TiO_2/WO_3/noble metal nanoarchitectures' photocatalytic activity: "from the degradation intermediates to structural peculiarities"

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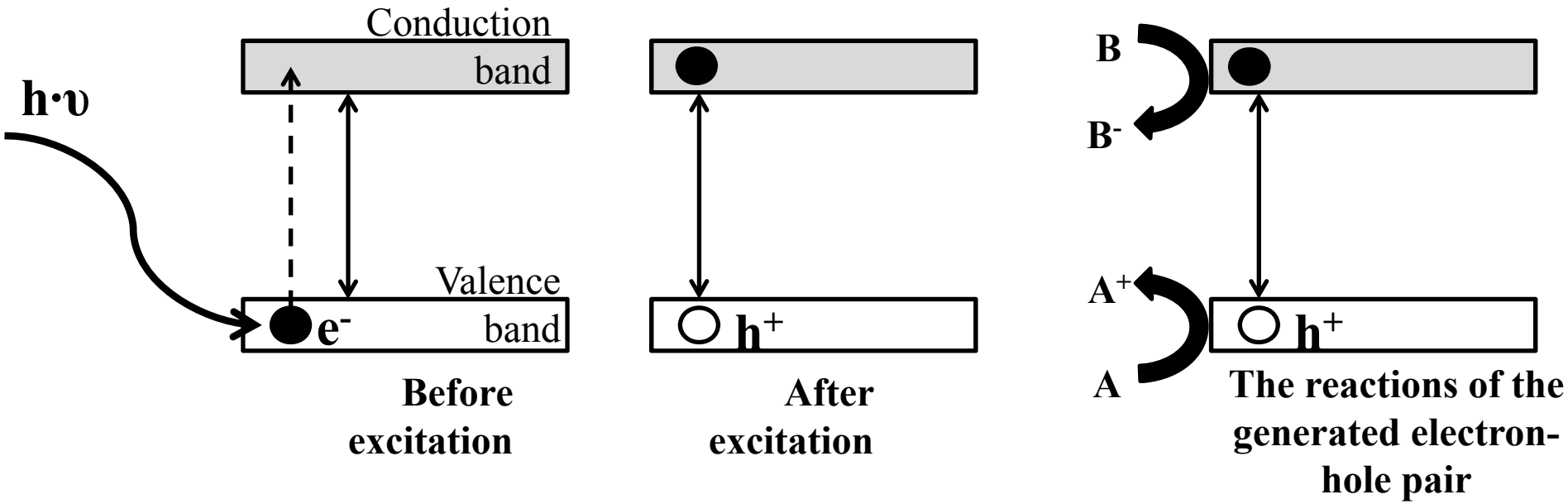
Introduction

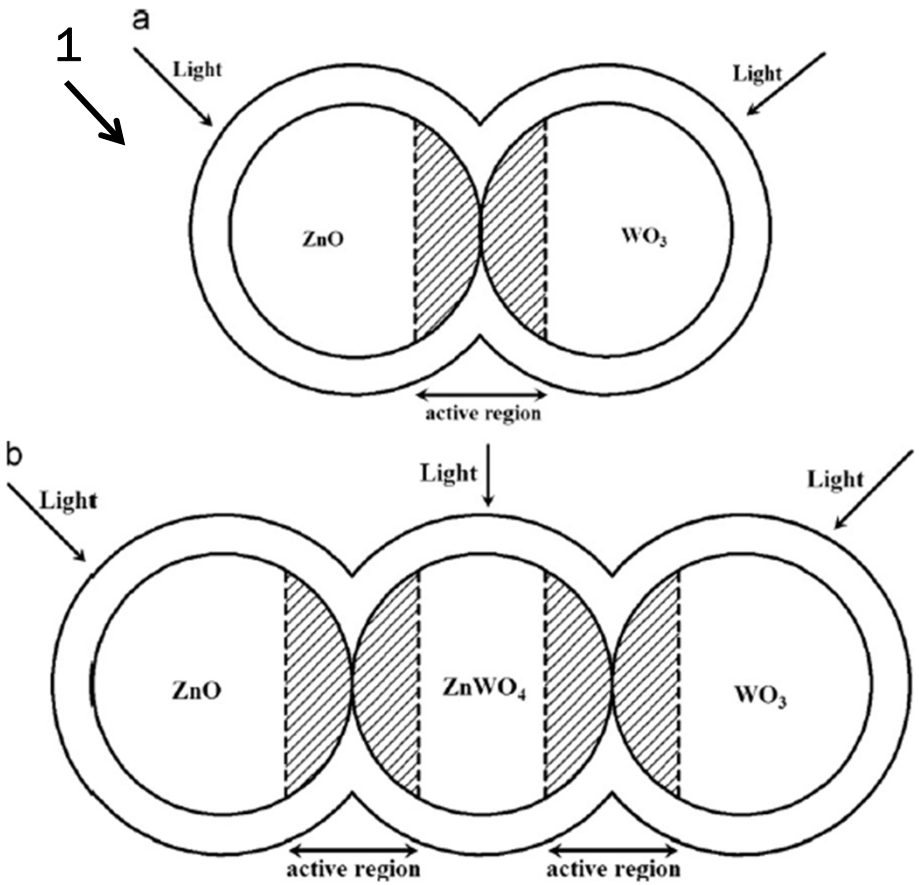
- **Photocatalysis?**
  - Electron-hole generation, under UV- or visible light
  - The charge carriers are participating in complex reaction chains - pollutant degradation

