Electronic Structures, Optical Properties and High Pressure Study of Nanostructured Titanium Dioxide

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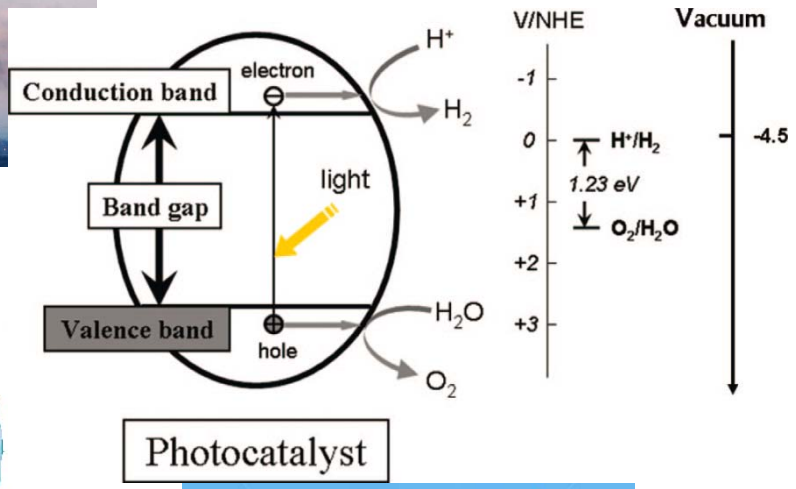
Sham's Group Workshop

Why TiO_2 Nanomaterials?

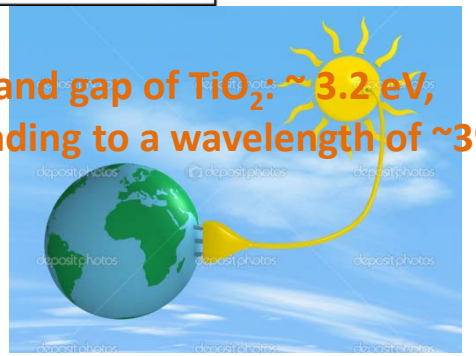
1. TiO_2 is a kind of semiconductor.



Photocatalyst

2. Nanostructured TiO_2 can provide high surface-to-volume ratio.

Band gap of TiO_2: ~ 3.2 eV, corresponding to a wavelength of ~390 nm



Chen, X.; Shen, S.; Guo, L.; Mao, S. S. *Chemical Reviews* **2010**, *110*, 6503.

Problems need to be concerned

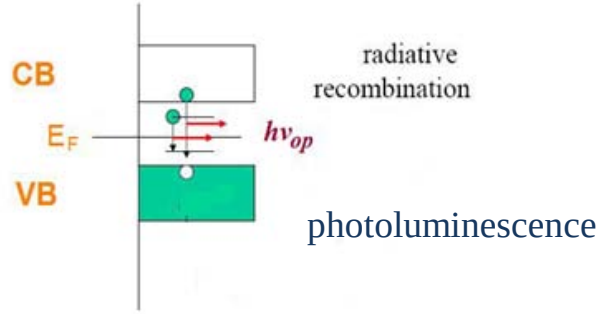
1. Polymorph: anatase, rutile and brookite in ambient pressure

High Pressure Study &
X-ray Absorption Near Edge Structure (XANES)

Anatase has shown the highest photocatalytic activity

2. Defects: recombination centers

X-ray Exited Optical Luminescence (XEOL)



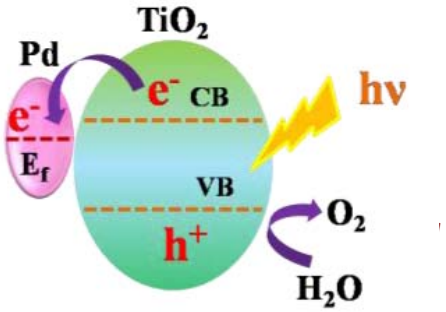
3. Morphology: nanotubes, naowires, nanoparticles and so on

