

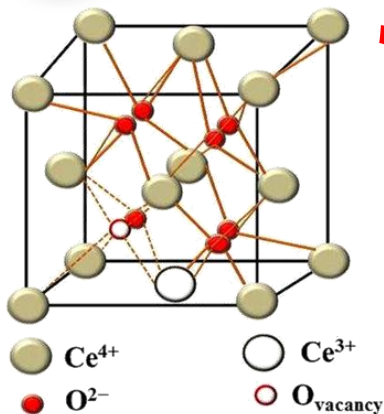
纳米二氧化铈在细菌表面的 生物转化及毒性机制

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
 $\text{Ce}^{3+}/\text{Ce}^{4+}$ 的可逆转化
催化生成/清除ROS

应用广



护理品/药物



电极材料



催化剂

产量大

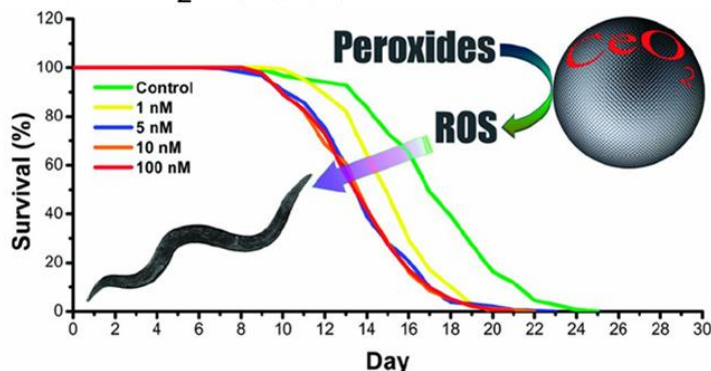
2016年全球市场规模：9100 tons

U.S. nanoceria market revenue by application
2014 - 2025 (USD Million)



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 $\rightarrow$ 环境相关低剂量暴露

0.01-100 nmol/L $\rightarrow$ 0.0001 nmol/L

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Nanoparticles Shorten Roundworms' Lives
Stomachache: Even at low concentrations, cerium oxide nanoparticles harm *C. elegans*

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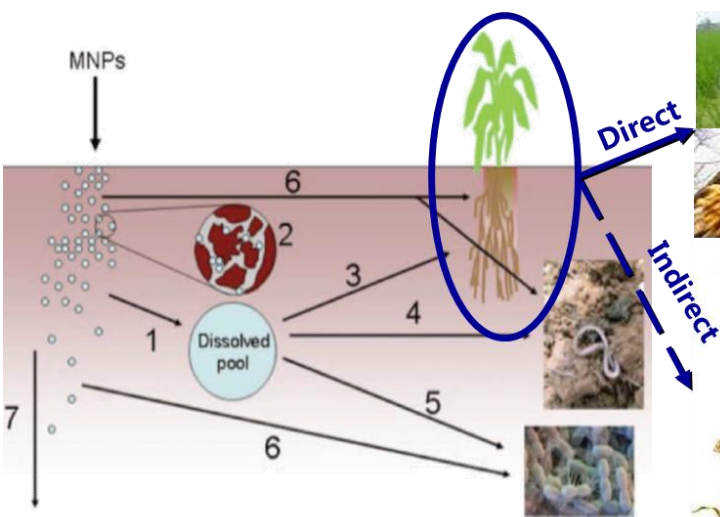
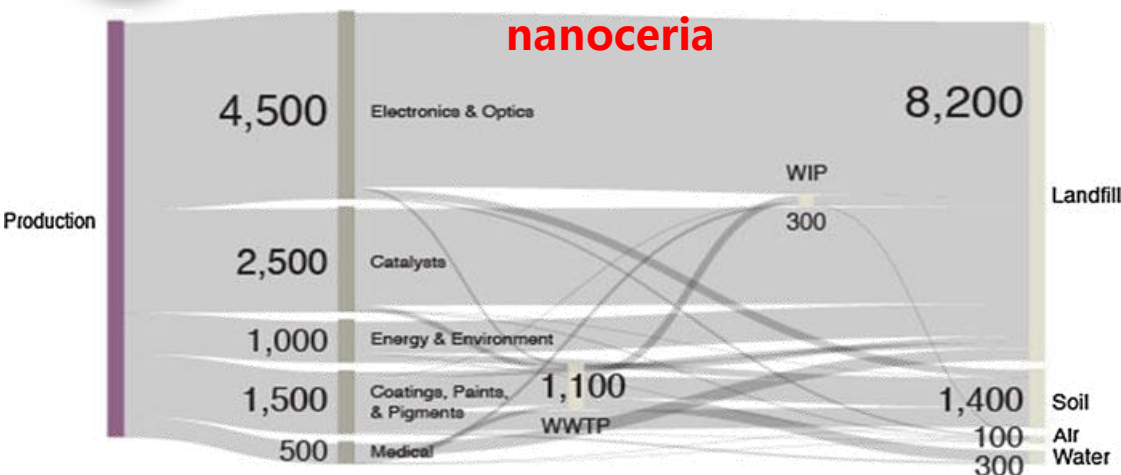
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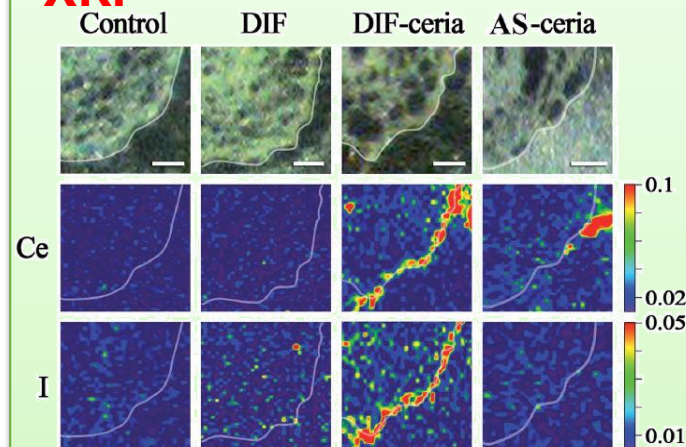
关键环节：迁移&转化



