

11- Luglio, Unione Industriale, Via Fanti 17, Torino

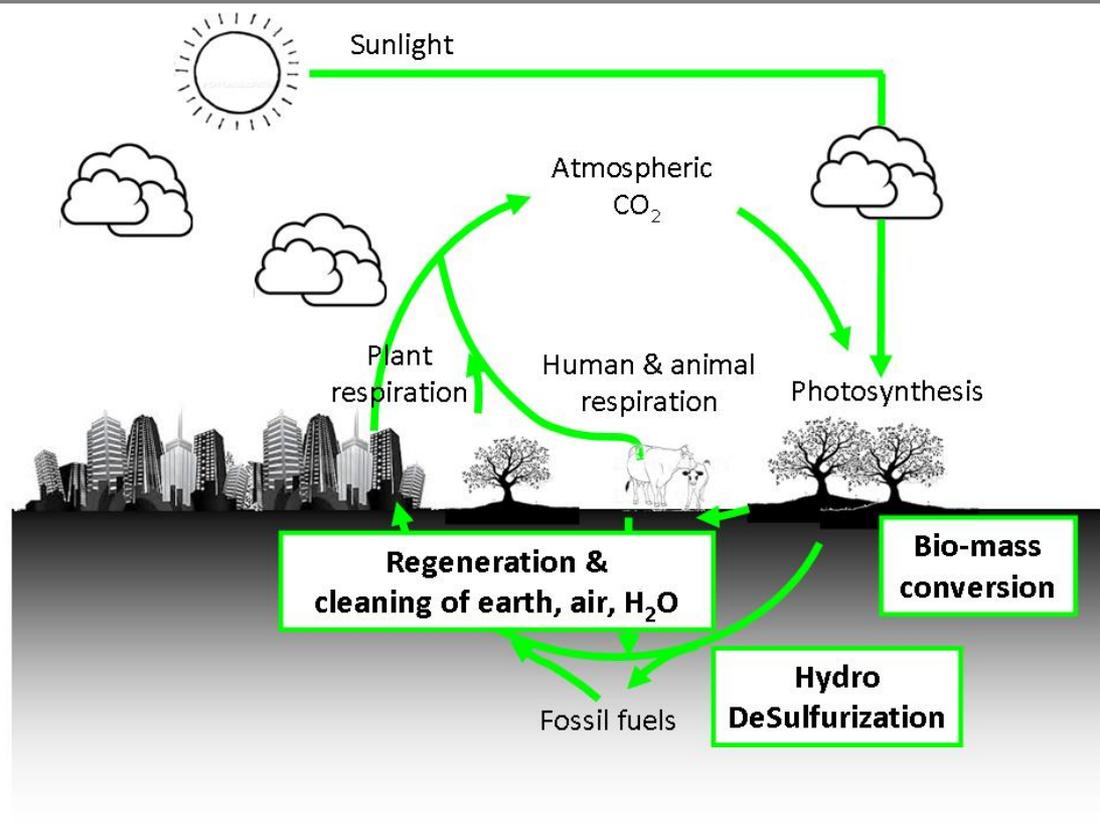


Materiali per l'energia e le "clean technologies"



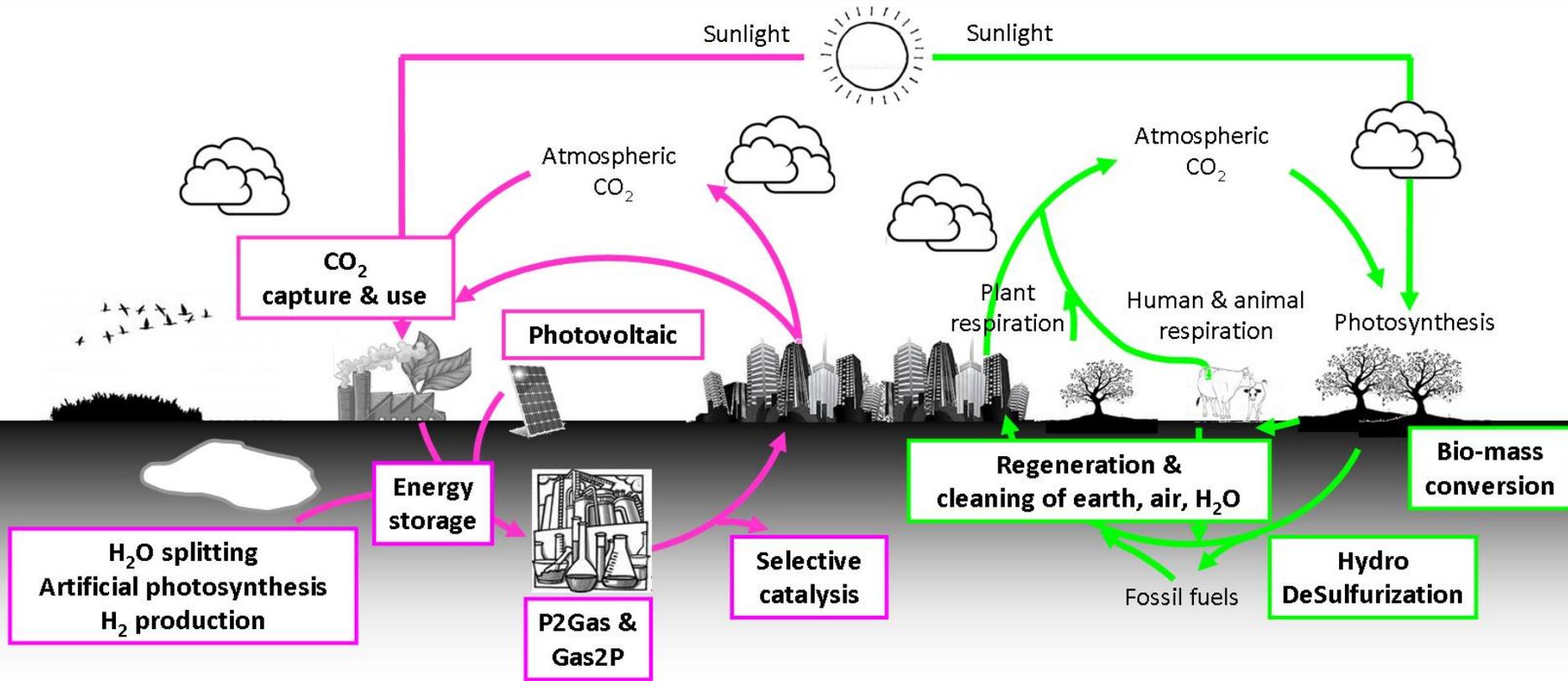
Silvia Bordiga

Il carbonio è un mattone fondamentale per tutte le forme di vita sulla Terra, e il suo riciclo naturale dall'atmosfera è un processo perpetuo, ma...



...il tempo richiesto per la “capitalizzazione” dell’energia solare in risorse fossili è ordini di grandezza superiore a quanto l’uomo possa aspettare.

Il ciclo del carbonio basato sulla fotosintesi naturale può essere integrato da...

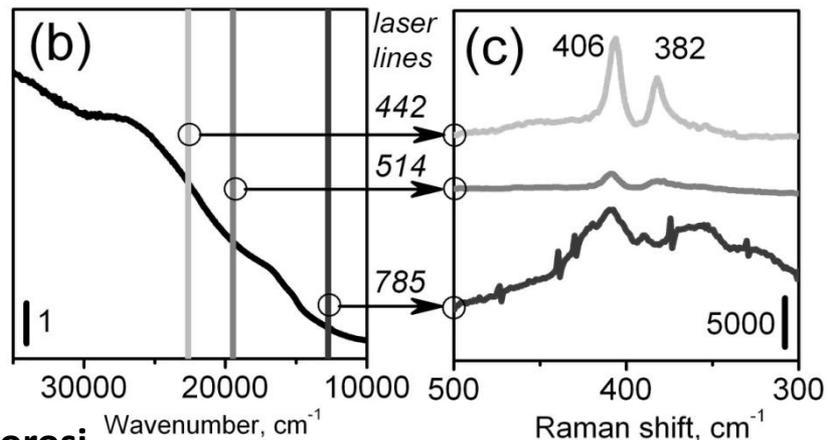
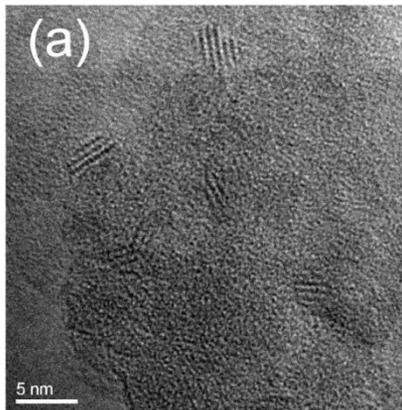


...un ciclo del carbonio antropogenico di tipo chimico, basato sulla cattura della CO₂ e sul suo riciclo in combustibili e materiali.



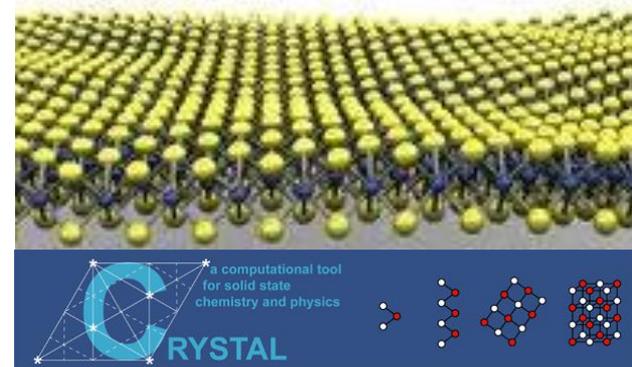
HydroDeSulfurization

A. Damin

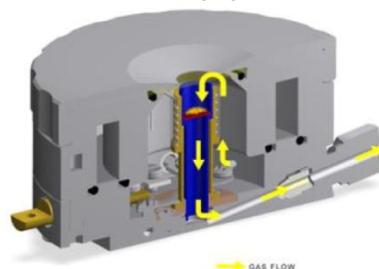
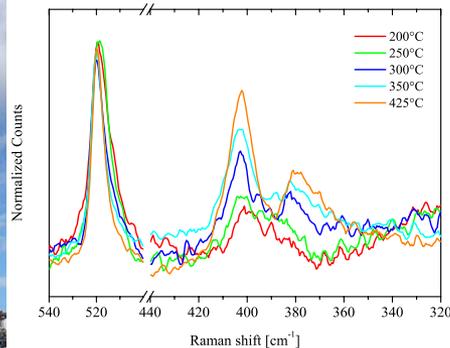
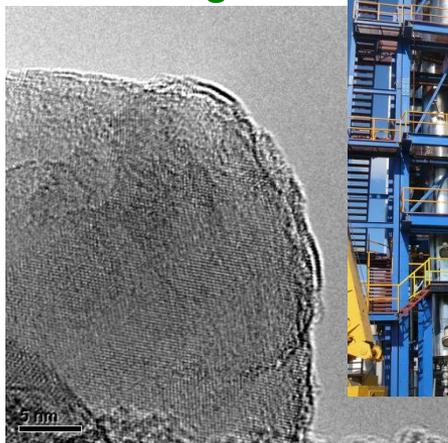


