Nanocarbon-metal oxide junctions in electrocatalytic energy processes

Michele Melchionna

Email: melchionnam@units.it

UNIVERSITÀ
DEGLI STUDI DI TRIESTE

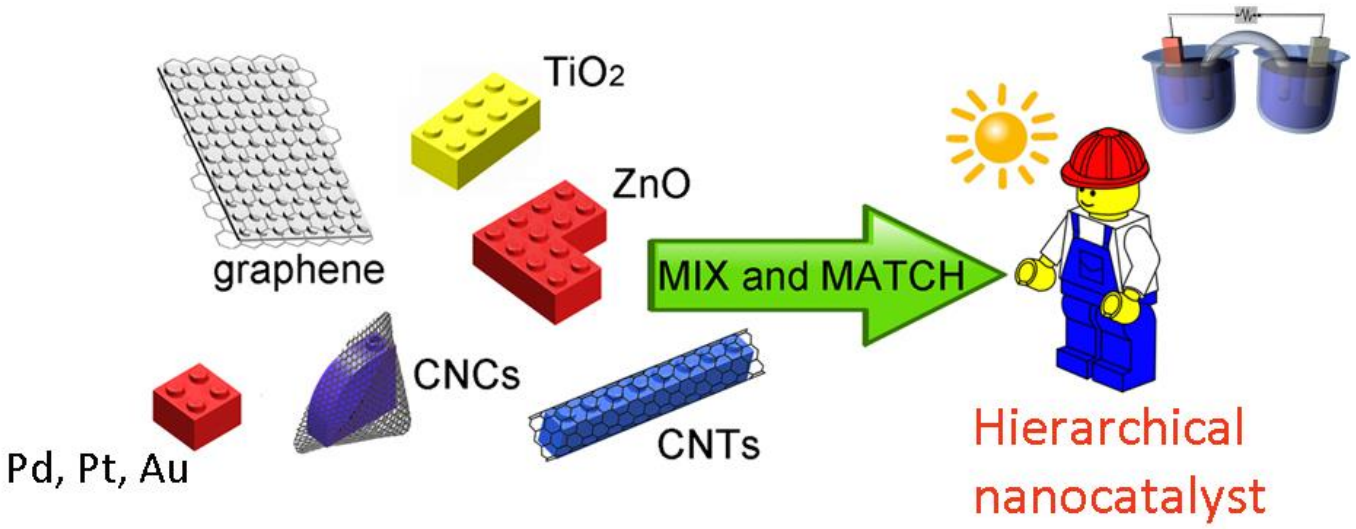
Ljubljana
5th February
2020

Nanostructure-based (electro)catalysis

"God made solids, but surfaces were the work of the Devil"

Wolfgang Pauli

Carbon nanostructures/metal oxide interfaces



CO_2 reduction

H_2 evolution

N_2 reduction

H_2O oxidation

O_2 reduction

Photocatalysis:

Semiconducting metal oxide:
Excited charges generation

Nanocarbon: electron or hole sink.
Retard of the recombination rate

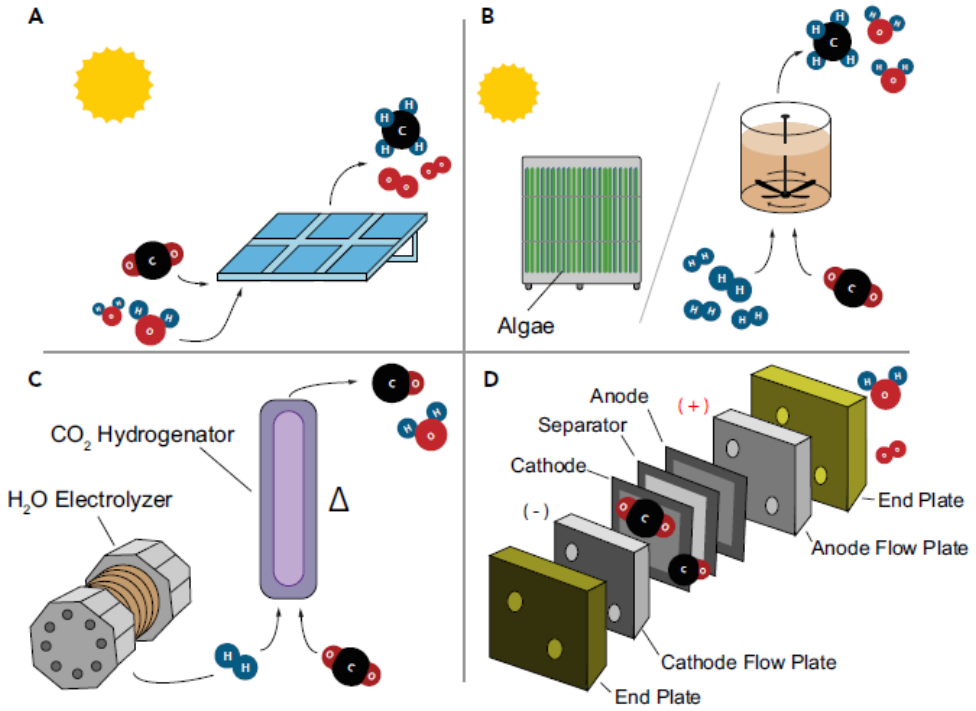
Electrocatalysis:

Semiconducting metal oxide:
Different roles (catalyst, capturing agent, co-catalyst…)

Nanocarbon: improve electron transfer

M. Melchionna, M. Prato, P. Fornasiero *Catal. Today* **2016**, *277*, 202-213

Carbon nanostructures/metal oxide interfaces



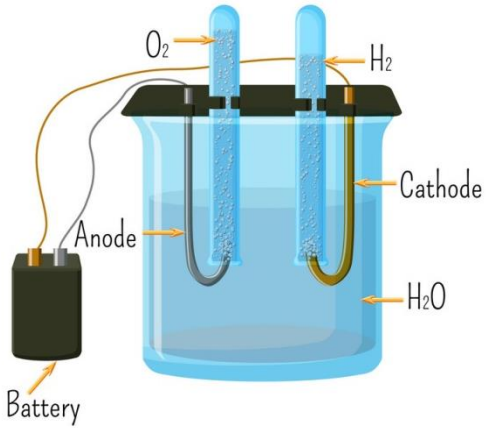
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ $E^\circ = -0.53V$

