Hybridisation and mesostructuring as tools towards advanced energy materials
Research overview

**Synthesis**

Nanocarbons: CNT fibres, aerographite, graphene

Hybrids & 2D Heterostructures:
TMO@TMO, NC@TMO & G@ Sb, Bi, MoS$_2$

Ordered mesoporous films vis BCP self-assembly:
Metal oxides/nitrides, carbon, glasses, zeolites

Metal-organic frameworks (MOFs)
Polyoxametallates (POMs)

**Fundamental studies**

Interfaces: liquid-solid and solid-solid
Dynamics: charge/energy transfer, diffusion
Mechanism: photocatalysis, sensing, bioactivity, stability

**Applied studies**

Energy: photocatalysis, artificial photosynthesis, photovoltaics
Environment: water/air purification, CO$_2$ reduction
Medicine: bioactivity/tissue engineering, drug delivery, biosensors, antibacterial coatings
1. Heterogeneous photocatalysis
2. Nanocarbon-inorganic hybrids
3. Hydrogen evolution through sacrificial water splitting
4. Model systems: mechanisms & interfacial charge transfer
5. Ordered mesoporous photocatalysts
6. Summary and outlook
Heterogeneous photocatalysis

Important photocatalytic applications

ENVIRONMENT
- Removal of pollutants (VOCs, odours, NOx, tobacco)
- Degradation of xenobiotica (pesticides, hormons, drugs)
- Self cleaning surfaces

HEALTH
- Destruction of bacteria, microbes, virus
Important photocatalytic applications

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HEALTH
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ENERGY
• Hydrogen production from water
• Conversion of CO₂ to methanol

FINE CHEMICALS
• Selective oxidations of alkanes, alkenes, and alcohols to aldehydes and ketons,
• propene to propylene oxide
Catalysis is the **acceleration of a chemical reaction** due to the pure presence of a substance called catalyst that is not consumed in the process.

A catalyst provides an **alternative reaction path** with lower activation energy, hence it affects the kinetics of the reaction without altering its thermodynamics.

A catalyst **enables a specific reaction** while greatly decelerating all other reactions.

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**1835**

Jöns J Berzelius

Definition

**1880**

Wilhelm Ostwald

Systematic work
**Photocatalysis:** photons instead of thermal energy to accelerate chemical reactions

**Homogeneous photocatalysis**
- same phase, mostly liquid
- activated species (O$_2^/-$/OH·)
- molecular (photo)catalysis

**Heterogeneous photocatalysis**
- different phases, mostly solid-liquid
- solid state inorganic compounds
- Catalysis happens at the interface

**Advantages:**
- ambient conditions
- high selectivity, alternative pathways
- “non-reactive” educts
Mechanistic steps in heterogen. photocatalysis

1 Reactant:
- Diffusion
- Adsorption

2 Irradiation:
- $e^-/h^+$ pair formation
- Charge recombination
- Charge transport/transfer

3 Chemical reaction:

4 Product:
- Desorption
- Diffusion

Reduction
Photoelectrochemistry
$H_2$ production

$O_2/H_2O_2$

$O_2^-/OH^-$

Adsorbed pollutant

$H_2O/OH^-$

$OH^-$

Adsorbed product

Oxidation
Organic pollutant degradation
Self-cleaning / Sterilisation
$O_2$ production

$E_{ph} > E_g$
### Nanocarbon-Composites

- CNTs as a filler in organic/inorganic matrix → low carbon loading
- Synthesis via mechanical “ex-situ” mixing → discrete building blocks
- Combines individual properties

### Nanocarbon-Hybrids

- Functional material as a thin layer on CNT surface → high carbon loading
- Synthesis from molecular precursor „in-situ“ → nanocarbon as substrate
- Interfacial processes → new properties

- thin layer of TiO$_2$ nanoparticles on CNTs
- heat and charge transfer processes

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1. Nanocarbon-inorganic hybrids

