The search for Sustainable Catalysts for Fuel Cells and Water Splitting: MetalFree or Noble Metal-Free Nanomaterials

Tewodros (Teddy) Asefa

Department of Chemistry and Chemical Biology
Department of Chemical and Biochemical Engineering
Rutgers Institute for Advanced Materials, Devices and Nanotechnology
Rutgers Energy Institute

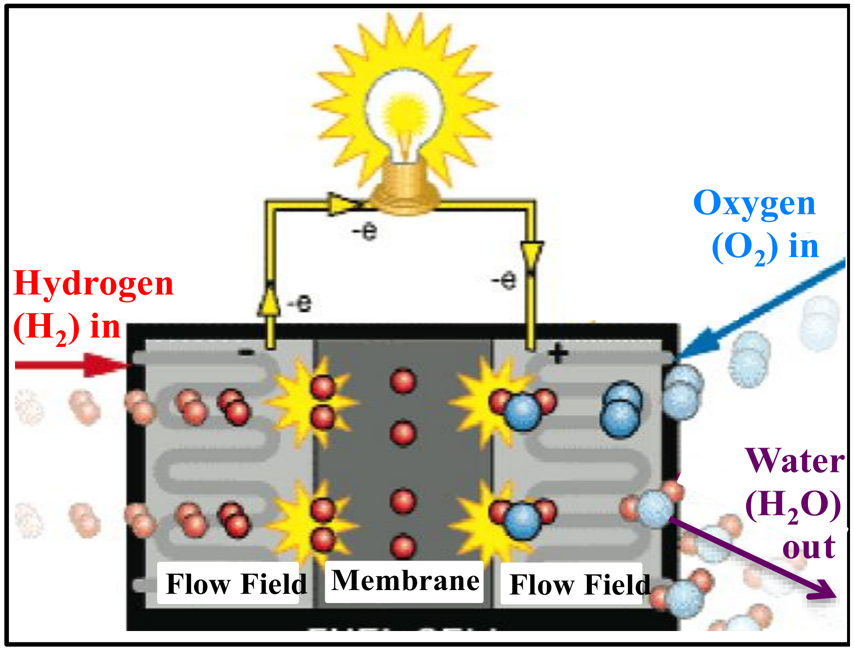
Rutgers, The State University of New Jersey
New Brunswick, New Jersey, USA

Sus Nano Conference - Venice, Italy, March 2015

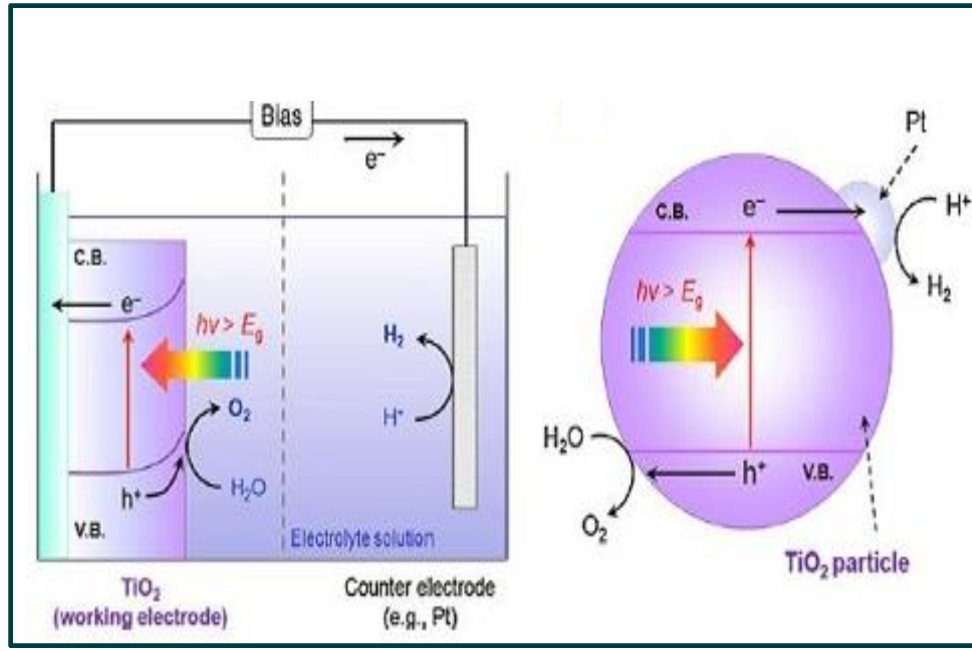
RUTGERS

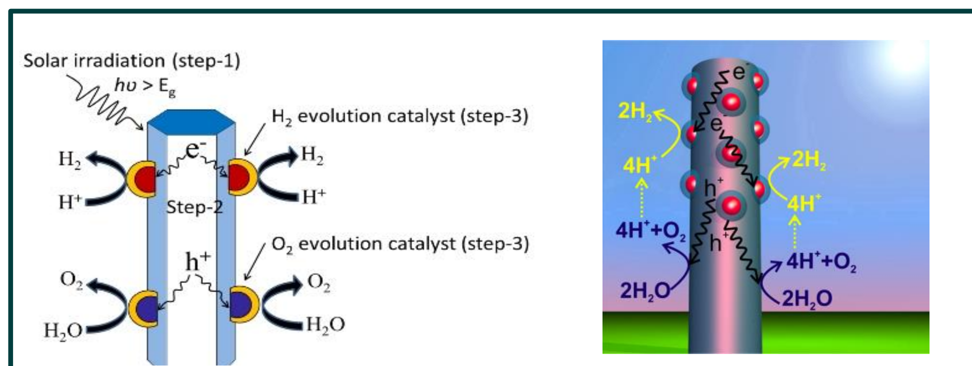
Fuel Cells and Water Splitting Catalysis

Fuel Cells



Water Splitting



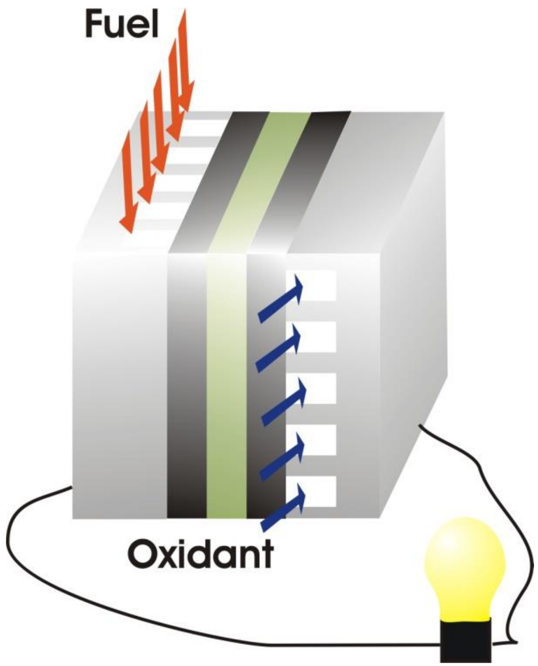


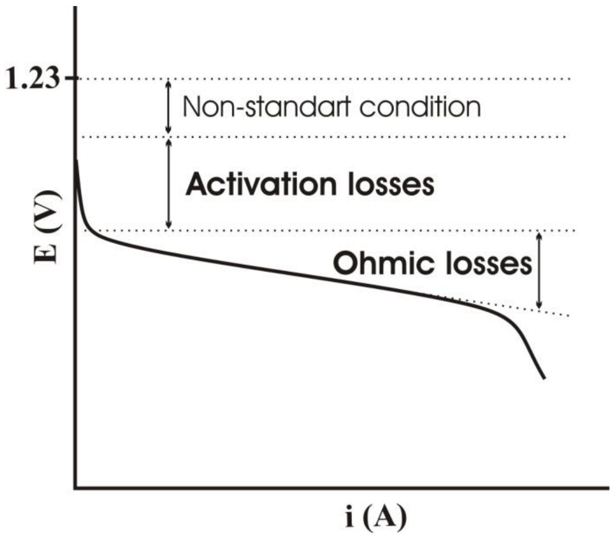
Giwirth et al., *Inorg Chem*. **2010**, *49*, 3557.
Kibria et al., SPIE, DOI: 10.1117/2.1201501.005751

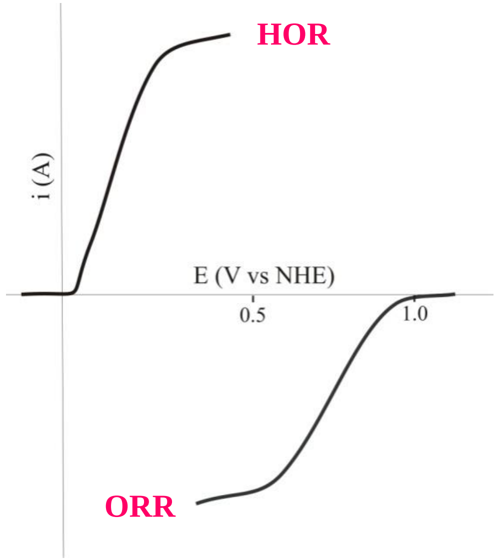
Fuel Cells

$$H_2 \longrightarrow 2H^+ + 2e^- \quad E^0 = 0.0\ V\ (NHE)$$

$$O_2 + 4H^+ + 4e^- \longrightarrow H_2O \quad E^0 = 1.23\ V\ (NHE)$$

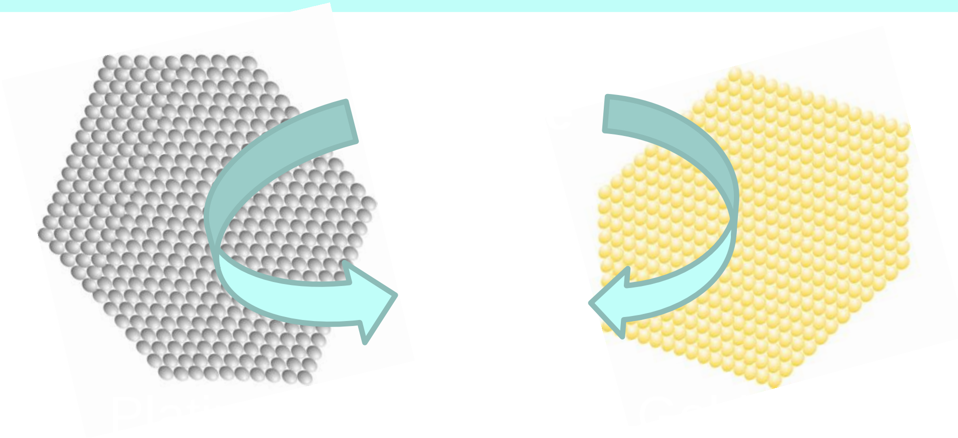




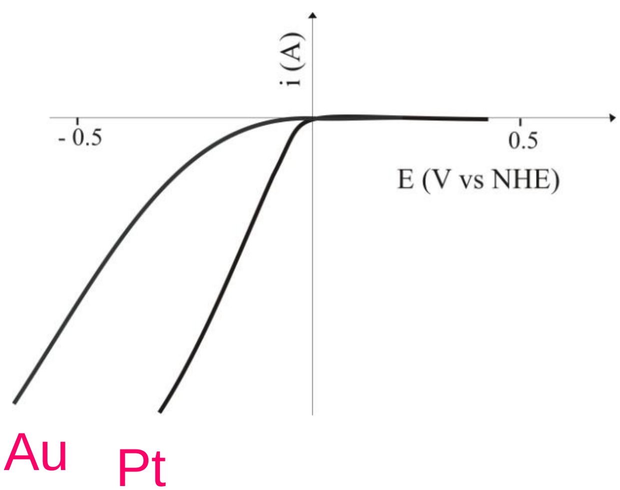


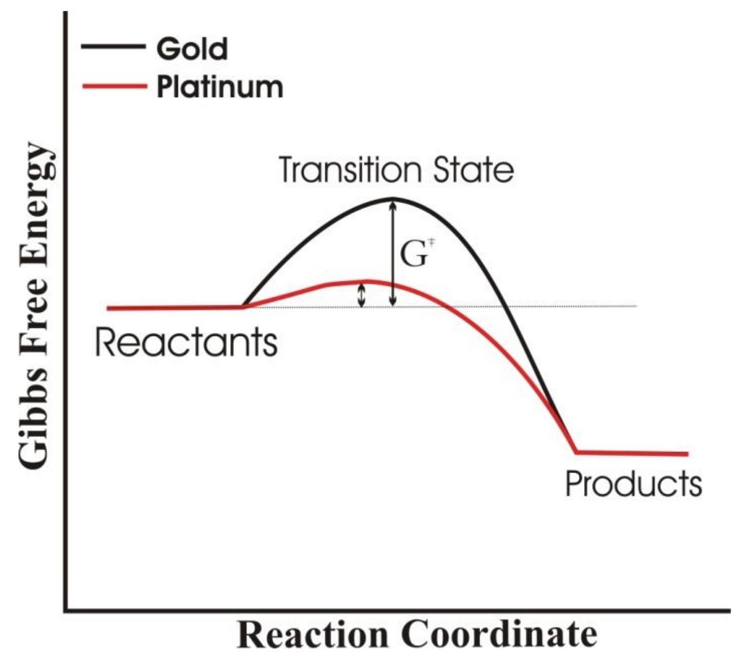
Possible Fuels: H_2, Hydrazine, Methanol, Ethanol, Ascobic acid...

Catalysts and Electrocatalysis



Overpotential = Activation barrier





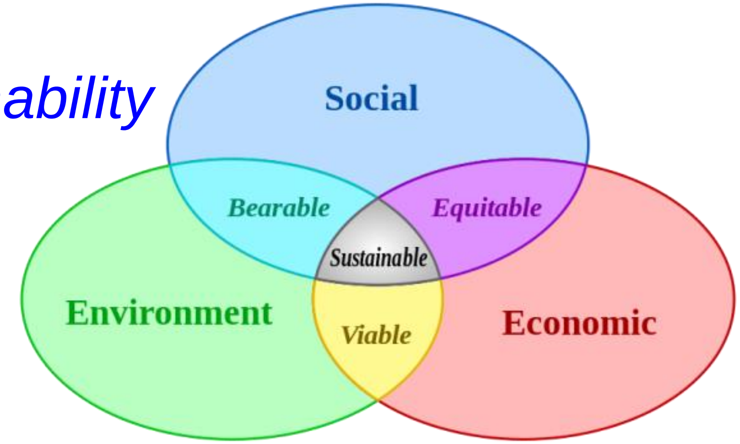
$2H^+ + 2e^- \rightarrow H_2$ $E_0 = 0.0$ V (NHE)

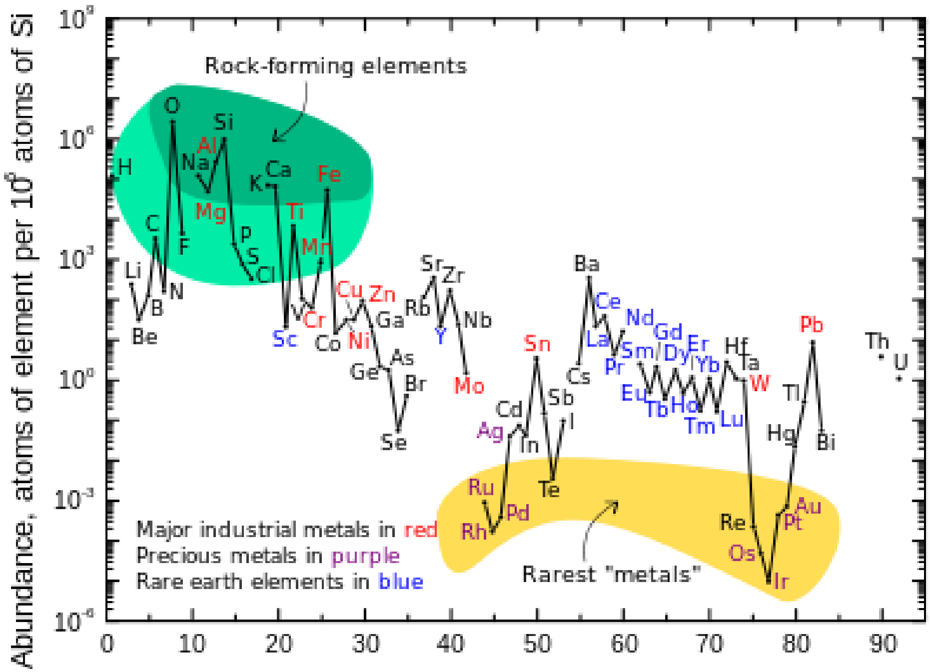
Designing Non-Conventional Electrocatalysts

Efficiency:

- Low overpotetial
- High current density
- Low ohmic loss

Sustainability

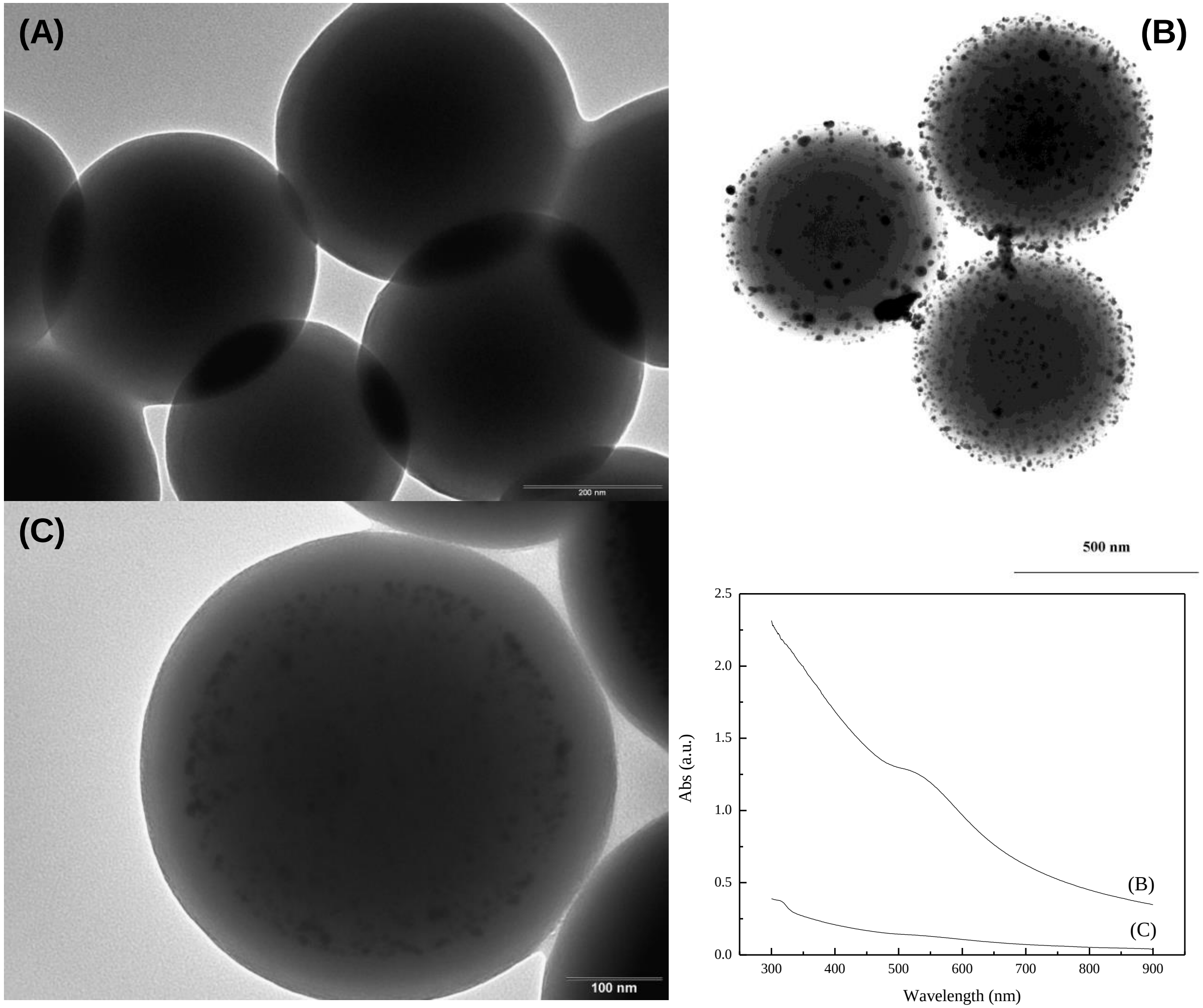


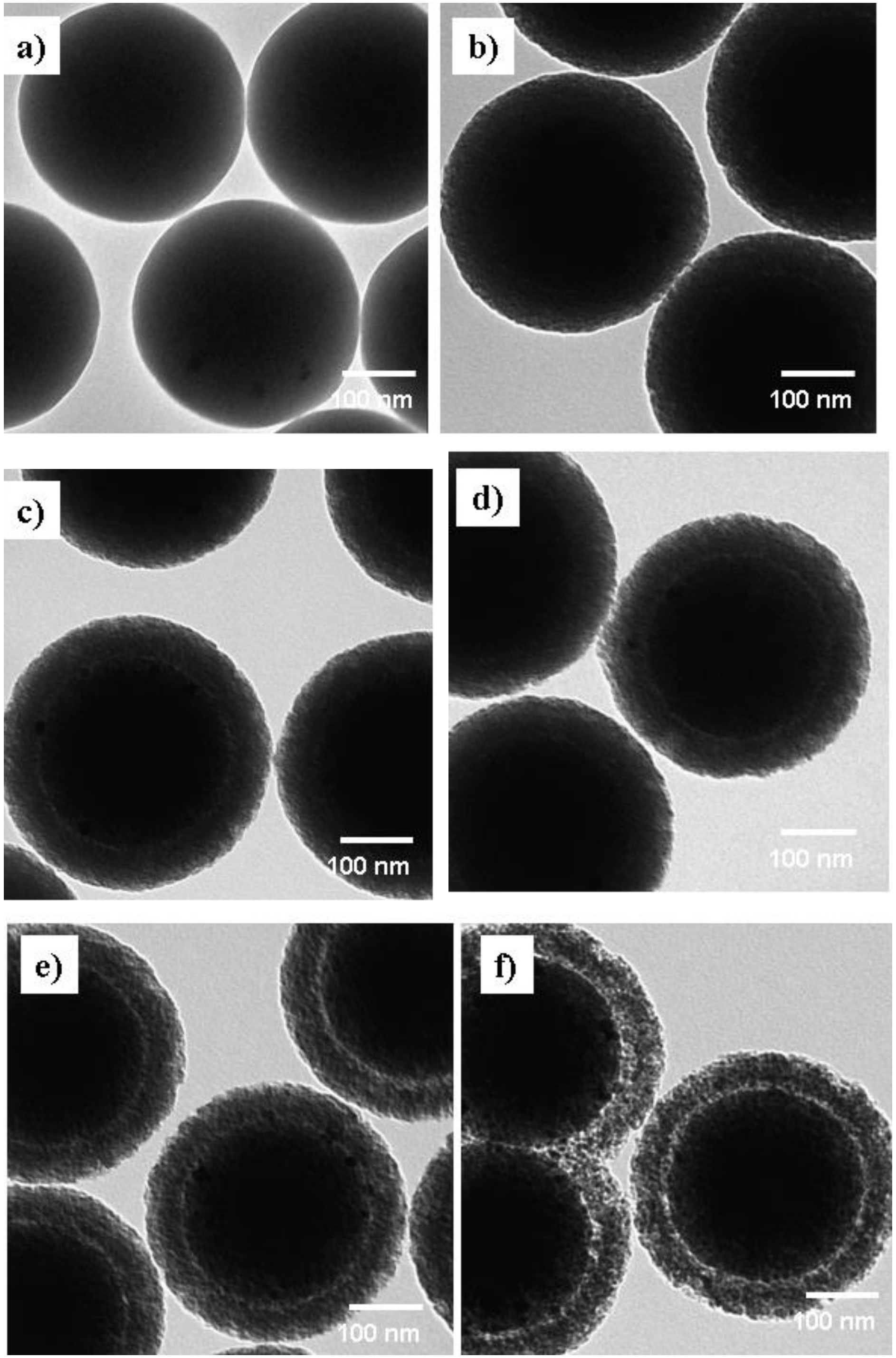


Wikipedia

- Based on abundant elements
- Nontoxic
- High density of active sites
- High surface area
- Low electrical resistance
- Robust
- High selectivity

Core-Shell-Shell Nanospheres



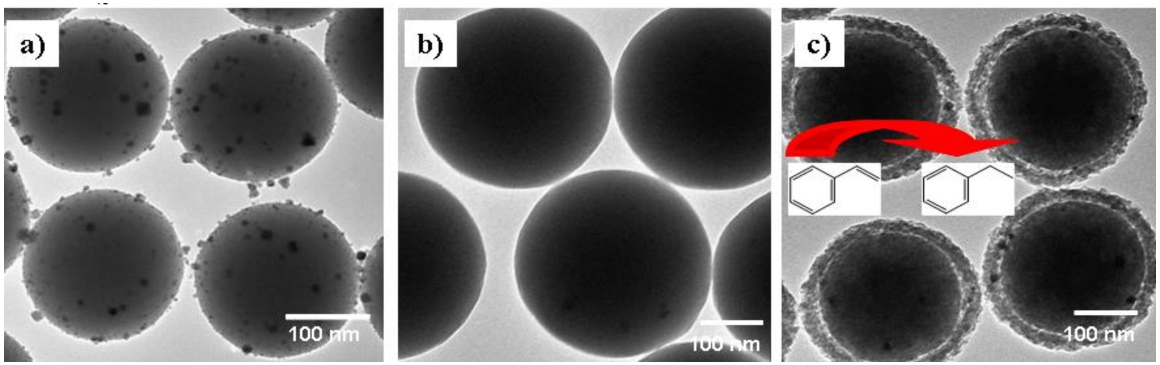


Controlled Etching

TEM images of SiO_2/Pd-NP/SiO_2 nanospheres (a) and SiO_2/Pd-NP/Porous-SiO_2 nanospheres after etching for:
(b) 50, (c) 60, (d) 70, (e) 80 and (f) 100 min.
Scale bars = 100 nm in all images.

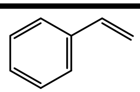
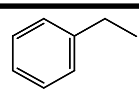
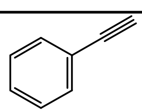
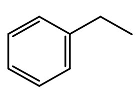
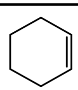
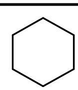
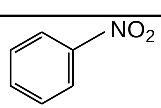
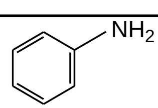
Wang, Y.; Asefa, T., *J. Mater. Chem.*, **2010**, *20*, 7834-7891.

Core-Shell-Shell Nanospheres as Efficient Catalysts

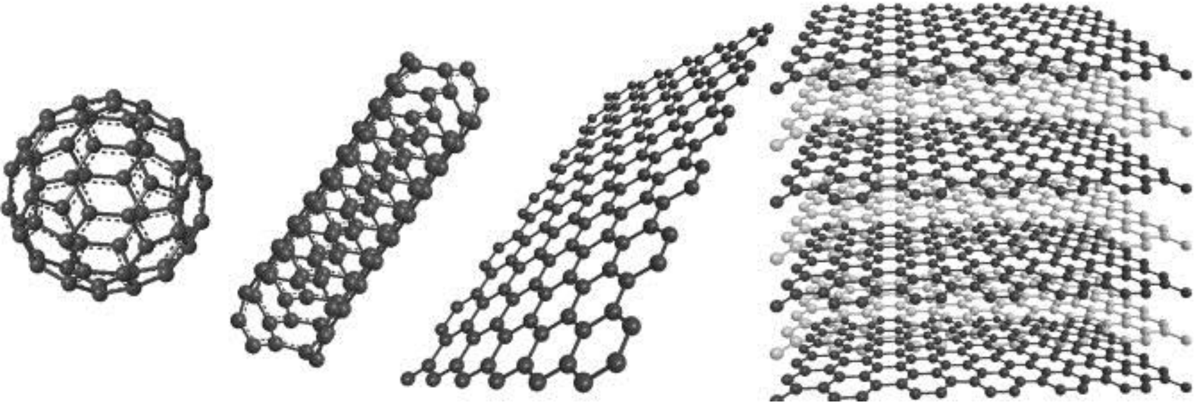


Wang, Biradar, Asefa et al., *J. Mater. Chem.*, **2010**, *20*, 7834.

Hydrogenation

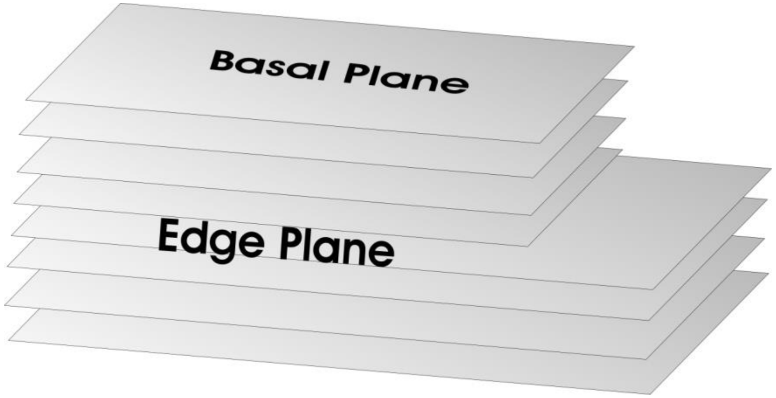
Substrate	Product	Time [h] /T [C]	Conversion [%]	Selectivity [%]	TOF [h^{-1}]
		0.5 / 25	~100	~100	5,181
		0.5 / 25	~100	~100	5,407
		1 / 50	96	~100	2,812
		3 / 50	91	~100	263

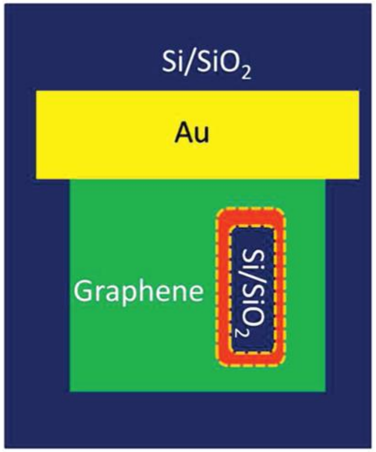
Carbon Nanostructures for Electroatalysis

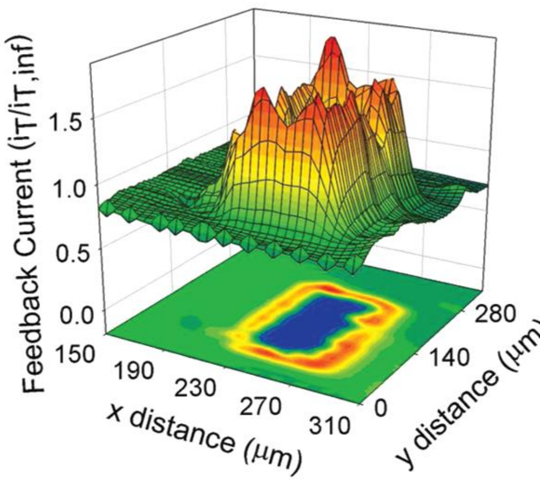


Pumera et al. Trends in Analytical Chemistry (2010)

Scanning electrochemical microscope image of graphene and graphene imperfection show that the electron transfer kinetics is higher at regions with greater defect density compared to those with lower density.



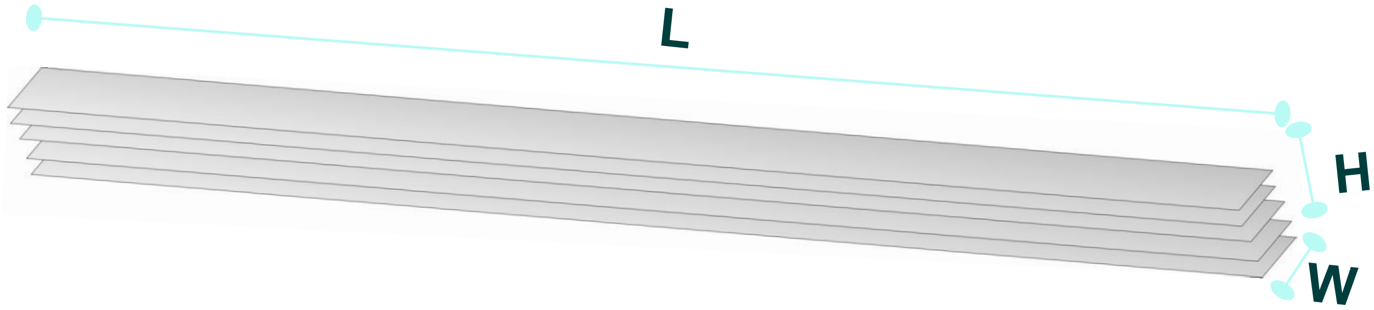




Tan, Abruña, et. al, *ACS Nano* **2012**, *6*, 3070.

