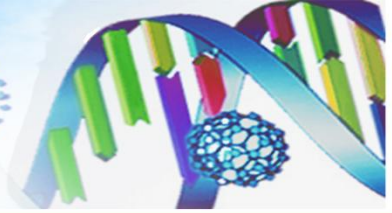
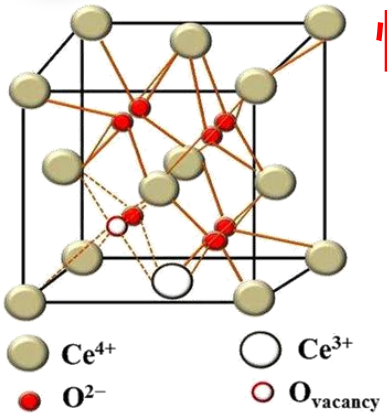


纳米二氧化铈在细菌表面的生物转化及毒性机制

何潇

中国科学院高能物理研究所

纳米二氧化铈（nanoceria）



性能优异

很强的储存/释放氧的能力

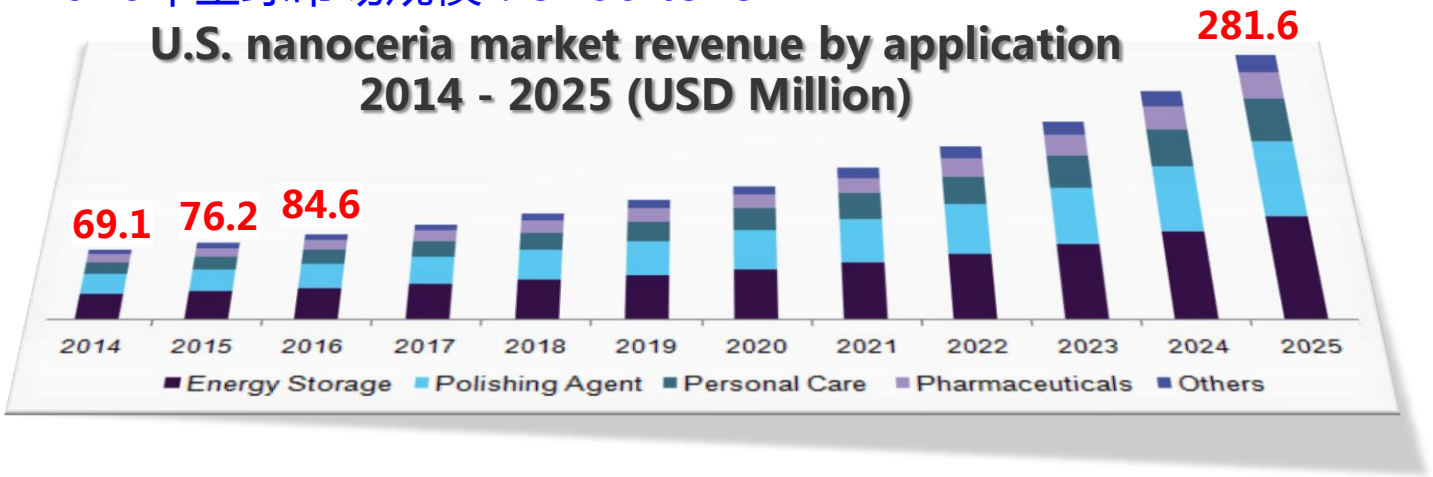
Ce^{3+}/Ce^{4+}的可逆转化

催化生成/清除ROS

应用广

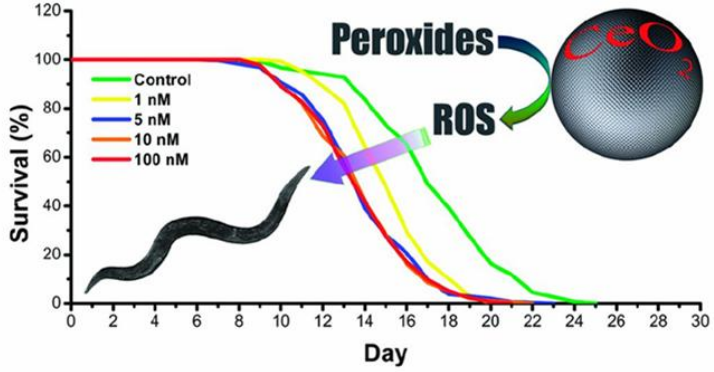
产量大

2016年全球市场规模：9100 tons



Nanoceria的环境生物效应研究：必要性

率先开展**环境相关低剂量暴露研究**（颗粒浓度：~0.1 pmol/L），并发现纳米CeO_2的负面效应。

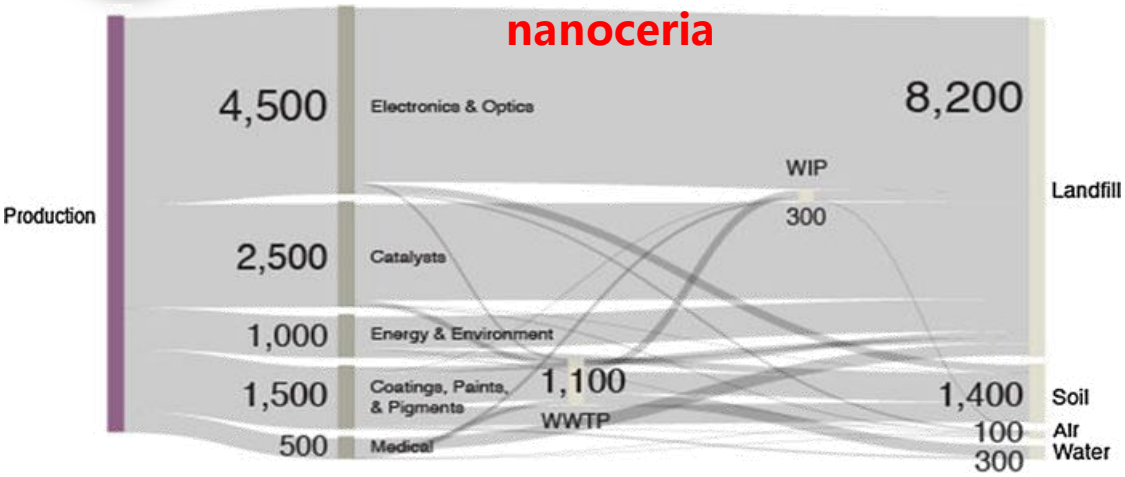


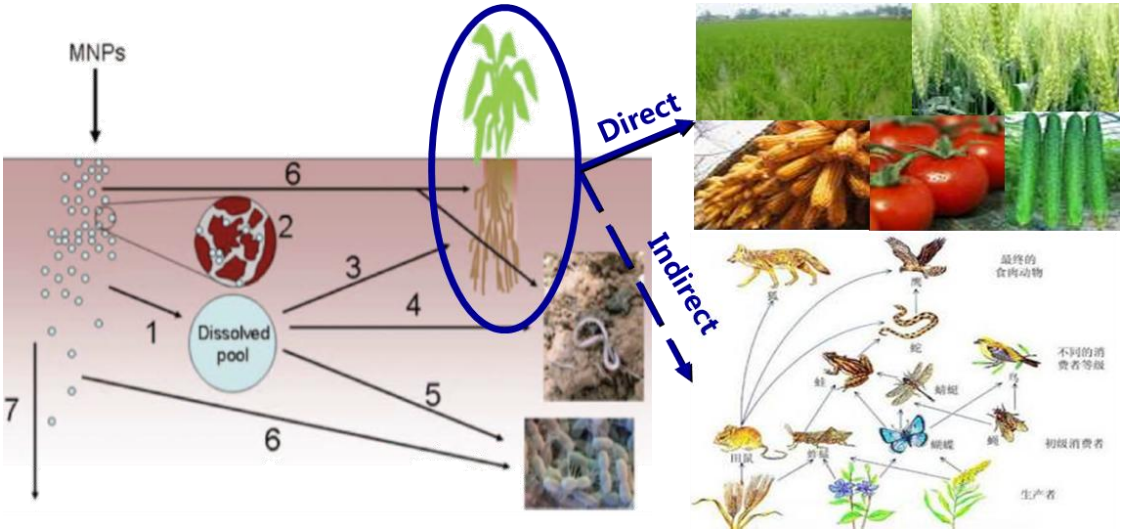
暴露介质中的CeO_2含量：	0.172 ng/g
每条线虫体内CeO_2含量：	~20 fg
	~5 ng/g