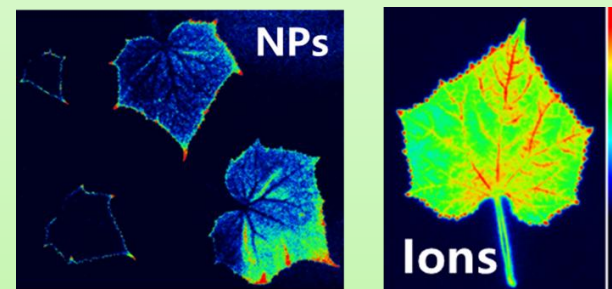
J Nanopart Res 2013, 15, 1692



XRF



Radiotracer



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

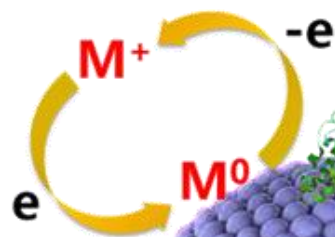
Sulfidation

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

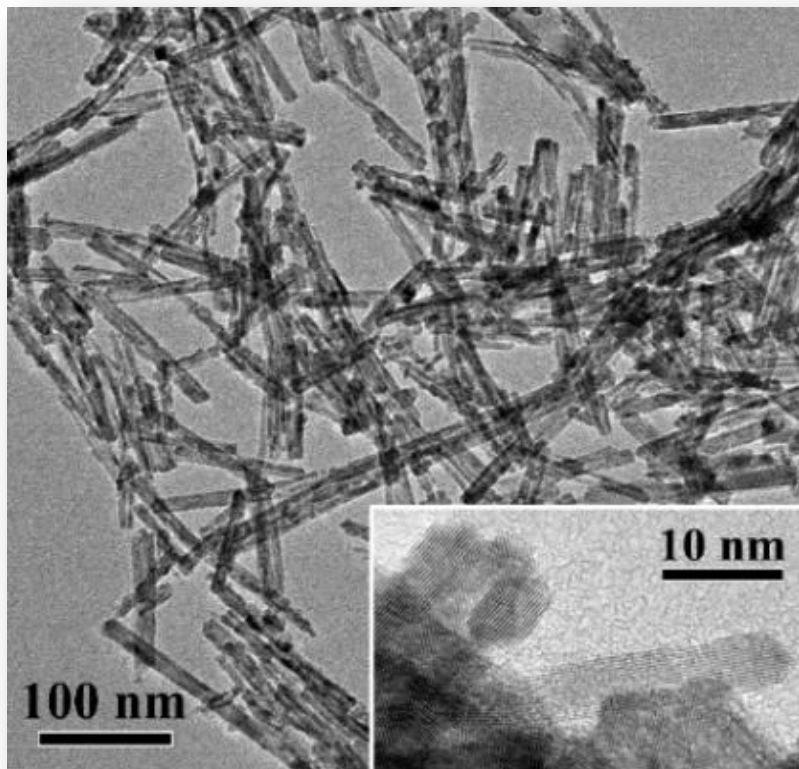
Acc Chem Res 2013, 46: 761

Small 2013, 9(9-10): 1482

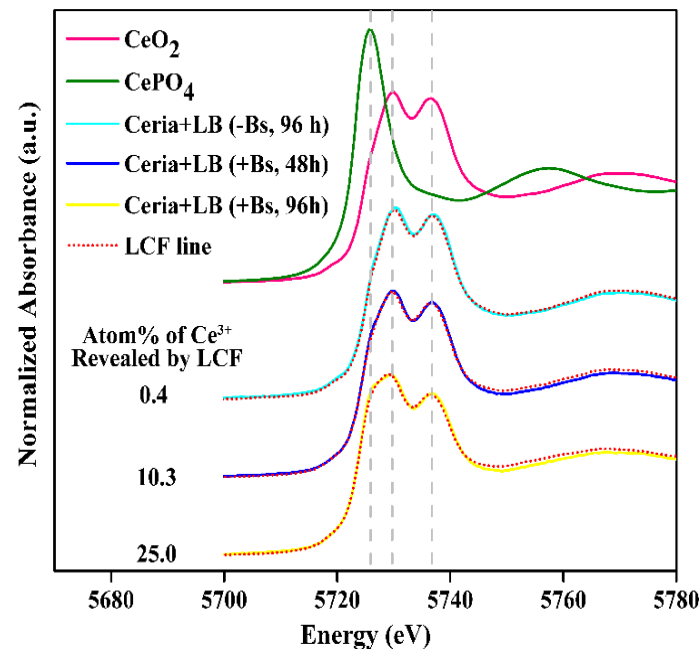
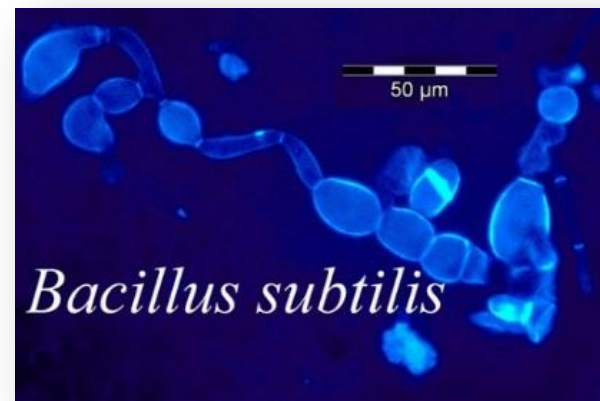




