Energy transfer mechanisms from plasmonic metal nanoparticles to core-shell black-TiO$_2$.

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Solar energy exploitation roadmap

2012

"excess" electrical energy

elektrolyzers (PEM)

H₂

catalysis

CH₃OH, CH₄, DME, etc.

2020

PEC
H₂ prod.
(Conc. solar, bioH₂,...)

elektrolyzers (PEM)

H₂

catalysis

CH₃OH, DME, olefins, etc.

2030

artificial leaves

in chemical industry to increase use of renewable energy

distributed energy and chemicals

Photocatalytic water splitting

Water splitting using TiO$_2$

1972 2014

- Absorption, bandgap $1.23 \text{ eV} < E_g < 2.5 \text{ eV}$
- Charge carriers transport
- Band energy position
- Surface features for maximizing interfacial charge transfer
- Stability, cost, non-toxicity

Chen et. al., Chem. Rev. 2010, 110, 6503–6570; http://solarfuelshub.org/
**TiO$_2$ + & - and solutions**

**TiO$_2$**

- large availability
- cheapness
- stability
- non-toxicity

**N-doped TiO$_2$**

- Hydrogenated TiO$_2$

**drawback is absorption only in UV region**

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Chen et al., Chem. Rev. 2010, 110, 6503–6570
Localized Surface Plasmon Resonance (LSPR)

Collective oscillation of surface free electrons

\[ d_{NM} \ll \lambda_{inc} \]

Intense, localized electromagnetic field

PLASMON RESONANCE ADVANTAGES

Coupling of optical & electronic properties

Catching all the solar spectrum-tunable absorption through nanostructures control

**LSPR - Applications**

1. Metal oxide - Metal nanoparticles coupling

   Metal oxide photoactivity increased (LEMF)


2. Plasmonic-induced photoactivity

   Plasmon resonance to excite the metal oxide

**TiO₂ supported-Au nanoparticles**

1. **Hot e⁻-transfer**
   - Band alignment $\rightarrow$ Schottky barrier height ($\phi_{SB}$)
   - $\text{Au/TiO}_2, \phi_{SB} \sim 0.9 \text{ eV}$
   - $\Delta \varepsilon \sim 1 \text{ eV}$

2. **Energy Transfer (PRET)**
   - Intra band-gap defect states
   - $V_{Os}$, slightly below CB
   - Non-metal doping, slightly above VB

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[Image of diagram with labels and annotations]
Aim of the work

Use CL spectroscopy better discern the **2 mechanisms**

- **P25 TiO$_2$**: no intra band-gap states
- **Black-TiO$_{2-x}$**: defect states below the CB

Au nanoparticles loading: **1 wt.%**

to evaluate **charge transfer** and **induced electric field** variations

Excitation of Au plasmon band ($\lambda > 400$nm)

(TiO$_2$ band gap $\sim 3.0 - 3.2$ eV)
Photocatalysts synthesis

P25-TiO$_2$
commercial TiO$_2$ powder, 500° C in O$_2$

black-TiO$_2$
Nanoactive™ commercial TiO$_2$ powder, 500° C in H$_2$

\[ \text{Au, Pt NPs deposition (1 wt.%):} \]
\[ \text{HPtCl}_6/\text{HAuCl}_4 + \text{NaBH}_4 \]

Photocatalysts characterization

X-ray Diffraction

Uv-vis

TEM

Catholuminescence spectroscopy

Plasmon-photoactivity

\[
\begin{align*}
\text{H}_2\text{O} & \longrightarrow \text{H}_2 + 0.5\text{O}_2 \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \longrightarrow 3\text{H}_2 + \text{CO}_2
\end{align*}
\]

H$_2$O photosplitting / methanol photoreforming

@CNR-ISTM
Black TiO$_2$ 1

- P25-TiO$_2$, $\sim 80$ wt.% A + $\sim 20$ wt.% R
- b-TiO$_2$, $\sim 81$ wt.% A + $\sim 19$ wt.% R
- Nanoactive - TiO$_2$, 100 wt.% amorphous

1. Red shift of absorption – $E_g$
2. Continuous absorption 400-800nm

EPR and XPS analysis indicate that Ti$^{3+}$ is present only in the core of black TiO$_2$ NPs.
Black TiO$_2$ vs. P25

Black TiO$_2$: crystalline core / amorphous shell

P25: fully crystalline nanocrystal
Crystalline core/disordered shell morphology
$V_O$s in the bulk anatase crystalline phase - disordered NP surface stoichiometric.
Bandgap narrowing $\rightarrow$ synergisty $V_O$s / surface disorder.
Plasmon-photoactivity 1

