Polyoxometalates:

from inorganic chemicals to energy materials

Prof. Pedro Gómez-Romero

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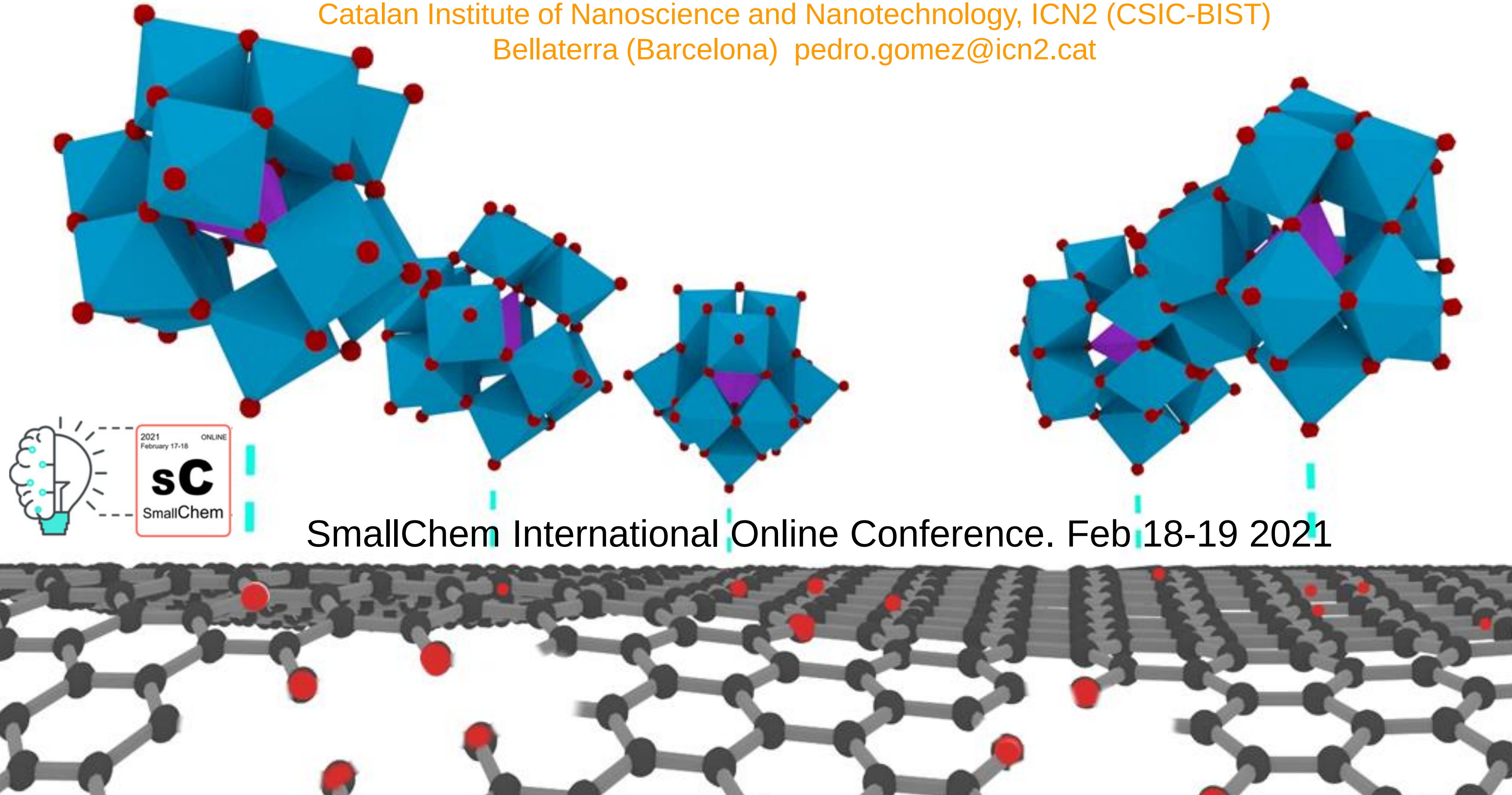
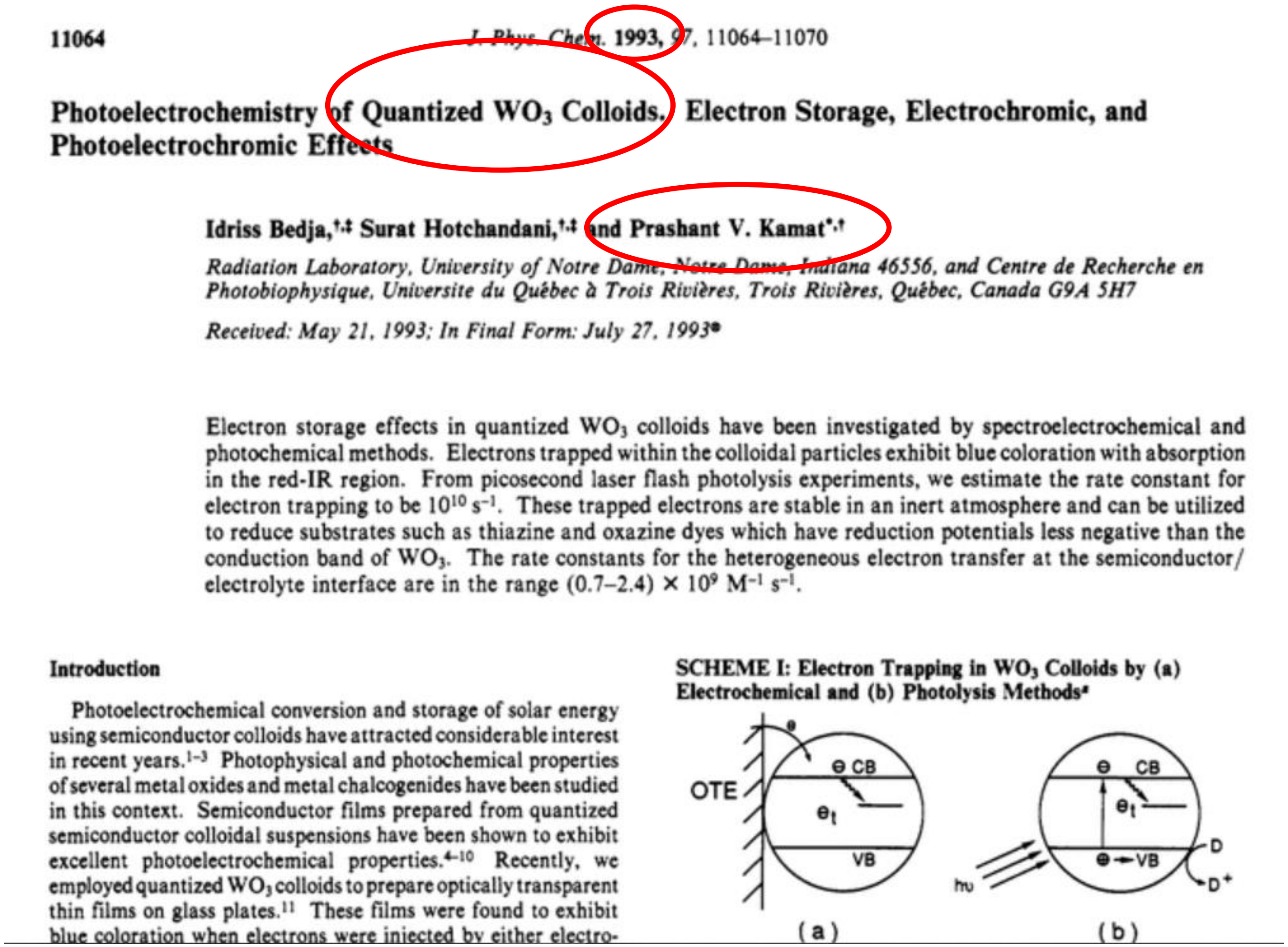


SmallChem International Online Conference. Feb 18-19 2021

Polyoxometalates:
A story with some history



11064 J. Phys. Chem. 1993, 97, 11064–11070

Photoelectrochemistry of Quantized WO_3 Colloids. Electron Storage, Electrochromic, and Photoelectrochromic Effects

Idriss Bedja,[†,‡] Surat Hotchandani,[†,‡] and Prashant V. Kamat[*,†]

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Centre de Recherche en Photobiophysique, Universite du Québec à Trois Rivières, Trois Rivières, Québec, Canada G9A 5H7

Received: May 21, 1993; In Final Form: July 27, 1993[*]

Electron storage effects in quantized WO_3 colloids have been investigated by spectroelectrochemical and photochemical methods. Electrons trapped within the colloidal particles exhibit blue coloration with absorption in the red-IR region. From picosecond laser flash photolysis experiments, we estimate the rate constant for electron trapping to be 10^{10} s^{-1}. These trapped electrons are stable in an inert atmosphere and can be utilized to reduce substrates such as thiazine and oxazine dyes which have reduction potentials less negative than the conduction band of WO_3. The rate constants for the heterogeneous electron transfer at the semiconductor/electrolyte interface are in the range (0.7–2.4) × 10^9 M^{-1} s^{-1}.

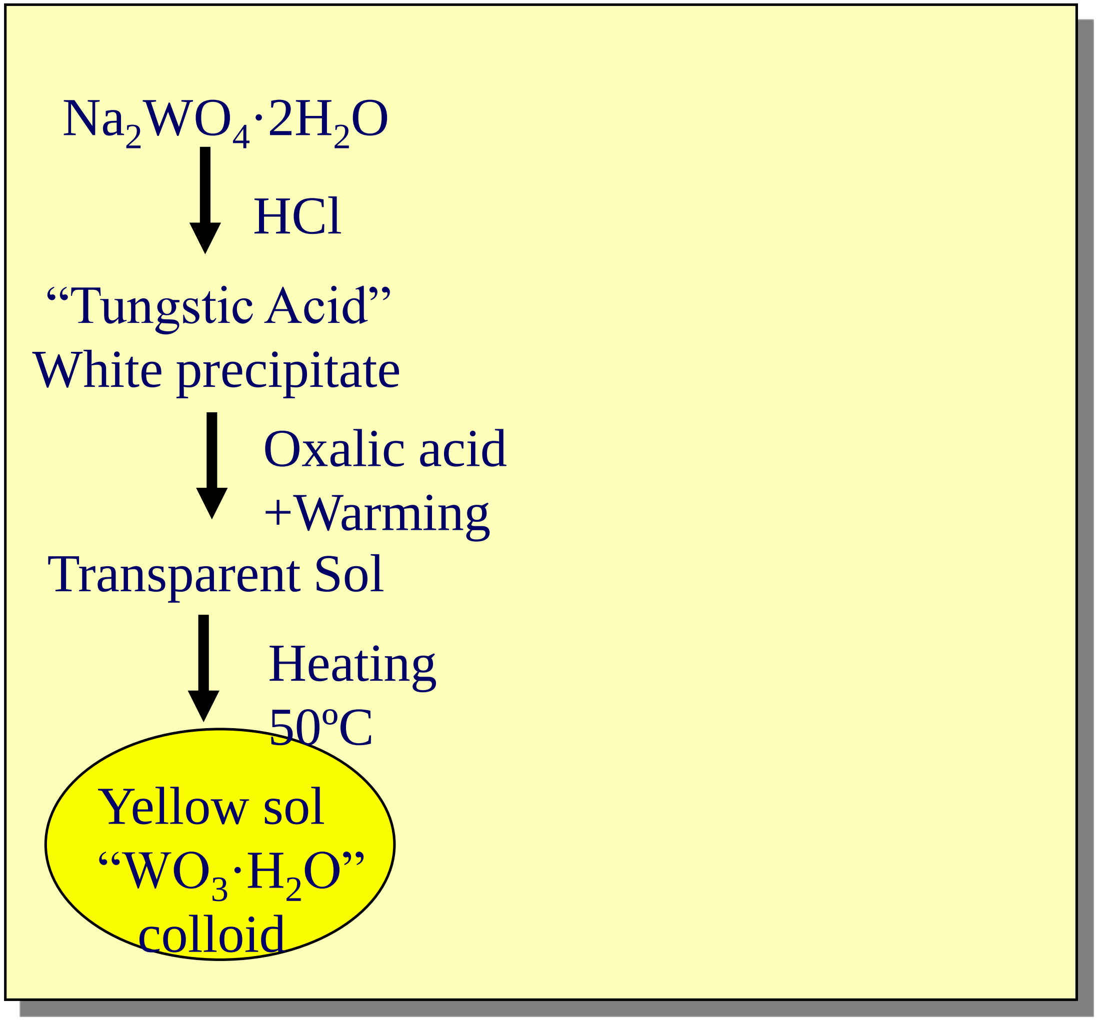
Introduction

Photoelectrochemical conversion and storage of solar energy using semiconductor colloids have attracted considerable interest in recent years.[1-3] Photophysical and photochemical properties of several metal oxides and metal chalcogenides have been studied in this context. Semiconductor films prepared from quantized semiconductor colloidal suspensions have been shown to exhibit excellent photoelectrochemical properties.[4-10] Recently, we employed quantized WO_3 colloids to prepare optically transparent thin films on glass plates.[11] These films were found to exhibit blue coloration when electrons were injected by either electro-

SCHEME I: Electron Trapping in WO_3 Colloids by (a) Electrochemical and (b) Photolysis Methods[a]