高剂量暴露 → 环境相关低剂量暴露

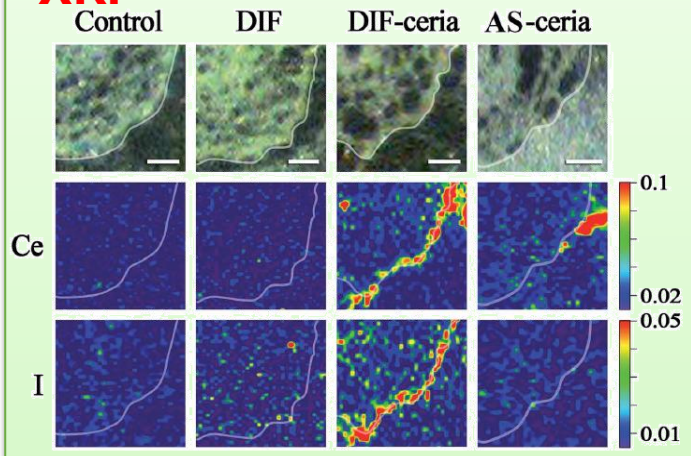
0.01-100 nmol/L → 0.0001 nmol/L

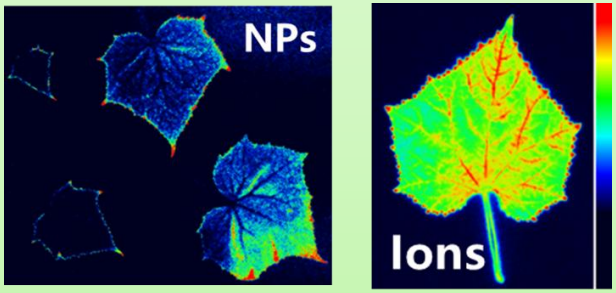
关键环节：迁移&转化





J Nanopart Res 2013, 15, 1692





Environ Sci Technol 2018, 52: 7921
RSC Adv 2015, 5:4554
Metallomics 2011, 3:816

纳米材料的生物转化

Agglomeration/deagglomeration

Adsorption/desorption

Complexation

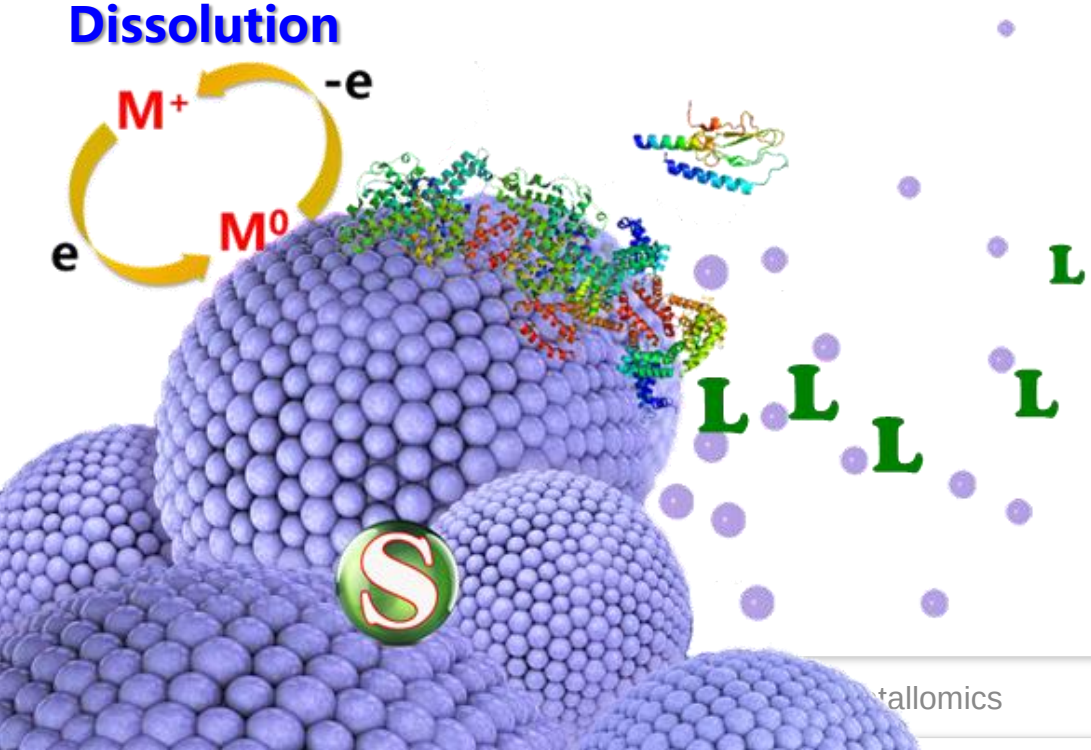
Sulfidation

Redox

Dissolution

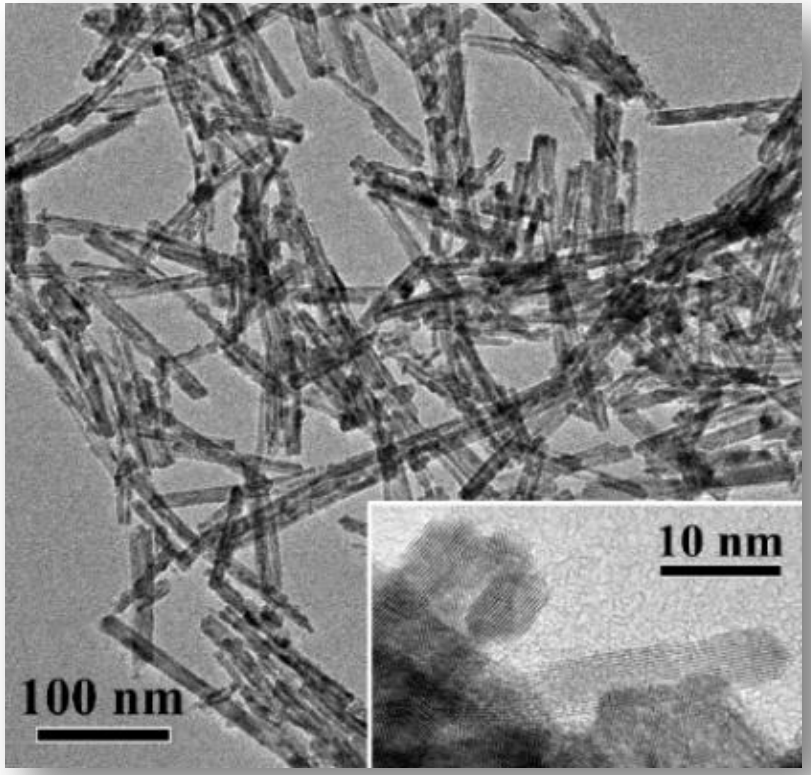
in situ

nano-bio interface

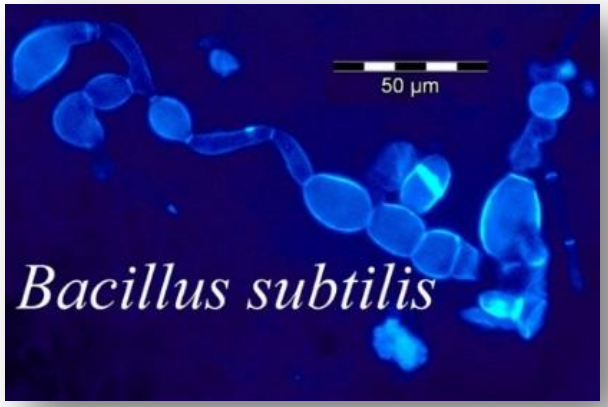


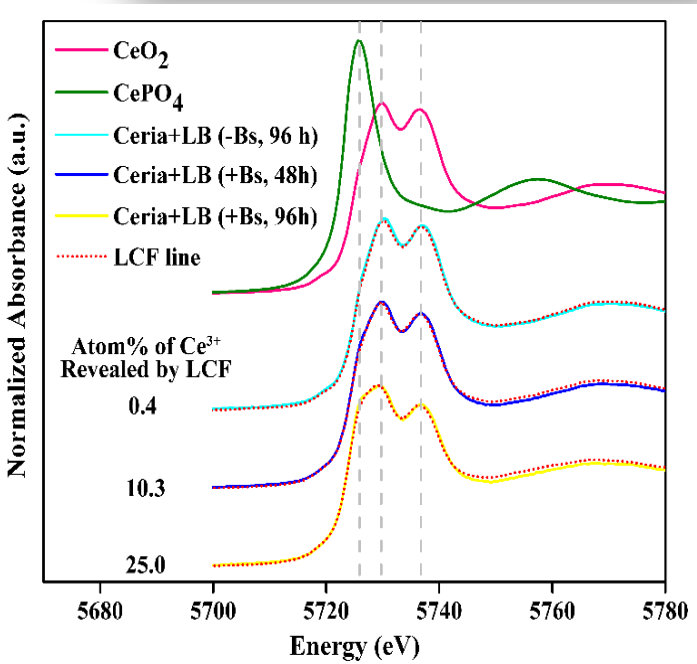
Environ Sci Technol 2018, 52: 7921
Environ Sci Technol 2017, 51: 5215
Environ Sci Technol 2015, 49: 10667
Environ Sci Technol 2012, 46: 1834
Environ Sci Technol 2011, 45: 3725
