Hyperfine interactions in hydrogenated TiO$_2$ thin films and powders for photocatalytic reactions

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Why study TiO$_2$:H?

TiO$_2$+ H$_2$ Plasma → Black TiO$_2$

Lots of defects (V$_{O}$, V$_{H}$, Ti)

- Absorption improved
- More electron-hole pairs
- Better performance?

Absorption

3 hours of H treatment

Pristine-TiO$_2$  H-TiO$_2$-30s  H-TiO$_2$-1min  H-TiO$_2$-3min  H-TiO$_2$-5min  H-TiO$_2$-20min
Why study TiO$_2$:H?

- doesn’t alter structure
- photocatalytic performance rates better
- defects (Ti$^{2+}$, Ti$^{3+}$ V$_o$, V$_H$)

Generation rates for methane and CO in the photocatalytic reduction of CO$_2$ with H$_2$O through H-TiO$_2$: H$_2$

Light absorption

TiO$_2$ $\rightarrow$ H$_2$ 30 sec $\rightarrow$ H$_2$ 1 min
Investigation of

- local defects induced with plasma in the nanostructured TiO$_2$ materials by PAC and eMS having a significant impact on the electron-hole recombination;
- dopants and H$_2$ interactions i.e. possibly leading to a “new” black TiO$_2$;
- charge transfer?
- defects evolution under various atmospheres and conditions.

**OBJECTIVES**

**Sample production & characterisation (PVD, CVD, XPS, UV/Vis, TEMS, CEMS)**

**TU Ilmenau**

**TDPAC & eMS measurements**

**ISOLDE**
PAC SPECTROSCOPY at ISOLDE

- $^{111m}$Cd is used in doping of TiO$_2$ and only at ISOLDE
- Experience and sufficient amount of setups
- Interactions of Cd with V$_H$, V$_0$ and Ti defects
  - + no after-effect

How?

As a function of

- sample stoichiometry with different amount of defects H$_2$ annealing and measuring temperature from 450-700 K

Implantation depth at 30 keV is $\sim$ 10-12 nm ($^{111m}$Cd in TiO$_2$)
Complement of the PAC study:

- Probe-host or probe-defect interaction
- Valence/(spin) state of probe atom \((X^{n+})\)
- In earlier work (2014)* Ti and Vo defects were probed

**HOW?**

As a function of

- Sample stoichiometry
- Annealing and measuring temperature

Implantation depth at 30 keV is \(~ 11-16\) nm \((^{57}\text{Mn in TiO}_2)\)

The eMS setups

The old setup:
• Limitations (such as temperatures, additional vibrations, long-sample-changing option)
• Complexity of extension for chemical experiments

The new setup:
• UV irradiation (laser 365 nm, 3B class)
• Better vibration isolation
• Less pumping time
• Compact & easy to assemble for a run
• Precise T-control
• Compatible with old cryo, magnetic lids
FEASIBILITY OF CURRENT PROPOSAL


eMS spectra of TiO$_2$:H-RT
TU Ilmenau/ISOLDE 2017

- Fe$^{2+}$ S=0 or S=2?
- Fe$^{3+}$?
- Does H act as an electronic donor?
- Leading to a charge transfer?

Fe$^{3+}$ + Ti$^{3+}$ $\leftrightarrow$ Fe$^{2+}$ + Ti$^{4+}$?
**TiO₂ pristine films (TDPAC)**

Schell et al, JAP 121, 145302 (2017)

![Graph](image1.png)

\[ ^{111}\text{In}(^{111}\text{Cd}) \text{ in TiO}_2 \]

Rutile structure
\[ \omega_0 \sim 100 \text{ Mrad/s} \]
and \[ \eta \sim 0.1 \]

![Graph](image2.png)

\[ ^{111}\text{mCd}(^{111}\text{Cd}) \text{ in TiO}:\text{H}_2 \]

Rutile structure
\[ \omega_0 \sim 100 \text{ Mrad/s} \]
and \[ \eta \sim 0.2 \]
**TU-Ilmenau/ISOLDE 2017**

**TiO₂ hydrogenated films (TDPAC)**

Two local environments with static nuclear quadrupole interactions:

**Site 1**: well-defined frequency for Cd at the Ti-site with distortion caused by the presence of H atoms ($\eta \sim 0.5$).