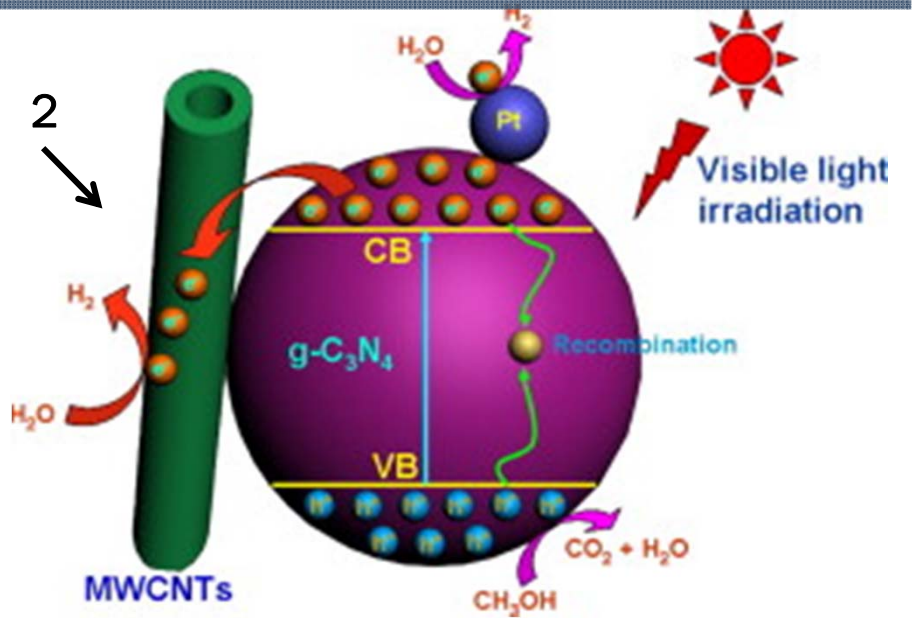


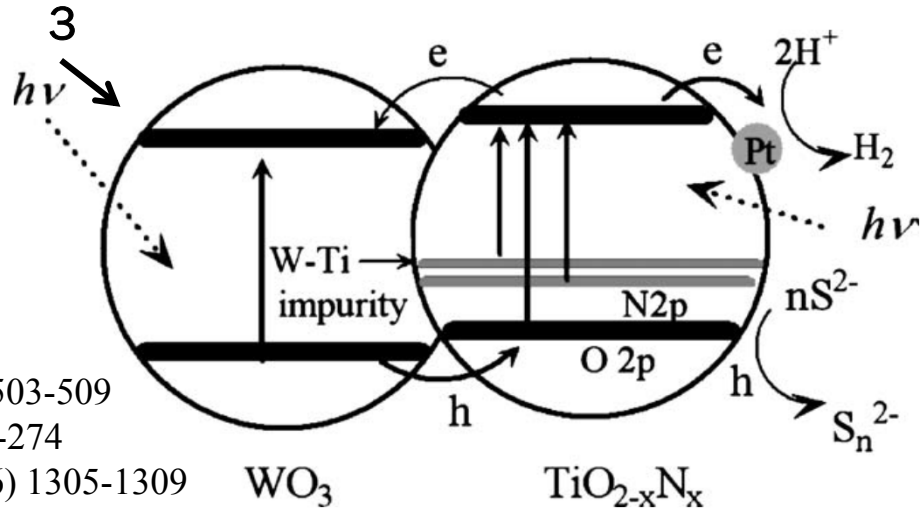
Introduction

- **Composite materials – why are we making them?**
  - To exploit the components' synergistic effects - photocatalysis
    - Increased adsorption properties (carbon materials)
    - Activity under visible light (WO_3)
    - Photocatalytic hydrogen production (Pt or Au)
- **The composites used in photocatalysis**
  - Semiconductors (TiO_2, WO_3, SnO_2, CdS, etc.)
  - Noble metals (Au, Pt, etc.)
  - High adsorption capacity materials (clay minerals, carbon nanotubes, etc.)