Colloidal? Nano? WO_3

Colloidal WO_3



$Na_2WO_4 \cdot 2H_2O$

HCl

"Tungstic Acid"
White precipitate

Oxalic acid
+Warming

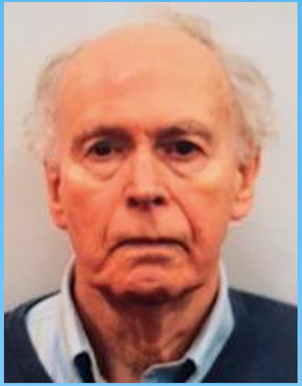
Transparent Sol

Heating
50ºC

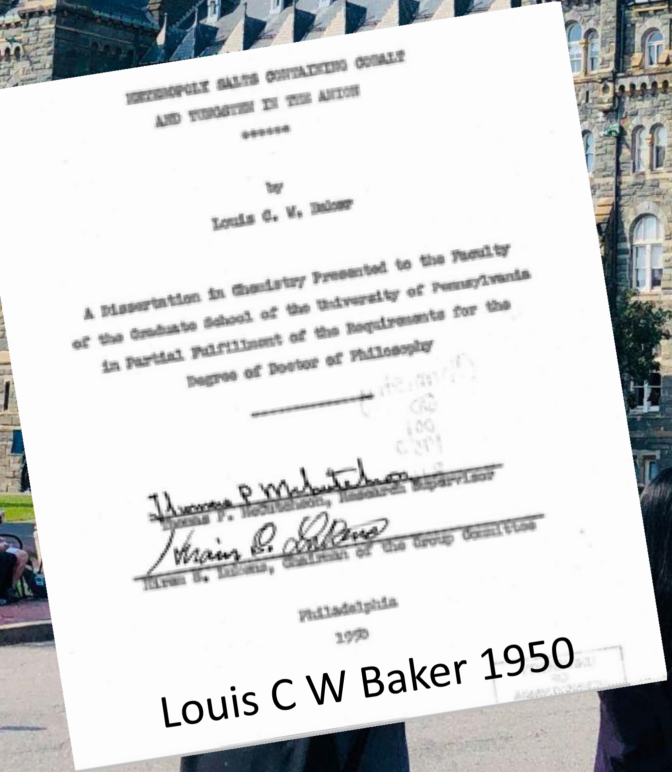
Yellow sol
"$WO_3 \cdot H_2O$"
colloid

Georgetwon U.

Prof.Louis C W Baker



Prof. Michael T Pope



HETEROPOLY SALTS CONTAINING COBALT
AND TUNGSTEN IN THE ANION
******

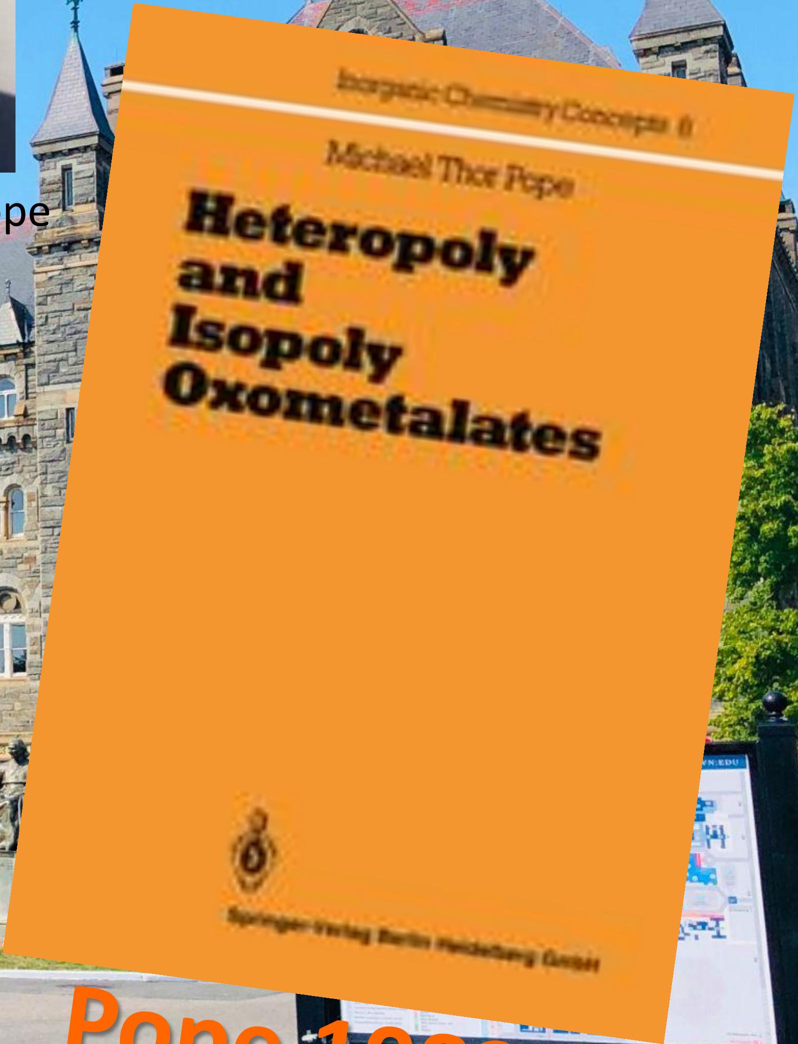
by
Louis C. W. Baker

A Dissertation in Chemistry Presented to the Faculty
of the Graduate School of the University of Pennsylvania
in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy

Thomas P. McCutcheon
Thomas P. McCutcheon, Research Supervisor
Hiram S. Lukens
Hiram S. Lukens, Chairman of the Group Committee

Philadelphia
1950

Louis C W Baker 1950



Inorganic Chemistry Concepts 8

Michael Thor Pope

Heteropoly and Isopoly Oxometalates

Springer-Verlag Berlin Heidelberg GmbH

Pope 1983

POMs: Unchanged structure upon reduction

5658 J. Am. Chem. Soc. **1991**, *113*, 5658–5663

Crystal Structures of α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{6-}$ and Its Heteropoly Blue 2e Reduction Product, α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{8-}$. Structural, Electronic, and Chemical Consequences of Electron Delocalization in a Multiatom Mixed-Valence System

Nieves Casañ-Pastor,† Pedro Gomez-Romero,† Geoffrey B. Jameson, and Louis C. W. Baker*

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057.

Received February 14, 1991

Abstract: This paper reports for the first time X-ray crystal structures for a parent heteropoly complex and for its heteropoly blue reduction product. The potassium salt of the former complex, α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{6-}$, is ordered in space group $P6_222$; and the potassium salt of its two-electron heteropoly blue reduction product, α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{8-}$, is disordered in space group $Pm3m$. The structures were refined to $R(\text{on } F) = 0.034$ and $R(\text{on } F) = 0.044$, respectively. Except for a shortening of each central Co–$\mathrm{O_{tet}}$ distance, by 0.03 Å, and a consequent corresponding increase in W–$\mathrm{O_{tet}}$ distances, the reduction caused remarkably little change in interatomic distances within the complex. Very slight lengthening of W–W distances between edge-sharing $\mathrm{WO_6}$ octahedra, upon reduction, and a corresponding contribution toward slight shortening of the W–W distances through corner-sharing between $\mathrm{WO_6}$ groups, as suggested by previous data, were near the limits of statistical significance. On the other hand, the reduction apparently creates sizable new energy barriers to atomic displacements for both W's and O's. The displacement parameters for all of those atoms in the heteropoly complex decrease markedly, upon its reduction, while such parameters remain unchanged for all of the atoms not in the complex ($\mathrm{H_2O}$'s and $\mathrm{K^+}$'s). The attendant significantly enhanced rigidity of the reduced complex is consistent with increased kinetic stability of heteropoly blue products to substitution and to degradation by base. The increased resistance to atom displacements in the heteropoly blue species may be seen as a consequence of the additional energy factor involved in maintaining favorable orbital overlaps for the delocalization of the added electrons. While the delocalization of the "blue" electrons presumably does involve thermal hopping of those electrons among W atoms, the greatly decreased displacement parameters, observed for the O's as well as the W's, suggest the importance of a ground-state delocalization mechanism involving partial "blue" electron residency in molecular orbitals that involve oxygen atoms. The increase in negative charge on bridging O atoms is consistent with their increased nucleophilicity and with the above-cited changes in Co–$\mathrm{O_{tet}}$ and W–$\mathrm{O_{tet}}$ distances. Those changes imply that the central $\mathrm{Co^{II}O_4}$ tetrahedron is slightly more isolated from the rest of the W–O framework in the reduced species. This is consistent with a pronounced decrease, upon reduction, in the magnitude of the large isotropic shift for the ^{183}W NMR signal.

Background

Heteropoly complexes resemble discrete fragments of metal oxide structures of definite sizes and shapes.[1-6] They maintain their identities in aqueous and nonaqueous solutions as well as in ionic crystals. Many heteropoly complexes can be made which contain various combinations of d-transition metals at specific

electron hopping process from one addendum (e.g., W or Mo) atom to the next and a ground-state delocalization (gsd)[6] pre-

---

(1) Baker, L. C. W. In *Advances in the Chemistry of the Coordination Compounds*; Kirschner, S., Ed.; Macmillan: New York, 1961; pp 608ff.

(2) Souchay, P. *Polyanions et Polycations*; Gauthier-Villars: Paris, 1963.

Keggin structure

5662 J. Am. Chem. Soc., Vol. 113, No. 15, 1991

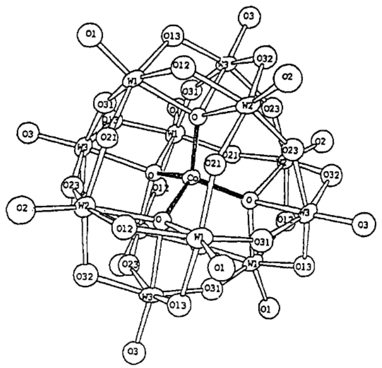
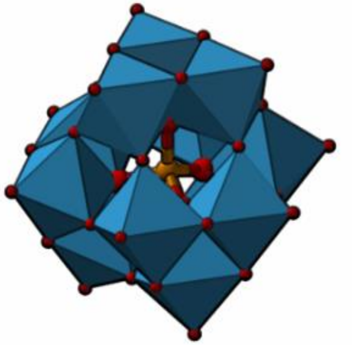


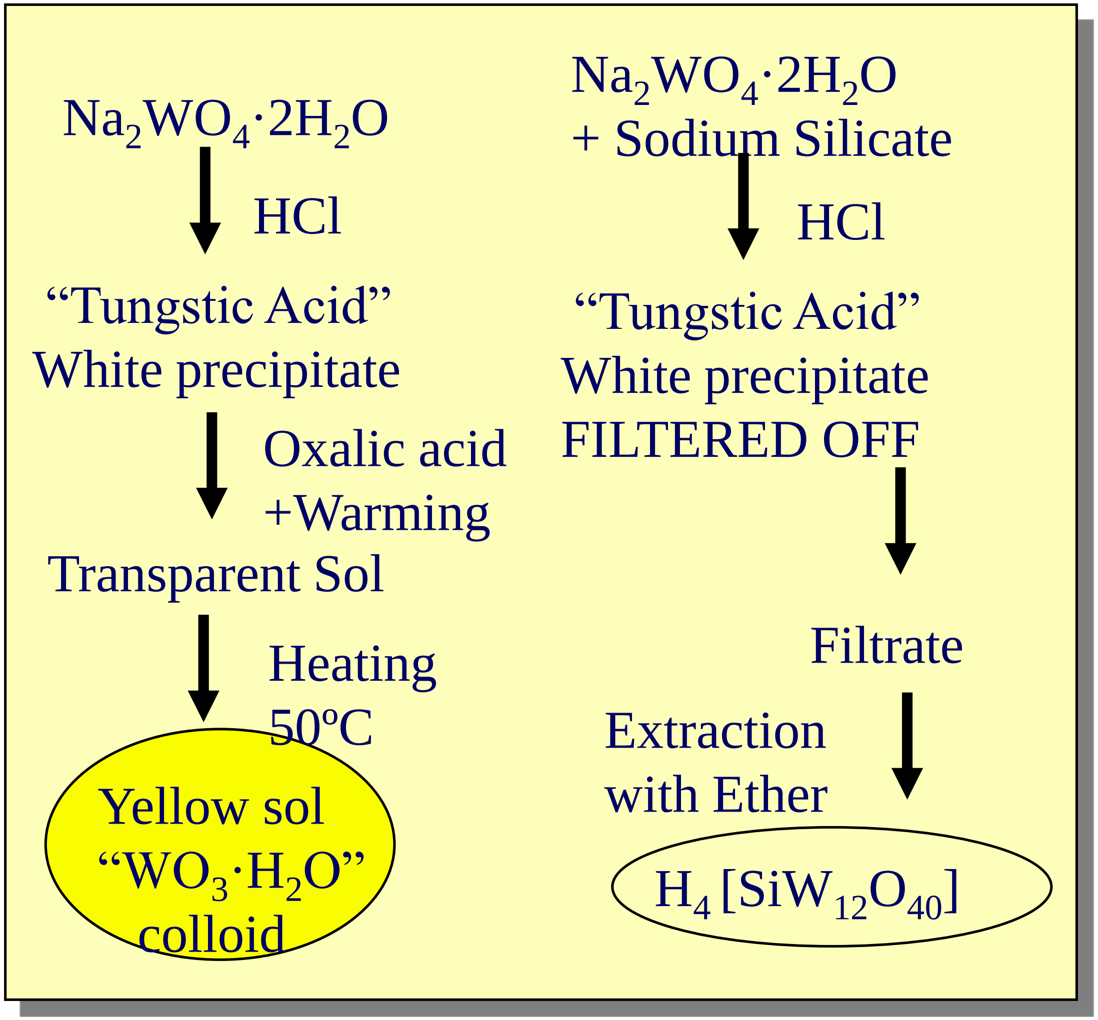
Figure 2. Perspective ORTEP diagram for oxidized species α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{6-}$. Except for much smaller atomic displacement elipsoids, an ORTEP diagram for the reduced species α-$[\mathrm{Co^{II}W_{12}O_{40}}]^{8-}$ would not show atomic positions that are detectably different from those for this oxidized species when drawn on this scale.