Nanoceria与细菌的相互作用



Length: 168 ± 18 nm
Width: 8.5 ± 1.5 nm





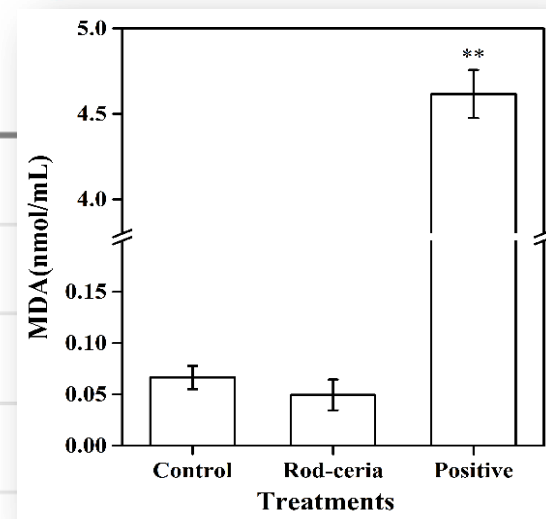
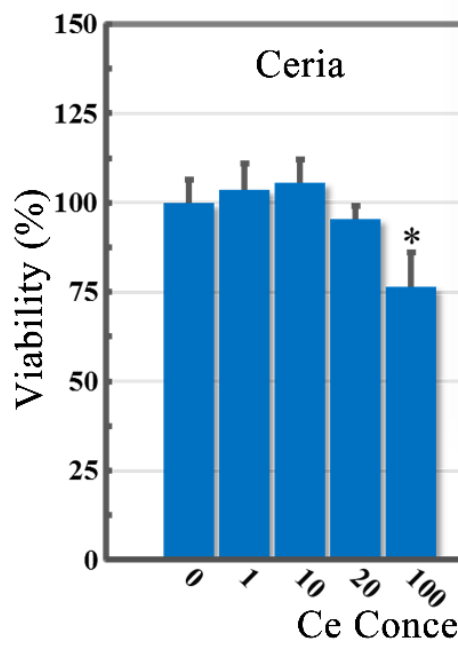
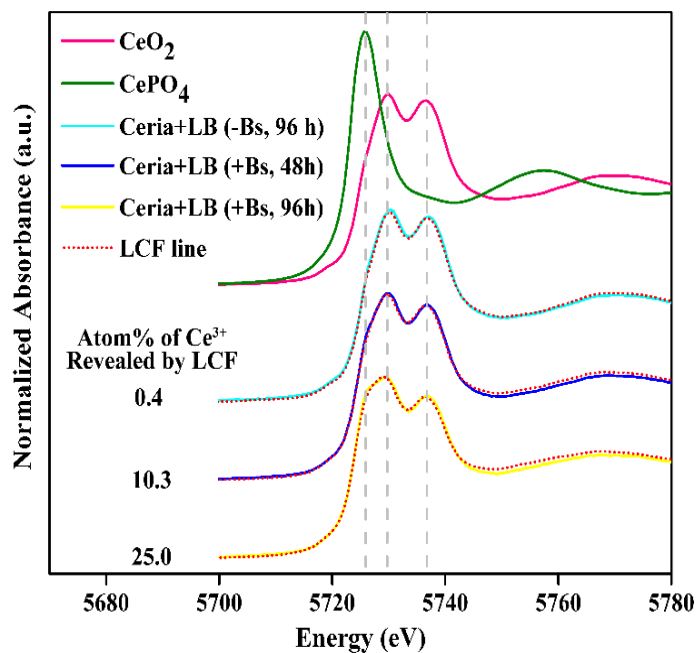
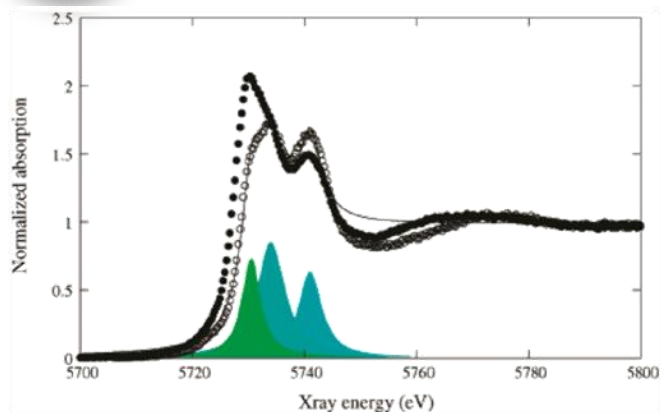
Nanoceria的细菌毒性机制？

2006年即发现了nanoceria与E. coli作用后:

① 部分Ce(IV)被还原为Ce(III)

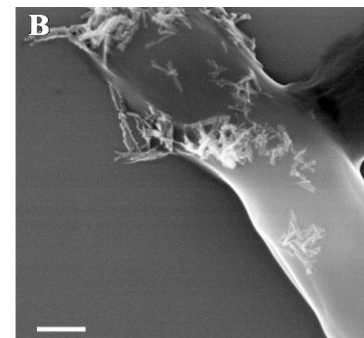
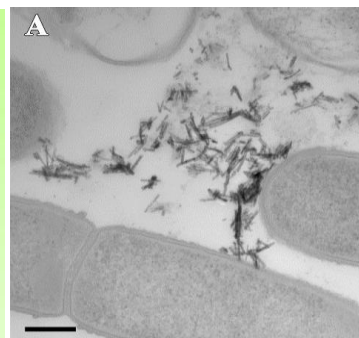
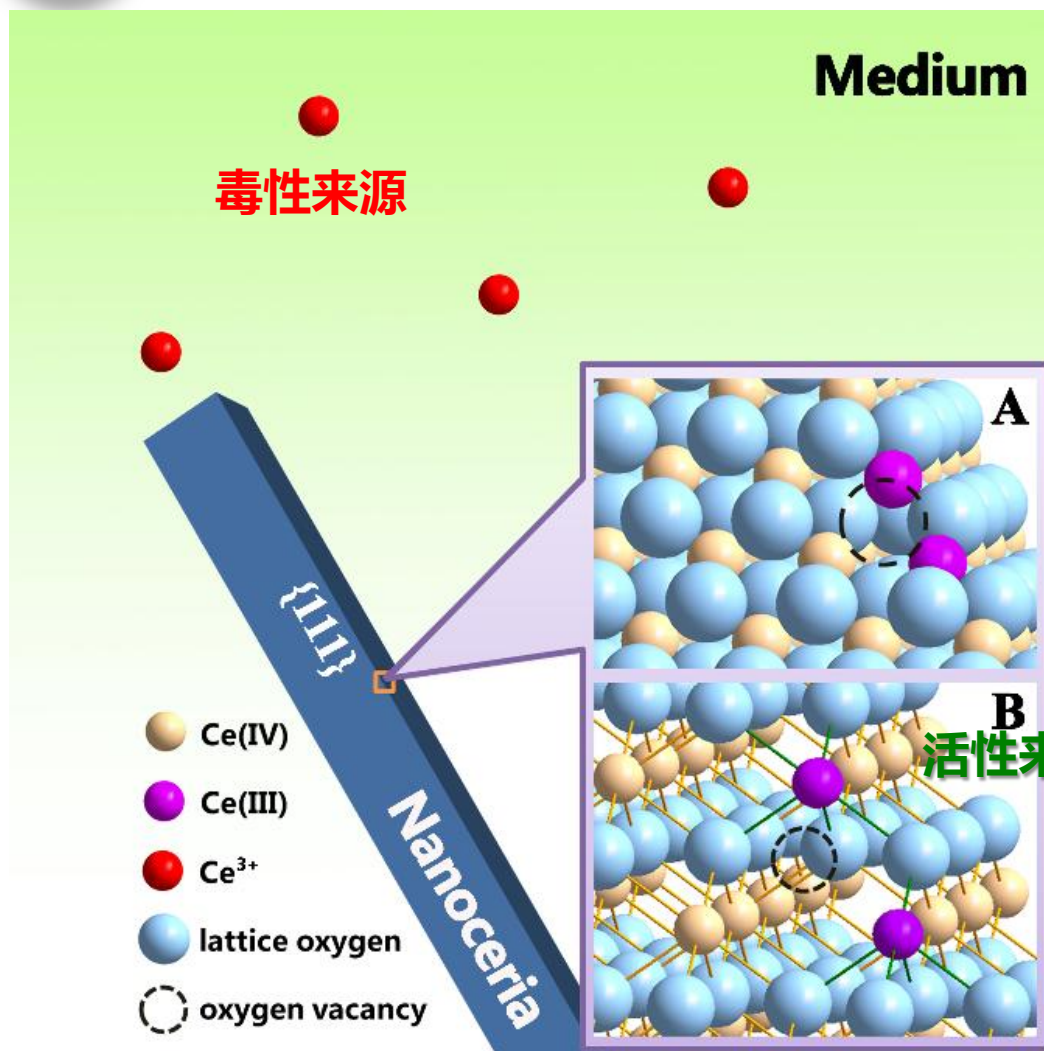
② 还原发生在细菌表面

