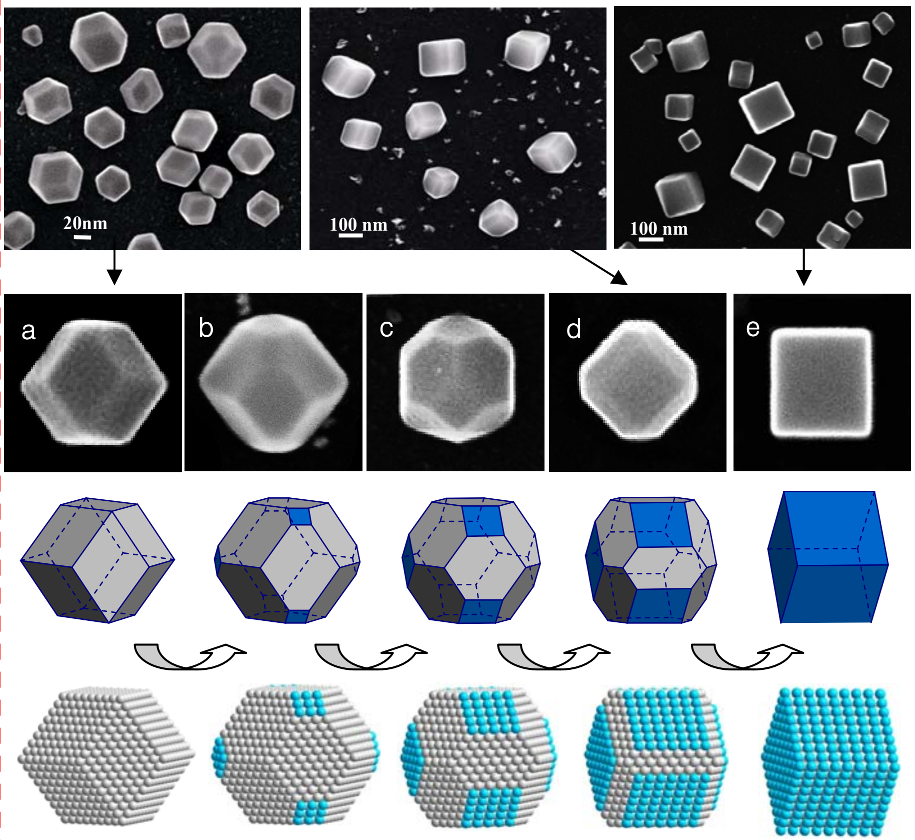
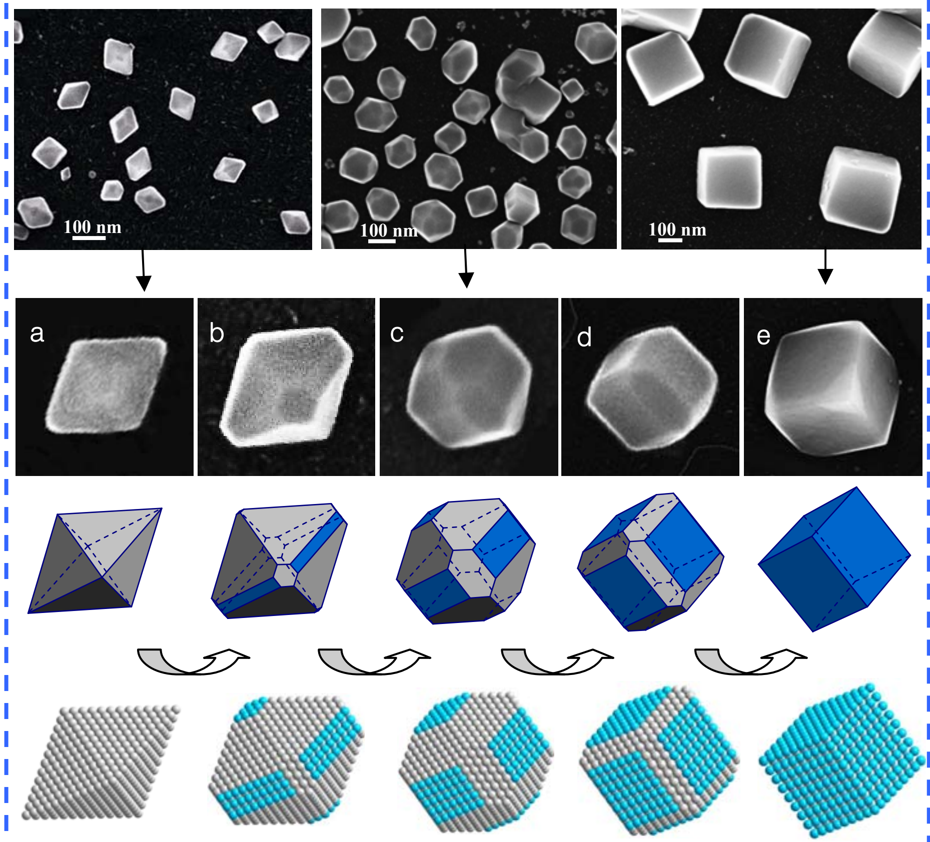
生长电位对Fe纳米粒子形貌的影响



E_{growth}	-1.03 V	-1.035 V	-1.05 V	-1.06 V	-1.07 V
t_{growth}	900 s	600 s	600 s	300 s	300 s

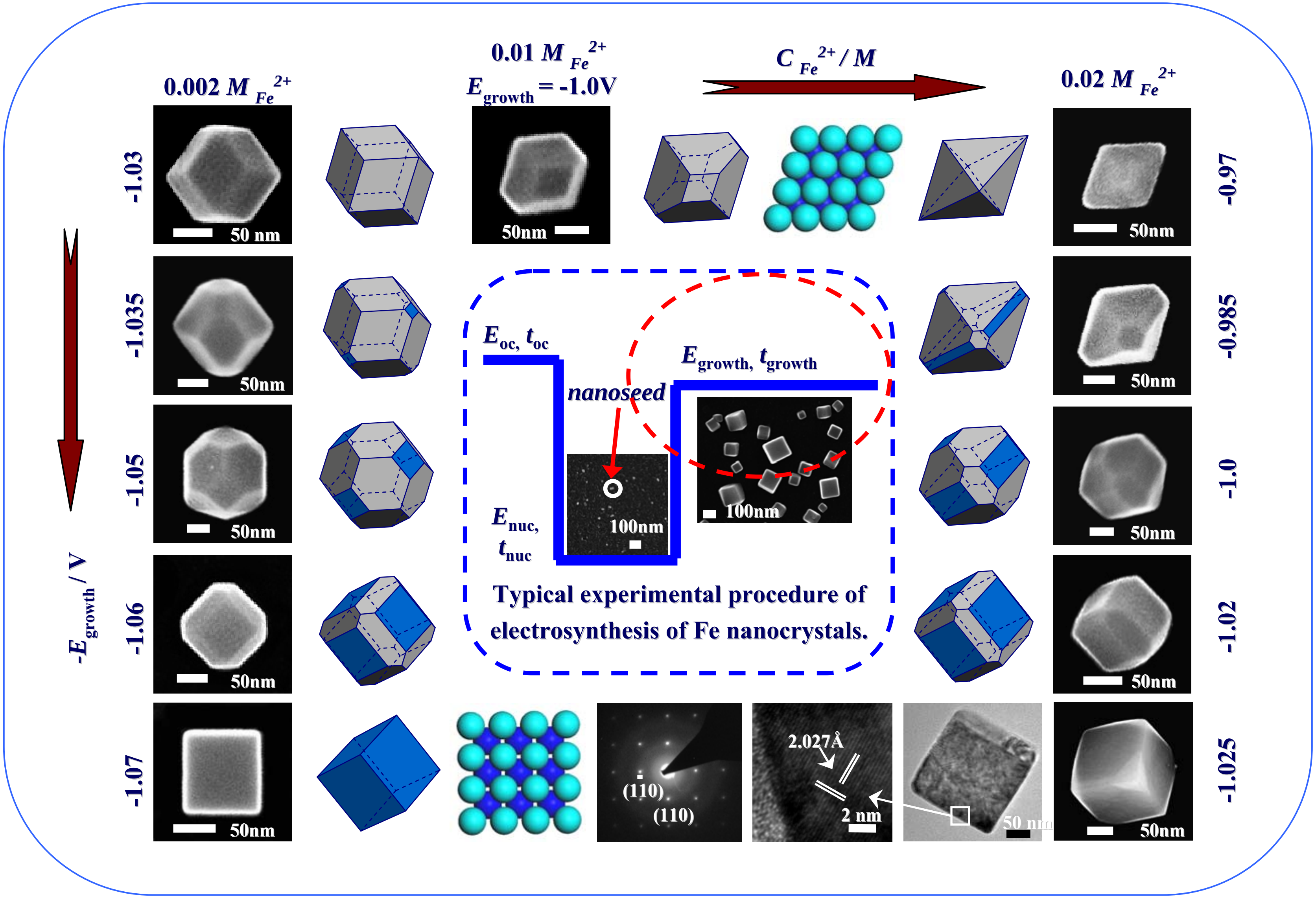
Fe NCs electrosynthesized in 0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solution,