The two paths to Nano-WO_3

Colloidal WO_3

Polyoxotungstates



$Na_2WO_4 \cdot 2H_2O$

HCl

"Tungstic Acid"
White precipitate

Oxalic acid
+Warming

Transparent Sol

Heating
50ºC

Yellow sol
"$WO_3 \cdot H_2O$"
colloid

$Na_2WO_4 \cdot 2H_2O$
+ Sodium Silicate

HCl

"Tungstic Acid"
White precipitate
FILTERED OFF

Filtrate

Extraction
with Ether

$H_4[SiW_{12}O_{40}]$

Same chemistry

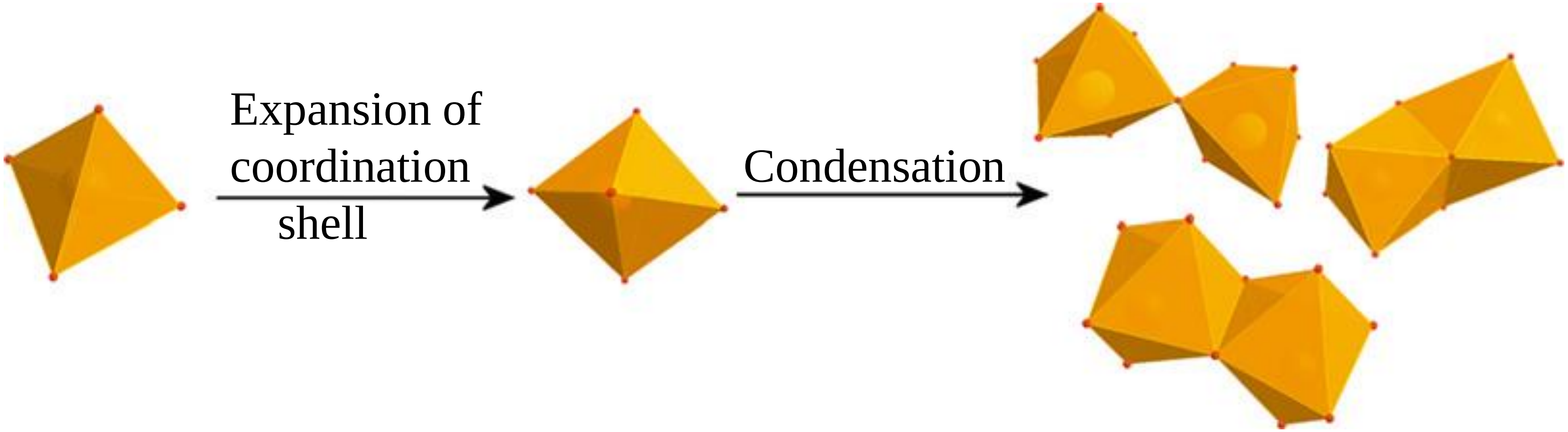
Top-Down

Bottom-Up

Two different
approaches

Polyoxometalates

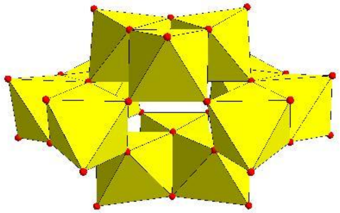
Formation



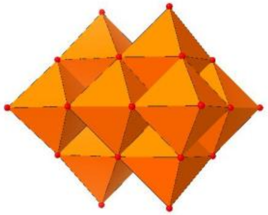
Self-assembly process, whereby the tetrahedral metal {MO4} expands into octahedra {MO6} and then condenses into larger assemblies sharing oxygen ligands, where M commonly is Mo, W, or V.

Polyoxometalates

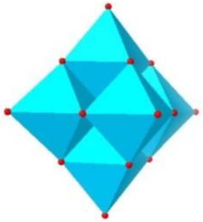
Isopoly-oxometalates (isopolyanions)



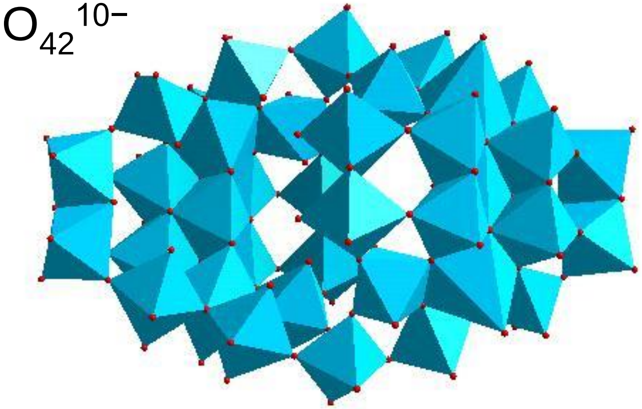
Paratungstate B, $H_2W_{12}O_{42}^{10-}$



Decavanadate, $V_{10}O_{28}^{6-}$



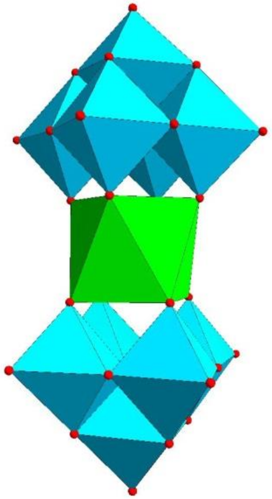
Lindqvist hexamolybdate, $Mo_6O_{19}^{2-}$



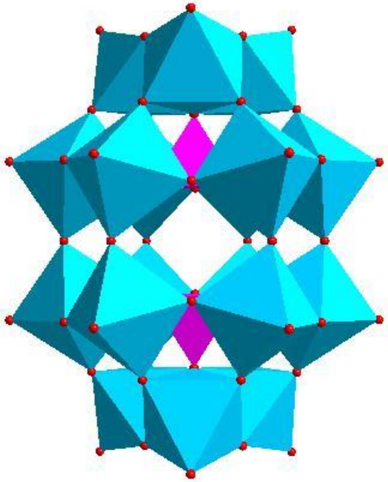
Mo36-polymolybdate, $Mo_{36}O_{112}(H_2O)_{16}^{8-}$

Polyoxometalates

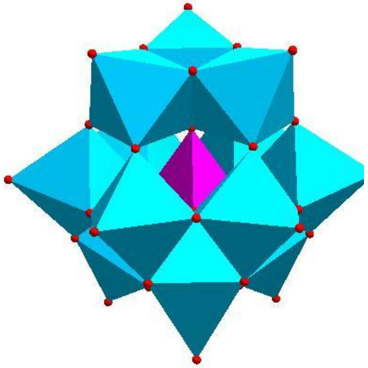
Heteropoly-oxometalates (heteropolyanions)



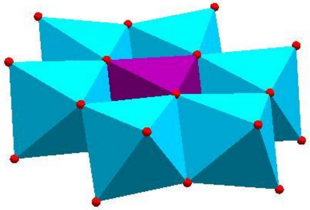
Weakley-Yamase structure, $XM_{10}O_{36}^{n-}$