$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$ $E^\circ = -0.61V$

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ $E^\circ = -0.38V$

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ $E^\circ = -0.24V$

$CO_2 + e- \rightarrow CO_2^{\bullet -}$ **$E^\circ = -1.90V$.**



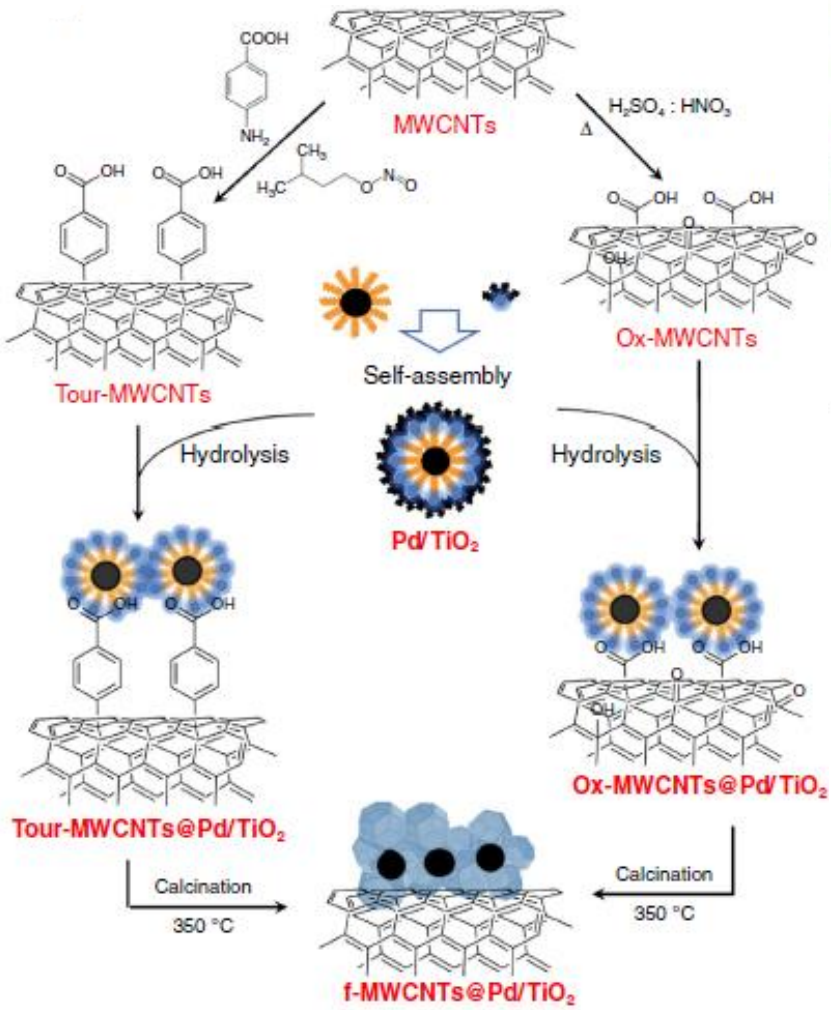
$2H_2O \rightarrow 2H_2 + O_2$

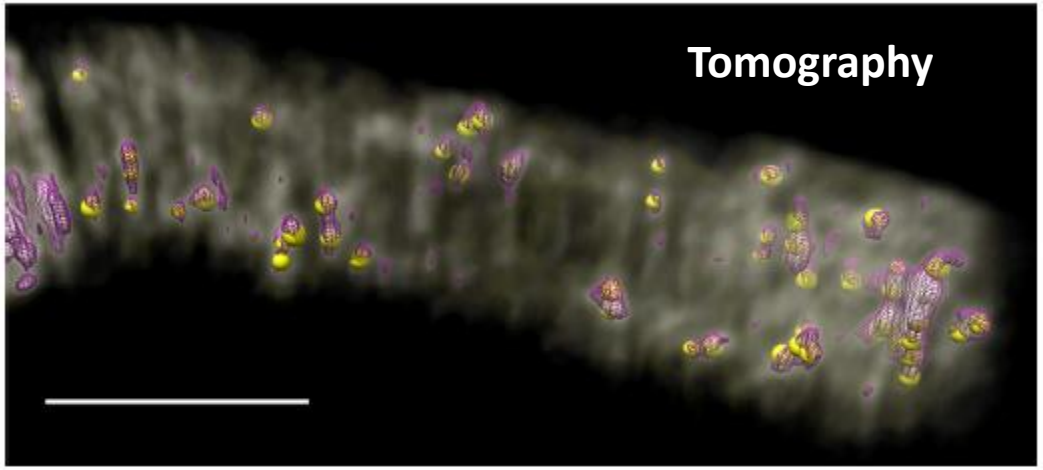
Anode: $2H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$ $E^o = +1.23$ V

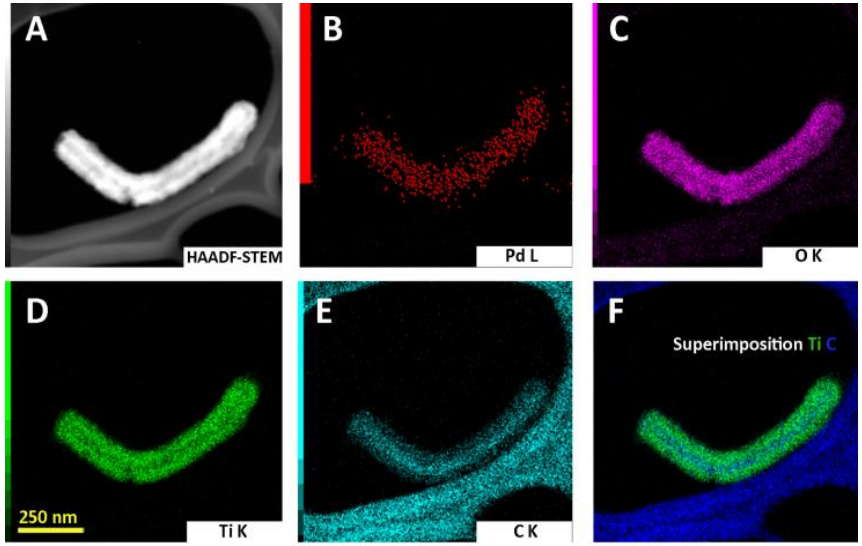
Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^o = 0.00$ V

