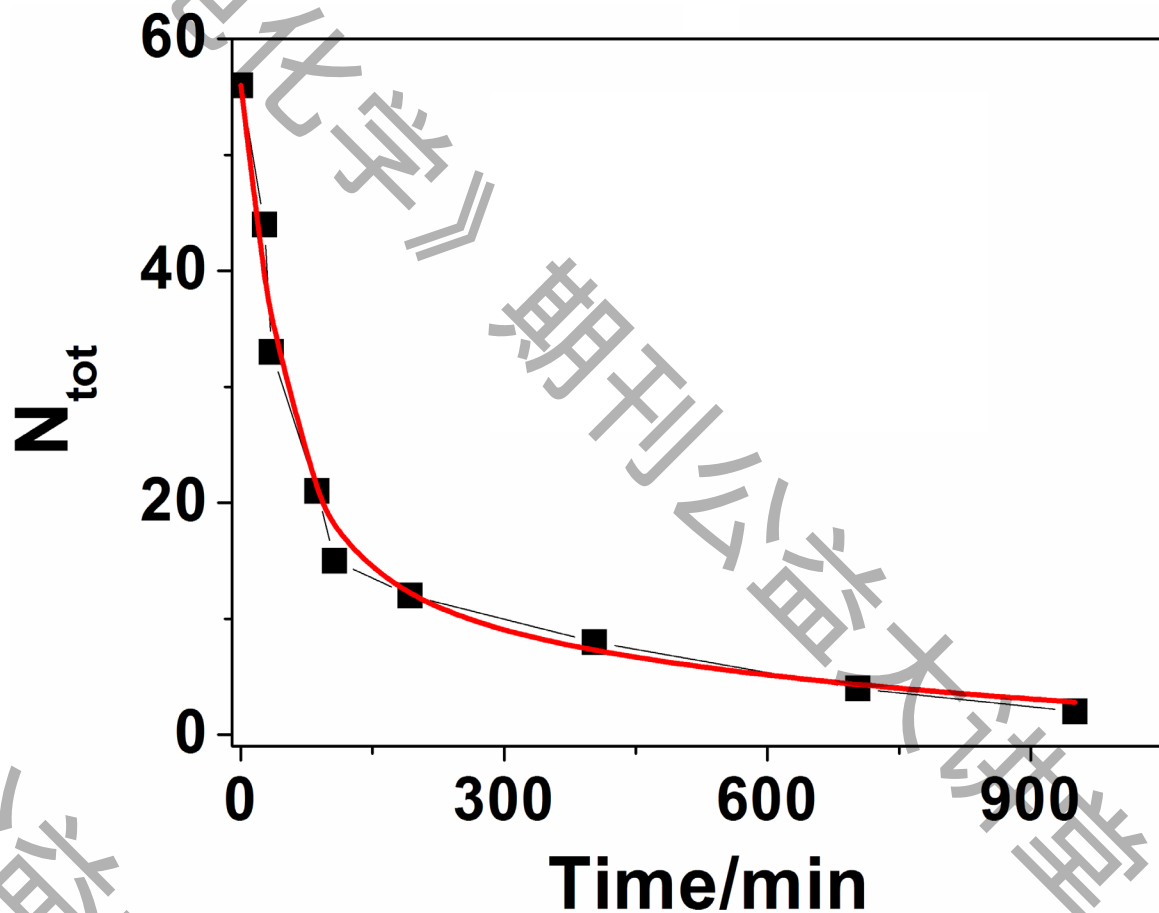
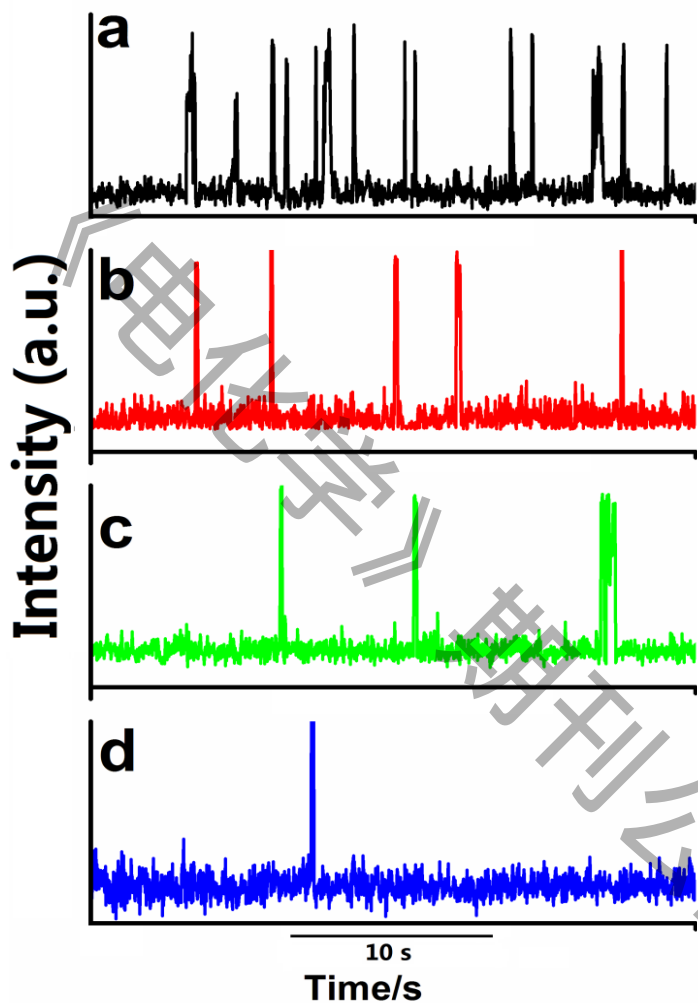
Effect of HOR on the morphology/size of Pt





(b) Pt nanoprisms

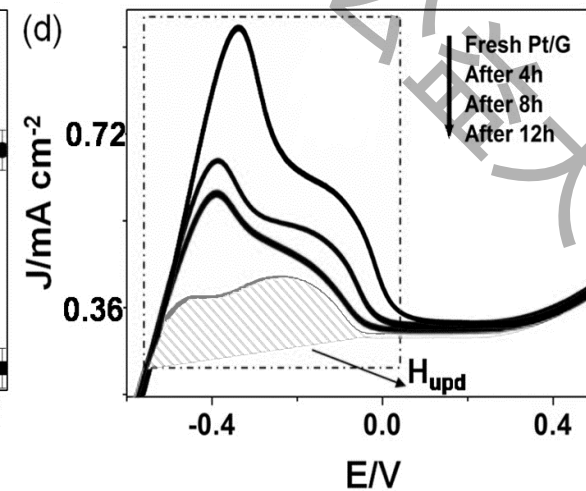
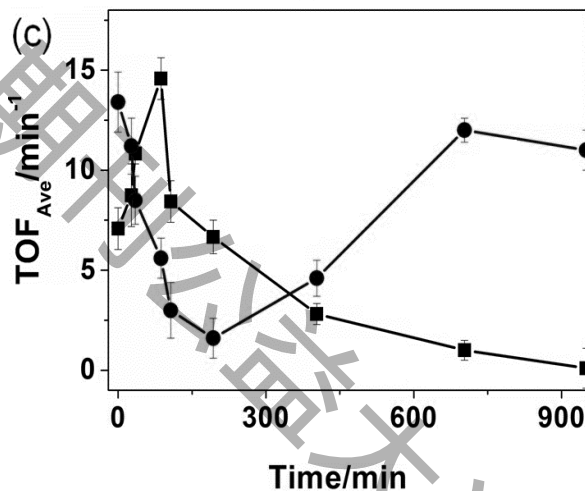
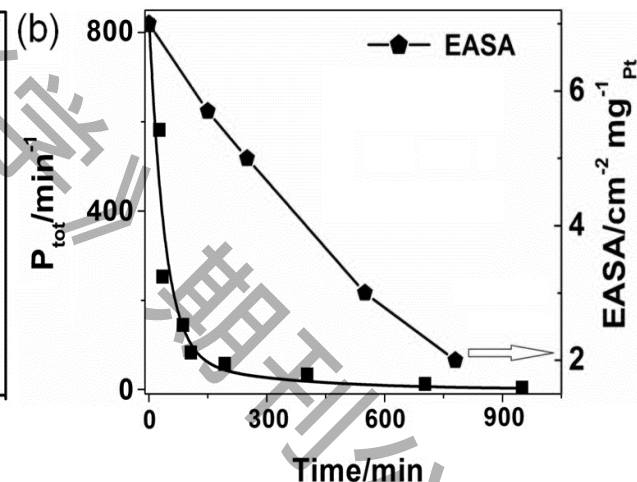
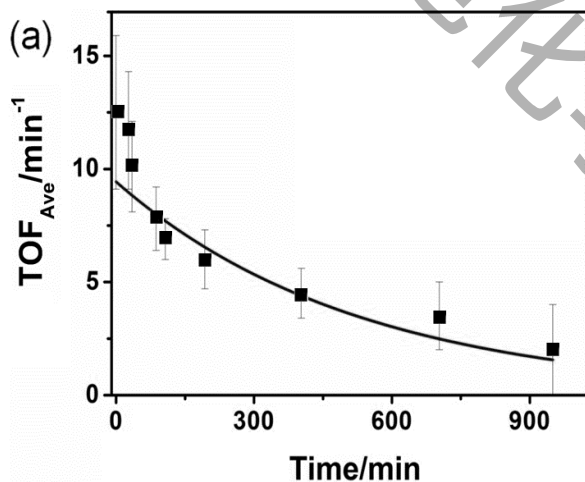




$$N_{tot} = a * \exp(-b * t) + (N_{tot,0} - a) * \exp(-d * t)$$

$$TOF_{Ave} \propto \exp(-r_s * t)$$

$$P_{tot} = TOF_{Ave} \cdot N_{tot}$$



2% :
activity
regeneration
3%:
incubation
period

$$P_{tot} = P_f \exp(-b * t) \cdot \exp(-r_f * t) + P_s \exp(-d * t) \cdot \exp(-r_s * t)$$