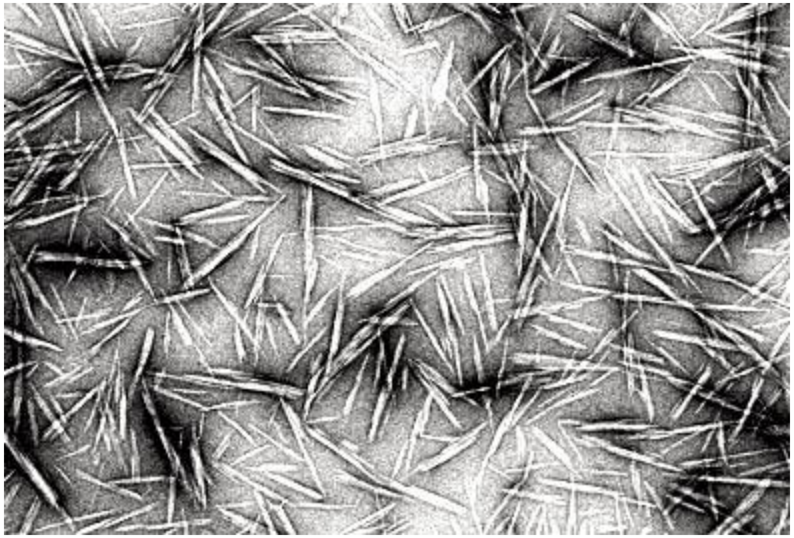
Graphene defect has higher reactivity

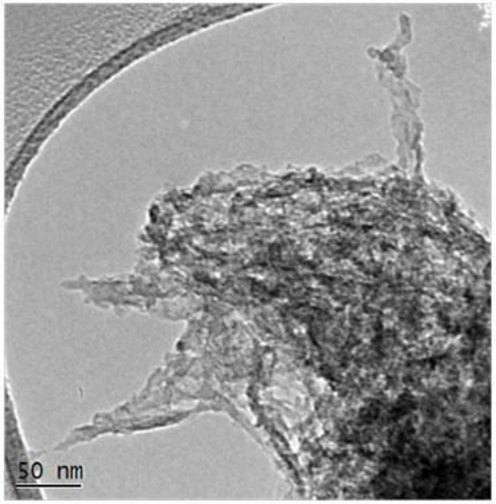
Carbon Nanoneedles



$L >> H \approx W$

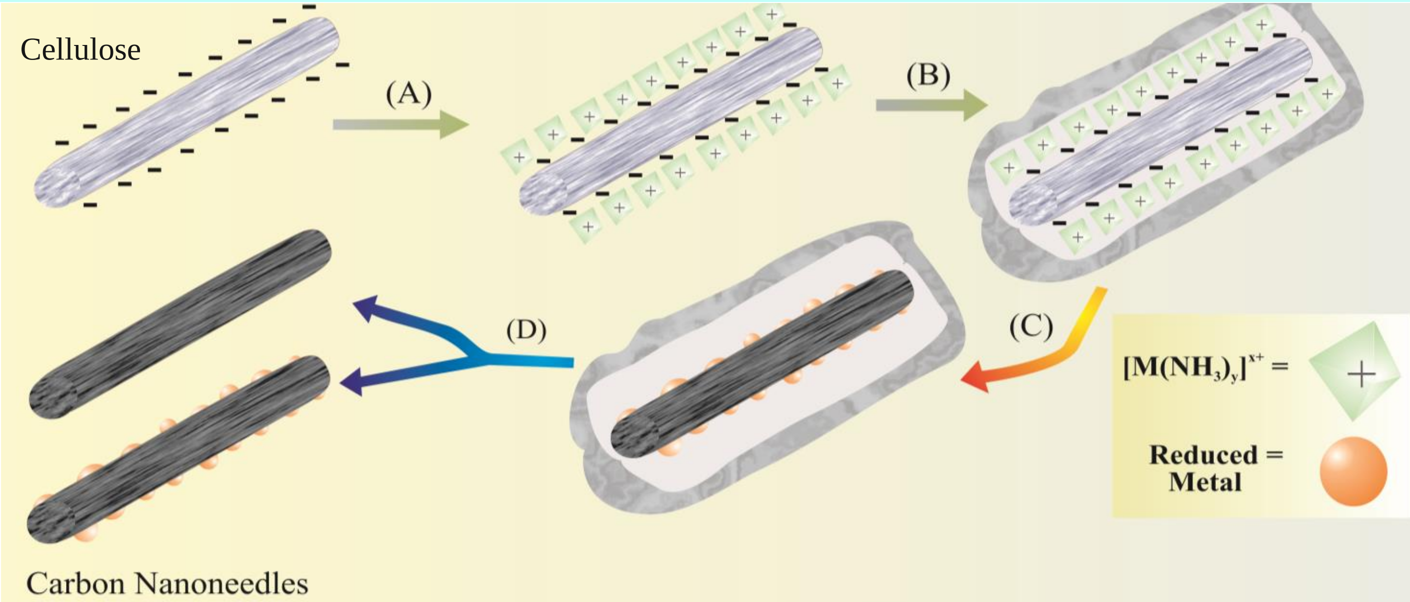
Cellulose Nanocrystal as precursor

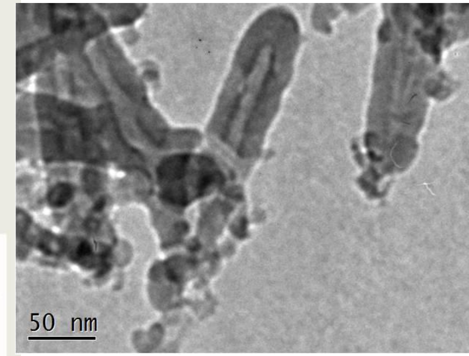


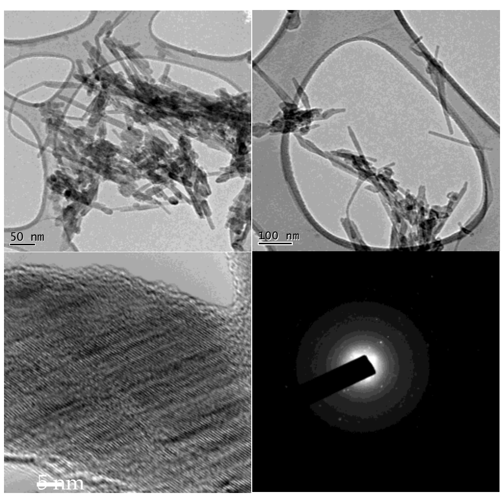


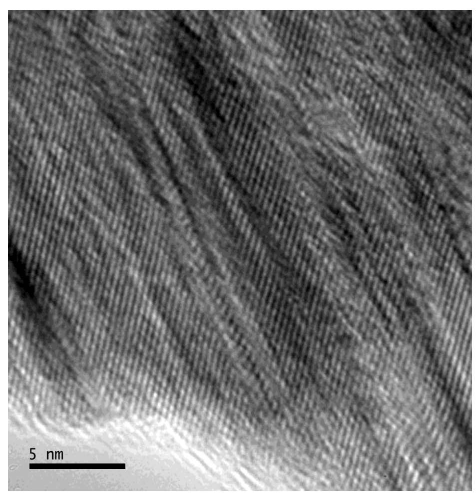
http://cerig.efpg.inpg.fr/dossier/LGP2-scientific-report-2006-2009/page20.htm

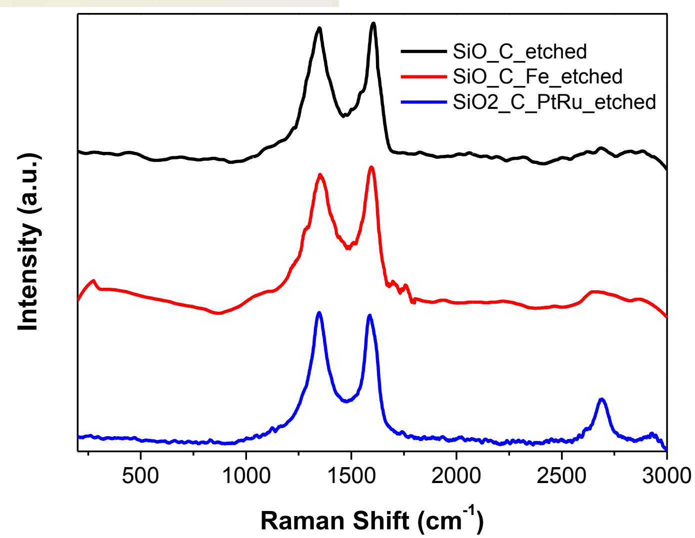
Cellulose-Derived Layered Graphite/Silica and Graphite Nanofibers











Silva, Asefa, et al. *Angew. Chem. Int. Ed.* **2012,** *51*, 7171.

Carbon Nanoneedles

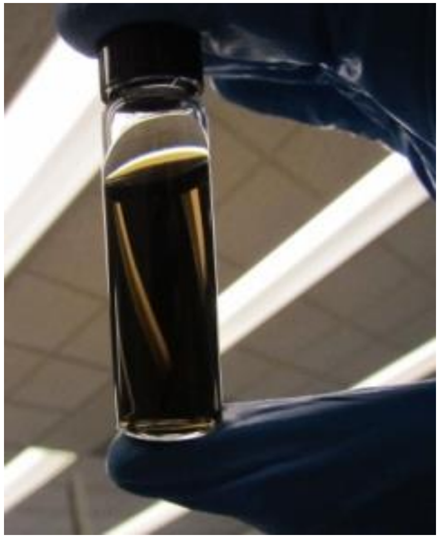
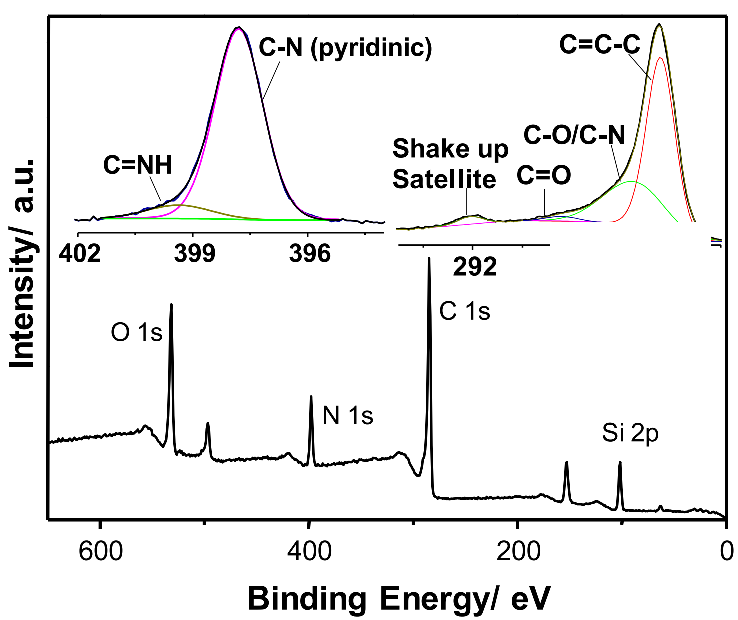
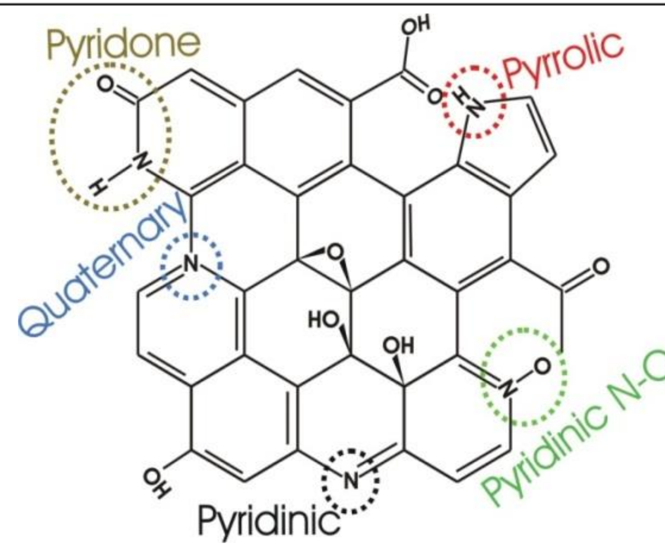


Table 1. XPS data for CNNs prepared from the $[(Fe(NH_3)_6]^{3+}$ route.

Element	C			O	N		Fe
	C=C-C	C-O/C-N	C=O		C-N (pyridinic)	C=NH	
Binding Energy (eV)	284.4	285.5	288.4	532.3	397.8	399.4	711.3/732.1*
Atomic percentage (%)	35.5	19.1	1.1	25.1	17.5	1.6	>0.1





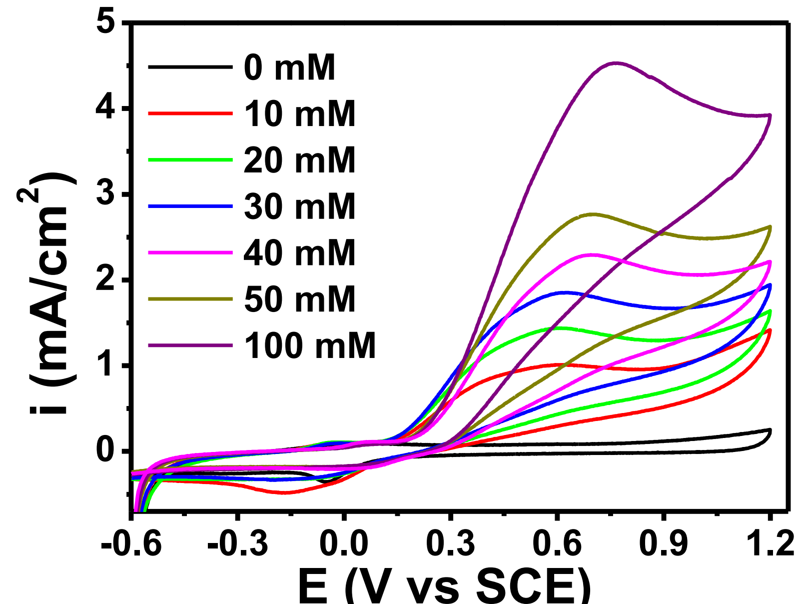
Graphite Nanofibers for Electroxidation of Hydrazine

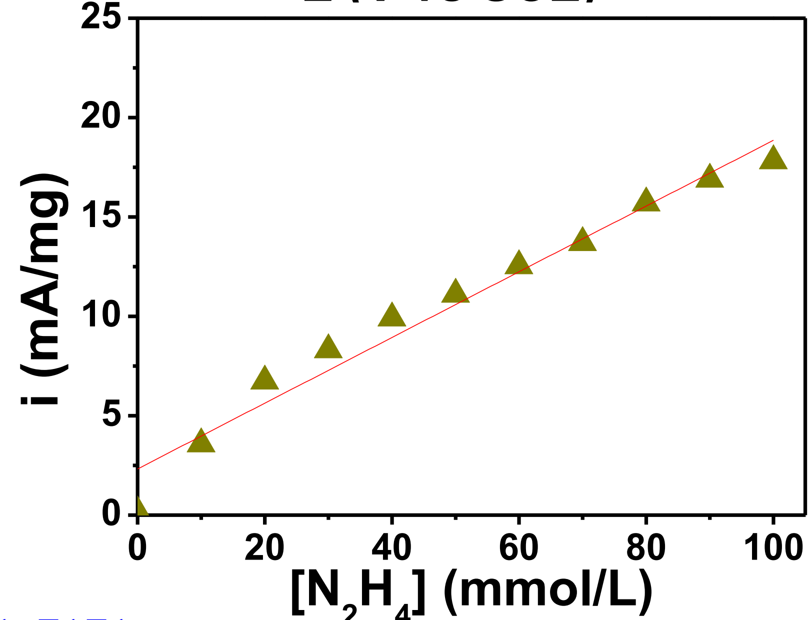
Hydrazine Oxidation for Fuel Cells

$$\text{Anode}: \; N_2H_4 + 4OH^- \leftrightarrows N_2 + 4H_2O + 4e^-$$
$$E^o = -0.33\ \text{V/RHE}$$

$$\text{Cathode}: \; O_2 + 2H_2O + 4e^- \leftrightarrows 4OH^-$$
$$E^o = +1.23\ \text{V/RHE}$$

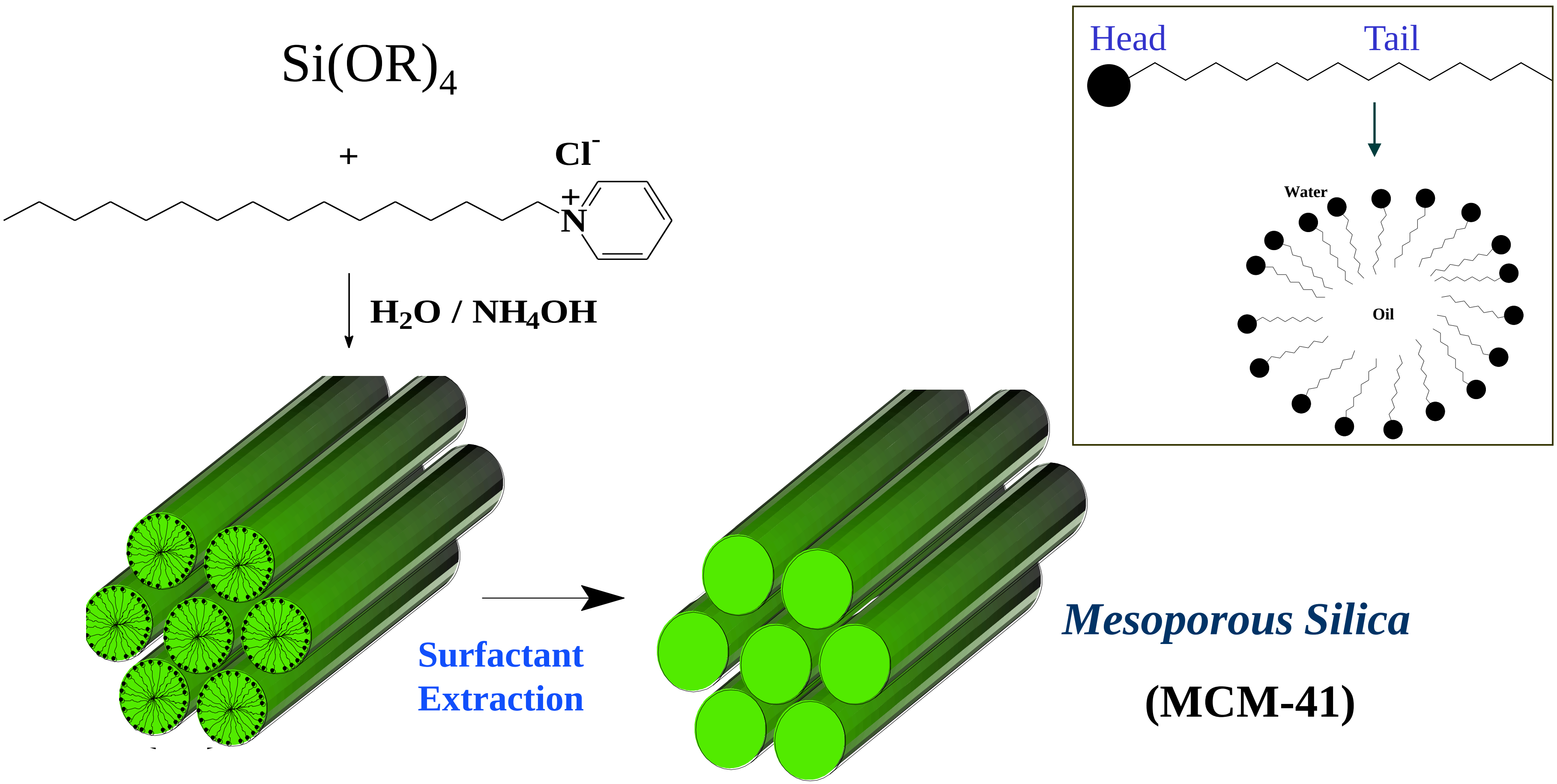
$$\text{Cell Reaction}: \; N_2H_4 + O_2 \leftrightarrows N_2 + 2H_2O$$
$$E^o = +1.56\ \text{V/RHE}$$





Silva, Asefa, et al. *Angew. Chem. Int. Ed.* **2012,** *51*, 7171.