Different synthesis methods

Affecting the overall efficiency of water-splitting

4. Band gap: band gap engineering

5. Cocatalysts: Pt, Pd, Au



Ye, M. D.; Gong, J. J.; Lai, Y. K.; Lin, C. J.; Lin, Z. Q. *J. Am. Chem. Soc.* **2012,** *134, 15720.*
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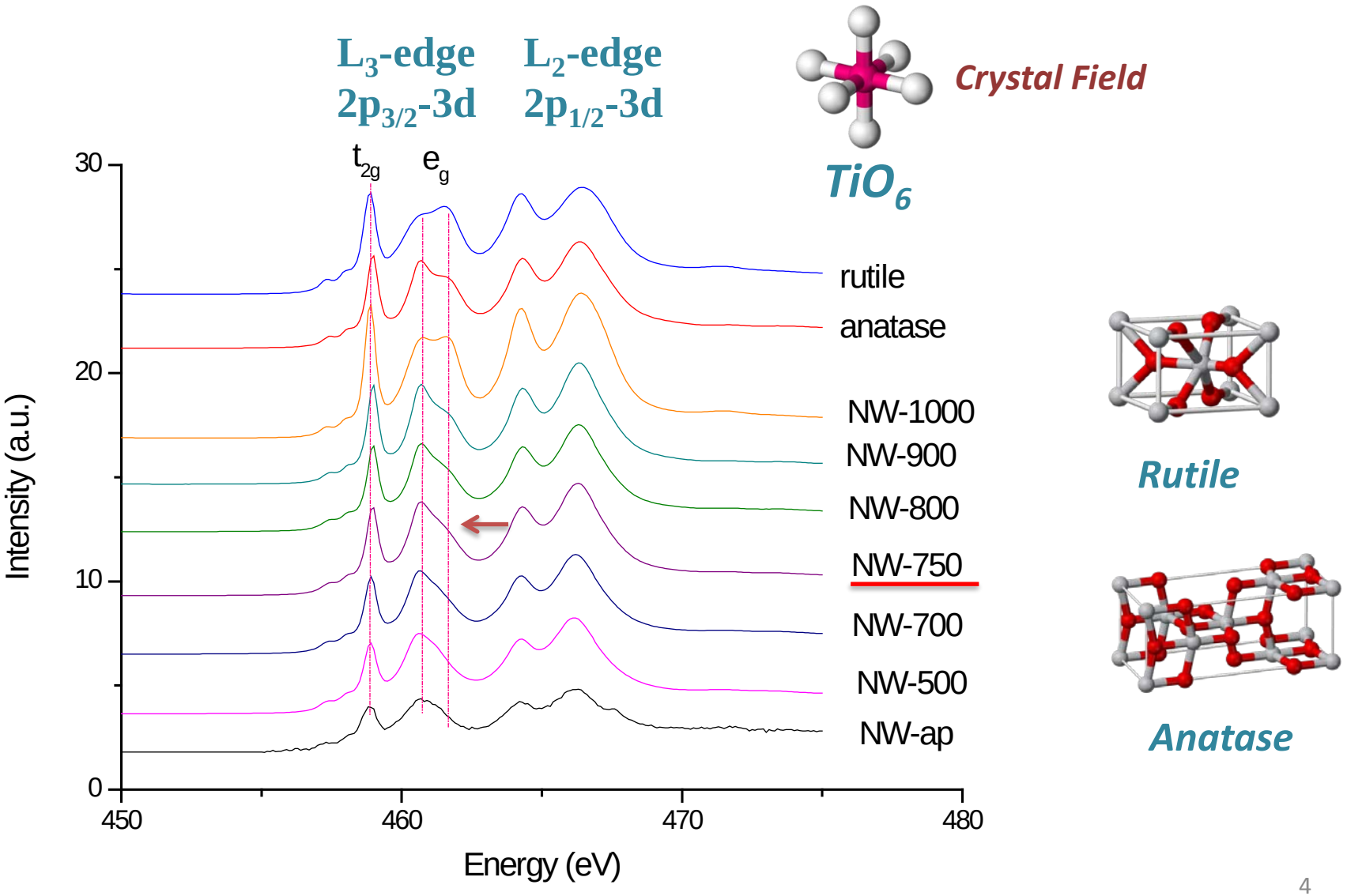
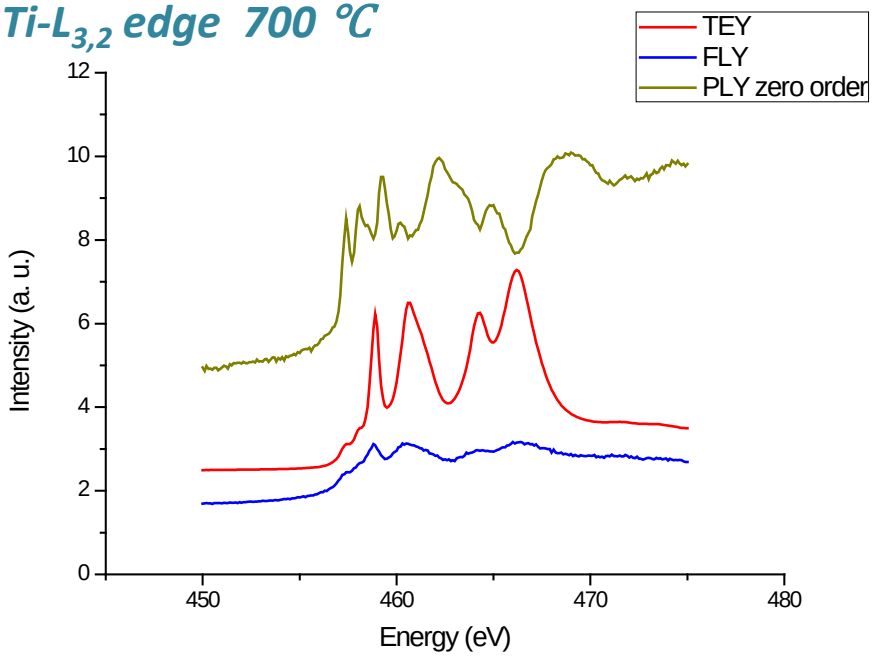
XANES Study of TiO_2 Nanowires