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Ce³⁺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、 $\Delta\text{Ce}^{3+} > 5\%$

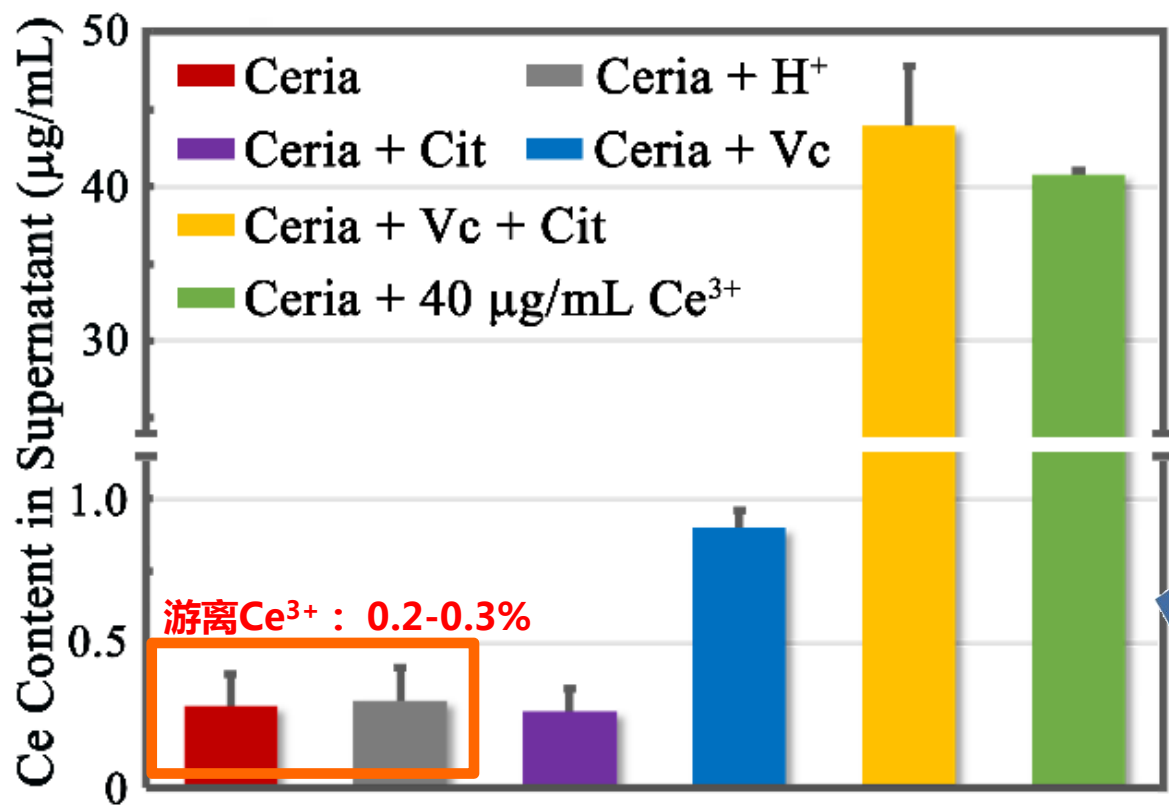
STXM

真空(10^{-6} torr)、X射线辐照



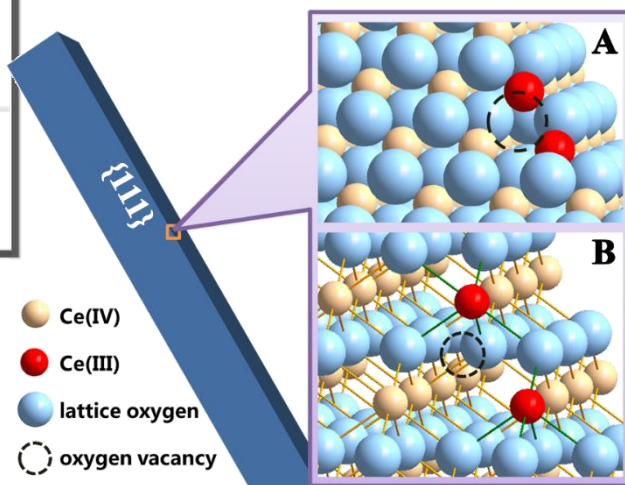


Nanoceria的解离条件