Mesoporous Silica-Based Multifuctional Materials

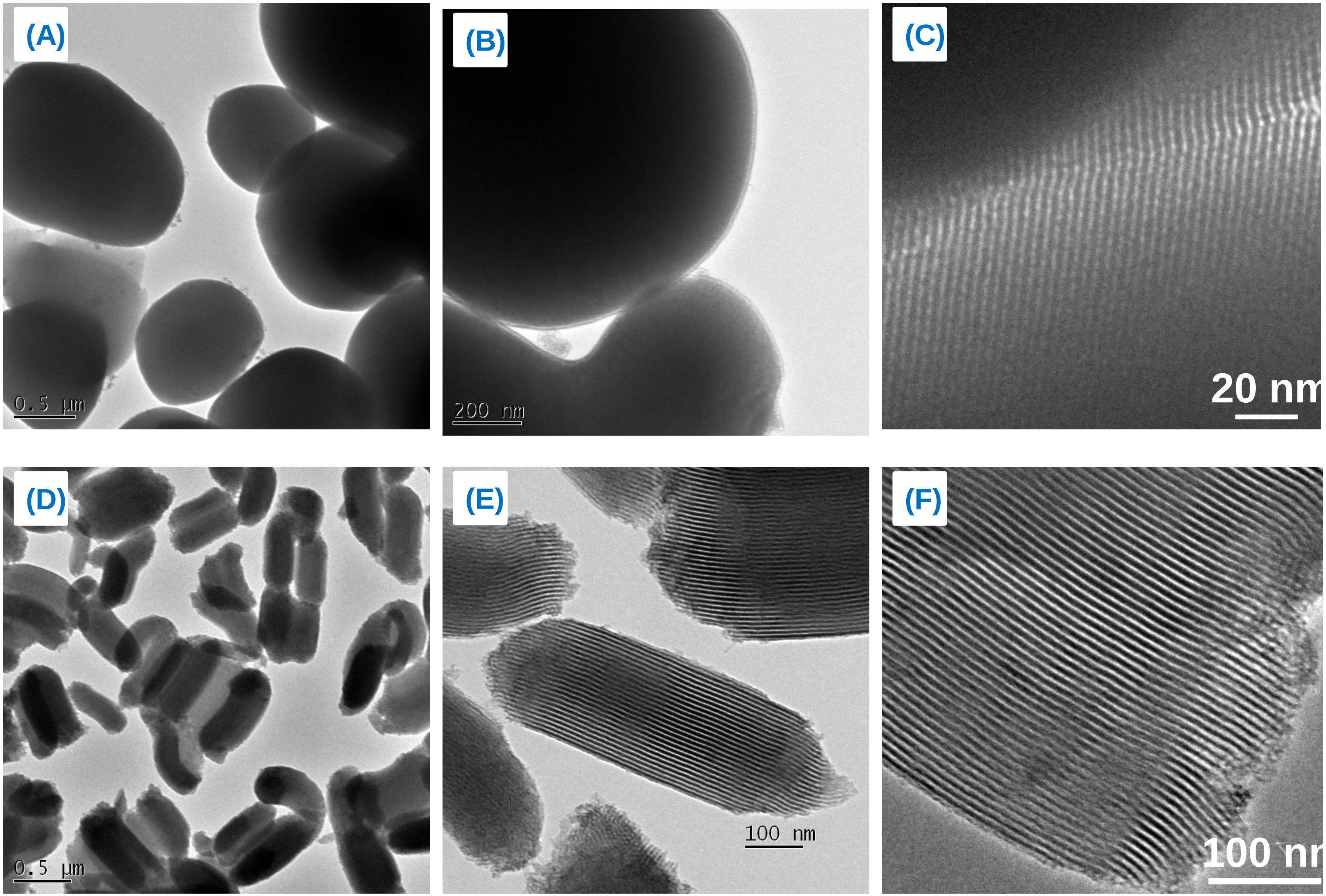


Kresge et al., *Nature* 1992

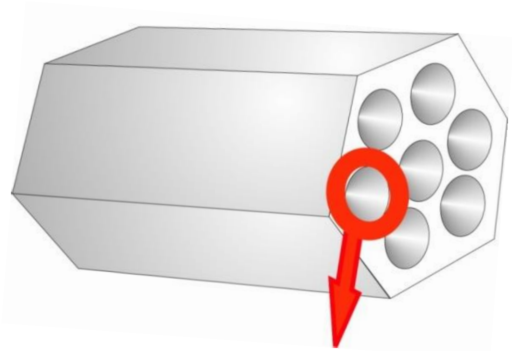
Mesoporous Silica Nanoparticles

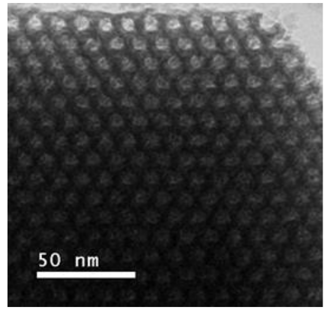
MCM-41

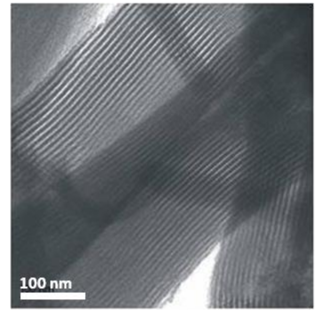
SBA-15



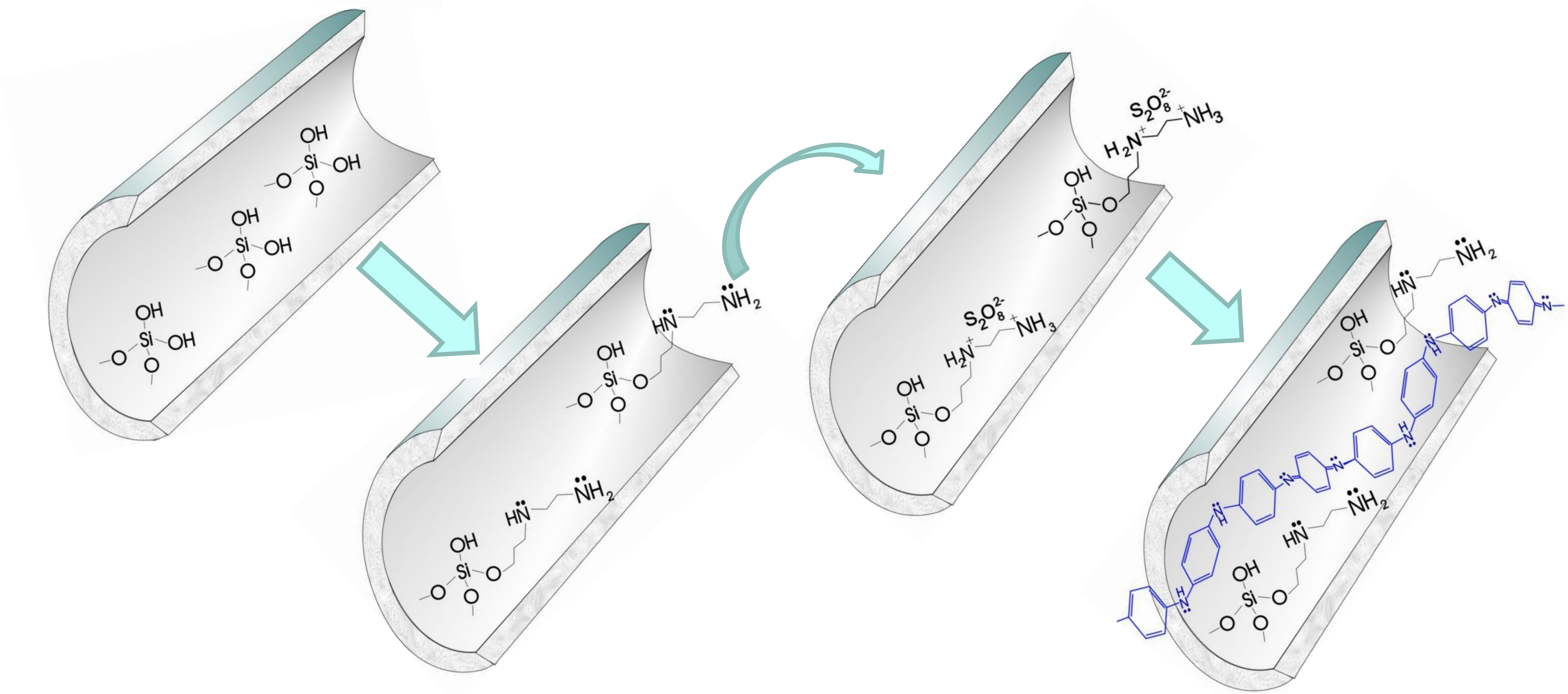
Mesoporous Silica Supported Polyaniline as Electrocatalyst





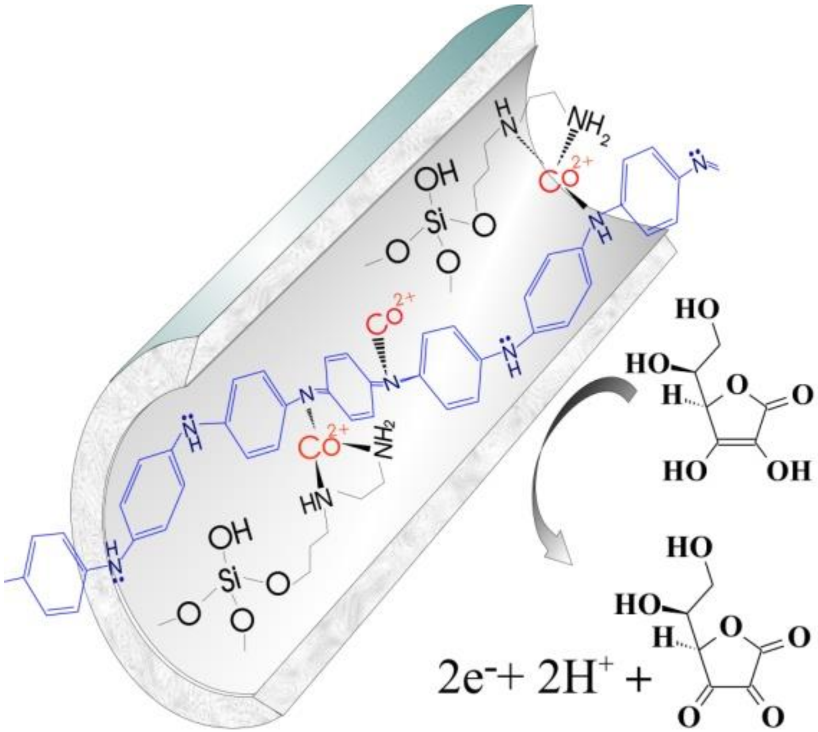


Mesoporous Silica

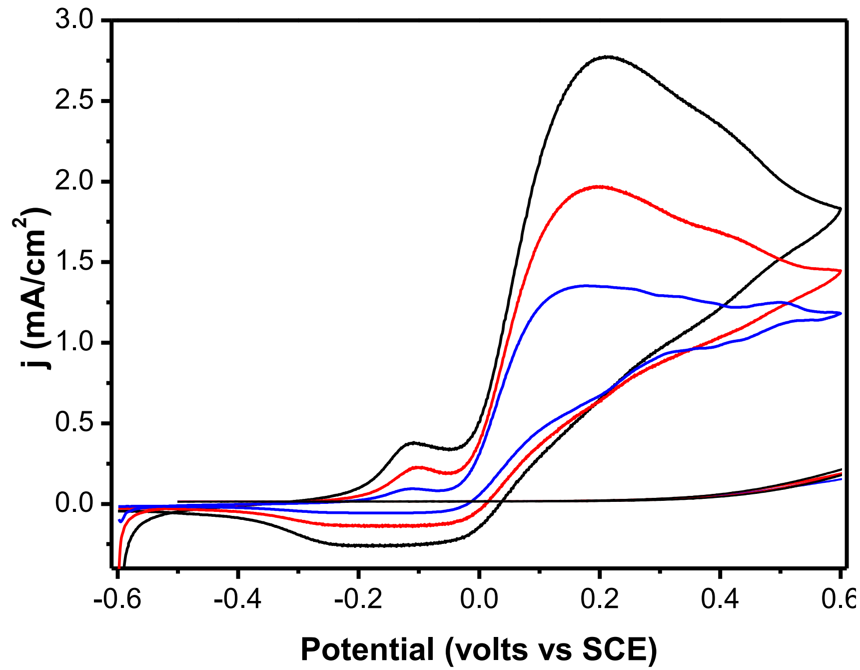


Silva, Asefa, *Adv. Mater.* **2013**, *24*, 1878.

Electrocatalysis for Hydrazine Oxidation

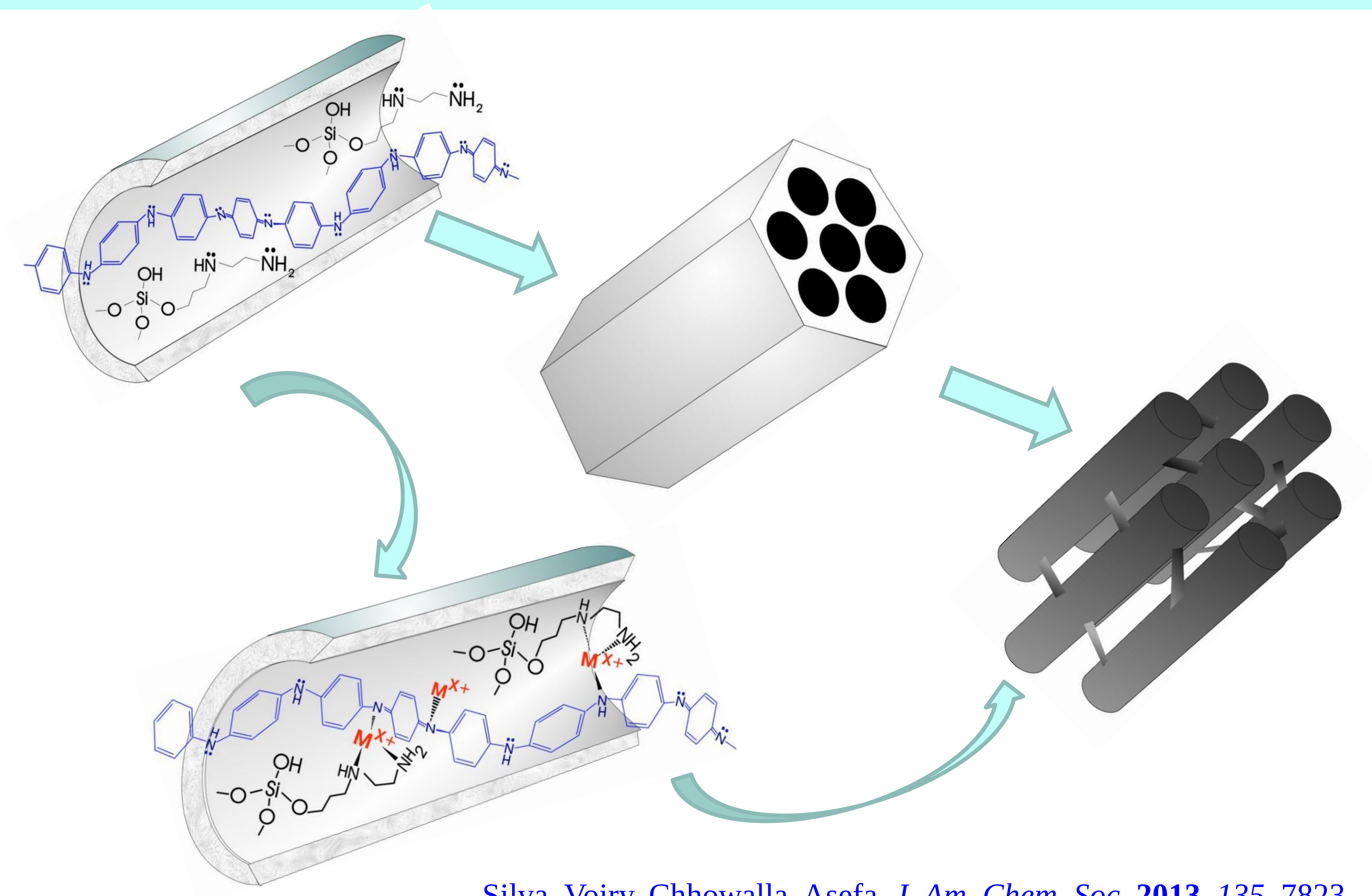


Glassy Carbon + Pani/SBA Electrode



Glassy Carbon Electrode

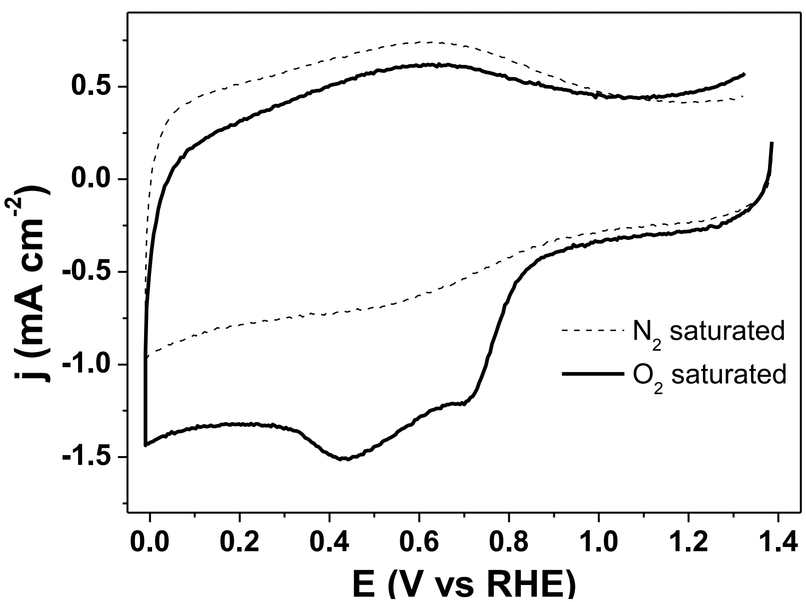
Polyaniline-Derived N- and O-Doped Mesoporous Carbons as Electrocatalyst for Oxygen Reduction Reaction

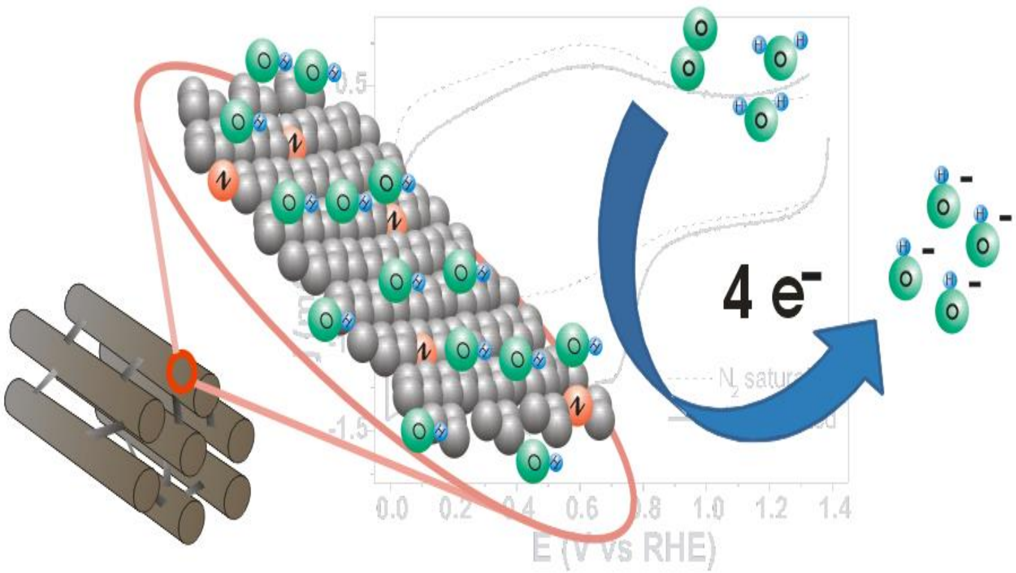


Silva, Voiry, Chhowalla, Asefa, *J. Am. Chem. Soc.* **2013**, *135*, 7823

Heteroatom-Doped Mesoporous Carbons: Efficient Electrocatalyst for Oxygen Reduction Reaction (ORR)

$O_2 + 4H^+ + 4e^- \longrightarrow H_2O \quad E^0 = 1.23\ V\ (NHE)$





* Among the most efficient, metal-free electrocatalyst for ORR.