$\Delta G = 237$ kJ mol^{-1}

A versatile hierarchical material: CNT@TiO_2@Pd

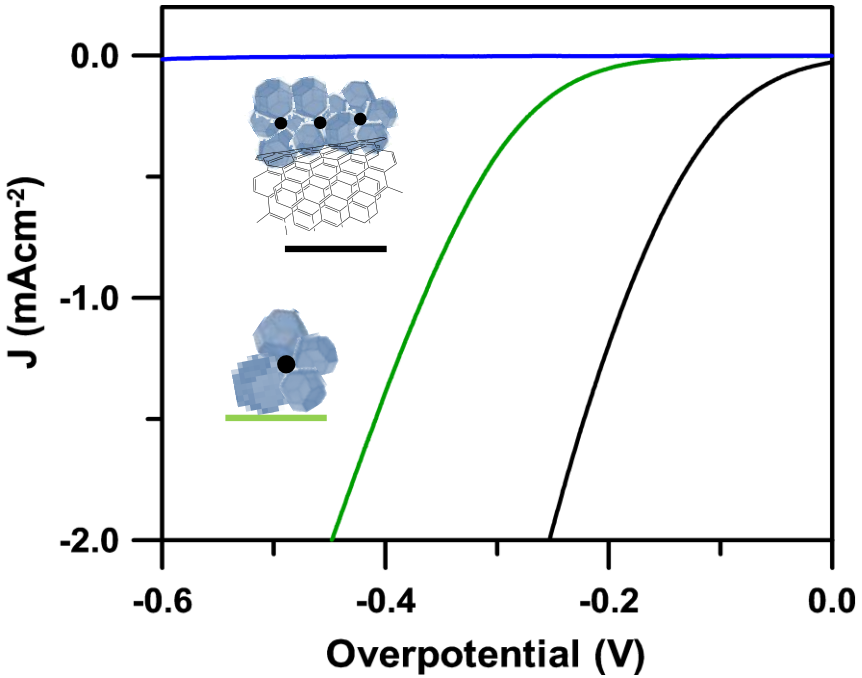




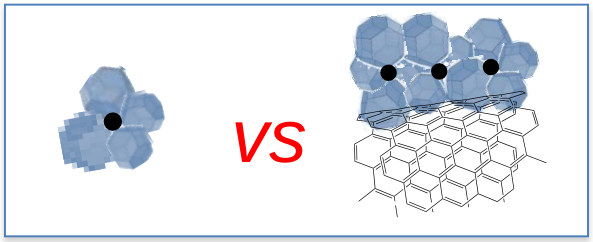


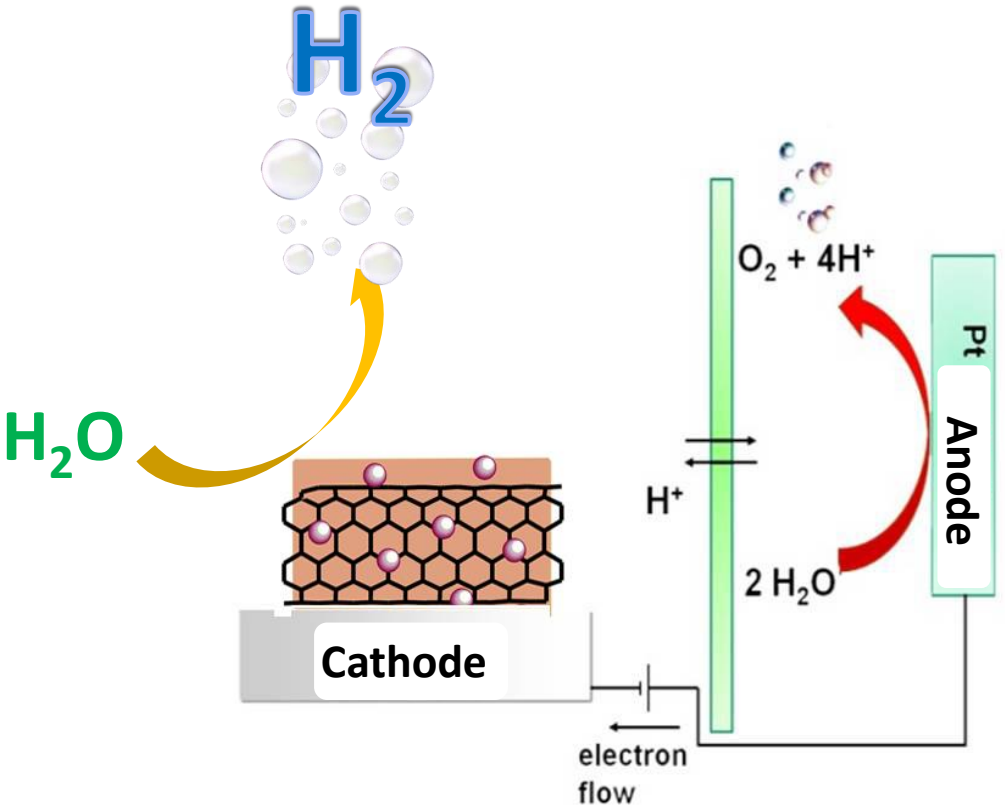
Nature Communications **2016**, *7,* article number: 13549

Electrocatalytic H_2 production: Effect of the CNTs



Linear Sweep Voltammetry for f-MWCNT@Pd/TiO_2 (black) Pd/TiO_2 (green) and bare GC electrode (blue).

