Covalent Functionalization of Carbon NanoTubes (CNTs) and their Application to Catalytic Water Splitting (Energy Storage)

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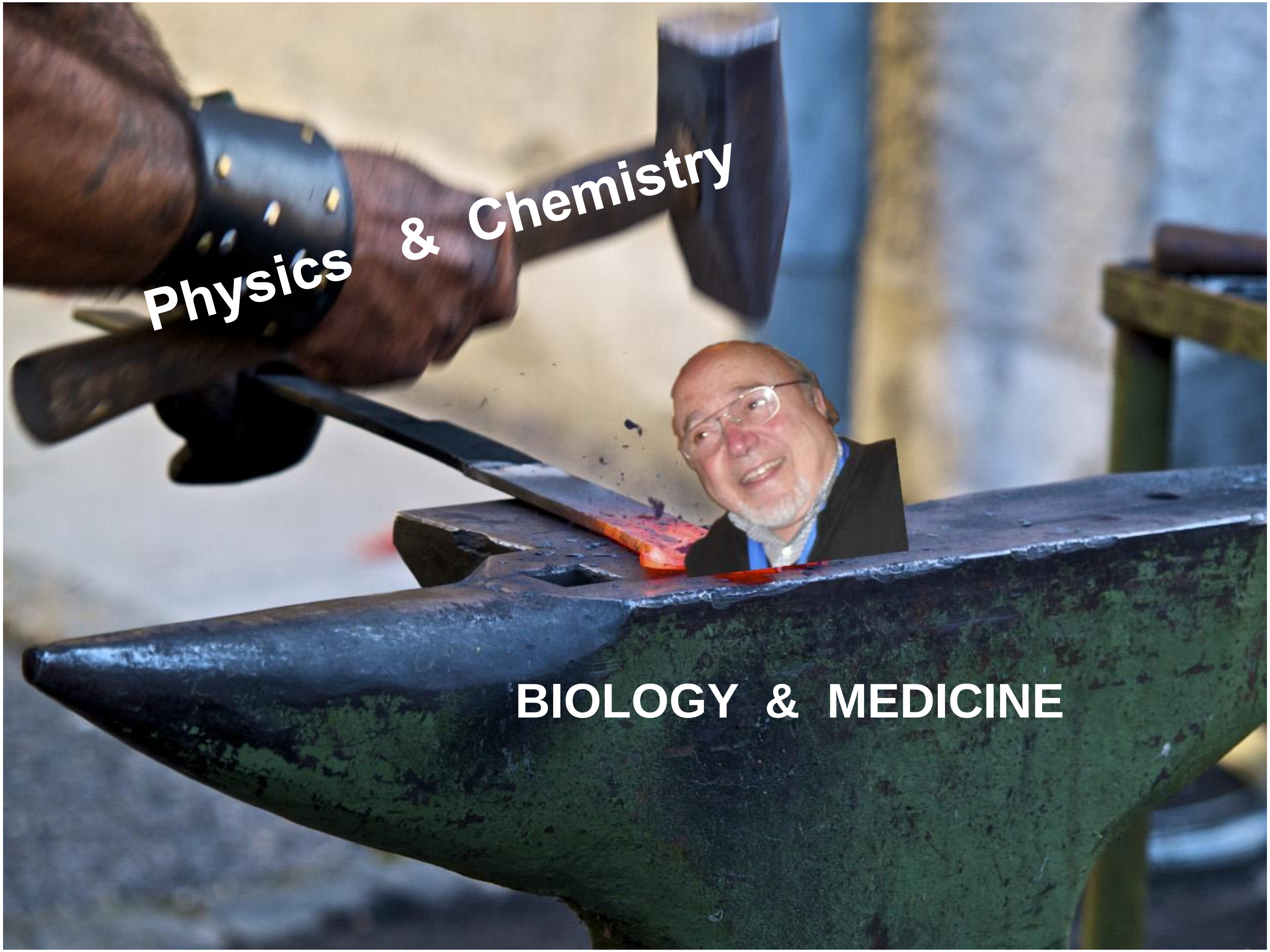
I HAVE BEEN HAPPY BUT IN A TOUGH SPOT AL OF MY CAREER (~LIFE!)



The artwork is by Mauro Melli, 4th year grad student at SISSA in Trieste (IT)

Let me start giving credit where credit is due

- This work has been the PhD thesis work of a Sissa student (**Francesca Maria Toma**) who, when she came to Trieste looking for a place where to do her PhD, told me that what she was looking for in leaving her University (Padova) was intellectual independence.
- I accepted her on the spot without even asking any reference about her.
- One of the best decisions that I have ever taken!

Many thanks to the SENIL group!

Barbara Sanavìo, Biotechnologist

Fouzia Bano, Physicist

Dr.Francesca M. Toma, Chemist

dr. Loredana “the boss” Casalis

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Maurizio Prato

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To other members of the SENIL Lab

Dr. F. Bano, Dr. D. Scaini, Dr. P. Parisse, , Dr. M. Castronovo, Mr. M. Melli

Acknowledgements

Prato's Group: Italian universities are overcrowded!

Acknowledgements

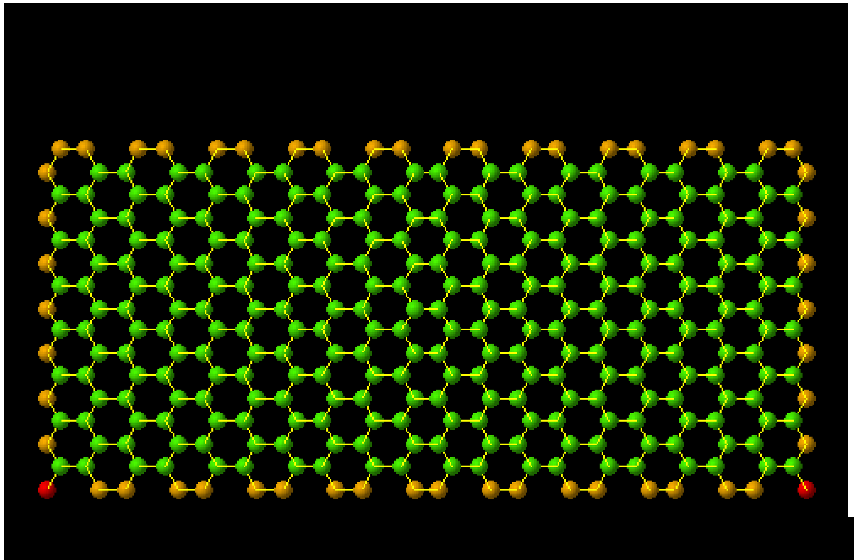
Dr. Mauro Carraro

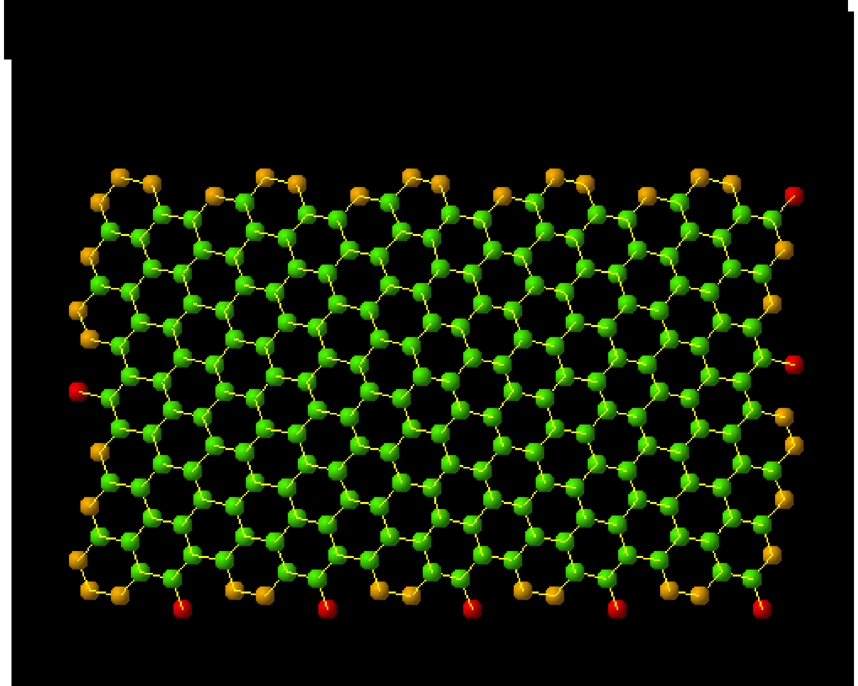
Dr. Marcella Bonchio

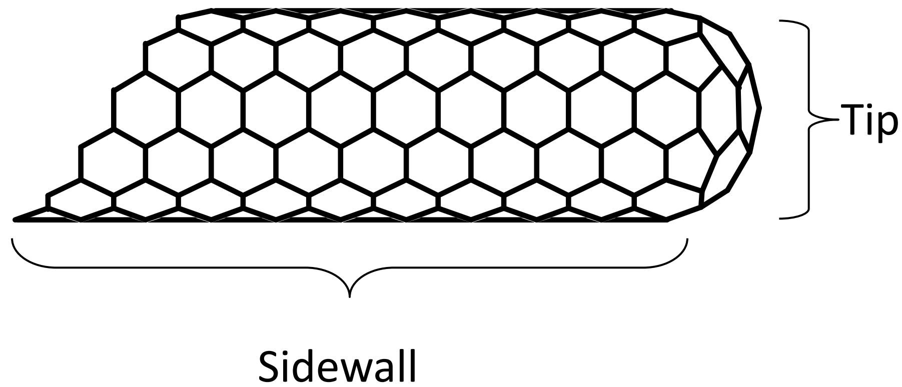
Dr. Andrea Sartorel

The Università di Padova Team

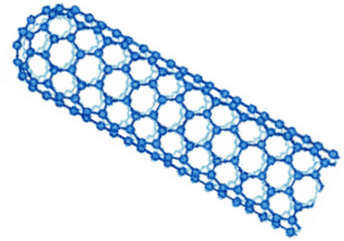
Introduction: CNTs



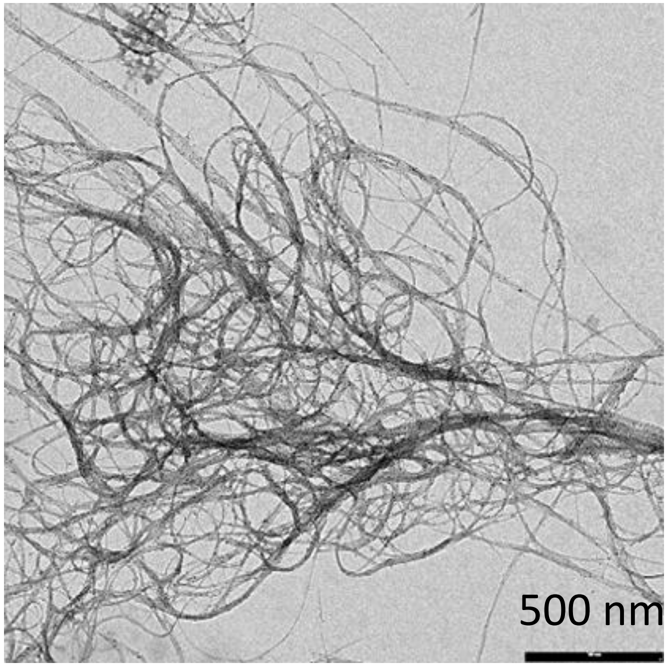




Introduction: CNTs



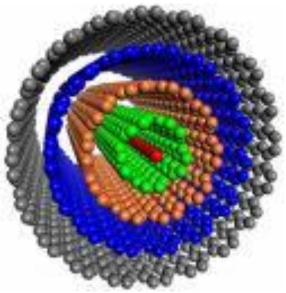
SWCNTs

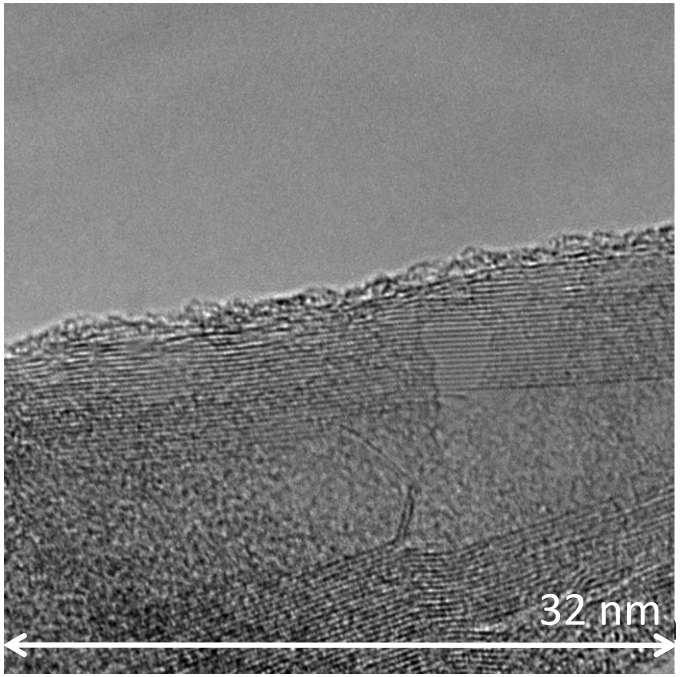


Cylinders of graphene rolled into tubes (diameter 0.7-1.2 nm)