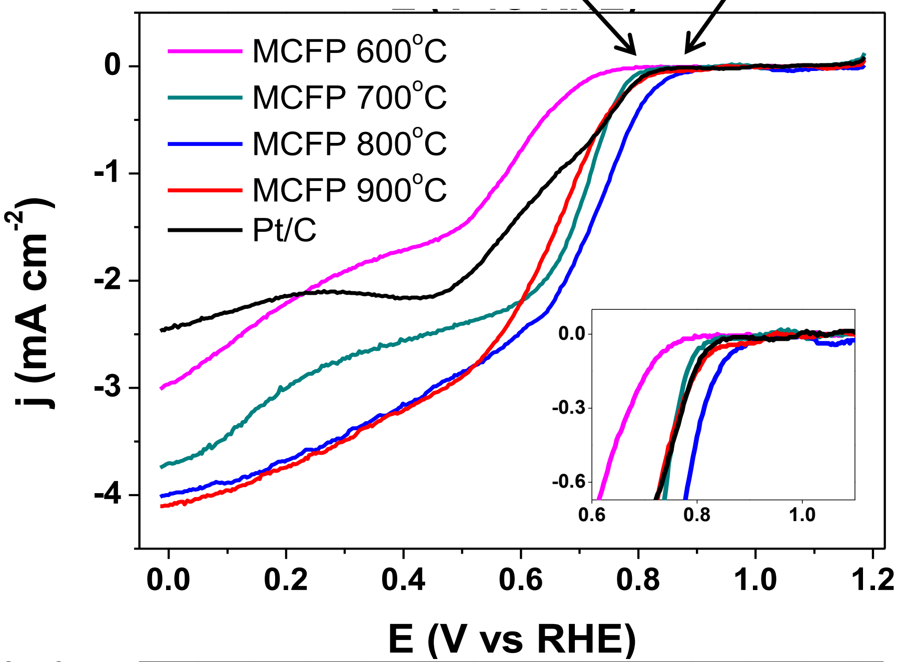
* Among the most efficient mesoporous carbon electrocatalyst for ORR.

Nitrogen-Doped Mesoporous Carbon: Efficient Electrocatalyst for Oxygen Reduction Reaction (ORR)

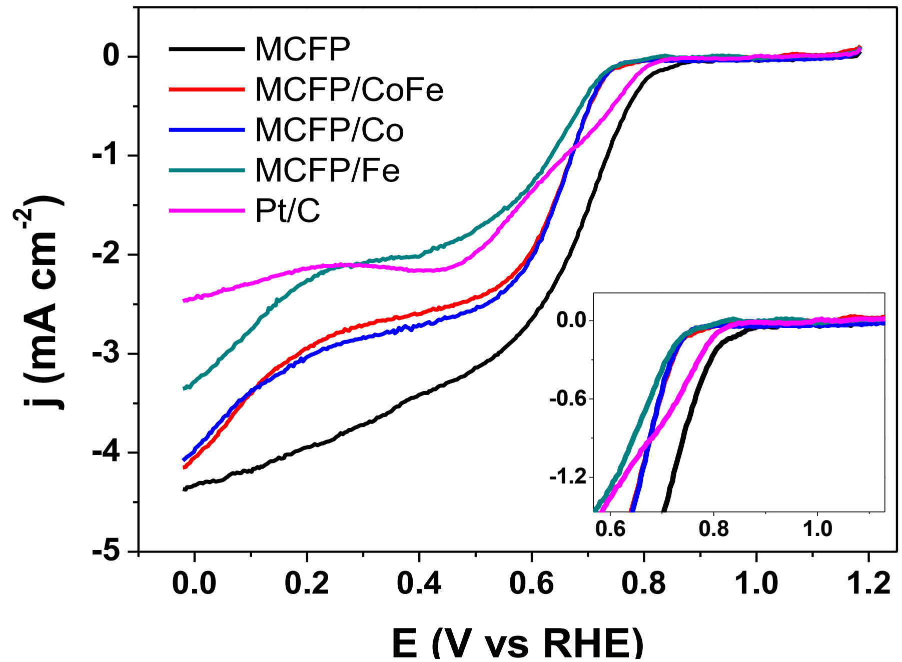
Electrocatalytic activity increases

Onset potential of Pt/C (benchmark catalyst)

Onset potential of our catalyst

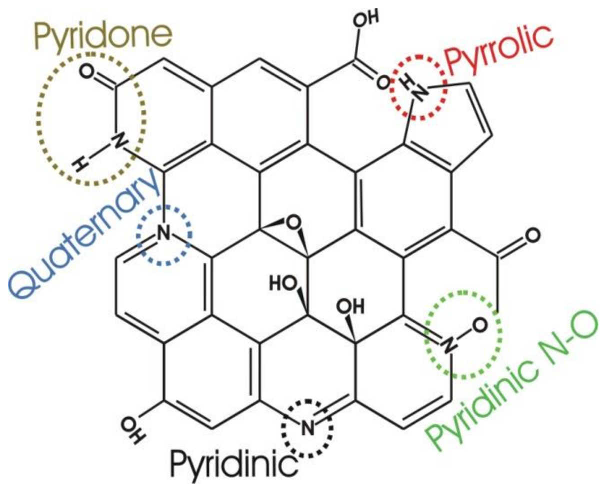


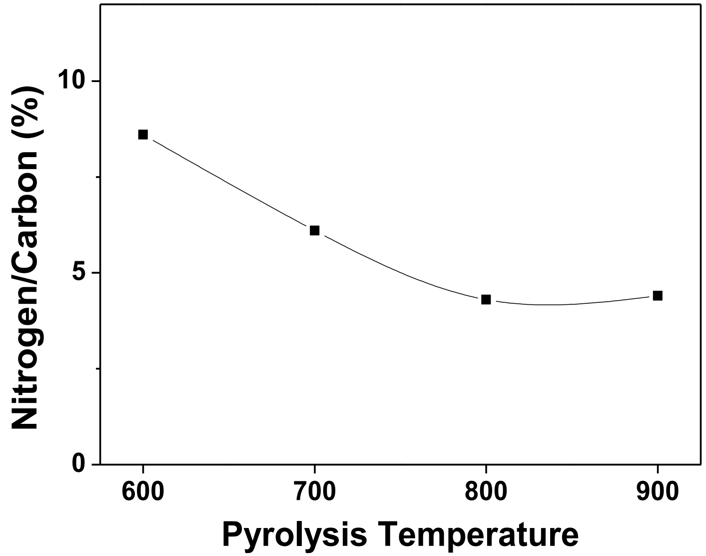
* We also found out that metals can actually compromise electrocatalytic activity (unlike in the case of L. Dai. *et al*. Science 2011).

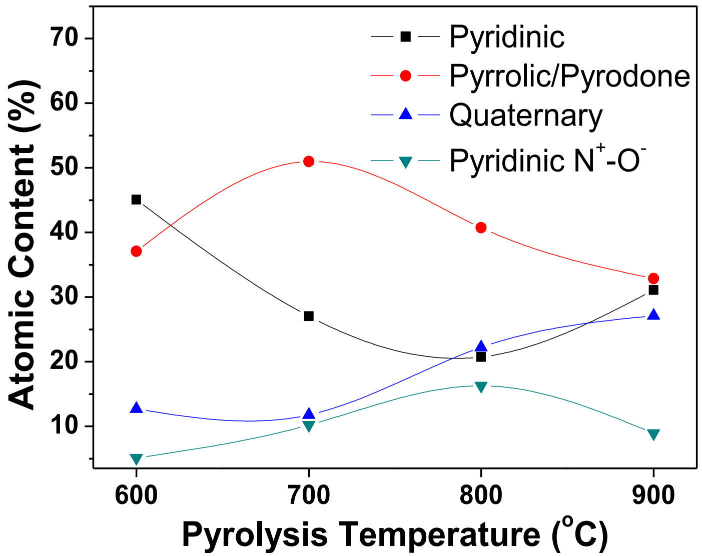


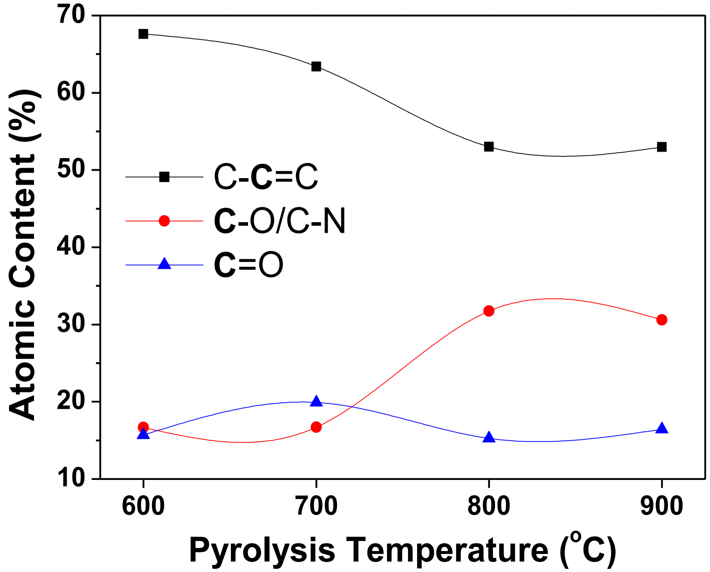
Silva, Voiry, Chhowalla, Asefa, *J. Am. Chem. Soc.* **2013**, *24*, 1878.

Compositional Studies

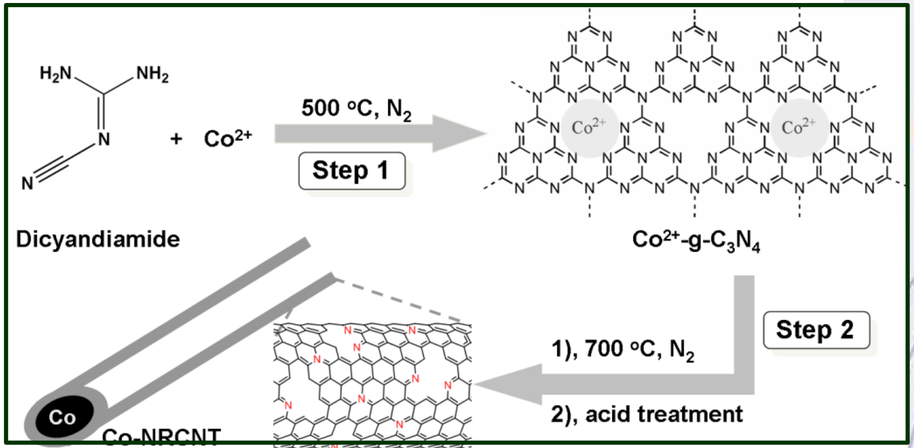


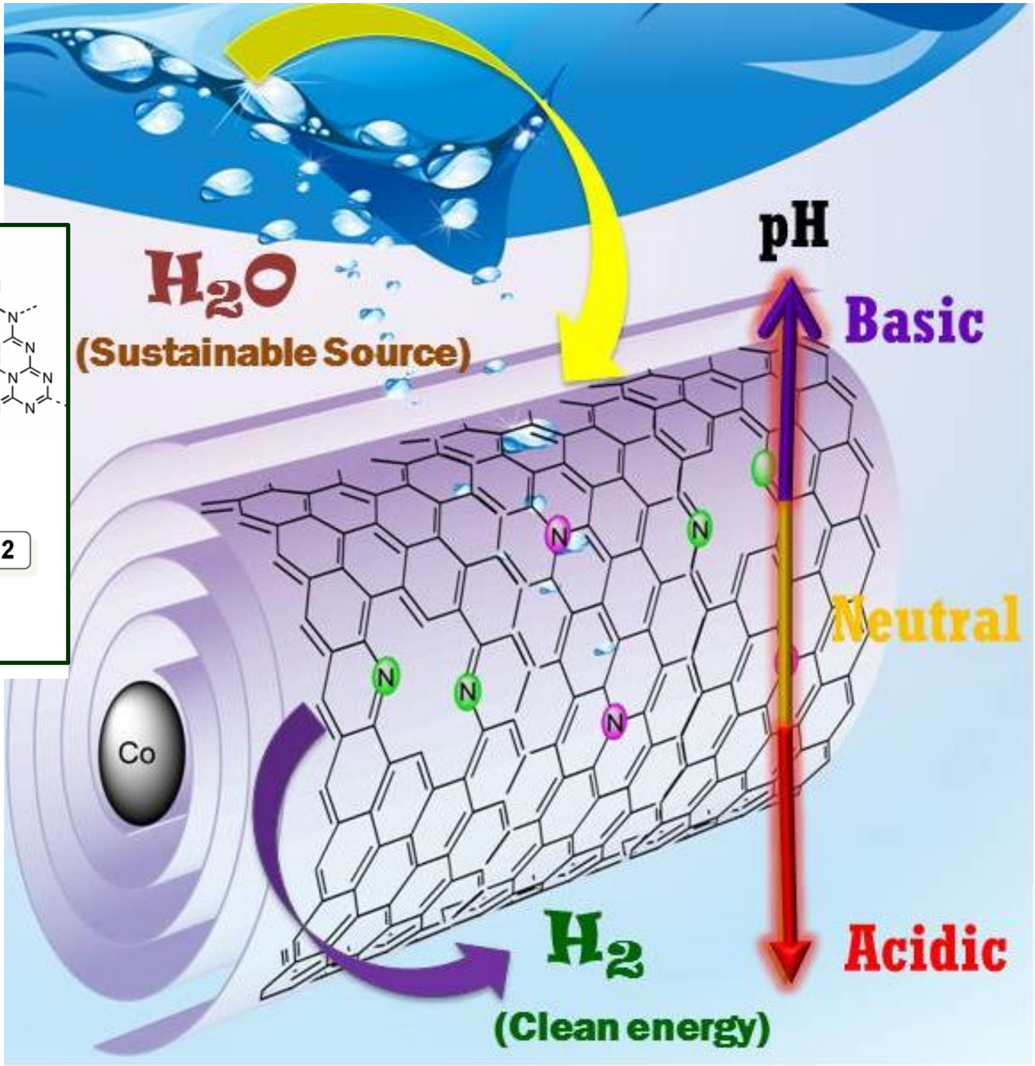






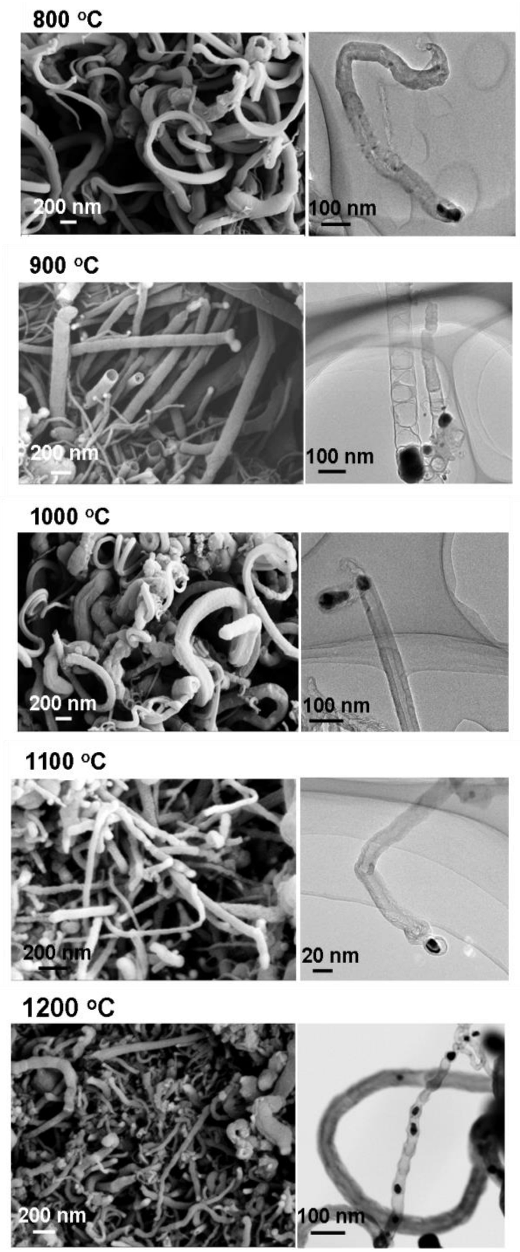
Nitrogen-Doped MWCNTs: Efficient Electrocatalyst for Hydrogen Evolution at All pH Values