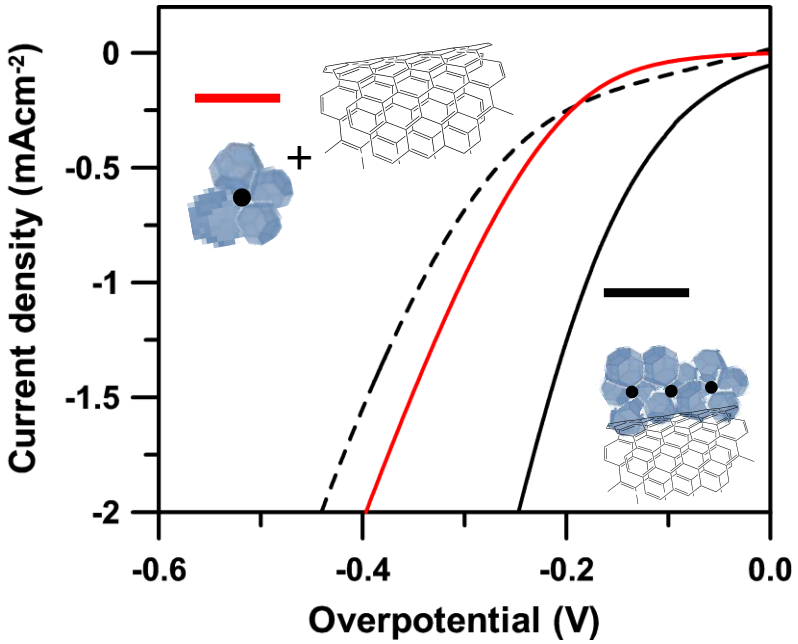


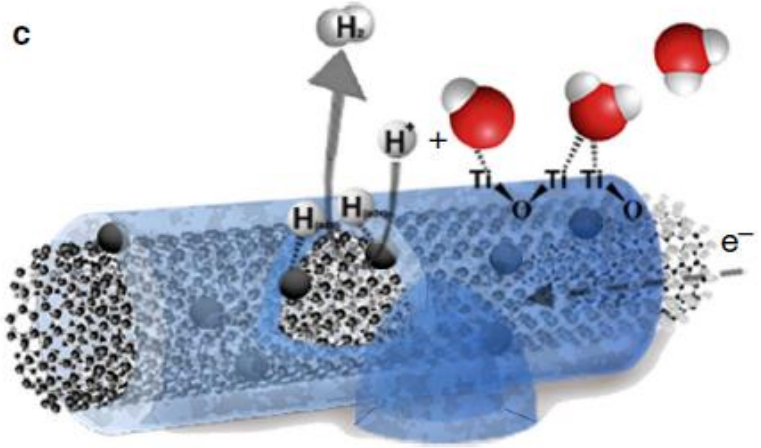


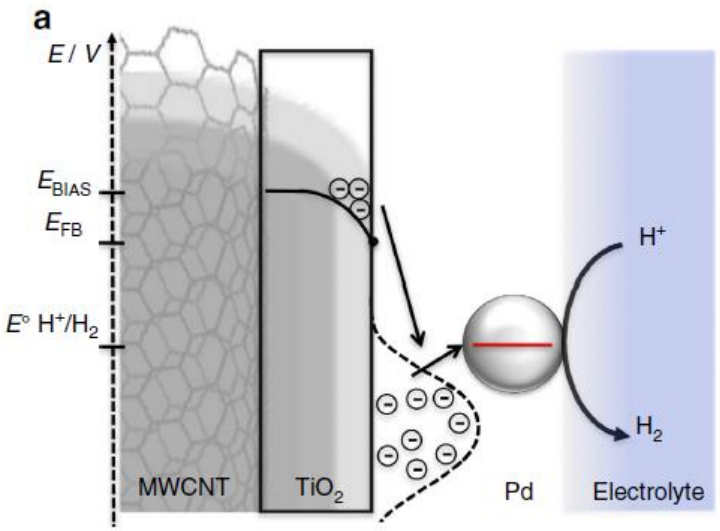
200 mV reduction in the overpotential

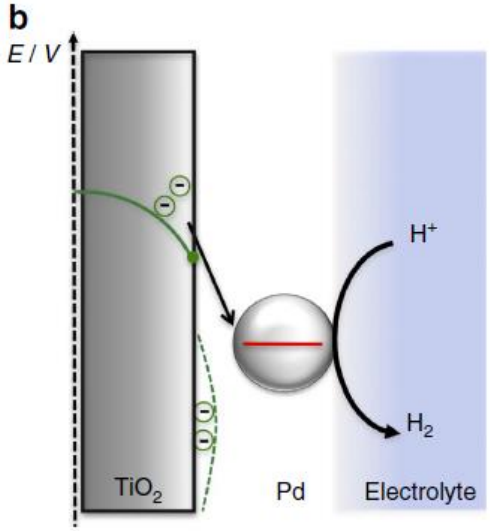
Nature Communications **2016**, *7,* article number: 13549