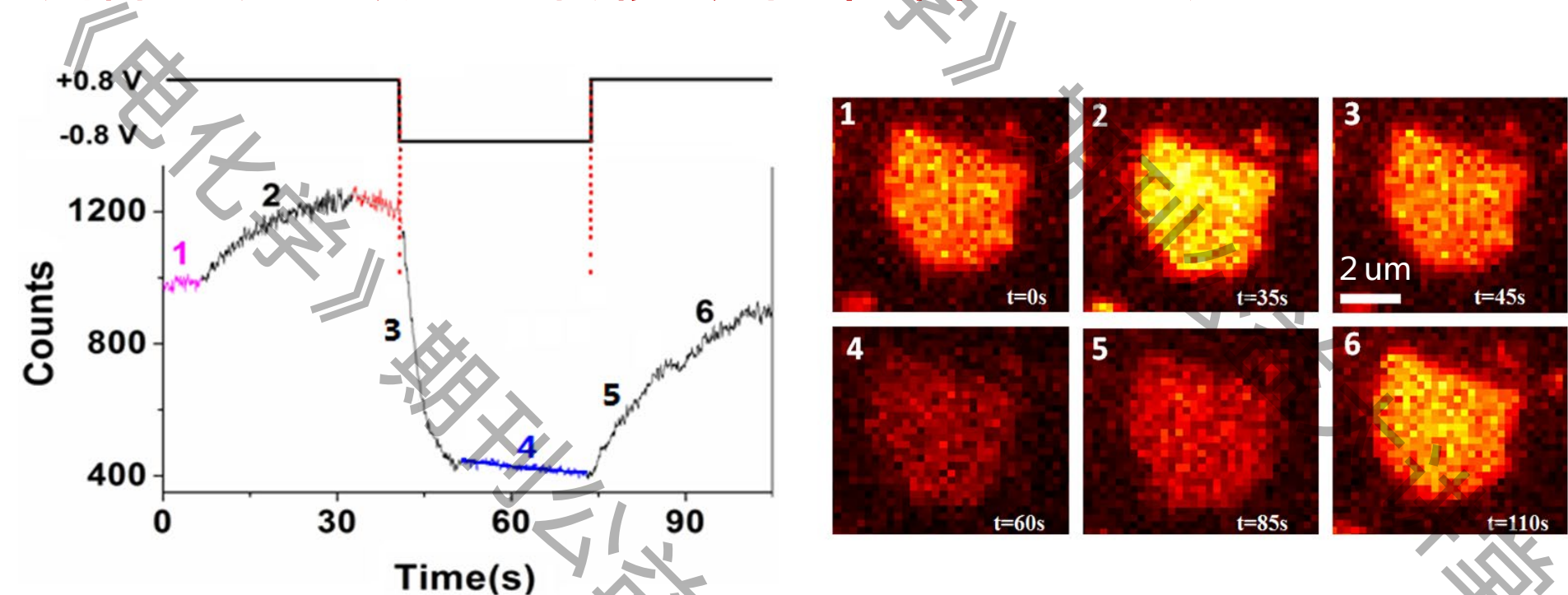
By combining SMFM with traditional electrochemical method, we revealed that the decay of catalytic performance of Pt/C mainly could be attributed to the electrocatalysis-induced electro-etching of Pt nanoparticles. **The lowly active but highly stable active particles determine the long-term operation stability of nanocatalysts.** These new understandings are useful for the rational design of high efficient functional materials.

单颗粒水平上定量评估催化剂活性组成及其动态变化过程的新方法



Example Three: 从个性化信息到精准设计

缺陷驱动高效电子转移 提高材料导电能力



缺陷调控单片石墨烯可逆电子转移

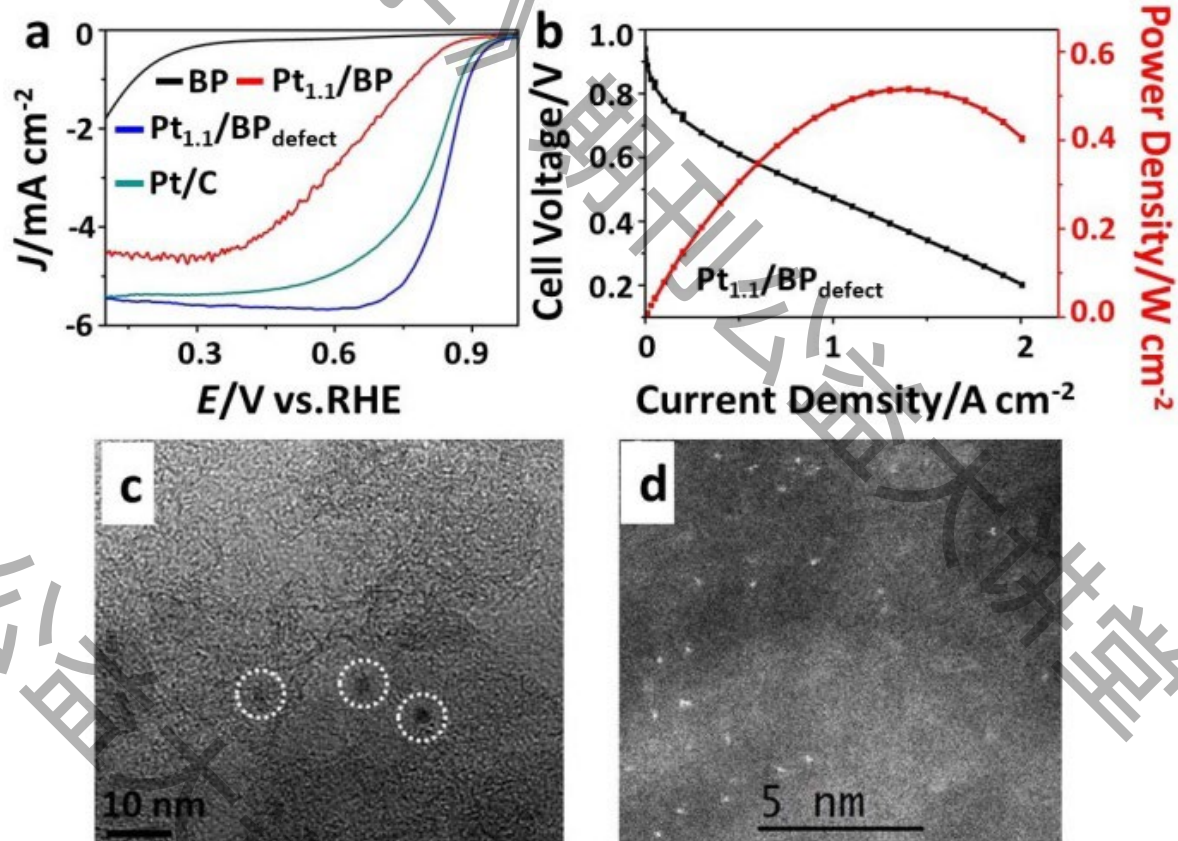


从个性化信息到精准设计的初探

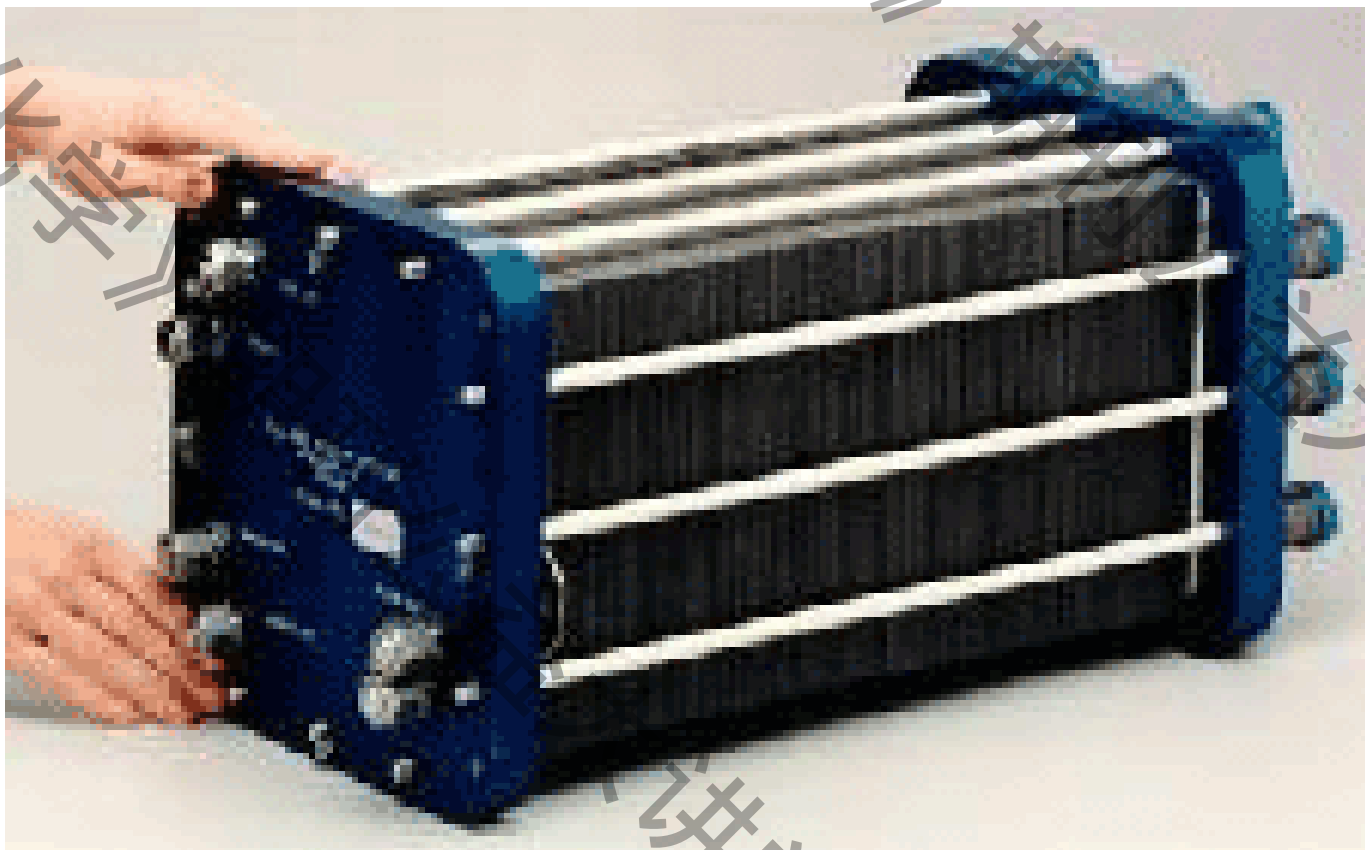
碳缺陷铆定的Pt单原子ORR催化剂

Pt 利用率

$0.09 \text{ g}_{\text{Pt}} \text{ kW}^{-1}$



Part B: Pt-free/Low Pt electrocatalysts For Fuel Cells



Our goal: For the commercialization of fuel cells, finally we need an alternative to Pt with super-high performance and super-low cost.

