Challenging nanomaterials for sustainable processes

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“Nanotechnology and NanoApplication”
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The 90 natural elements that make up everything

How much is there? Is that enough?


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The famous Carlin-type gold ores of Nevada are often found in limestone or lime-rich shales. Tens of millions of ounces of gold have been mined from rocks just like this.
ETHICAL COBALT EXTRACTION

Replacing noble metals with base metal (?)
INTRODUCTION

To sustainable satisfy population needs

- Extensive use of renewable energy sources and raw materials
- More efficient processes for production of energy and chemicals

Design of new catalytic materials with improved properties for new sustainable processes
MEE RESEARCH ACTIVITIES

Air pollution abatement
- Three Way Catalysts
- CH₄ combustion

Water purification by photocatalysis
- Doped TiO₂
- Bi₂O₃-based materials
- Metal tungstates

H₂ & Fuels production
- CH₄ partial oxidation
- Steam reforming of renewable compounds
- Photocatalytic reforming of oxygenated compounds
- Synthesis of valuable organic compounds

H₂ purification
- Water Gas Shift
- Preferential Oxidation of CO
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H$_2$ PRODUCTION TECHNOLOGIES

1. HCs
   - Thermal reforming
   - Syn-gas
   - H$_2$ production
     - MeOH synthesis
     - NH$_3$ synthesis
     - Fisher-Tropsch

2. 2$^{nd}$ generation EtOH/Glycerol
   - Thermal reforming
   - Syn-gas

3. 2$^{nd}$ generation EtOH/Glycerol
   - Photoreforming
   - Chemicals
   - Distributed H$_2$ Production

PHOTOCATALYTIC H₂ PRODUCTION

WATER SPLITTING

BIOMASS OXIDATION

PHOTOCATALYTIC H₂ PRODUCTION

Photoreforming of oxygenated compounds

H₂ PRODUCTION FROM ETHANOL

Possible pathway

\[
\begin{align*}
\text{OH} & \quad \rightarrow \quad \text{CH}_2\text{CH}_2 \\
\text{H}_2 & \quad \rightarrow \quad \text{accumulated in solution} \\
\text{OH}^* & \quad \rightarrow \quad \text{CH}_4 + \text{CO} \quad \text{(not detected)} \\
\text{H}_2 & \quad \rightarrow \quad \text{H}_2 \\
\text{not detected} & \quad \rightarrow \quad \text{CH}_4 + \text{CO}_2 \\
\text{H}_2 & \quad \rightarrow \quad \text{H}_2 \\

\text{ChemCatChem} 3 (2011), 574-577
\]
TUNING TiO$_2$ COMPOSITION

$$2\text{NH}_4^+ \rightarrow \begin{array}{c} \text{OH} \text{OH} \\ \text{H}_3\text{C} \text{O} \text{O} \text{O} \text{Ti} \text{O} \text{O} \text{O} \text{CH}_3 \end{array} \rightarrow 2^-$$

+ Urea

$160^\circ C \times 24h$

$\rightarrow \text{TiO}_2$

$\text{R + A}$

Rutile

Anatase

$\text{TiO}_2$

Brookite

$\text{A + B}$

$\text{A + B}$

TUNING TiO₂ COMPOSITION

Ethanol/water solution
Simulated sunlight

Pt 0.2 wt% added as co-catalysts

**Per mass**

**Per surface area**

**Brookite:**
- Favorable electronic properties
- Well defined morphology and exposed facets

**TiO$_2$ BROOKITE NANORODS**

Per mass

**Per surface area**

**Proc. Nat. Acad. Sci., 113** (2016), 3966-3971
50 fs ultraviolet (4.0 eV) pump pulse

\[
\frac{\Delta T}{|\Delta T_{MAX}|} = A_1 e^{\frac{t}{\tau_1}} + A_2 e^{\frac{t}{\tau_2}}
\]

➢ Increase life-time of electron/hole pairs with length
Formation of hybrid materials