Introduction

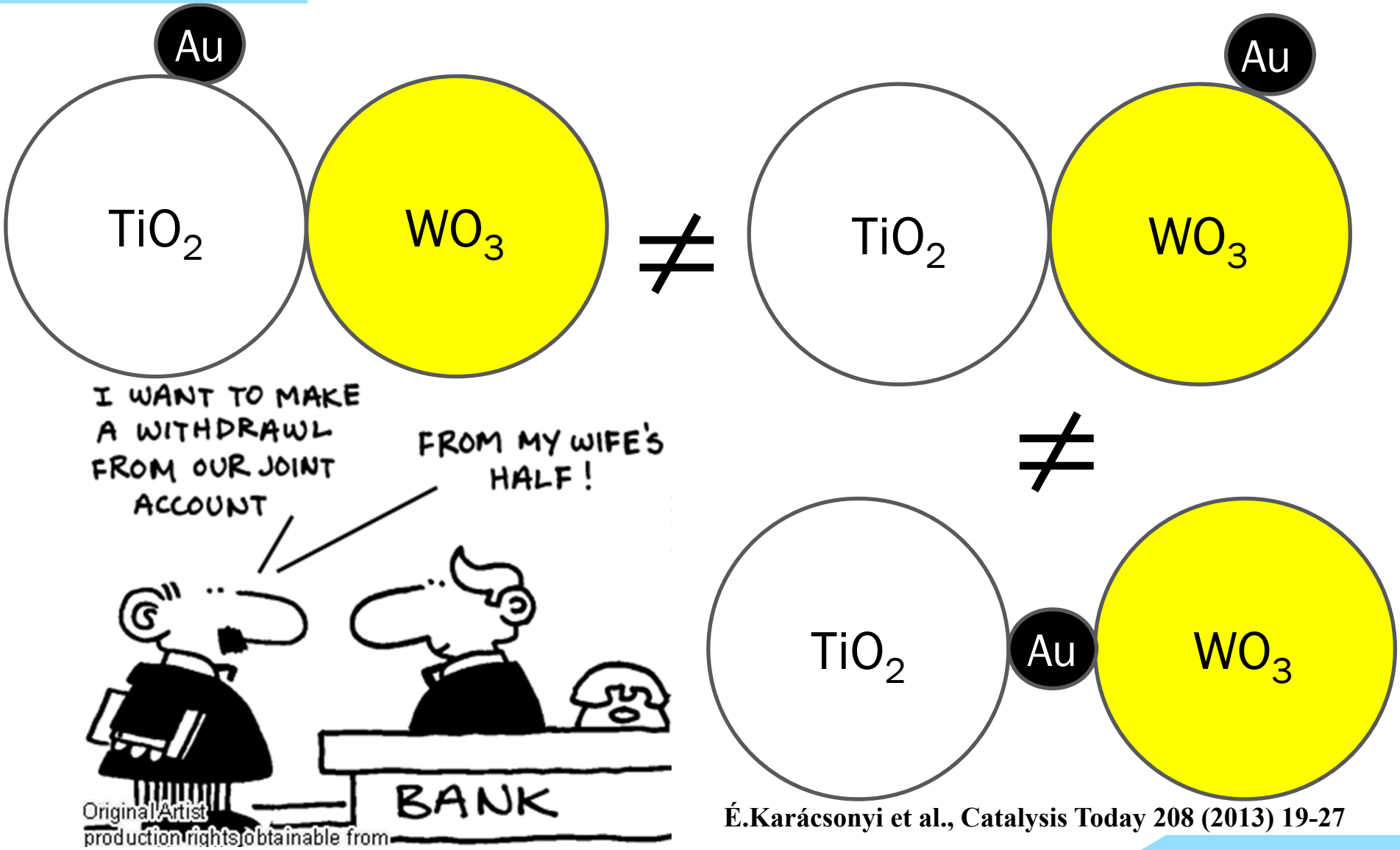






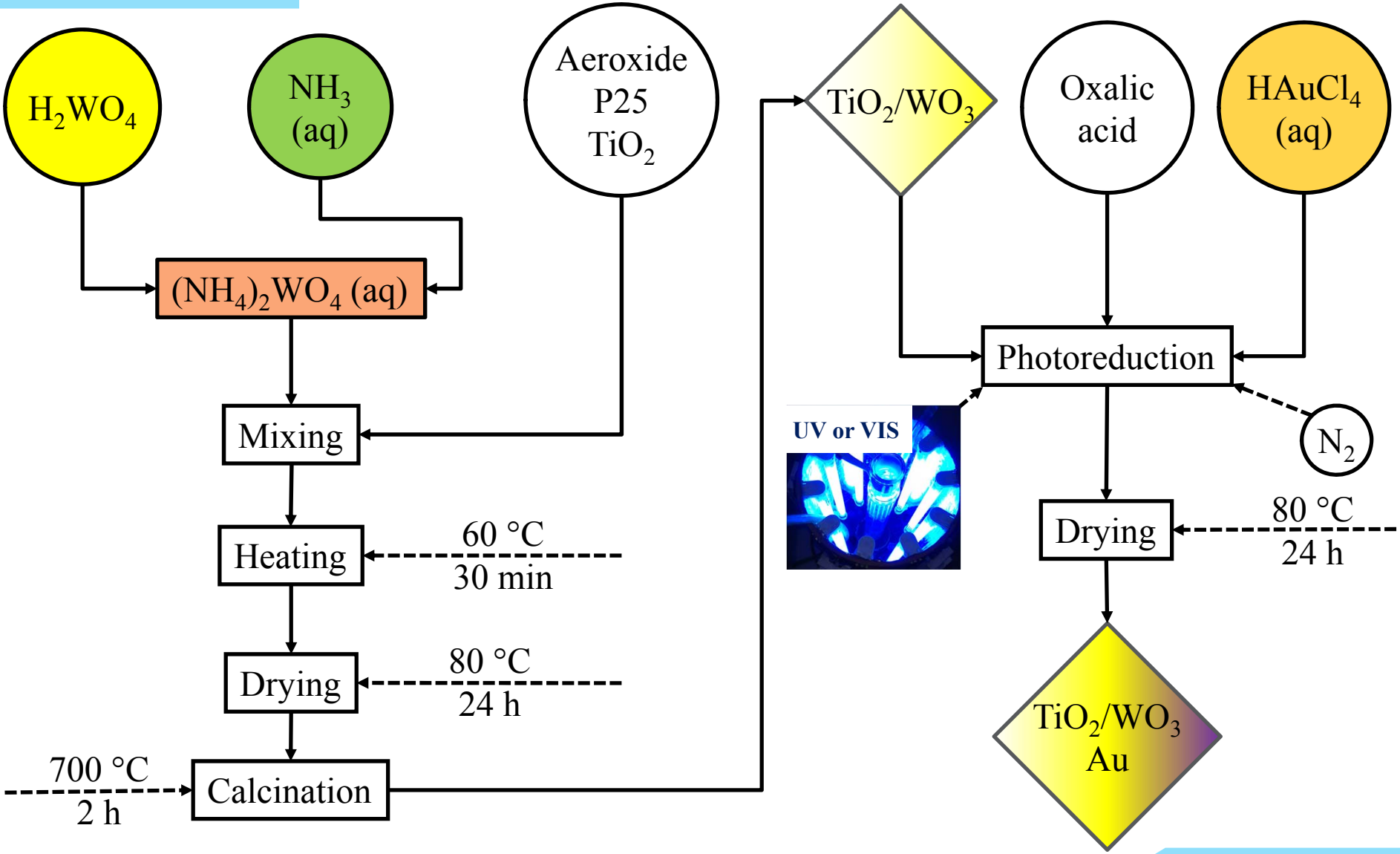
[1] Y. Wang, L. Cai, Y. Li, Y. Tang, C. Xie, Physica E 43 (2010) 503-509
[2] L. Ge, C. Han, Appl. Catal. , B: Environ. 117-118 (2012) 268-274
[3] H. Yang, L. Guo, W. Yan, H. Liu, J. Power Sources 159 (2006) 1305-1309

Introduction



É.Karácsonyi et al., Catalysis Today 208 (2013) 19-27