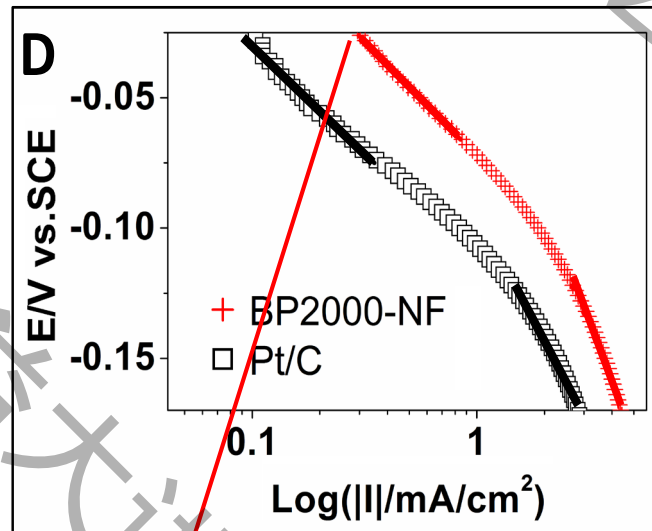
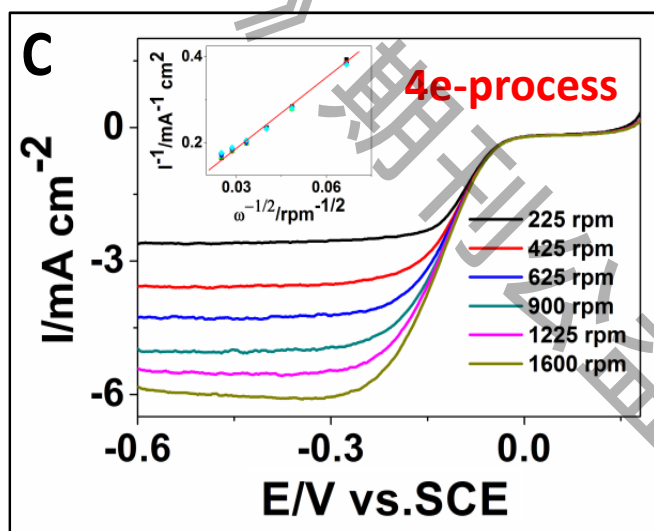
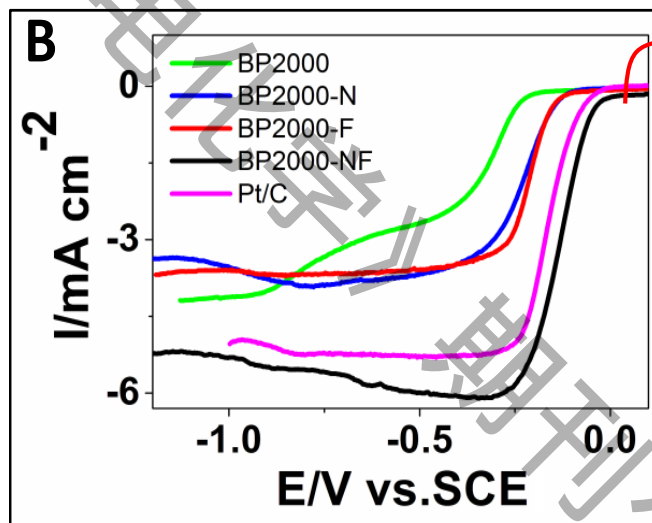
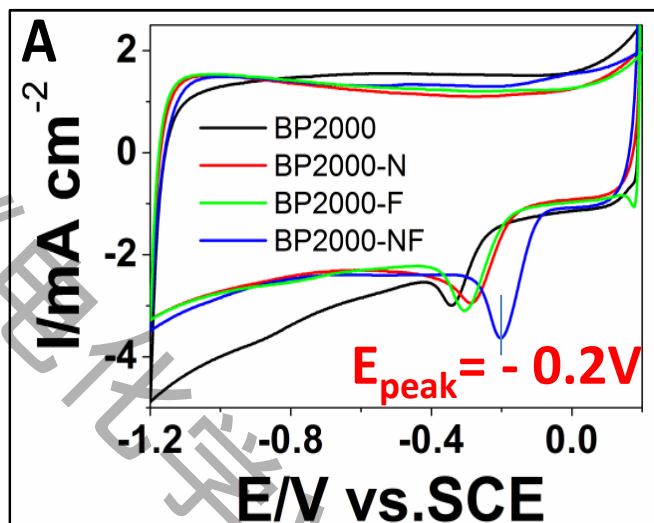
Cheapest and most sustainable: Commercial Carbon black



Product: High performance and low cost

With the best price/performance ratio

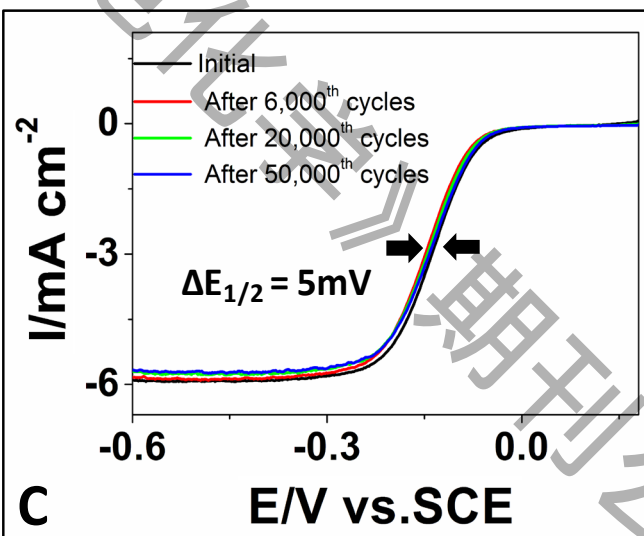
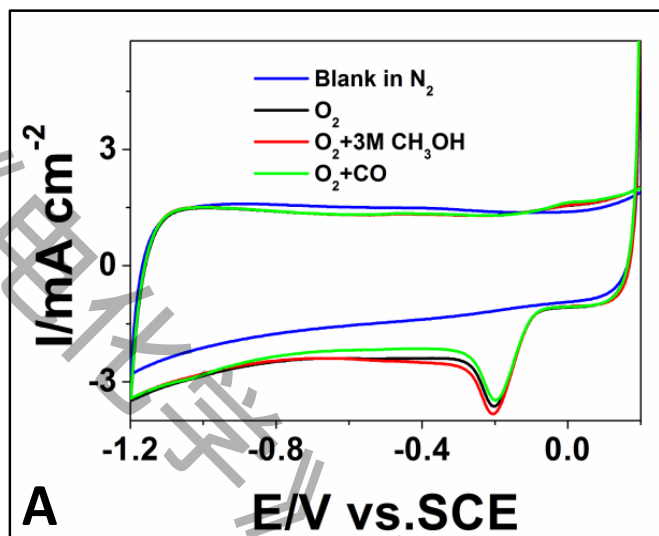
In 0.1 M KOH: Super-high performance



Tafel plots

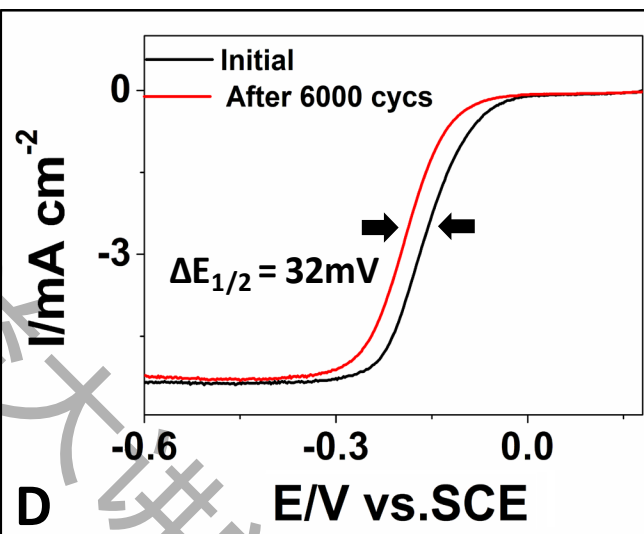
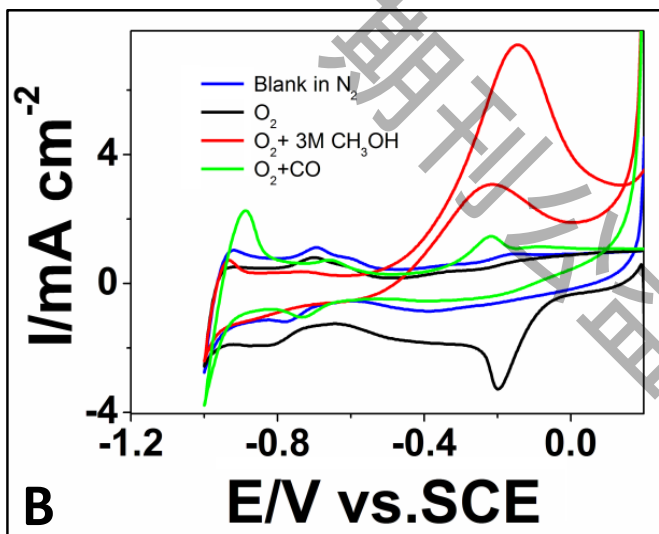
A **much** higher exchange current density ($3.0 \times 10^{-3} \text{ mA/cm}^2$) than Pt/C

Super-high tolerance to poison and long-term operation stability



Cycling between
-1.2 ~ 0.2 V 200mV/s
 O_2 saturated KOH

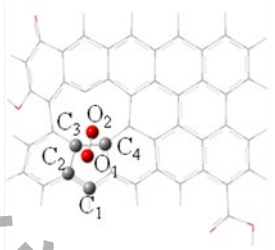
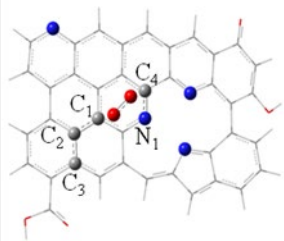
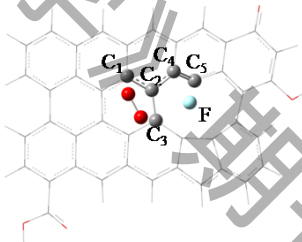
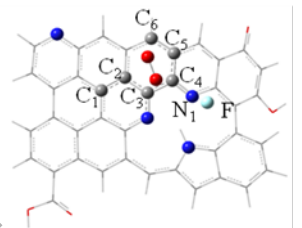
➔ BP2000-NF



➔ Pt/C

Quantum Chemical Calculation

Table 1: The optimized structures for CB-O₂ systems and their geometry parameters in solution phase.