Effect of the interfacing and nanostructuring







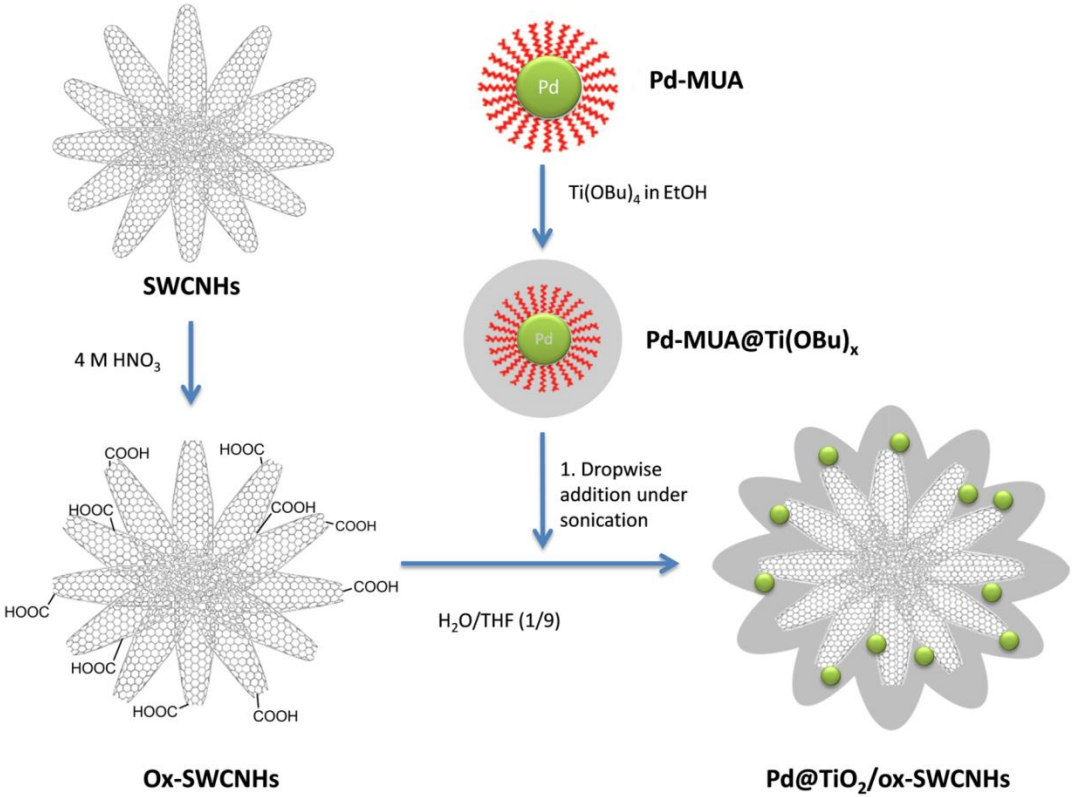


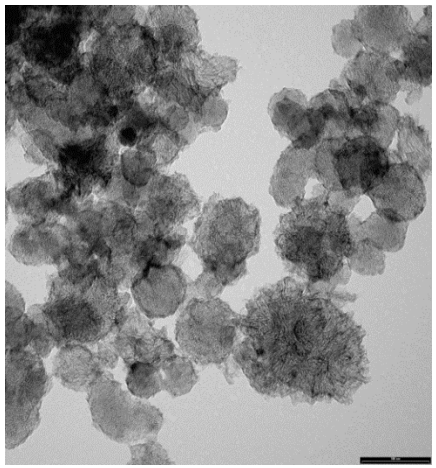
Presence of surface state at the interface CNT/TiO_2 : free electrons