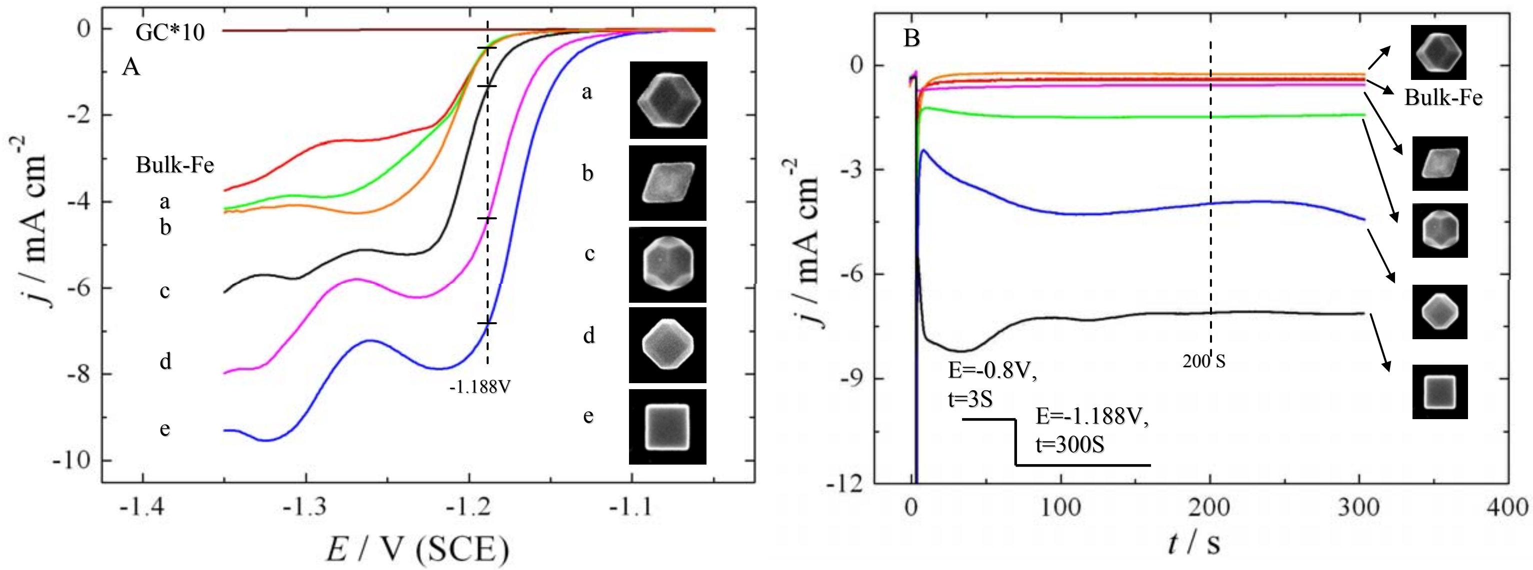
-0.97 V	-0.985 V	-1.0 V	-1.02 V	-1.025 V
900 s	900 s	600 s	300 s	300 s

Fe NCs electrosynthesized in 0.02 M $FeSO_4$ + 0.1M Na_2SO_4 solution,

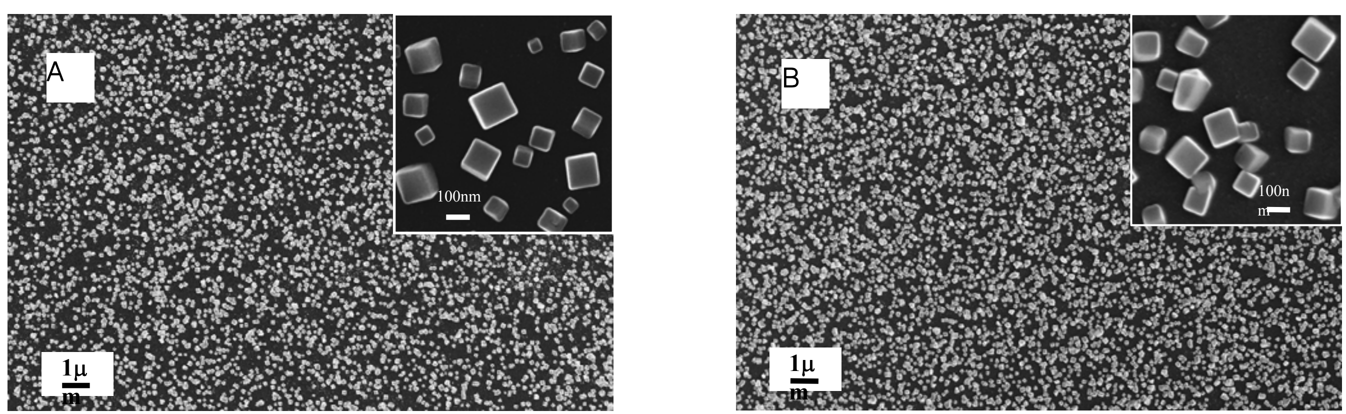
Fe纳米粒子合成条件－形貌全图



不同形貌Fe纳米粒子电催化活性及稳定性研究

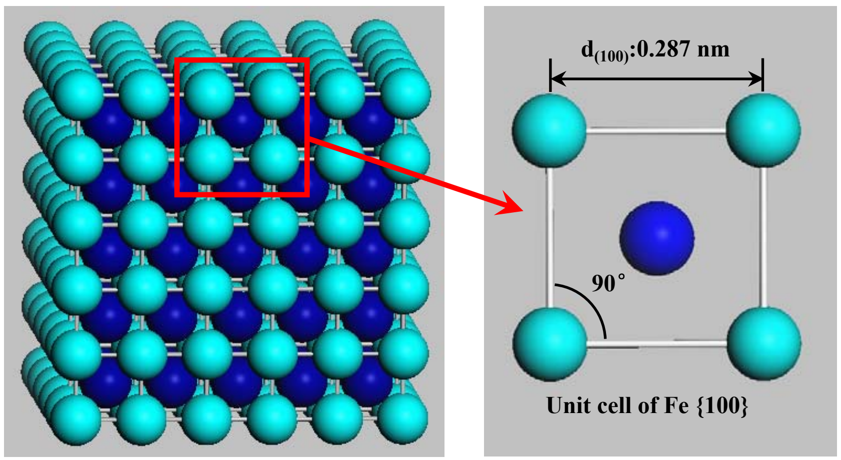


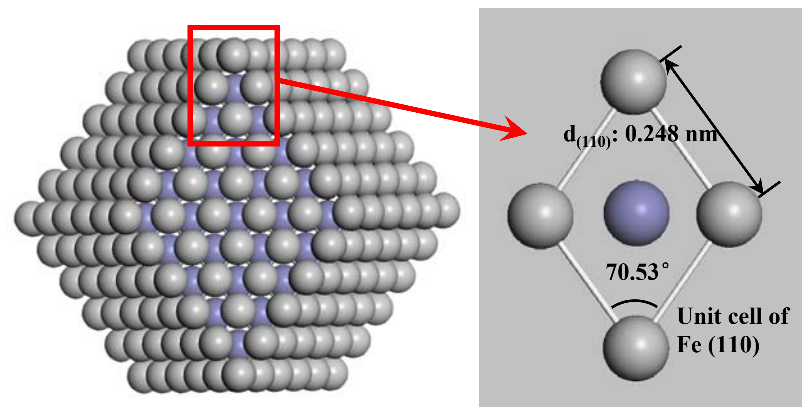
The electrocatalytic property of Fe NCs towards Nitrite reduction. (A) *j-E* curves recorded on nano-Fe/GC electrodes of Fe NCs with different shape in 0.01 M $NaNO_2$ + 0.2 M NaOH solution, scan rates 1 mV s^{-1}; (B) Steady j-t curves of nitrite reduction on nano-Fe/GC electrodes of Fe NCs of different shape.