Compound	a+O ₂	b+O ₂	c+O ₂	d+O ₂
Structure				
^a E _g (eV)	1.726	1.584	1.556	0.770
^b D _{O-O} (Å)	1.217	1.241	1.254	1.258
^c e _{O₂} (e)	-0.02	-0.21	-0.31	-0.33
^d E _{ad} (eV)	-0.04	-0.20	-0.36	-0.39

Note: ^aE_g: The energy gap between HOMO and LUMO for models **a**, **b**, **c** and **d** without O₂ adsorption.

^bD_{O-O}: The bond length for O₂.

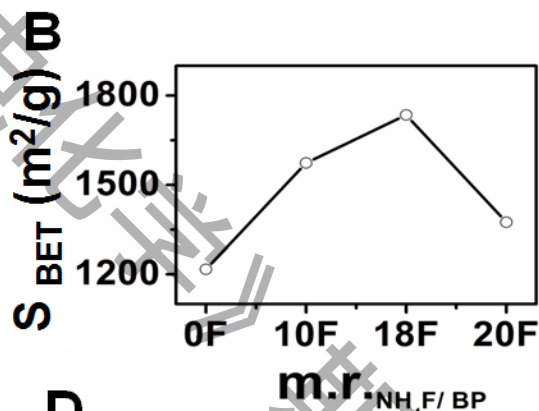
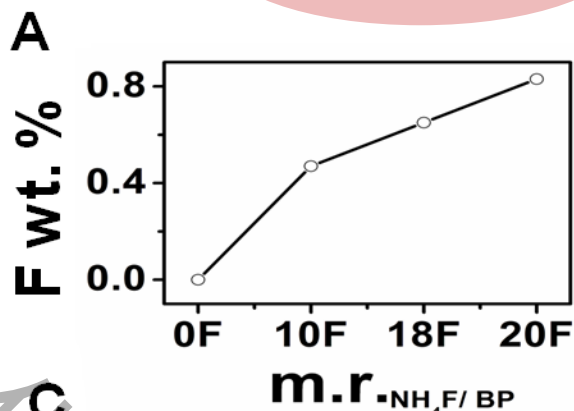
^ce_{O₂}: The charge O₂ possesses.

^dE_{ad}: The adsorption energy, and it is equal to E_{ad} = E(CB-O₂) - E(CB) - E(O₂), in which E(CB-O₂), E(CB) and E(O₂) is the total energy for CB-O₂ system, separated CB and separated O₂ molecule.

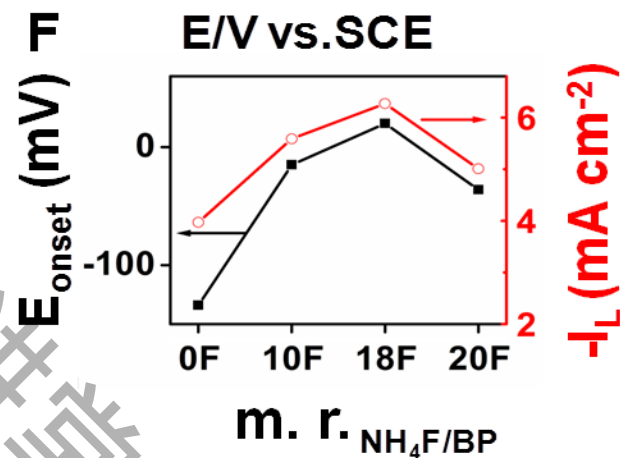
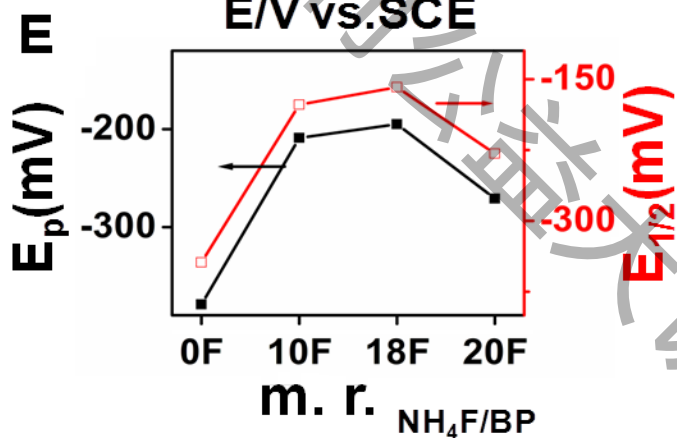
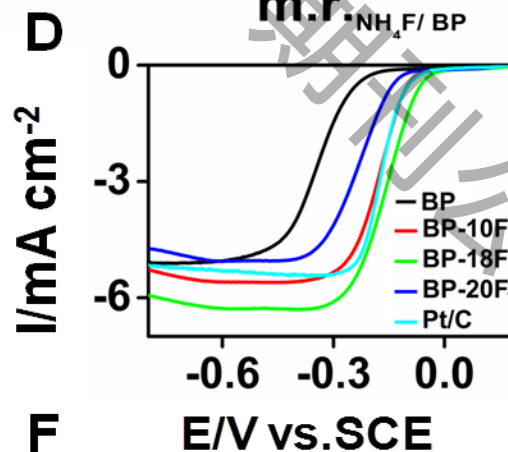
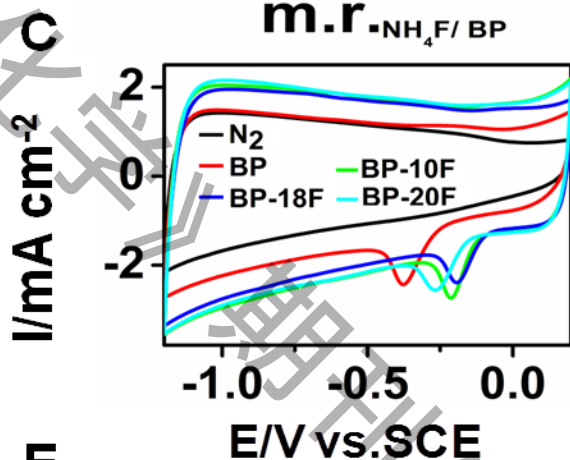
The co-doping of N,F can greatly enhance the ORR electrocatalytic activity!!

Predict: CB-NF > CB-F ≥ CB-N > CB

Predict: $CB-NF > CB-F \geq CB-N > CB$



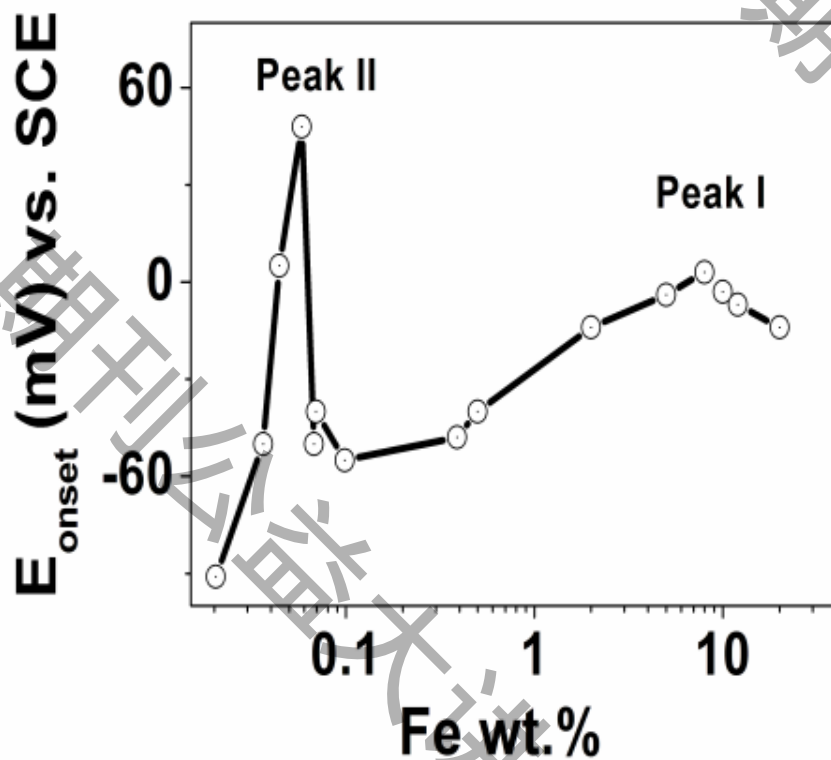
CB-F



Non-precious metal catalysts for ORR

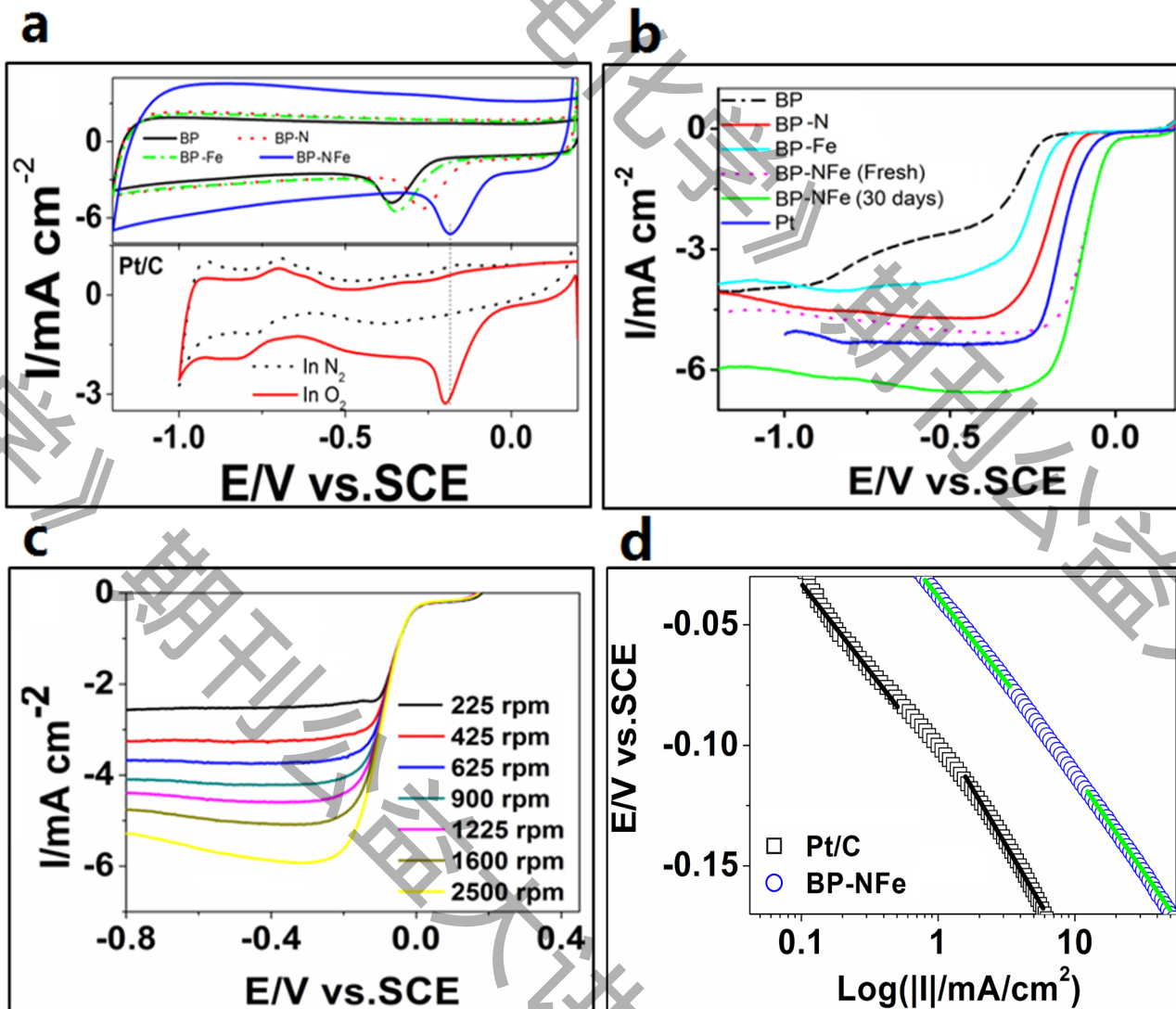
High Performance Oxygen Reduction Electrocatalysts based on Cheap Carbon Blacks, Nitrogen and Trace Iron