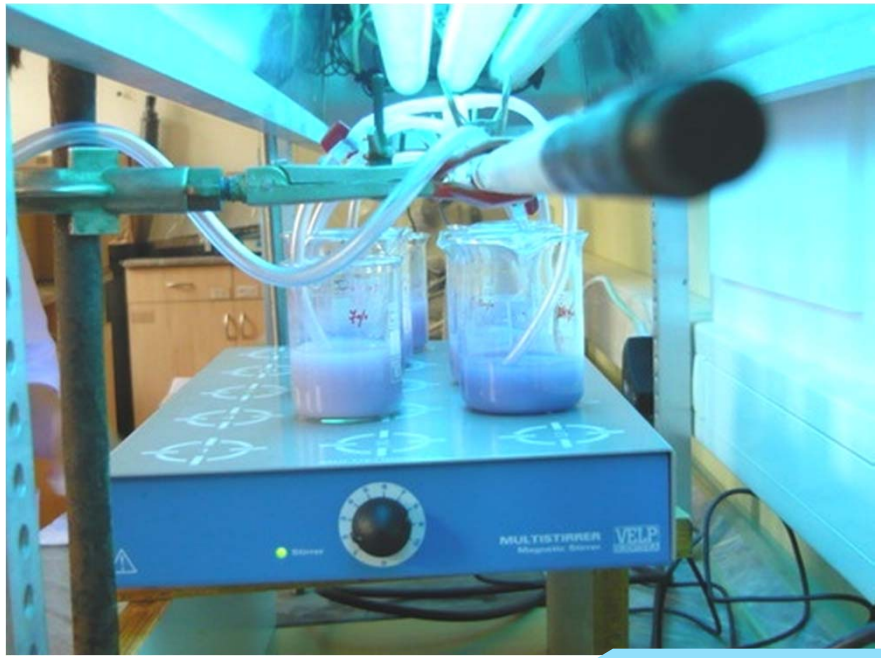
Synthesis


H_2WO_4
NH_3 (aq)
Aeroxide P25 TiO_2
$(NH_4)_2WO_4$ (aq)
Mixing
Heating
60 °C
30 min
Drying
80 °C
24 h
700 °C
2 h
Calcination
TiO_2/WO_3
Oxalic acid
$HAuCl_4$ (aq)
Photoreduction
UV or VIS
N_2
Drying
80 °C
24 h
TiO_2/WO_3 Au

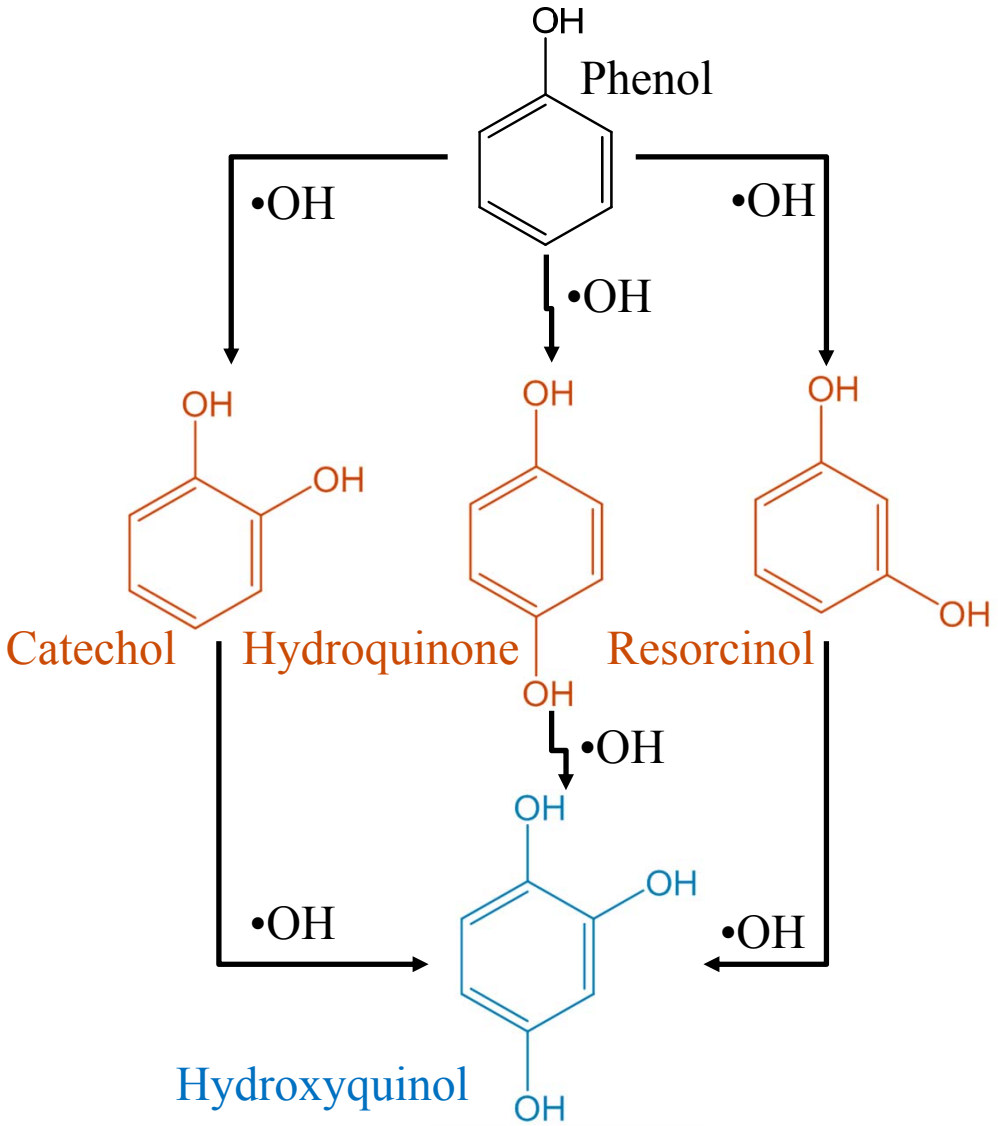
Experimental set-up for the degradation experiments