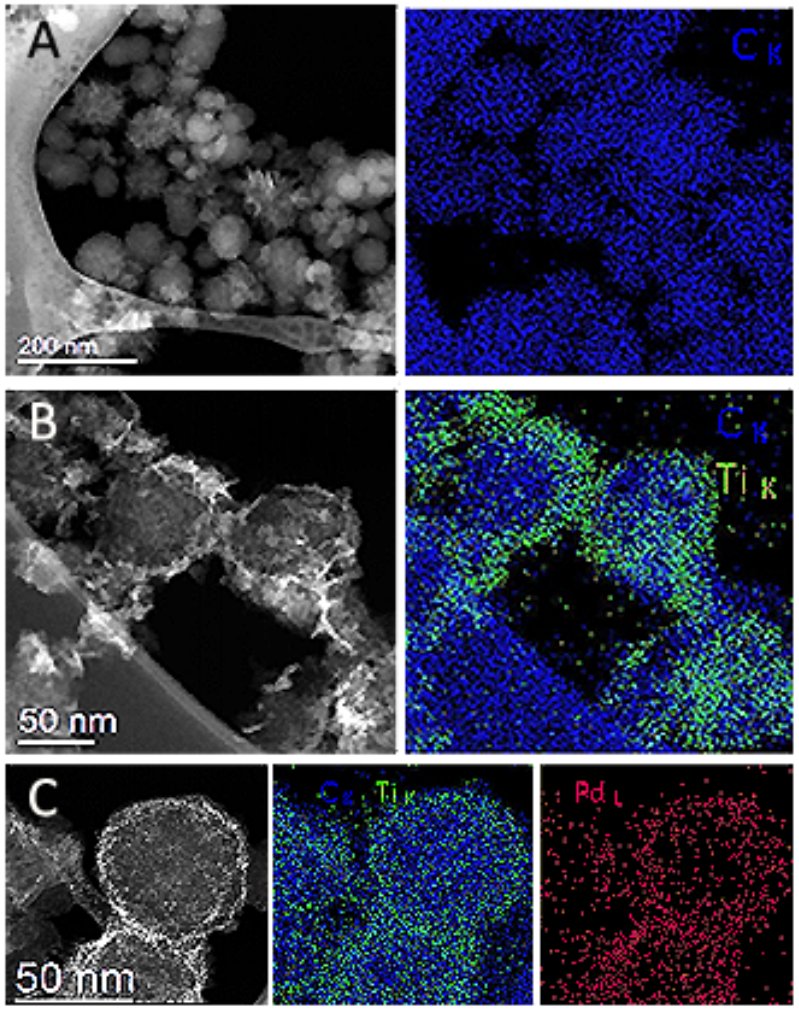
Better coupling with Pd nanoparticles

Faster kinetics

CO_2 reduction: Carbon nanohorns@TiO_2@Pd

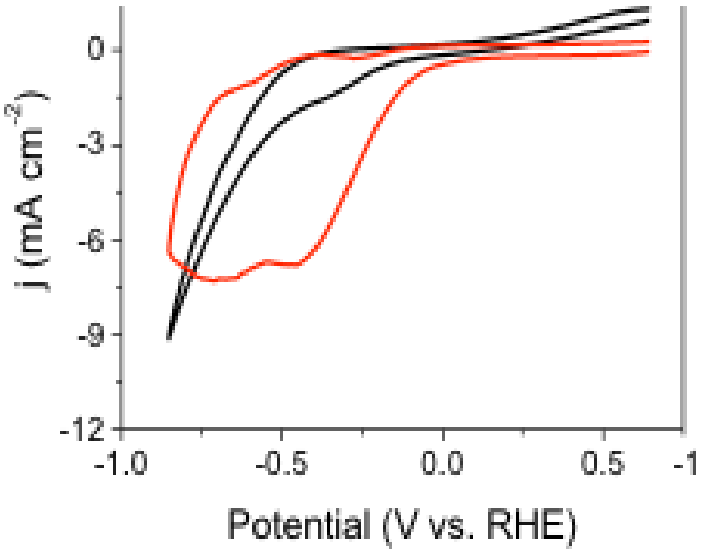


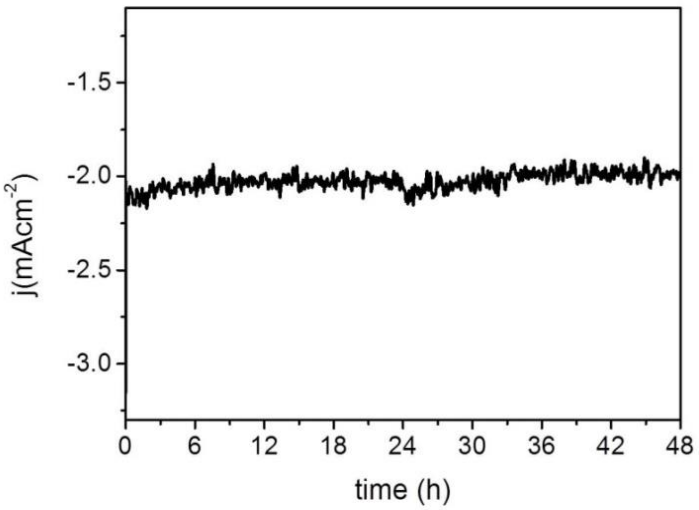


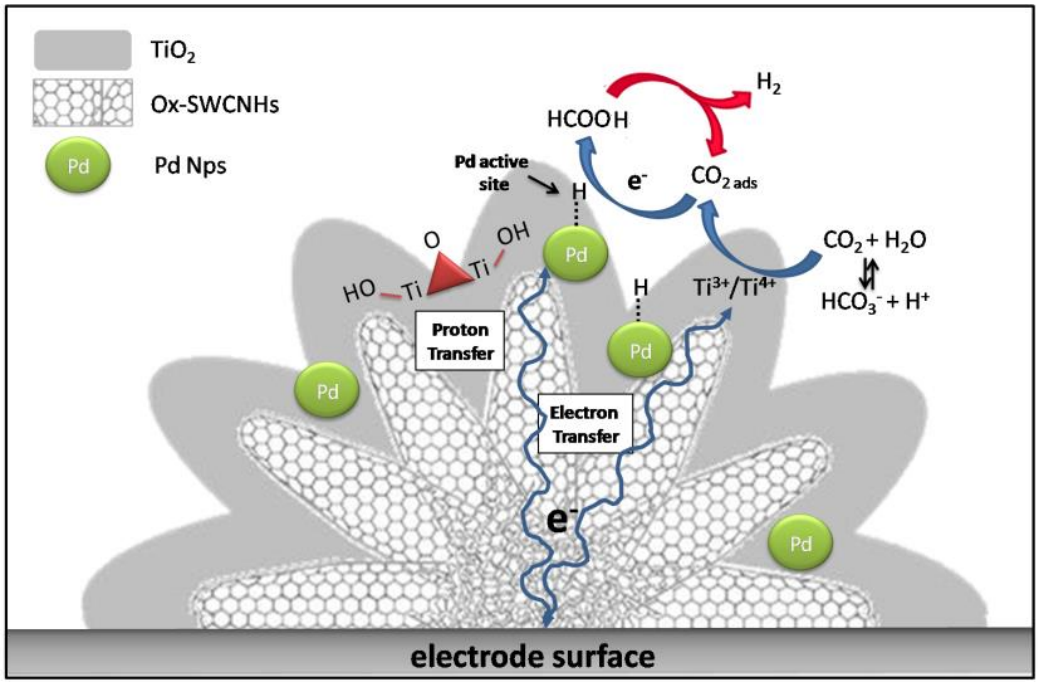


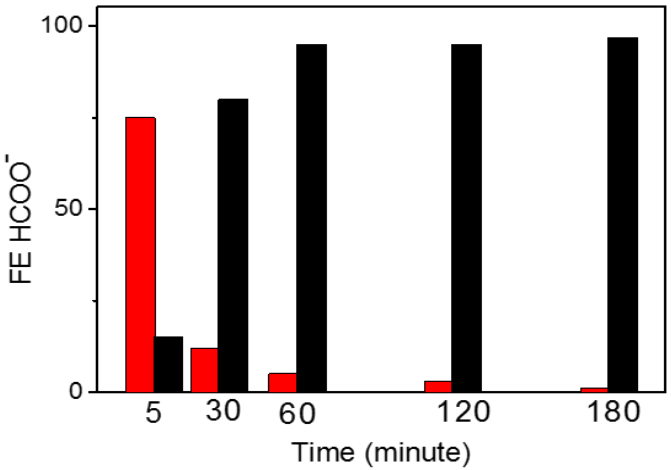
Energy Environ. Sci. **2018**, *11*, 1571-1580