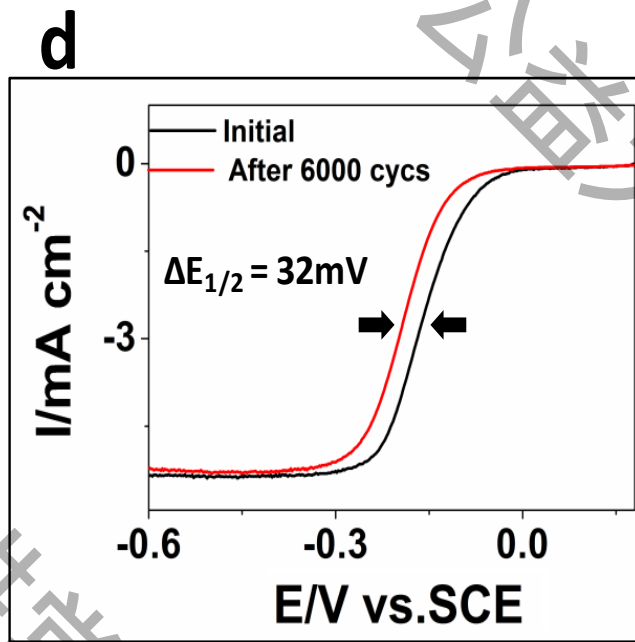
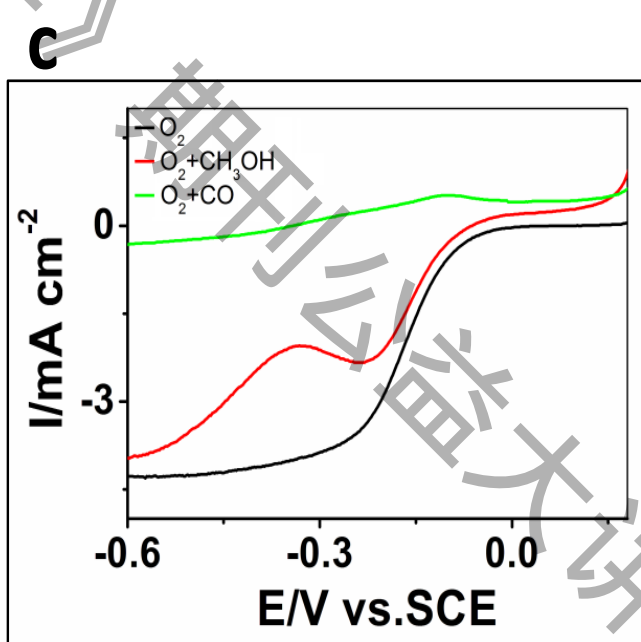
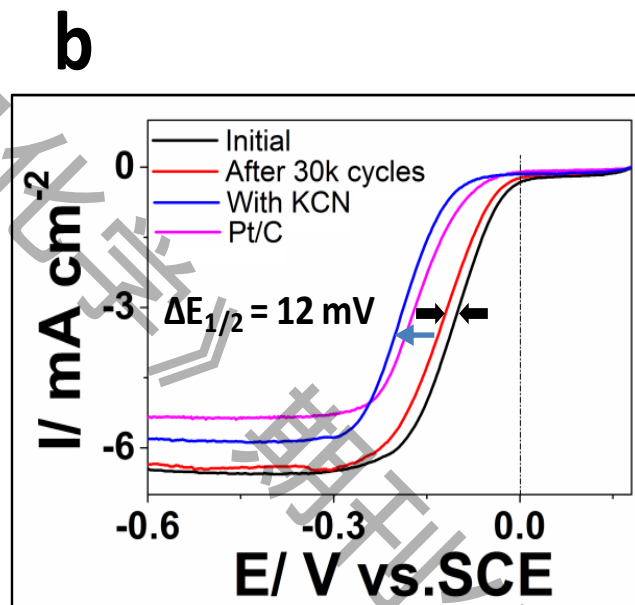
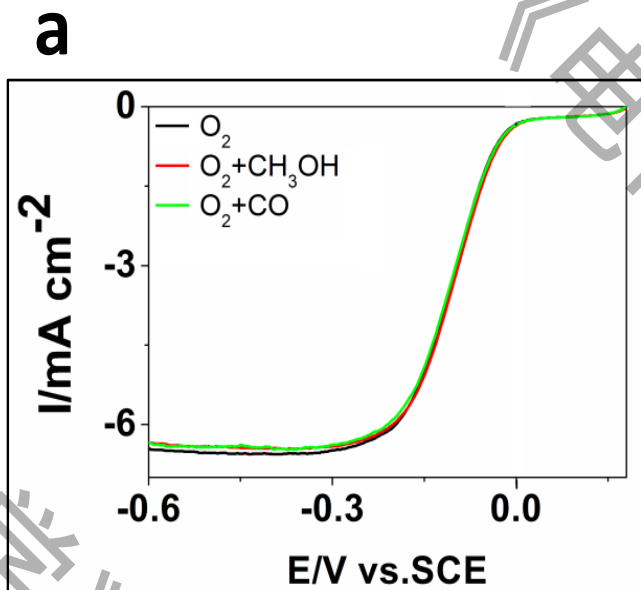
Adv. Mater. Liu, J. Xu, W. et al. 2013, 25, 6879-6883

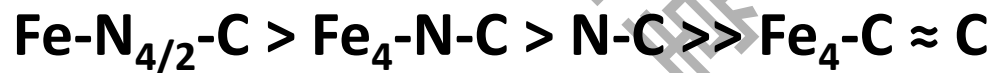
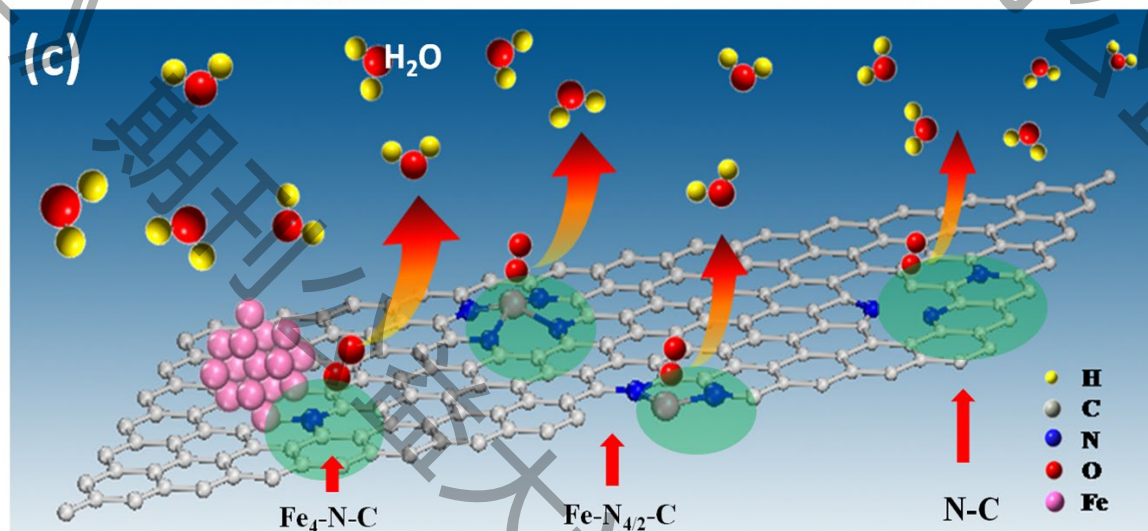
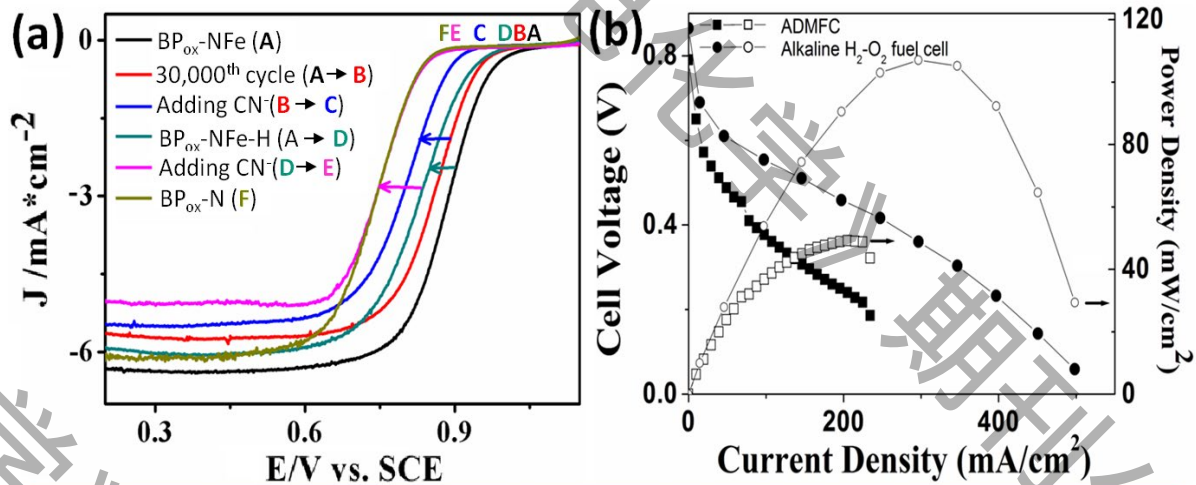