MoS₂ in vetri di SiO₂ porosi

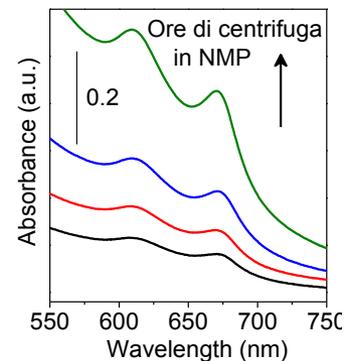
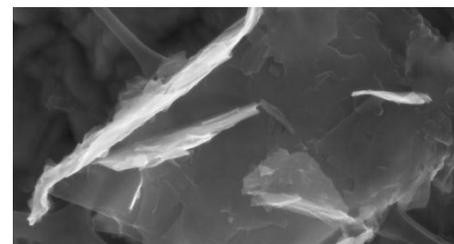
R. Dovesi



S. Bordiga



MoS₂ centrifugato in NMP

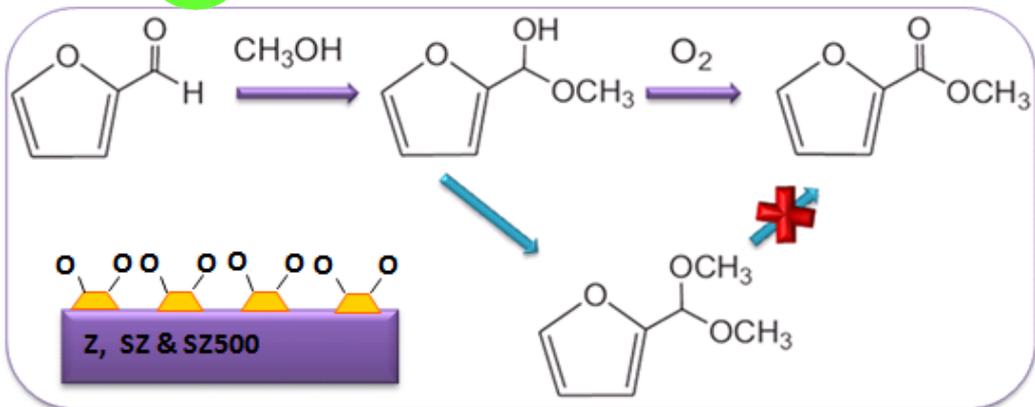


F. Cesano



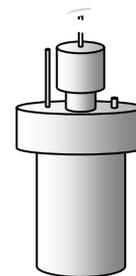
MoS₂ su TiO₂

Bio-mass conversion



No different by-products under the experimental conditions.

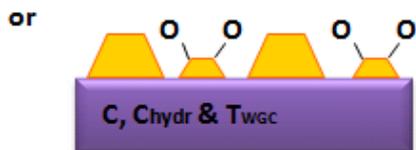
1000 rpm



150 mL MeOH
150 mL Furfural
100 mg Catalyst

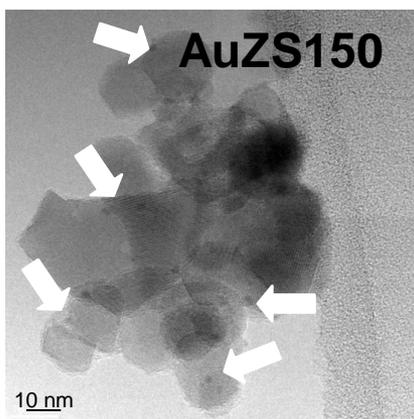
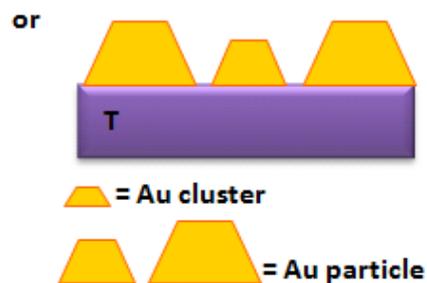
6 bar of O₂,
methanol, 120 °C.

F. Boccuzzi, M. Manzoli



PRIN 2008 : G. Centi (Me), UniTO: F. Boccuzzi

“Upgrading” catalitico della frazione C₅ in bioraffinerie lignocellulosiche



“Particelle d’oro altamente disperse si dimostrano attive e selettive nella conversione di FURFURALE verso furoati e acido 2,5 dicarboxy-furanico”

F. Pinna et al., *Catalysis Today*, (2012) DOI: 10.1016/j.cattod.2012.01.033.

M. Signoretto, et al. *Appl. Catal. B*, 129, 2013, 287

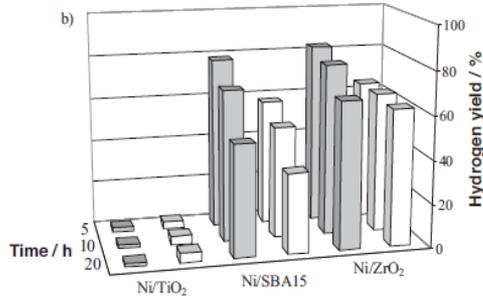
M. Signoretto, et al. *Green Chemistry*, 2013, submitted.



Bio-mass conversion

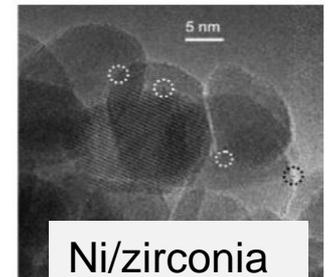
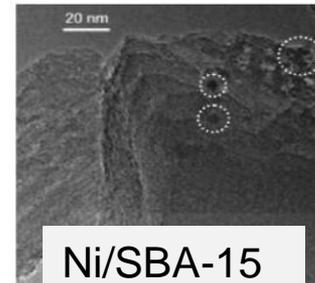
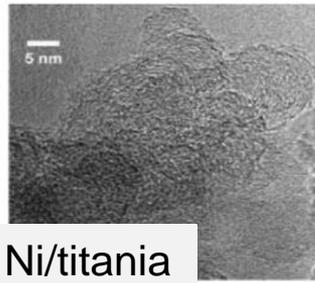
L'idrogeno è "green" solo se prodotto da fonti rinnovabili

Il glicerolo (≈10% sottoprodotto del bio-diesel da reazioni di transesterificazione di oli vegetali estratti dalle bio-masse) può essere sottoposto a reazione di "steam reforming"

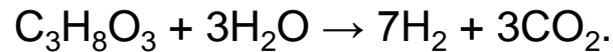


G. Cerrato

Immagini HR-TEM di catalizzatori esausti a base di Ni supportato.



V. Nichele, et al. *Appl. Catal. B: Environmental*, 111-112, 2012, 225



Strategie di ottimizzazione del pretrattamento enzimatico e delle popolazioni microbiche per la produzione di idrogeno da scarti agricoli



Progetto regionale: HyStrEM

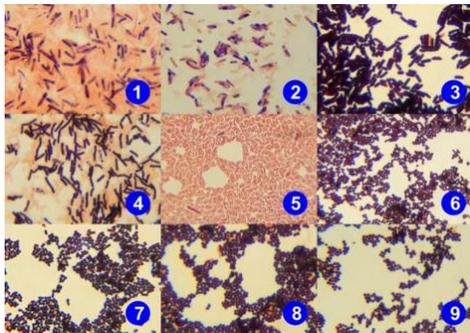
Proponente: UniTO, Francesca Valetti

AGO Renewable SpA

Asja Ambiente Italia S.p.A.

CCS Aosta S.r.l

La Licata B et al. *Int. J. Hydrogen Energy*, 2011, 36, 7861



S. Morra et al. 2012 G.R. Conference Barga (Lucca)

G. Gilardi, F. Valetti

Il progetto prevede lo sviluppo di sistemi integrati commercializzabili. Si forniscono ceppi misti stabilizzati ed i protocolli di pre-trattamento a basso costo e alta resa. Possibile anche sistemi bi-stadio, dove la produzione di idrogeno è seguita dalla produzione di metano.

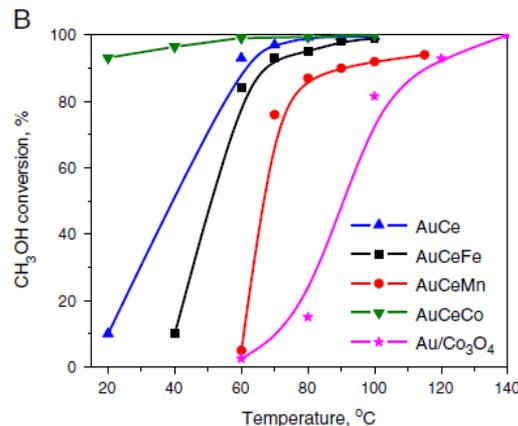
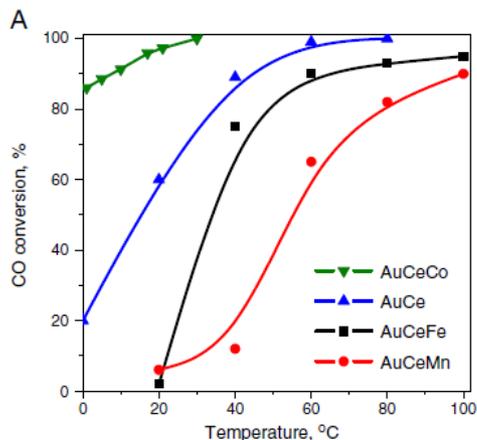




Regeneration & cleaning of air, earth, H₂O

NANOGOLD Project

F. Boccuzzi, M. Manzoli, F. Vindigni



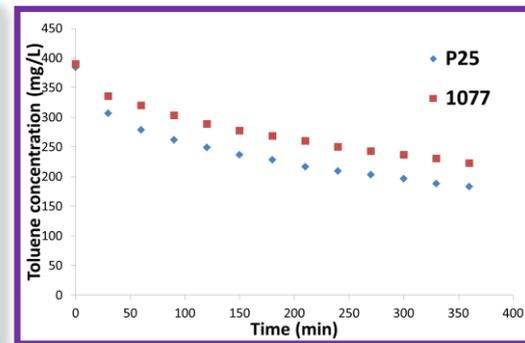
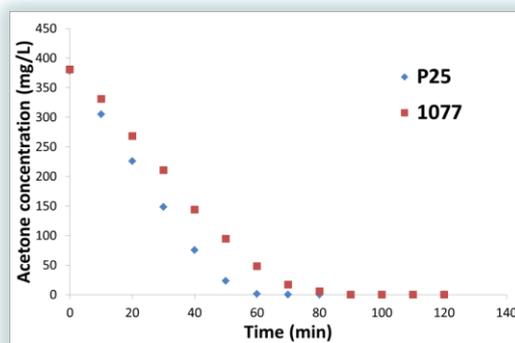
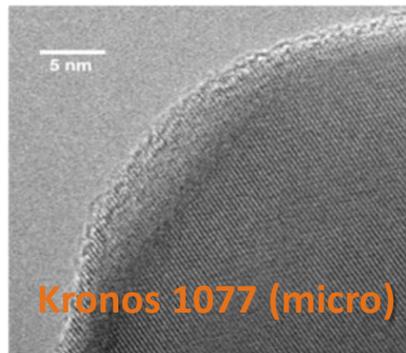
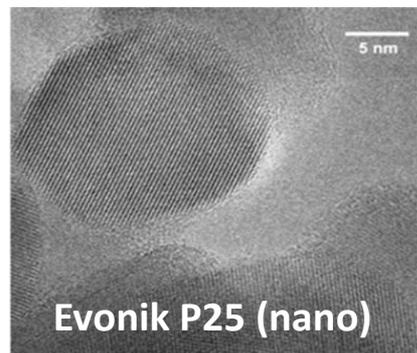
AuCeCo > AuCe > AuCeFe > AuCeMn

Il sistema Au su Ossido di cerio/Ossido di cobalto mostra la totale conversione di CO a RT e di CH₃OH a 40 ° C.