Pd@Ti(OR)_4 Core-shell

MWCNT-COOH

Self-assembling

Calcination at 350°C

Hydrolysis

Green Chem. 19 (2017), 2379-2389
Pd@TiO$_2$/CARBON NANOTUBES

After calcination

- Porous Pd@TiO$_2$ shell around CNT
- Anatase phase

EF-TEM

*Green Chem.* 19 (2017), 2379-2389
Pd@TiO$_2$/CARBON NANOTUBES

**Ethanol/water solution**

**Glycerol/water solution**

H$_2$ production under UV-vis irradiation

*Green Chem. 19 (2017), 2379-2389*
Pd@TiO$_2$/CARBON NANOTUBES@Fe

Before

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Before.png" alt="Catalyst Before" /></td>
<td><img src="After.png" alt="Catalyst After" /></td>
</tr>
</tbody>
</table>

After

Purification by magnetic separation

1. Sonication
2. Hydrolysis

![Images showing before and after purification](Images.png)

Pd@TiO$_2$/CARBON NANOTUBES@Fe

EtOH : H$_2$O = 1:1
UV-vis irradiation

Pd@TiO$_2$/Fe@CNT-magnetic
Pd@TiO$_2$/Fe@CNT-filtered
Pd@TiO$_2$

Pd@TiO$_2$/CARBON NANOTUBES@Fe

EtOH : H$_2$O = 1:1
Simulated Sunlight irradiation

Easily reusable by magnetic recovery from the reaction mixture!!!
✓ Materials active under visible light ($\lambda > 420$nm)

✗ Not sustainable
Sacrificial Electron Donor
Effect of molecular structure
PHENOTIAZINE-BASED DYES

Effect of molecular structure

Active & Stable

ChemSusChem 8 (2015), 4216-4228
PHENOTIAZINE-BASED DYES

Effect of aromatic structure

Phenotiazine

Phenoxazine

Carbazole

![Chemical structures and spectra](image)
PHENOTIAZINE-BASED DYES

Effect of aromatic structure

High energy of LUMO

Ligand-to-Metal Charge Transfer

TRIPHENYLAMINE-BASED DYES

Toward sustainability

EtOH / water solution as sacrificial electron donor
\( \lambda > 420 \text{ nm} \)

Figure 2. Structure of the dyes investigated in this study.
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Electric Vehicles Smart Fleets

Electric Unmanned aerial vehicles
ELECTRIC / HYBRID AIRCRAFT

2 hrs 250 Kg of batteries

1 MJ/Kg

43 MJ/Kg

7 hrs 260,000 Kg of batteries
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

\[ \text{Ru-doped ZnIn}_2\text{S}_4 \] 
\[ \text{acceptorless dehydrogenative C-C coupling} \]

Representative diesel fuel precursors (DFPs):
- Linear-chain DFPs:
  - C10-2 (R^1 = H, R^2 = H)
  - C11-3 (R^1 = H, R^2 = Me)
  - C12-2 (R^1 = Me, R^2 = Me)

- Branched-chain DFPs

Other oligomers + H\(_2\) → diesel fuels + other alkanes

\[ \text{Pd/Nb}_2\text{O}_3\cdot\text{Yb(CF}_3\text{SO}_4)_3 \] 
\[ \text{hydrodeoxygenation} \]
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

Doped-ZnIn$_2$S$_4$ photocatalysts

Nature Energy 4 (2019), 575-584
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

Ru-ZnIn$_2$S$_4$ photocatalyst

2,5-DMF
0.56 g of DPF g$_{\text{cat}}^{-1}$ h$^{-1}$
3.3 mmol of H$_2$ g$_{\text{cat}}^{-1}$ h$^{-1}$
AQY 15.2 %

Nature Energy 4 (2019), 575-584
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

Ru-ZnIn$_2$S$_4$ photocatalyst

Nature Energy 4 (2019), 575-584
VISIBLE-LIGHT-DRIVEN COPRODUCTION OF DIESEL FUEL PRECURSORS AND HYDROGEN

Ru-ZnIn$_2$S$_4$ photocatalyst

Radical mechanism confirmed

Nature Energy 4 (2019), 575-584
Ru-ZnIn$_2$S$_4$ photocatalyst: role of Ru

- Decreased band gap
- Stabilization of e$^-$/h$^+$ pairs
- Reduction of Ru ions to Ru(0) justifies slight deactivation

Nature Energy 4 (2019), 575-584
Materials manipulation at nanoscale level and precise assembly of nano-building blocks in hierarchical materials can lead to a step change in photo-, electro- & catalytic performances.