Environ Sci Technol Lett 2017, 4: 380
Angew Chem Int Ed, 2015, 6: 5820
ACS Nano 2012, 6: 9943
Nanotoxicology 2015, 9: 262
Nanotoxicology 2015, 9: 1
Nanotoxicology 2012, 6: 233
Nanotoxicology 2011, 5: 743
Environ Sci： Nano 2019, 10.1039/C8EN01002A
Environ Sci： Nano 2019, 10.1039/C8EN01089G
Environ Sci： Nano 2014, 1: 459
Environ Pollut 2017, 224: 392
Environ Pollut 2017, 220B: 1400
Environ Pollut 2015, 198: 8
Environ Pollut 2015, 196: 194
Sci China Chem 2015, 58: 761
Acc Chem Res 2013, 46: 761
Small 2013, 9(9-10): 1482

Nanoceria与细菌的相互作用

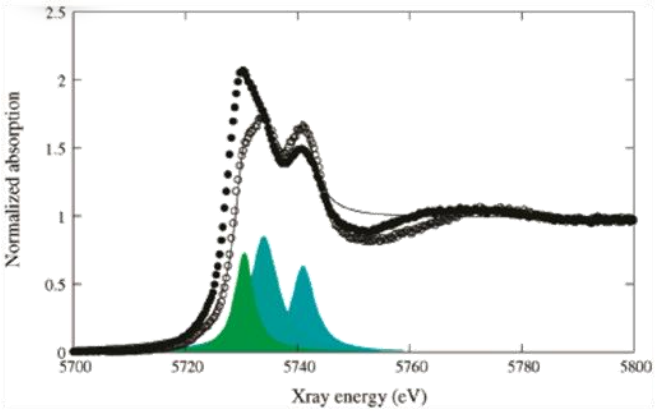


Length: 168±18 nm
Width: 8.5±1.5 nm





Nanoceria的细菌毒性机制？

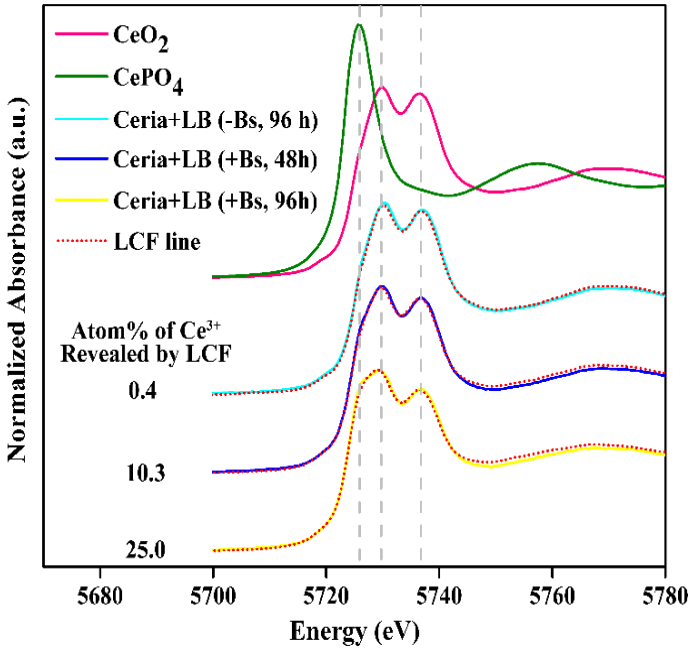


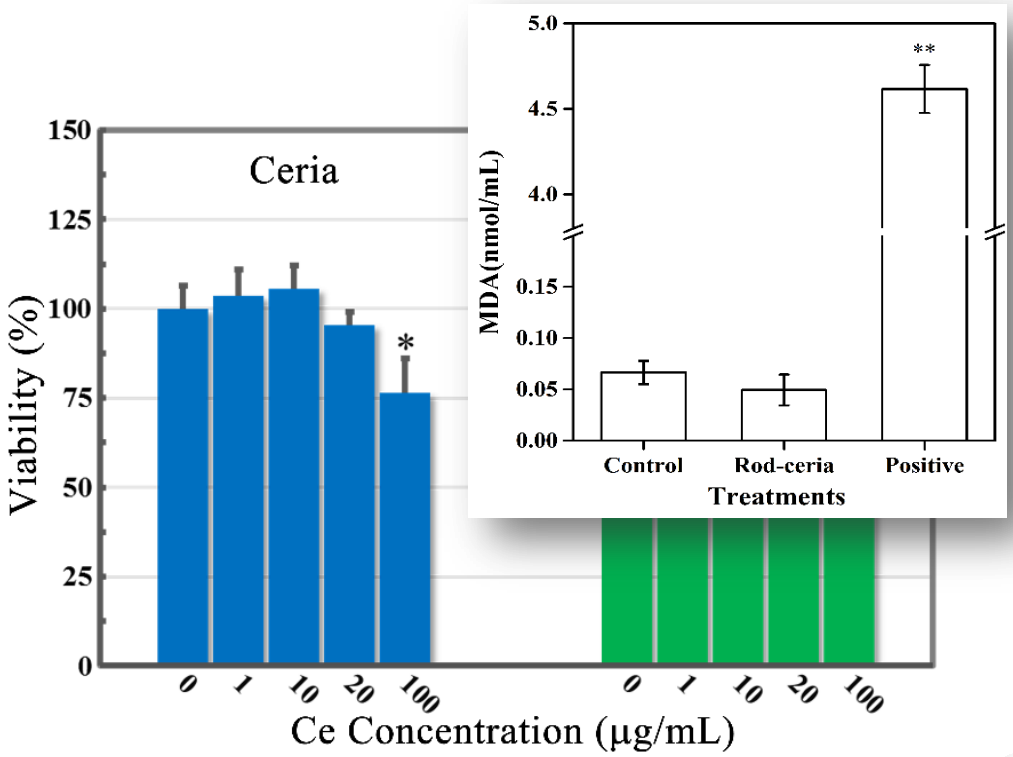
2006年即发现了nanoceria与E. coli作用后:

① 部分Ce(IV)被还原为Ce(III)

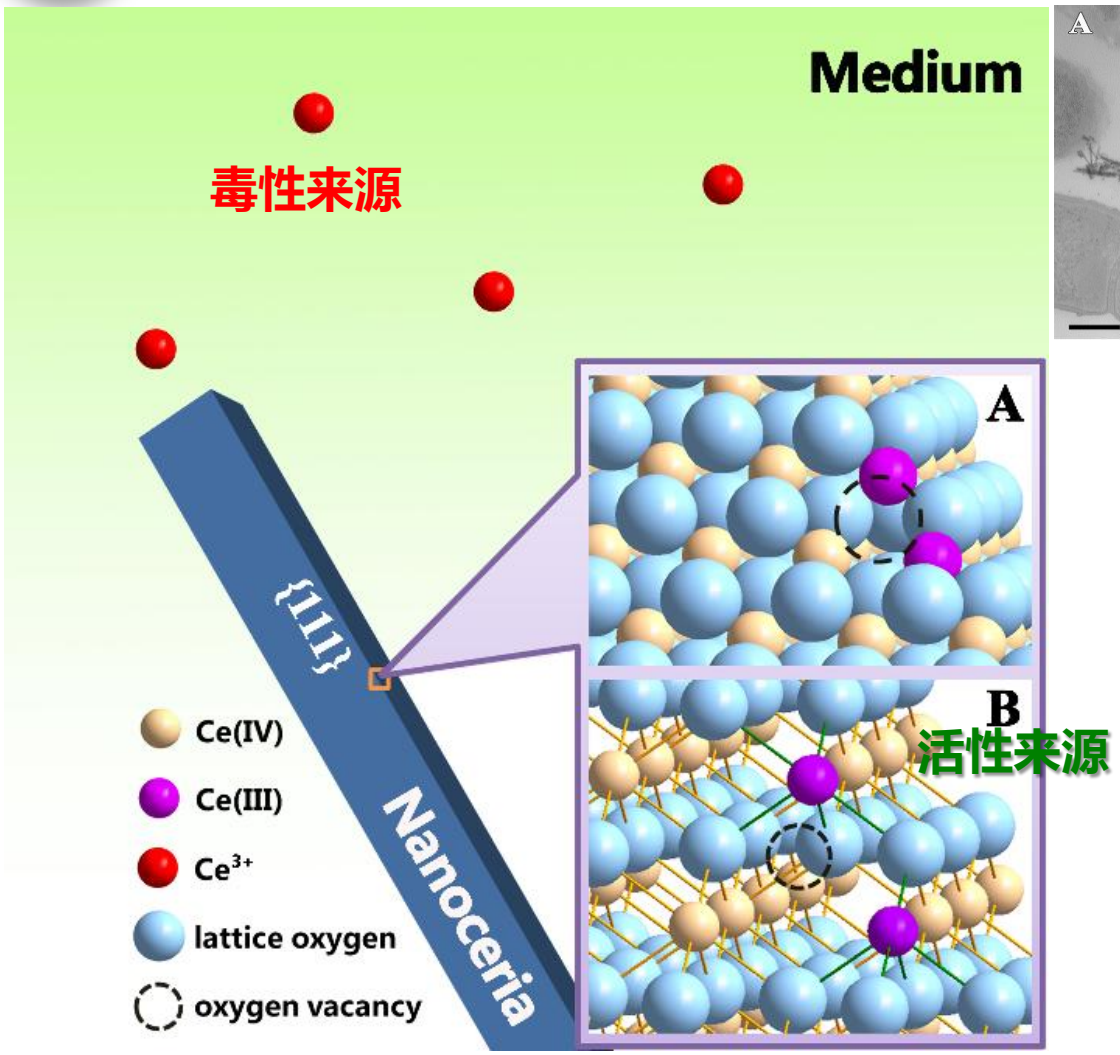
② 还原发生在细菌表面

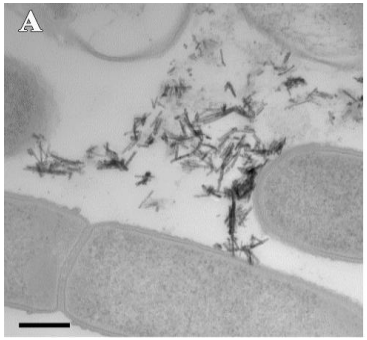
③ Ce(IV)的氧化性导致毒性 ✗

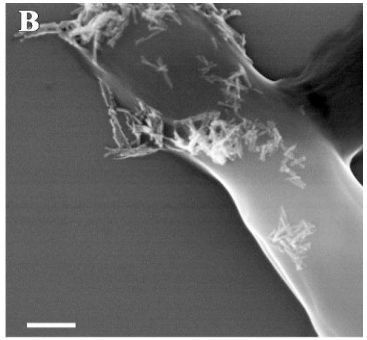




还原后是否发生解离？







ICP-MS/OES

需要预分离NPs和Ce^{3+}离子

XPS

超高真空（$<10^{-8}$ torr）、X射线辐照

EELS

超高真空（$<10^{-9}$ torr）、电子束辐照

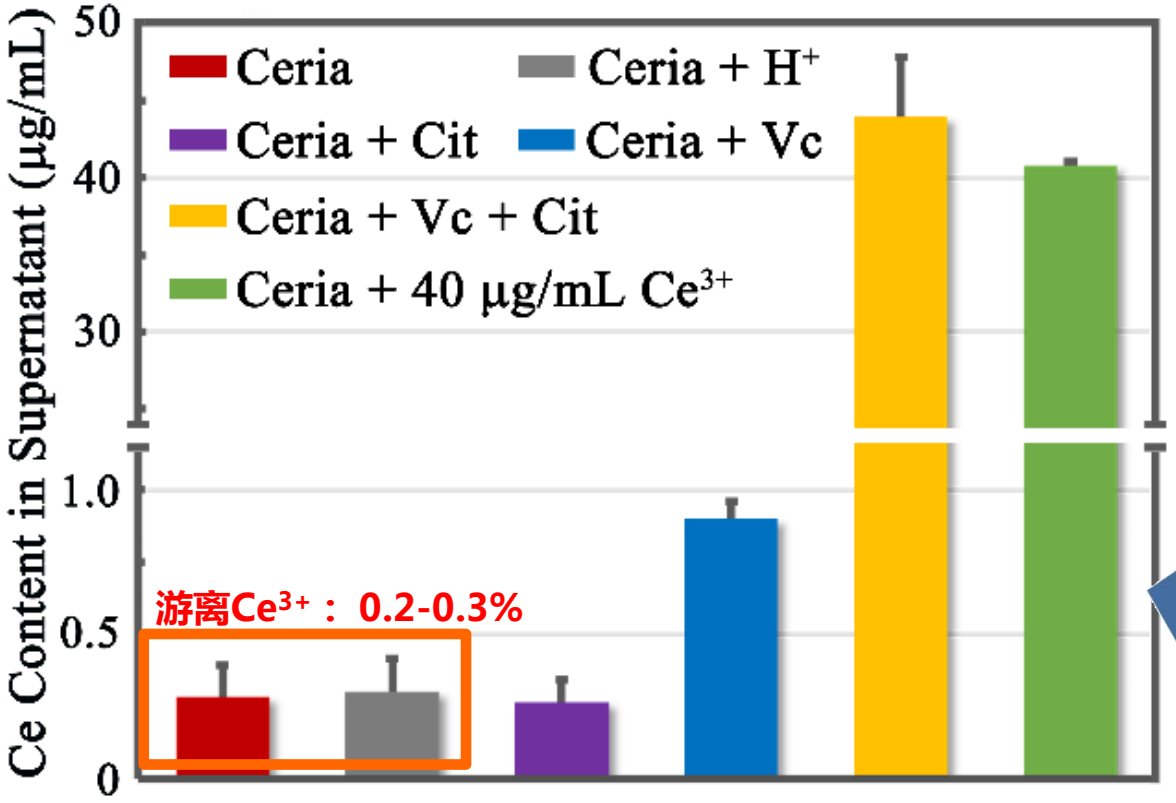
XAFS