Fotodegradazione di NO_x e VOC_s da parte di TiO₂: Nano- vs Microparticelle

G. Cerrato, V. Crocellà

Degradazione di Acetone



Degradazione del toluene



C.L. Bianchi et al. , *Appl. Catal. B-Environ.* 2013, DOI: 10.1016/j.apcatb.2013.02.047



Regeneration & cleaning of air, earth, H₂O

Sintesi e caratterizzazione di Ossidi semiconduttori modificati allo scopo di modulare proprietà fotochimiche ed elettriche.

E. Giamello, M. Chiesa, M.C. Paganini, S. Livraghi

Targets:

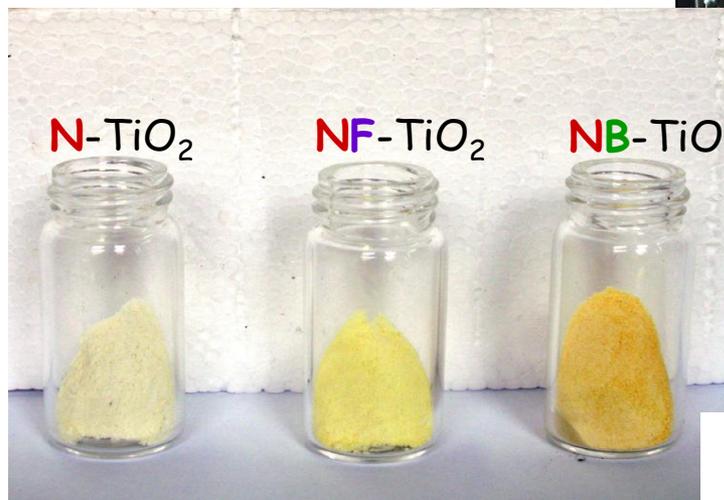
utilizzo di luce visibile in processi fotocatalitici, modificazioni della conducibilità della matrice.

- Ossidi semiconduttori drogati con non metalli
- Ossidi misti solubili. Eterogiunzioni ossido ossido. Particelle "core shell".

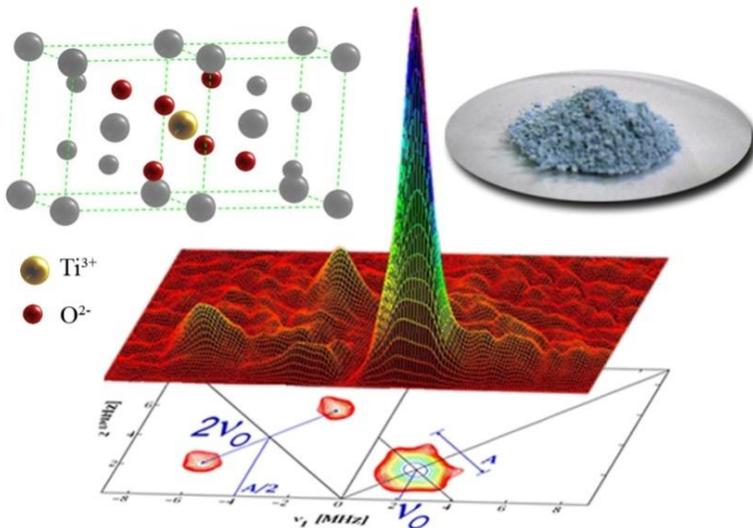
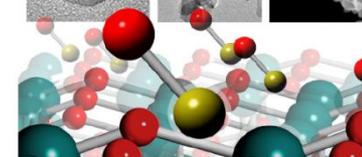
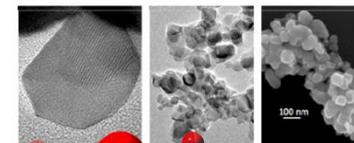
Intorno locale di Ti³⁺ in TiO₂ arricchito con ¹⁷O.



Sintesi CVD



G. Spoto, L. Mino



S. Livraghi et al. *Angew. Chem. Int. Ed. Engl.* 2011, 50, 8038.;

G. Barolo et al. *J. Phys. Chem. C*, 2012, 116, 20887;

M. Chiesa et al. *Phys. Chem. Chem. Phys.* 2013, 15, 9435.

S. Livraghi et al. *J. Phys. Chem. C* 2011, 115, 25413;

C. Gionco, C. et al. *Chem. Mater.* 2013, 25, 2243;

FIRB 2012

**"Oxides at the nanoscale:
multifunctionality and applications"**

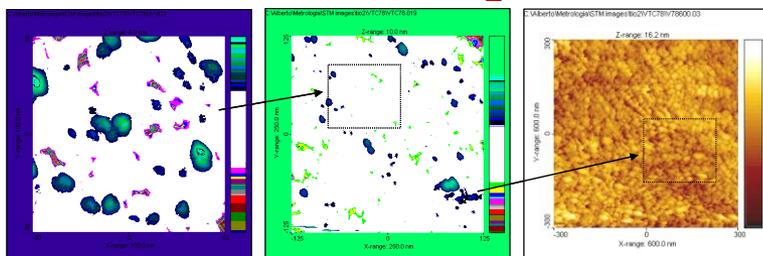


Regeneration & cleaning of air, earth, H₂O

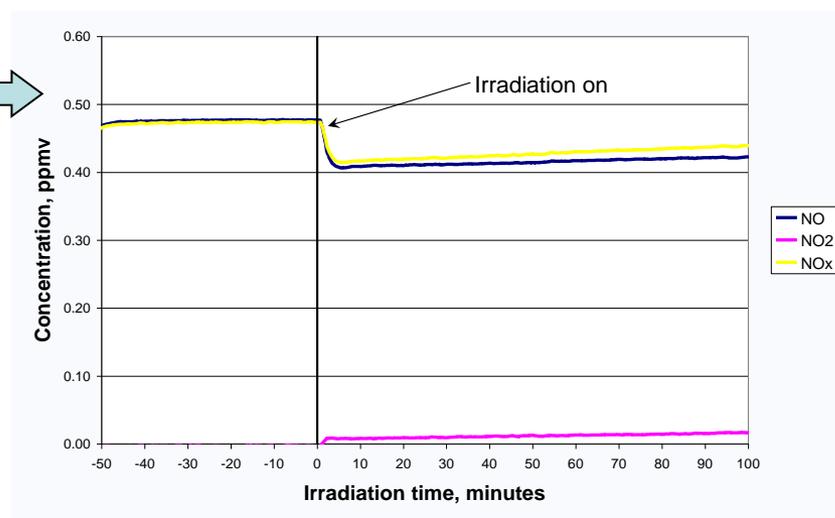
Rivestimenti fotocatalitici, auto pulenti, auto sterilizzanti a base di film di TiO₂.



Esempi di film di TiO₂ su vetro



Immagini STM

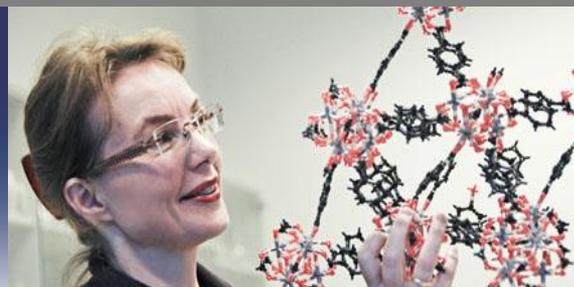
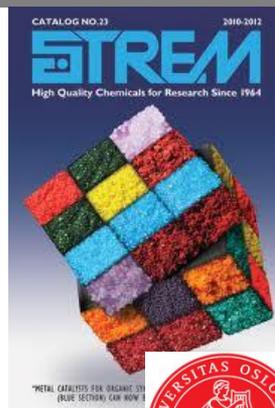
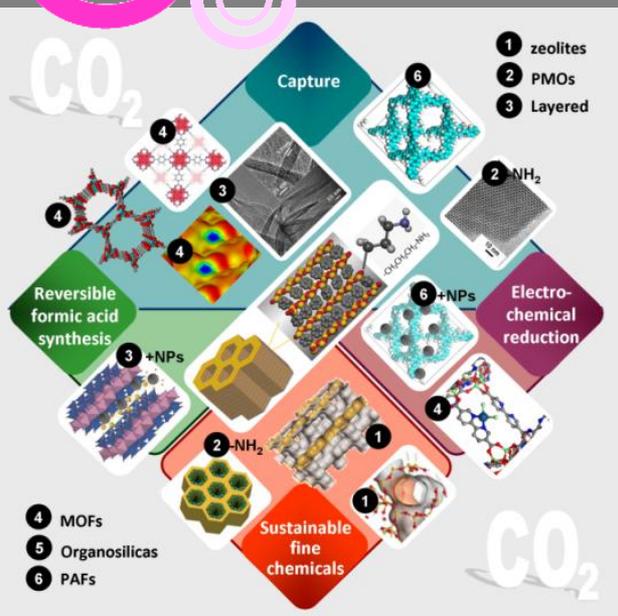


NOx Abatement

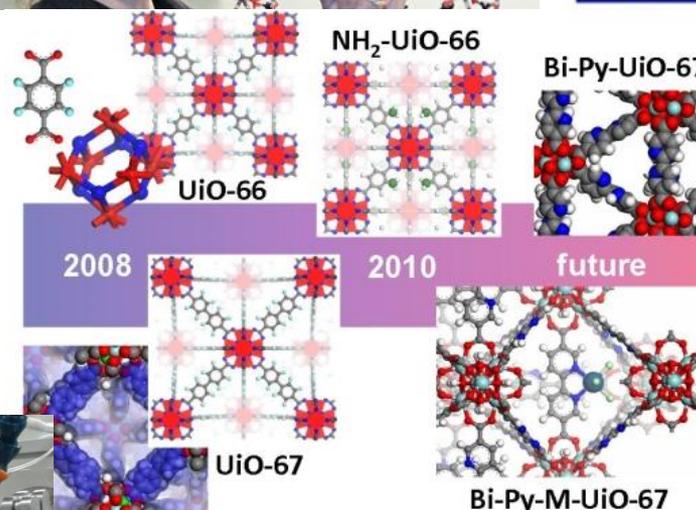
C. Minero, V. Maurino

Valter Maurino, Claudio Minero, Ezio Pelizzetti "Preparation of Firmly-Anchored Photocatalytically-Active Titanium Dioxide Coating Films with non-gelled organic-doped Precursors", Brevetto Europeo n°EP1205243, pubblicato il 15/05/2002

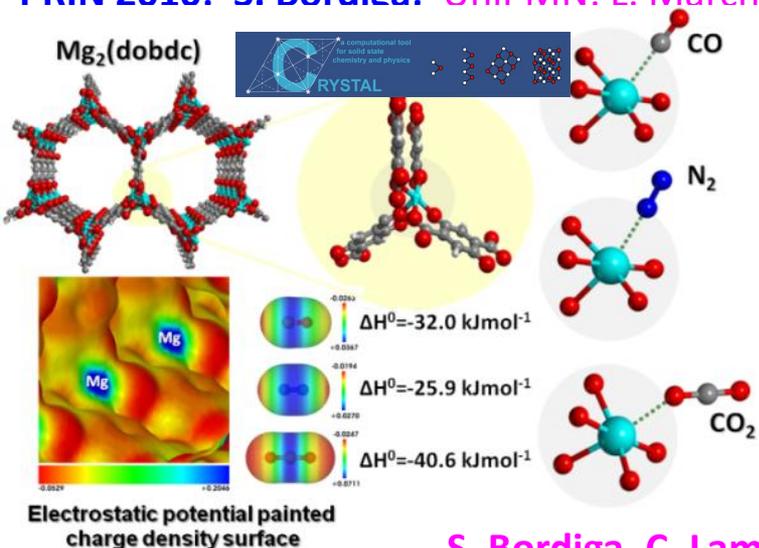
CO₂ capture and use



nano
MOF



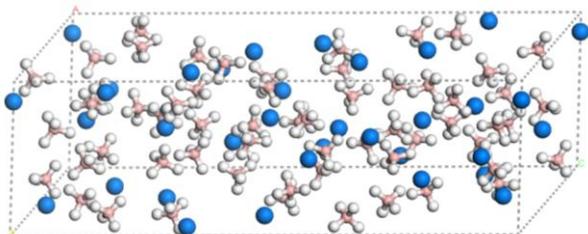
PRIN 2010: S. Bordiga. UniPMN: L. Marchese et al ...