Dawson structure, $X_2M_{18}O_{62}^{n-}$



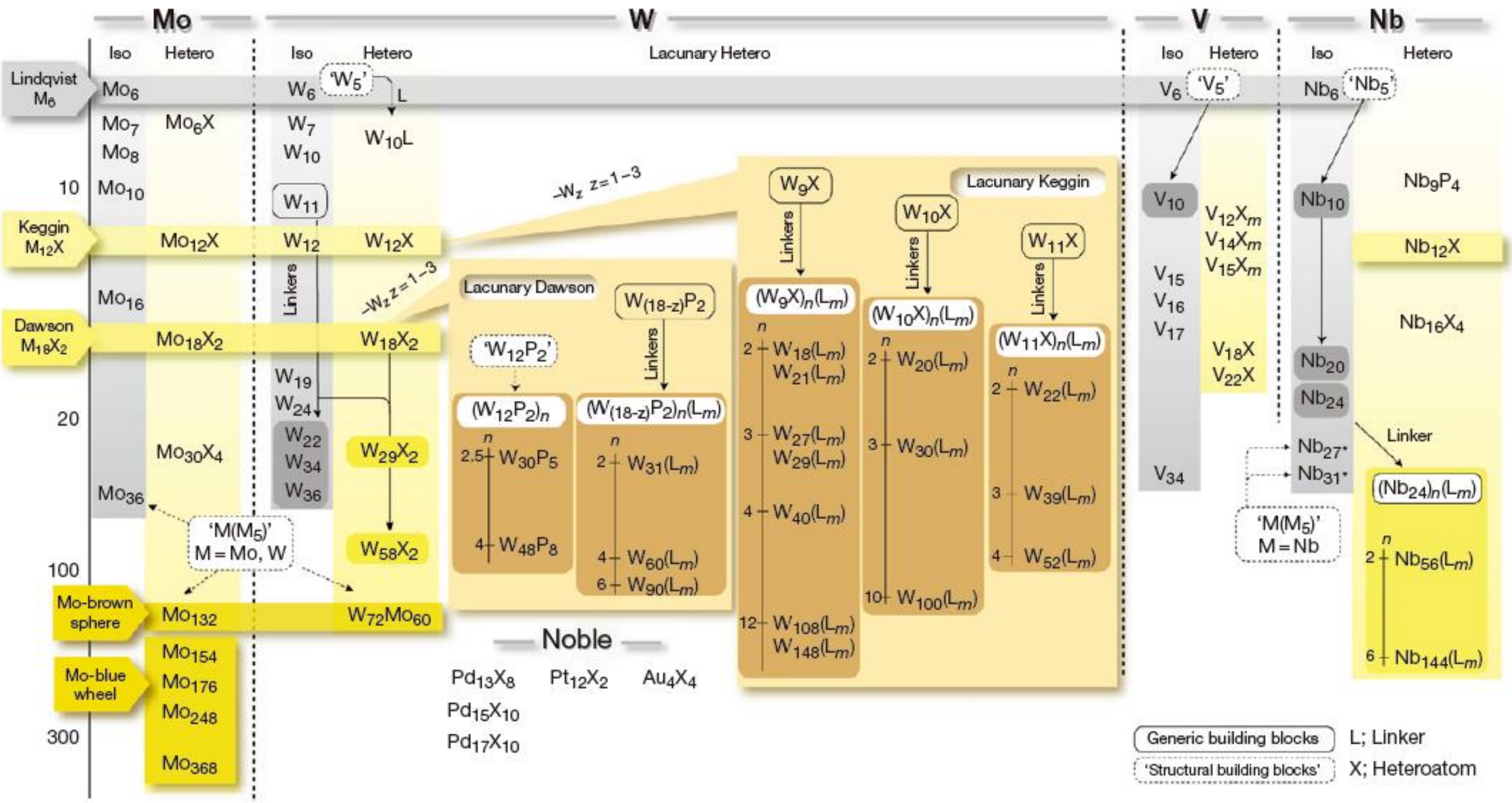
Keggin structure, $XM_{12}O_{40}^{n-}$



Anderson structure, $XM_6O_{24}^{n-}$

Polyoxometalates

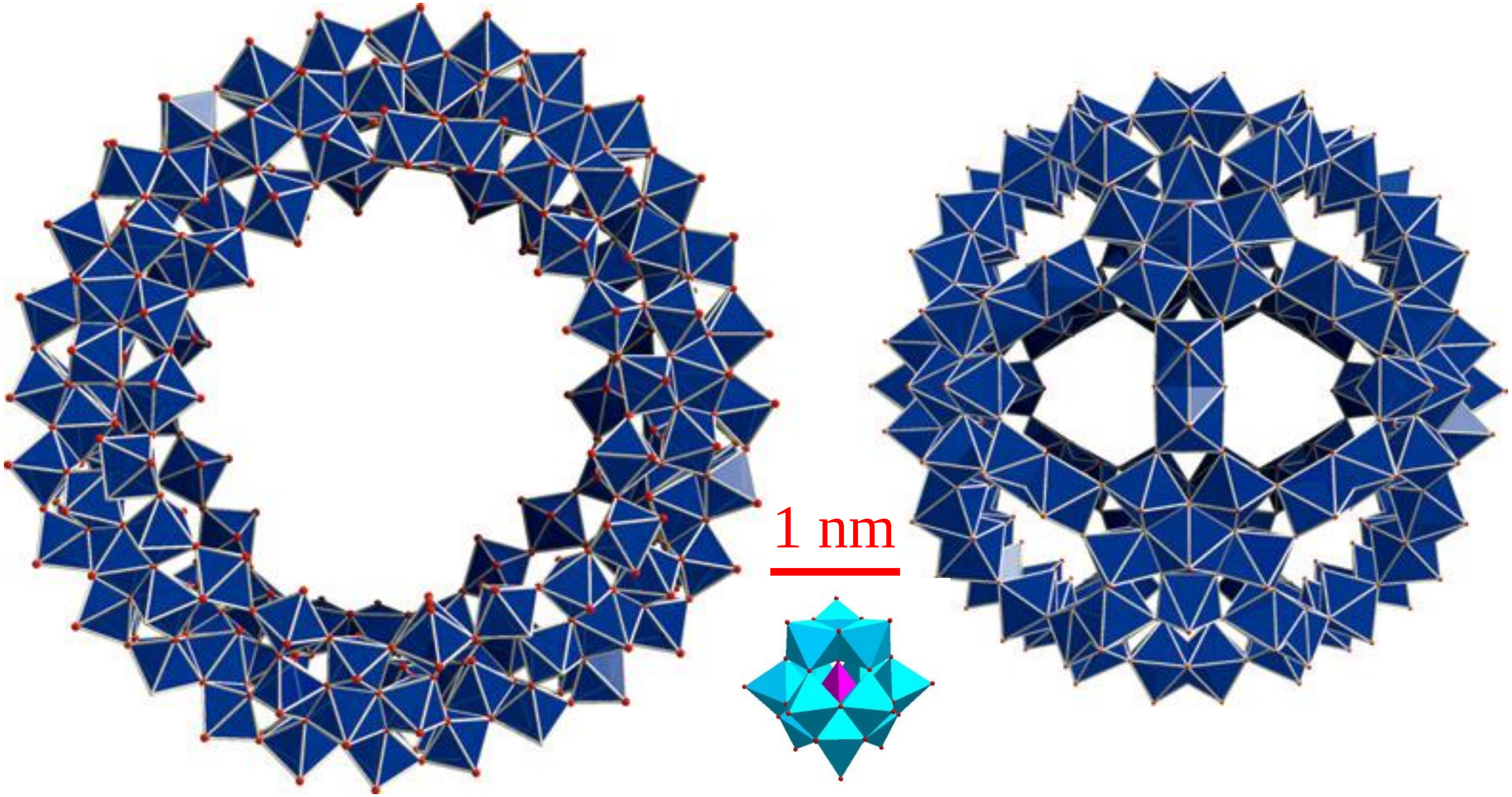
Taxonomy



Hutin M., Rosnes M.H., Long D.-L. and Cronin L. Polyoxometalates: Synthesis and Structure – From Building Blocks to Emergent Materials. In: Jan Reedijk and Kenneth Poeppelmeier, editors. Comprehensive Inorganic Chemistry II, Vol 2. Oxford: Elsevier; 2013. p. 241-269.

Polyoxometalates

From 1nm to Giant clusters



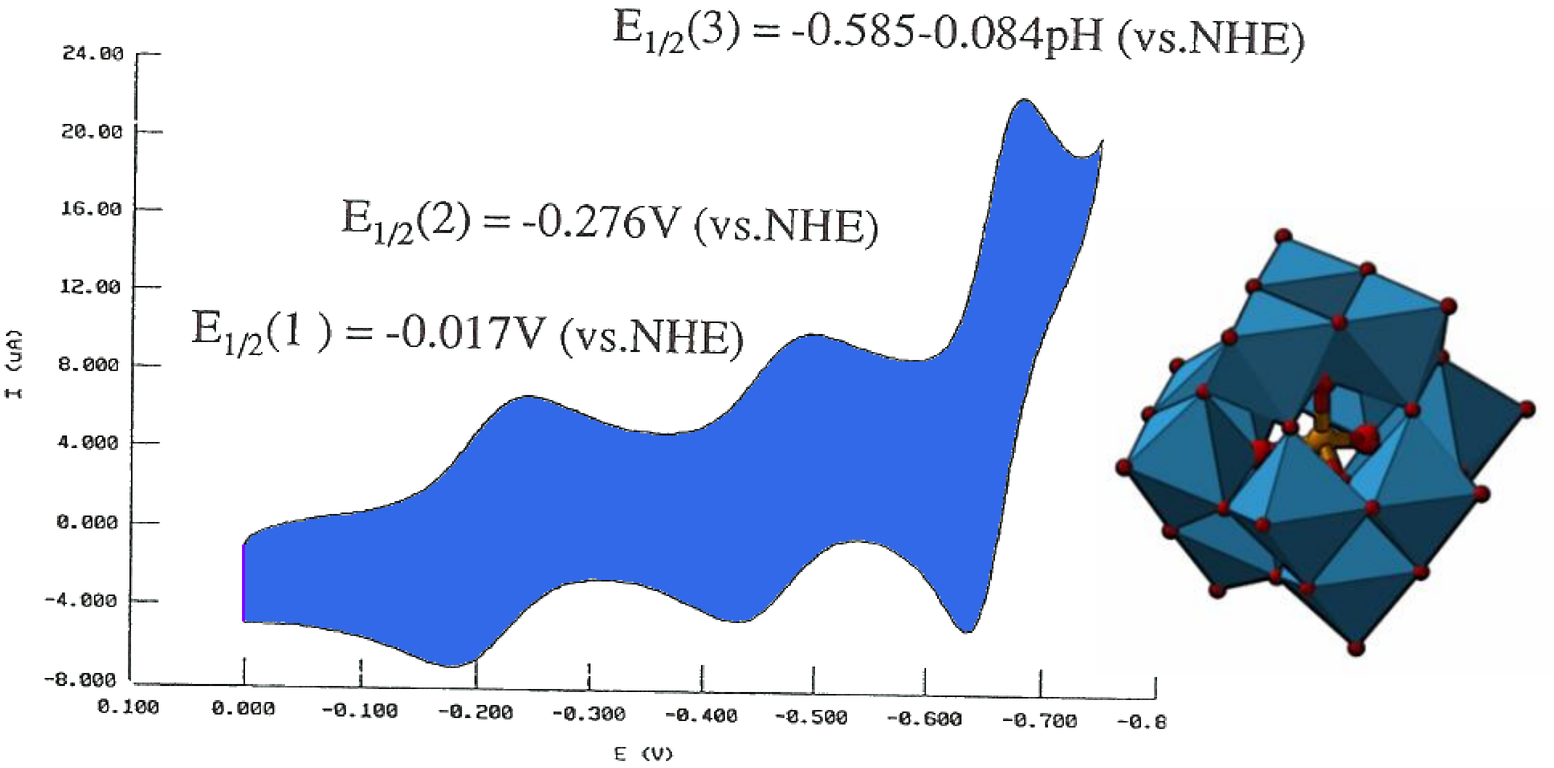
Polyhedra representation of the {Mo154} (left) and {Mo132} (right). Color scheme: Mo, blue (polyhedra); O, red.

Comprehensive Inorganic Chemistry II: From Elements to Applications, (2013), vol. 2, pp. 241-269

RedOx Chemistry of POMs

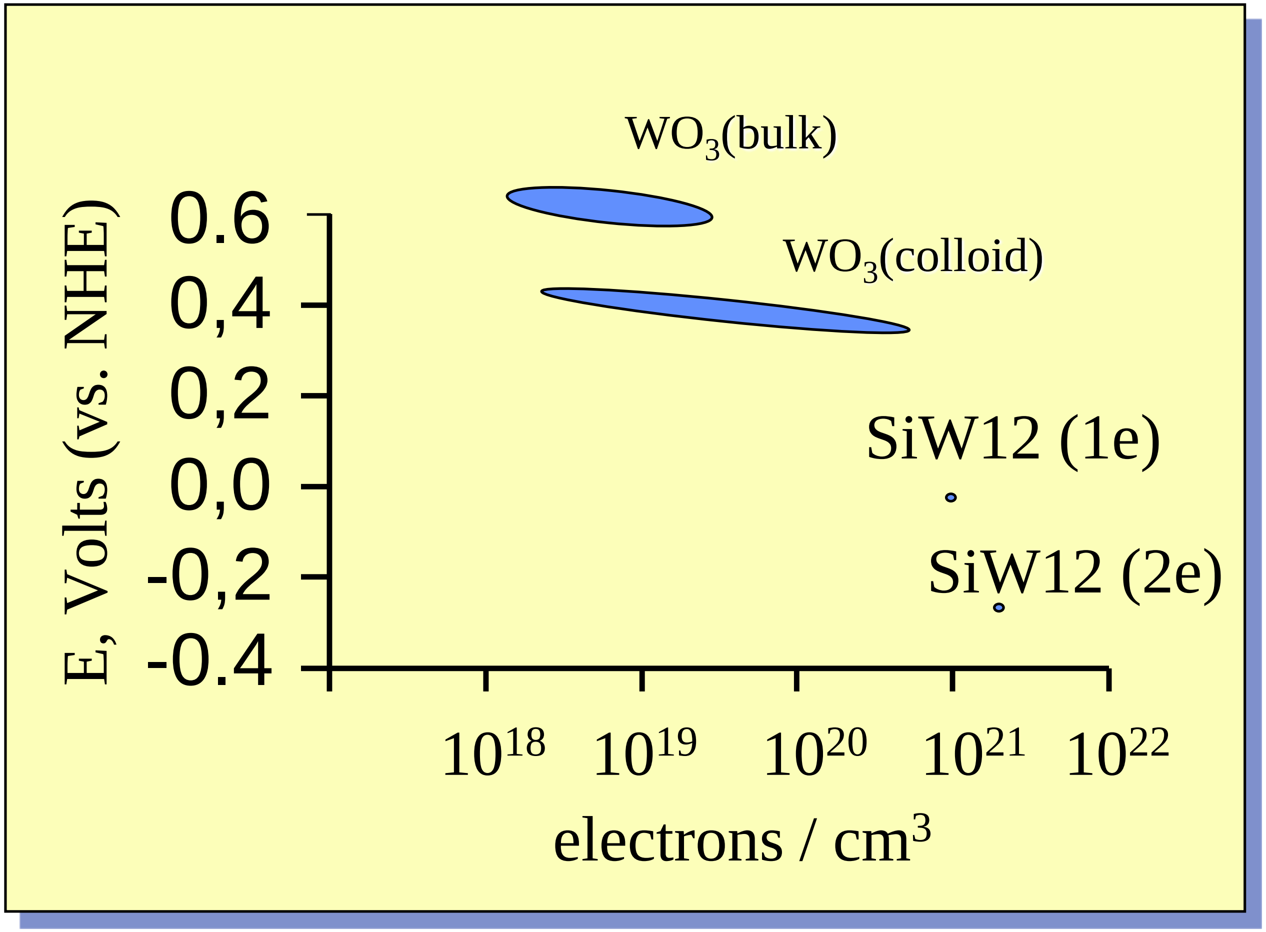
Cyclic Voltammogram (CV) of H_4 [$SiW_{12}O_{40}$] (SiW12)

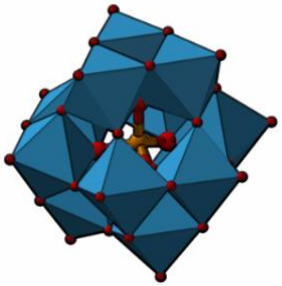
H_4 [$SiW_{12}O_{40}$] (aq.HCl), pH=0.8



Photoredox Chemistry in Oxide Clusters. Photochromic and Redox Properties of Polyoxometalates in Connection with Analog Solid State Colloidal Systems.
Pedro Gómez-Romero* et al J.Phys.Chem. **1996**, 100(30), 12448-54.