常压、X射线辐照、$\Delta Ce^{3+}>5\%$

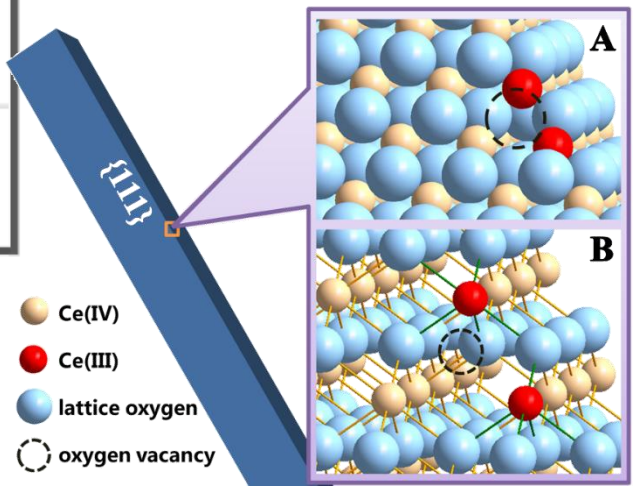
STXM

真空(10^{-6} torr)、X射线辐照

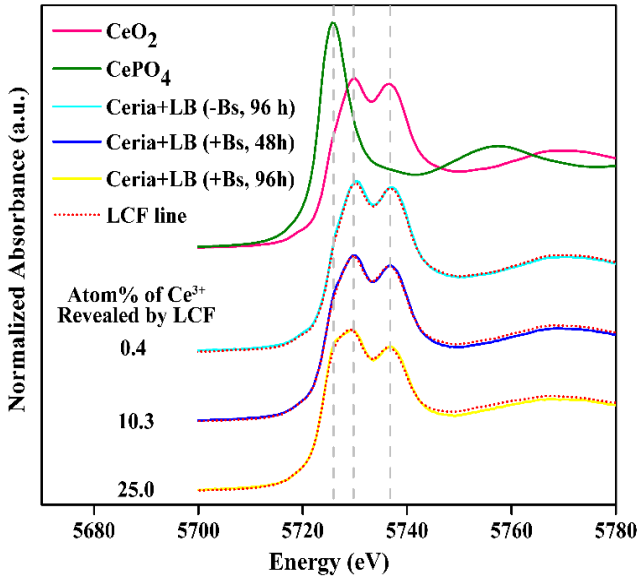
Nanoceria的解离条件

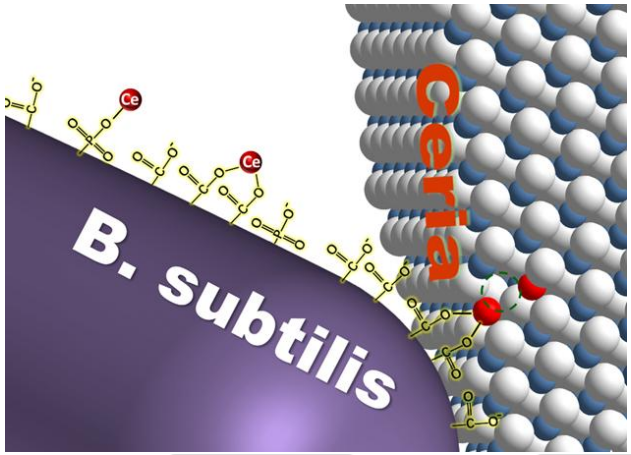


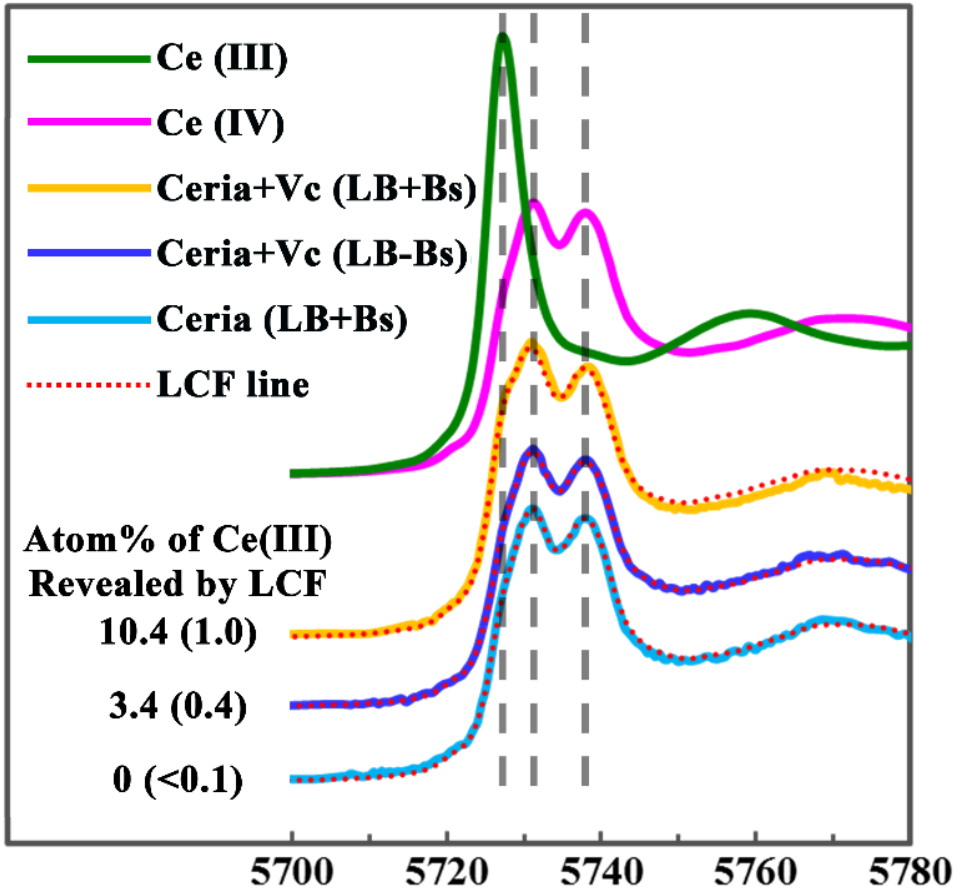
还原剂
多齿螯合剂



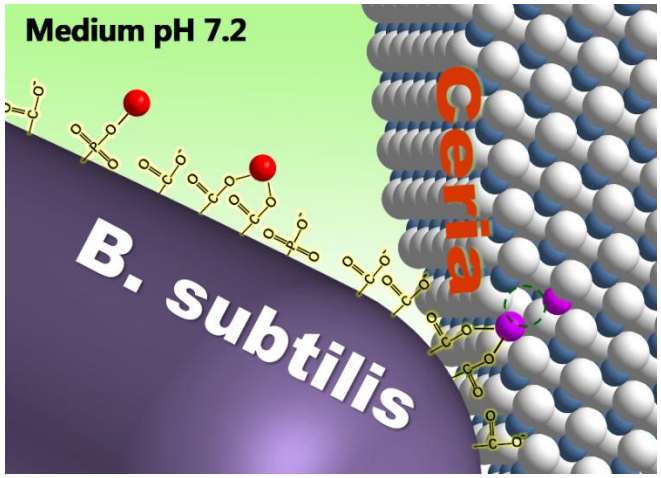
Nano-bio作用：还原&多齿螯合

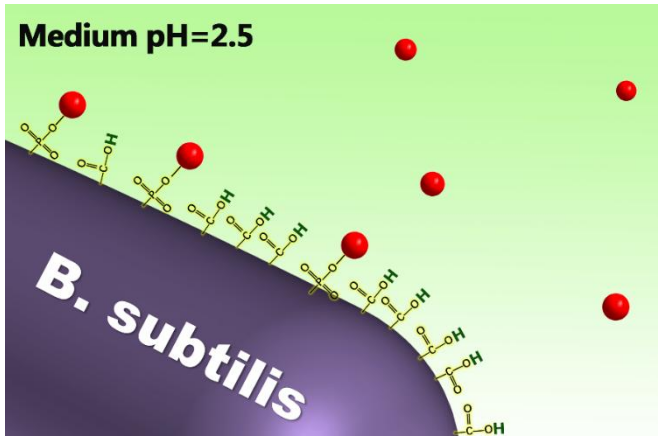