J. G. Vitillo J.G et al., *ChemSusChem*, 4, 2011, 1281
 Kandiah M., et al., *Chem. Mater.* 22, 2010, 6632
 Dietzel P. et al. *Chem Commun.* 2008, 5125
 Valenzano L., et al., *J. Phys. Chem. C*, 114, 2010, 11185
 Valenzano L., et al, *Catal. Today* 182, 2012, 67
 Cavka J.H., et al *J. Am. Chem. Soc.* 130, 2008, 13850.
 C. Lamberti et al. *Chem Soc. Rev.*, 39, 2010, 4951
 S. Bordiga et al., *Chem Soc Rev*, 39, 2010, 4885

S. Bordiga, C. Lamberti, F. Bonino, J.G. Vitillo, V. Crocellà, G. Ricchiardi, B. Civalleri

Hydrogen Storage



Calcoli termodinamici $Mg(BH_4)_2$



E. Albanese et al., *J. Alloy. Compd.*, 2013, in press
 M. Baricco et al. *J. Alloy. Compd.*, 536 (2012) S216
 E. Pinatel et al. *Calphad* 39 (2012) 80
 O. Zavorotynska et al. *J. Phys. Chem. C*, 115 (2011) 18890

Idruri complessi

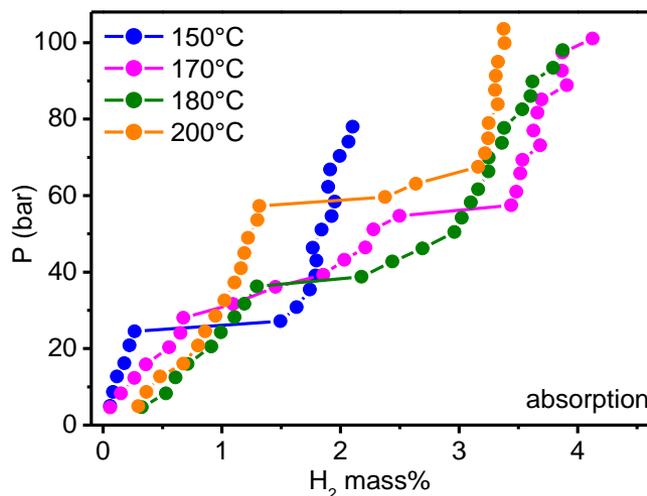
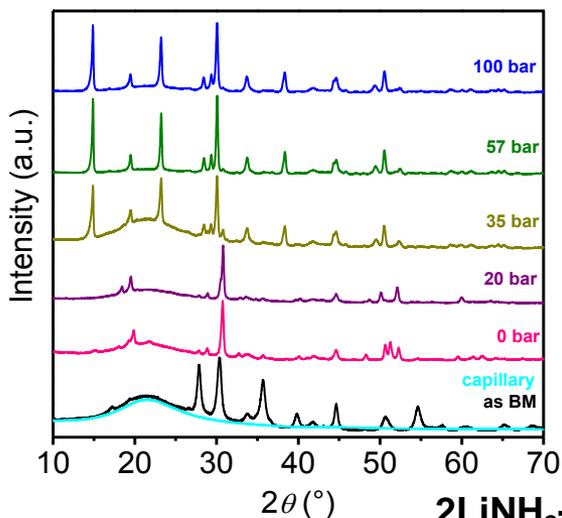
Idruri metallici

Serbatoio per idrogeno
 a base di $LaNi_{4.8}Al_{0.2}$



Progetto Regionale
H2FC, FA-H2FC, STERIN

XRD misurati lungo l'isoterma a 170°C



M. Baricco, J. G. Vitillo, B. Civalleri, C. Nervi

L. Battezzati, P. Rizzi, A. Castellero,

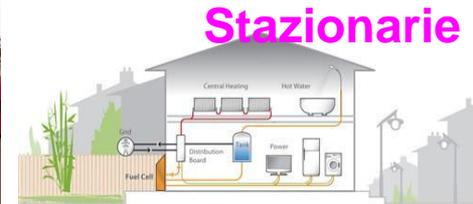
Energy Conversion

Membrane Polimeriche Elettrolitiche per Celle a Combustibile

Sintesi di polimeri a conduzione protonica alternativi al NAFION con caratteristiche superiori, soprattutto in termini di tempo di vita della membrana.



Mobili



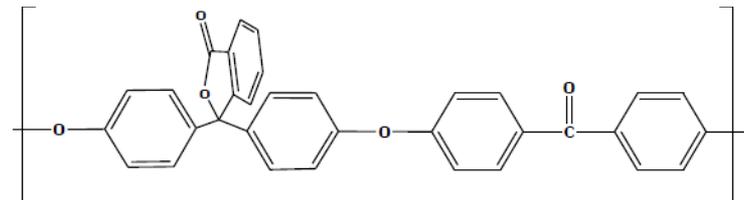
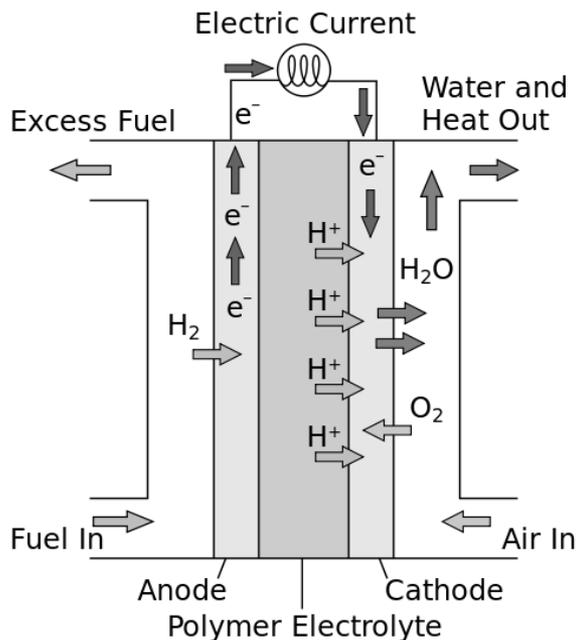
Stazionarie

applications



Portatili

A. Lulianelli et al. *Int. J of Hydrogen Energy* 35 (2010) 12688.
F. Trotta, *J. of Applied Polymer Science* 117-4 (2010) 2258



Esempio di unità base di un **polimero a conduzione protonica** che è caratterizzato da buona resistenza meccanica, stabilità alle ossidazioni, elevata temperatura di transizione vetrosa e buona solubilità.

P. Luda, F. Trotta

Photovoltaic

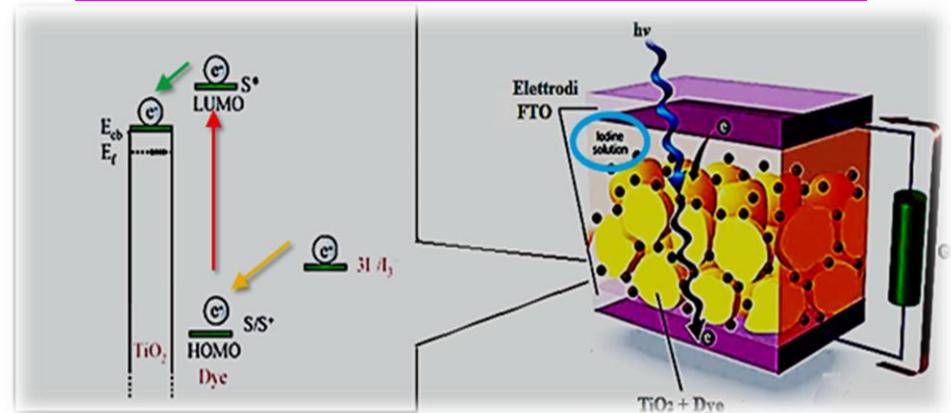
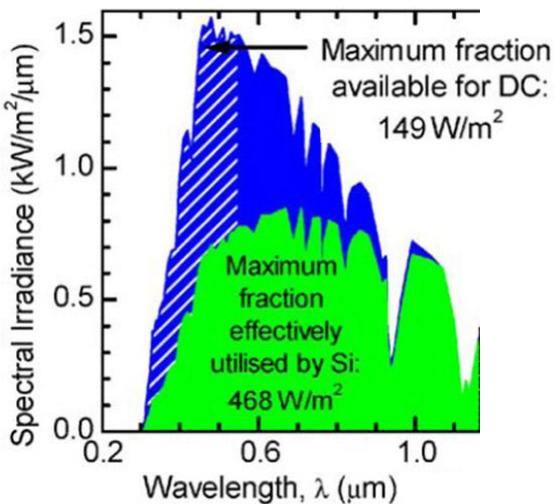
Nuove molecole foto-attive nel “down-shifting” per applicazioni in celle fotovoltaiche a base di silicio policristallino



Progetto Regione Piemonte: DYE-HARD
UniTO, UniPMN SIVE, V-ENERGY, IN.TE.CO, SE



Le celle solari “Dye-sensitized” (DSCs) sono una promettente alternativa alle celle convenzionali a base di giunzioni p-n



Architettura di una tipica cella DSC:

- un ossido conduttivo su un substrato di vetro o plastica
- uno strato mesoporoso di un semiconduttore nanocristallino (TiO_2)
- un “sensibilizzatore” ancorato alla superficie
- un elettrolita con una coppia ionica with (*i.e.* I^-/I_3^-)
- un contro-elettrodo di metallo dove il mediatore ionico è rigenerato

Molecole organiche poco costose in matrici polimeriche per conferire proprietà di emissione a λ sensibilmente inferiori rispetto alle λ assorbite.