Polyoxometalates (POMs) as models for quantum-sized oxides





Effect of particle size on flat-band potential

P. Gomez-Romero Solid State Ionics 1997, 101-103, 243-248

Comparative analysis

POLYOXO-TUNGSTATES

- photoreducible
- e- storage
- 10 A diameter
- monodisperse
- reproducible synthesis
- controlled composition
- well-known structure
- stable in solution
- lower potentials
- more tunability

WO_3 COLLOIDS

- photoreducible
- e- storage
- 20-450 A
- polydisperse
- uncontrolled parameters with unknown effect
  - pH
- unknown structure
- less stable (ageing, coagulation)

Polyoxometalates as photoelectrochemical models for quantum-sized colloidal semiconducting oxides
P. Gomez-Romero Solid State Ionics 1997, 101-103, 243-248

How to…

Design materials with POMs

↓

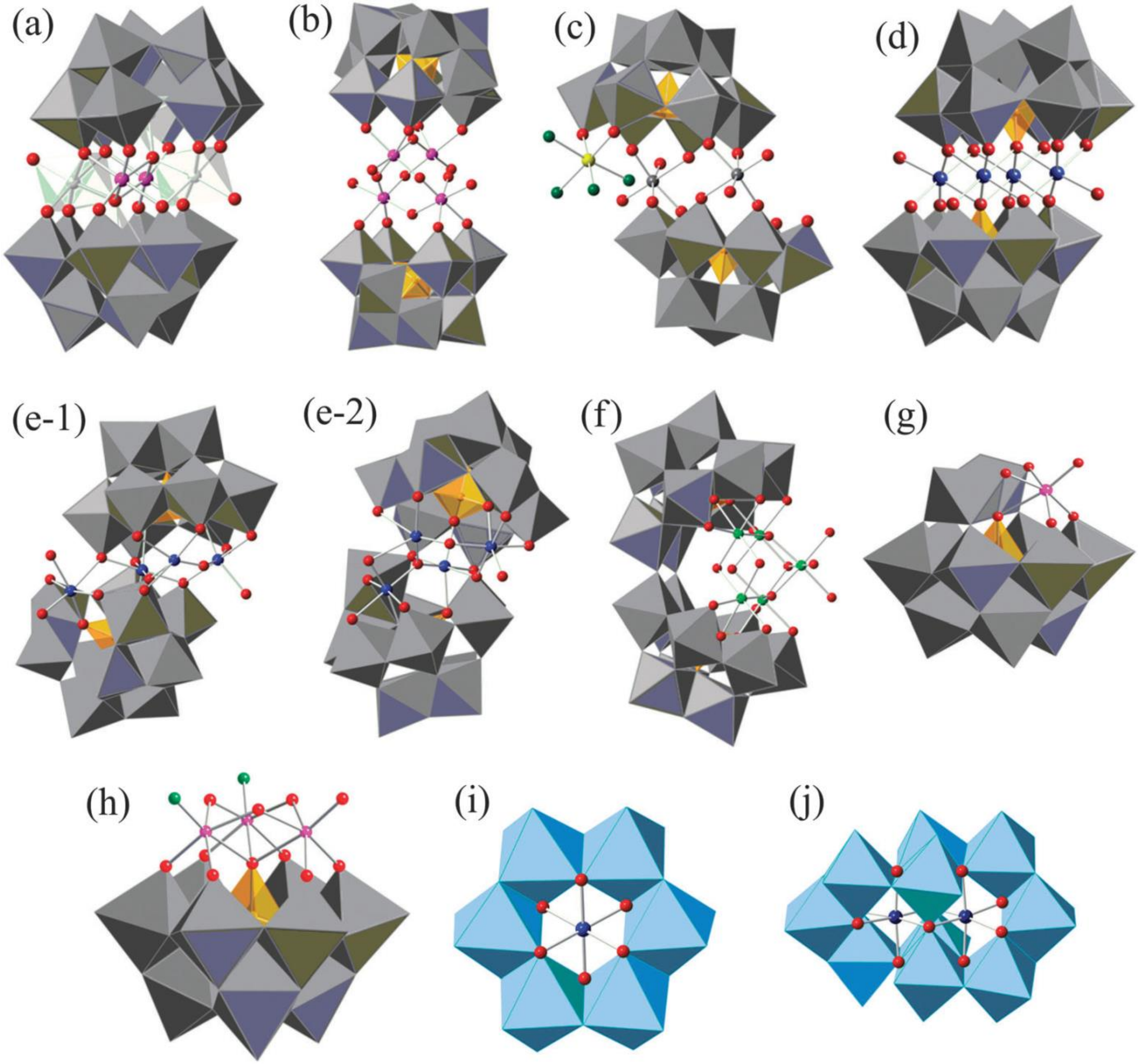
Energy Storage

Energy Conversion

Photo-
Electro-catalysis
Borras-Almenar

Polyoxometalates

Derivatives



Polyoxometalate water
oxidation catalysts and the
production of green fuel

Hongjin_Lv, et al.
Chem. Soc. Rev., 2012,41, 7572

How to…

Design materials with POMs

Energy Storage

Energy Conversion

Electrolytes

Electrodes

conducting matrix
+
electroactive POM

Hybrid material

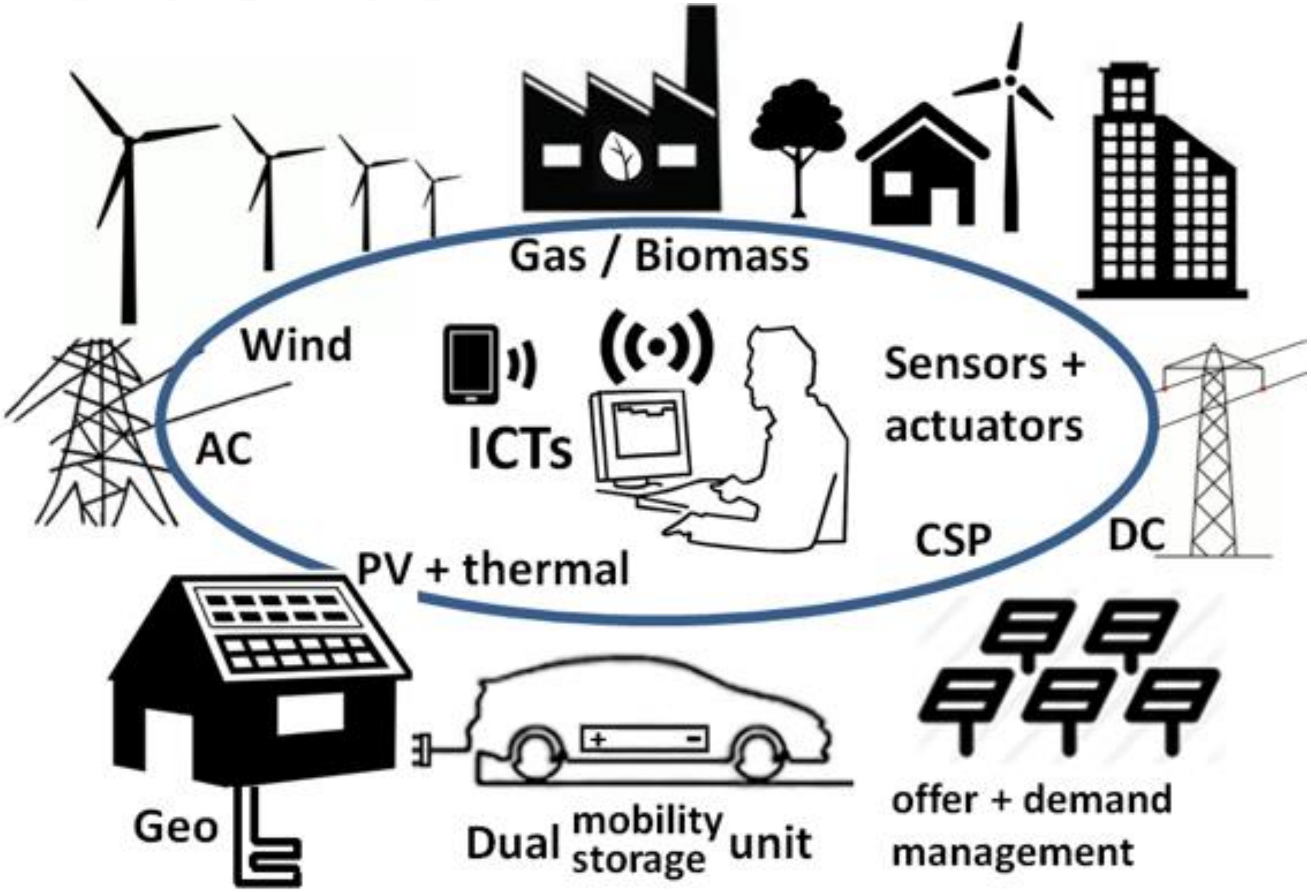
Electrochemical energy storage in transition

Towards flexible solid-state supercapacitors for smart and wearable electronics
D. P. Dubal,* N.R. Chodankar, D-H. Kim and P. Gomez-Romero*
Chemical Society Reviews, **2018,** 47(6), 2065-2129

Centralized AND Distributed Energy

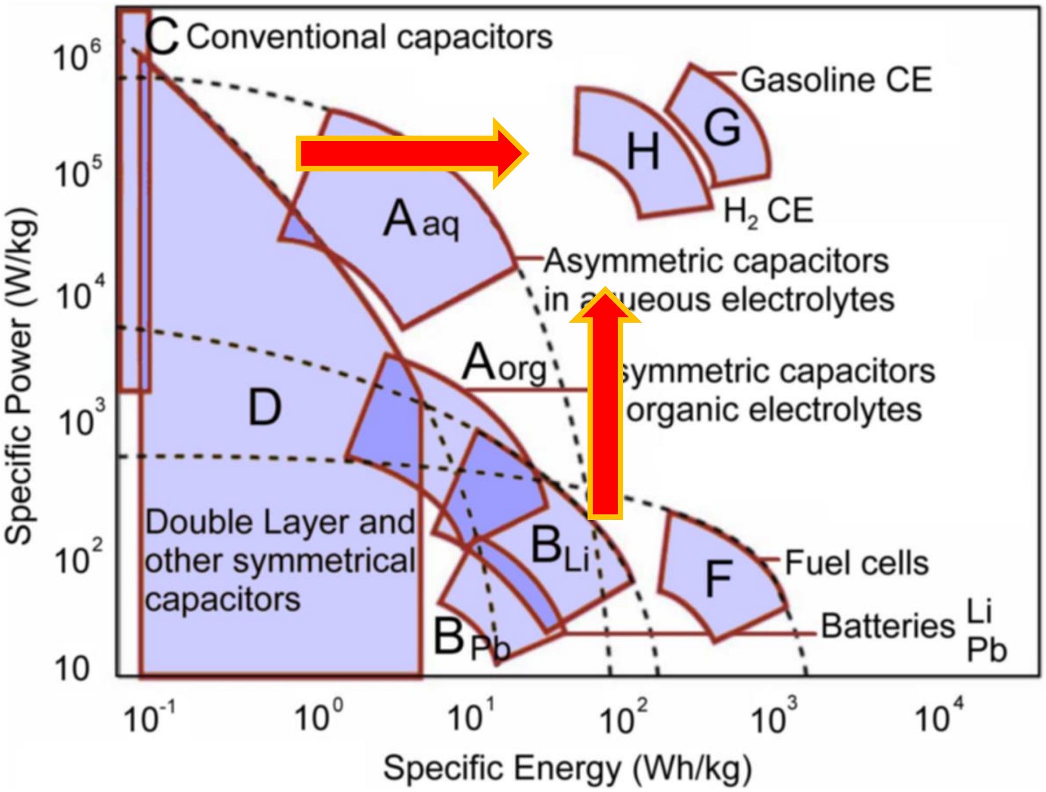
Smart Grids

Internet of Things



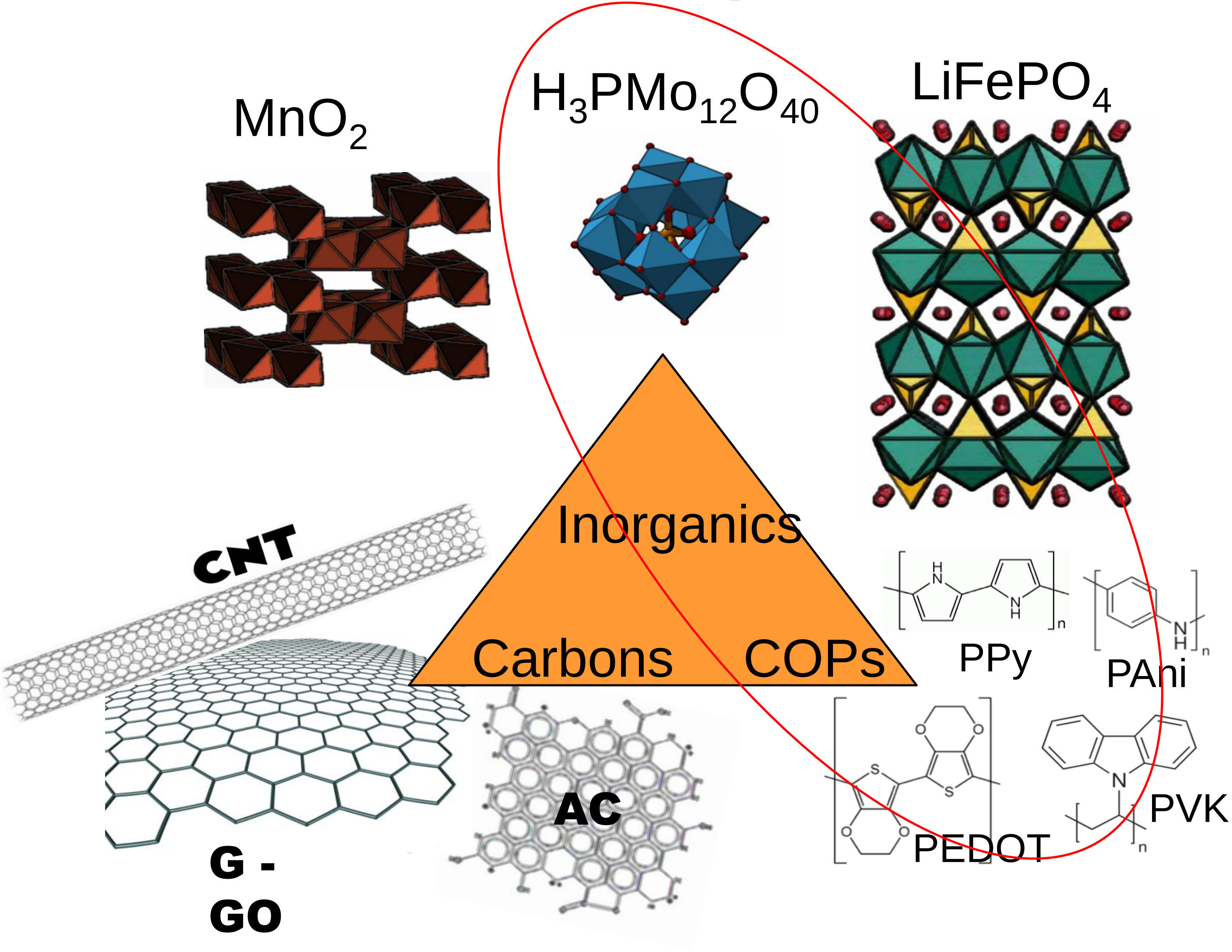
Batteries vs. Supercapacitors

Ragone Plot: the energy storage chessboard



Hybrid Energy Storage. The merging of battery and supercapacitor chemistries.
D. P. Dubal, O. Ayyad, V. Ruiz, and P. Gomez-Romero* Chem.Soc.Rev. 44(7):1777-90 **2015**