Photovoltaic devices
- larger photocurrents
- higher efficiencies
- improved lifetime

Photonics/field emitters
- improved electron emission densities
- lower turn-on and threshold fields
- stabler and longer performance

Chemical sensors
- improved sensitivity
- lower operation temperature
- faster response time

Electrocatalysis/Catalysis
- improved activity & selectivity
- smaller particles/less material
- positive support effects

Photocatalysis
- extended absorption range
- improved activity/selectivity for the
  * degradation of organic compounds
  * destruction of virus and bacteria
  * production of hydrogen from water

Batteries/Supercaps
- larger capacity & energy density
- faster & deeper charging/discharging
- reversible and stable performance
- lighter weight
1. Nanocarbon-inorganic hybrids

**Materials requirements**

1. **Electronic structure: light absorption**
   - Need materials with suitable bandgap
     a) small enough for maximum absorption
     b) large enough to oxidise water and organic compounds
     c) stable towards degradation
     d) positioned correctly with respect to reactions

**CNTs in hybrid materials**

DSSC, “Grätzel cell“:
- i.e. Ru$^{2+}$ - bipyridine complex
1. Nanocarbon-inorganic hybrids

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2. **Crystal structure/Interfaces: charge recombination**
   - Need crystalline and defect-free materials
   - Need charge separation through el. field/material interface

**CNTs in hybrid materials**

**Photosensitiser:**
- increased absorption range

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1. **Nanocarbon-inorganic hybrids**

1. band-to-band recombination
2. trap-assisted recombination
1. Nanocarbon-inorganic hybrids

**Materials requirements**

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<th>3. Morphology: Transport, sorption and reaction</th>
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<td>Need nanostructured functional materials with</td>
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<td>a) desired surface properties (i.e. hydrophilicity)</td>
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<td>b) large surface area (adsorption):</td>
</tr>
<tr>
<td>particle size vs absorption cross-section</td>
</tr>
<tr>
<td>c) controlled mesopores (diffusion)</td>
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| 4. Stability, cyclability, durability, cost, toxicity |

**CNTs in hybrid materials**

**Photosensitiser:**
increased absorption range

**Charge acceptor:**
reduced charge recombination

**Heat sink and substrate:**
substrate for smaller particles, controlled porosity, new phases

**Structural material:**
mechanical integrity, light-weight
Synthesis of nanocarbon hybrids

Carbon nanotubes: the most useful nanocarbon?

<table>
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<tr>
<th>Property</th>
<th>SWCNTs</th>
<th>MWCNTs</th>
<th>Graphite</th>
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<tr>
<td>Specific gravity</td>
<td>0.8 g/cm³</td>
<td>&lt; 1.8 g/cm³</td>
<td>2.26 g/cm³</td>
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<tr>
<td>Young’s modulus</td>
<td>~1.4 TPa</td>
<td>~0.3-1 TPa</td>
<td>1 TPa (in plane)</td>
</tr>
<tr>
<td>Strength</td>
<td>50-500 GPa</td>
<td>10-60 GPa</td>
<td></td>
</tr>
<tr>
<td>Resistivity</td>
<td>5-50 µΩ cm</td>
<td>50 µΩ cm (in plane)</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>3000 Wm⁻¹K⁻¹</td>
<td>3000 Wm⁻¹K⁻¹ (in plane)</td>
<td>6 Wm⁻¹K⁻¹ (in plane)</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>Negligible</td>
<td>Negligible</td>
<td>-1 x 10⁻⁶ K⁻¹ (in plane)</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>600-800 °C in air</td>
<td>2800 °C in vacuum</td>
<td></td>
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2 to 9.6 wt% ferrocene in toluene
Synthesis of nanocarbon hybrids

Choice of nanocarbons

Key characteristics

- Type (SW/MW, NHs, G/GO)
- Dimensions (length, diameter)
- Purity / Yield (metals, C60, C)
- Crystalline quality, defects
- Chirality (semi vs metallic)
- Entanglements, alignment
- Surface chemistry (functional.)