TEM

MWCNTs

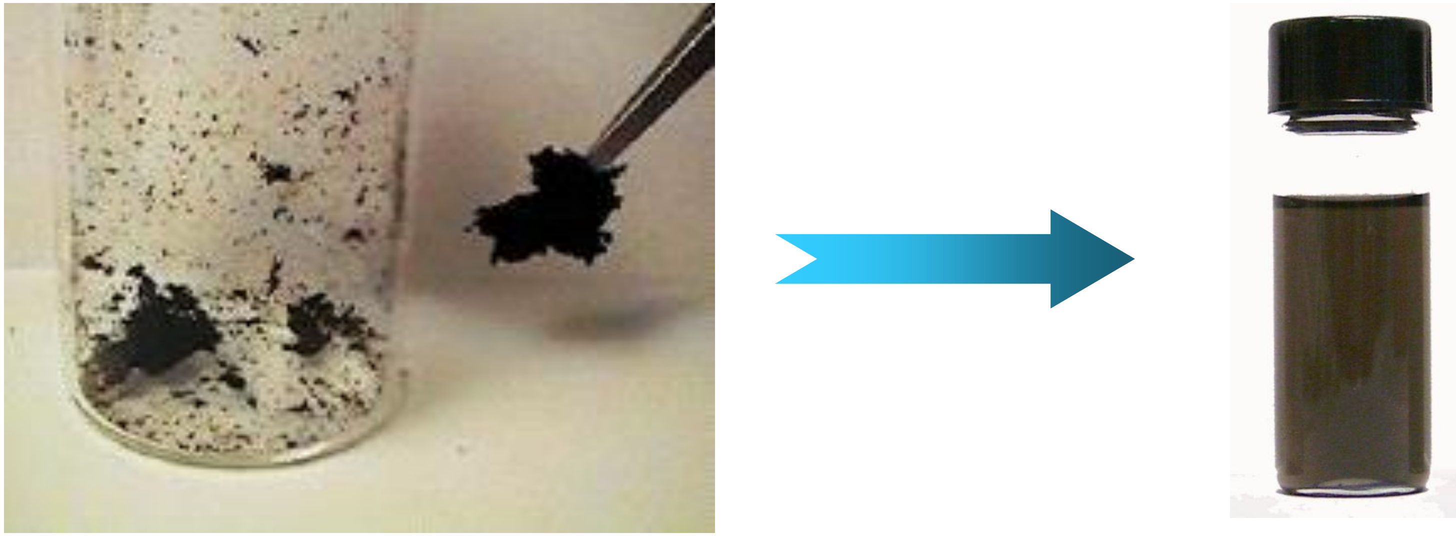




Concentric arrangement of numerous cylinders (diameter up to 100 nm)

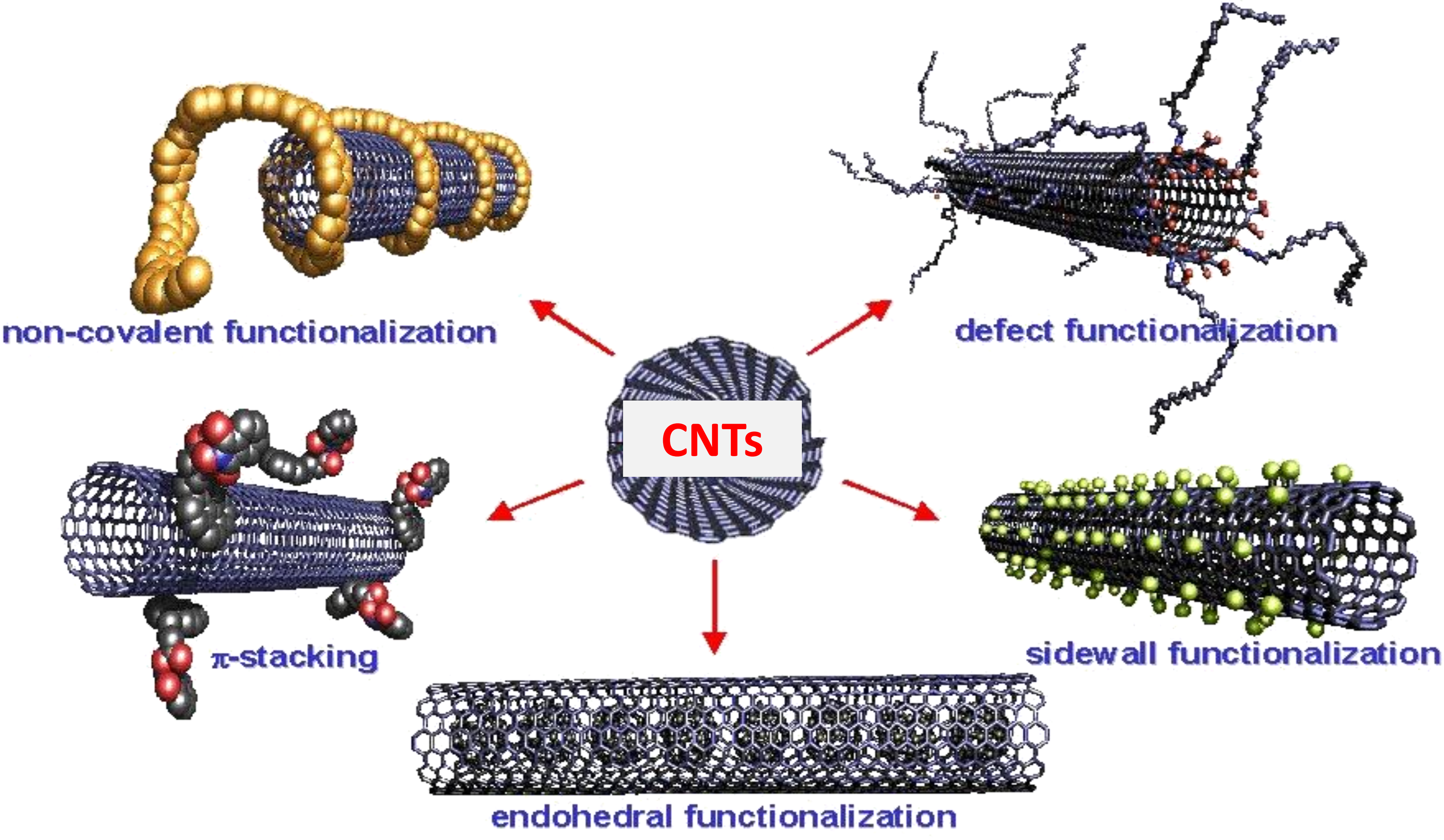
TEM

Why do we functionalize CNTs?



- To allow their easier manipulation
- To allow the investigation of CNT properties in solution and use them in syntesizing nanostructures that are meant to work in solution
- To render CNT biocompatible and to integrate them into living systems/

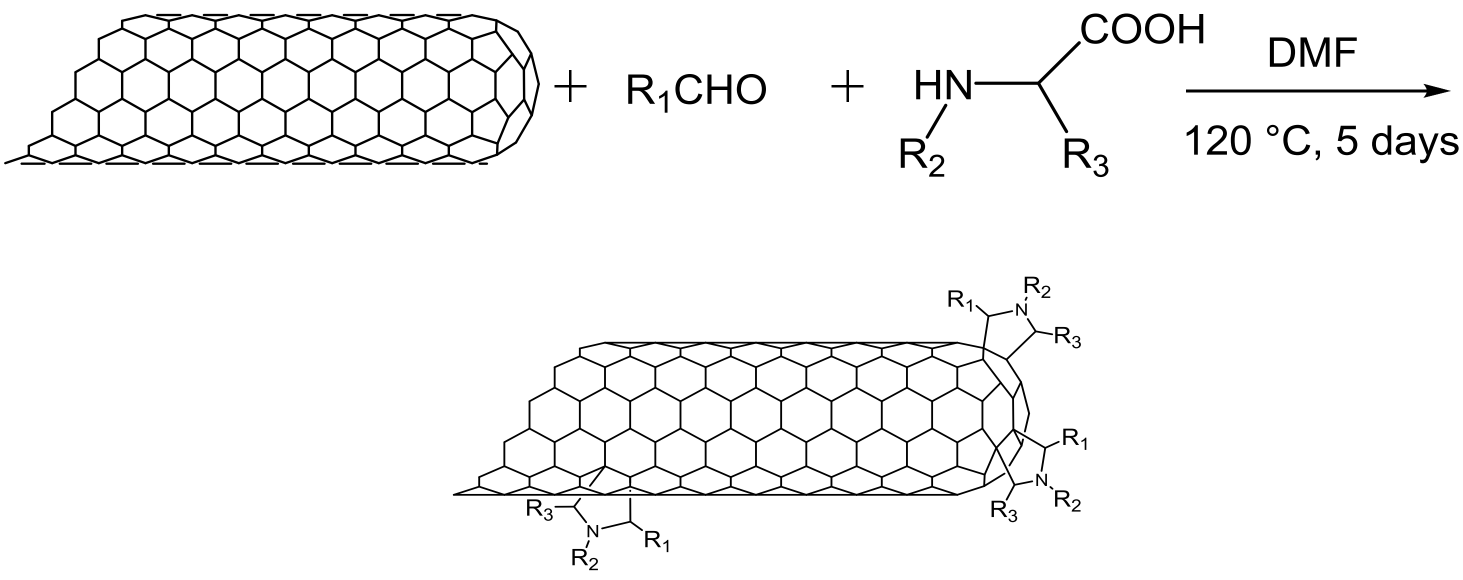
CNT functionalizations



Hirsch *Angew. Ch. Int. Ed.* **2002**, *41*, 1853-1859.

1,3-dipolar cycloaddition reaction (the "Prato reaction")

- **As first step, we use the 1,3-dipolar cycloaddition**
- **We use MWCNTs 20-30 nm**



Georgakilas., *Journal of American Chemical Society*, **2002,** *124* (5), 760-761.

Properties and applications of CNTs

Unusual mechanical, thermal and electrical properties give CNTs promising applications

Electrical applications: (1 Example) **Fast field effect transistors**: 80 GHz is the current record! = the night sky photon of 4 x 1/cm i.e. far IR !

Biological applications (2 examples): **drug delivery**, contrast agents, biosensors, last but not least **substrates for cell growth**

ELECTRICAL PROPERTIES

Progress in Carbon Nanotube Electronics and Photonics

Phaedon Avouris and Richard Martel (IBM)

Abstract

Carbon nanotubes are prime candidates for FETs fabrication because of their exceptionally high carrier mobility, low capacitance, and strong optical response (direct bandgap). Although these properties compare very favorably with those of crystalline silicon, ***several issues related to their synthesis, processing, and assembly have challenged efforts for making electronic and photonic devices.*** Tremendous progress, nevertheless, has been achieved over the years,..................
Fast FETs , Photodetectors and LEDs..

MRS BULLETIN • VOLUME 35 • APRIL 2010 • www.mrs.org/bulletin

APPLIED PHYSICS LETTERS 94, 243505 2009

80 GHz field-effect transistors produced using high purity semiconducting single-walled carbon nanotubes

L. Nougaret,1 H. Happy,1,a G. Dambrine,1 V. Derycke,2 J. -P. Bourgoin,2 A. A. Green,3 and M. C. Hersam3
A CEA (F) CNRS (F) Northwestern U.(USA).collaboration.

BIOLOGICAL APPLICATIONS CNT
toxicity

- Toxicological properties of nanomaterials are not negligible: a lot of studies are still necessary to assess chronic and long term toxicity
- Purity, solubility and length of the material determine the degree of toxicity
- **Pure, soluble (i.e. functionalized) and short CNTs show negligible toxicity**

Sayes *Toxicology Letters* **2006**, *161*, 135-142;
Poland *Nature Nanotechnology* **2008**, *3*, 423-428.