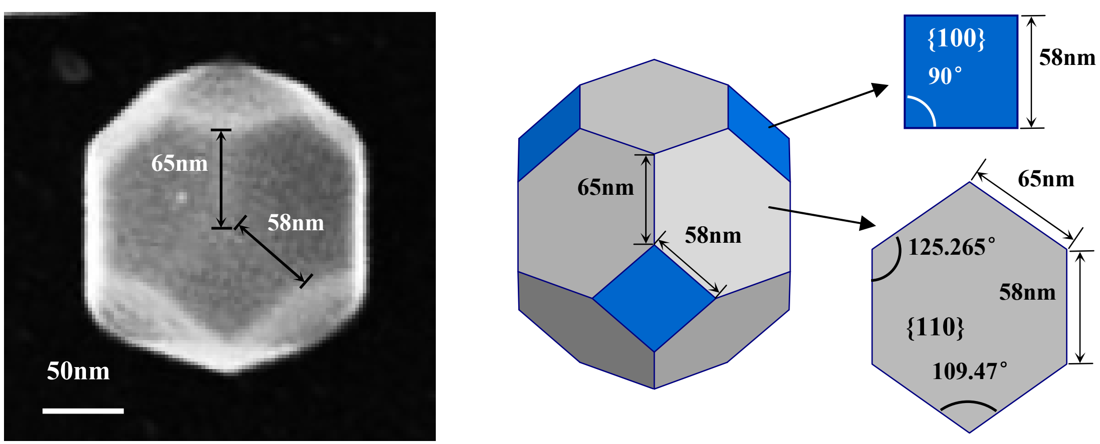


Comparison of SEM images of cube Fe NCs before (A) and after (B) elecrtocatalytic reduction of nitrite.

催化剂表面原子开放度 (*R*) 的计算



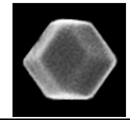
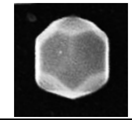
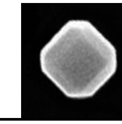
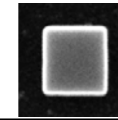


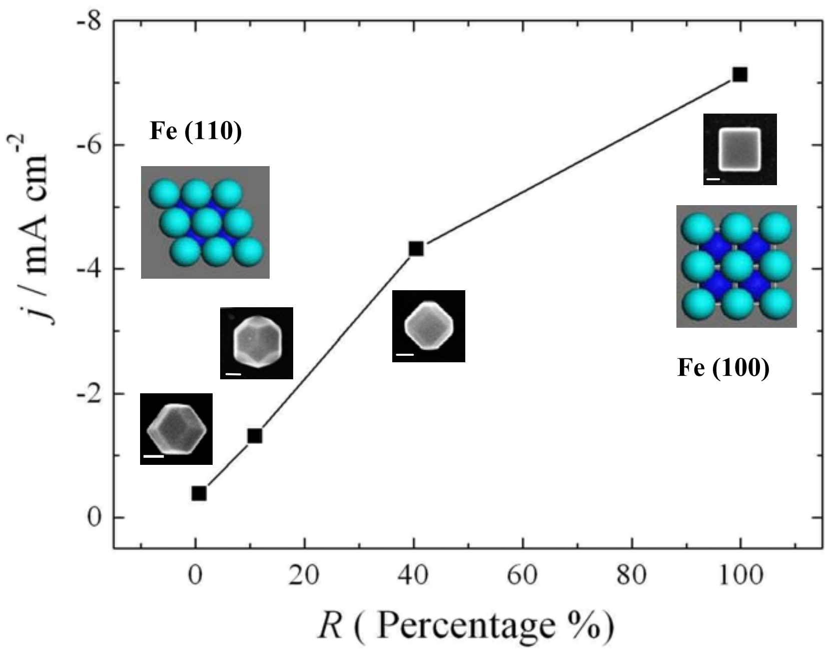


$$R = \frac{N_{\text{active atoms}}}{N_{\text{total surface atoms}}} \times 100$$

$$N_{\text{active atoms}} = N_{100} + N_{\text{conner}} + N_{\text{edge}}$$

催化剂表面原子开放度(*R*)与催化活性之间的关系

Shapes of Fe NCs	bulk-Fe				
R / %	----	0.77	10.93	40.57	100
E_{onset} / V (@ j = -0.07 mA.cm^{-2})	-1.181	-1.182	-1.131	-1.093	-1.084
j / mA.cm^{-2} (@ E = -1.188V, measured from CVs of Fig.4.10A)	-0.40	-0.385	-1.308	-4.32	-6.82
j / mA.cm^{-2} (@ E = -1.188V and t =200 s, measured from Fig.4.10B)	-0.389	-0.261	-1.486	-3.985	-7.126



j **was measured at –1.188 V in *j*-*E* curves, the scale bar in all SEM images is 50 nm.**

本章小结

1. 发展了程序电位阶跃电沉积法，成功地在GC电极表面电沉积制备了由封闭结构的{110}晶面组成的菱形十二面体和四方双锥Fe纳米晶体 。

2. 通过对生长电位（E_{growth}）和沉积液浓度的调控，改变了纳米粒子表面各（hkl）密勒指数二维晶核的生长速度，进而实现对Fe纳米晶体形状和表面结构的精确调控。

3. 结合不同形状Fe纳米粒子，求算其各自的表面原子开放度(*R*)。并将*R*值与其催化活性关联，获得Fe纳米粒子电催化剂活性随(*R*)增加而升高的变化规律 。