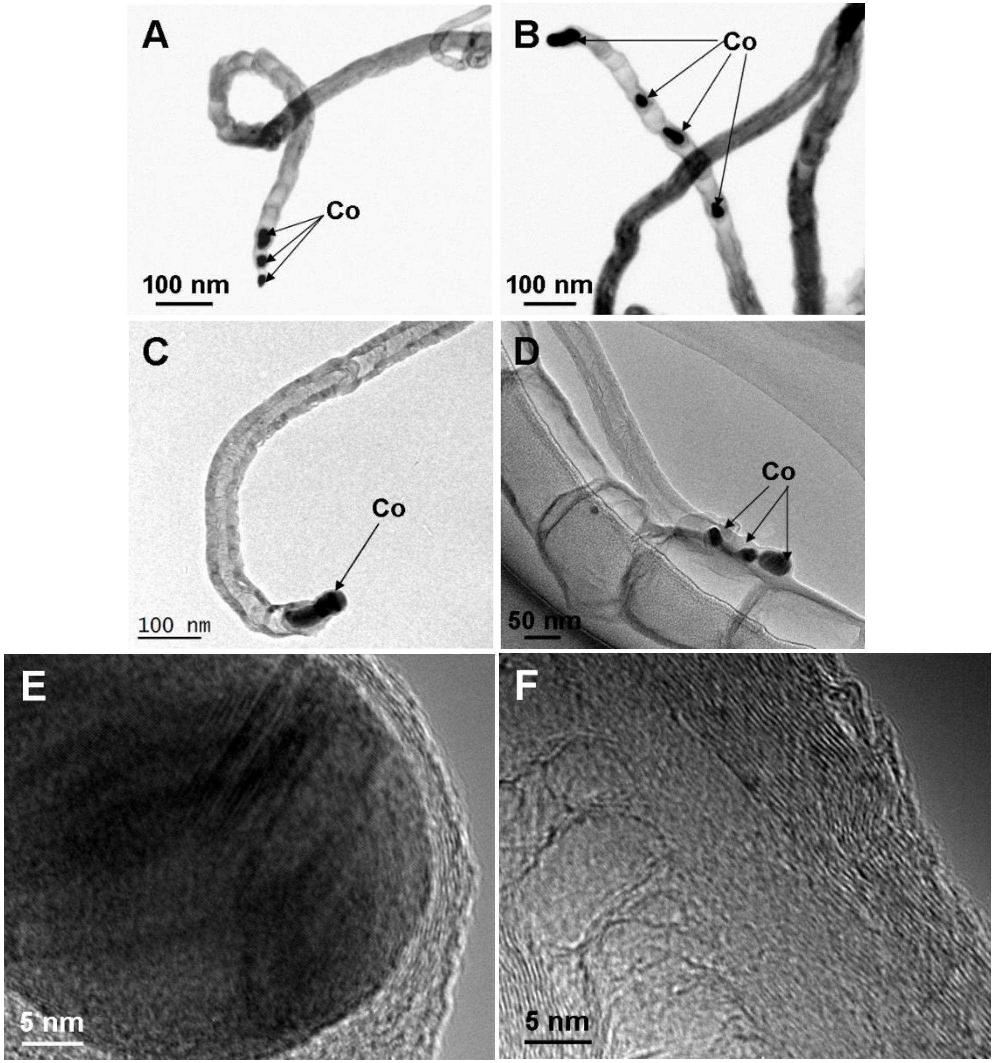




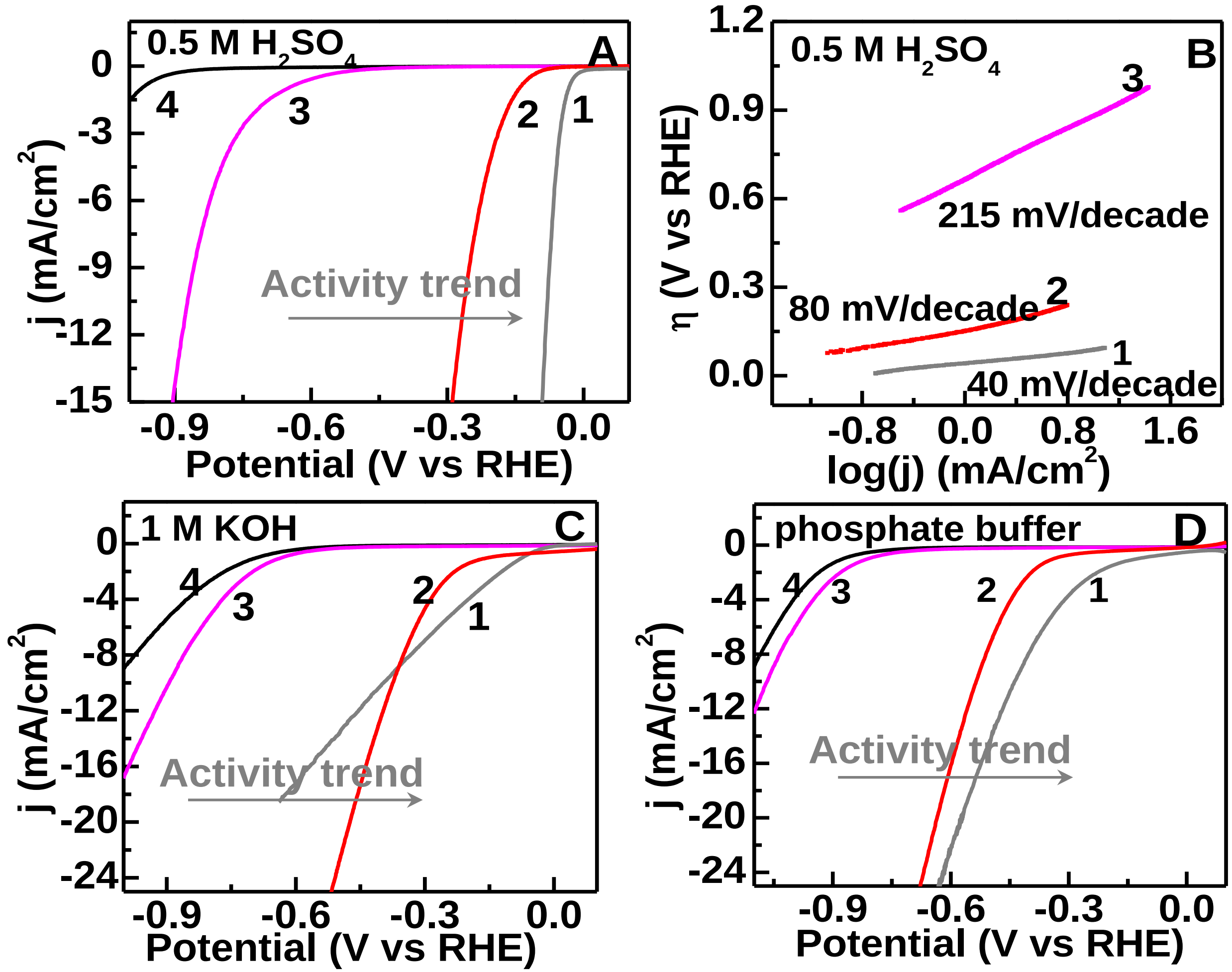
Zou, Huang, Goswami, Silva, Sathe, Asefa, *Angew Chem. Int. Ed*. **2014**, *53*, 4372.

Characterizations



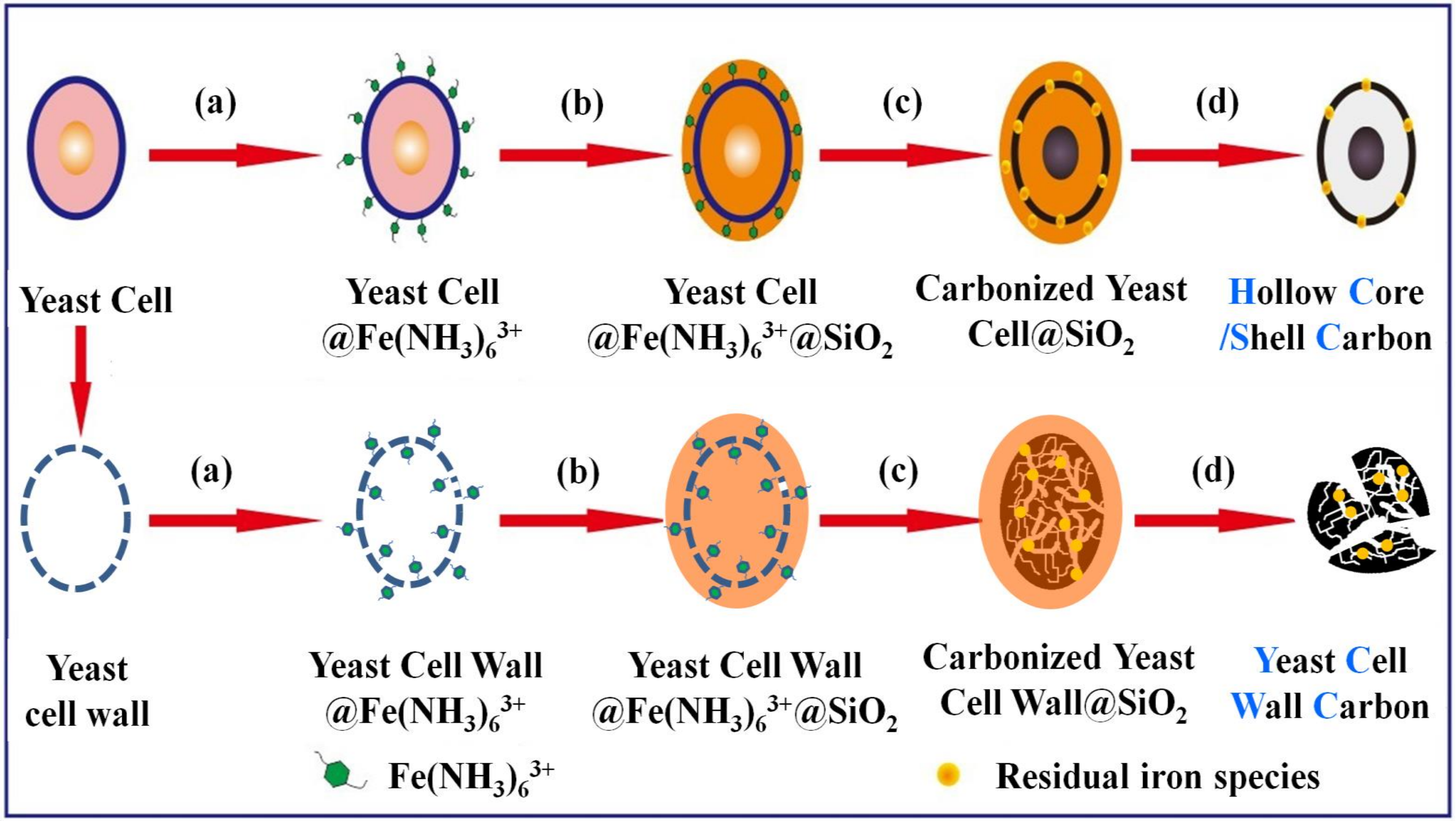


Electrocatalysis Results at Different pH Values



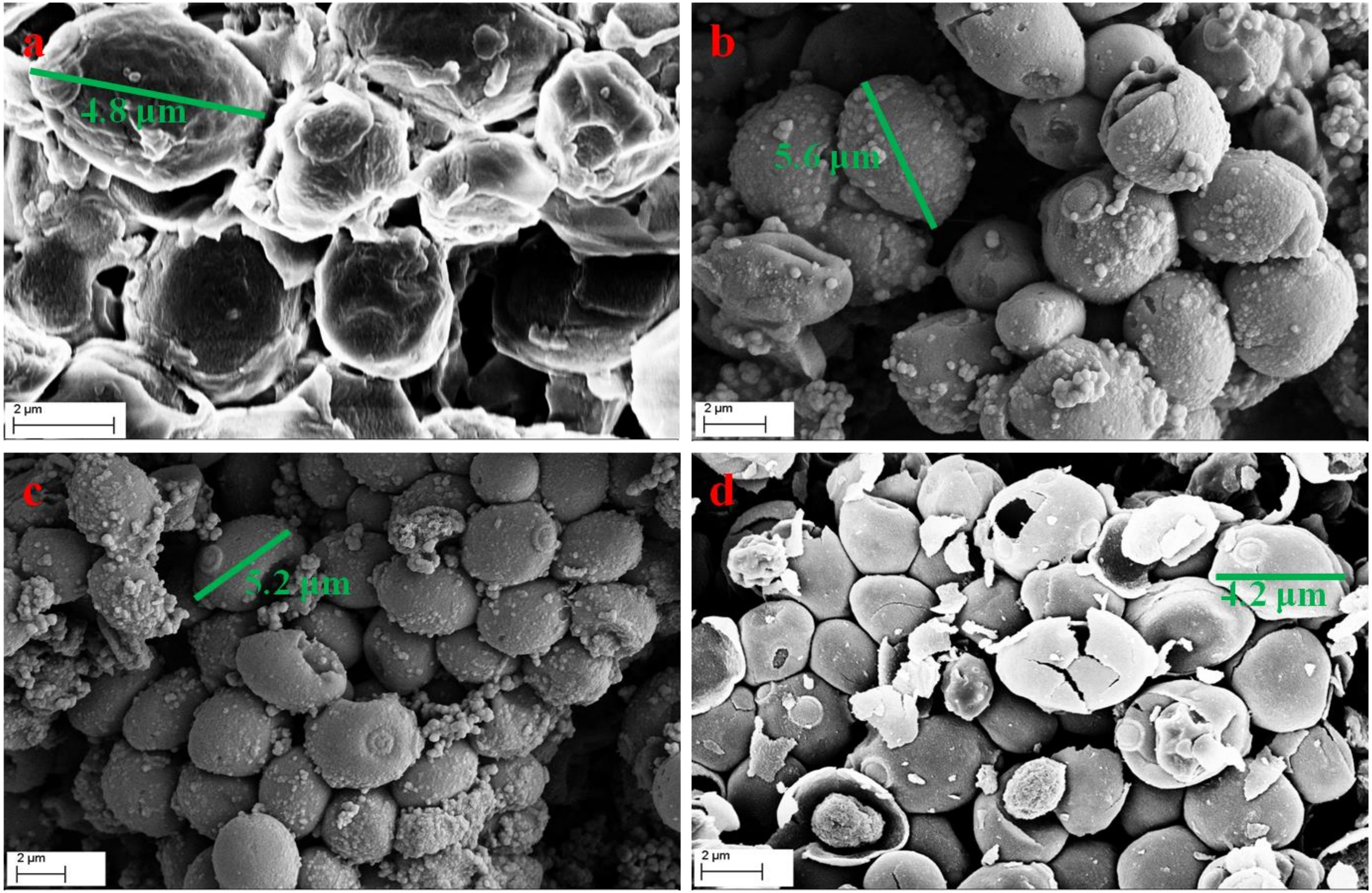
(A) Typical linear sweep voltammetry (LSV) curves in 0.5 M H_2SO_4 (pH = 0), (B) the corresponding Tafel plots in H_2SO_4 solution, and typical LSV curves in (C) 1 M KOH (pH = 14) and (D) phosphate buffer (pH = 7) solutions. Sample labels are: **1,** 1 wt. % Pt/C; **2,** Co-NRCNTs; **3,** MWCNTs; and **4,** no catalyst.

Yeast-Derived Heteroatom-Doped Carbon Nanomaterials as Electrocatalysts

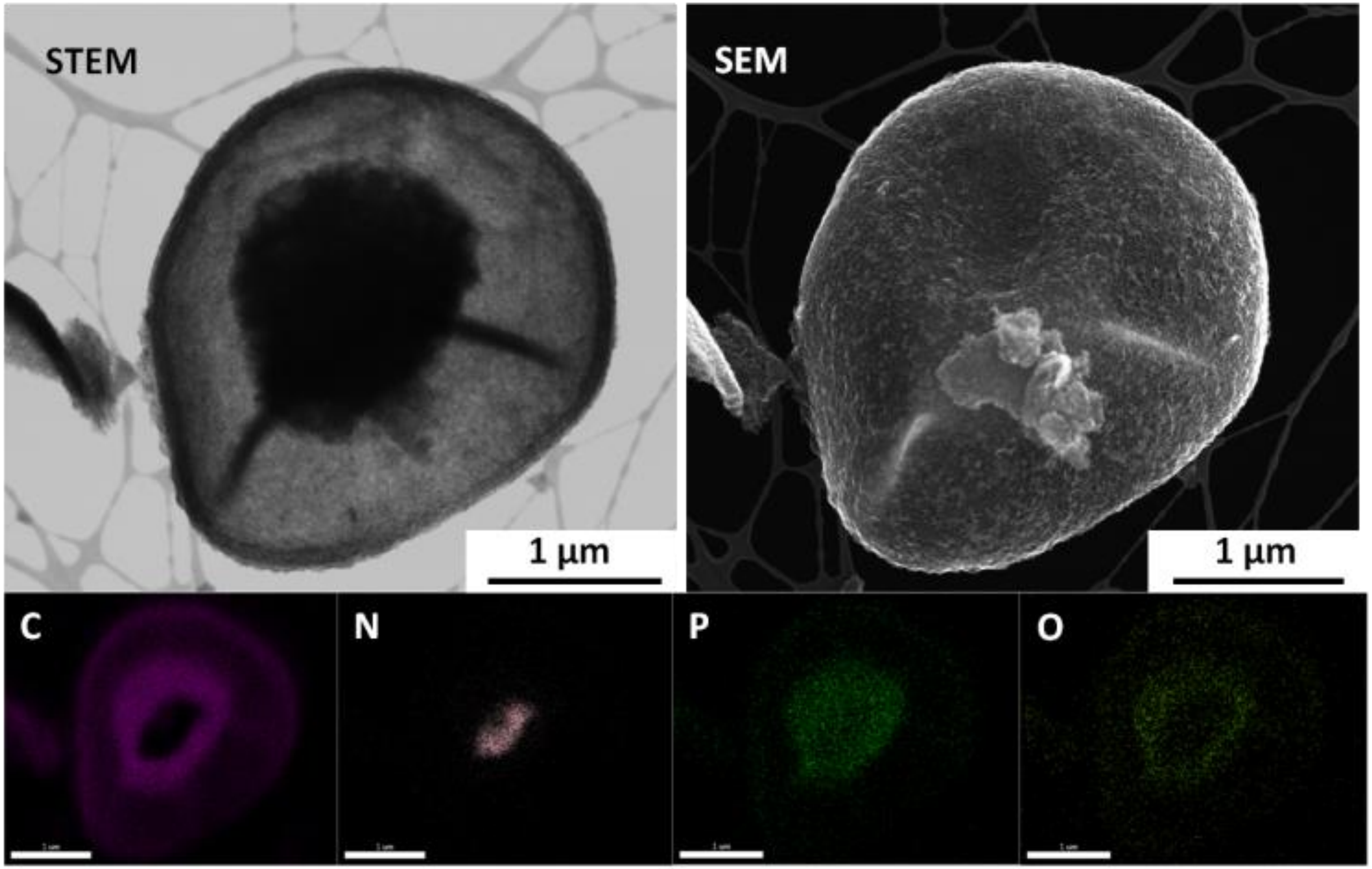


Procedures used for making heteroatom-doped hollow, core/shell carbon and yeast cell wall carbon from yeast cell and yeast cell wall, respectively: a) adsorption of $[Fe(NH_3)_6]^{3+}$ ions around yeast cells, b) deposition of silica shells around cells, c) high temperature treatment of the yeast/metal ions/silica, and (d) removal of the silica shells.