Ti-$L_{3,2}$ edge 700 ℃



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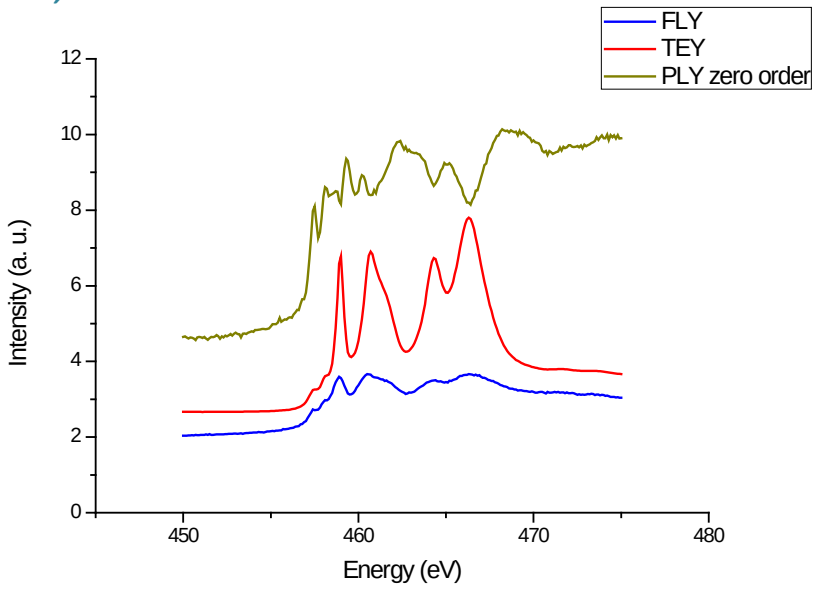