Testing conditions:

- *Run time*: 180 minutes
- *Irradiation*: UV ($\lambda \approx 365$ nm)
- *Degraded organic compound:* 0.5 mM phenol
- *Purging gas*: air
- *Catalyst "concentration"*: 1.0 g/L

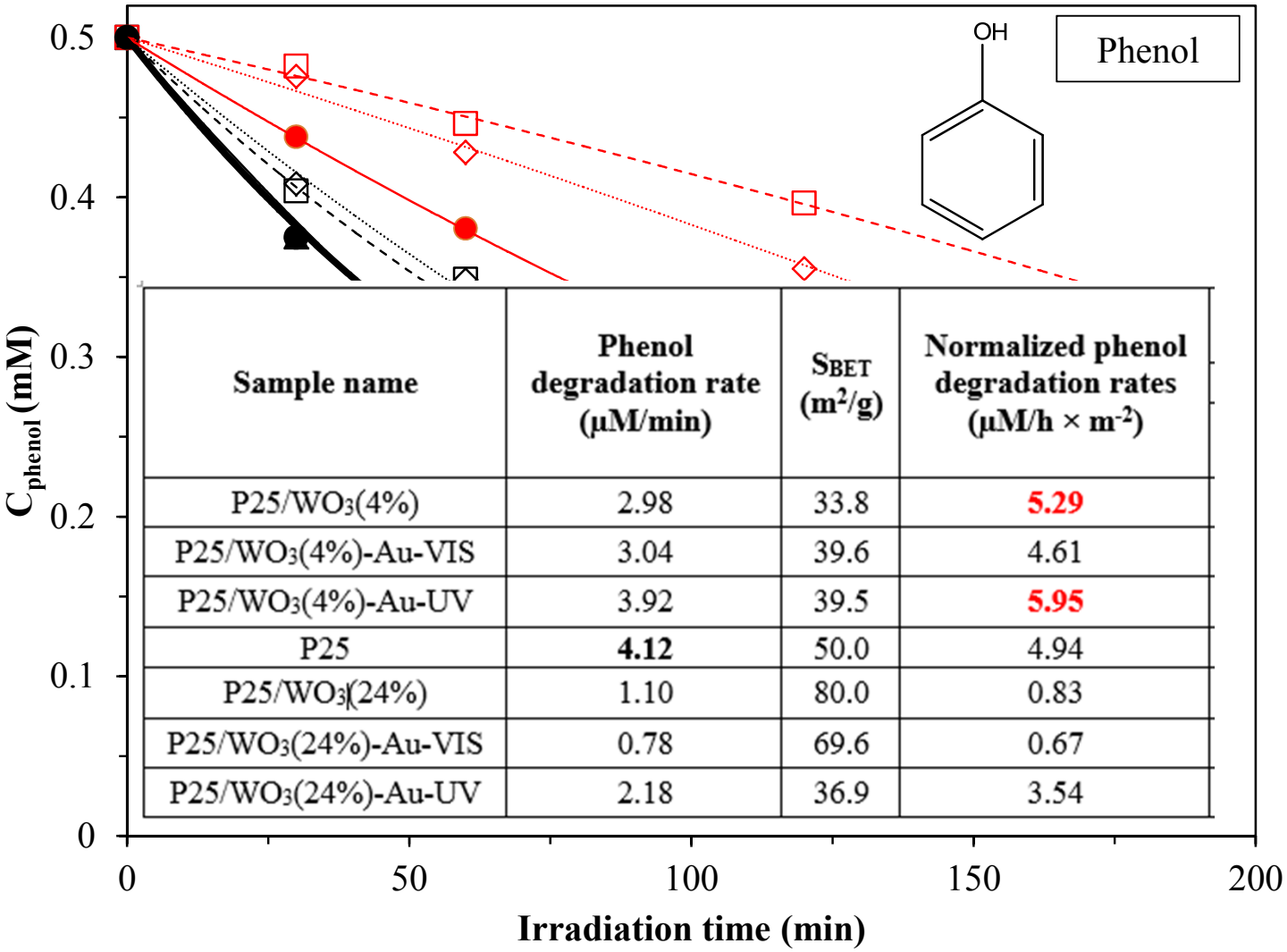


Degradation pathway of phenol



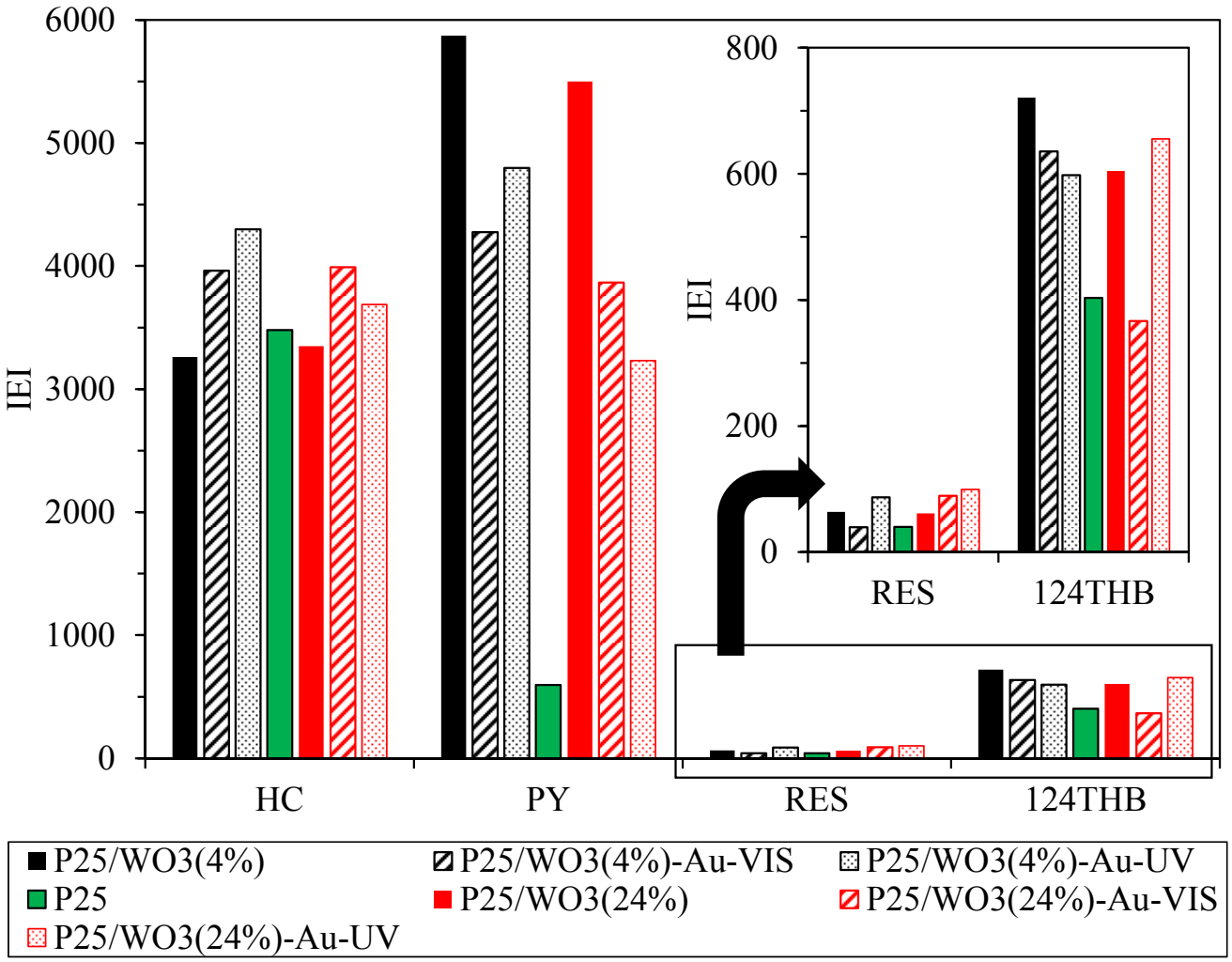
- **Phenol**
  - Important base chemical for several commercial products
  - Significant industrial pollutant in wastewaters and natural pollutant of thermal waters
- **Removal**
  - Via photocatalysis
    - Efficient
    - Cheap
    - Energy-friendly
    - Degradation intermediates (ECR) 1272/2008 [EU-GHS/CLP])

Results – degradation of phenol

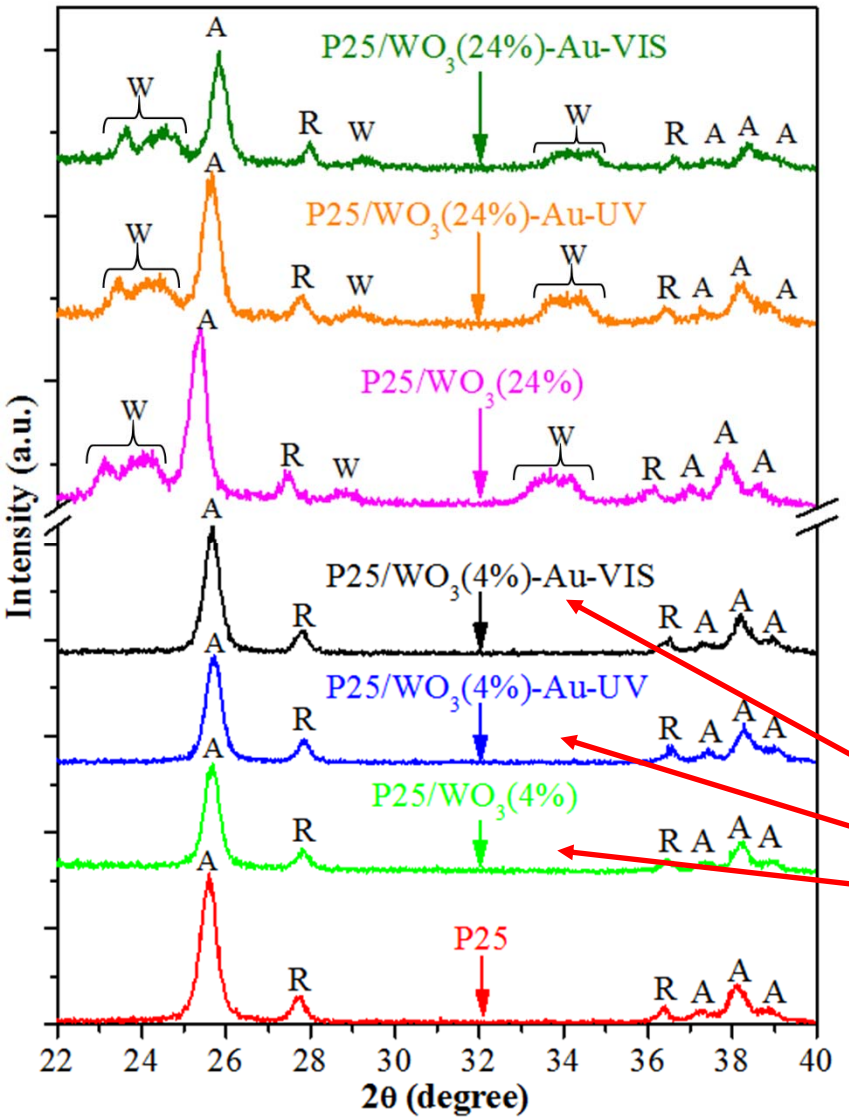


Sample name	Phenol degradation rate (μM/min)	S_{BET} (m^2/g)	Normalized phenol degradation rates (μM/h × m^{-2})
$P25/WO_3(4\%)$	2.98	33.8	**5.29**
$P25/WO_3(4\%)$-Au-VIS	3.04	39.6	4.61
$P25/WO_3(4\%)$-Au-UV	3.92	39.5	**5.95**
P25	**4.12**	50.0	4.94
$P25/WO_3(24\%)$	1.10	80.0	0.83
$P25/WO_3(24\%)$-Au-VIS	0.78	69.6	0.67
$P25/WO_3(24\%)$-Au-UV	2.18	36.9	3.54