Cheap BP2000 (BP), melamine ($\text{C}_3\text{H}_6\text{N}_6$) and FeCl_3

BP-NFe with Fe 0.05 wt. %, N 2.4 wt. %

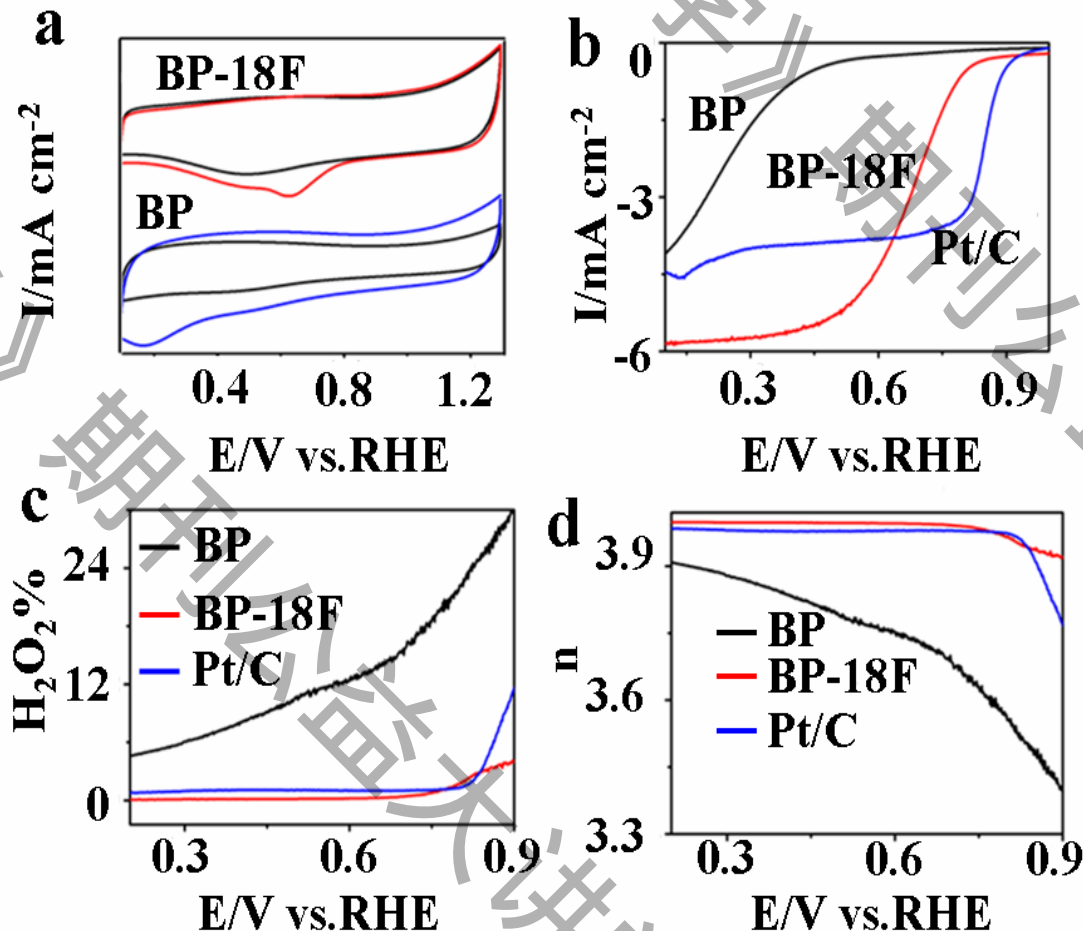




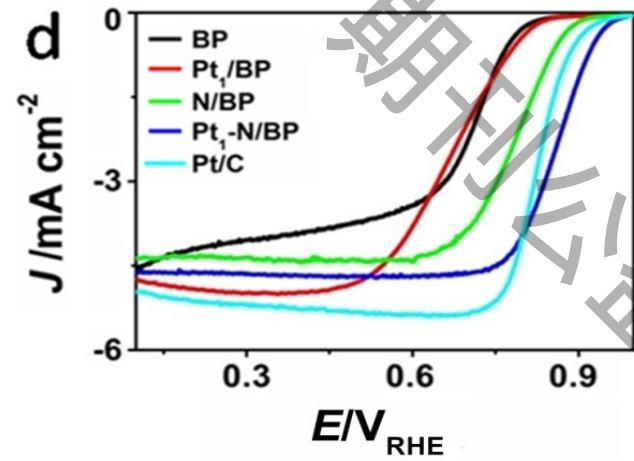
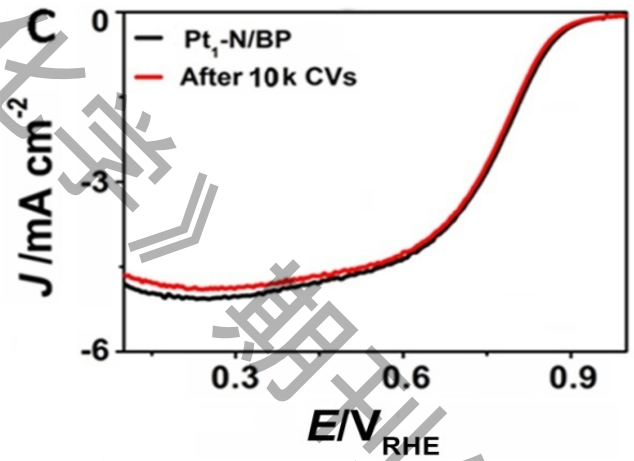
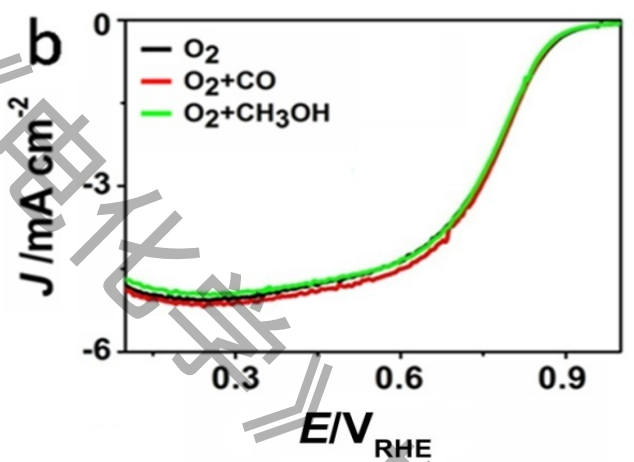
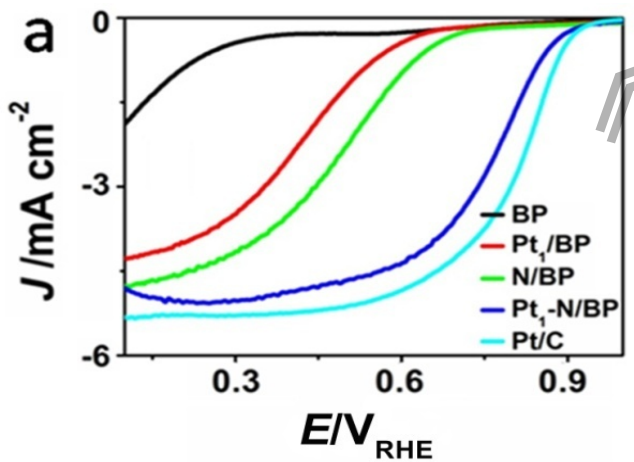


Another big challenge in this field of Pt-free catalysts:

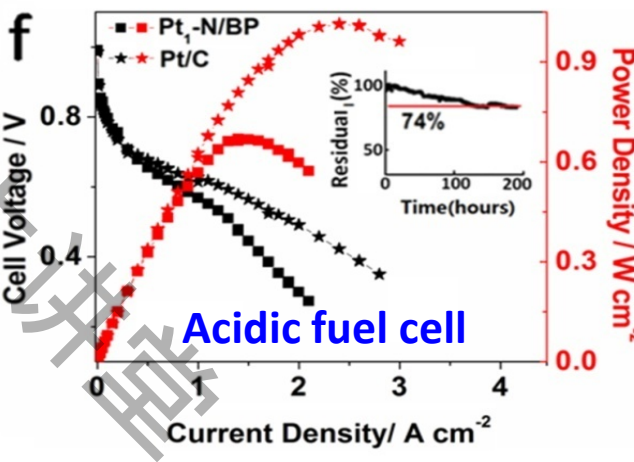
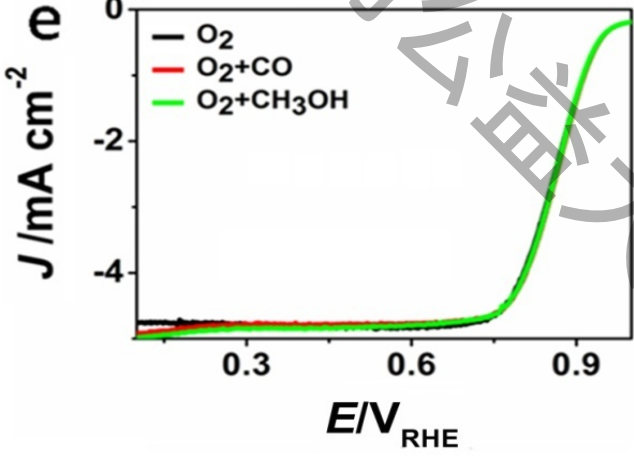
In acidic condition, the performance of non-precious metal or metal-free catalysts for ORR is not as good as Pt/C.