CNT BIOLOGICAL APPLICATIONS: SIRNA DELIVERY

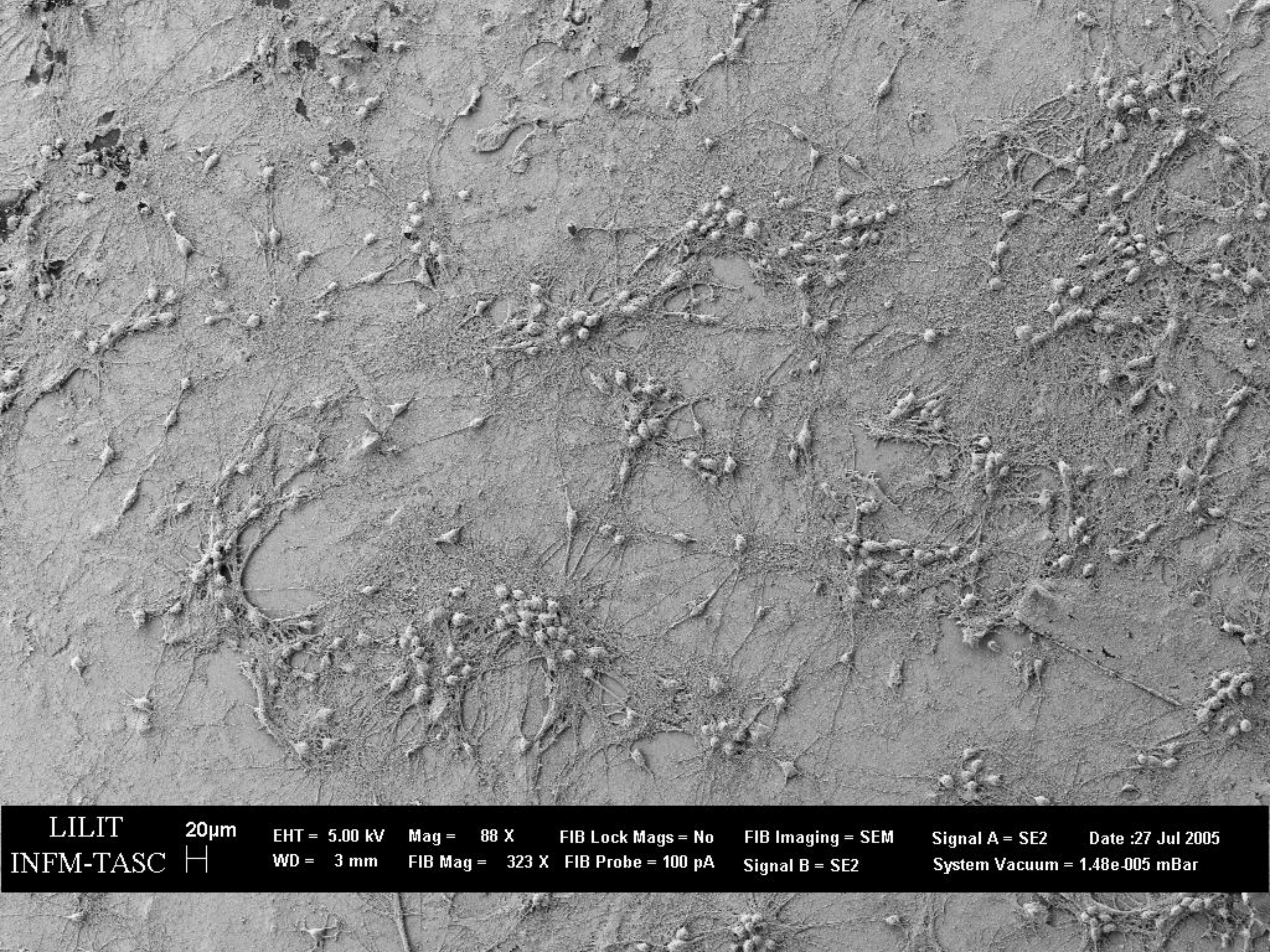
(NOT TODAY STORY!)

In collaboration with Dr. K. Al-Jamal and Prof. K. Kostarelos, Nanomedicine Lab-Centre for Drug Delivery Research, London; and Dr. Alberto Bianco, CNRS, Institut de Biologie Moléculaire et Cellulaire, Immunologie et Chimie Thérapeutiques, Strasbourg, France

CNT BIOLOGICAL APPLICATIONS: NEURONAL CELL SUBSTRATES

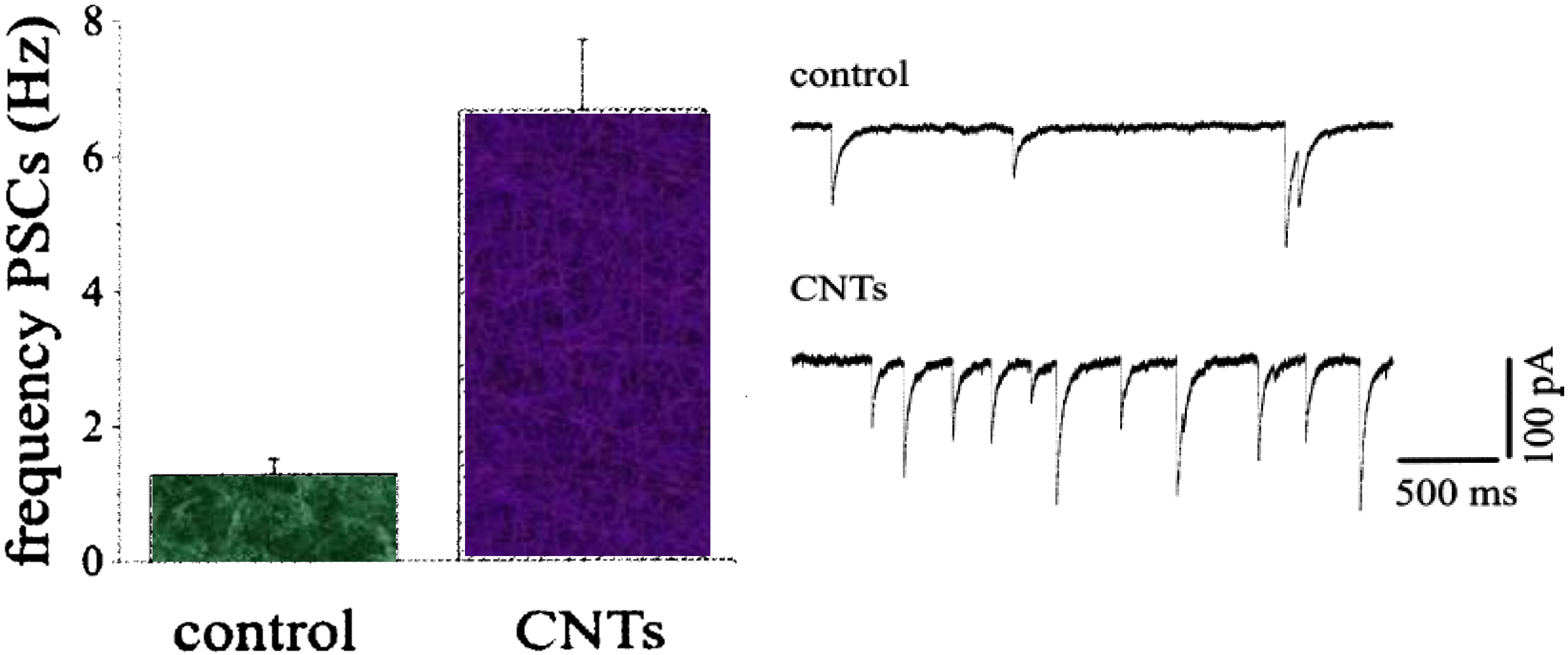
ALSO NOT TODAY' STORY!

In collaboration with Giada Cellot and Prof Laura Ballerini, neurophysiologists from the Life Science Department, B.R.A.I.N., University of Trieste.


LILIT
INFM-TASC
20µm
EHT = 5.00 kV
WD = 3 mm
Mag = 88 X
FIB Mag = 323 X
FIB Lock Mags = No
FIB Probe = 100 pA
FIB Imaging = SEM
Signal B = SE2
Signal A = SE2
Date :27 Jul 2005
System Vacuum = 1.48e-005 mBar

CNT substrates for neuronal cultures: background

- Neuronal cells grown on CNT substrates displayed an increase in spontaneous activity (on average a six-fold increase in the frequency of post-synaptic currents with respect to the control

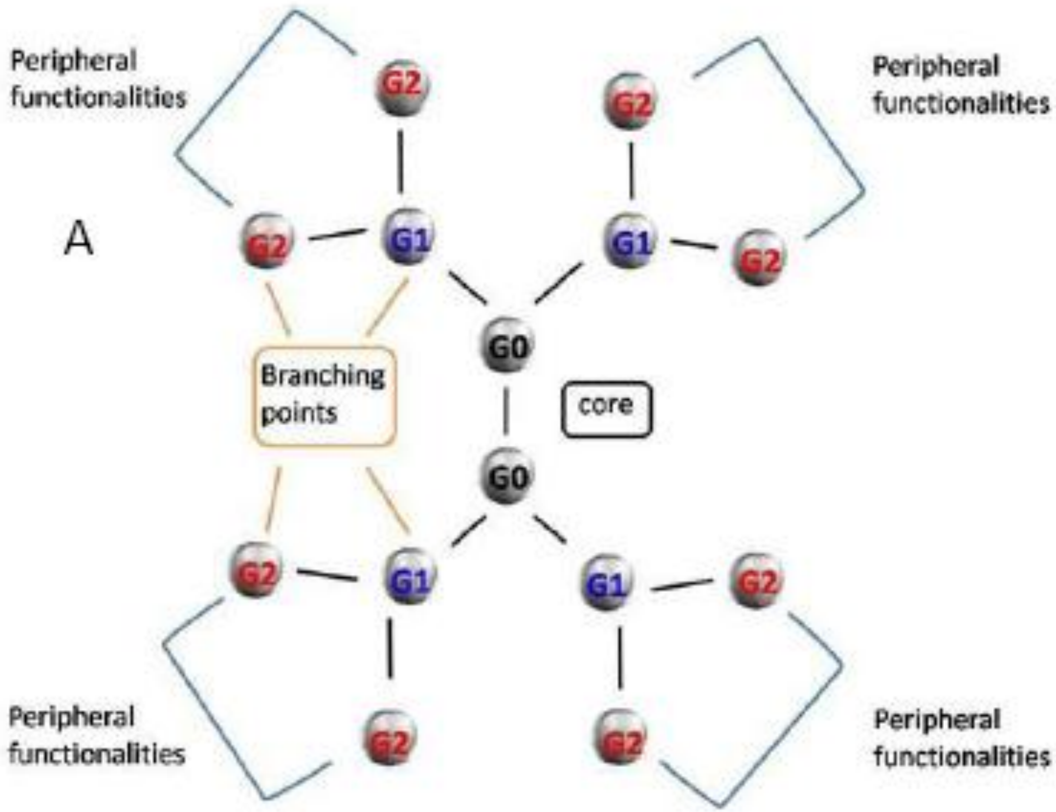


Lovat et al *Nano Letters* **2005**, 5, 1107-1110.

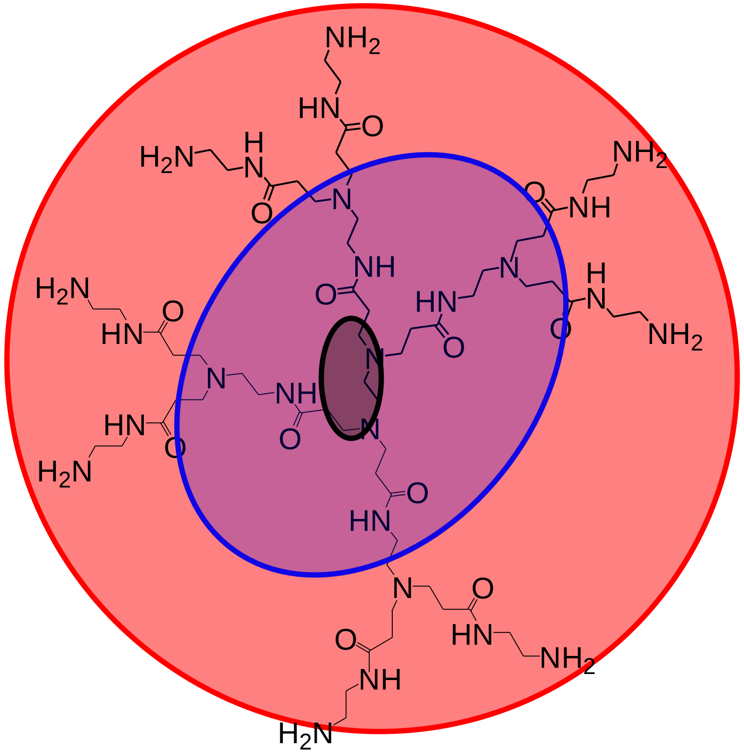
TODAY's STORY is about ENERGY!