论文答辩提纲

1、研究背景介绍

2、结果与讨论

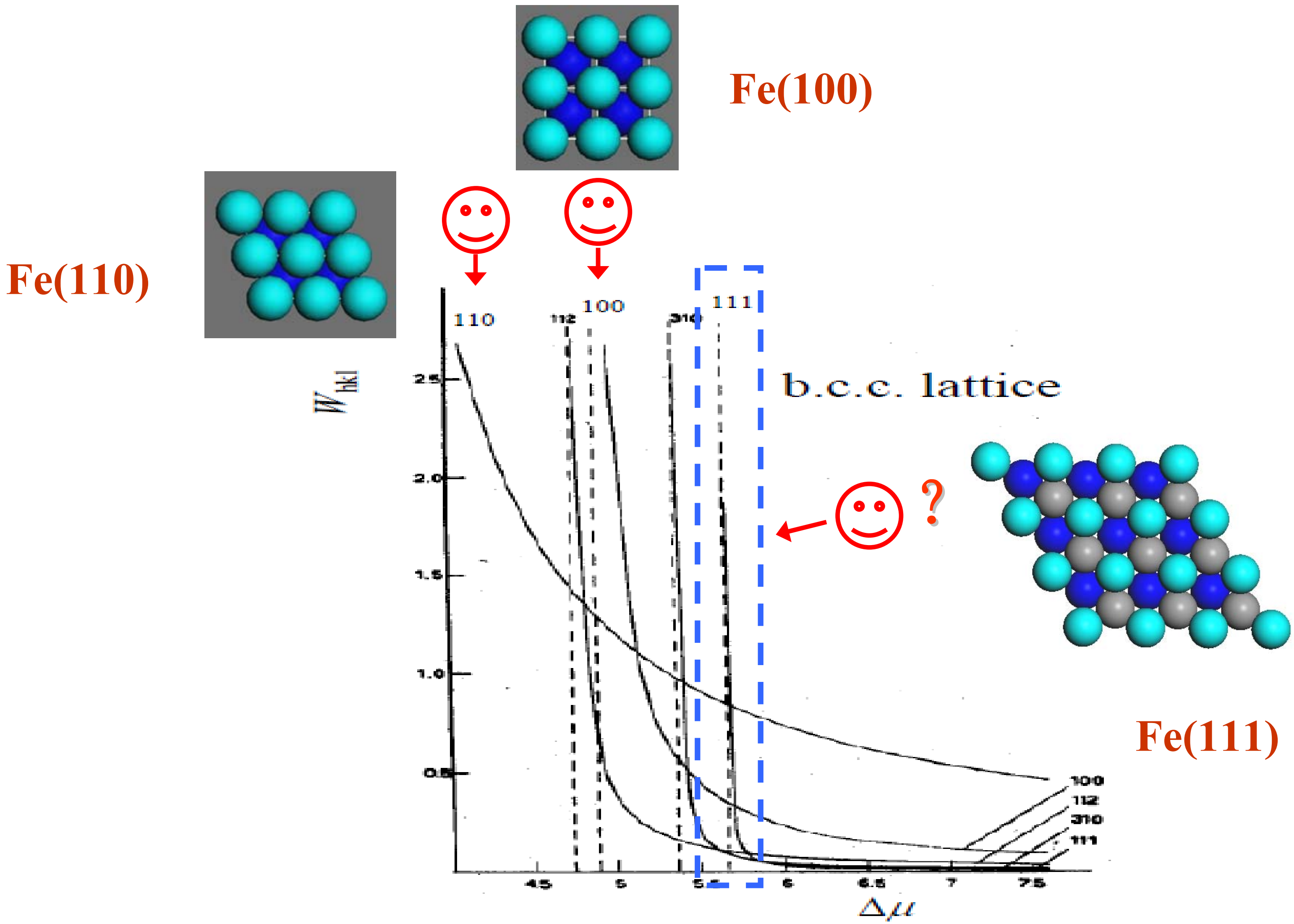
(1) 立方体Fe纳米粒子的制备、表征与性能。

(2) 菱形十二面体、四方双锥和十八面体等一系列Fe纳米粒子的形貌控制合成。

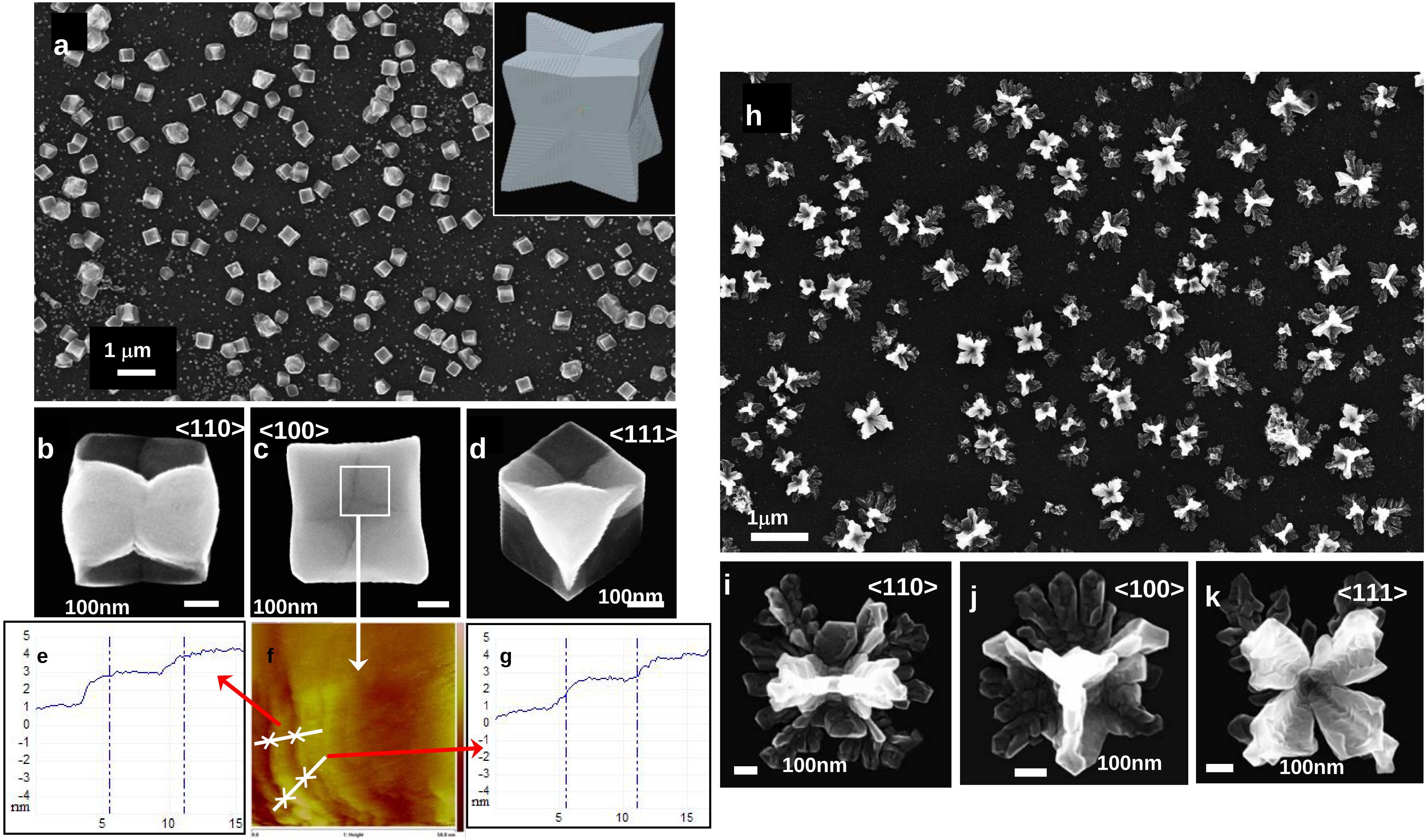
(3) 八极子、枝晶和平行连晶形Fe纳米粒子的制备与性能。

3、结论

运用二维晶核生长理论指导更开放结构晶面的制备

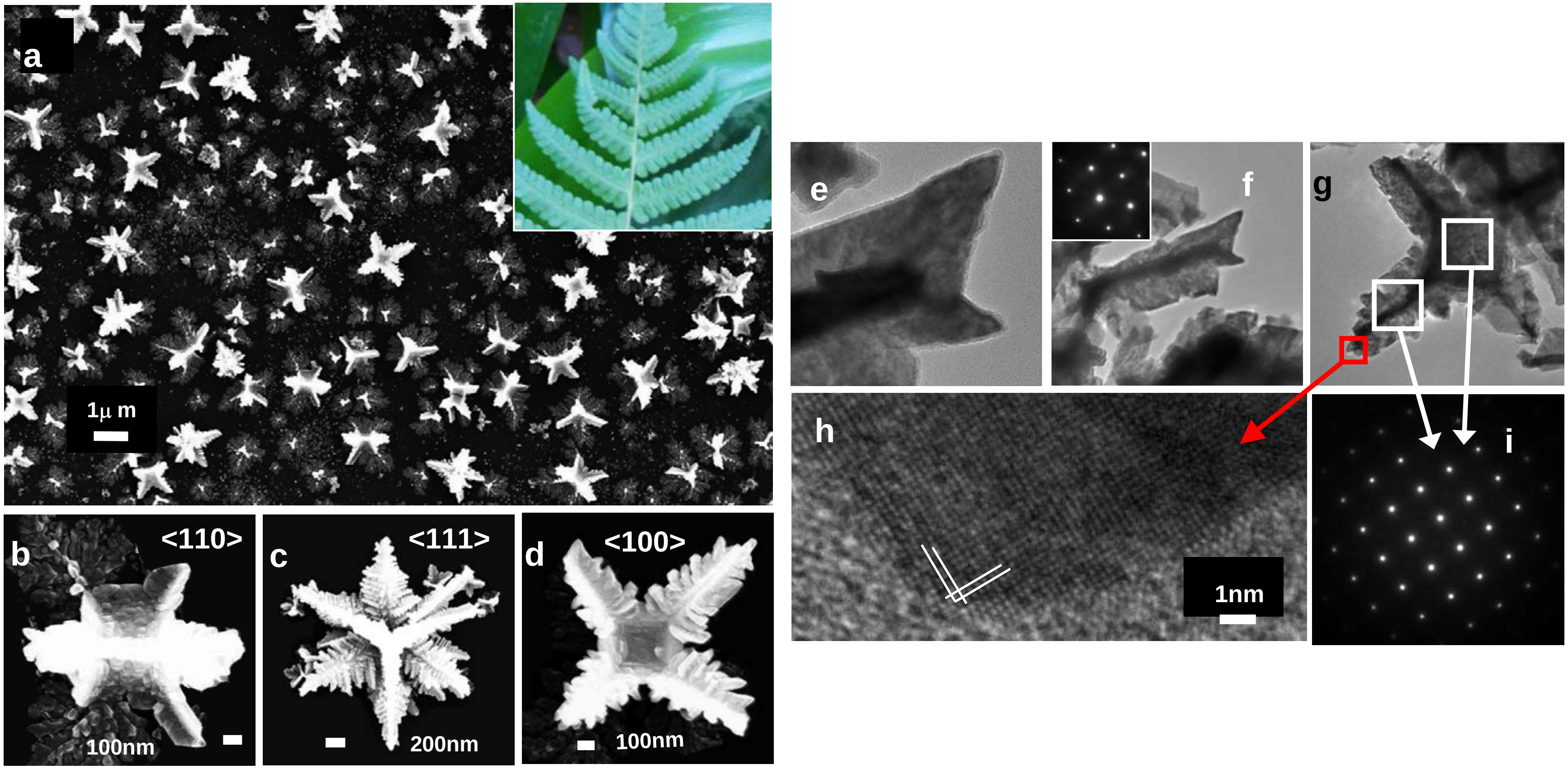


八极子及枝晶Fe纳米粒子制备与表征



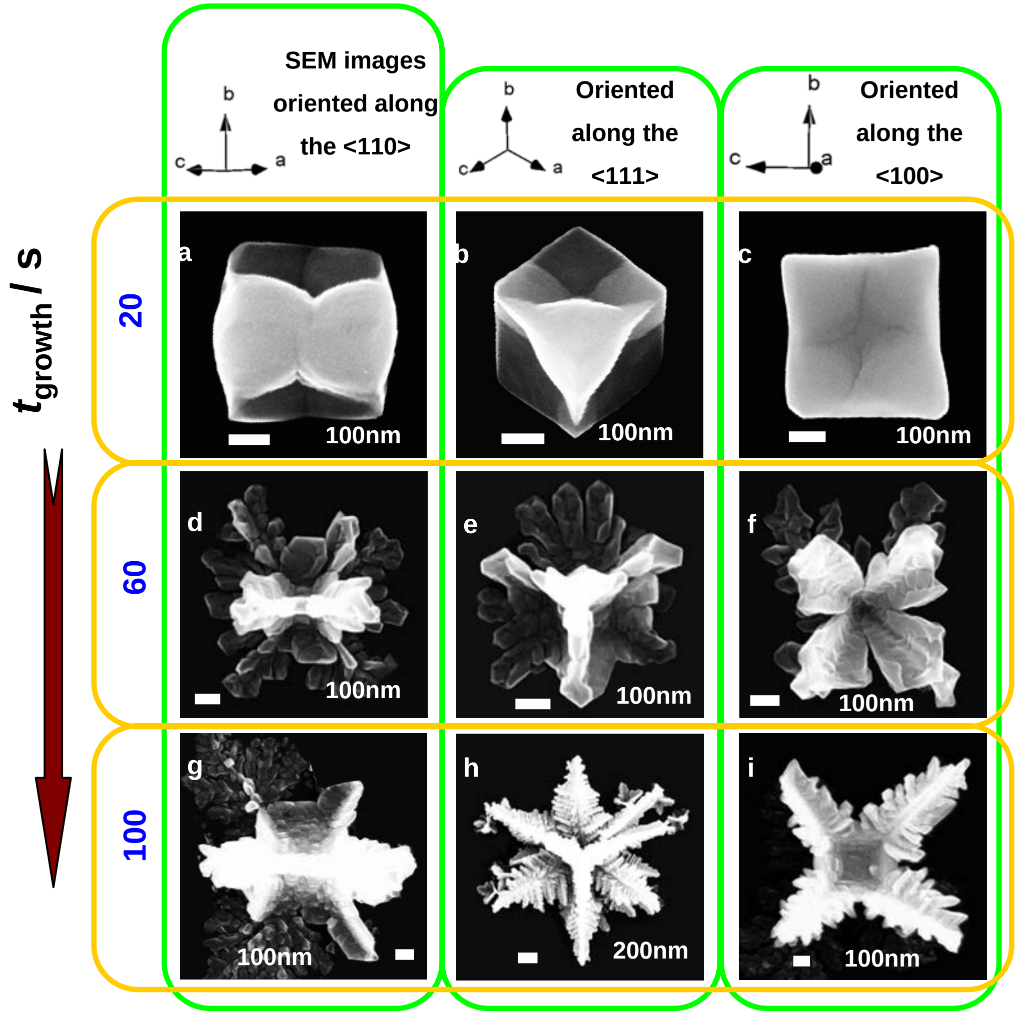