Results – degradation intermediates accumulated

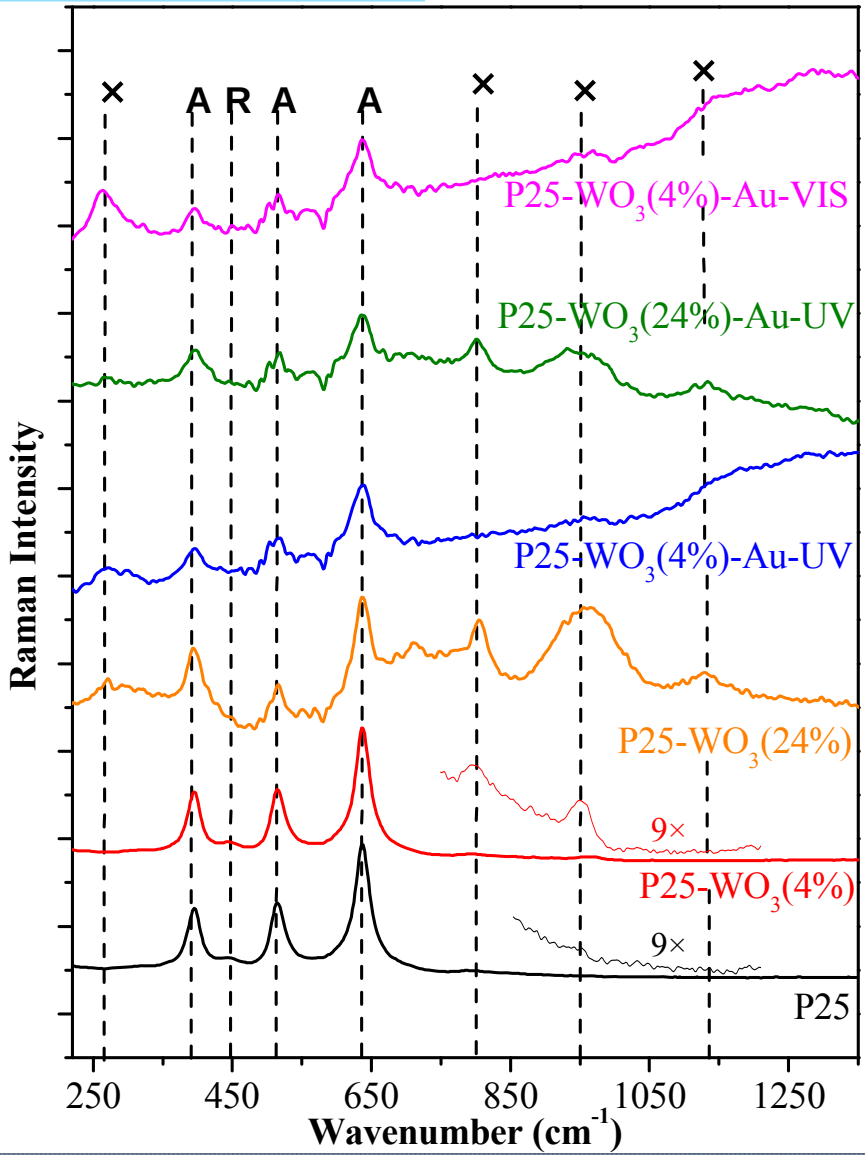


Results – X-ray Diffraction

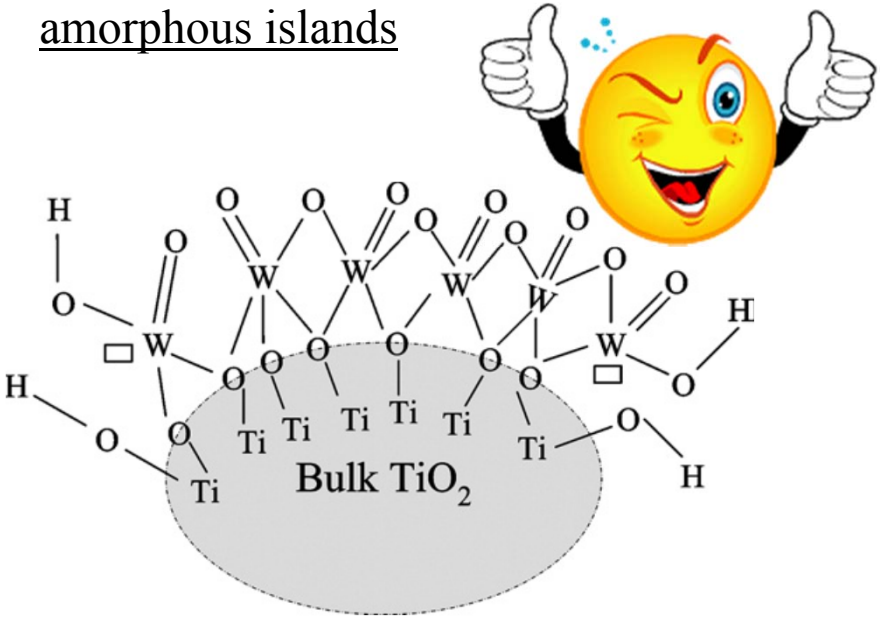


- **TiO_2**
  - *Crystal phase composition*: 89 wt. % - A
    11 wt. % - R
  - *Crystallites' size*: 15-20 nm anatase (A)
    35-40 nm rutile (R)
- **WO_3**
  - *Crystal phase composition:* monoclinic (W)
  - *Crystallites' size*: 22-25 nm