CO_2 reduction: CO_2 electroreduction to formic acid



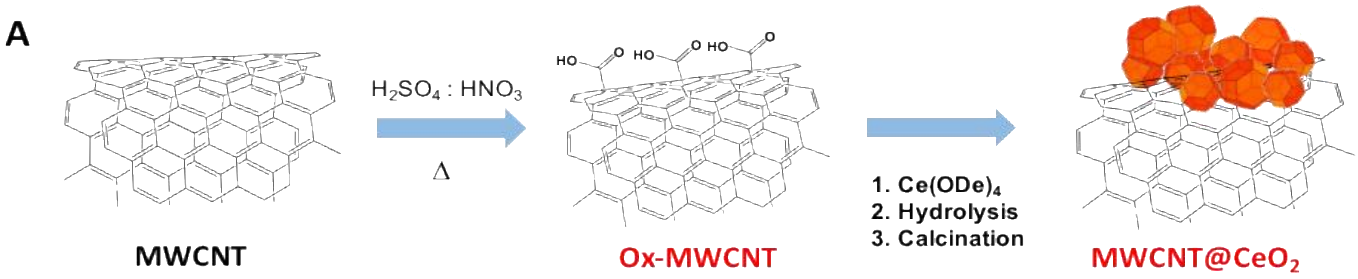


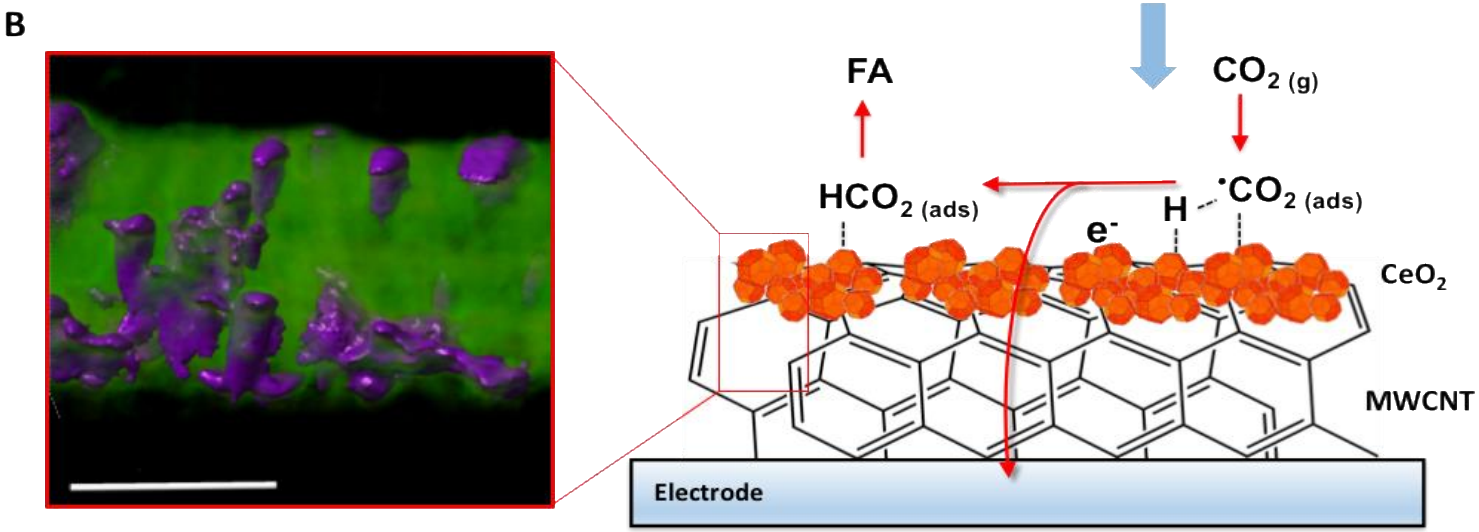


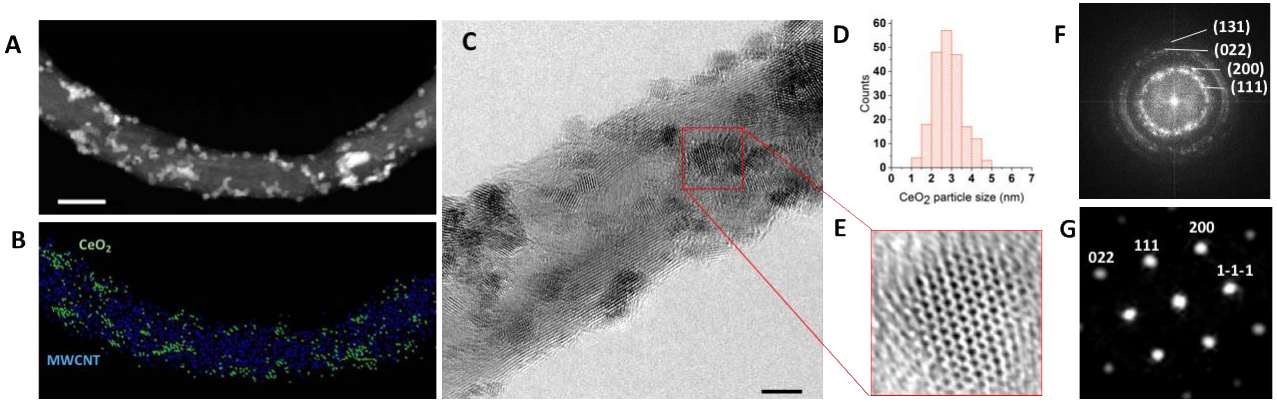


Energy Environ. Sci. **2018**, *11*, 1571-1580

Get rid of noble metals: Carbon nanotubes/CeO_2

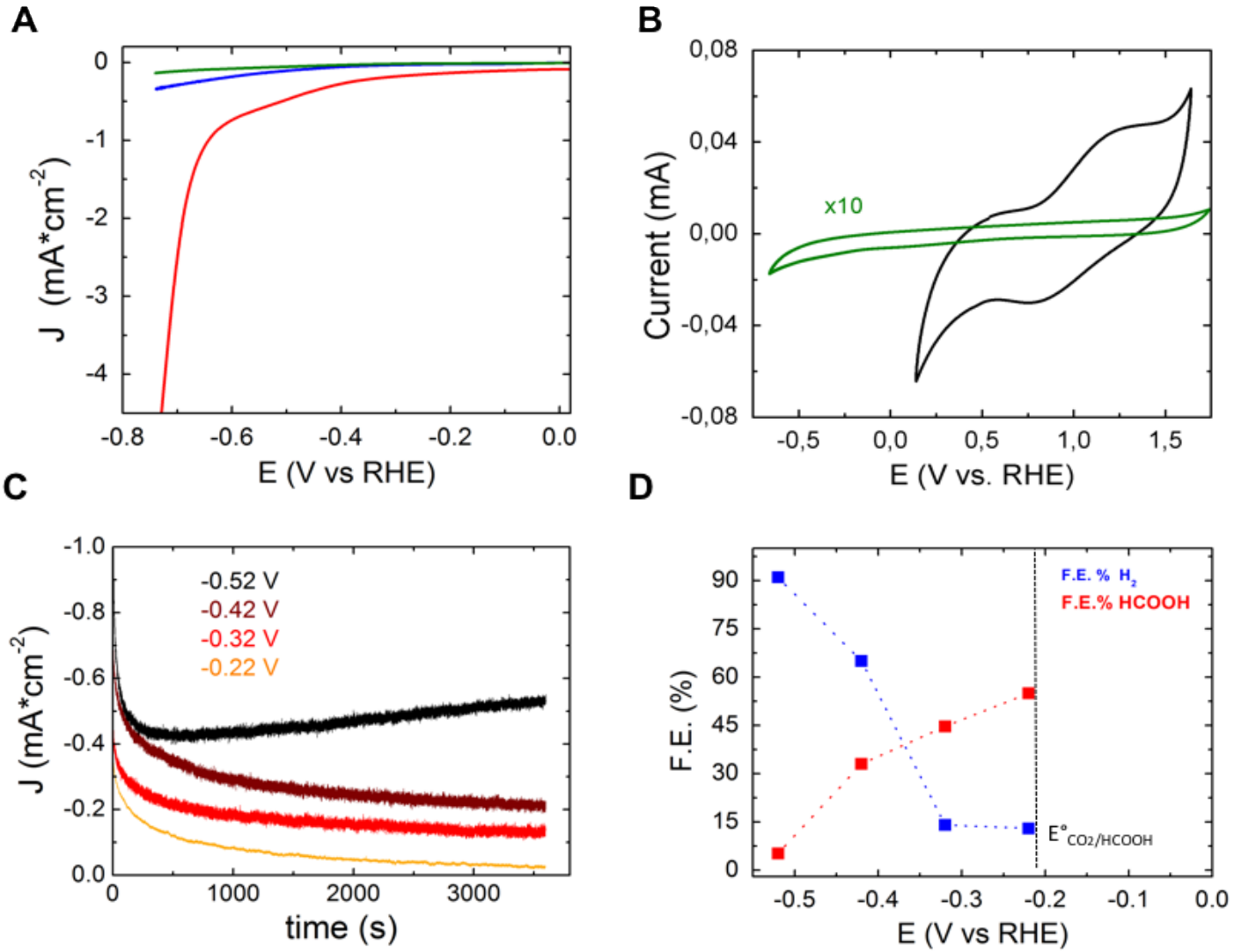






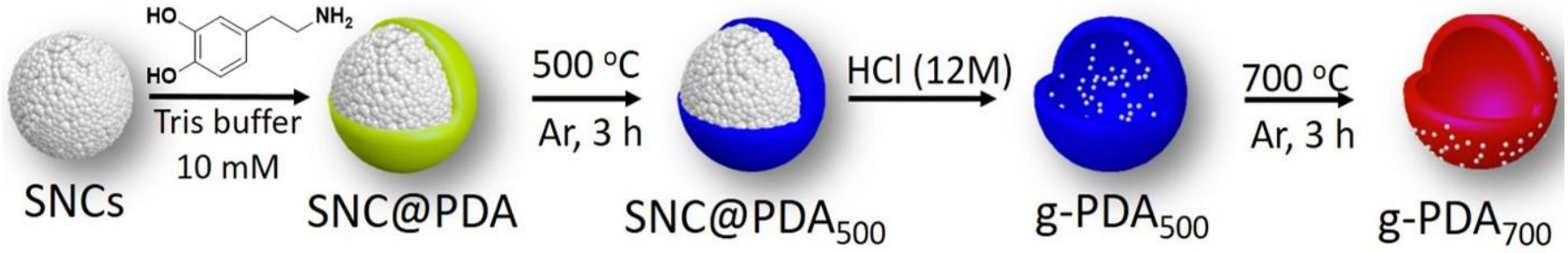
Submitted (under review)

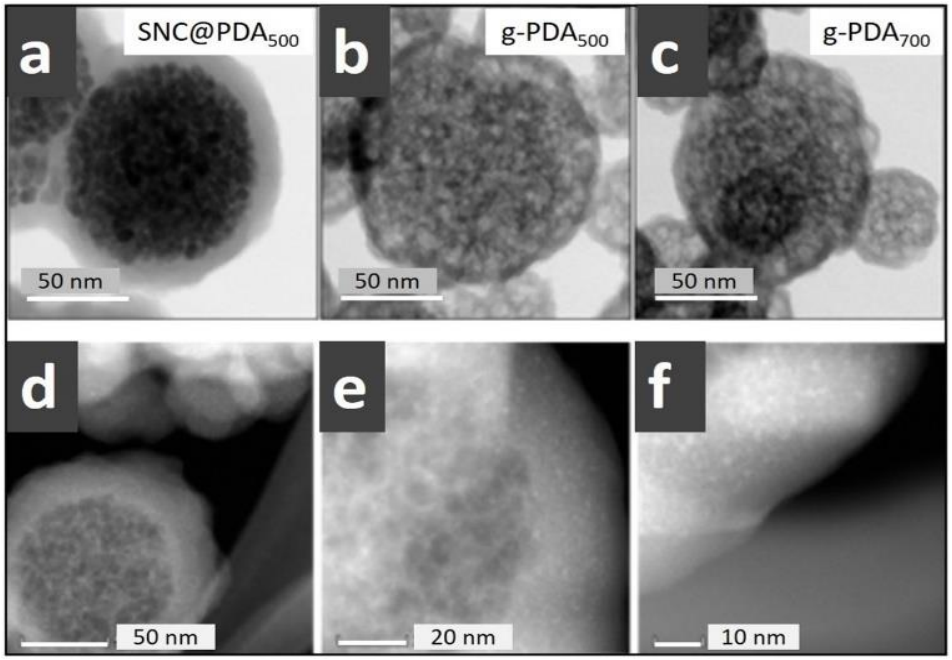
Get rid of noble metals: Carbon nanotubes/CeO_2



O_2 reduction: Ex-solution Surface modification

SNC = superparamagnetic nanoparticle clusters of γ-Fe_2O_3





Sample	E_{onset} (V)	$E_{applied}$ (V)	$j^{[1]}$ (mA cm^{-2})	x_{H2O2} (%)
$SNC@PDA_{500}$	0.67	0.6	-0.098	72
		0.5	-0.22	62
$g\text{-}PDA_{500}$	0.64	0.6	-0.11	63
		0.5	-0.14	28
$g\text{-}PDA_{700}$	0.60	0.6	-0.30	9
		0.5	-0.42	8

Collaboration with Prof. Darko Makovec and Dr. Slavko Kralj

ACS Appl. Nano Mater. **2019**, *2*, 6092-6097

Conclusions and perspectives

Nanocarbons can be useful components in the design of hierarchical catalysts for Electrocatalytic applications