C. Barolo, G. Viscardi

Photovoltaic

Standardizzazione delle proprietà di particelle nanometriche di TiO₂

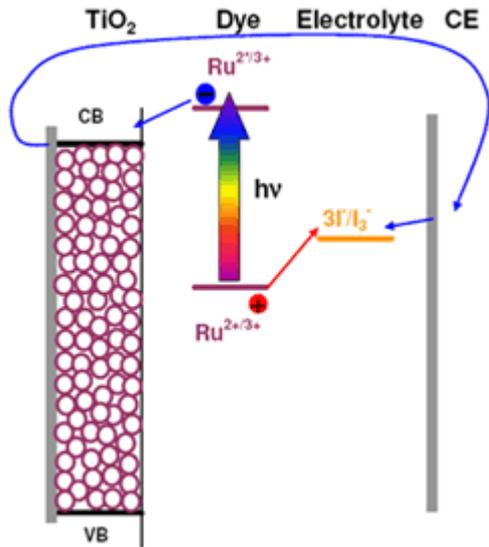
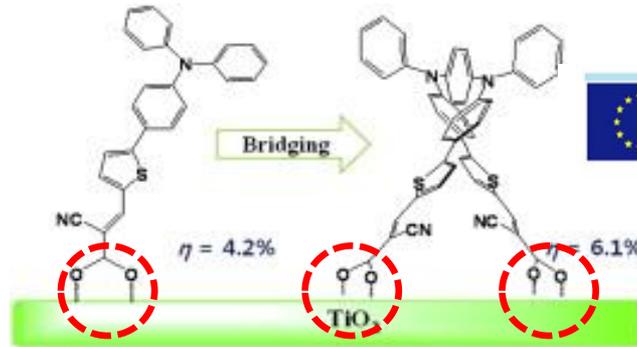
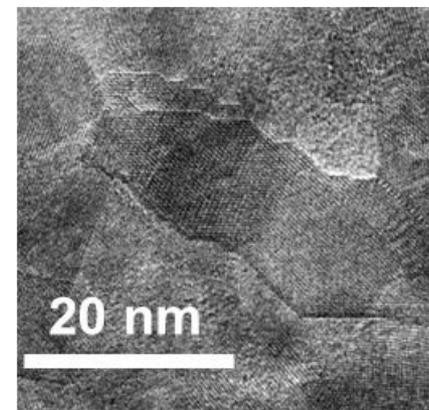


Figure 1. Schematic of electron pathway in a DSC system



Quali superfici?

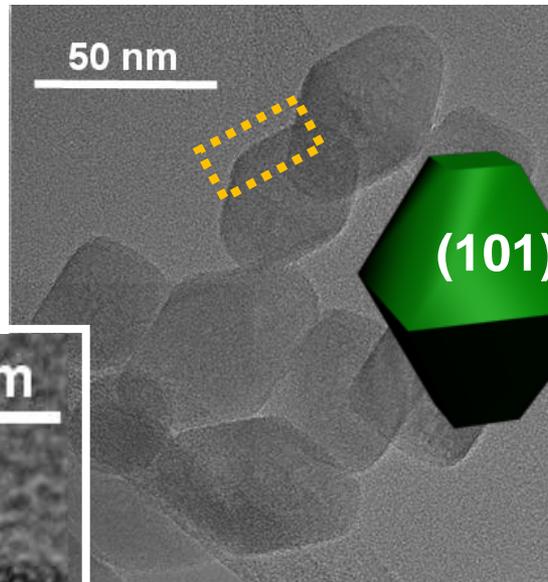
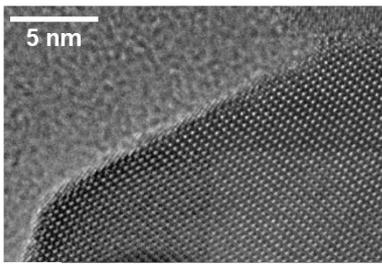
TiO₂ T-SP (Solaronix*)
(*a "Graetzel spin-off")



FP7-NMP SETNanoMetro

" Shape-engineered TiO₂ nanoparticles for metrology of functional properties: setting design rules from material synthesis to nanostructured devices"

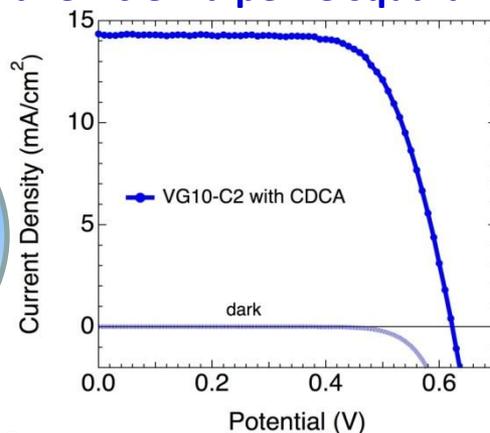
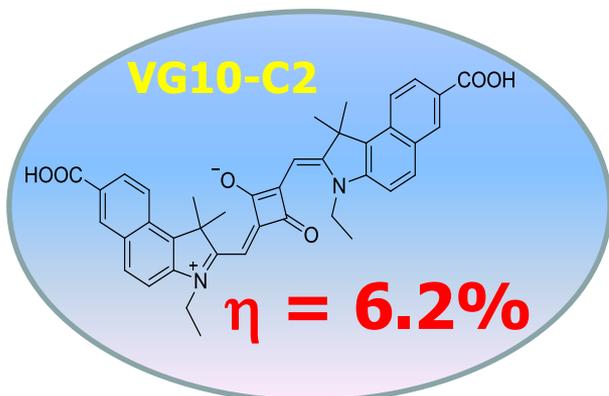
G. Martra, V. Maurino, G. Spoto and INRIM (Rossi)



TiO₂ Nps con forme e dimensioni ben definite

Photovoltaic

VG10-C2 PV ha il record mondiale di efficienza per le squaraine simmetriche.



La sintesi con le microonde permette:
Sintesi più veloce; Maggiori rese
Maggior purezza del prodotto

Barolo et al, Chem. Commun., 2012, 48, 2782

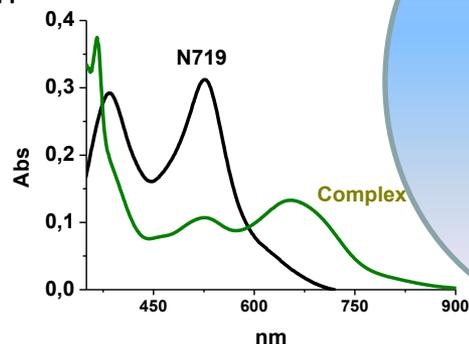
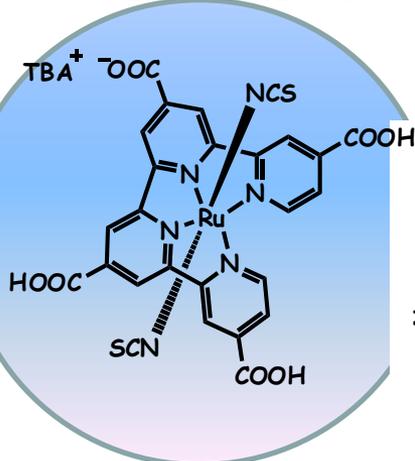
Barolo C. et. al. RSC Advances, (2012), 2, 2748.

Barolo C. et al. Chem. Commun. (2012), 48, 2782–2784.

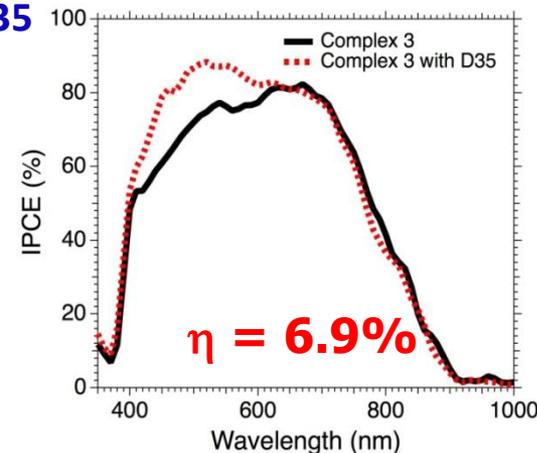
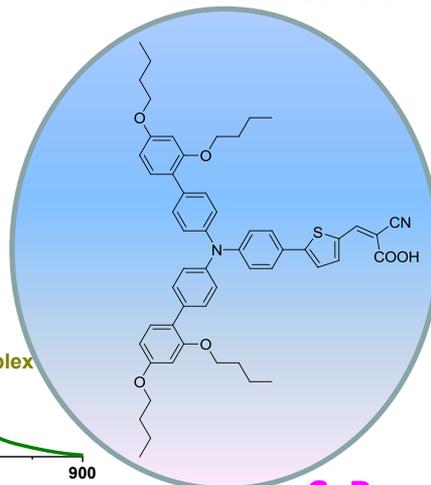
G. Viscardi, C. Barolo, N. Barbero, L. Bonandini

Sensibilizzatori "Pancromatici" per TiO₂

Barolo, C. et al. ChemSusChem (2013) DOI:
10.1002/cssc.201200973



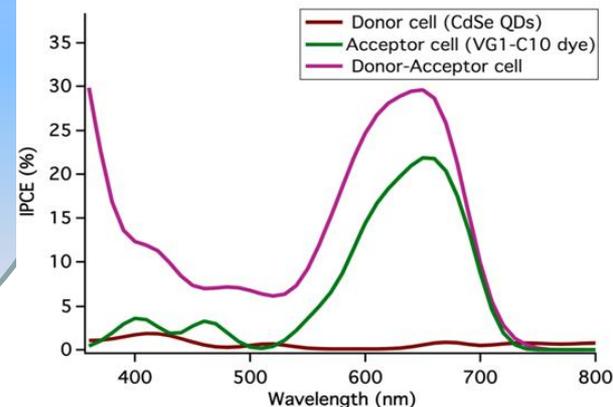
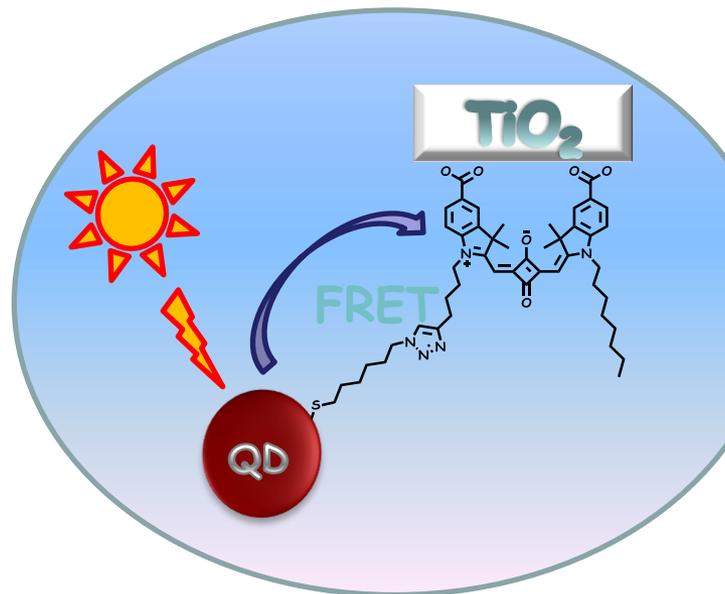
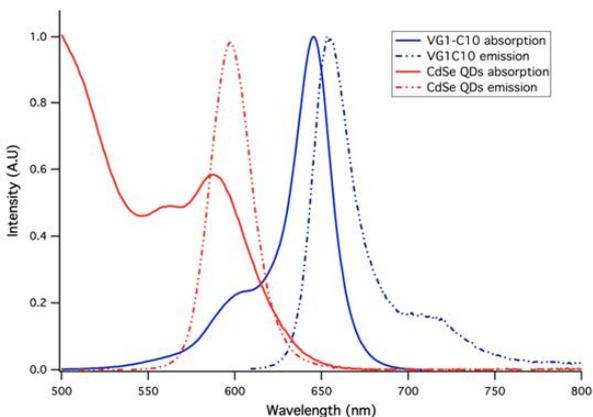
Co-sensitization with D35



C. Barolo, R. Buscaino

Photovoltaic

Uso di Quantum dots e di squaraine organiche per la messa appunto di celle DSC



Cell type	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/mV	FF	$\eta @ 1 \text{ sun}$
VG1-C10 dye	2.73	542	0.536	0.79
VG1-C10 dye + CdSe QDs (FRET cell)	3.25	653.4	0.69	1.48
Δ	+16%	+17%	+23%	+47%

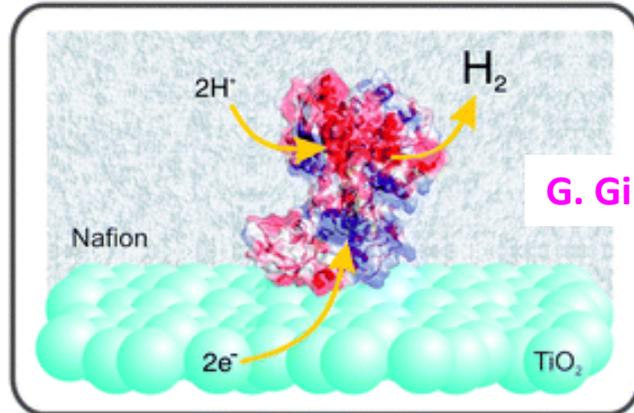
Barolo C. et. al. RSC Advances, (2012), 2, 2748-2752.
 Barolo C. et al. Chem. Commun. (2012), 48, 2782-2784.