SEM image of Fe NCs electrosynthesized in 0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solutions, E_{growth}=-1.2V; (a-g) t_{growth}=20s; (h-k) t_{growth}=60s

蕨状单晶Fe纳米粒子形貌的表征



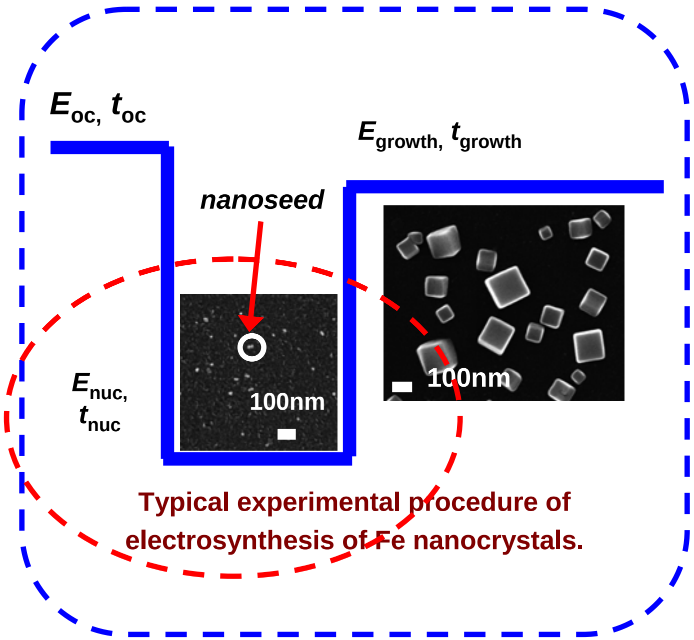
SEM and TEM images of Fe NCs electrosynthesized in 0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solutions, E_{growth}=-1.2V; t_{growth}=100s