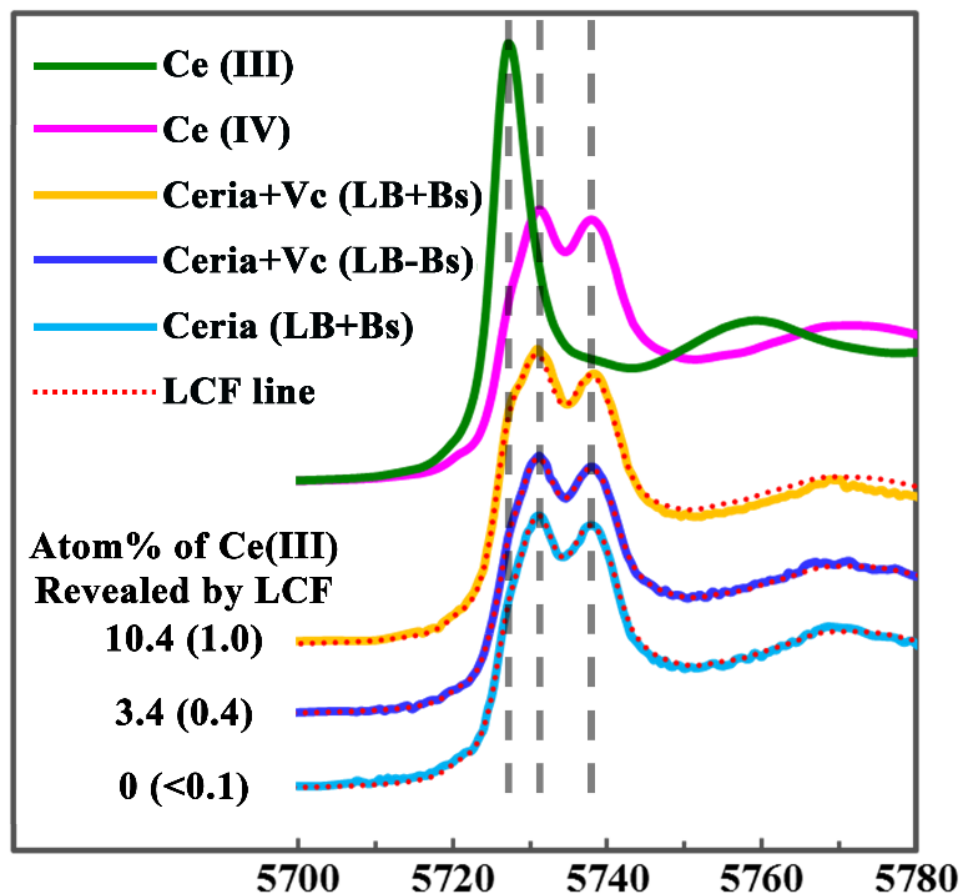
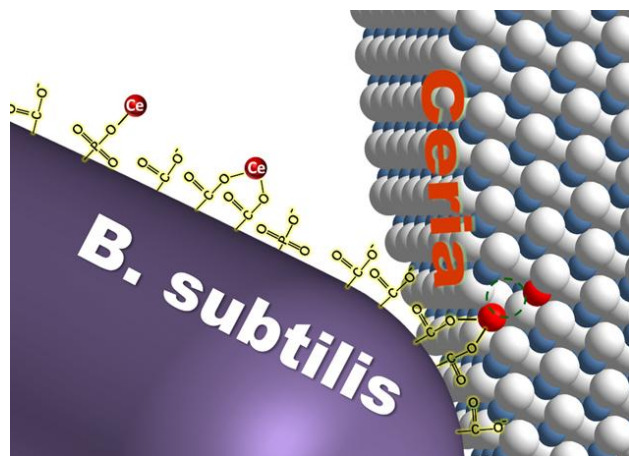
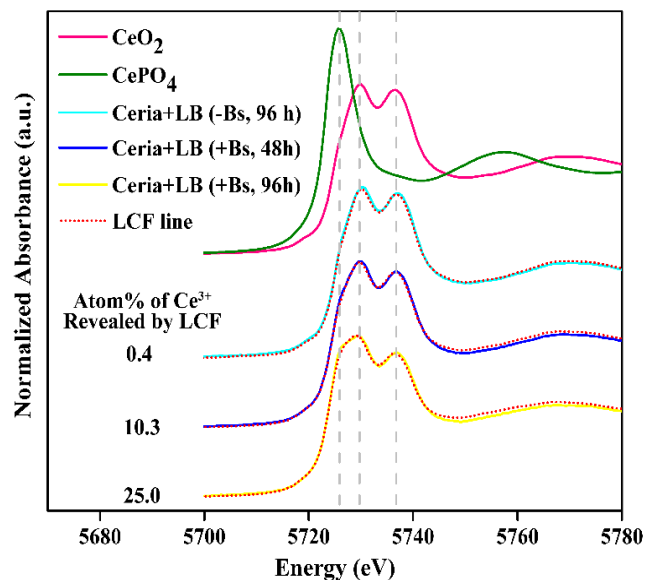
游离Ce³⁺: 0.2-0.3%

还原剂
多齿螯合剂



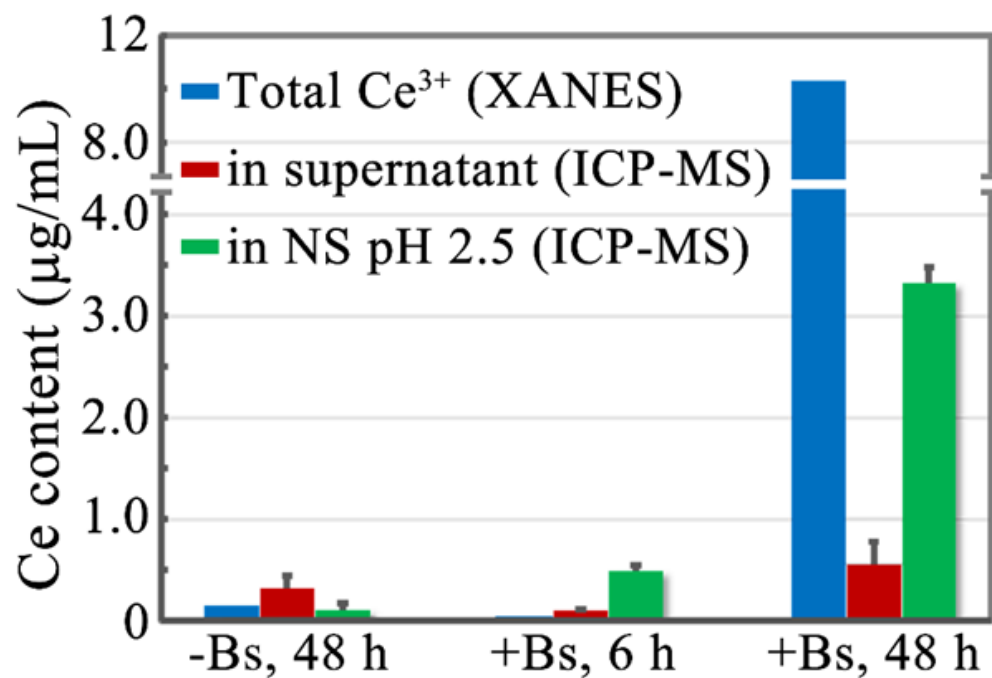
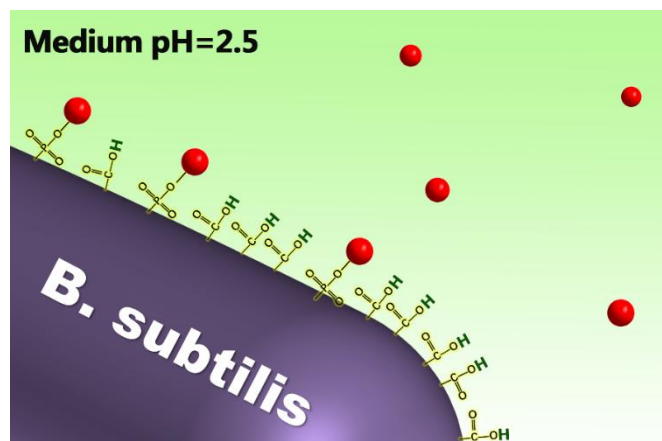
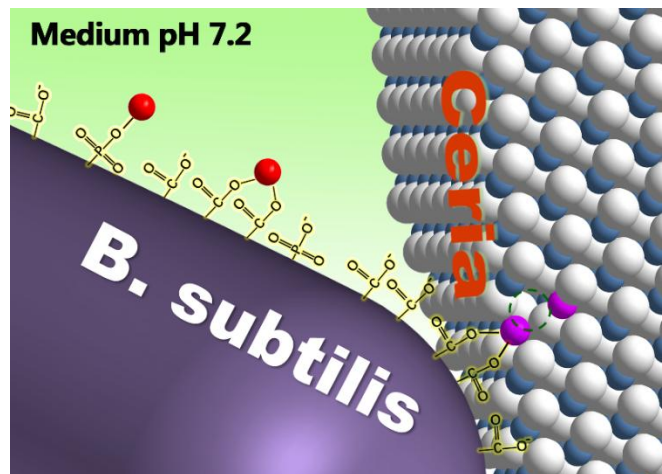