G. Viscardi, J. Park, P Quagliotto

H₂ production

L'idrogeno può essere prodotto dall'acqua per "photo-, thermal-, electrochemical- splitting"

FP7-Energy SOLHYDROMICS



G. Gilardi, F. Valetti

[FeFe]-Idrogenasi sono efficienti catalizzatori naturali che possono essere usati per produrre H₂. L'ancoramento di [FeFe]-hydrogenase CaHydA è stato ottenuto per la prima volta su un elettrodo fatto di TiO₂ (anatasio). **L'enzima interagisce e scambia elettroni con l'elettrodo e catalizza la produzione di H₂ con un'efficienza del 70%.**

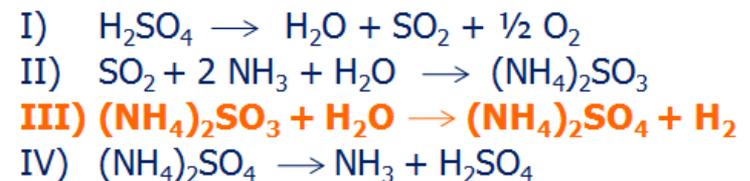
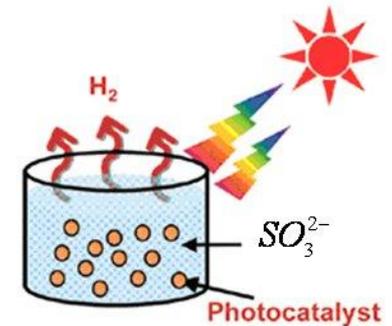
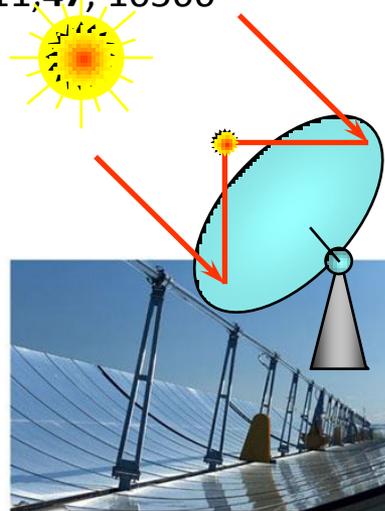
S. Morra et al. *Chem. Commun.*, 2011, **47**, 10566

Energia solare

- fornisce energia termica
- guida la formazione di H₂ molecolare attraverso un processo fotocatalitico.

Processo Fototermocatalitico

ENEA Casaccia Roma

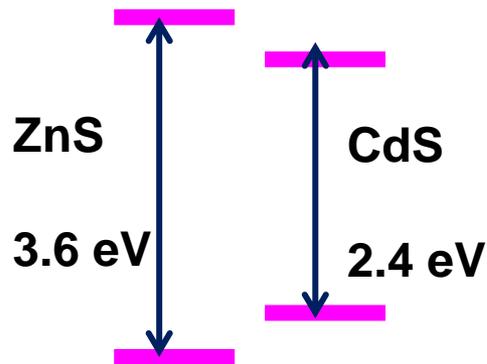


PRIN 2009, UniPMN, E. Gianotti, **UniTO: G. Berlier**

H₂ production

Una alternativa "green" a CdS

- particelle di ZnS

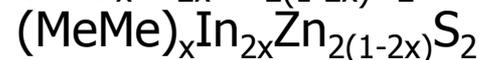


Ingegnerizzazione della "Band gap" verso il visibile

- drogaggio con Me=Ag, Ni, Cu, Mn, Co

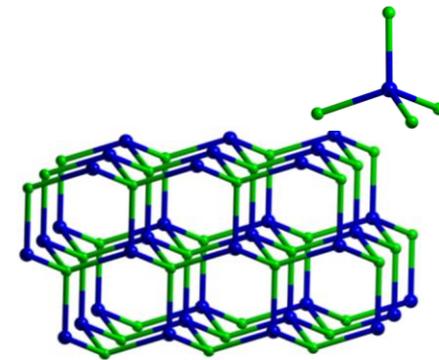
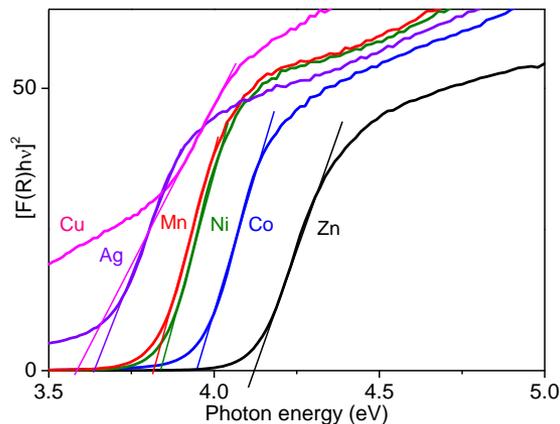


- Sintesi di soluzioni



Per modulare il band-gap si può pensare di "drogare" ZnS

Samples	E_g exp (eV) (x=0.05)	E_g calc (eV) (x=0.06)
Zn_{1-x}Ni_xS	3.84	3.69
Zn_{1-x}Mn_xS	3.82	3.54
Zn_{1-x}Co_xS	3.94	3.68
Zn_{1-x}Cu_xS	3.59	3.71
Zn_{1-x}Ag_xS	3.64	3.57
ZnS	4.12	3.70



G. Berlier, A. Ferrari

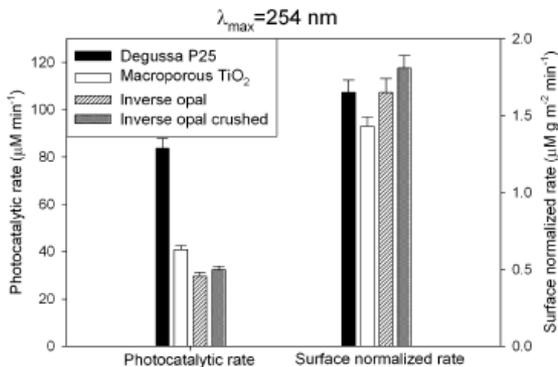
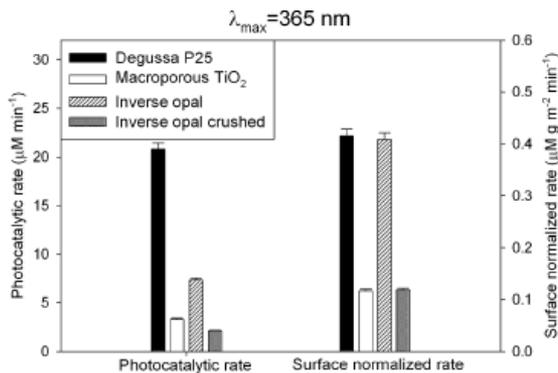
Artificial Photosynthesis

PHOTORECARB. Progetto di Ateneo UniTO 2012

La fotosintesi artificiale si realizza in una cella foto elettrochimica a schema "Z"

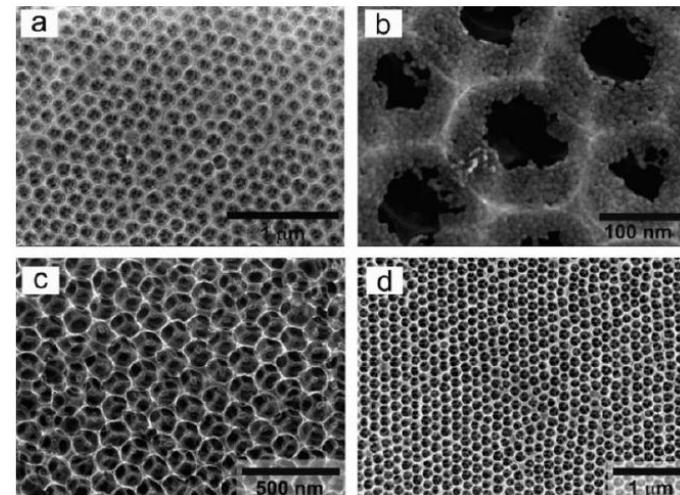
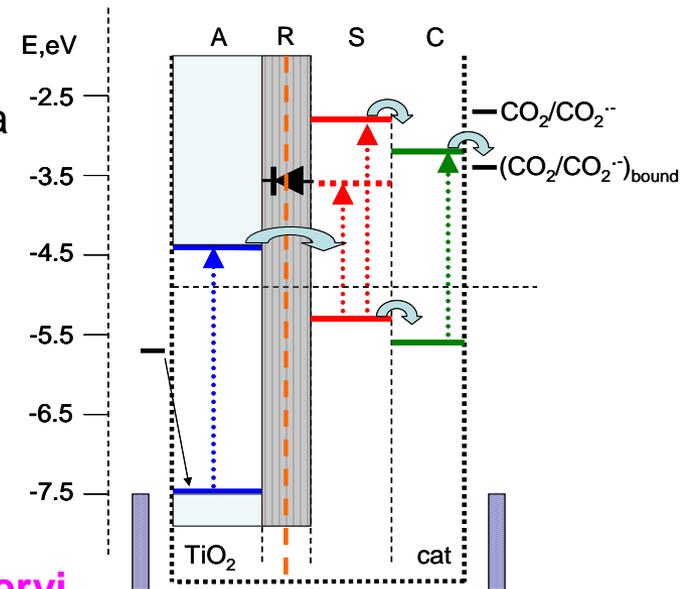
L'anodo (A-R) è costituito di una'opale inverso a base di TiO_2 accoppiato ad un opportuno catalizzatore a cui l'acqua si ossida. L'anodo è fisicamente separato dal catodo

F. Sordello et al. Chem Commun, 2011, 47, 6147



C. Minero, G. Viscardi, C. Nervi

Il principale materiale che caratterizza la cella è una forma speciale di TiO_2 (opale inverso) che ha proprietà ottime per quanto concerne la cattura della luce, "Harvesting"