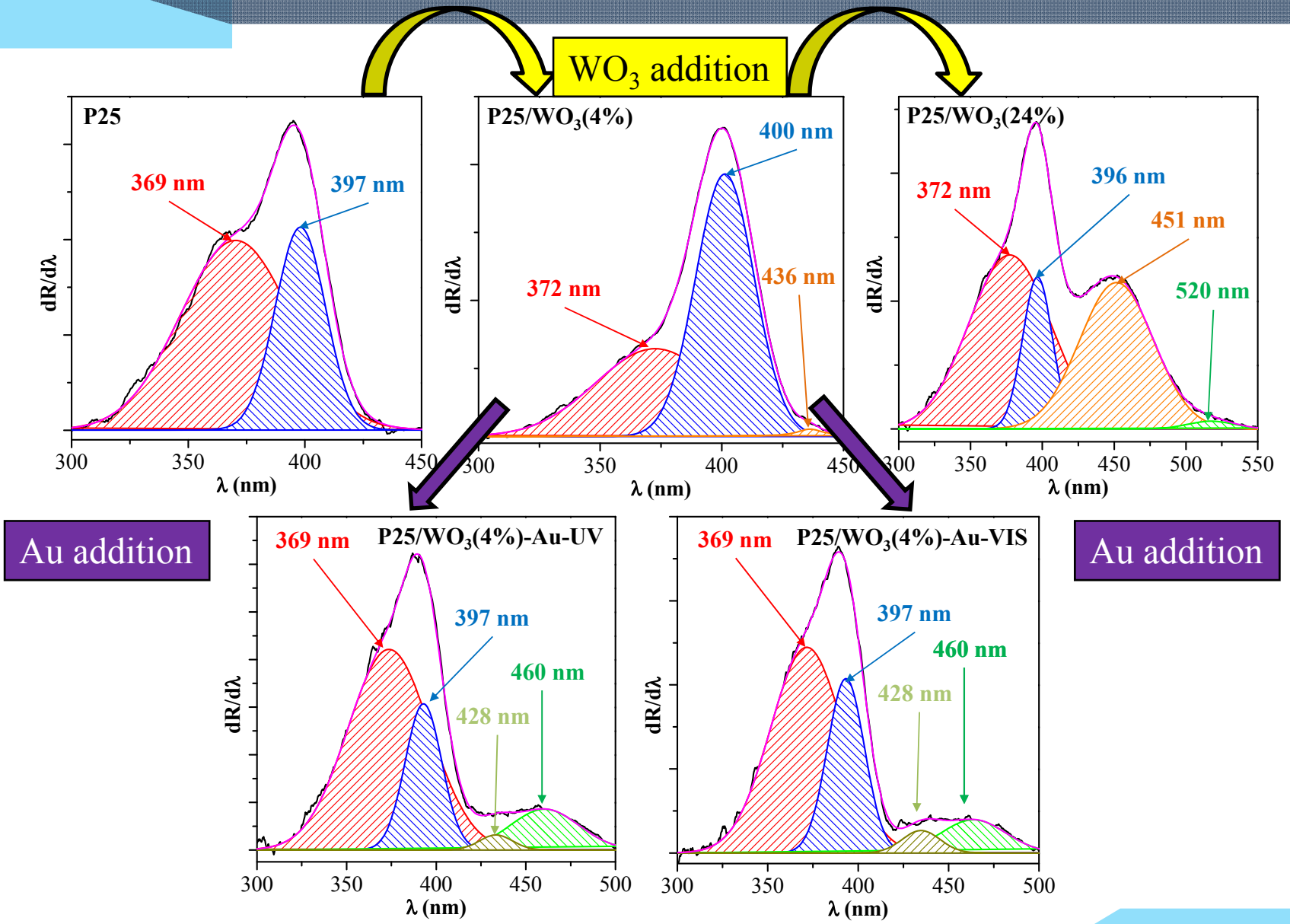
Results – Raman spectroscopy



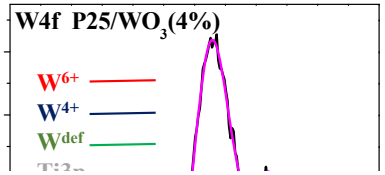
- **TiO_2**
  - *Crystal phase composition*: confirms the presence of anatase and rutile
- **WO_3**
  - *Crystal phase composition:* confirms the presence of crystalline WO_3
  - Indicates the presence of anchored amorphous islands

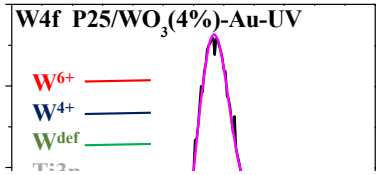


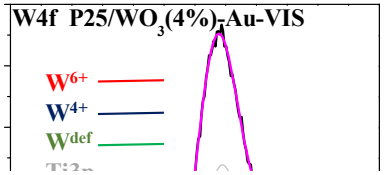
Results – Diffuse Reflectance spectroscopy

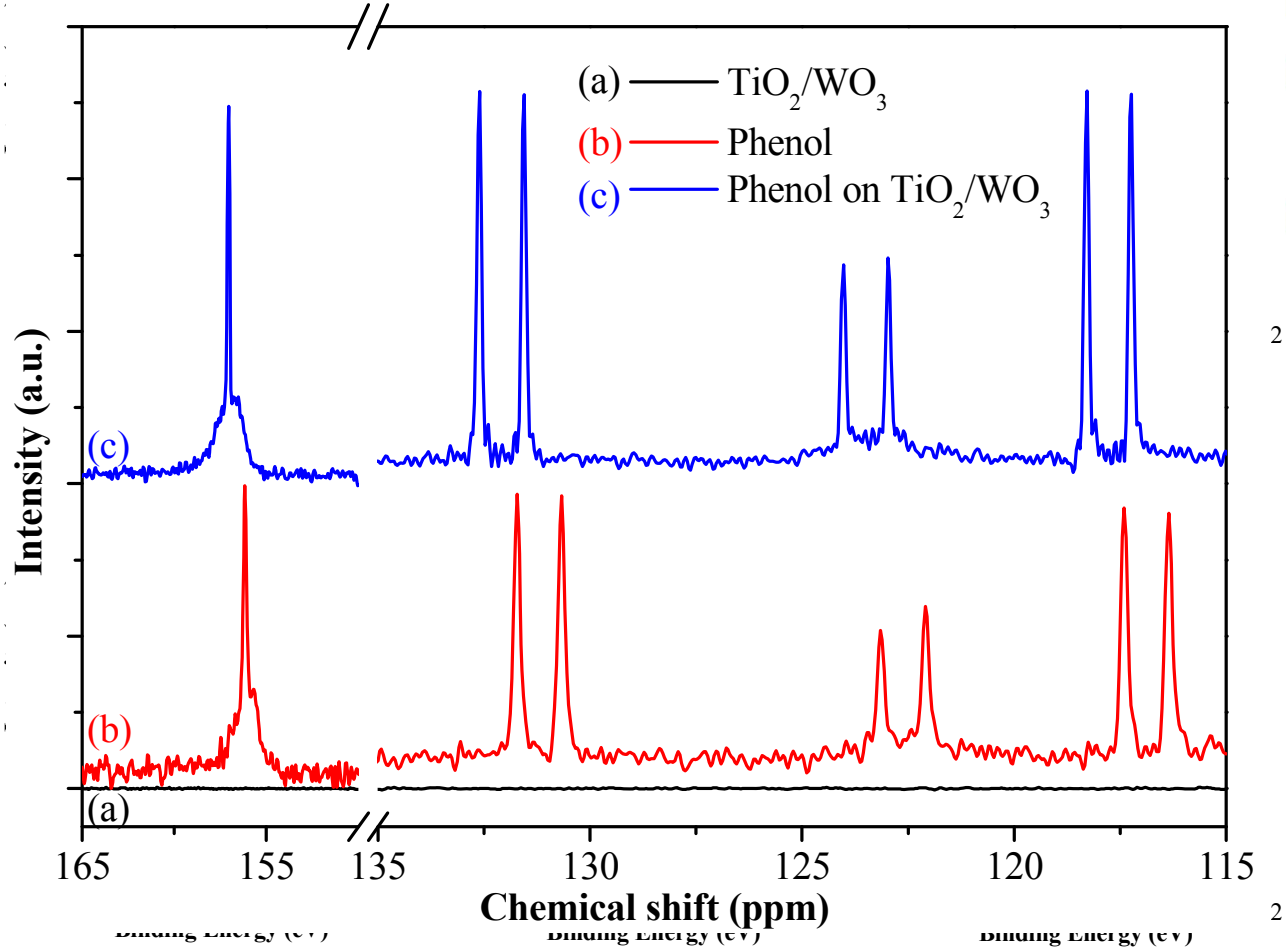


Results – X-ray photoelectron spectroscopy/ 13C-NMR



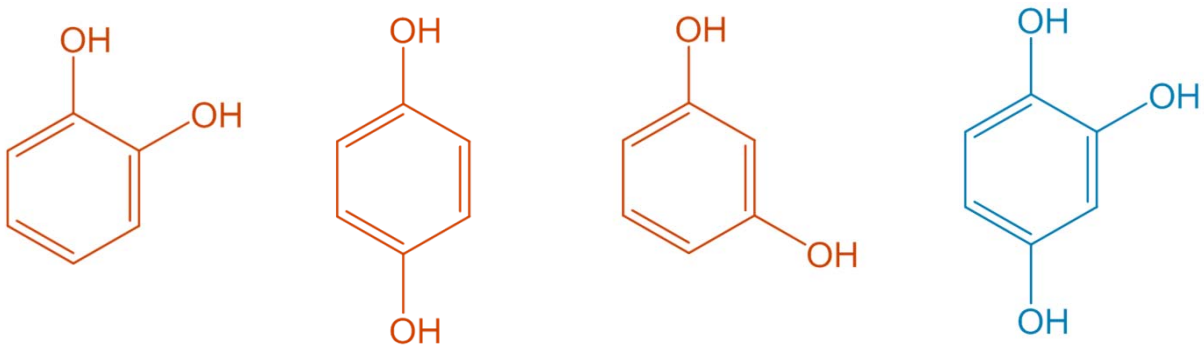






- **Structural features**
- *W - Doping – Ti^{3+}*
- *Crystalline WO_3 – W_{def}, W^{6+}*
- *Amorphous WO_3 – W_{def}, W^{4+}*
- **No evidence of possible phenol anchoring**
- **Solid state - 13C-NMR**