Nano-bio作用：还原&多齿螯合



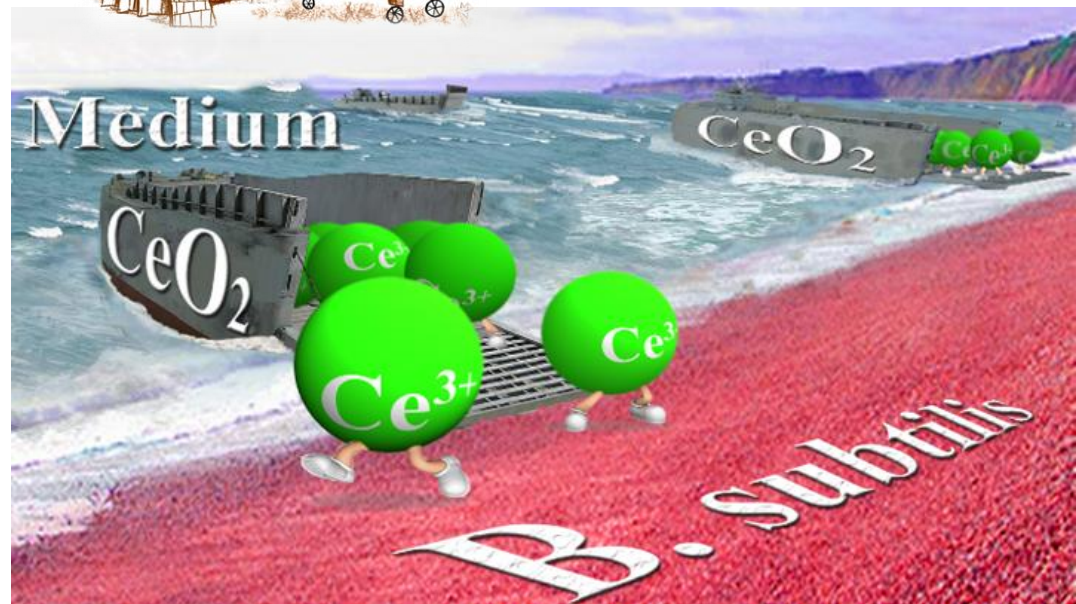
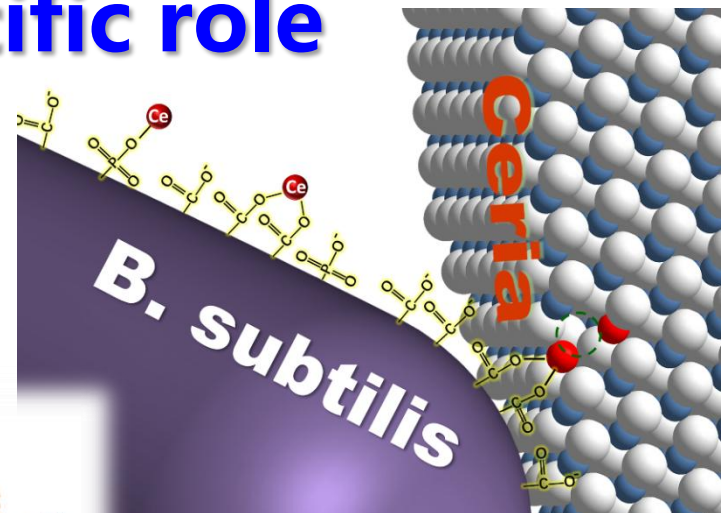
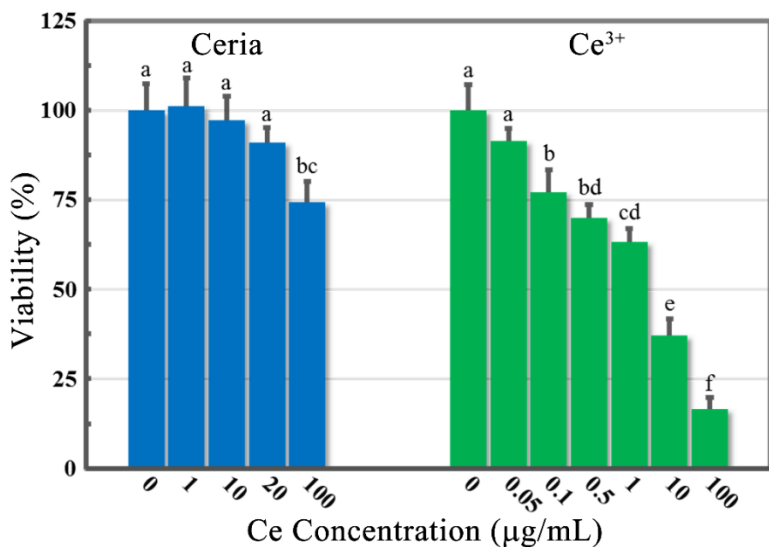
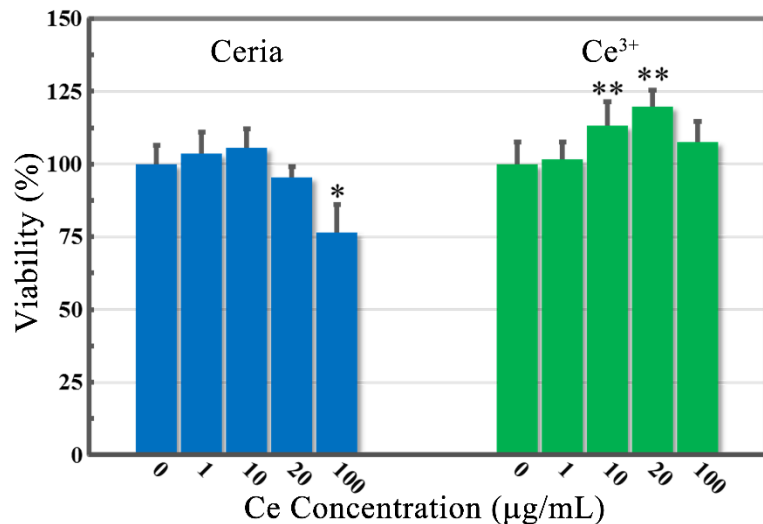