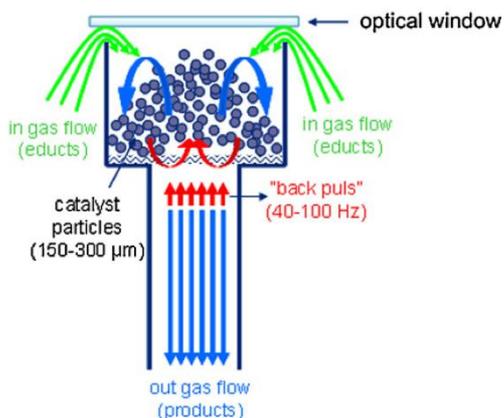
Power 2 Gas/Liquid



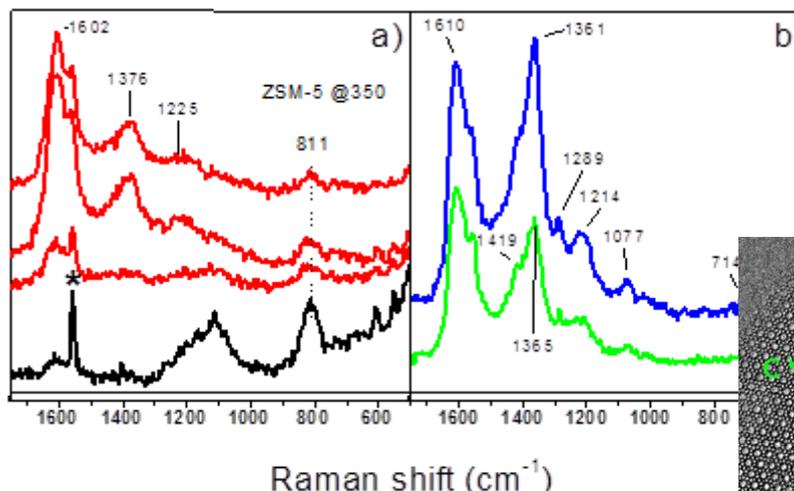
HALDOR TOPSOE
The Catalyst and Technology Company

U. Olsbye, et al. *Angew. Chemie* 51, (2012). 5810

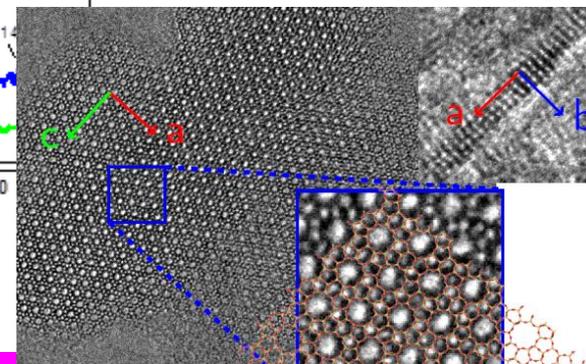
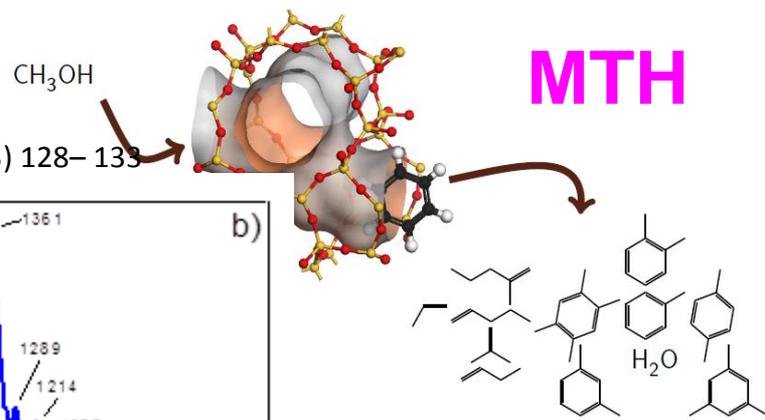
S. Bordiga, F. Bonino,



P.Beato et al. *Catalysis Today* 205 (2013) 128–133



B.T. Lønstad Bleken et al. *PCCP*, accepted



Gas 2 Power



COST Action CM0904 Intermetallic Compounds in Methanol Steam Reforming

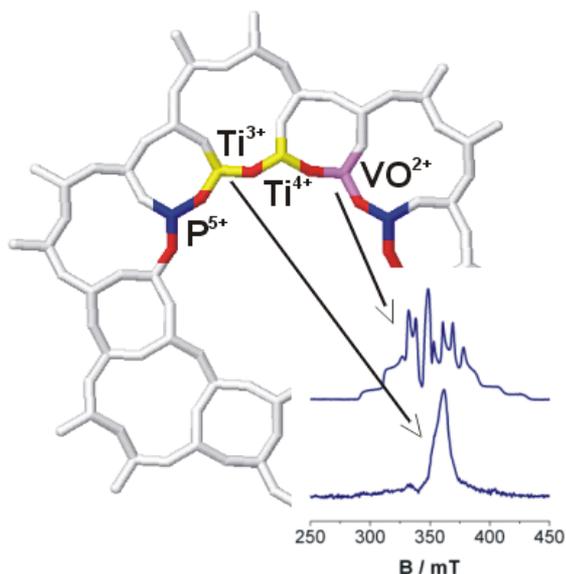
E. Groppo

Selective Catalysis

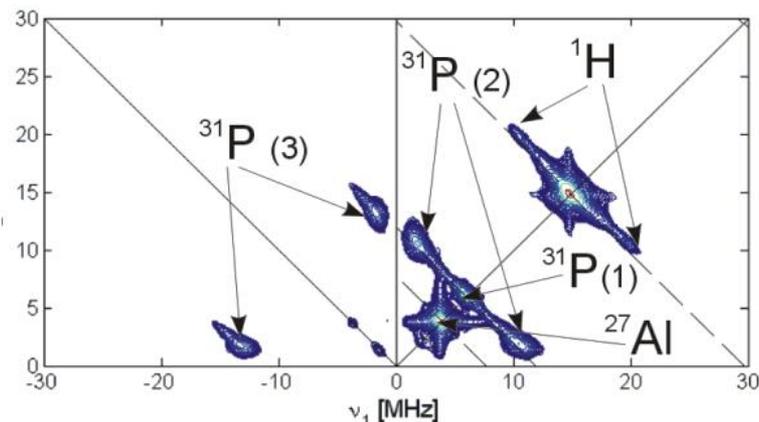
Catalizzatori mono- e bi-metallici per ossidazione selettiva a base di ioni di transizione (Ti, Ni, Co) dispersi in matrici porose di alluminio fosfati

Alta selettività, basse temperature di reazione (100 °C) , uso di ossigeno come agente ossidante

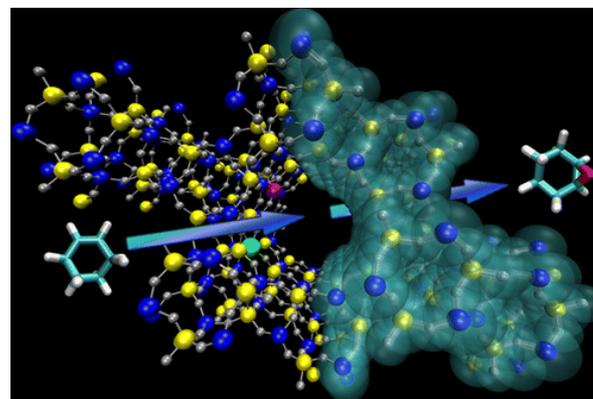
- S. Maurelli et al. S.; *P. C. C. P.* **2010**, *12*, 10933.
S. Maurelli et al., *P. C. C. P.* **2012**, *14*, 987.
S. Maurelli, et al. *S. J. Am. Chem. Soc.* **2011**, *133*, 7340



- S. Maurelli et al., *Chem. Commun.* **2012**, *48*, 8700.
R. Leithall et al. *J. Am. Chem. Soc.* **2013**, *135*, 2915.
C. Novara, C. et al. *Phys. Chem. Chem. Phys.*, **2013**, *15*, 11099.



E. Giamello, M. Chiesa, S. Maurelli



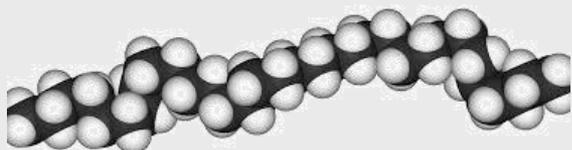
Selective catalysis: olefin polymerization



From olefins...

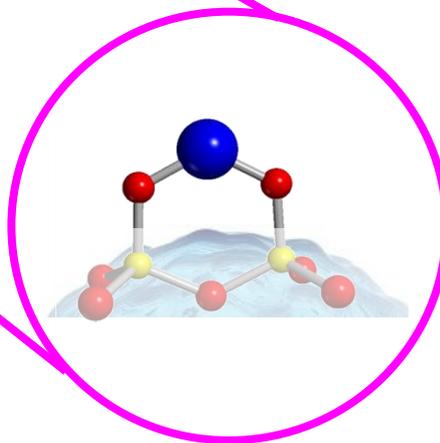
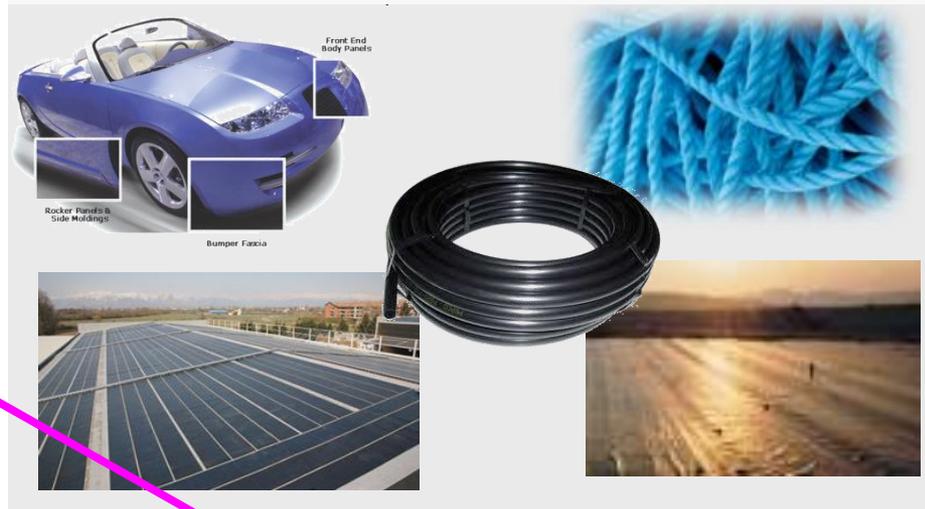


CATALYST



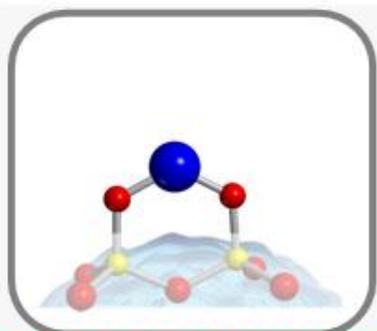
... to polyolefins

A wide range of advanced materials



Selective catalysis: olefin polymerization

CATALYSTS



ADVANCED MATERIALS



HDPE

ADVANCED APPLICATIONS

e.g. insulating cables



electronics

e.g. geomembranes



agriculture



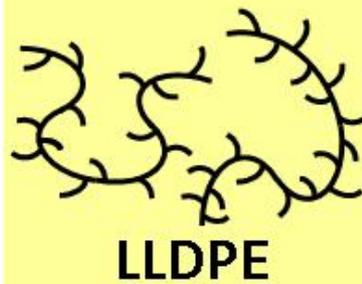
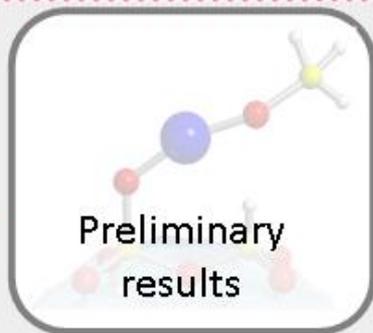
e.g. shade nettings



e.g. oil recovery

surfactants

R_3SiH



LLDPE

Pyrrole



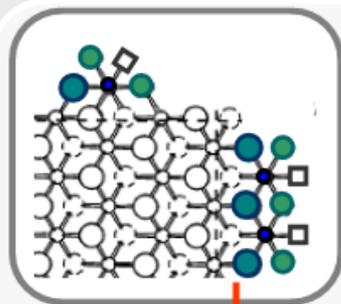
$AlEt_3$



α -olefins

Selective catalysis: olefin polymerization

CATALYSTS



ADVANCED MATERIALS



ADVANCED APPLICATIONS



construction

(ID/ED)*

?