In HClO_4



In KOH



Acidic fuel cell

$0.29 \text{ g}_{\text{Pt}} \text{ kW}^{-1}$

$0.13 \text{ g}_{\text{Pt}} \text{ kW}^{-1}$

Pt utilization

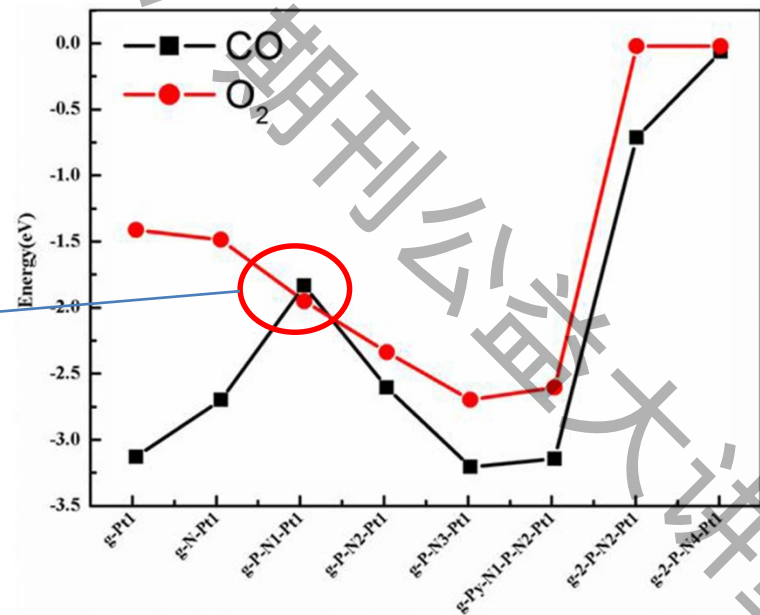
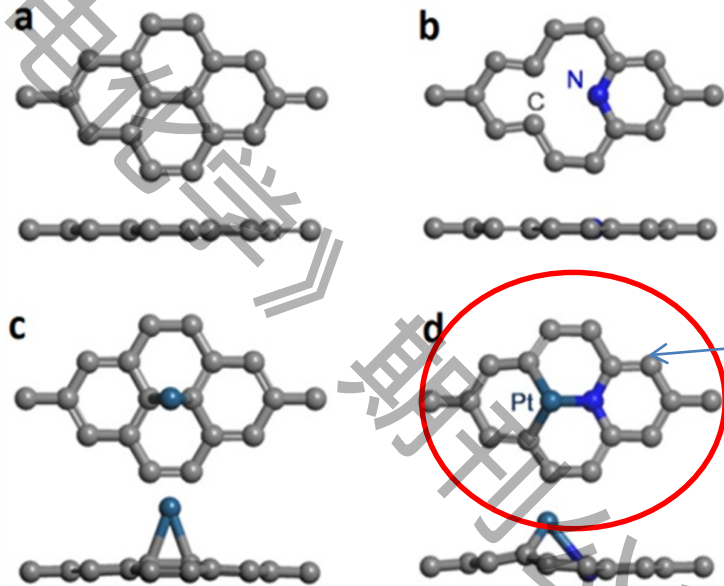
Samples	Pt consumption/ $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	References
Pt₁-N/BP	0.13 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	In this work
Fe/N/C	0.33 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	Nat. Commun. 2 , 416(2011)
S-Fe/N/C	0.39 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	Angew. Chem. Int. Ed. 54 , 9907(2015)
Fe/N/C	0.33 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	<i>PNAS</i> 112 , 10629(2015)
PANI-Fe-C	0.45 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$	<i>Science</i> 332 , 443(2011)

2017 DOE target: **0.18 $\text{g}_{\text{Pt}} \text{ kW}^{-1}$**

Durability in fuel cell

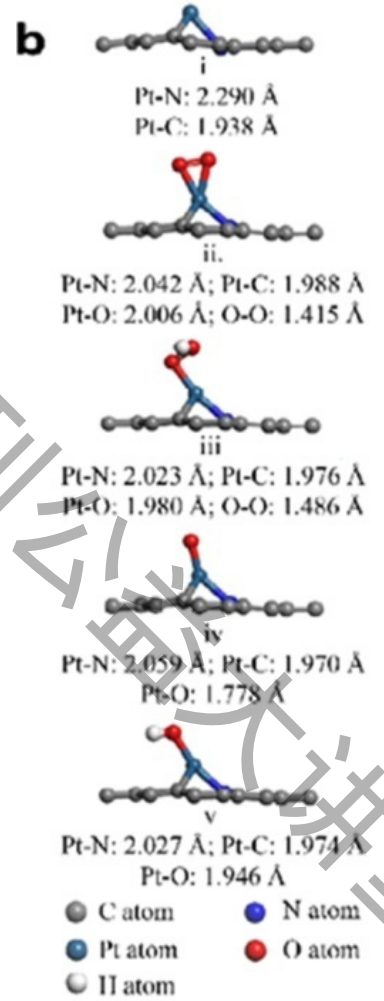
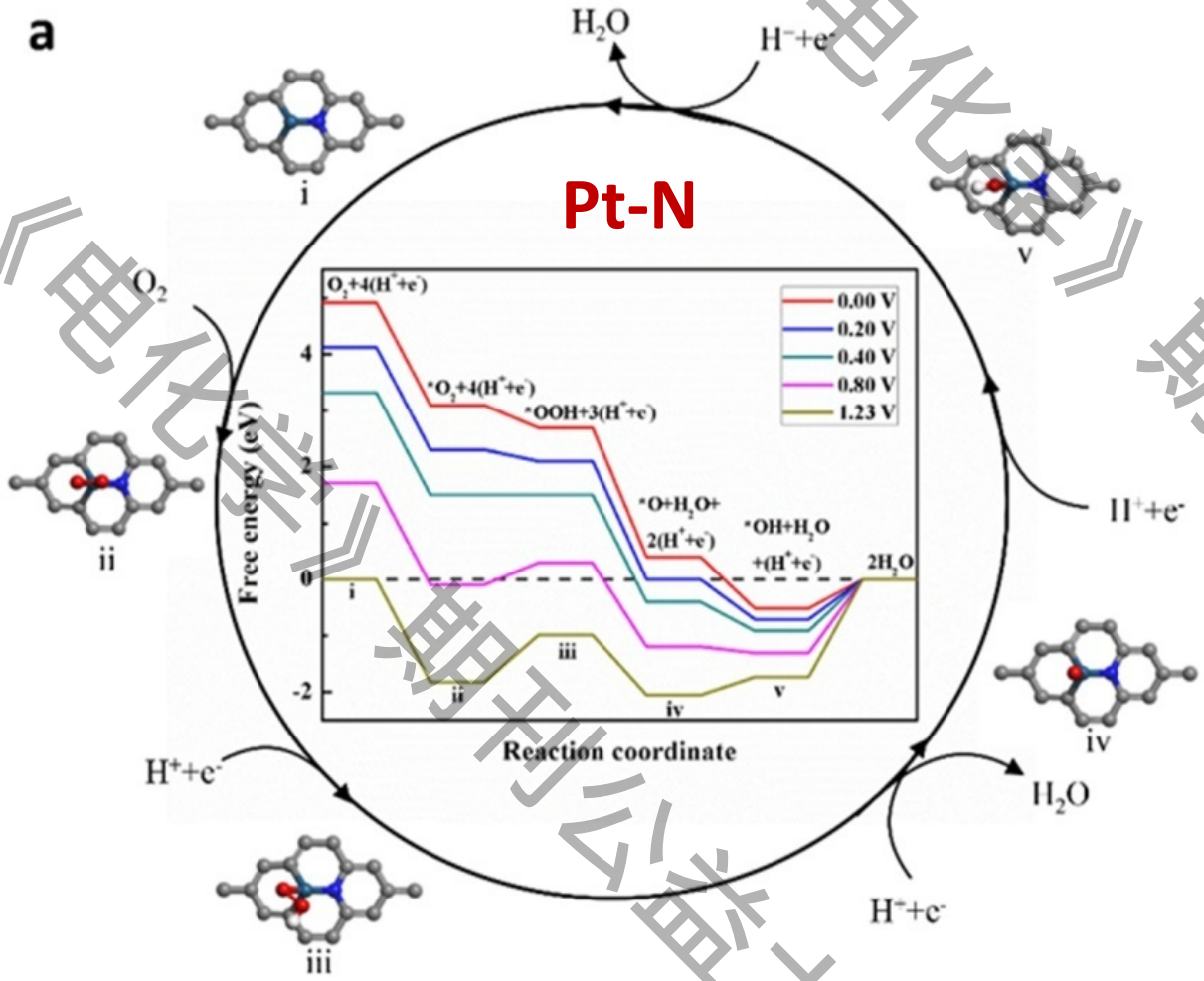
Samples	Current remained after a period of time at 0.5 V	References
Pt ₁ -N/BP	74% remained after 200 hours at 80°C	In this work
Pt ₁ -N/BP	90% remained after 200 hours at 70°C	In this work
S-Fe/N/C	28% remained after 100 hours at 80°C	Angew. Chem. Int. Ed. 54 , 9907(2015)
Fe/N/C	44% remained after 100 hours at 80°C	<i>Science</i> 324 , 71(2009)

Pt is more stable than any other non-precious atoms in acid!



Pt₁-N₁

Pyridinic N



Nat. Commun. 2017; 8:15938

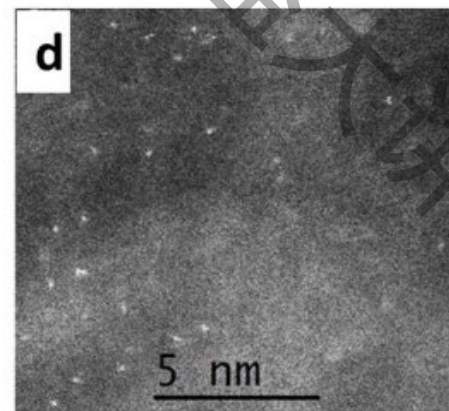
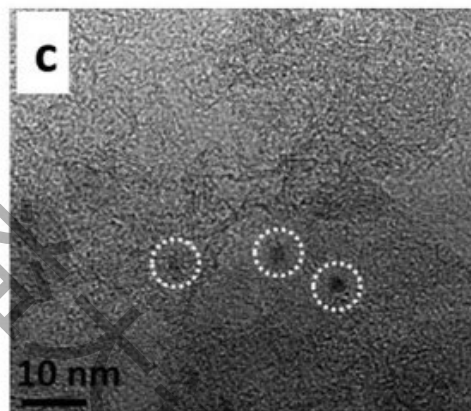
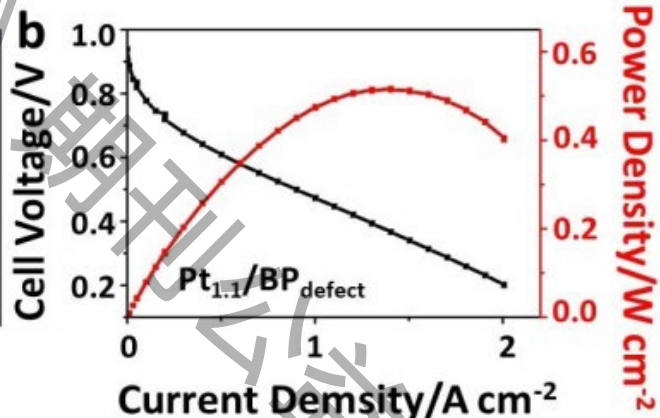
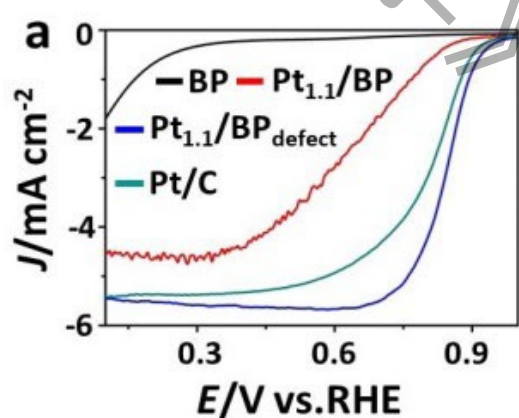


从个性化信息到精准设计的初探

碳缺陷铆定的Pt单原子ORR催化剂

Pt 利用率

$0.09 \text{ g}_{\text{Pt}} \text{ kW}^{-1}$



Summary:

1. Demonstrate a class of high performance Pt or metal-free ORR catalysts from **cheap and sustainable** carbon blacks;
2. The high performance (high activity, stability and tolerance to poisons) and super-low cost of these CB-based ORR electrocatalysts (CB-NF, CB-F or CB-NFe) make them the **best price/performance ratio** ever obtained for ORR;
3. ADMFC data unambiguously substantiate these CB-based non-Pt catalysts are the **most promising alternative** to Pt or other rare materials as ORR catalysts in alkaline fuel cells;
4. Open up **the possibility** of making other high performance cheap carbon-based metal-free catalysts for ORR.