Nanoceria解离的直接证据





离子毒性 & Particle-specific role





工具篇



工欲善其事 必先利其器



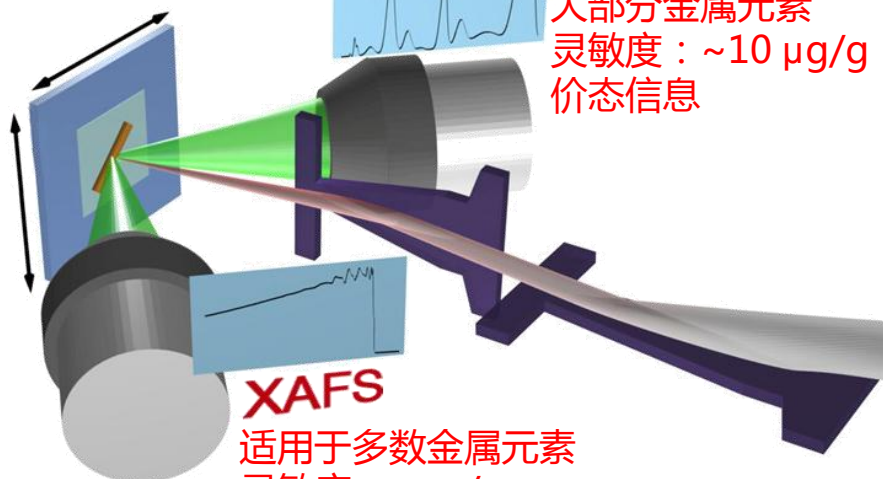
化学形态分析方法

XRF(μ XANES), XAFS, STXM(μ XANES)



XRF

适用于多数金属元素
空间分辨率： $\sim \mu\text{m}$
大部分金属元素
灵敏度： $\sim 10 \mu\text{g/g}$
价态信息

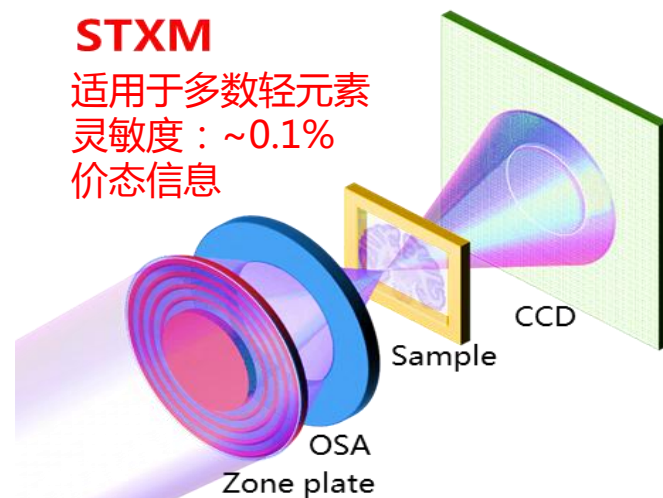


XAFS

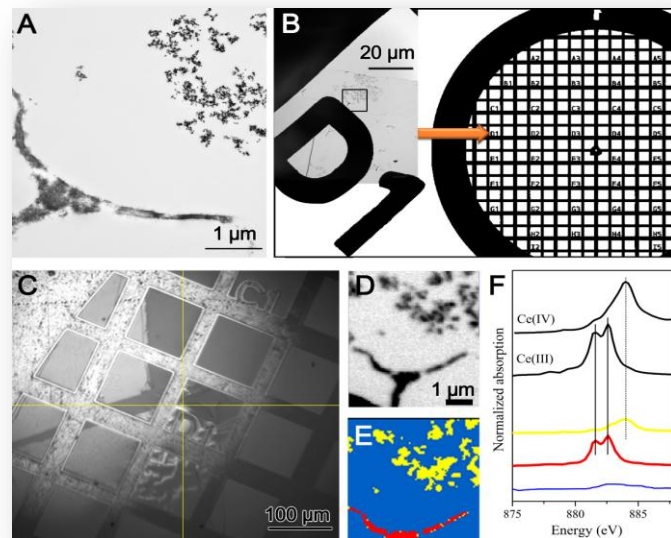
适用于多数金属元素
灵敏度： $\sim \mu\text{g/g}$
价态、键长、配位等信息

STXM

适用于多数轻元素
灵敏度： $\sim 0.1\%$
价态信息



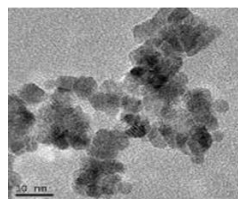
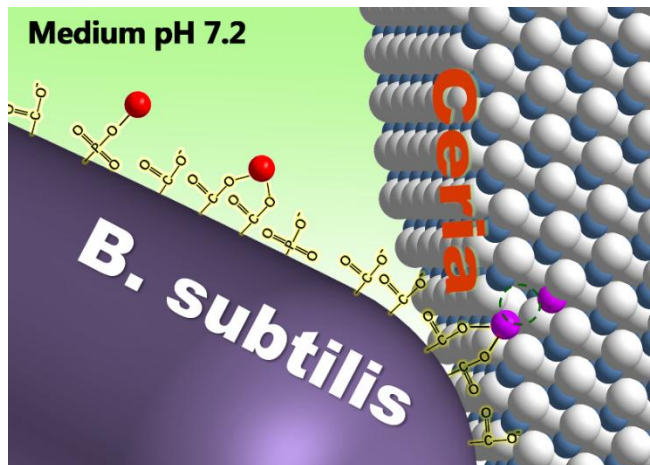
通过与TEM联用，可对1 ppm含量的元素进行纳米尺度上的化学形态分析



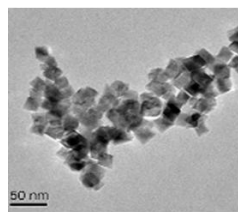
He X, et al. **Methods Molecular Biology**, Vol. 1894: Nanotoxicity. 2019, Springer Nature.