Combining CNTs with Polymers: Dendrimer/CNT Hybrid

- A dendrimer is a synthetic branched oligomer with tunable nanoscale size



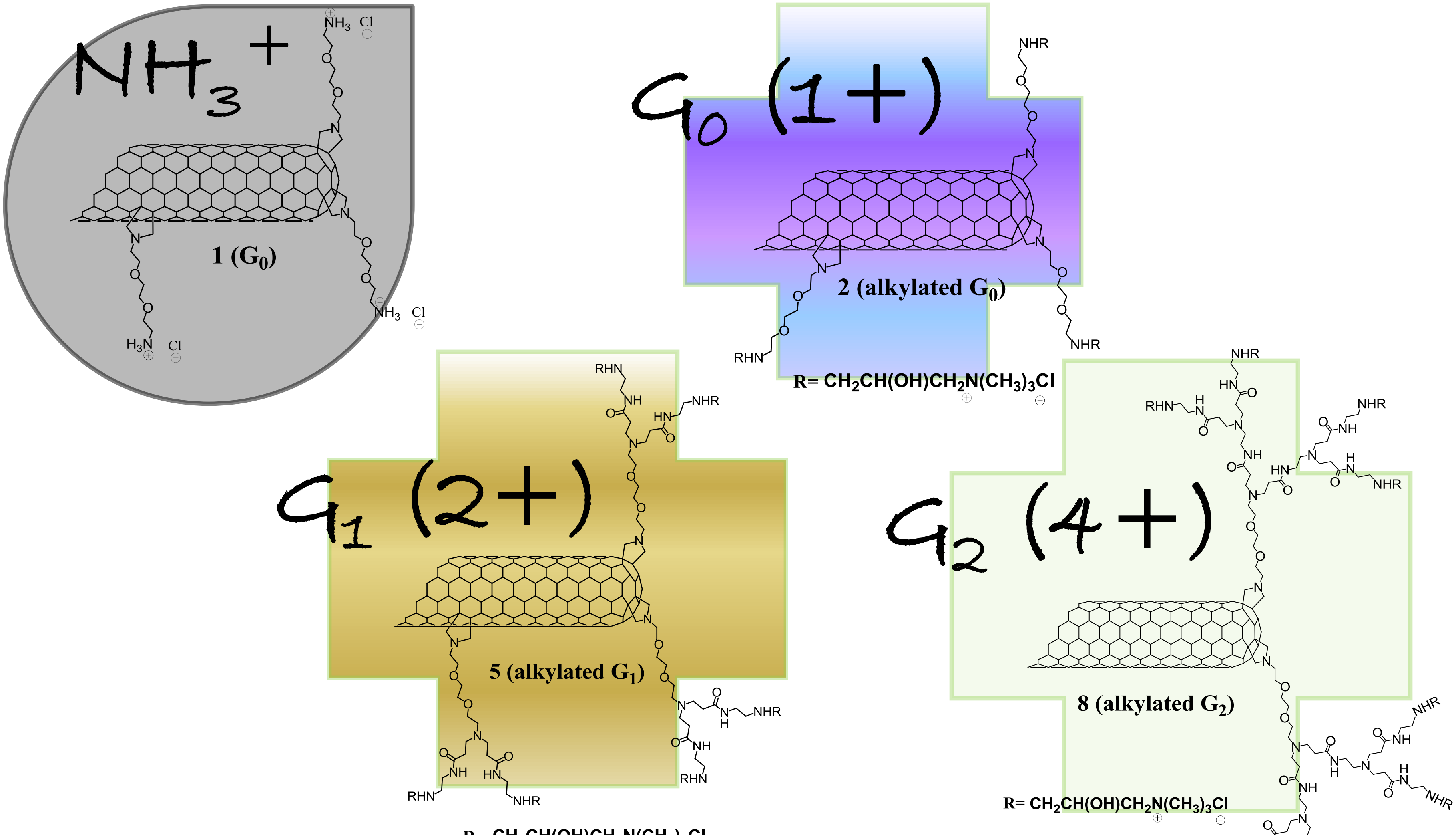
Dendrimers:



the PAMAM example

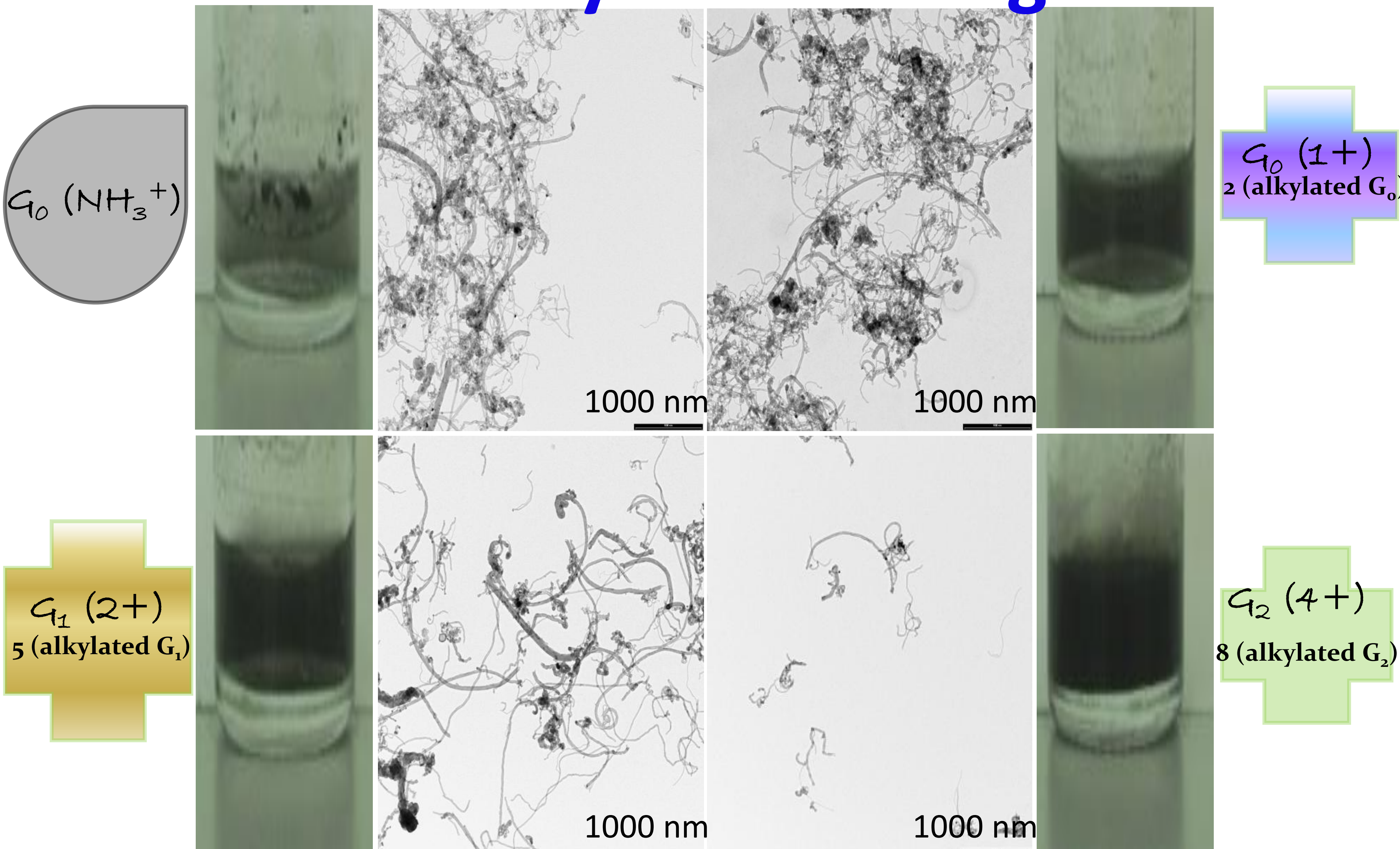
Tomalia et al. *Polymer J.*, **1985**, *17*, 117-132.

Dendron functionalized MWCNTs: summary



Herrero, Toma , et al., *J. Am. Chem. Soc.*, 2009, *131* (28), 9843-9848.

Solubility + TEM images



Herrero, Toma , et al., *J. Am. Chem. Soc.*, **2009,** *131 (28)*, 9843-9848.

ENERGY APPLICATIONS: CNTs FOR CATALYTIC WATER SPLITTING

In collaboration with the groups of Dr. M. Bonchio (University of Padova), Prof. F. Paolucci (University of Bologna) and Prof. M. Prato (University of Trieste).

Energy thirst and artificial photosynthesis

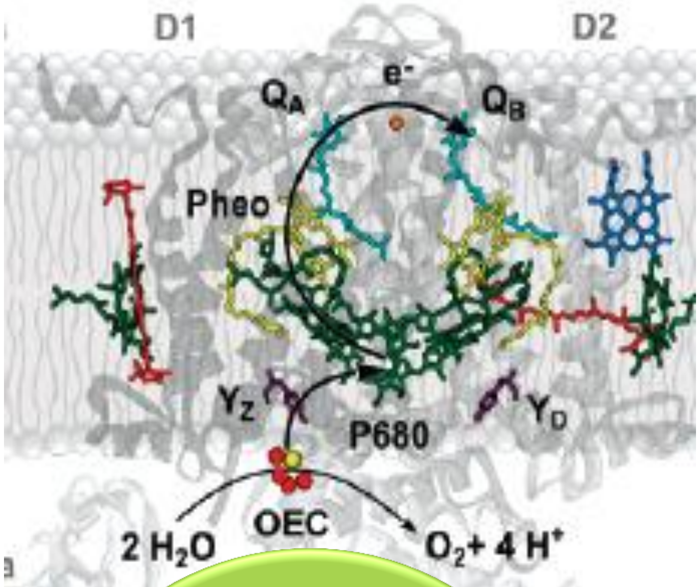
We need to reduce pollution and to find out a solution to the universal thirst for energy.

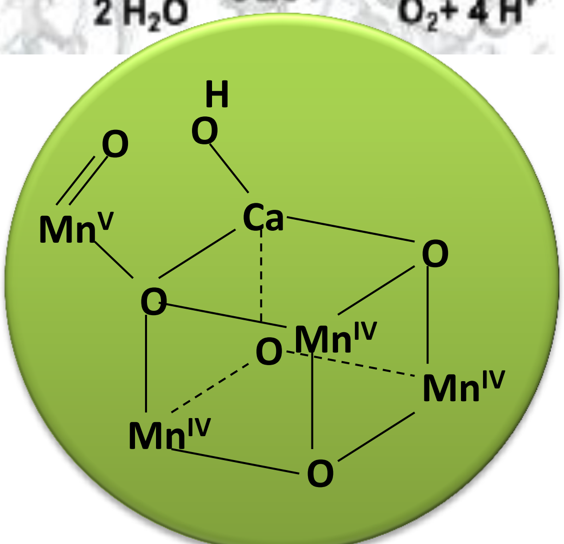
- Human energy current usage is ~ 24 TW
- Sun is giving us 120,000 TW
- Attractive and clean exploitation of solar energy (2/100 of 1% is not a major perturbation !)
- Mimicking Nature!