Our window to the hybrid material landscape



MnO_2

$H_3PMo_{12}O_{40}$

$LiFePO_4$

Inorganics

Carbons

COPs

CNT

G - GO

AC

PPy

PAni

PEDOT

PVK

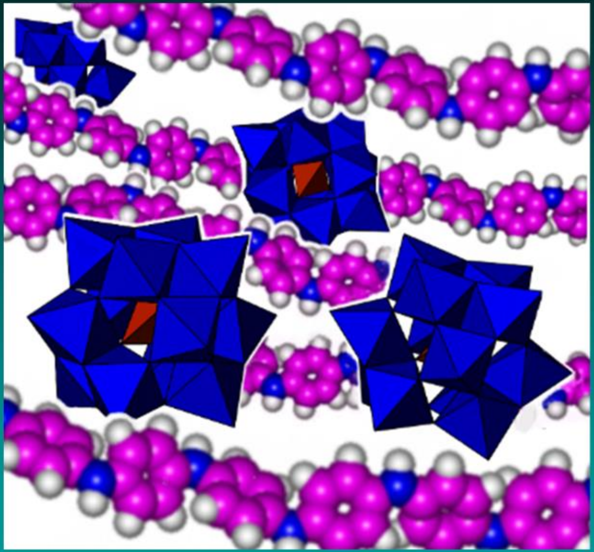
POMs and COPs

Integration of POMs in Conducting Polymers to form Hybrid (Organic-Inorganic) Nanocomposite Materials

•Applications:

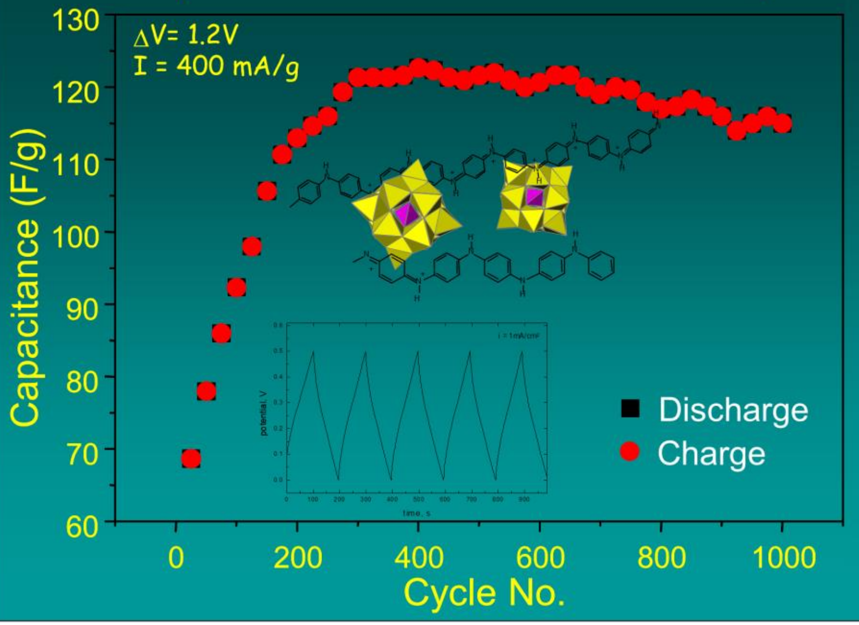
Energy storage
Catalysis
Magnetic
Sensors
Multifunctional
…

PAni/PMo12



Polyaniline $[PMo_{12}O_{40}]^{3-}$

Example: PAni/PMo12 electrochemical capacitor

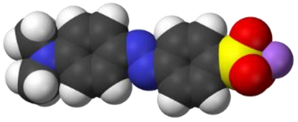


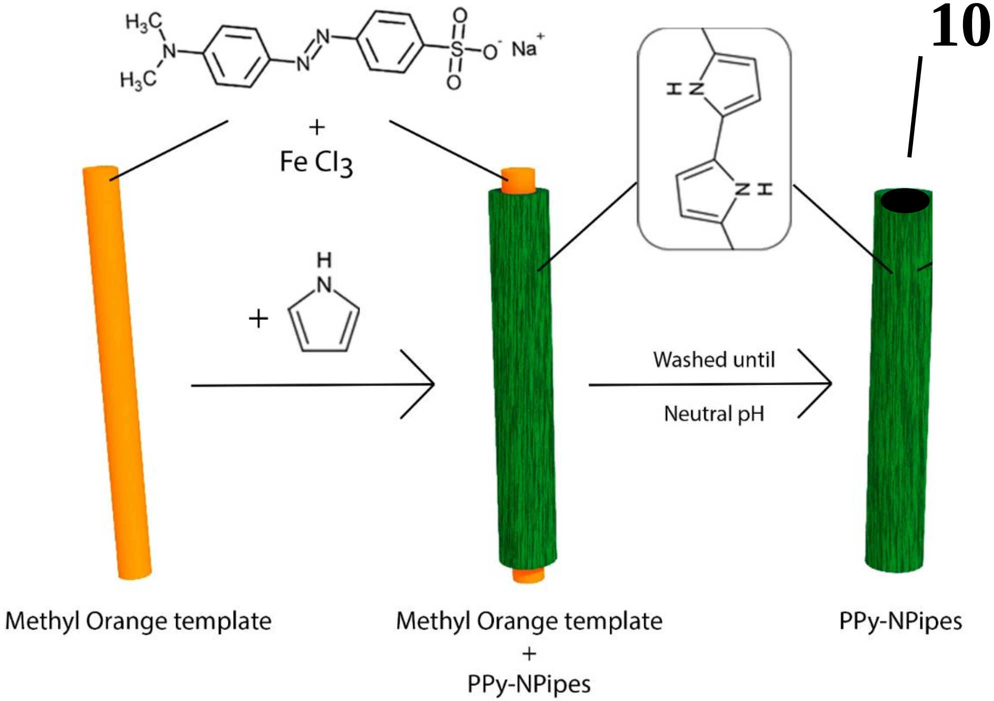
[1]P. Gómez-Romero, M. Lira-Cantú *Adv. Mater*. 9(2) **1997** 144-7.
[2] M. Lira-Cantú and P. Gómez-Romero* Chem.Mater. **1998**, 10, 698-704.
[3] PGomez-Romero Hybrid Organic-Inorganic Materials. In Search of Synergic Activity. Adv.Mater. **2001**, 13(3), 163-174.
[4] P Gómez-Romero*, M Chojak, K Cuentas-Gallegos, JA. Asensio, P Kulesza, N Casañ-Pastor and M Lira-Cantú. Electrochem. Commun. **2003**, 5, 149-153
[5] M. Lira-Cantú, P. Gómez-Romero, Chapter 7 of "Functional Hybrid Materials" P. Gómez-Romero and C. Sánchez (Editors). ISBN 3-527-30484-3 - Wiley-VCH, Weinheim, **2004**