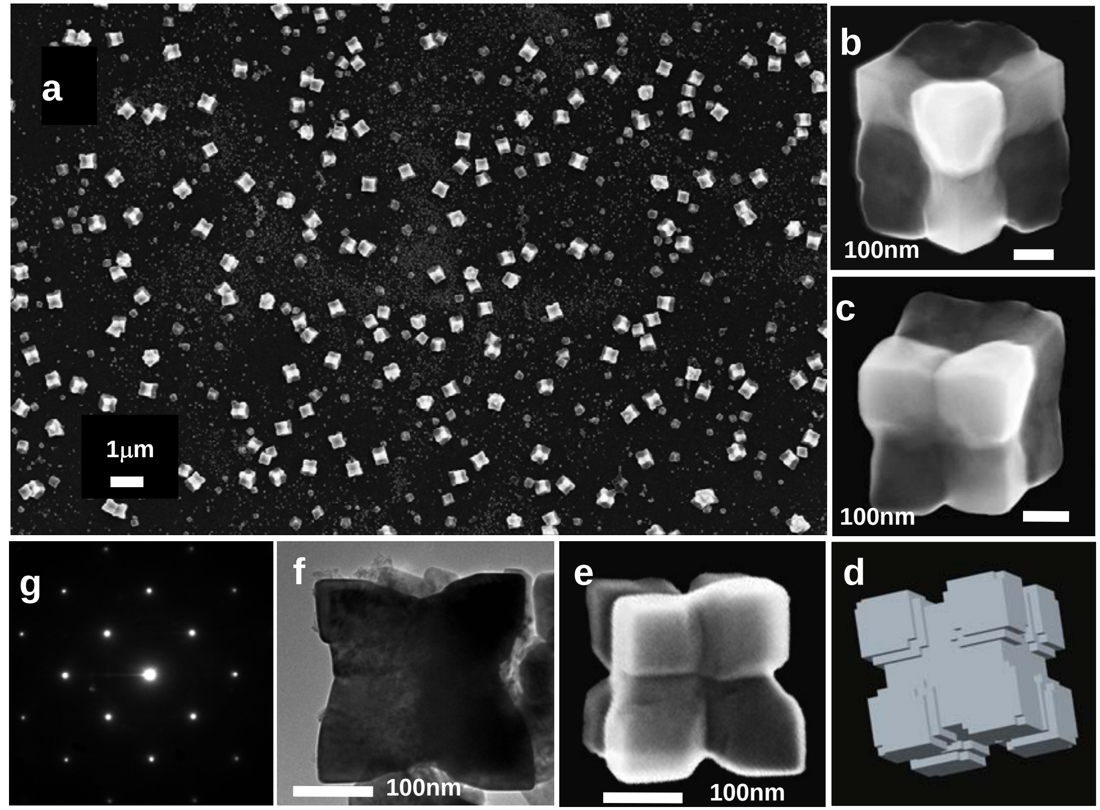
八极子—枝晶Fe纳米粒子生长过程



The relationship between t_{growth} and the shapes of the single-crystalline dendritic Fe Nanostructures

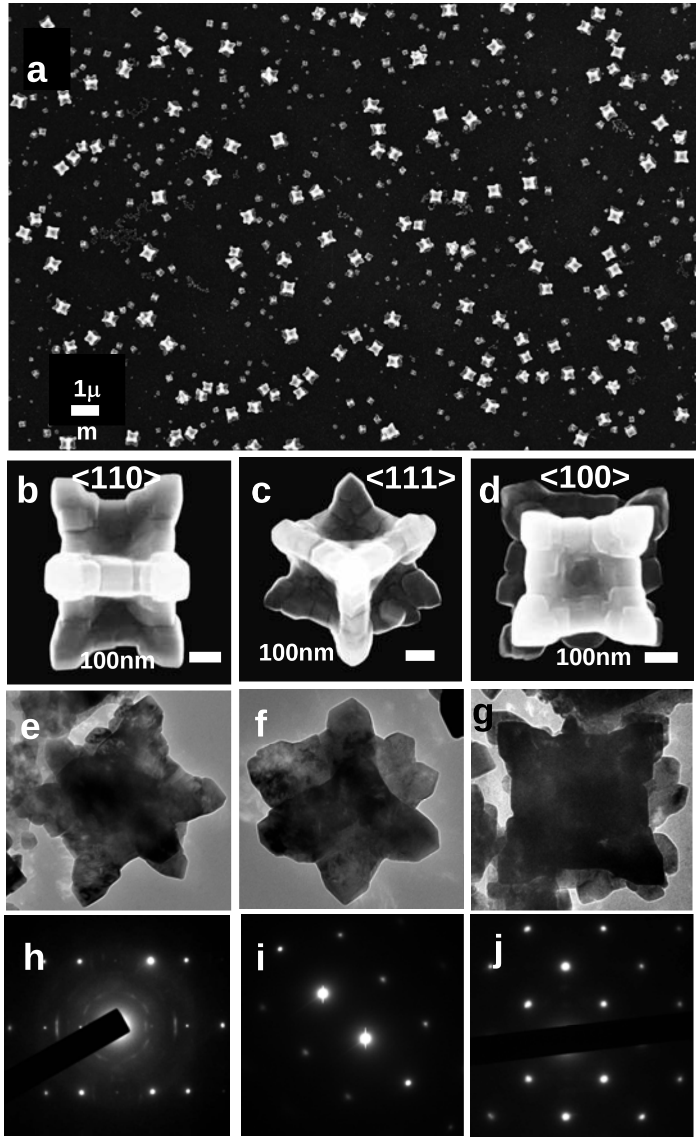
成核时间和成核电位对Fe纳米粒子最终形貌的影响



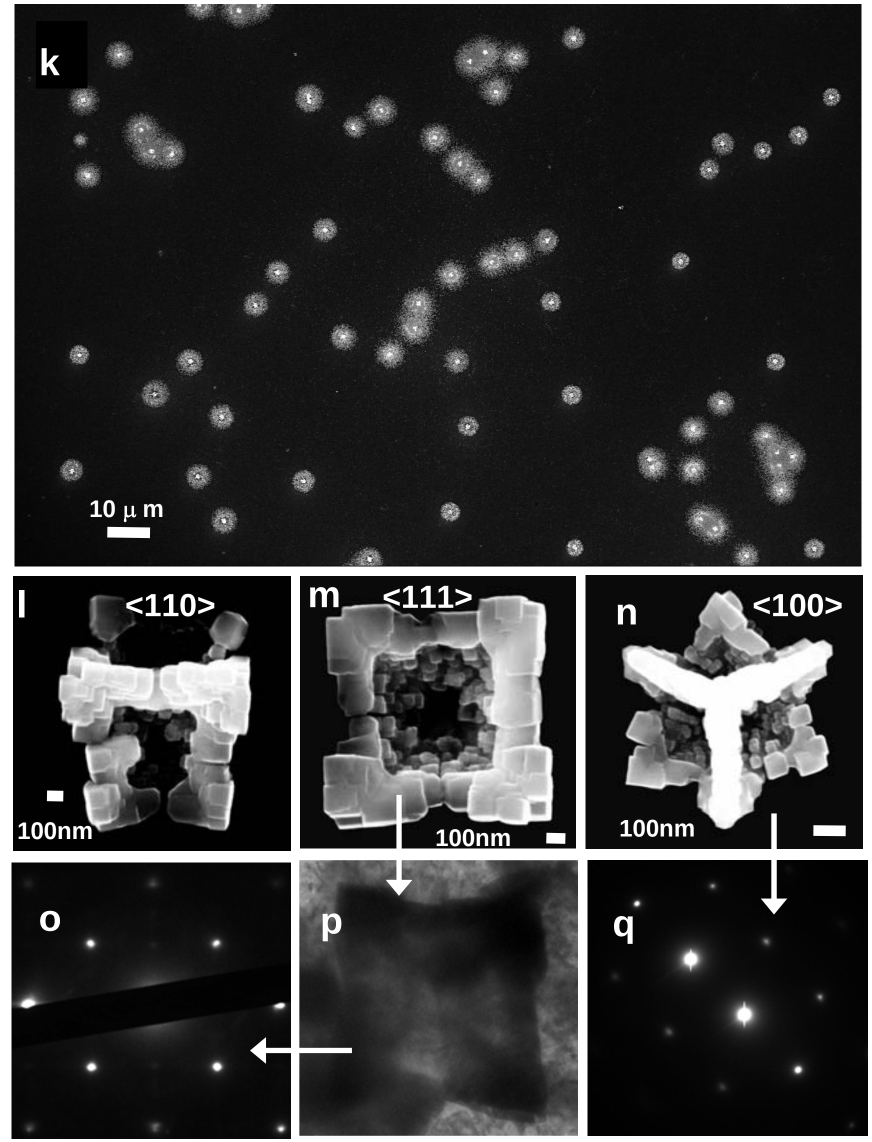


(a) SEM image of Fe NCs electrosynthesized in 0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solutions, E_{nuc}=-1.4V，t_{nuc}=2s; E_{growth}=-0.9V， t_{growth}=72s; (b,c,e) three typical high magnified SEM images of octapods Fe NCs oriented nearly along the <111>, <110> and <100> axes (d) the geometrical models of octapods Fe NCs; (b-d) three typical high magnified SEM images of octapods Fe NCs oriented nearly along the <110>, <100> and<111> axes; (f,g) TEM image and SAED pattern of octapods Fe NC recorded along <100> direction.