Aerographite (K. Schulte)

OMC gyroids (U. Wiesner)
Synthesis of nanocarbon hybrids

Choice of attachment

- irregular coating of non-uniform thickness
- lots of agglomerated particles

Non covalent: benzyl alcohol as linking agent

Synthesis of nanocarbon hybrids

Non-covalent modification with aromatic linkers

ZnO NWs
Sputtering and Hydrothermal (Shearer et al, Adv. Mater. 2012)


„Nano-Petals“ of V$_2$O$_5$ by solvothermal reaction (Dieterle, unpublished)

Al$_2$O$_3$ with ALD (Kemnade et al, Nanoscale 2015)
Photocatalytic hydrogen evolution

- Band-gap = 3.9 eV
- Ta(OEt)5 as precursor
- BA as surfactant
- 48 h @ 180°C, 2h @ 500/700 °C

Evaluation of H$_2$ evolution

- 200W Hg lamp (inner radiation)
- 20 mg/200 ml
- 50% methanol
- 0.5% Pt (photodeposition)
- online detection of H$_2$, O$_2$, CO, CO$_2$ (Emerson X-Stream)

G. Haselmann, D. Eder, ACS Catalysis, 2017
Photocatalytic hydrogen evolution

Nanoparticles, gap

Single-crystalline film, Ohmic contact

Higher activity of H2:
- better charge transport
- better charge transfer
  (Ohmic vs tunneling)
- altered band structure

With Pt: 1520 μmol/h
Without Pt: 1190 μmol/h

20 mg/200 ml
50% methanol
0.5% Pt (photo)
How can we measure interfacial charge or energy transfer?

→ Photoluminescence: requires luminescent materials (e.g. ZnO)
→ DLS-TPCS (Dual Light Source Photocurrent Spectroscopy)
→ CIMPS (Controlled Intensity Modulated PhotoSpectroscopy)
→ Pump-probe femtolaser spectroscopy (M. Bonn, MPI Mainz)

Where is hydrogen formed?

i.e. triple-phase boundaries, tips of CNTs

XPS/UPS; unpublished

Photoluminescence spectroscopy
Quenching effect: Charge transfer, energy transfer, size/interparticle effects, CNT absorption

New model system:
→ thin inactive barrier layer (Al$_2$O$_3$) between CNTs and ZnO
→ distance-dependent PL studies to distinguish charge and energy transfer
Atomic layer deposition (ALD)
- introduction of Al₂O₃ barrier layer (2-100 nm)
- pyrenecarboxylic acid (PCA) as linker
- additional deposition of fluorescent ZnO
Interfacial charge and energy transfer

Photoluminescence spectroscopy & photocatalysis

- PL quenching up to at least 50 nm
- linear correlation with thickness
- Influence of crystallinity and permittivity

Model:
- charge transfer into $\text{Al}_2\text{O}_3$
- $e^-$ conduction limitation
- charge injection into CNTs

Interfacial charge and energy transfer

Photoluminescence spectroscopy & photocatalysis

HER decreased with 2 nm Al$_2$O$_3$

→ “Triple phase boundaries“ as active sites
→ Porous nanocarbon-inorganic hybrids
→ Self-assembly of triblock-terpolymers
(PI-b-PS-b-PEO) → 3D gyroidal pores
Summary and Outlook

Heterogeneous photocatalysis with great prospects for energy/environment

Nanocarbon-inorganic hybrids as next-generation photocatalysts

→ Interfacial, structural, electronic engineering
→ Quantification of interfacial processes
→ Reaction mechanism, origin of catalyst deactivation
→ Ordered mesoporous hybrids

Interplay between Chemistry, Physics and Materials Science

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Thank you for your attention!

FG: Materials for Energy, Environment and Medicine

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