**Site 2**: major fraction at 150°C and 200°C

Hydrogenation treatment with high frequency distribution. Higher EFG asymmetry in respect to site 1 ($\eta \sim 1$).
Mössbauer spectroscopy under light irradiation

Sample: CdS:57Fe(0.2%)

# BEAM TIME REQUEST

## Perturbed Angular Correlations Studies

<table>
<thead>
<tr>
<th>Required isotope</th>
<th>Implanted beam</th>
<th>Probe element</th>
<th>Type of experiment</th>
<th>Intensity [at/μC]</th>
<th>Target / Ion source</th>
<th>Atoms per sample</th>
<th>Ne of shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{111m}$Cd (48 min)</td>
<td>$^{111m}$Cd</td>
<td>$^{111}$Cd</td>
<td>γ-γ PAC</td>
<td>$10^8$</td>
<td>Molten Sn; plasma</td>
<td>$2 \times 10^{10}$</td>
<td>3</td>
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</tbody>
</table>

## Mössbauer studies

<table>
<thead>
<tr>
<th>$^{57}$Mn (1.5 min) + TESTING of eMS</th>
<th>$^{57}$Mn</th>
<th>$^{57}$Fe</th>
<th>eMS</th>
<th>$2 \times 10^8$</th>
<th>UCx, RILIS (Mn)</th>
<th>$1 \times 10^{12}$</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td>2</td>
<td>2</td>
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FUNDING INVOLVED

BMBF
Bundesministerium für Bildung und Forschung

Erforschung kondensierter Materie mit Großgeräten
Ausbau und Unterhalt der Einrichtungen an ISOLDE/CERN
Germany, contract: 5K16SI1
Thank you for your attention!
Similar frequency value (257 Mrad/s) in respect to the well-defined frequencies obtained with H:TiO$_2$ (300 Mrad/s), but since it had no H and the sample was a single crystal, it presents lower EFG asymmetry:

$^{111m}$Cd:TiO$_2$ Syngle Crystal

$\omega_0 \sim 257$ Mrad/s  
and $\eta \sim 0$

**Table 1** Hyperfine fitting parameters of PAC experiments performed in TiO$_2$ single crystals

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>$T_M$ (K)</th>
<th>EFG</th>
<th>$\omega_0$ (Mrad/s)</th>
<th>$\eta$</th>
<th>$\sigma$ (Mrad/s)</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>implanted$^{111m}$Cd/Cd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>257(14)</td>
<td>0</td>
<td>0.175(12)</td>
<td>0(1)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>implanted$^{111m}$Cd/Cd + $^{111}$In/Cd</td>
<td>465</td>
<td>1</td>
<td>100.0(7)</td>
<td>0.15(2)</td>
<td>0.0(1)</td>
<td>12(2)</td>
</tr>
<tr>
<td>b</td>
<td>2</td>
<td>182(2)</td>
<td>0.99(3)</td>
<td>15(2)</td>
<td>42(3)</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>295</td>
<td>1</td>
<td>99.01(16)</td>
<td>0.175(12)</td>
<td>0(1)</td>
<td>70</td>
</tr>
</tbody>
</table>

Cd can attract the vacancies according to partial pressure. The missing / attenuated fractions are likely due to multiple attracted vacancies (or charging / discharging vacancies) that alter the environment.
Additional information TDPAC

$^{111m}\text{Cd}^{(111\text{Cd})}$

- $^{111}\text{In}$, $t_{1/2} = 2,8047\text{ d}$
- EC 99.99%
- $^{111m}\text{Cd}$, $t_{1/2} = 48.54\text{ m}$

Levels and transitions:

- $\gamma_1$: 171 keV
- $\gamma_2$: 245 keV
- $\mu(5/2^+) = -0.766(3)\mu_N$
- $Q(5/2^-) = +0.74(8)\text{ b}$
- $A_{22}(^{111m}\text{Cd}) = 0.1786$
- $A_{22}(^{111}\text{In}) = -0.1782$

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$^{57}\text{Mn}/^{57}\text{Fe}$

$^{57}\text{Mn}^+ (T_{1/2} = 85.4 \text{ s})$  

$^{57}\text{Co}^+ (T_{1/2} = 271.74 \text{ d})$

$\beta^{-}$  

$I = \frac{5}{2}$

$57^{*}\text{Fe}$  

136 keV (8.7 ns)

EC

$\langle E_r \rangle = 40 \text{ eV}$

$\frac{3}{2}$

$57^{*}\text{Fe}$  

14.4 keV (97.8 ns)

$\gamma$ - rays

$\frac{1}{2}$

$57\text{Fe}$  

0