Natural Photosynthesis

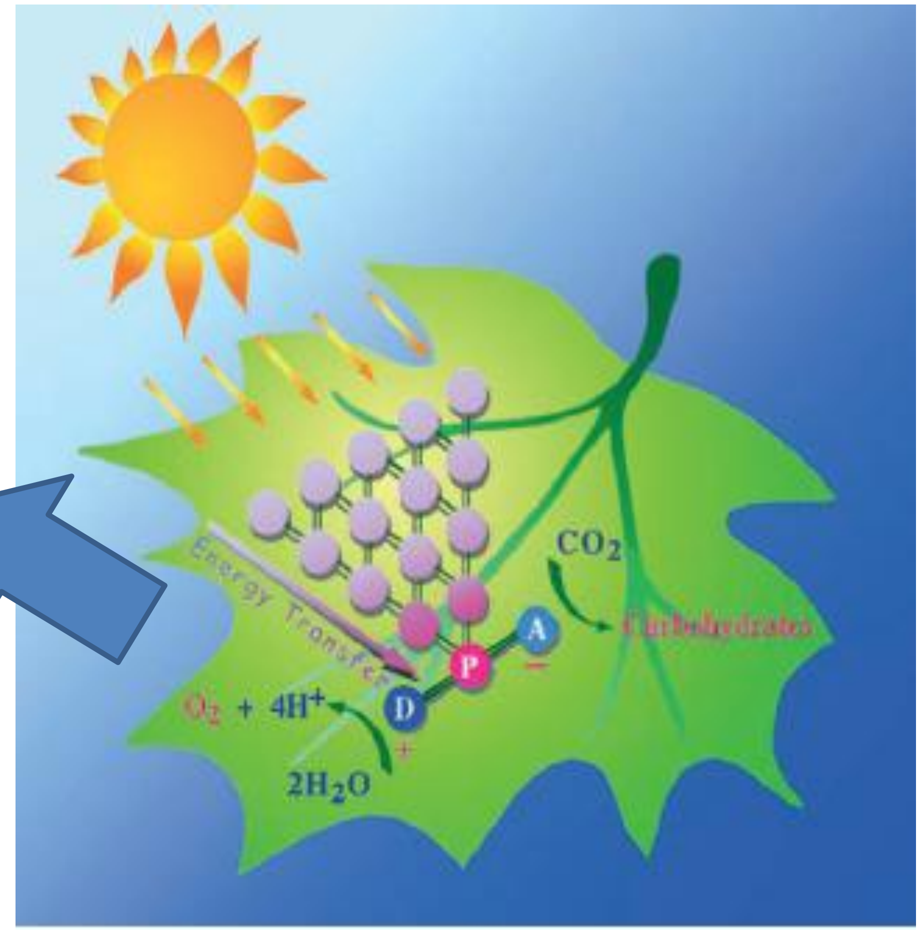
$$6\ H_2O + 6\ CO_2 + 48\ h\nu \longrightarrow C_6H_{12}O_6 + O_2$$

PS II





Oxygen Evolving Center (**OEC**)



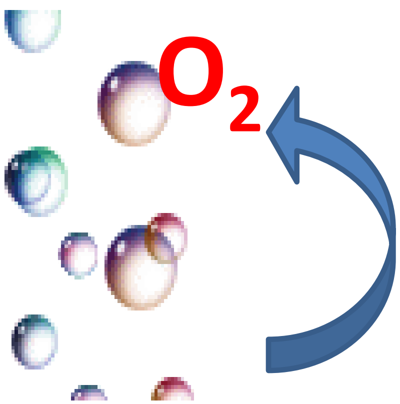
A very simplified sketch of key processes in natural photosynthesis

N. Armaroli, V. Balzani, *Angew. Chem. Int. Ed.* **2007**, *46*, 52.

What we can do

- Immediate exploitation of fully renewable and sustainable sun light resource.
- Energy storage: H_2 economy
  (a caveat: a lot of the calculations on H2 storage in the literature are wrong)
- Energy release: fuel cells

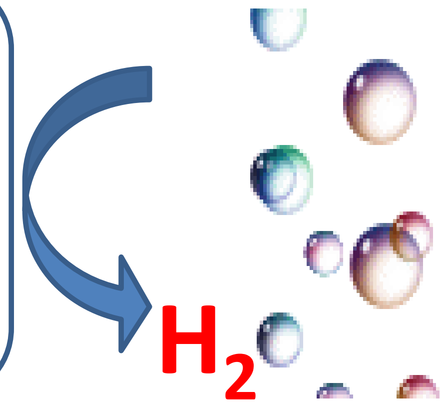
<u>Splitting</u> of water into **Hydrogen** and **Oxygen** is a high-energy process



$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

$$4H^+ + 4e^- \rightleftharpoons 2H_2$$

$$2H_2O \longrightarrow 2H_2 + O_2$$



- Thermal splitting of water requires temperatures above 2500°C

-Electrochemical splitting of water is efficient E= –1.23 V

<u>the 2H$_2$O/O$_2$ half reaction is considerably complex</u>

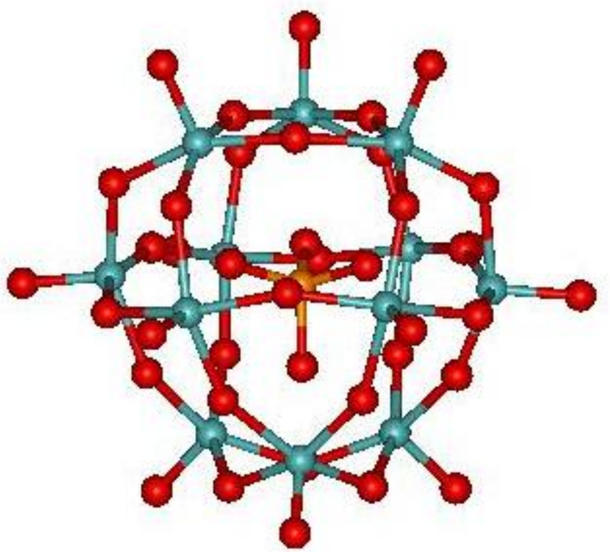
- ✓ **the removal of 4-electrons from 2 H_2O molecules**
- ✓ **the removal of 4 protons**
- ✓ **the formation of a new oxygen-oxygen bond.**

POLYOXOMETALATES (POMs)

anionic aggregates of early transition metals (Mo^{VI}, W^{VI}, V^{V}, etc) and oxygen

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

X = P, Si
M = Mo, W



α–KEGGIN (1934)

$[XM_{12}O_{40}]^{n-}$

STABLE WITH RESPECT TO THERMAL and OXIDATIVE DEGRADATION

TUNABLE SOLUBILITY by COUNTERION METATHESIS

INORGANIC LIGANDS FOR BIO-RELEVANT METALS: Fe,Mn, Ru, etc

Polyoxometalate Chemistry from Topology via Self-Assembly to Applications (Eds.: M. Pope, A. Muller), Kluwer Academic Publishers, Dordrecht, the Netherlands, **2001** . b) D. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105 – 121.

POLYOXOMETALATES (POMs)

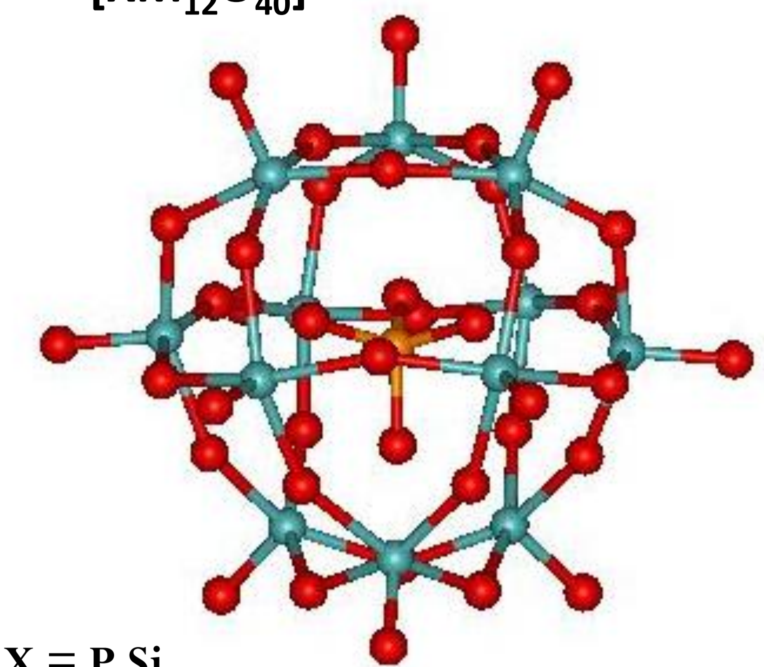
anionic aggregates of early transition metals (Mo^{VI}, W^{VI}, V^{V}, etc) and oxygen

"catalysts for water oxidation are so rare that the discovery of a new family is cause for celebration." **NATURE 2008, 451, 778.**

T. J. Meyer,

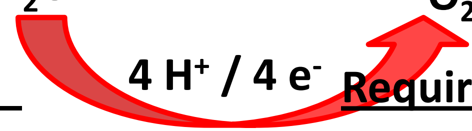
α–KEGGIN (1934)

$[XM_{12}O_{40}]^{n-}$



X = P, Si
M = Mo, W

$2\ H_2O$ → **O_2**

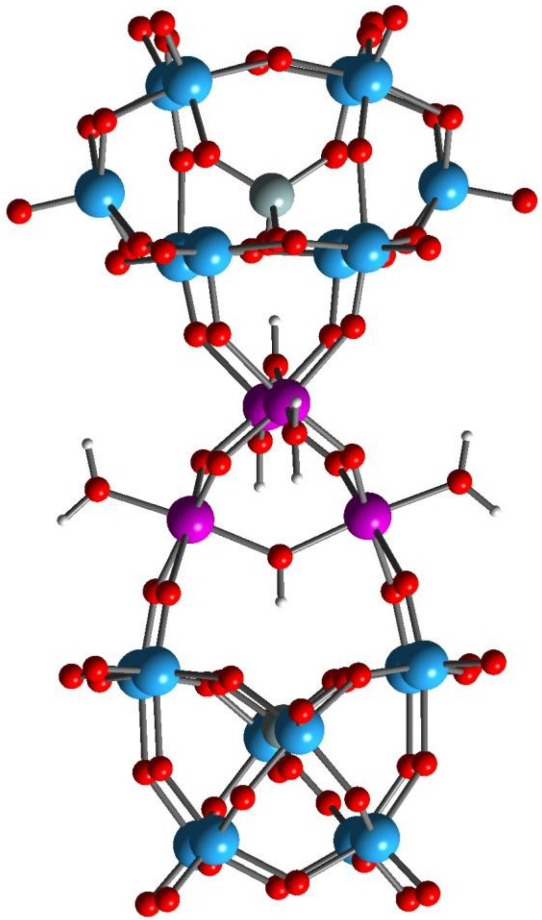


$4\ H^+ / 4\ e^-$

Catalyst's Requirements

- ✓ **Available oxidation states** ***($4\ e^-$ are released)***
- ✓ **Proton transfer ability** ***($4\ H^+$ are released)***
- ✓ ***Mechanism of O-O bond formation***

The synthesis of $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\gamma\text{-}(SiW_{10}O_{36})_2]^{10\text{-}i}$ is carried out in the Bonchio Group

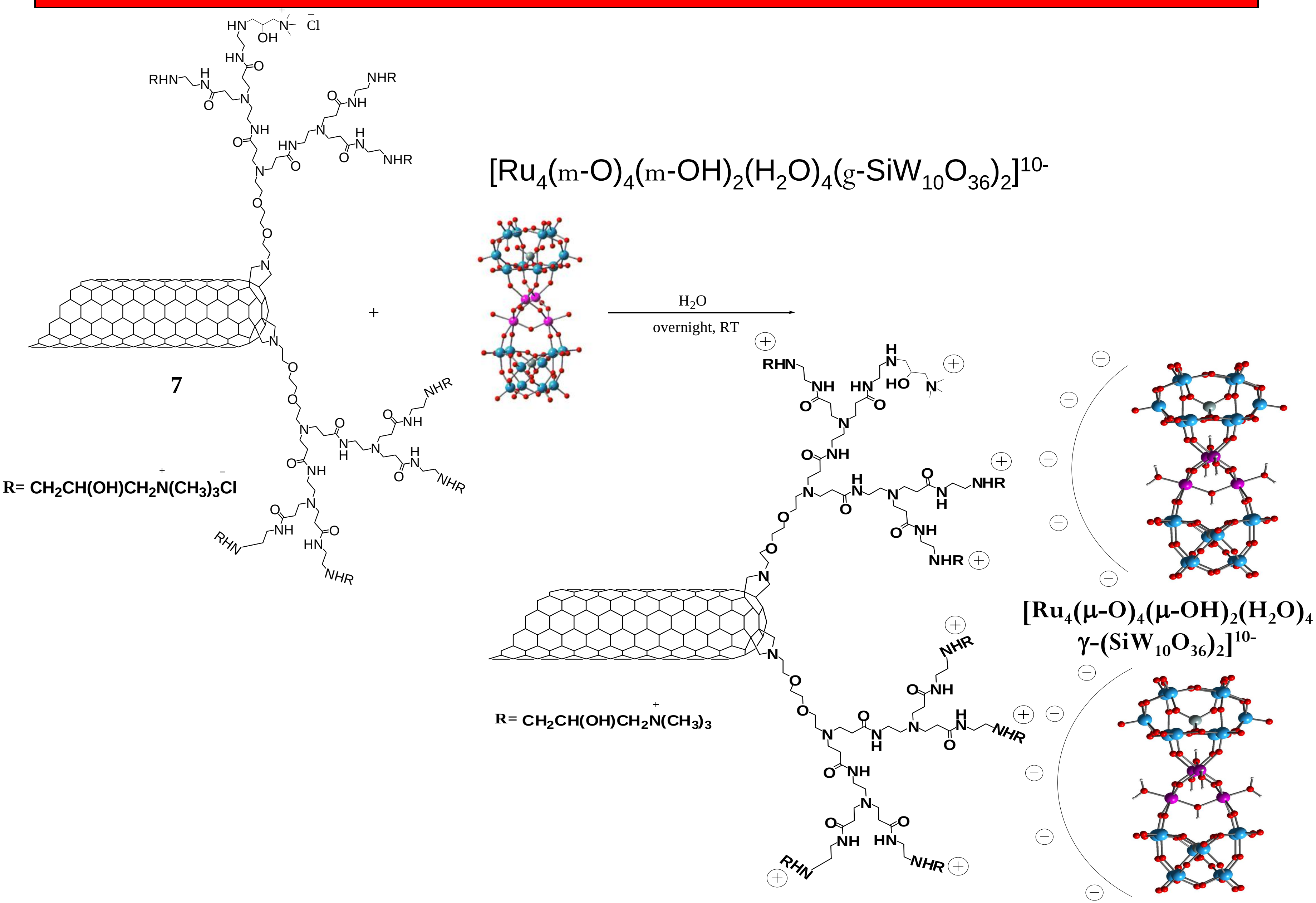


85% yield **Ru_4POM**

A. Sartorel, M. Carraro, G. Scorrano, R. De Zorzi, S. Geremia, N.D. McDaniel, S. Bernhard, M. Bonchio
J. Am. Chem. Soc. **2008**, *130*, 5006. Highlight by Georg Suess-Fink *Angew. Chem. Int. Ed.* **2008**, 47, 5888 – 5890