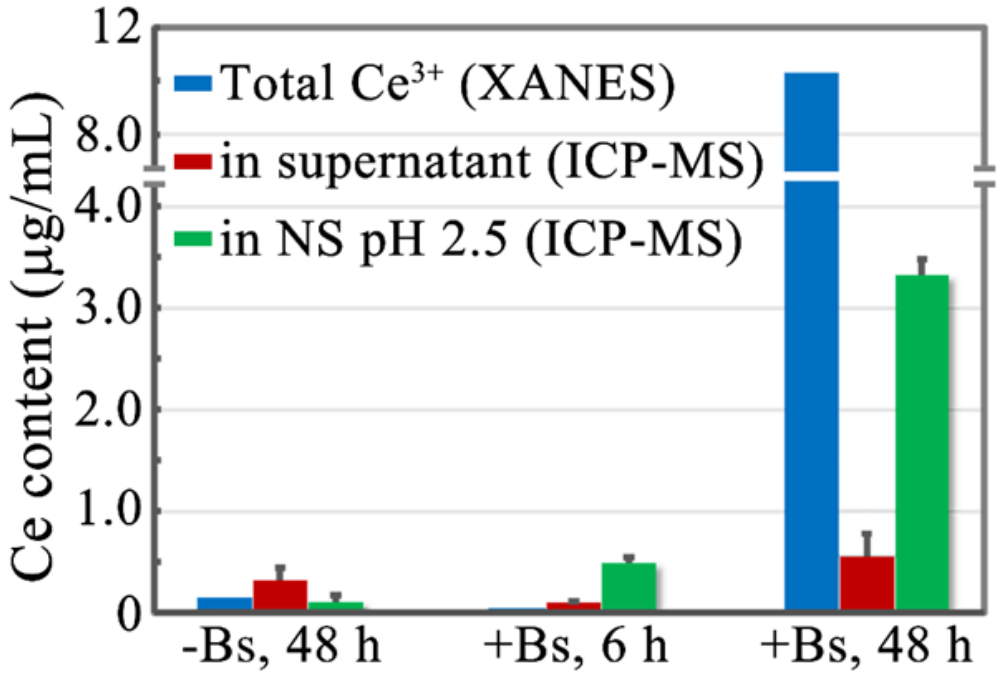




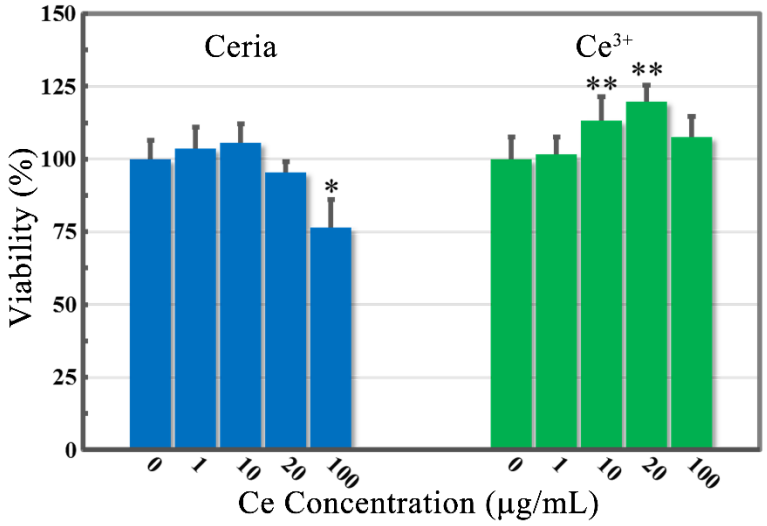
Nanoceria解离的直接证据

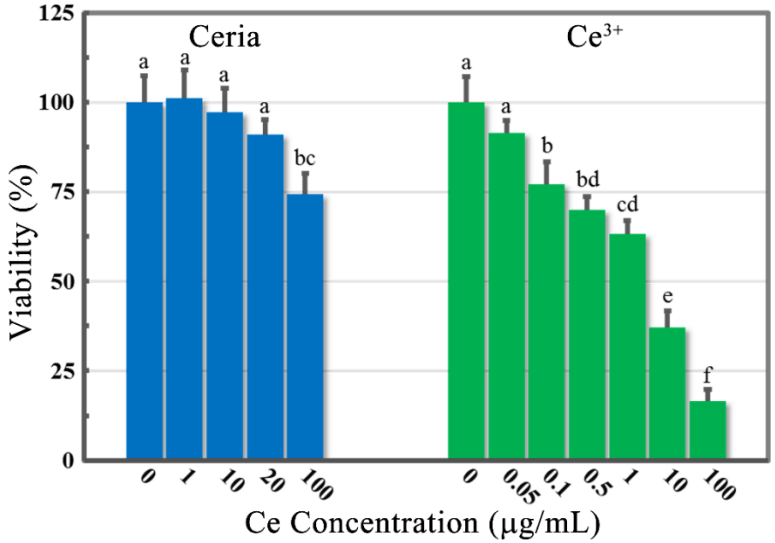


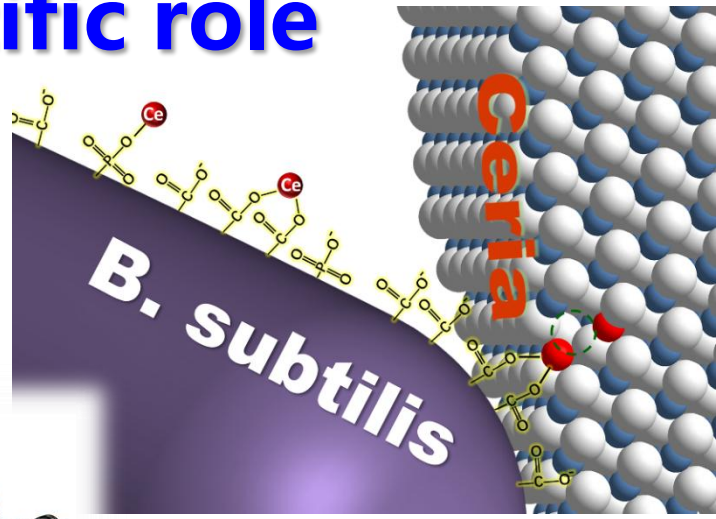


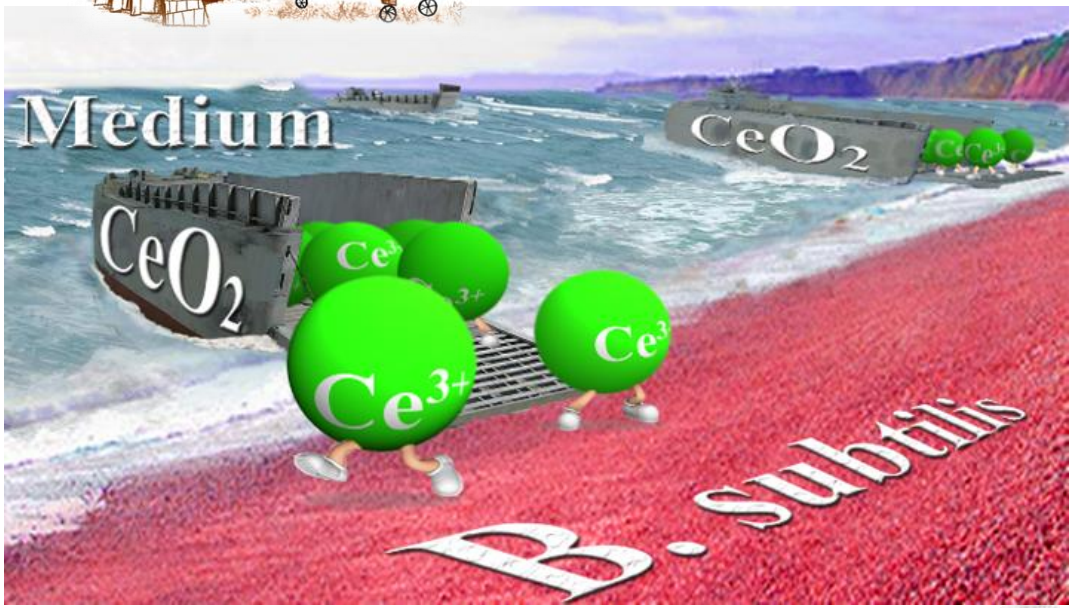


离子毒性&Particle-specific role









工 具 篇

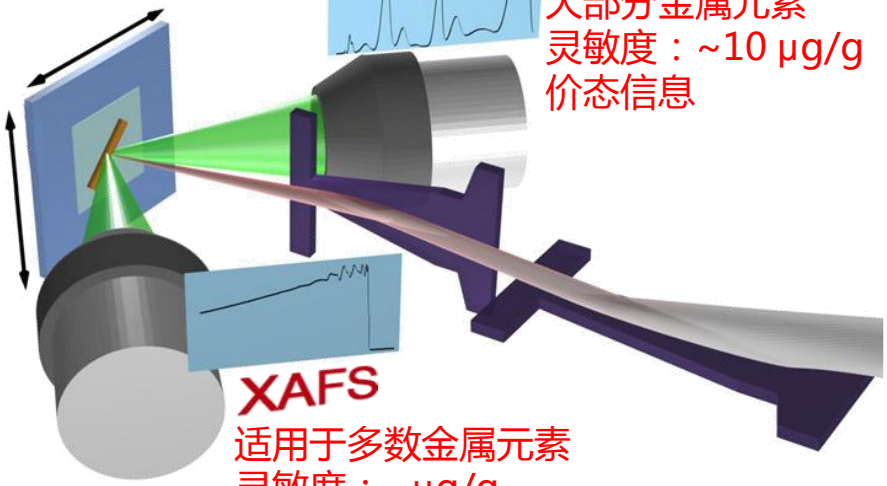
工欲善其事 必先利其器

化学形态分析方法

XRF(μXANES), XAFS，STXM(μXANES)