The importance of Nano Micro structure

Polypyrrole Nanopipes

MO =

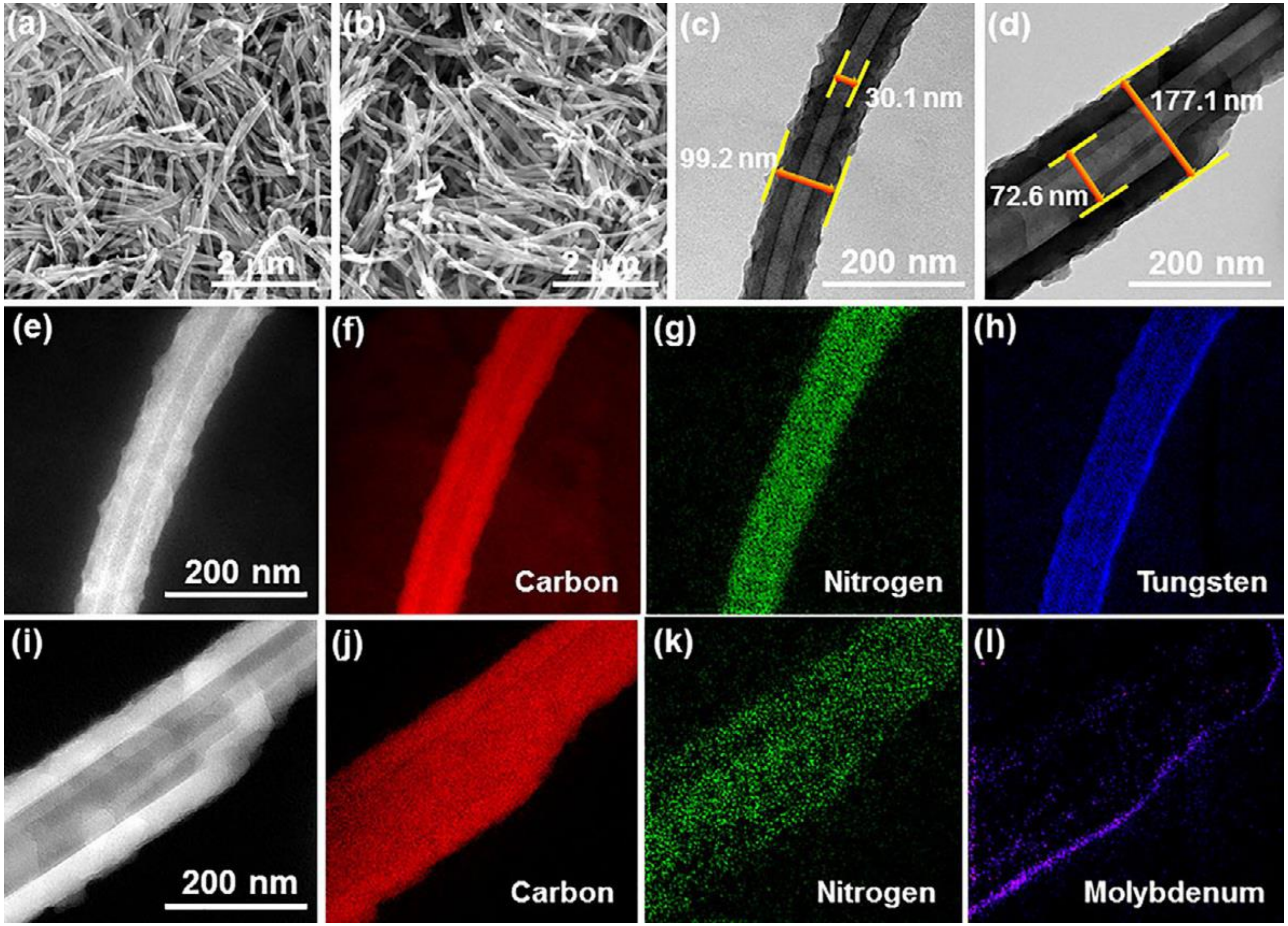




100 nm diameter

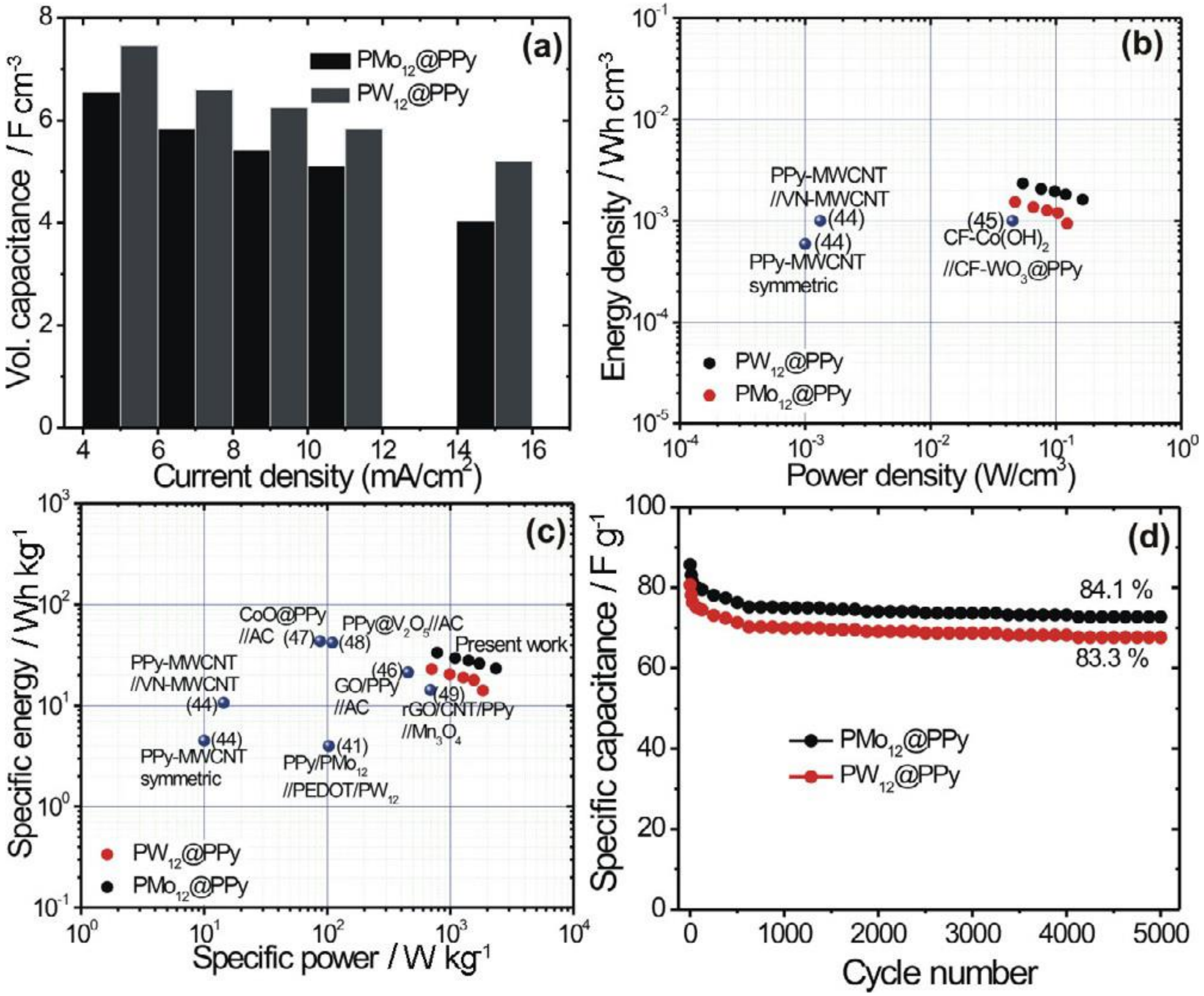
© Marta Castells

PPy NanoPipes and their Hybrids

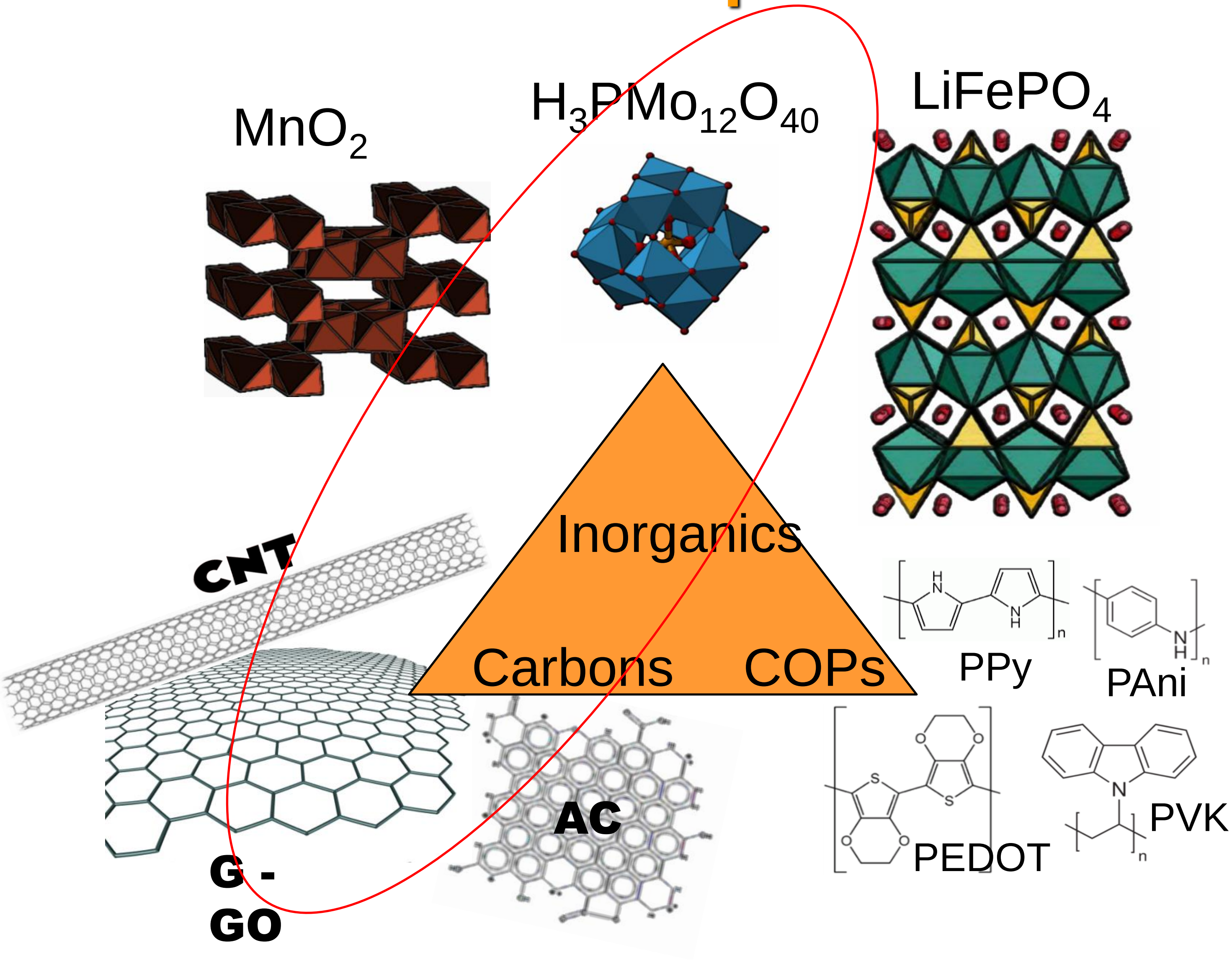


Functionalization of PPyNanopipes with Redox-Active Polyoxometalates for High Energy Density Supercapacitors
D. P. Dubal, B. Ballesteros, A. A. Mohite, P. Gómez-Romero, ChemSusChem **2017**, 10, 731-737.

PPy NanoPipes with POMs

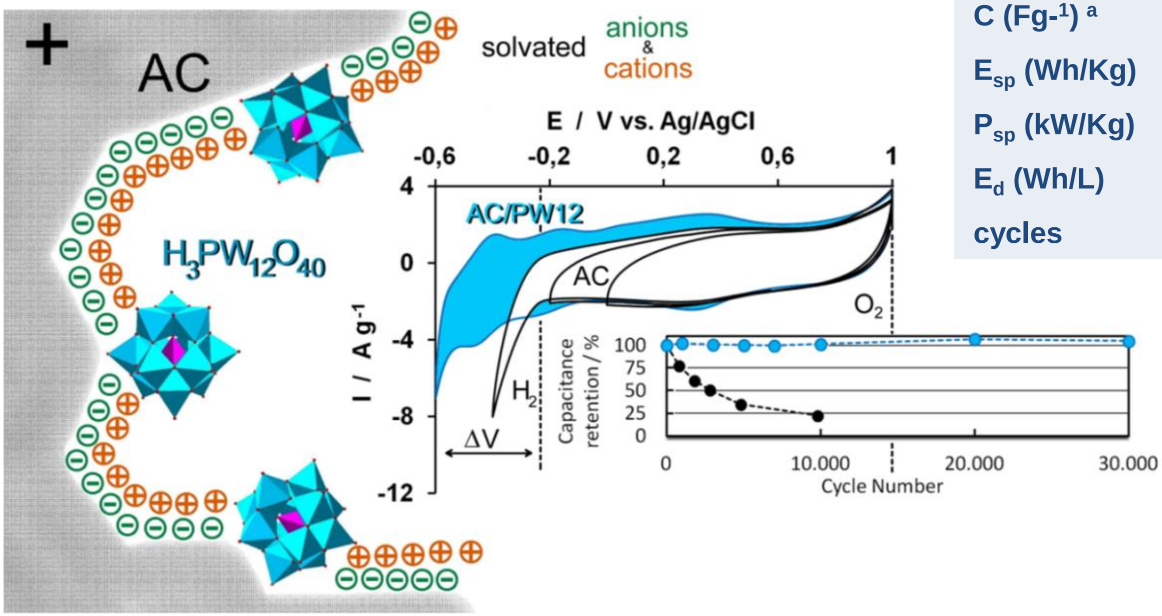


Our window to the hybrid material landscape



Hybrid Energy Storage:
Hybrid electrode materials

Hybrid Activated Carbon-$H_3PMo_{12}O_{40}$

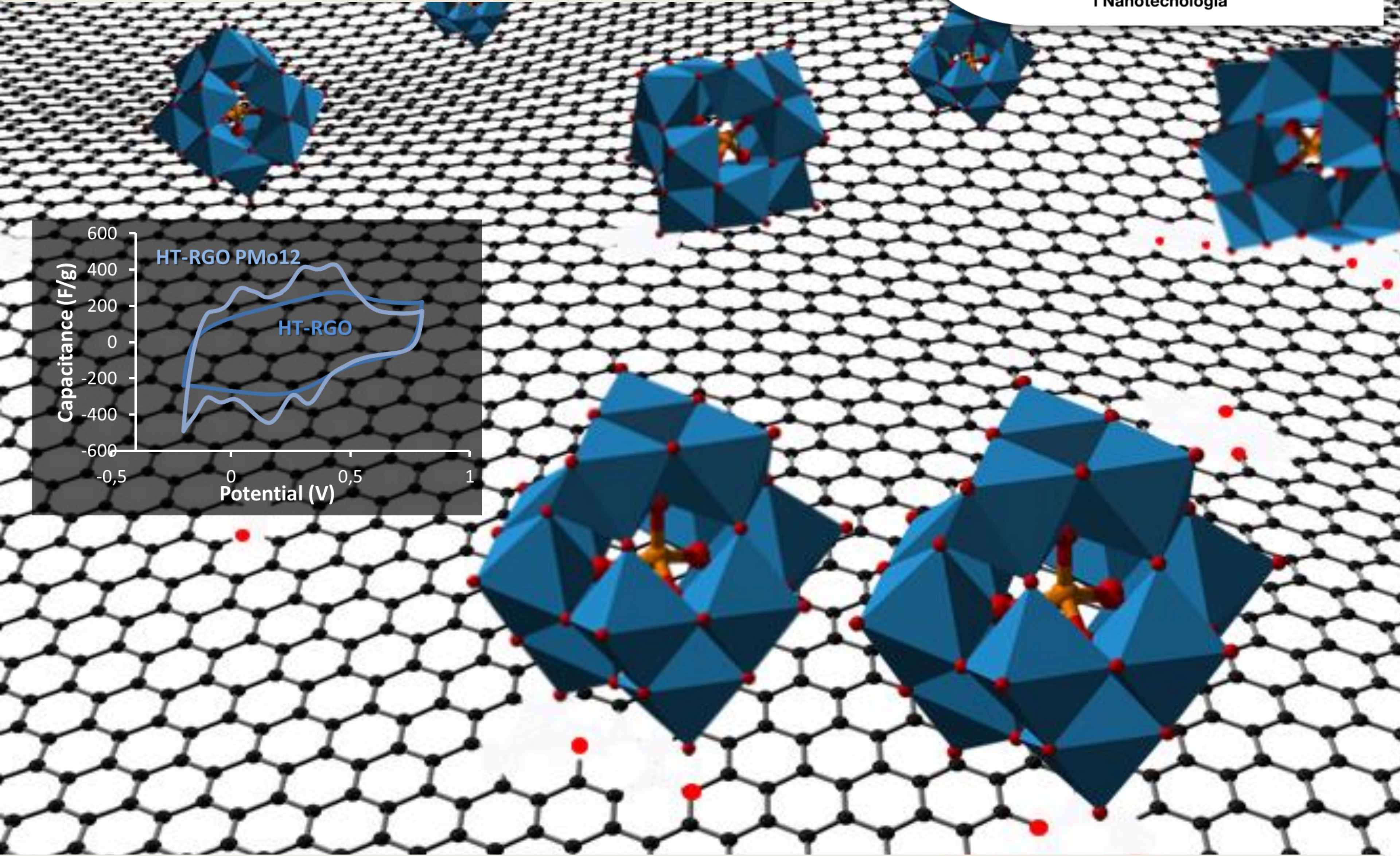


	AC	AC-PW12
C (Fg^{-1}) [a]	185	254
E_{sp} (Wh/Kg)	4.05	4.96 (1.6 A/g)
P_{sp} (kW/Kg)	45	115
E_d (Wh/L)	1.55	2.32
cycles	10,000	> 30,000 (6 A/g)

1.6V
in 1M H_2SO_4 !