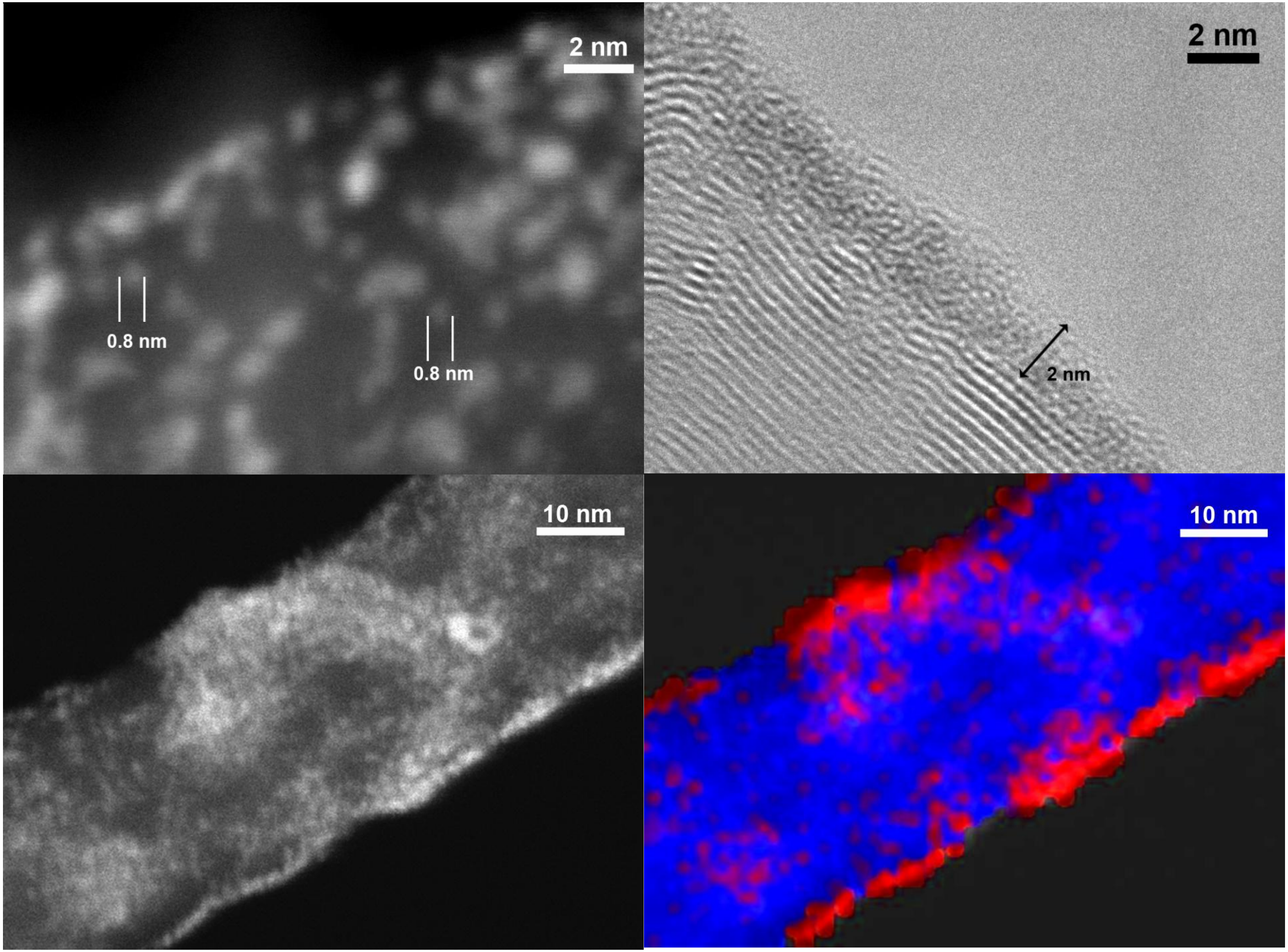
And the assembly of the POMs with the Dendrimer functionalized CNTs is ELECTROSTATIC in nature

POLYOXOMETALATES (POMs) AND CNTs

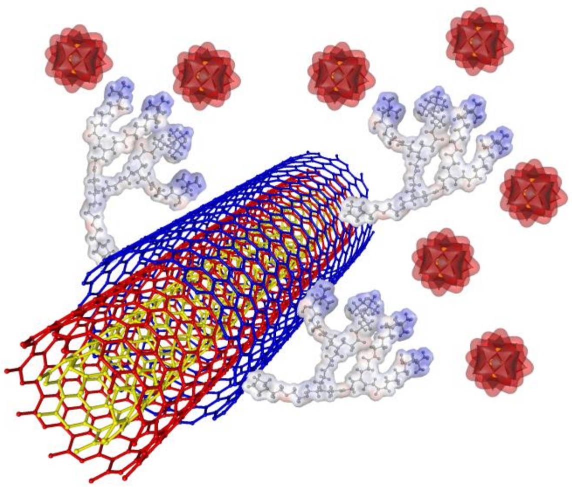


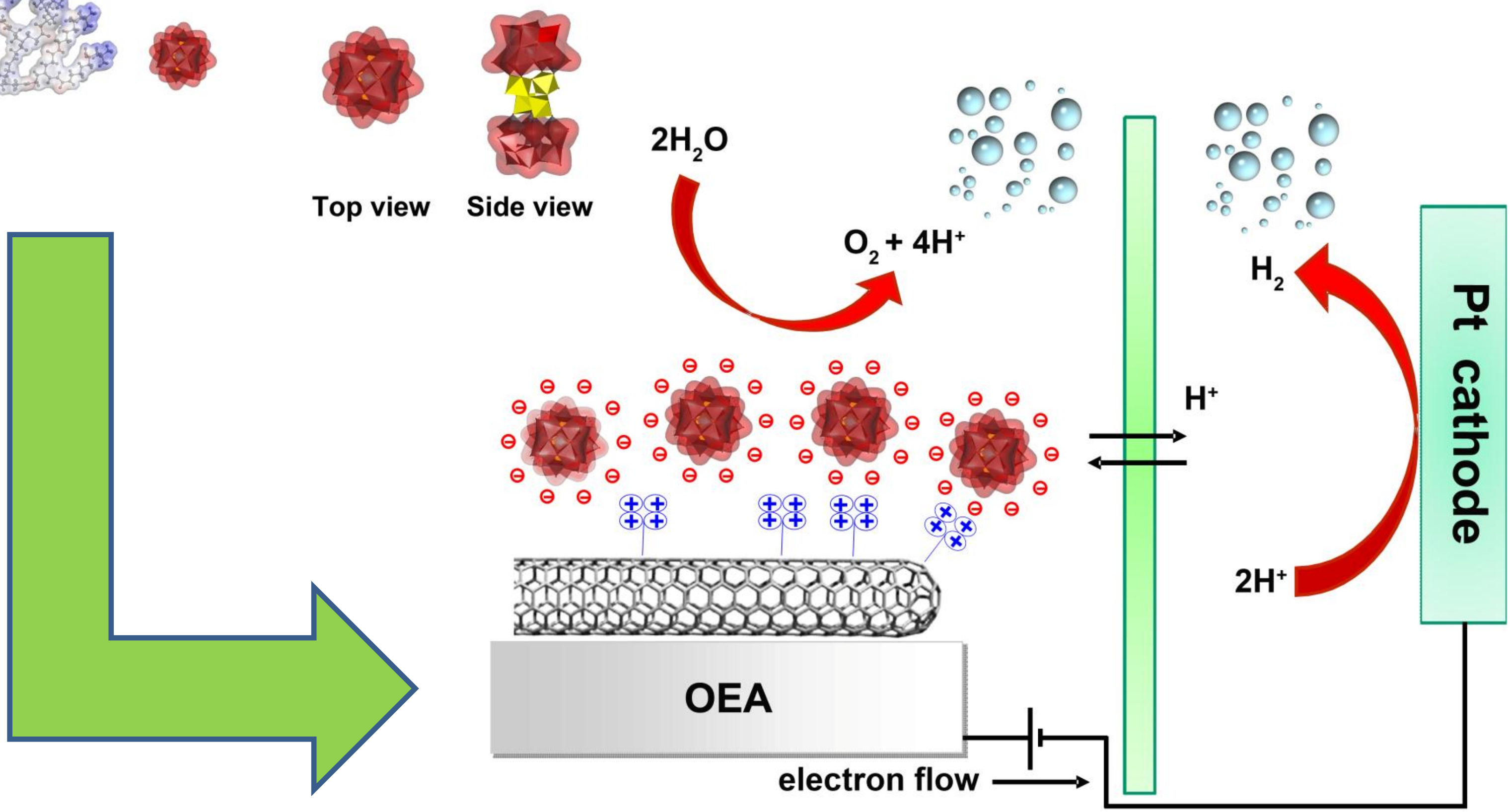
Toma, Sartorel et al *Nat Chem*; accepted