Opportune interface with other phases and make it functional (rational synthetic design)

Translation of fundamental knowledge to large scale devices

For catalysis: Advanced techniques (*in situ* or *in operando*) to aid understanding of mechanism

Computational chemistry to help design

ACKNOWLEDGEMENTS

Thank You!

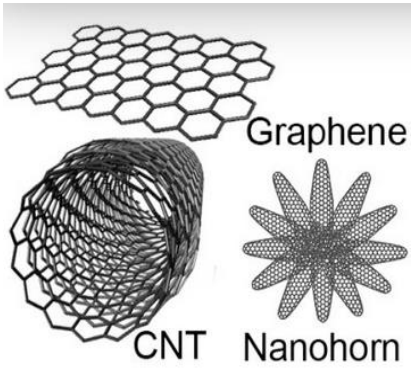
Prof. Marcella Bonchio (Universita' di Padova))
Prof. Francesco Paolucci (Universita' di Bologna)
Prof. Claudio Tavagnacco (Universita' di Trieste)
Dr. Victoria Bracamonte (National University of Cordoba)
Dr. Giovanni Valenti (Universita' di Bologna)
Dr. Lucia Nasi (IMEM-CNR, Italy)
Dr. Manuela Bevilacqua (ICCOM-CNR)

MultiComp

https://www.marchesanlab.com/multicomp

FREE REGISTRATION !
12-13 Mar 2020
TRIESTE

ORAL SLOTS AVAILABLE!



Confirmed Speakers

Prof. Paola Ayala (University of Vienna, Austria)
Prof. Jan Peters MBE (Katalytic, UK)
Prof. Maurizio Prato (University of Trieste & CIC BiomaGUNE, Spain)
Dr. Lok Kumar Shrestha (NIMS, Japan)
Dr. Jonathan P. Hill (IPC, Japan)
Felicite Ruddock (LJMU, UK)

cost
EUROPEAN COOPERATION IN SCIENCE & TECHNOLOGY