平行连晶Fe纳米粒子生长过程

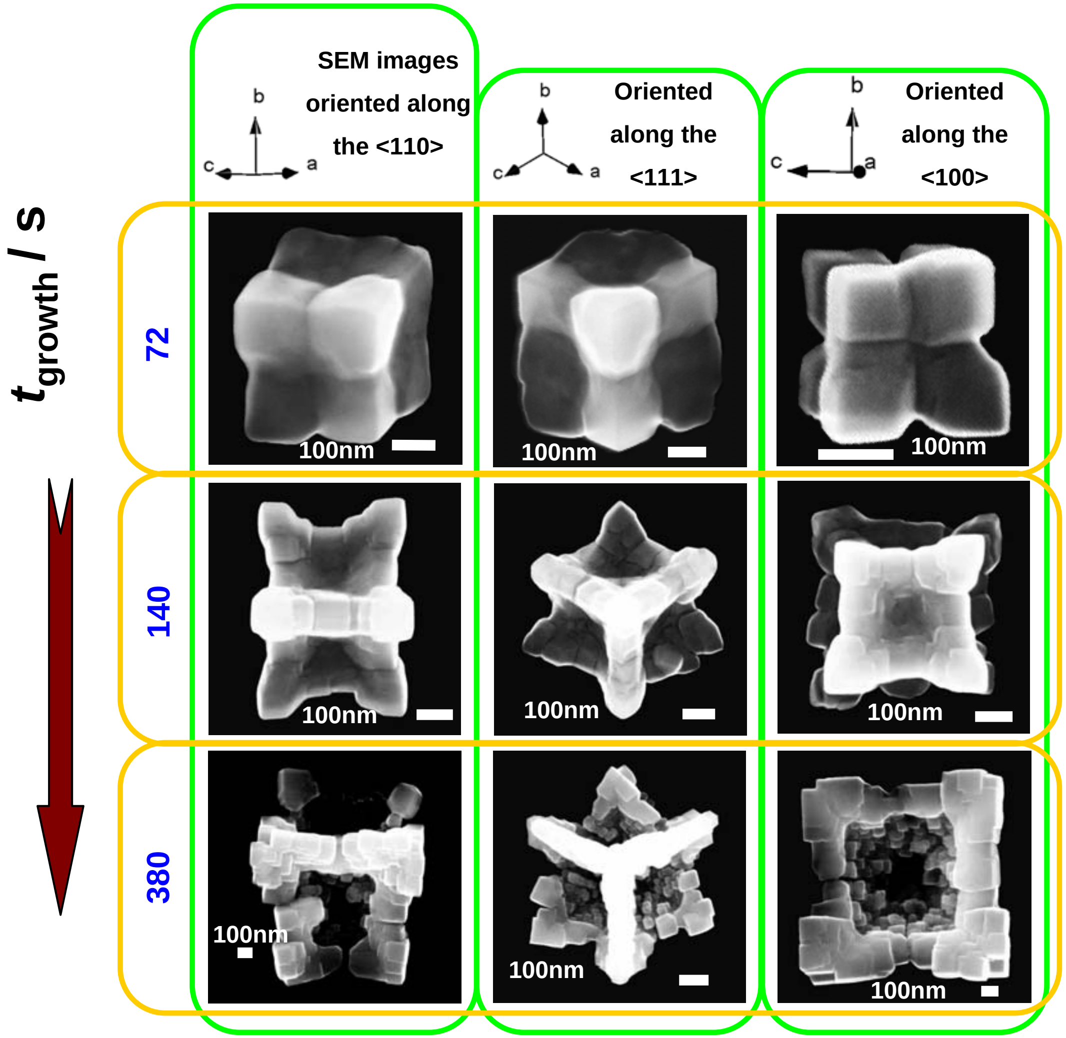


0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solutions, E_{nuc}=-1.4V， t_{nuc}=2s; E_{growth}=-0.9V， t_{growth}=*140s*;



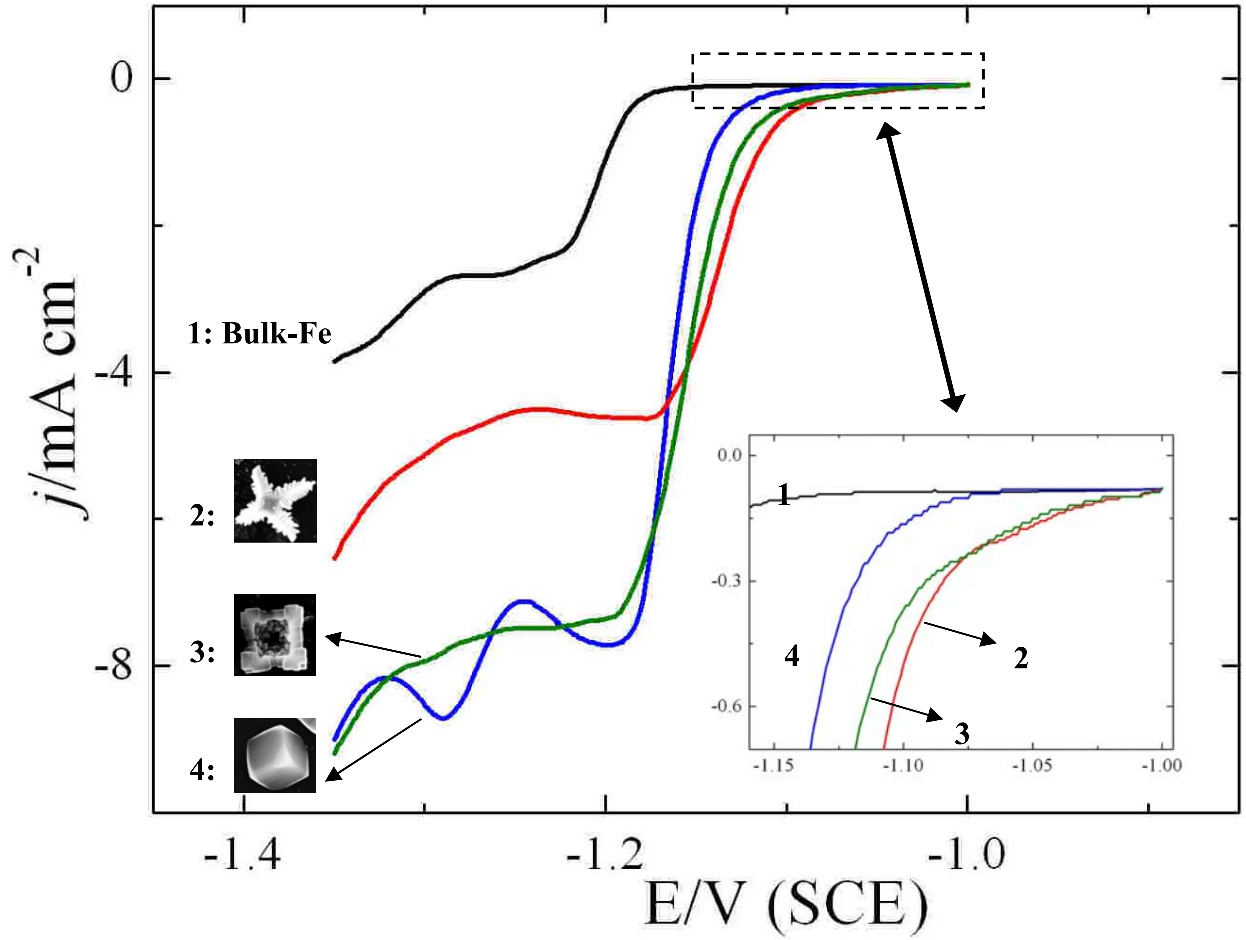
0.002 M $FeSO_4$ + 0.1M Na_2SO_4 solutions, E_{nuc}=-1.4V， t_{nuc}=2s; E_{growth}=-0.9V， t_{growth}=*380s*;

八极子－平行连晶Fe纳米粒子生长过程



The relationship between t_{growth} (E_{nuc}=-1.4V， t_{nuc}=-2s); and the shapes of the single-crystalline parallel intergrouth Fe Nanostructures

枝晶，平行连晶Fe纳米粒子催化活性研究



The electrocatalytic property of Fe NCs towards Nitrite reduction. *j-E* curves recorded on nano-Fe/GC electrodes of Fe NCs with different shape in 0.01 M $NaNO_2$ + 0.2 M NaOH solution, scan rates 1 mV s^{-1}.