TEM Characterization

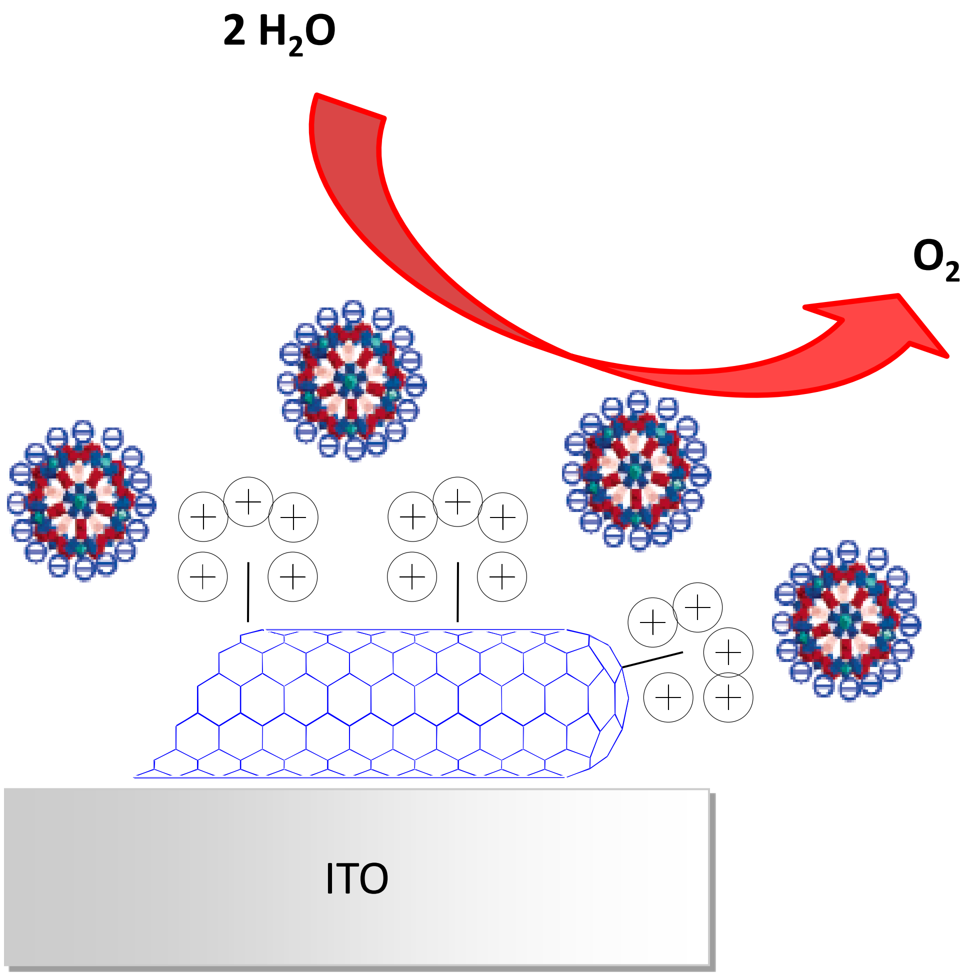


Our goal: From hybrid material to nanostructured electrode



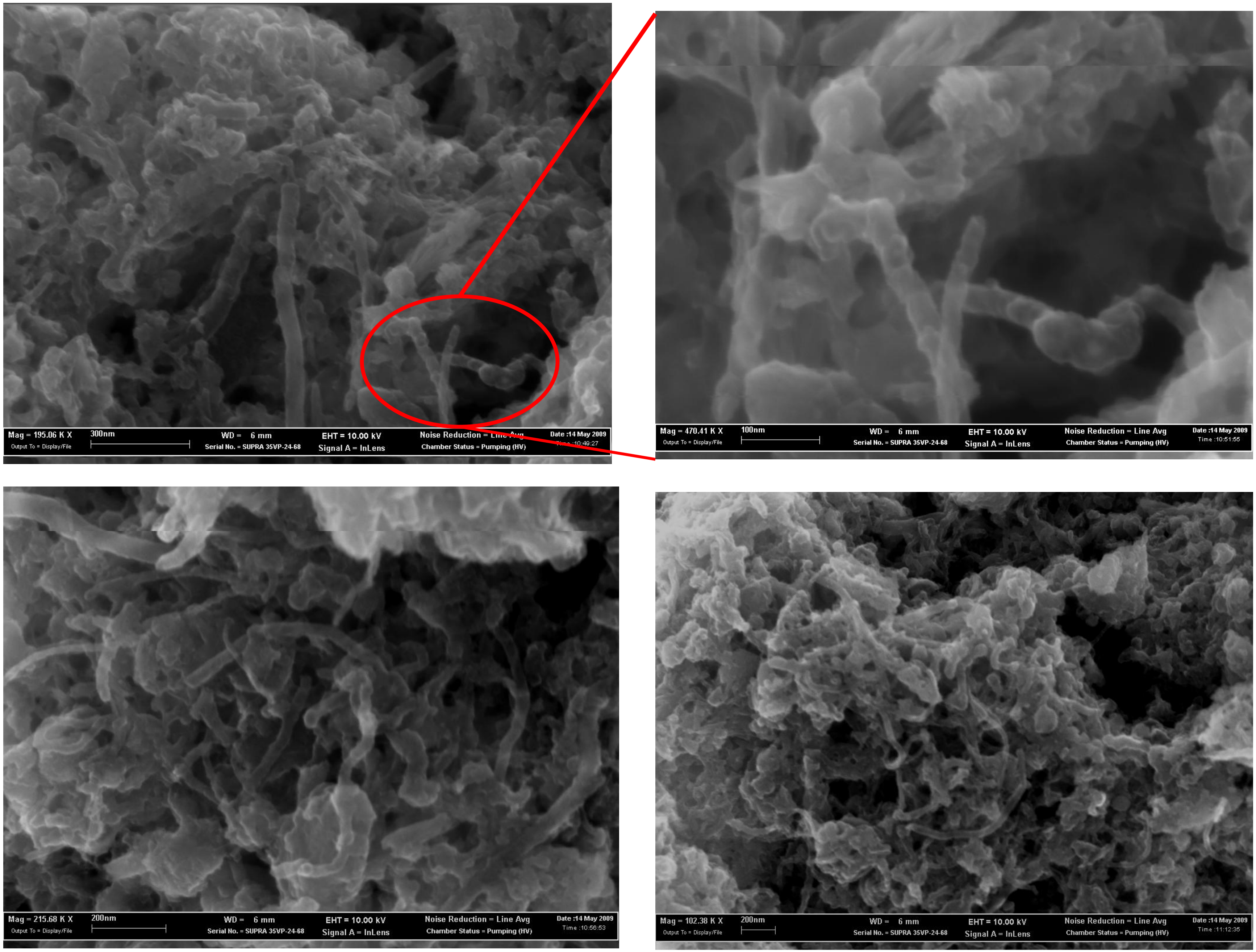


Why a nanostructured electrode



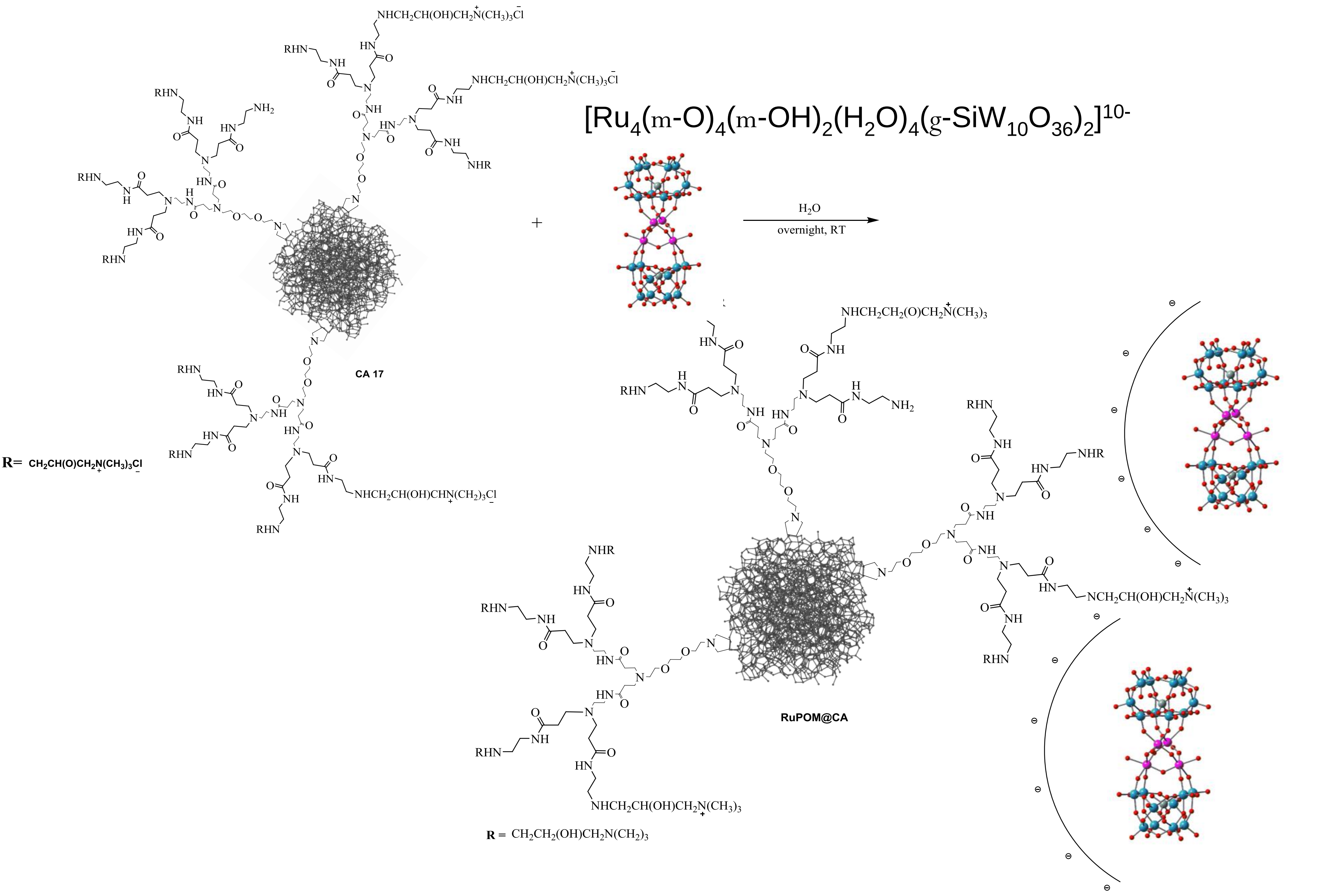
- provide heterogeneous support to the catalyst
- control the material morphology
- increase the surface area
- funnel the sequential electron transfer to the electrode, and thus favour energy dispersion and relieve catalytic fatigue

NT+ POM su ITO



Mag = 195.06 K X
300nm
WD = 6 mm
EHT = 10.00 kV
Signal A = InLens
Serial No. = SUPRA 35VP-24-68
Chamber Status = Pumping (HV)
Date :14 May 2009
Mag = 470.41 K X
100nm
WD = 6 mm
EHT = 10.00 kV
Noise Reduction = Line Avg
Signal A = InLens
Serial No. = SUPRA 35VP-24-68
Chamber Status = Pumping (HV)
Date :14 May 2009
Mag = 215.68 K X
200nm
WD = 6 mm
EHT = 10.00 kV
Noise Reduction = Line Avg
Signal A = InLens
Serial No. = SUPRA 35VP-24-68
Chamber Status = Pumping (HV)
Date :14 May 2009
Mag = 102.38 K X
200nm
WD = 6 mm
EHT = 10.00 kV
Noise Reduction = Line Avg
Signal A = InLens
Serial No. = SUPRA 35VP-24-68
Chamber Status = Pumping (HV)
Date :14 May 2009