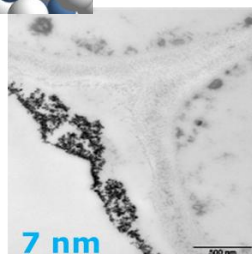
分析方法比较



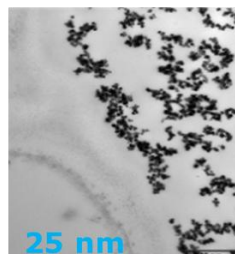
7 nm CeO₂ NPs



25 nm CeO₂ NPs



7 nm

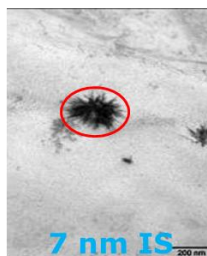


25 nm

5 days



7 nm



7 nm IS



25 nm

14 days

ICP-MS/OES

需要预分离NPs和Ce³⁺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、 $\Delta\text{Ce}^{3+} > 5\%$

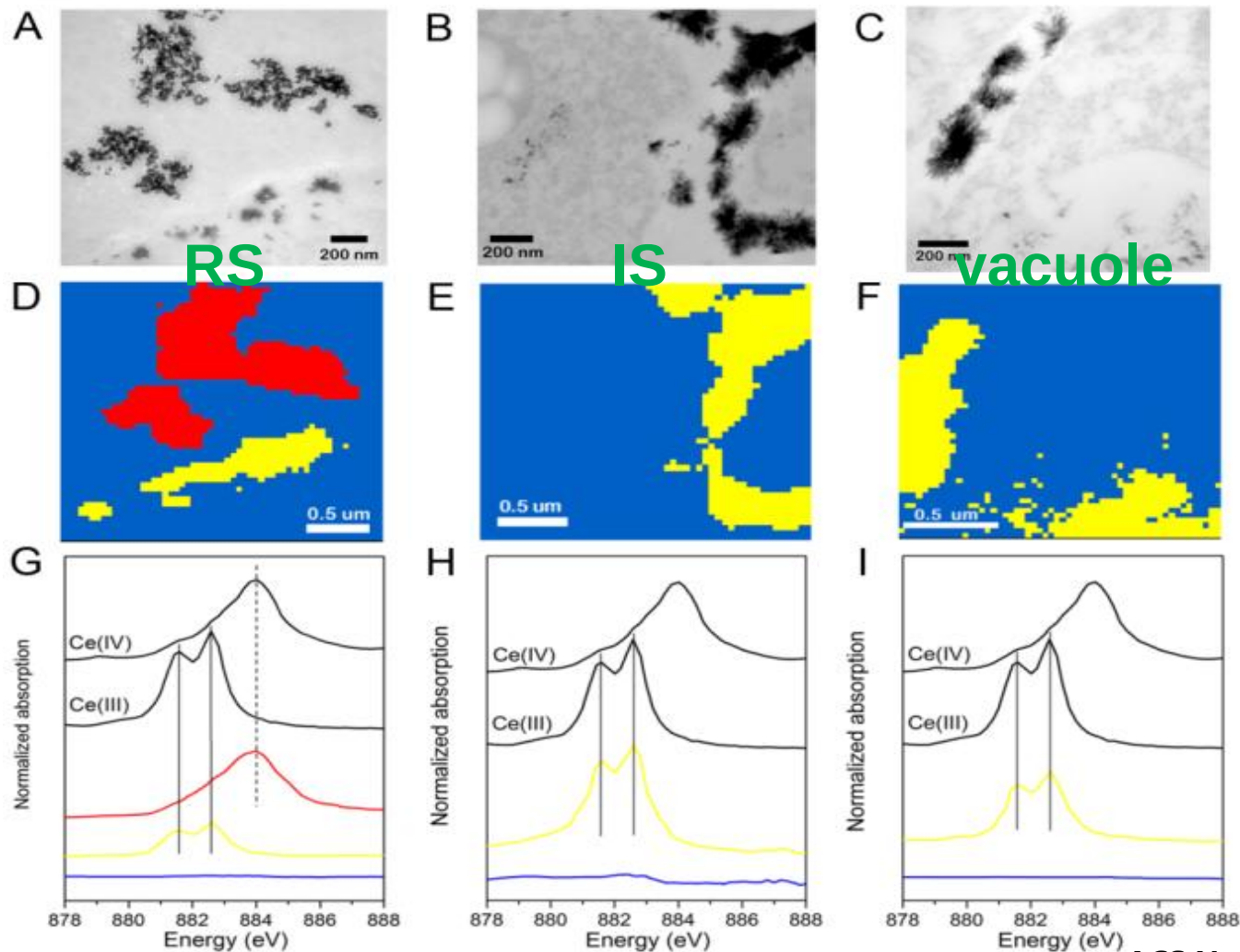
STXM

真空(10^{-6} torr)、X射线辐照





Ce的微区形态及分布特征

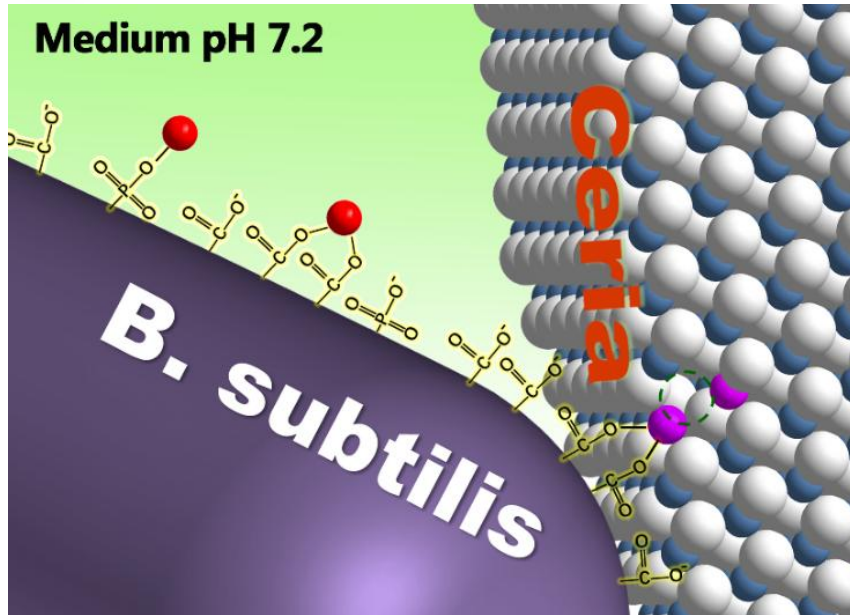


ACS Nano 2012, 6(11): 9943
Environ Sci Technol 2015, 49: 10667





组学方法



Metallomics
Genomics
Transcriptomics
Proteomics
Metabolomics





谢谢 !

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纳米中心

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陈春英
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地质与地球物理所 :

杨蔚