《电化学》

《电化学》

分享一点心得体会

《电化学》
期刊公益大讲堂

《电化学》
期刊公益大讲堂

好的碱性催化体系：活性、稳定性问题不大，但目前市场上缺乏成熟的高性能碱性电解质膜与之匹配；

酸性体系：

- 1、低 / 非铂电催化剂**活性**难以提高到与铂竞争的水平；
- 2、即使表观活性可以提高一些，但在酸性体系中的长时**稳定性**却是致命的，至少目前还没有很好的办法解决。

文献中报导的千千万万的这类低 非铂电催化剂**价值、出路**在哪里？

- 1、抛开性能这个指标，为各类催化材料的基础研究提供理想模型：比如Fe-N-C 体系，此类文章爆炸式增长加快了人们深刻全面、认识该体系的速度；
- 2、在廉价燃料电池中的应用. . . .

不是所有燃料电池都要用到车上 / 需要经受苛刻的工作考验



不是所有燃料电池都要用到车上 / 需要经受苛刻的工作考验

催化 / 膜材料 $\xrightarrow{\text{特性}}$ 高活性 / 高稳定性：比如汽车等
稳定性中等：家用发电系统；应急发电系统；

性价比：性能 / 价格

性能差些，但有价格优势

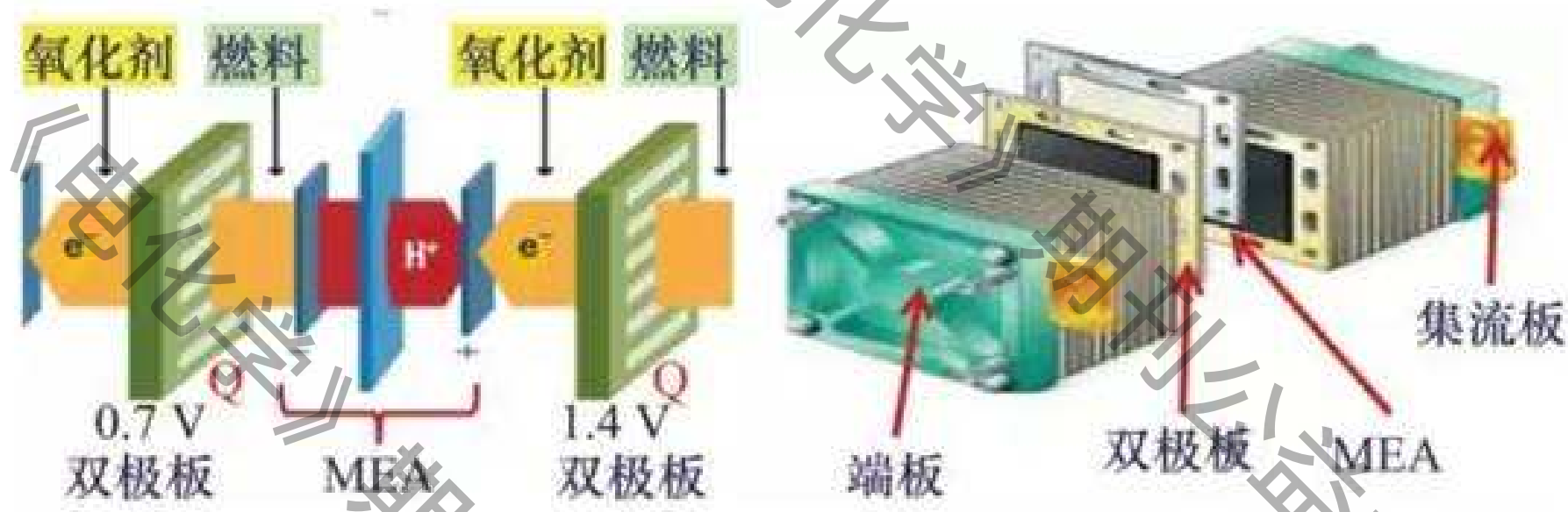
稳定性相对较差（比如可工作~几百小时）的电催化剂只要性价比合适，可以开发M E A可多次更换的廉价发电系统。（廉价催化剂、膜和碳纸）

活性很好，稳定性一般，或者活性中等但稳定性很好

开发批量制备工艺，降成本

物尽其用

“廉价燃料电池”



- 1、各部件都很便宜；
- 2、循环利用某些昂贵关键部件。
(更换廉价MEA) (类似共享单车)

凉山“330大火”

2019年3月30日18时许，四川省凉山州木里县雅砻江镇立尔村发生森林火灾，着火点在海拔3800米左右，地形复杂、坡陡谷深，交通、通讯不便。截至2019年4月4日15时15分，这次森林火灾已确认遇难31人。

扑救难点：

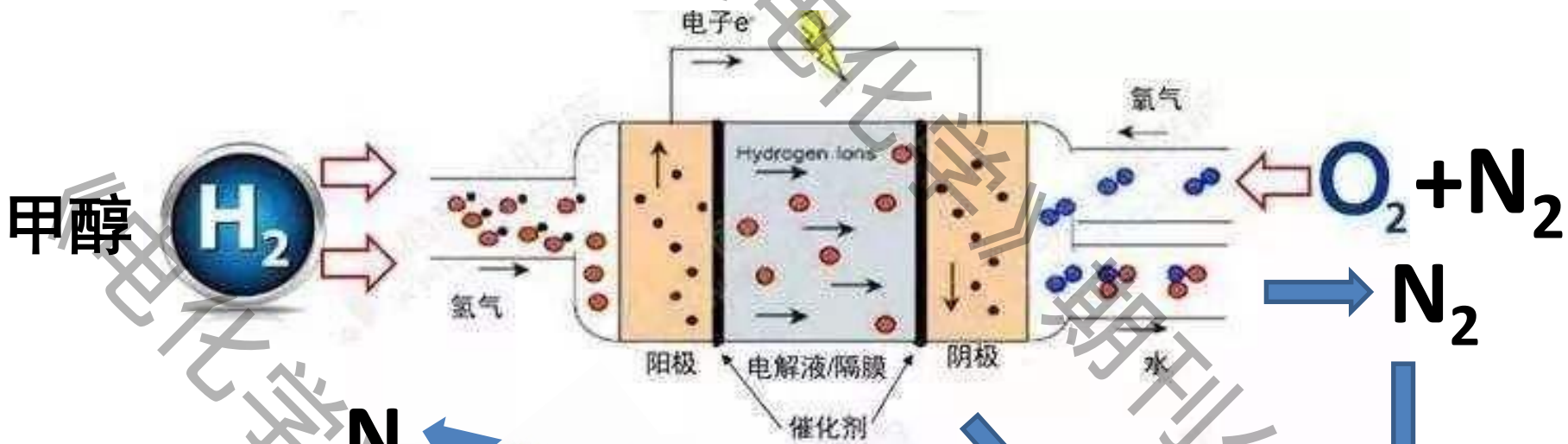
- 一：火场最高海拔约3700米，海拔高，风大且方向不定，火势难控制；
- 二：木里当地地形复杂，尤其是雅砻江沿岸一带山高坡陡，很多地方没有路，给灭火和搜救工作带来很大困难；
- 三：当地森林腐殖层较厚，火不易打熄；
- 四：山上取水非常困难。



不懂气体分离

2020年3月：
凉山西昌森林火灾致19人牺牲 - 四川发布

“廉价燃料电池”




民用+

尾气存储



高压储罐

氮气灭火系统分析

来自 维普 |  喜欢 0 阅读量 : 32

作者 : 尹静辉

摘要 : 氮气灭火系统是向防护区内释放纯氮气,将防护区内的氧气体积分数降低到物质持续燃烧所必须的体积分数(15%)以下而达到灭火目的的新一代灭火系统。氮气对臭氧层破坏系数(ODP值)为0,地球温暖化系数为0,是对人安全、对地球生态环境没有污染的环保产品。空气中所含氮气的比例为78%,灭火剂使用纯氮气,降低了灭火剂的充装使用成本。

关键词 : 纯氮 灭火系统 环保 低充装成本

氮气灭火系统是向防护区内释放纯氮气,将防护区内的**氧气体积分数降低到物质持续燃烧所必须的体积分数(15%)以下**而达到灭火目的的新一代灭火系统。氮气对臭氧层破坏系数(ODP值)为0,地球温暖化系数为0,是对人安全、对地球生态环境没有污染的环保产品。空气中所含氮气的比例为78%,灭火剂使用纯氮气,降低了灭火剂的充装使用成本。

Acknowledgement

1. Cooperators

Prof. Lin Zhuang, Wuhan University;

Prof. Gongquan Sun from DICP;

Prof. Jie Zeng from USTC;

Prof. Nanfeng Zheng from Xiamen U.;

Prof. Dijia Liu from Argonne National Laboratory;

Prof. Paul Alivisatos from UC Berkeley, USA

Prof. Bryan S. Pivovar from National Renewable Energy Laboratory, USA

2. Funding Support

Recruitment Program of Global “young Experts” of China; National Natural Science Foundation; National Basic Research Program of China

3. My group members



中国科学院长春应用化学研究所

[非画]作品欣赏



https://weibo.com/3714084647/profile?topnav=1&wvr=6&is_all=1#_rnd1590886689669