结　　论

1. 用CV和CA电沉积的方法，在玻碳（GC）基底上制备具有立方体结构的Fe单晶纳米粒子。并实现了对其粒径的控制。
2. 建立了对纳米Fe电极活化表面积的标定方法。
3. 发展程序电位阶跃电沉积方法，系统地实现了对Fe纳米晶体形状和表面结构的精确调控。成功地制备出具有完美晶型的菱形十二面体、四方双锥、一系列十八面体，以及立方体Fe单晶纳米粒子。
4. 运用程序电位阶跃电沉积法，成功地在GC电极表面电沉积制备了枝晶和平行连晶等单晶Fe纳米材料，并系统地研究了其生长过程。
5. 所制备的各种形貌Fe纳米粒子的电催化活性研究结论如下:

枝晶>平行连晶>立方体>十八面体>菱形十二面体≈四方双锥≈本体Fe

本论文的研究结果不仅从实验上验证了二维晶核生长理论。而且进一步证明在实现纳米催化剂形状控制与合成的征程中，电化学法是一种非常有效的方法。它为合成和制备更多、更高效的催化剂提供了有效的途径。

致　　谢

衷心感谢导师孙世刚教授的悉心指导和栽培！

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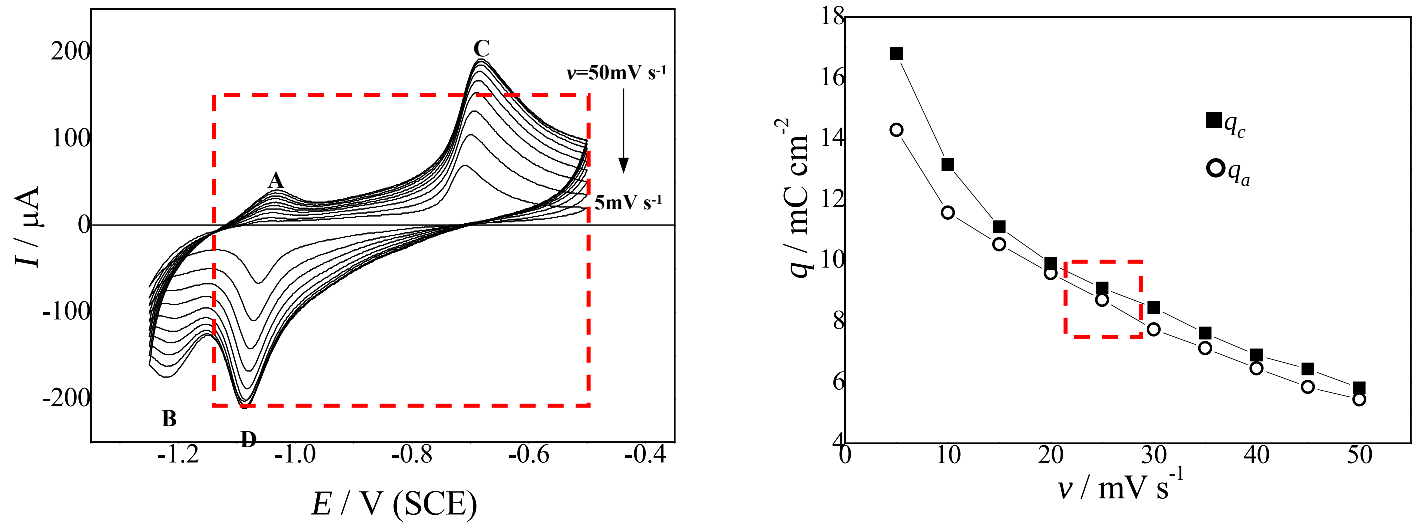
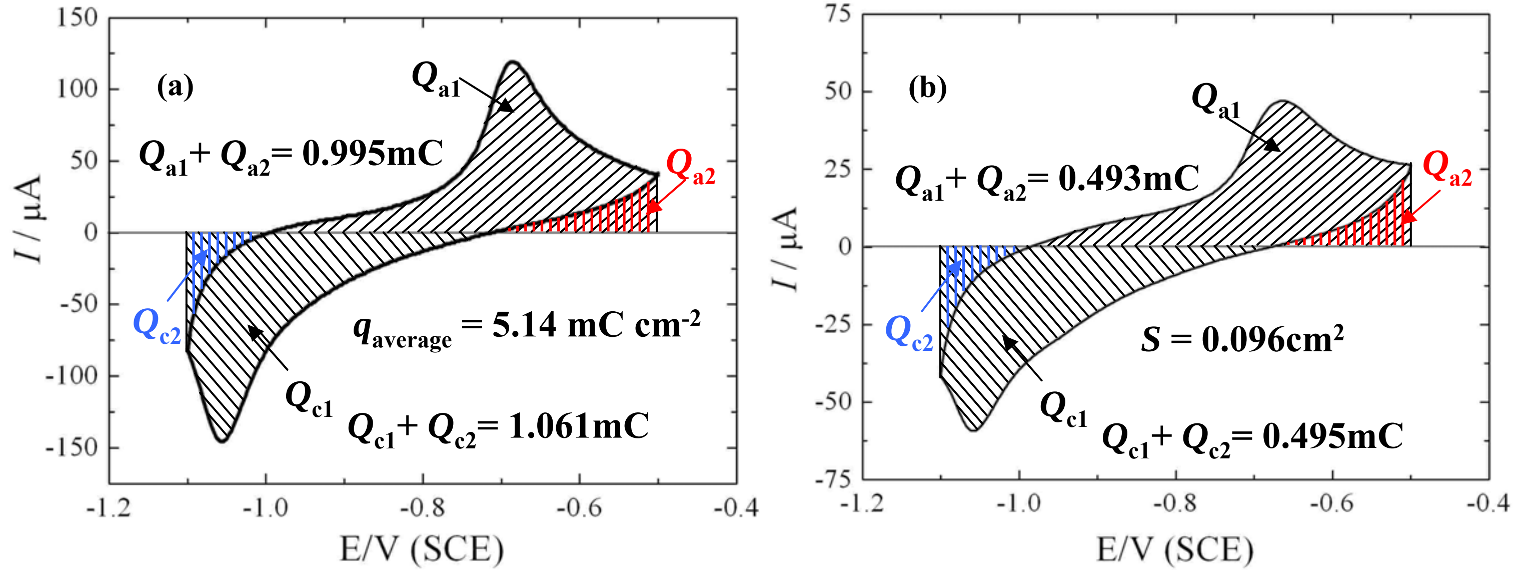
感谢所有帮助、支持过我的老师和同学们！

感谢答辩委员会各位老师的莅临！
敬请指正！

纳米Fe电极活性面积标定方法介绍





Cyclic voltammograms of bulk Fe (a) and cube nm-Fe/GC (b) electrodes, 0.2 M NaOH solution, scan rate 25 mV s^{-1}, with potential scan range between -1.1 and -0.5V.