We have great options for a sustainable world!

The future is bright but there are still lots of shadows.
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MEE RESEARCH GROUP
http://meeresearch.weebly.com/

THANK YOU ALL FOR YOUR KIND ATTENTION
MINING REQUIRES ENERGY
CH₄ & GREENHOUSE EFFECT

- Lifetime in the atmosphere is much shorter than CO₂
- More efficient at trapping radiation than CO₂

Impact of CH₄ on climate change is more than 25 times greater than CO₂

Source Identification and Quantification

NEEDS FOR CATALYTIC ABATEMENT

Anthropogenic sources

EPA, Emission Overview 2015
Pd-BASED CH₄ COMBUSTION CATALYSTS

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

**Noble metal-based catalysts (Pd, Pt, Au)**

- **2 active phases:** PdO and Pd

- High specific activity (PdO)
- Lower specific activity (Pd)

Al₂O₃

**Pd(5%)/La-Al₂O₃**

Pd-BASED CH₄ COMBUSTION CATALYSTS

Catalyze re-oxidation

Maximize PdO - CeO₂ interaction

O₂ from the gas phase

O₂ from a PROMOTER

REDUCIBLE OXIDES
**Pd@CeO$_2$ SUPRAMOLECULAR STRUCTURES**

Ce(IV) tetrakis(decyloxide)

**Hydrolysis conditions:**
THF + 30 eq H$_2$O (120 mol vs Ce) in 4 h

**MUA-Pd NPs**
MUA: 11-Mercapto Undecanoic Acid

**Pd core size:**
1.8 ± 0.2 nm

Dispersible in CH$_2$Cl$_2$, toluene, hexane

J. Am. Chem. Soc. 132 (2010), 1402-1409
Pd@CeO$_2$ FOR CH$_4$ COMBUSTION
Engine exhaust:
- Methane
- Higher hydrocarbons
- CO
- Soot
- NOx

Diesel oxidation catalyst
- Oxidation of methane, higher hydrocarbons, and carbon monoxide with a Pd catalyst

Catalyzed soot filter
- Wall-flow filter removes soot

Selective catalytic reduction
- Converting nitrogen oxides with aid of urea (which hydrolyzes to ammonia) into nitrogen and water

Tailpipe emissions:
- CO₂
- N₂
- H₂O

Water vapor

SO₂

Phosphates

PdO DEACTIVATION

Pd@CeO$_2$ FOR CH$_4$ COMBUSTION

Effect of water

0.5% CH$_4$, 2.0% O$_2$, 15% H$_2$O (if present), Ar balance, O$_2$/O$_2$(stoich) = 2, GHSV = 200000 mL g$^{-1}$ h$^{-1}$

ChemCatChem 7 (2015), 2038-2046
Pd@CeO$_2$ FOR CH$_4$ COMBUSTION

Fresh
Dry-aged
Wet-aged

850°C + O$_2$

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Accessible Pd surface area (m$^2$/g)</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Dry aged</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Reactivated after dry aging</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>Wet aged</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Reactivated after wet aging</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
Pd@CeO₂ FOR CH₄ COMBUSTION

- Reduction of PdO to Pd
- Increase in population of OH
- Wet aging reduces Pd accessibility
XPS-SRPES
Synchrotron Radiation PhotoEmission Spectroscopy

Surface Study

Pd@CeO$_2$ MODEL CATALYSTS

Conductive support
SURFACE STUDY: SO$_2$ POISONING

ALD

ITO/quartz

Al$_2$O$_3$/ITO/quartz

Pd@MOx/Al$_2$O$_3$/ITO/quartz

850°C calcination

**SURFACE STUDY: SO$_2$ POISONING**

- Choose layer composition
- Change thickness
- General applicability

Model materials comparable to real catalysts

850°C calcination

**ALD**

SURFACE STUDY: SO$_2$ POISONING

- **Surface area** 90-100 m$^2$g$^{-1}$
- **Pd accessible area** 3 m$^2$g$^{-1}$ (~ 60% D)
- **Similar activity in light off experiments**