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{H}_2 + 0.5\text{O}_2 \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow 3\text{H}_2 + \text{CO}_2
\end{align*}
\]

Water photosplitting
methanol photoreforming
Photoreforming device

- TiO$_2$ powders (14 mg) on quartz beads
- Photocatalytic Plexiglas cell + closed recirculation apparatus
- N$_2$ flow 40 mL min$^{-1}$
- Vapour feed from 20 vol.% MeOH/H$_2$O solution ($x_{\text{MeOH},l} = 0.1$)
- 300 W Xe arc lamp (solar simulator, cut off filter $\lambda > 400$ nm)
- H$_2$ + MeOH oxidation products monitored by on-line GC analysis
- T = 30 ± 2 °C and P$_i$ = 1.2 bar

Photoreforming activity

Un-filtered solar simulator light

M/P25 > M/b-TiO₂

Au/P25 ≈ Pt/P25 >> P25

Au/b-TiO₂ > Pt/b-TiO₂ >> b-TiO₂
Photoreforming selectivity

"Real" water photosplitting
Less photoreforming

Pt more selective than Au
“Pure” visible light ($\lambda > 400$nm)

- No $H_2$ for black TiO$_2$
- Au vs. Pt 360% enhancement
  
  (33% increase under unfiltered solar light)
CL System

CL spectroscopy system:
- Wavelength ranges:
  - Visible 280 – 830 nm
  - Ge NIR 800-1700 nm
  - Extended InGaAs Short-wavelength IR 1000-2500 nm
- Temperature: 6-300K

SE Microscope:
- Accelerating Voltage: 250 eV – 40 keV
- Beam Current: 100 pA – 10 μA
Two types of transitions can be distinguished:

- **Intrinsic emissions** which are due to **recombination of electrons and holes** across the fundamental energy gap, by interband transitions from the bottom of the conduction band to the top of the valence band. In the spectral region close to the energy gap it is possible to detect **free excitons or bound excitons**, with one of the carriers localized at an impurity centre.

- **Extrinsic luminescence** which is due to **radiative transitions involving states in the band-gap**, shallow or deep, mainly due to **native defects and impurities** complexes acting as donor or acceptor centers. Different processes of recombination between free carriers and trapped carriers can take place, basically indicated as free-to-bound (e.g. donor-to-free-hole $D^0 h$, free-electron-to-acceptor $eA^+$) and donor-to-acceptor pair (DAP) transitions.
P25 vs black TiO$_2$

2.77 eV = self-trapped exciton
2.62 eV = oxygen vacancies (V$_{Os}$)
2.36 eV = oxygen vacancies (V$_{Os}$)

MUCH HIGHER NUMBER OF DEFECT IN BLACK TiO$_2$
**Au, Pt – P25, black-TiO$_2$**

<table>
<thead>
<tr>
<th>CL component</th>
<th>Black TiO$_2$</th>
<th>Au/Black TiO$_2$</th>
<th>P25</th>
<th>Au/P25</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.77 eV</td>
<td>1975</td>
<td>1383</td>
<td>919</td>
<td>2253</td>
</tr>
<tr>
<td>2.62 eV</td>
<td>2224</td>
<td>3363</td>
<td>1284</td>
<td>1500</td>
</tr>
<tr>
<td>2.36 eV</td>
<td>4071</td>
<td>8045</td>
<td>2616</td>
<td>5200</td>
</tr>
</tbody>
</table>

Pt $\rightarrow$ luminescence quenching (better e$^-$/h$^+$ separation)

Au $\rightarrow$ luminescence enhancement (plasmonic interactions = energy transfer)
The disordered black-TiO$_2$ nanoparticle outer layer induces a reduced charge mobility $\rightarrow$ Less hot e$^-$ transfer.

The signal at 2.36 eV is doubled $\rightarrow$ PRET SPR(Au)$\rightarrow$V$_{O}$s TiO$_2$
Conclusions

1. Higher photoactivity of Au/TiO$_2$ vs Pt/TiO$_2$

2. Role of SPR and Plasmonic interactions

3. By Catholuminescence spectroscopy:
   
   Hot e$^-$ transfer: dominant process for non-defective titania

   Plasmon Resonance Energy Transfer: reduced band-gap black titania

   Role of intra band-gap oxygen vacancies defect states (CB)
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