XRF

适用于多数金属元素
空间分辨率：~μm
大部分金属元素
灵敏度：~10 μg/g
价态信息

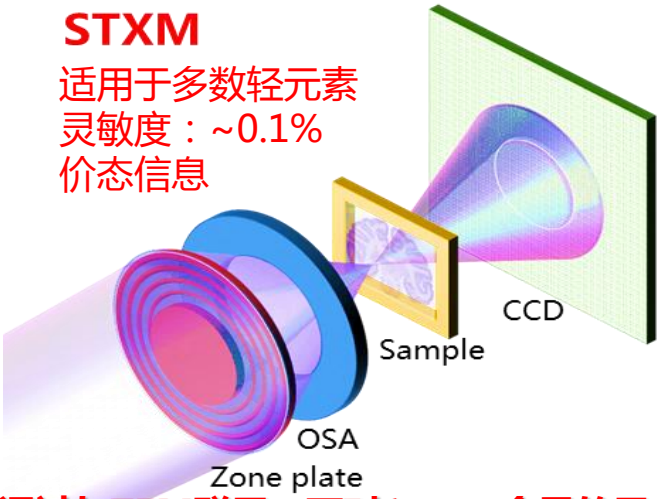


XAFS

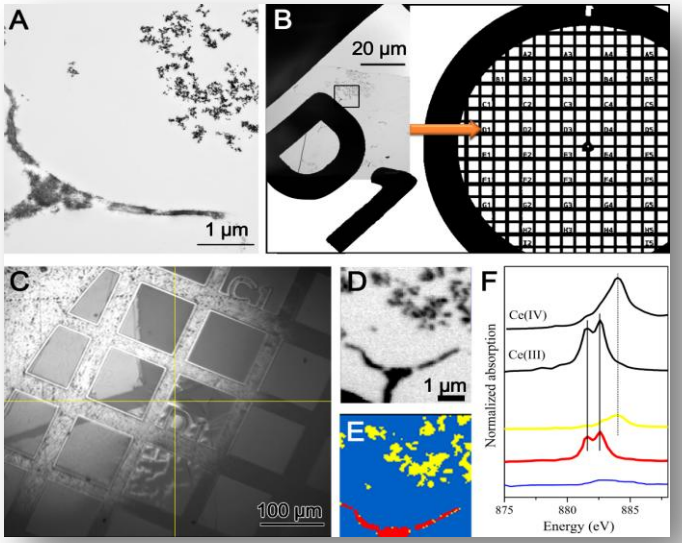
适用于多数金属元素
灵敏度：~μg/g
价态、键长、配位等信息

STXM

适用于多数轻元素
灵敏度：~0.1%
价态信息

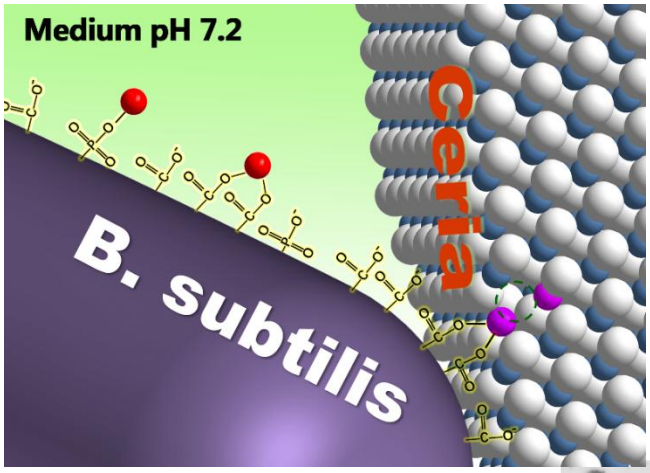


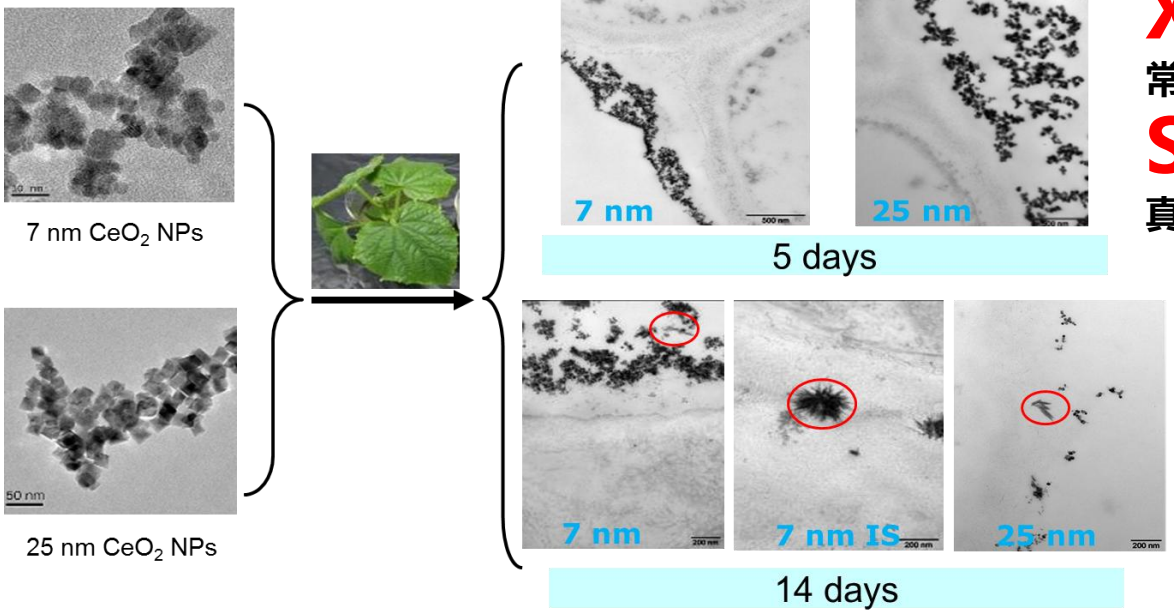
通过与TEM联用，可对1 ppm含量的元素进行纳米尺度上的化学形态分析



He X, et al. **Methods Molecular Biology, Vol. 1894: Nanotoxicity**. 2019, Springer Nature.

分析方法比较





ICP-MS/OES

需要预分离NPs和Ce^{3+}离子

XPS