![XRD graph](chart.png)

CeO$_2$ 80:20
60:40
40:60
20:80
ZrO$_2$

PdO

**References**

SURFACE STUDY: SO$_2$ POISONING

- **Low T**

**Graphical Data**

- CH$_4$ conversion (%)
  - Time (h)
  - Temperature: 325°C, 350°C, 400°C, 450°C
  - SO$_2$ concentration: 50 ppm
  - GHSV = 200000 mL g$^{-1}$ h$^{-1}$

**Chemical Reactions**

- SO$_2$ + PdO $\rightarrow$ SO$_3$ + Pd
- SO$_3$ + PdO $\rightarrow$ PdSO$_4$

**Textual Information**

- 0.5% CH$_4$, 2.0% O$_2$, SO$_2$ 50 ppm (if present), Ar balance, O$_2$/O$_2$(stoich) = 2
- Pd@ZrO$_2$, Pd@CeO$_2$, Pd@CZ, Pd

**Similar Performances**

- Complete deactivation

**References**

Sulfates formation/desorption

Catalytic Activity

Pd@ZrO₂ more resistant
Less sulfates formed and partial desorption

SURFACE STUDY: SO₂ POISONING

0.5% CH₄, 2.0% O₂, SO₂ 50 ppm (if present), Ar balance, O₂/O₂(stoich)=2, GHSV = 200000 mL g⁻¹ h⁻¹

SURFACE STUDY: SO$_2$ POISONING

Single Cations Sulfates

- At 600°C: no deactivation observed
- Modification of Ce and Zr spectra
- Zr signal not affected in CZ
- In CZ, sulfates are mostly formed on Ce

XPS

![XPS Spectra](image)

**Ce 3d**

- **CeO$_2$**

**Zr 3d**

- **ZrO$_2$**

**Pristine**

- **500°C SO$_2$/dry**

- **600°C SO$_2$/dry**

MEE RESEARCH ACTIVITIES

**Air pollution abatement**
- Three Way Catalysts
- CH$_4$ combustion

**Water purification by photocatalysis**
- Doped TiO$_2$
- Bi$_2$O$_3$-based materials
- Metal tungstates

**H$_2$ & Fuels production**
- CH$_4$ partial oxidation
- Steam reforming of renewable compounds
- Photocatalytic reforming of oxygenated compounds
- Synthesis of valuable organic compounds

**H$_2$ purification**
- Water Gas Shift
- Preferential Oxidation of CO
**H₂ PRODUCTION FROM GLYCEROL**

*Possible pathway*

Accumulated in solution
Formation of hybrid materials

**A**

- CNTs as electron sink

**B**

- CNTs as sensitizer

---

Pd@TiO$_2$/CARBON NANOHORN

**SWCNHs**

4 M HNO$_3$
1. Sonication 15min
2. Stirring 3h

**Ox-SWCNHs**

Pd-MUA

Ti(OBu)$_4$ in EtOH

Pd-MUA@Ti(OBu)$_x$

1. Dropwise addition under sonication

2. Sonication 30min
3. H$_2$O/THF (1/9)
4. Sonication 30’

**Pd@TiO$_2$/ox-SWCNHs**
Pd@TiO₂/CARBON NANOHO Horns

CVs measured in (---) N₂-saturated or (---) CO₂-saturated 0.10 M phosphate buffer solution pH 7.40, at 50 mV s⁻¹

Energy Environ. Sci. 2018
H₂ production under Simulated sunlight

Ethanol/water solution

- Homogeneous coverage of CNC by porous Pd@TiO₂ shell
- Anatase phase

Montini et al. Chem. Commun. 52 (2016), 764-767
PHENOTIAZINE-BASED DYES

Effect of wettability

Chem. Commun. 52 (2016), 6977-6980
PHENOTIAZINE-BASED DYES

Effect of co-adsorbents

Stable interaction between PTZ-GLU and GLUA

ACS Energy Lett. 3 (2018), 85-91
Single Atom Catalyst on high quality functionalized graphene