Results – Summary



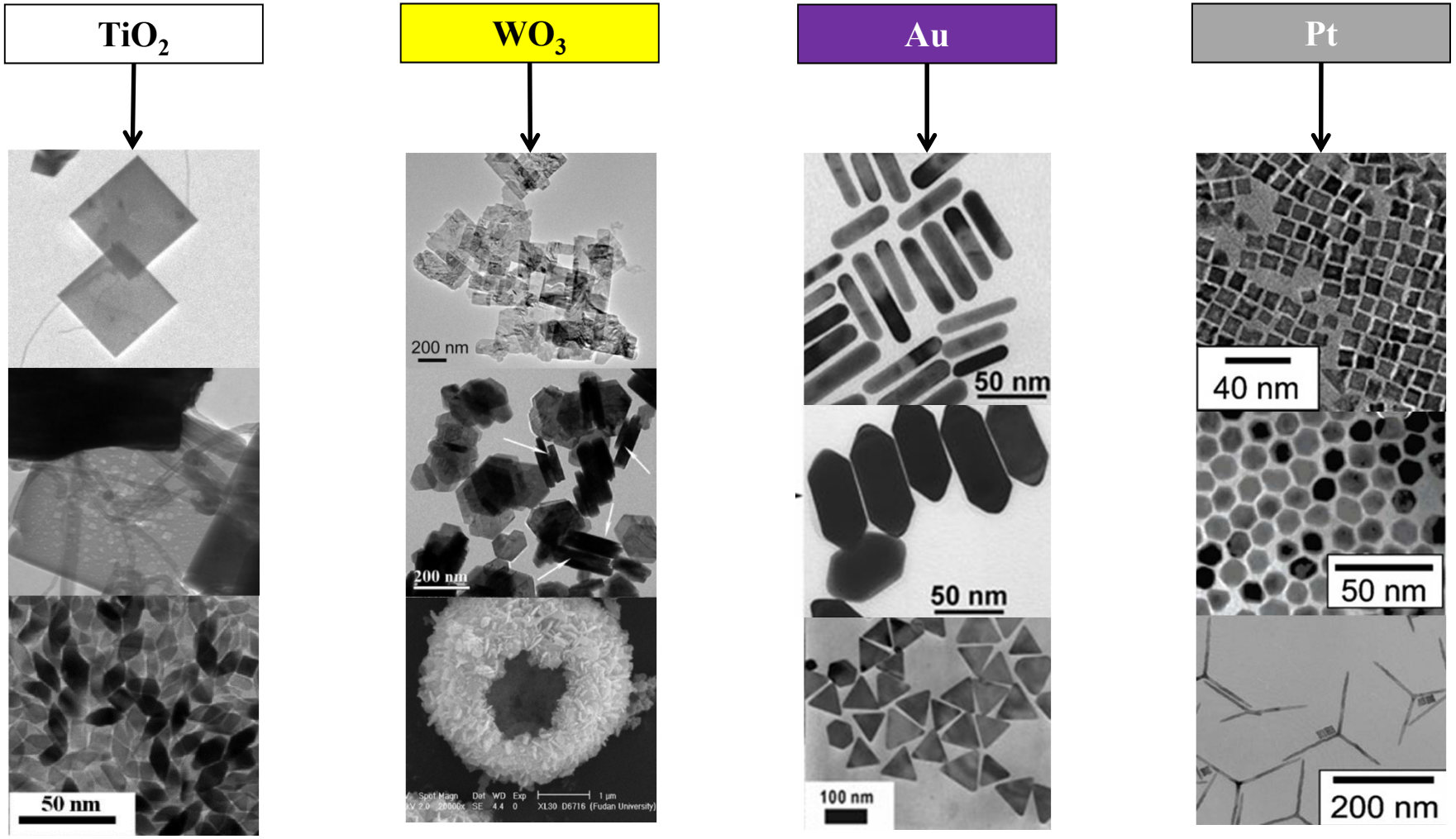
Intermediates

WO_3 addition

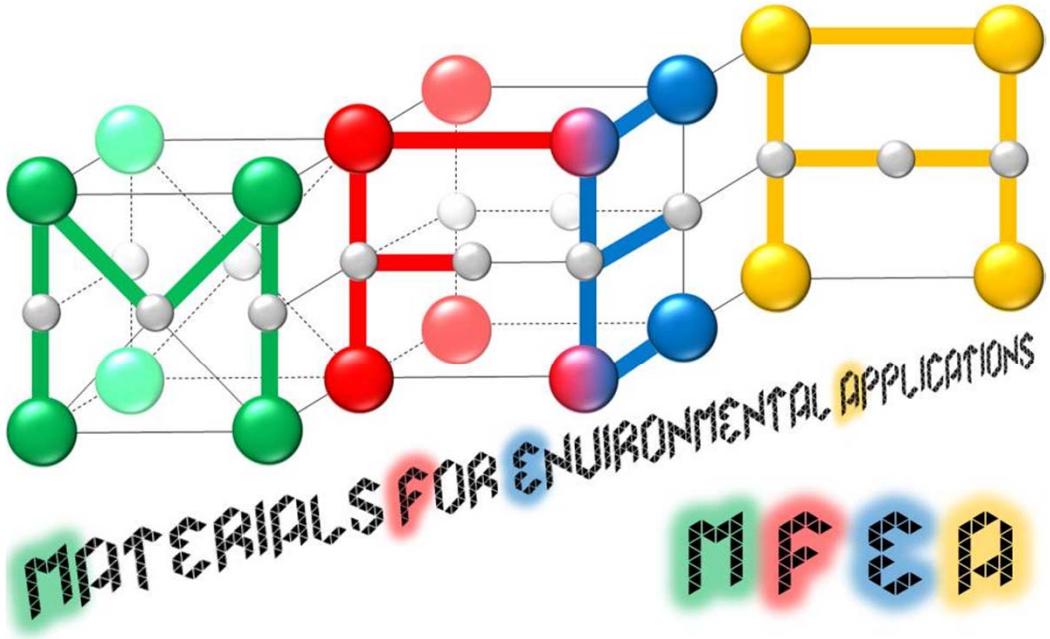
Au addition

Crystalline WO_3	Defects in WO_3	W doping	Amorphous WO_3	Responsible structural entities

Other related activities



5 Papers already submitted to: Applied Catalysis B, Advanced Materials, Catalysis Today



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Thank you for your attention