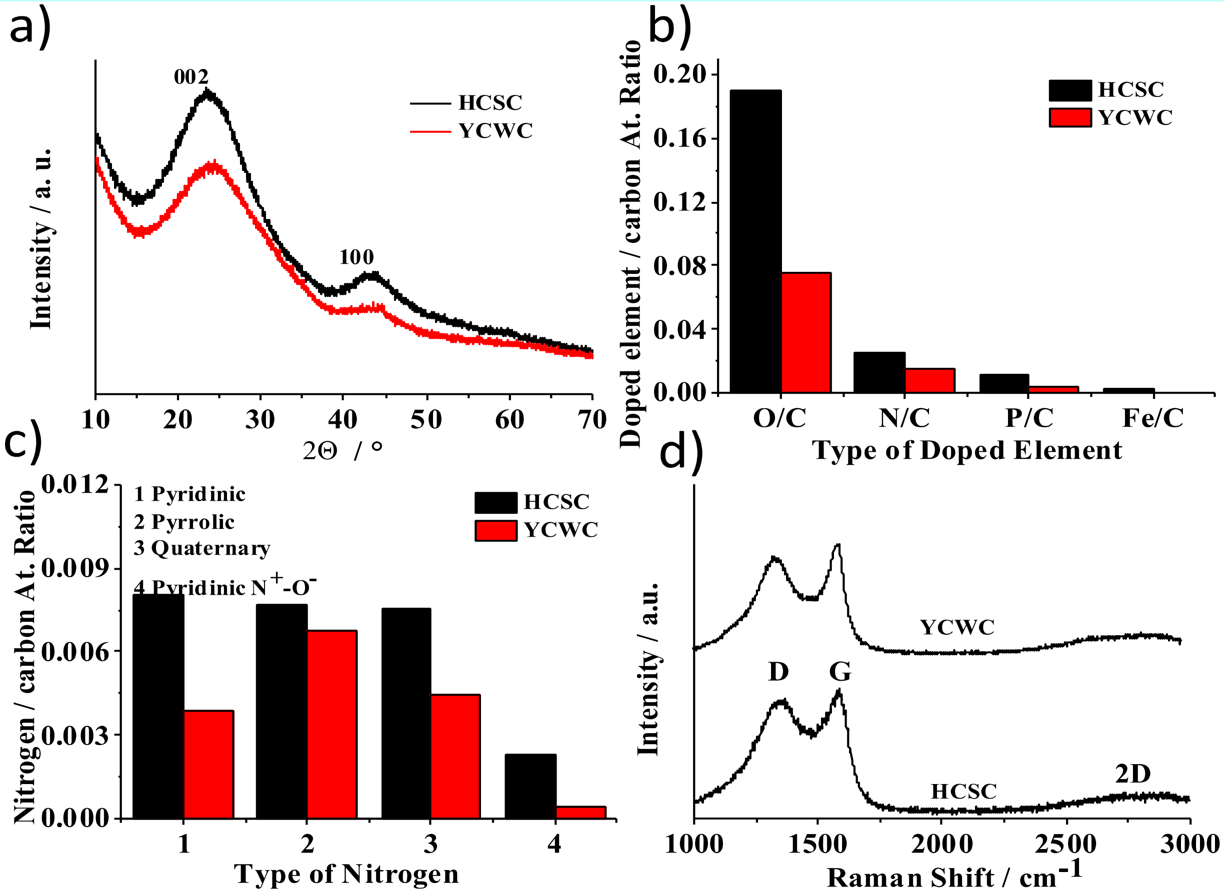
Huang, Asefa, et al. *ACS Appl. Mater. Interfaces*, 2015, 7,1978.



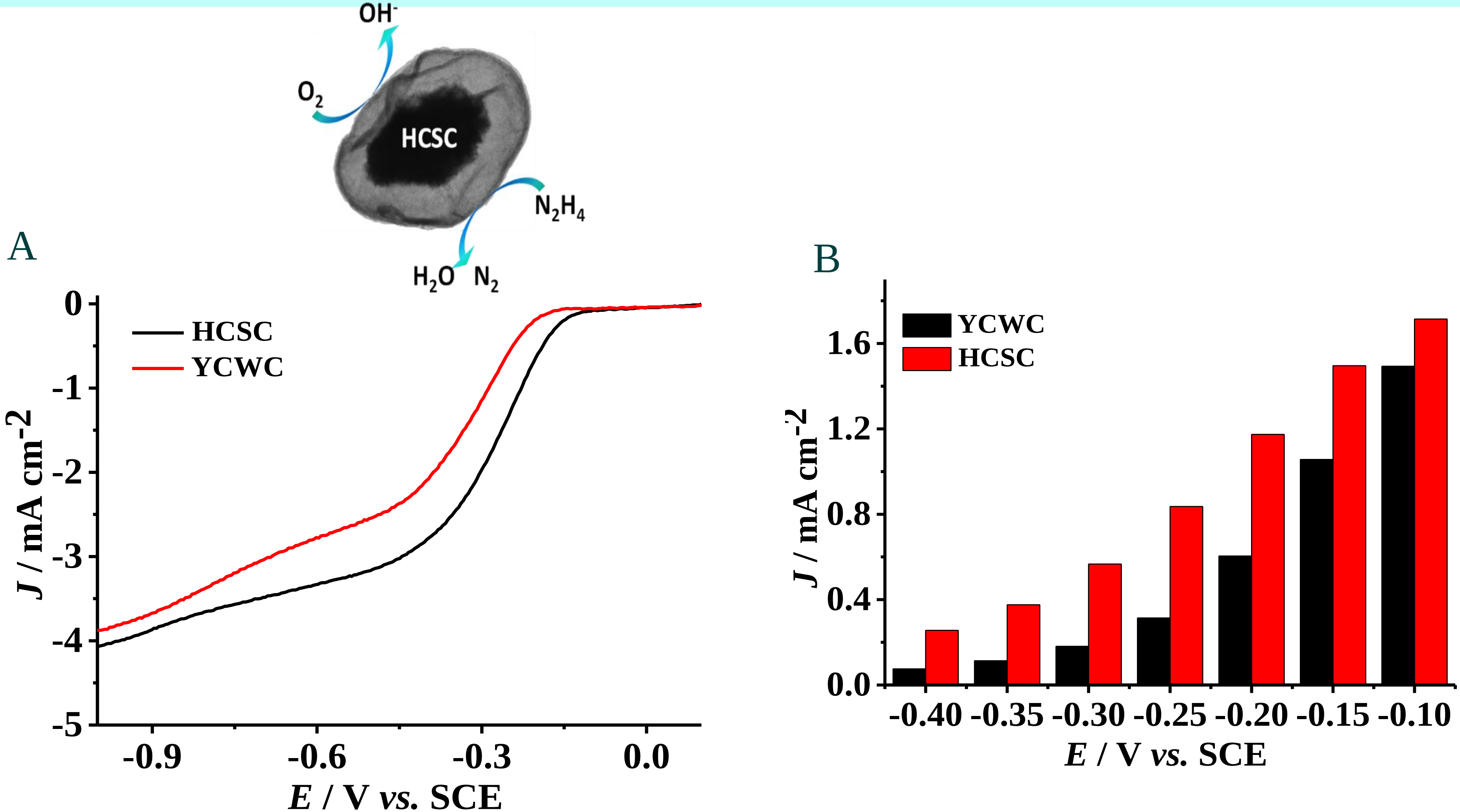
FESEM images of (a) yeast cells, (b) yeast cell@$[Fe(NH_3)_6]^{3+}$@SiO_2 microparticles, (c) carbonized yeast cell@SiO_2 microparticles and (d) hollow core/shell carbon (HCSC) microparticles.



STEM and SEM images of HCSC and elemental mapping results for C, N, P, and O atoms in them. The scale bars in all the images represent 1 µm.



(a) Polarization curves of ORR at 1600 rpm on HCSC and YCWC. (b) Comparison of kinetic current density (J_k) of ORR at various potentials on HCSC and YCWC. (c) Comparison of current density of HOR at various potentials on HCSC and YCWC in 32 mM hydrazine. (d) Chronoamperometric results in 50 mM hydrazine at -0.15 V for HCSC and YCWC.



(A) Polarization curves of ORR at 1600 rpm on HCSC and YCWC. (B) Comparison of current density of HOR at various potentials on HCSC and YCWC in 32 mM hydrazine.

Conclusions

- Novel carbon nanomaterials that can electrocatalyze various reactions were synthesized using two strategies:

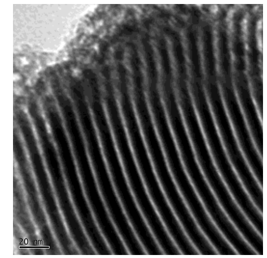
  1) core-shell nanostructuring, followed by carbonization and etching and

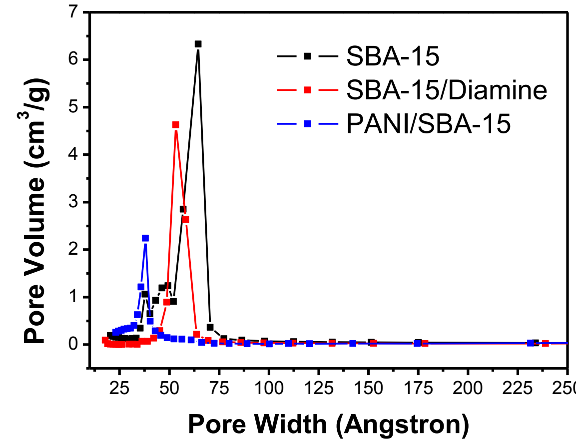
  2) nanocasting using mesoporous silicas

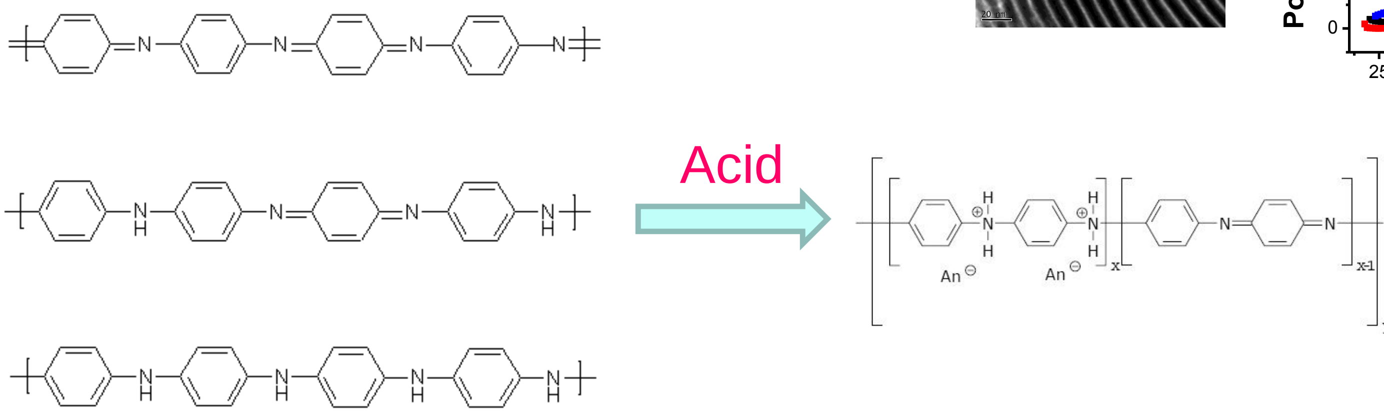
- The materials electrocatalytic activities are quite impressive compared with conventional catalysts such as Pt/C.

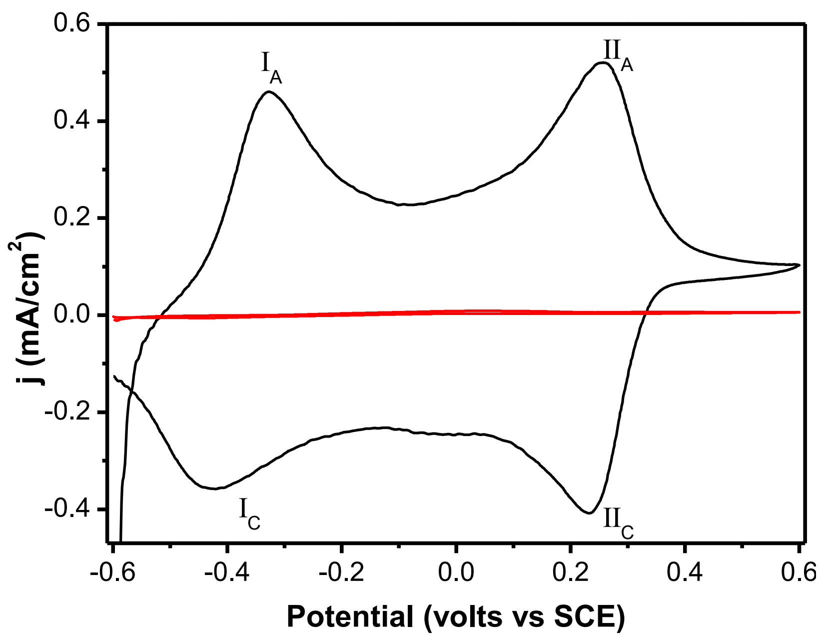
- The materials are composed of earth-abundant elements or do not contain noble metals.

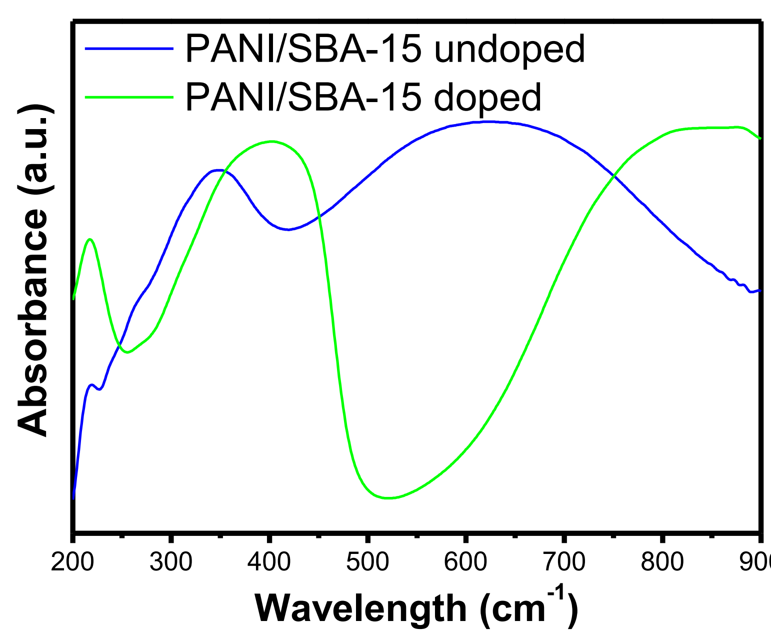
Characterizations











Acknowledgements

Asefa Group Members (Past and Present):

Dr. Krishna Sharma
Dr. Cole Duncan
Youwei Xie
Dr. Yan-Li Shi
Amy Otuonye
Dr. Yanfei Wang
Stephanie Flitsch
Dr. Zhimin Tao
Sean Quinlivan
Ridhima Obrai
Stephanie Flitsch
Mukund Patel
Chao Zhang
Nicholas Lavrov
Dr. Xiaoxin Zou
Katherine Koh

Robert Buckley
Rajiyalakshmi Vathyam
Johanna Weisebauer
Abhishek Anan
Richard Mishler
Dr. Ankush Biradar
Semonti Sinharoy
Dr. Randy Rarig
Elizabeth Blair
Peter Lobaccaro
David Brown
Cassidy Heneman
Natenapa Simpkins
Nicholas Phillips
Dr. Anandarup Goswami
Dr. Eun Woo Shi

Stephanie Hayes
Dr. Jafar Al-Sharab
Dhara Patel
Yesha Kathrani
Nicholas Pasquale
Dr. Sayantani Das
Gang Wang
Tobias Abel
Rafael da Silva
Elisabeth Wondimu
Dr. Saquib Ahmed
Archana Biradar
Rachit Jain
Peter Godar
Bryan Cargill
Dr. Bhaskar Sathe
Dr. Vitor Almeida

Funding:

- NSF - NanoEHS, CBET Program (2011-2015)
- NSF Grant, DMR-0804846 (2007-2014)
- NSF-ACIF Grant (2010); NSF Creativity Award(2011)
- Empire State Development Corporation (2007-2009)
- NSF CAREER Award, CHE-0645348 (2007-2012)
- Rutgers University (2009-), SU (2005-2009)
- EPA, Through CARTI – SU (2007-2009)

Collaborators:

- Prof. Flavio Maran, Padova (Italy)
- Prof. Jing Li (Rutgers)
- Prof. Alan Goldman (Rutgers)
- Prof. Charles Dismukes (Rutgers)
- Prof. Eric Schiff (Syracuse)
- Prof. V. Poleshittewar (TIFR, India)
- Prof. Marina Petrkhina (SUNY –Alb.)
- Prof. Jerry Goodisman (Syracuse)
- Prof. Dunbar Birnie (Rutgers)
- Prof. Jim Dabrowiak (Syracuse)
- Prof. Bob Niederman (Rutgers)
- Prof. Tamara Minko (Rutgers)

Acknowledgements

Asefa Group Members:

Dr. Krishna Sharma
Dr. Cole Duncan
Youwei Xie
Dr. Yan-Li Shi
Amy Otuonye
Dr. Yanfei Wang
Stephanie Flitsch
Dr. Zhimin Tao
Sean Quinlivan
Ridhima Obrai

Robert Buckley
Rajiyalakshmi Vathyam
Johanna Weisebauer
Abhishek Anan
Richard Fuller
Dr. Ankush Biradar
Semonti Sinharoy
Dr. Randy Rarig
Libby Blair
David Brown

Stephanie Hayes
Dhara Patel
Yesha Kathrani
Nicholas Pasquale
Flavian Ptrao
Gang Wang
Tobias Abel
Rafael da Silva
Elisabeth Wondimu

Funding:

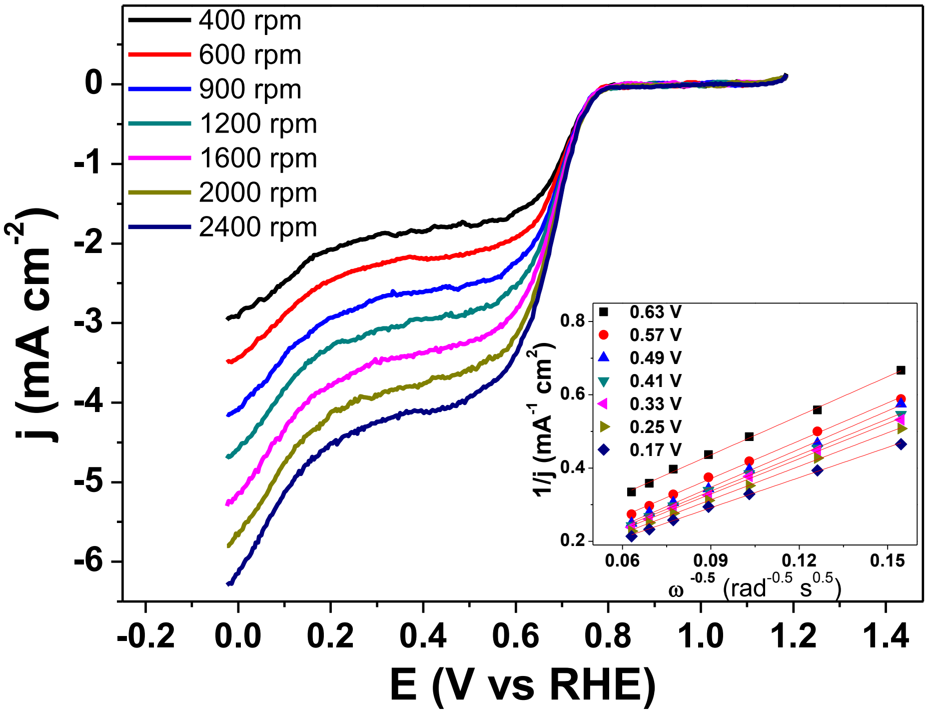
- NSF CAREER Award, CHE-0645348
- NSF Grant, DMR-0804846
- NSF-ACIF Grant
- NSF - NanoEHS, CBET Program

Collaborators

- Prof. Abdul-Kader Souid (Upstate Medical Univ. & Univ. of UAE)
- Prof. Jing Li (Chemistry, Rutgers)
- Prof. Eric Schiff (Physics Department, SU)
- Prof. Marina Petrkhina (Chemistry Department, SUNY – Albany)
- Prof. Jerry Goodisman (Chemistry Department, SU)
- Prof. Evgeny Dikarev (Chemistry, SUNY – Albany)
- Dr. Dunbar Birnie (MSE, Rutgers University)
- Prof. Bob Niederman (Biochemistry, Rutgers)
- Prof. Jim Dabrowiak (Chemistry Department, SU)

Electrocatalysis Results in ORR

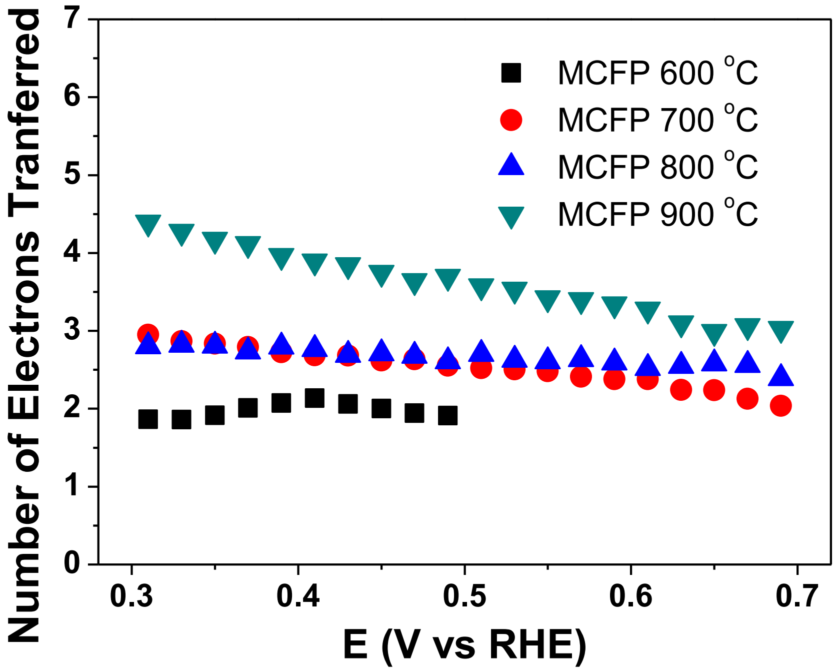
Rotating Disk Electrode (RDE) Based Studies



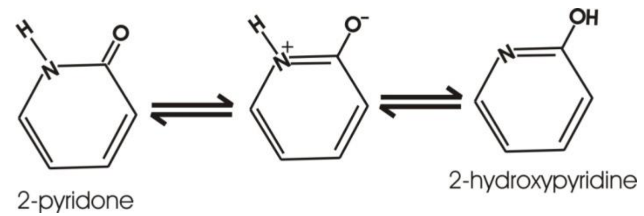
Koutecky–Levich Plot

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$

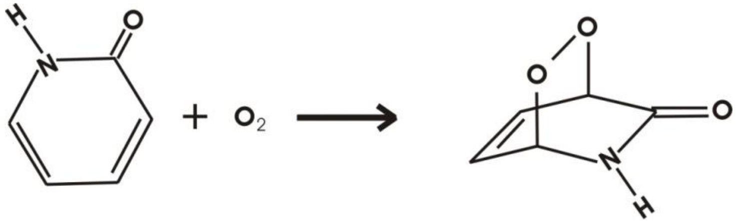
$$B = 0.62nFC_o(D_o)^{2/3}v^{-1/6}$$



Silva, Voiry, Chhowalla, Asefa, *J. Am. Chem. Soc.* **2013**, *24*, 1878.



Tautomerization between 2-pyridone and 2-hydroxypyridine.



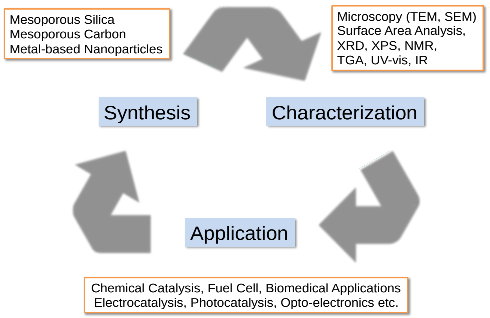
Representation of the addition reaction between molecular oxygen and a pyridone molecule, which lead to the of stable adduct. This process is easily verified when singlet oxygen is used.[1]

1. Matsumoto, M.; Yamada, M.; Watanabe, N. *Chem. Commun.* **2005**, 483.

RUTGERS

Asefa Nanomaterials Research Group

Department of Chemistry & Chemical Biology
Department of Chemical & Biochemical Engineering

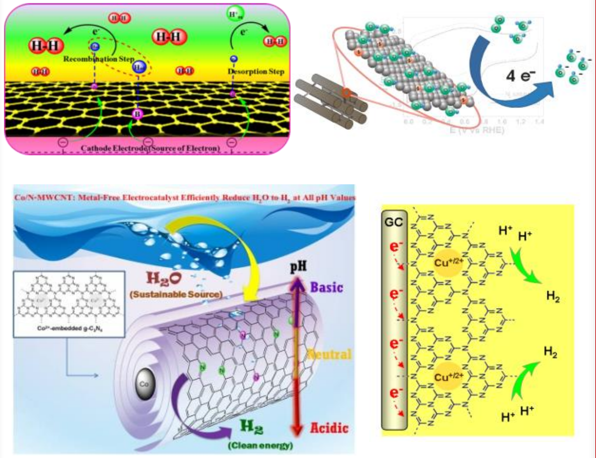


Prof. Tewodros (Teddy) Asefa
Tel.: (848) 445-2970; E-mail: tasefa@rci.rutgers.edu

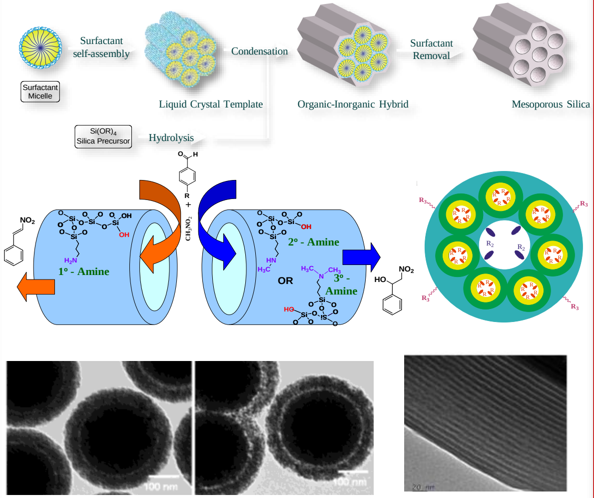
Development of Novel Multifunctional Nanomaterials, Investigation of their Properties, and Demonstration of their Potential Applications:

- Multifunctional nanocatalysts and heterogeneous nanocatalysis and photocatalysis
- Carbon nanomaterials for electrocatalysis, fuel cells, and solar-energy conversions
- Carbon nanomaterials energy storage
- Nanoporous catalysts, biocatalysts, and biotransformations
- Photovoltaic materials
- Multifunctional nanomedicines for targeted drug delivery and cancer treatment
- Nanostructured sensors and biosensors
- Nanoceramics and low-k nanomaterials
- New synthetic methods to novel nanomaterials
- Nanoporous materials for environmental remediation
- Development of novel mesoporous materials and heteroatom-doped nanoporous carbons

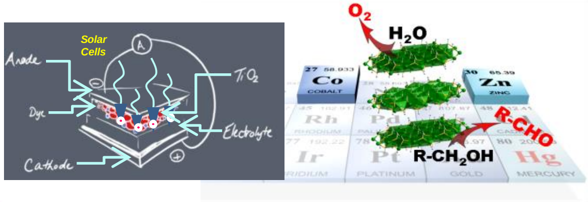
Carbon-based Nanomaterials for Renewable Energy Applications:



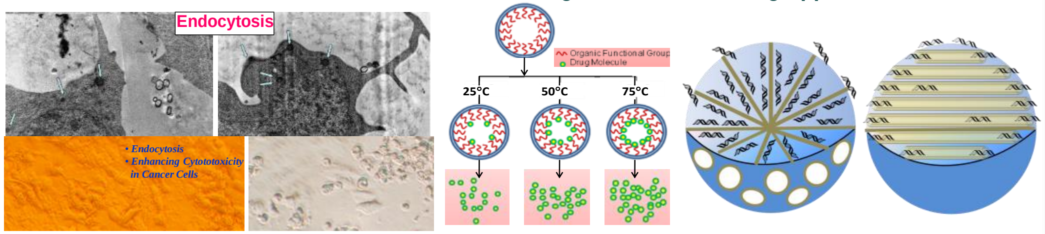
Silica-based Nanomaterials and their Applications:



Photovoltaics and their Applications

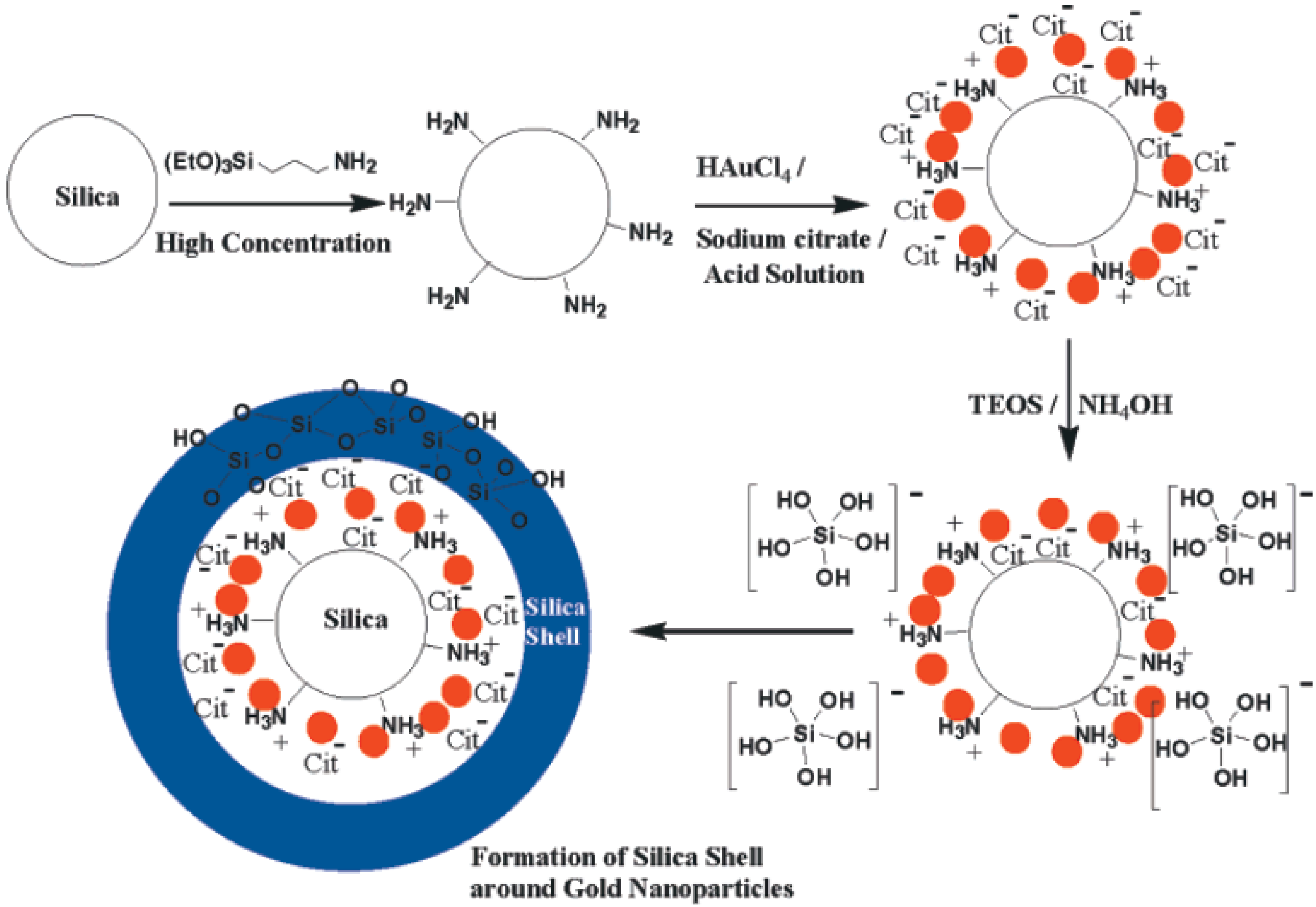


Nanomedicine and Nanomaterials for Biological and Biosensing Applications:

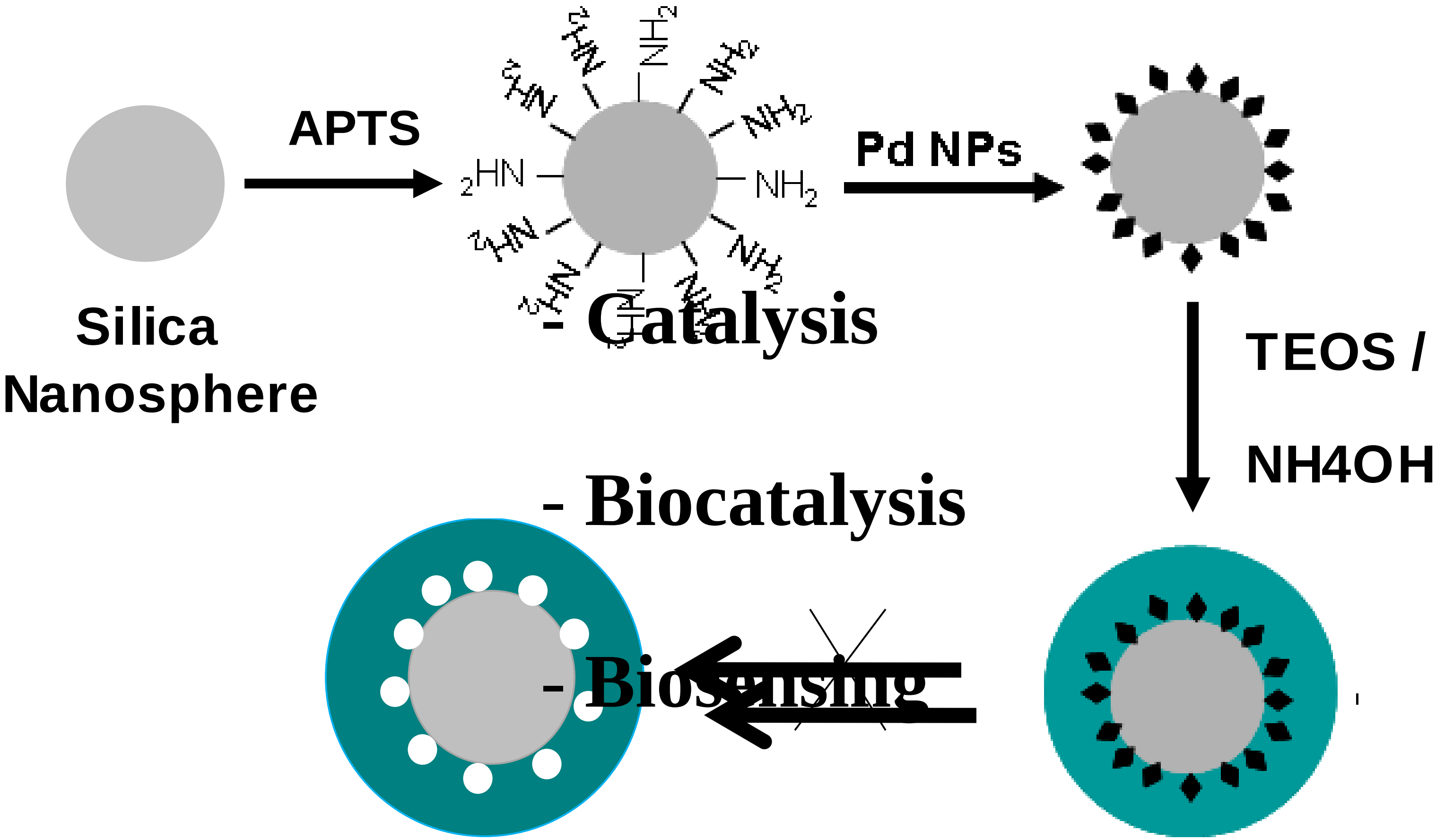


IAMDN

Mechanism of Formation of Core-Shell-Shell Nanoparticles



Core-Shell-Shell Nanoparticles and Controlled Etching of Outer Shells



- Catalysis

- Biocatalysis

- Biosensing