Oxidative homocoupling of substituted benzylamines

Aim of this work

Evaluation of the effect of the doping of TiO$_2$ with B and N on the production of valuable chemicals:

**Hydrogen**
by photoreforming of aqueous solutions containing ethanol or glycerol.

**Benzimidazole**
by an alternative process.

![Graph showing apparent first order constant for Methyl Orange degradation](image)


Synthesis of the supports

**Sol-gel method for TiO$_2$ supports**

1. \( Ti(BuO)_4 \) + EtOH / H$_2$O + HNO$_3$ → gel → Drying → Calcination

2. \( Ti(BuO)_4 + H_3BO_3 + H_2NCONH_2 \) + EtOH / H$_2$O + HNO$_3$ → gel → Drying → Calcination

B / Ti = 0.09
N / Ti = 0.05
Characterization of the supports

➢ Mixture of polymorphs
➢ High surface area
➢ Improved by B,N doping

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
</tr>
<tr>
<td>TiO₂</td>
<td>64</td>
<td>28</td>
</tr>
<tr>
<td>TiO₂-B,N</td>
<td>68</td>
<td>26</td>
</tr>
</tbody>
</table>
Deposition of the metal phase

Metal photodeposition

Support + metal nitrate \[\text{50\% water - 50\% ethanol} \quad \text{UV-vis irradiation} \rightarrow \text{Metal/TiO}_2 \quad \text{Metal/TiO}_2-B,N\]

HAADF-STEM

Pd 0.5wt\%
Ag 0.5wt\%
Pt 0.5wt%
Cu 1.0wt\%
H₂ production from ETHANOL

Gas phase

Effect of:
- Support
- Metal

![Graphs showing H₂ production vs. irradiation time](image)

- **Support**
  - Pd/TiO₂
  - Pd/TiO₂-B,N

- **Metal**
  - Cu/TiO₂
  - Ag/TiO₂-B,N
  - Pt/TiO₂-B,N
  - Cu/TiO₂-B,N

**Ethanol vs. Glycerol**

- Doping TiO₂, leaching is significantly reduced
- More stable performances for TiO₂-B,N supported catalysts
Synthesis of benzimidazole

**Conventional synthesis:**

Very toxic and carcinogenic

- T = 100 – 200 °C
- Strong acidic conditions
- Strong oxidants
Synthesis of benzimidazole

Conventional synthesis:

Very toxic and carcinogenic

➢ T = 100 – 200 °C
➢ Strong acidic conditions
➢ Strong oxidants

Communications

Heterogeneous Catalysis

One-Pot Synthesis of Benzimidazoles by Simultaneous Photocatalytic and Catalytic Reactions on Pt@TiO₂ Nanoparticles**

Yasuhiro Shiraishi,* Yoshitsune Sugano, Shunsuke Tanaka, and Takayuki Hirai


Scheme 1. One-pot synthesis of benzimidazole using a Pt@TiO₂ catalyst under photoirradiation.
Synthesis of benzimidazole

Alternative processes:

- Less toxic reagents
- Renewable and cheap solvent
Synthesis of 2-methylbenzimidazole

Conditions:
- 60 mL DNB/NA 2mM in EtOH 96%
- 150 mg Pd/TiO$_2$-B,N
- Ar flow, 30°C
- Simulated sunlight irradiation
Synthesis of 2-methylbenzimidazole

Conditions:
- 60 mL DNB/NA 2mM in EtOH 96%
- 150 mg Pd/TiO$_2$-B,N
- Ar flow, 30°C
- Simulated sunlight irradiation
Substituted 2-methylbenzimidazole

Further functionalization
Bromo derivative

GC/MS analysis

Pd

Pt

Ag

Cu
Bromo derivate

GC/MS analysis

Complete hydrode bromination

Selectivity > 90%

Pd
Pt
Bromo derivate

GC/MS analysis
Chloro derivate

GC/MS analysis

Selectivity ~ 95%

Pd, Pt
Methyl ester derivat

GC/MS analysis

Pd
Pt
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1936 – 2019

The sleep of reason produces monsters
Francisco Goya (1799)