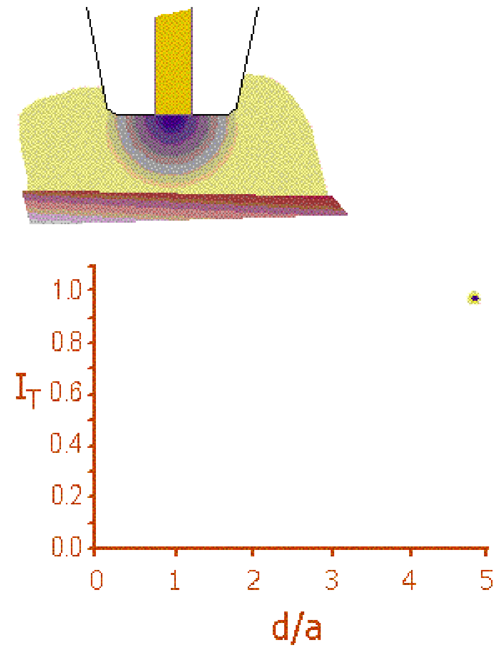
POMs AND Amorphous Carbon



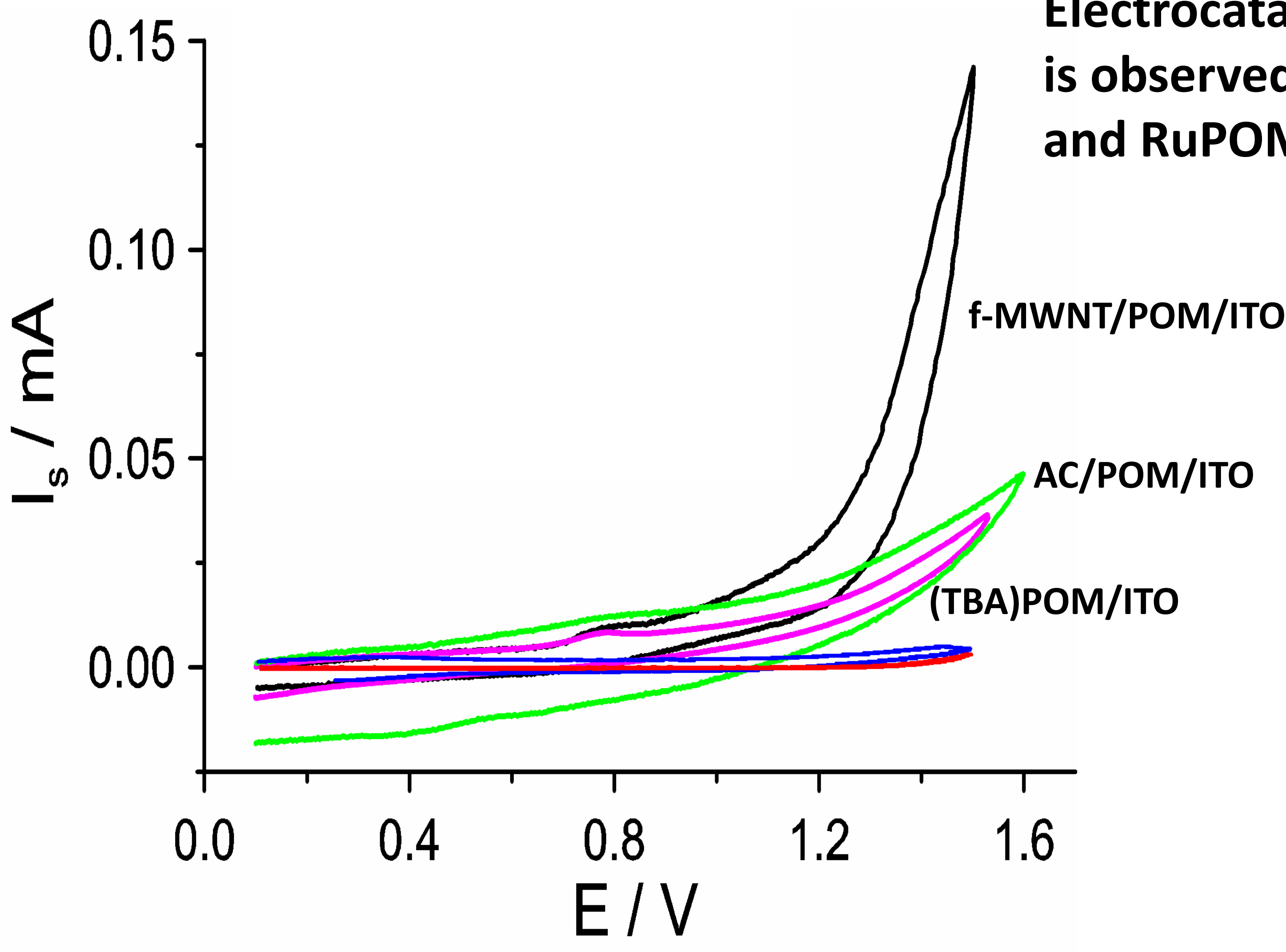
SECM: Scanning Electrochemical Microscopy

- It probes surface reactivity of materials at the microscopic scale.
- Redox reaction occurs and evolution of O_2 (insulating species) is monitored.
- The evolution of O_2 is measured by means of current intensity.
- Measurements can be performed at constant height or constant current

Insulator

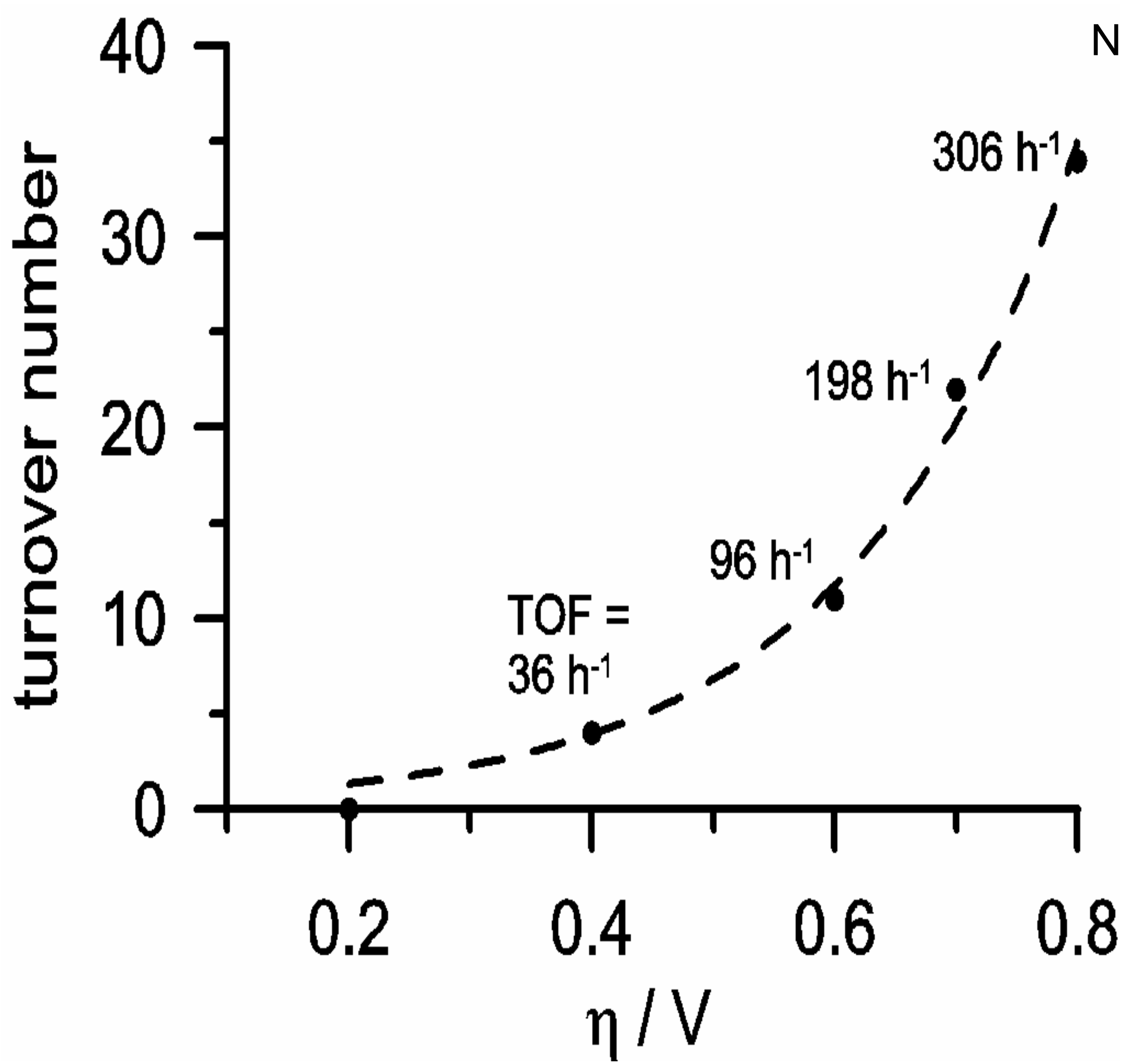


Cyclic Voltammetry



Electrocatalytic current is observed for RuPOM and RuPOM@CNS.

$$TON = \frac{n_{O_2}}{n_{POM}} = \frac{Q_s - Q_{POM}}{Q_{POM}}$$



NOCERA's #

is 8 !

A new technique developed by Princeton University engineers for producing electricity-conducting plastics could dramatically lower the cost of manufacturing solar panels.

By overcoming technical hurdles to producing plastics that are translucent, malleable and able to conduct electricity, the researchers have opened the door to broader use of the materials in a wide range of electrical devices.

Associte prof at Princeton Chem Eng Dept
Lynn Loo

Conclusion

- CNTs for energy applications: we have demostrated how CNTs can be useful in fabrication of nanostructured anode for water splitting

TLAZOCAMATL (Huhatl)

GRACIAS (Mexicano)

MAMNOON (Farsi)

ENKOSI (African)

THE END

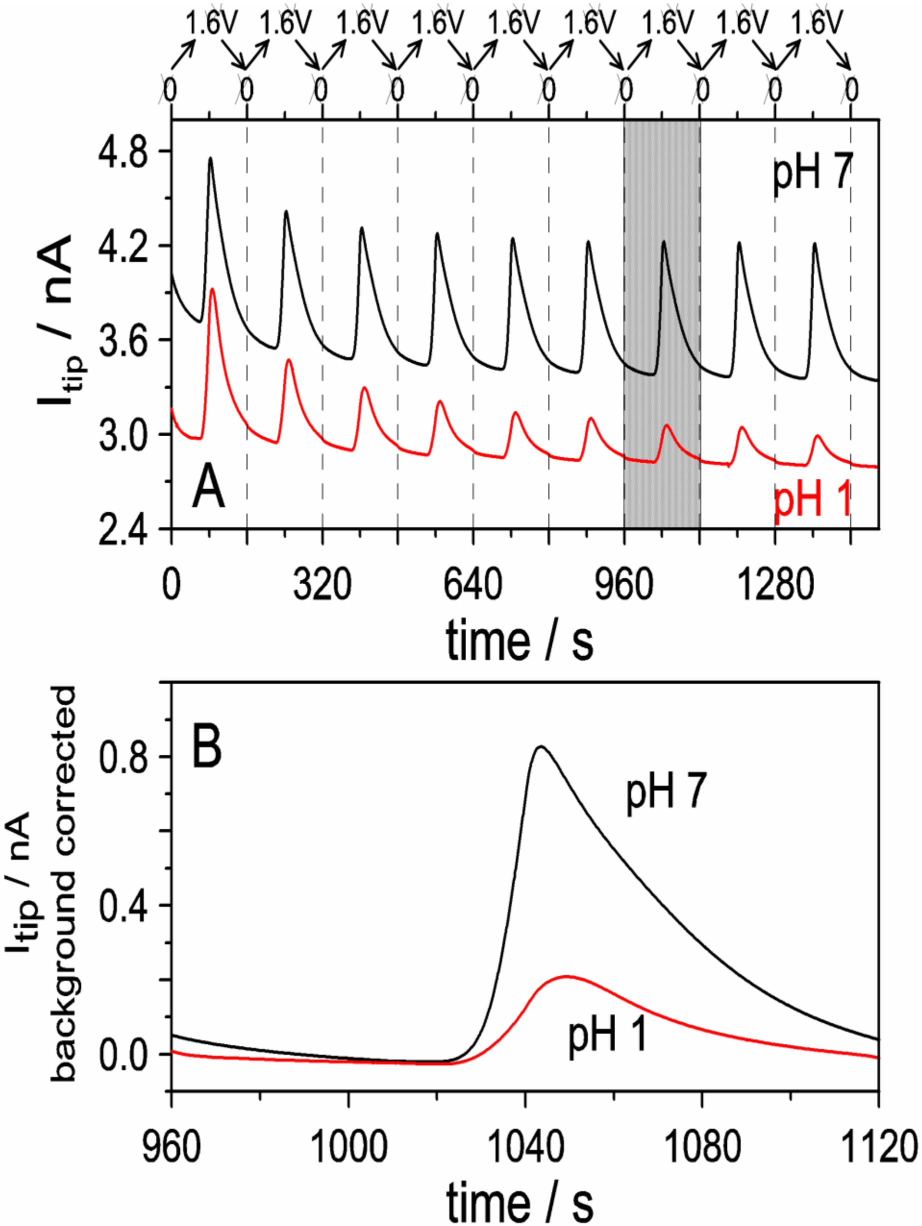
GRAZIE (Italian)

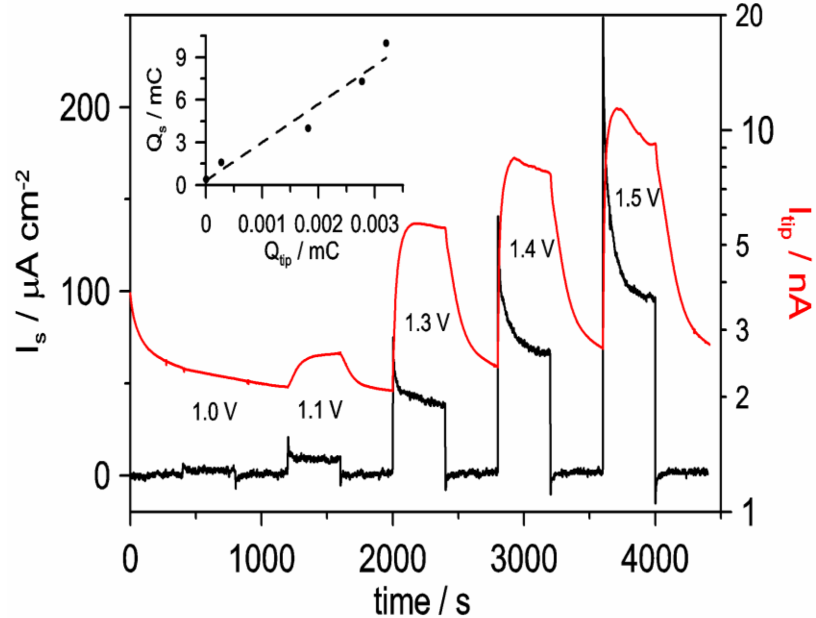
NGIYABONGA (Zulu)

THANK YOU (English)

DANKIE (Afrikaans)

Results





CHRONOAMPEROMETRY

I_s: substrate current (transfer of electrons between the POM film and the ITO electrode)

I_{tip}: tip current (measure of the flux of O_2 at the film/solution interface)

$Q_{POM} = 0.32$ mC $n_{POM} = 8.3\times10^{-4}$ μmol