**e.g. ID = aromatic diester*
ED = alkoxy silane



e.g. monofilaments for surgery



medical

(ID/ED)**

?



***e.g. ID = dibutylphthalate*
ED = 2,6-dimethylpyridine



e.g. high performance fabrics



textile

Old compounds, new understanding



nature
chemistry

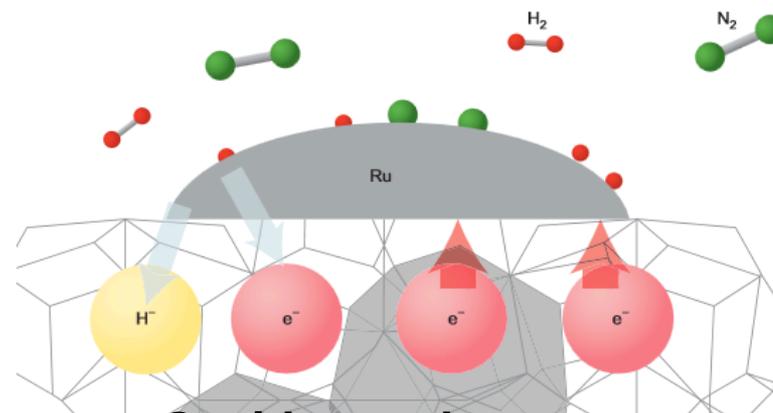
**Grandi sfide ci attendono per processi notissimi:
1–2% del consumo energetico mondiale è speso
per la sintesi dell'NH₃**

E. Giamello Nature Chemistry, 2012, 4, 869

Hosono, Hara e coll. (Nature Chem 2012, 4, 934) descrivono che un materiale “classico”, l'alluminato di calcio ($12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$) è stato modificato per ottenere un **ELETTURUO** $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} (e^-)_4$ che funziona come promotore del catalizzatore a base di particelle di Rutenio supportate, nella sintesi dell'ammoniaca.

Heterogeneous catalysis: Teaching an old material new tricks

Il promotore (un elettrondonor) ha un benefico effetto sia nell'attivazione di N₂ che nell'inibizione di H₂.



Ossido conduttore trasparente

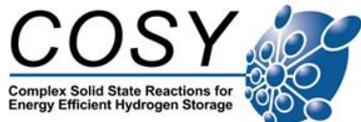
Si è osservato un aumento del TOF di 1 ordine di grandezza, se confrontato con il catalizzatore di puro Rutenio.

“Innovation in materials science is not always derived from completely new and exotic materials. A well-known, old structural material which, by the action of smart and learned scientists, has become a new, exciting functional material.

Grazie a...



Ministero dell'Istruzione, dell'Università e della Ricerca



©...per il supporto economico



Un ringraziamento personale.....



ad **Adriano Zecchina**

e a Tutti voi



...per il cammino insieme!



Regeneration & cleaning of air, earth, H₂O

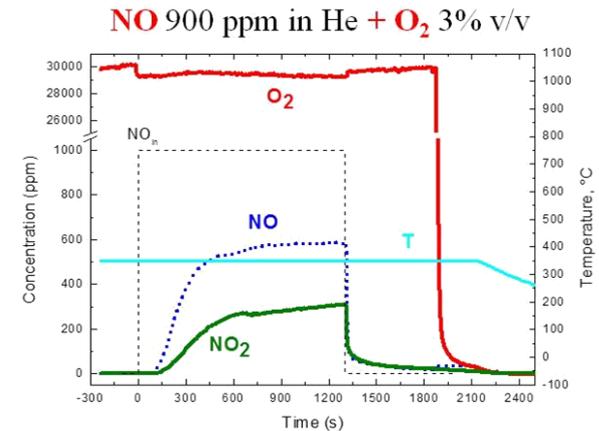
Catalizzatore Toyota

DeNO_x

Pt-Ba/Al₂O₃ (1 wt.% Pt, 16 wt.% Ba)

Lean Phase

Rich Phase

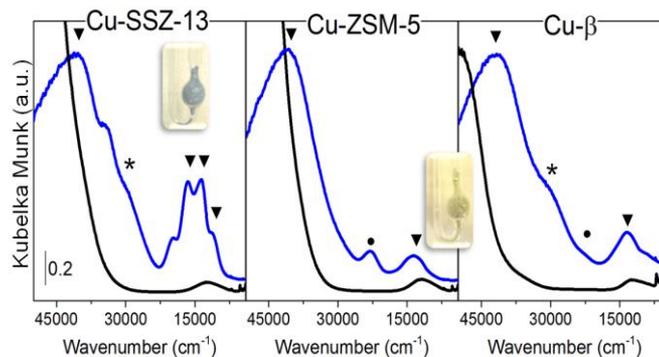
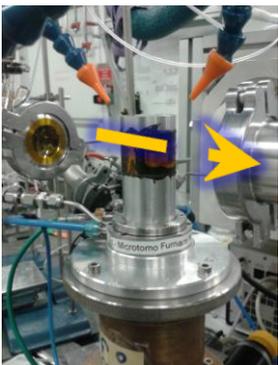


- F. Prinetto et al. *J. Phys. Chem C*, 114 (2010) 1127
- P. Forzatti et al., *J. Catal*, 274 (2010) 163
- S. Morandi et al., *Catalysis Today*, 176 (2011) 399
- S. Morandi et al., *PCCP*, in press

S. Morandi

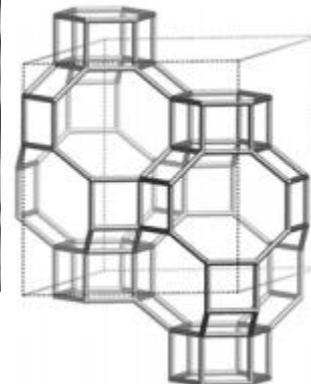
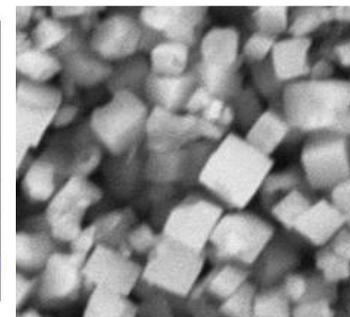
Cu-zeoliti

ESRF- BM-23 (Aprile 2013)



F. Giordanino, et al. *Dalton Transaction*, 2013 in press

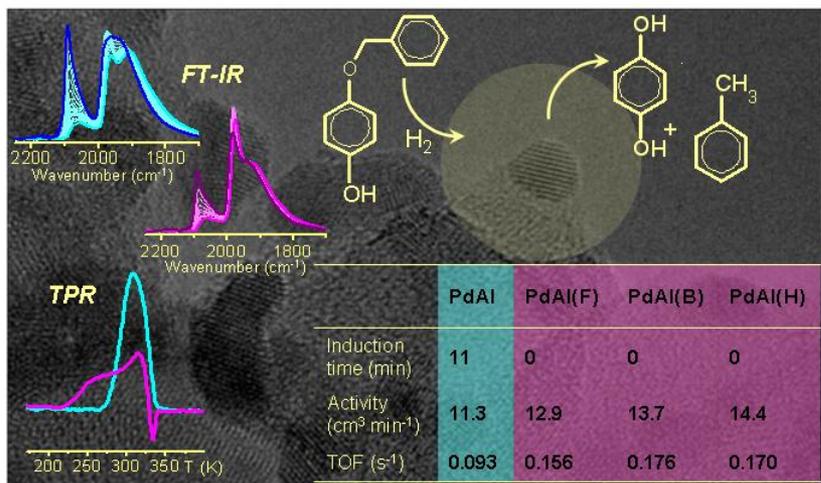
S. Bordiga, C. Lamberti



Selective catalysis: metal nanoparticles

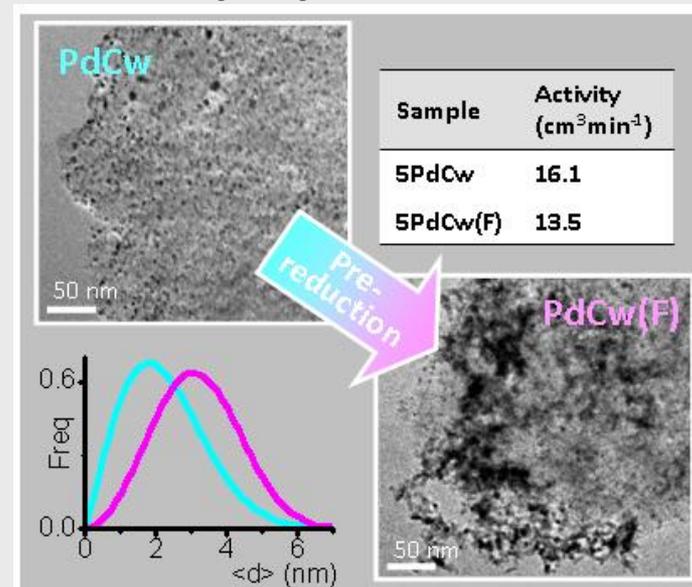
...for selective hydrogenation reactions

1) Structure-activity relationship

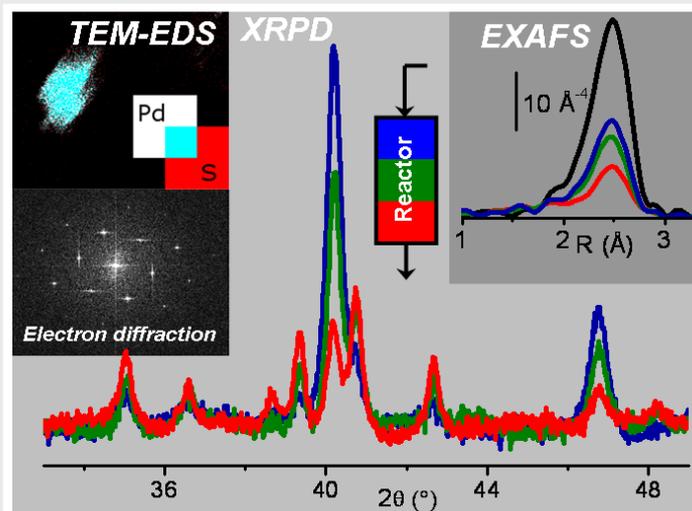


E. Groppo, et al. J. Catal. 287 (2012) 44.

2) Influence of preparation method



G. Agostini, et al. ACS Catal., submitted.



3) Deactivation of industrial catalysts

R. Pellegrini, et al. J. Catal. 280 (2011) 150.