超高真空（$<10^{-8}$ torr）、X射线辐照

EELS

超高真空（$<10^{-9}$ torr）、电子束辐照

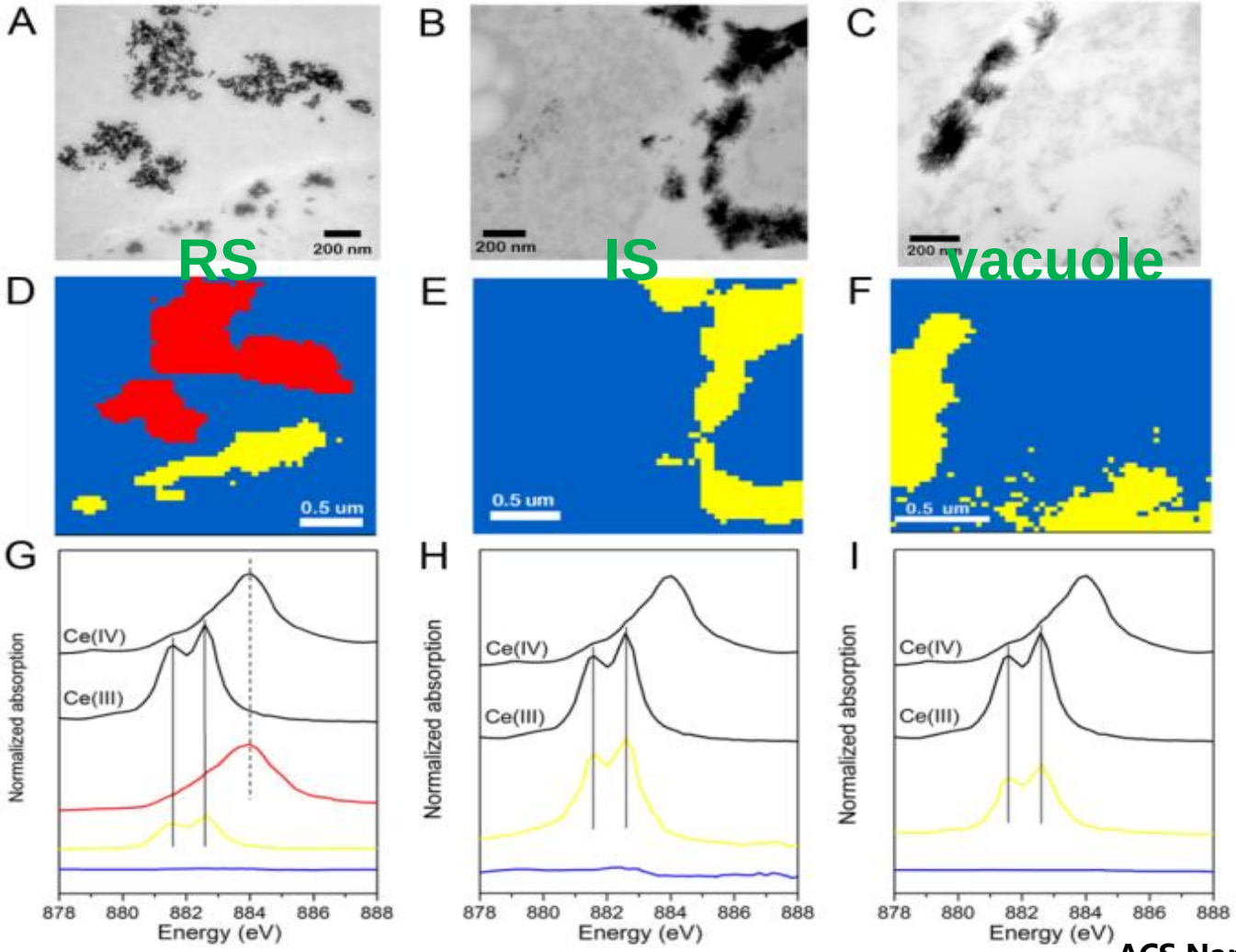
XAFS

常压、X射线辐照、$\Delta Ce^{3+}>5\%$

STXM

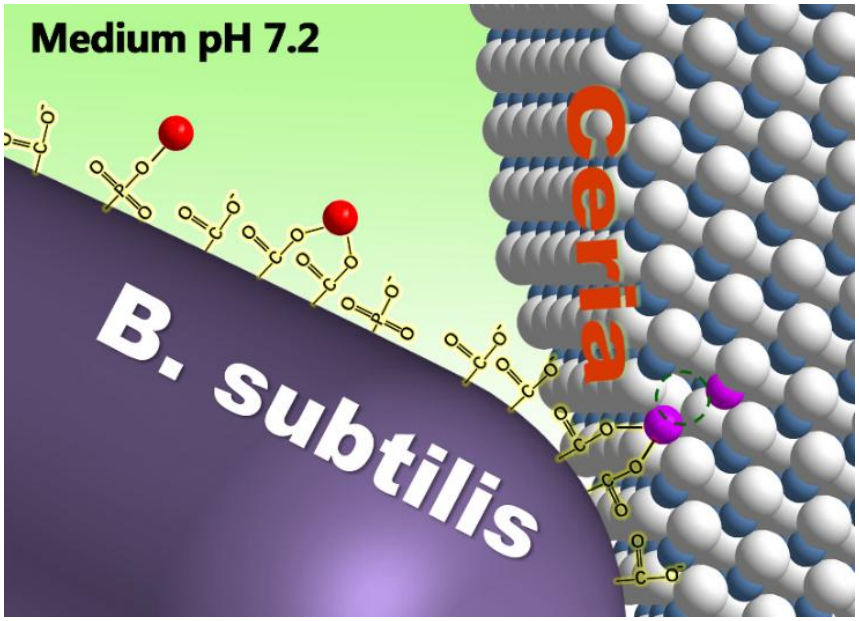
真空(10^{-6} torr)、X射线辐照

Ce的微区形态及分布特征



ACS Nano 2012, 6(11): 9943
Environ Sci Technol 2015, 49: 10667

组学方法



Metallomics
Genomics
Transcriptomics
Proteomics
Metabolomics

纳米中心
赵宇亮
陈春英
董凤良

高能所
张静
郑黎荣
安鹏飞

上海光源：
郜仁忠
郭智
张立娟
张祥志
许子健
甄香君

地质与地球物理所：
杨蔚

谢谢！

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