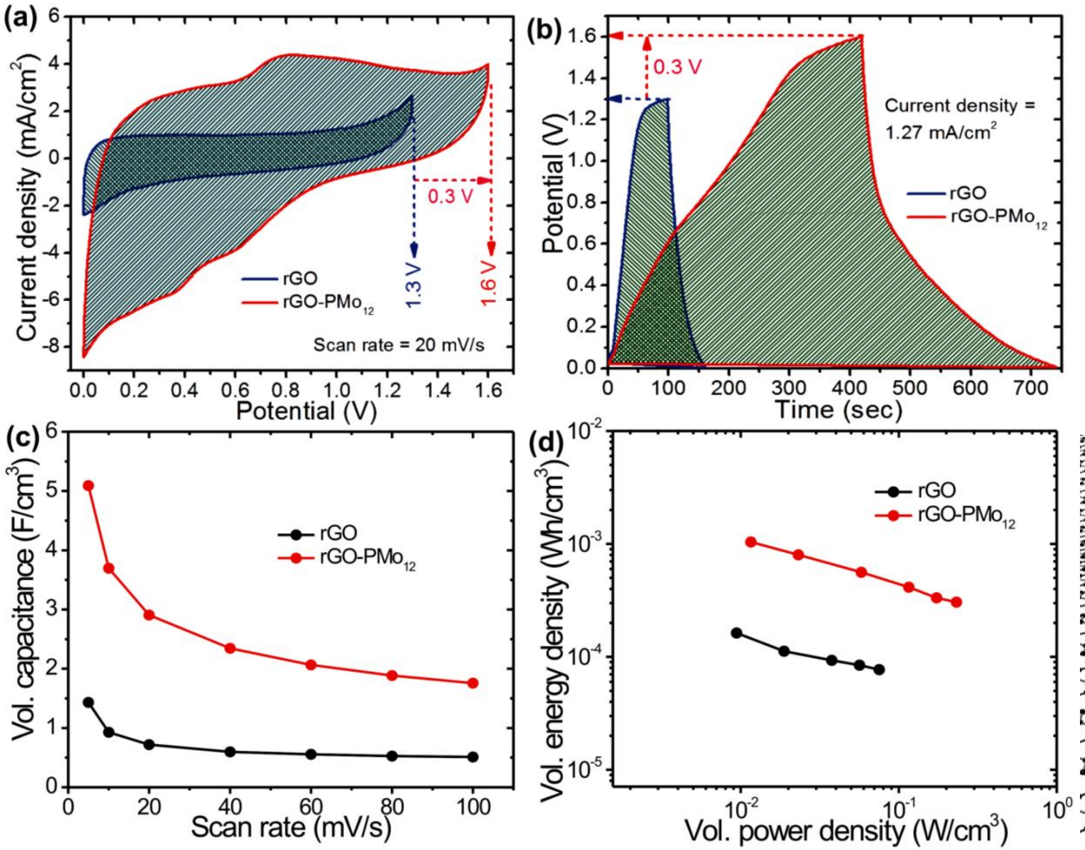
Hybrid Energy Storage: High Voltage Aqueous Supercapacitors based on Activated Carbon / Phosphotungstate Hybrid Materials.
J. Suárez-Guevara, V. Ruiz, P. Gomez-Romero J. Mater. Chem. A, **2014**, 2 (4), 1014-1021

Electroactive RGO-POM Hybrids



J. Suárez-Guevara, V. Ruiz, P. Gomez-Romero*, Phys. Chem. Chem. Phys. **2014**, 16 (38), 20411

Hybrid Graphene Polyoxometalate Electrodes

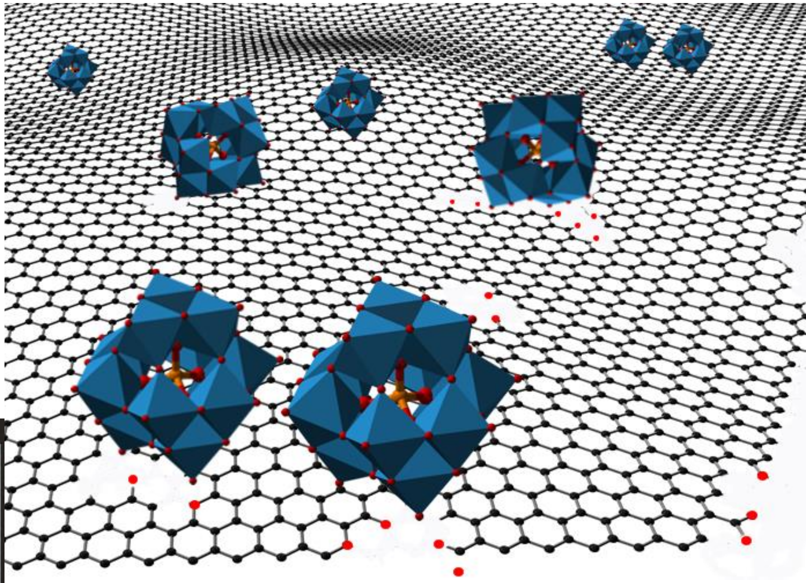


Hybrid Energy Storage:

Hybrid electrode materials

+ Electroactive electrolyte

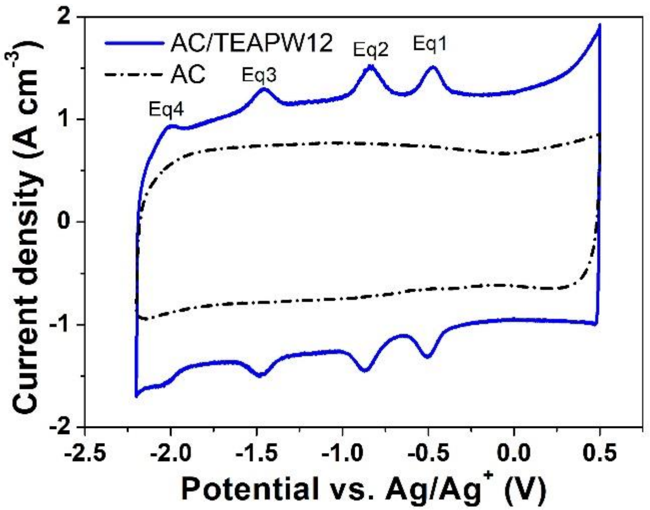
rGO / $H_3PMo_{12}O_{40}$ / HQ

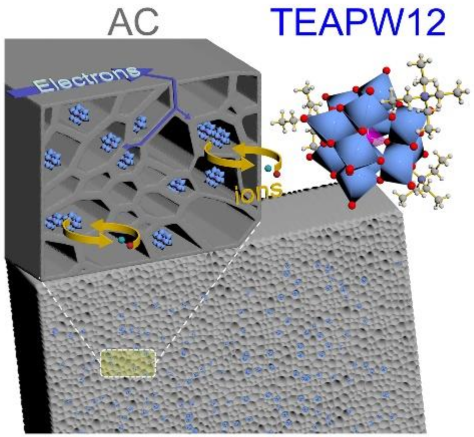


31 LEDs powered with a single rGO-PMo$_{12}$ symmetric cell with 0.2 M HQ doped polymer gel electrolyte.
30 s charge 2 min lit

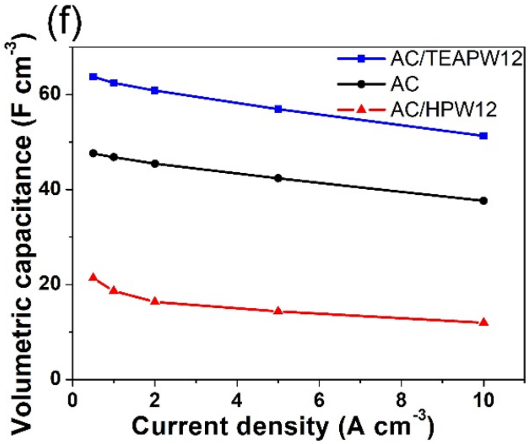
D.P. Dubal ... P. Gomez-Romero Journal of Materials Chemistry A, 2015, 3(46), 23483

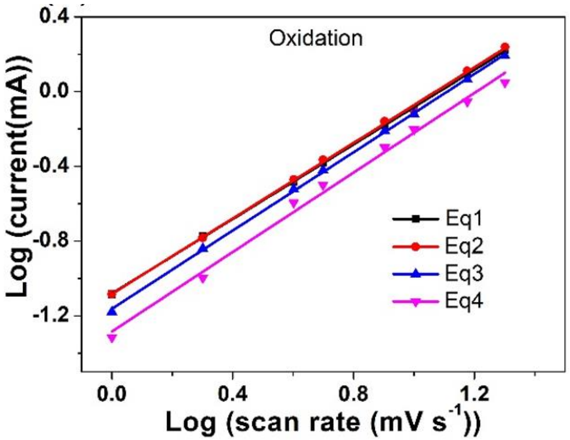
AC/POMs Hybrid electrodes in organic electrolytes





1M TEA BF_4
in CH_3CN





$$i = a v^{b}$$

current

scan rate

b=1
NOT
limited
by diffusion

Can polyoxometalates enhance the capacitance and energy density of activated carbon in organic electrolyte supercapacitors?
Jun-Jie Zhu, Raul Benages-Vilau, Pedro Gomez-Romero* Electrochimica Acta **2020** 137007

Conclusions

- Polyoxometalates have a very rich chemistry of their own.
- They are ideal quantum models for W, Mo or V oxides (i.e. with all 12 MO6 units on the surface of a Keggin anion)
- Their integration in e^--conducting or insulating matrices leads to synergic electrode or electrolyte materials respectively
- Hybrid electrodes show dual (Faradaic-capacitive) energy storage + more synergic effects (overpotentials leading to increased V and E
- Their utterly dispersed nature and reversible multi-electron redox chemistry can result in fast (not diffusion hindered) e^- transfer.
- But remember the importance of Nano- Micro-structure

NEO-Energy Lab

Prof. Pedro Gómez-Romero

ICN2
Institut Català
de Nanociència
i Nanotecnologia
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EARTHDAS

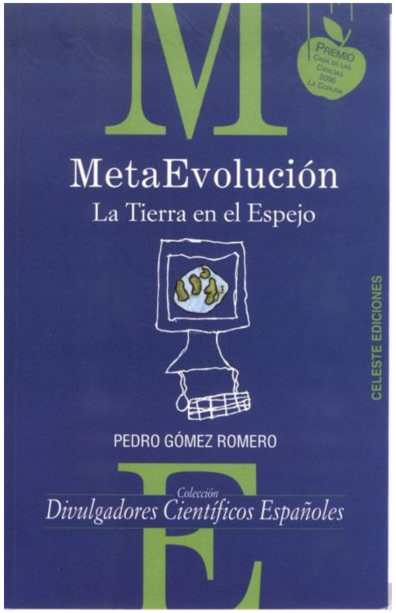
NEO-Energy Group @ ICN2 May 2019

Dani Rueda, Verónica Fabián, Bhawna Nagar, Pedro Gómez, Raúl Benages, Carlos Marchante, Rocío Rodríguez, Jun-Jie Zhu

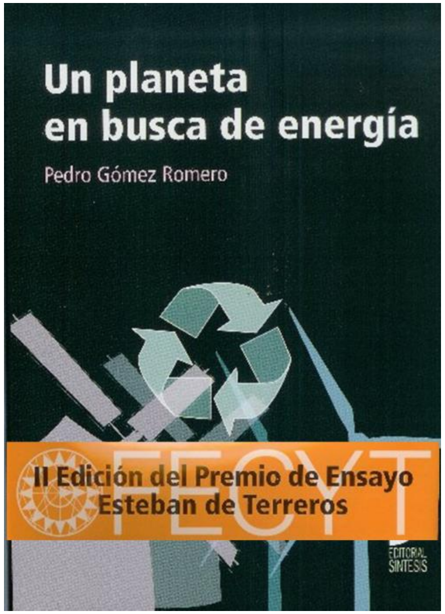
Gracias

… for your attention!

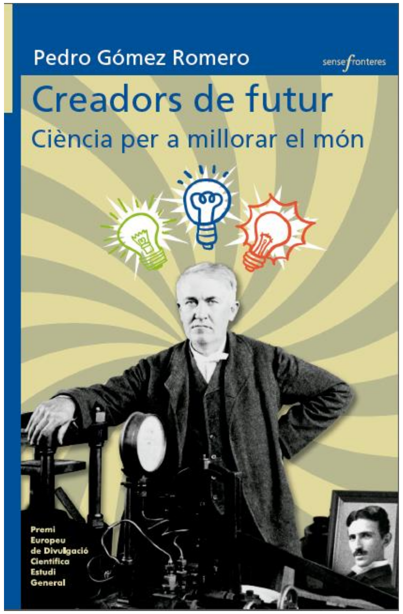
NEO-Energy Group.
Social communication of science



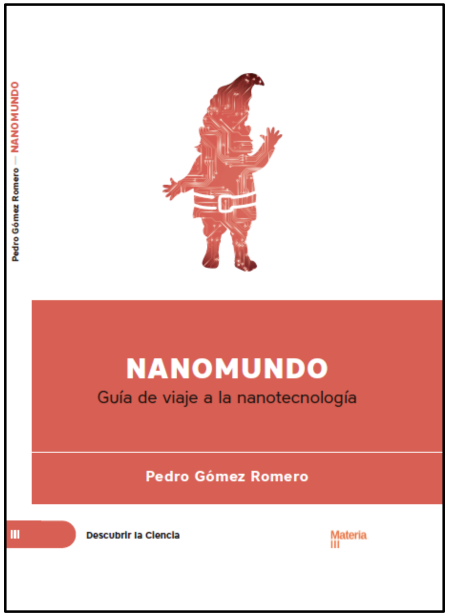
Celeste, 2001



Síntesis, 2007



Bromera, 2016



Materia/EP, 2016