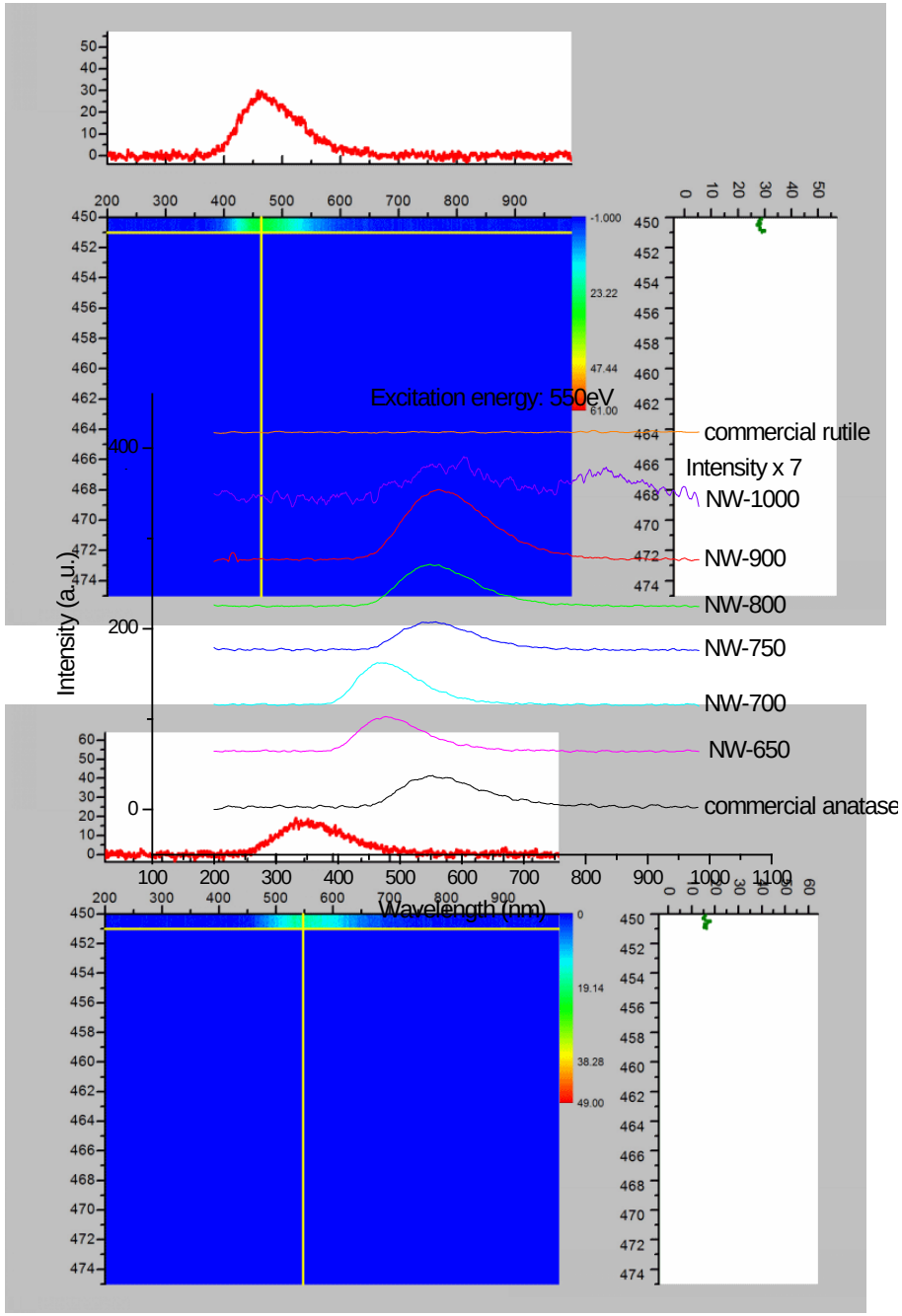
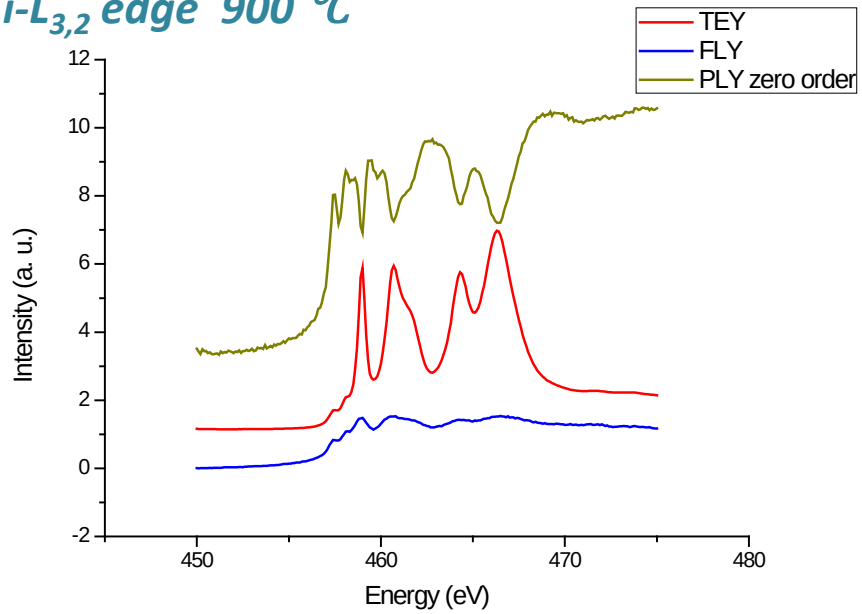
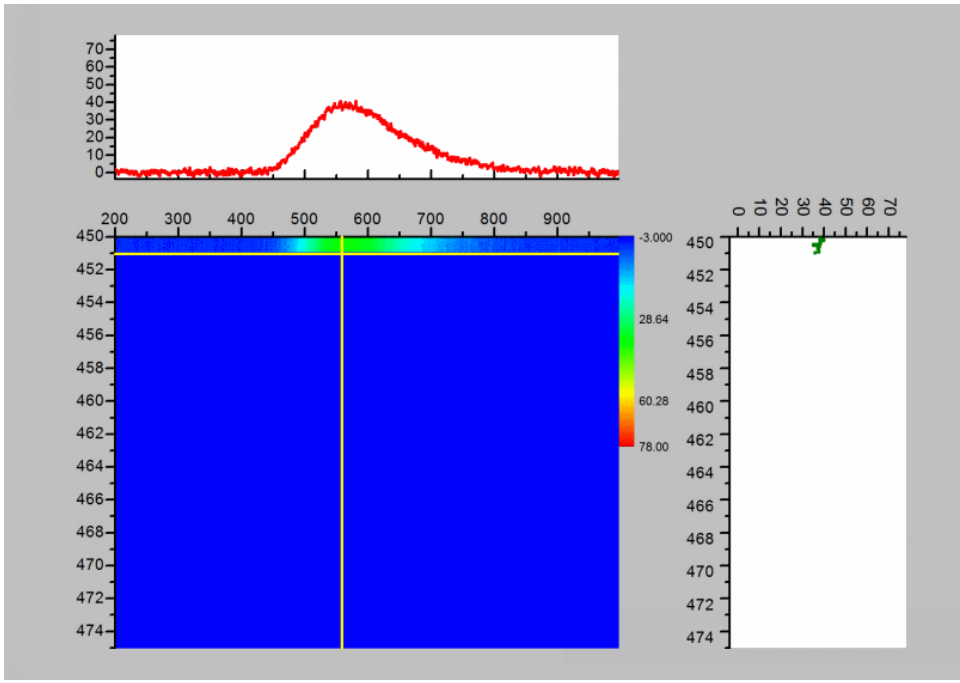


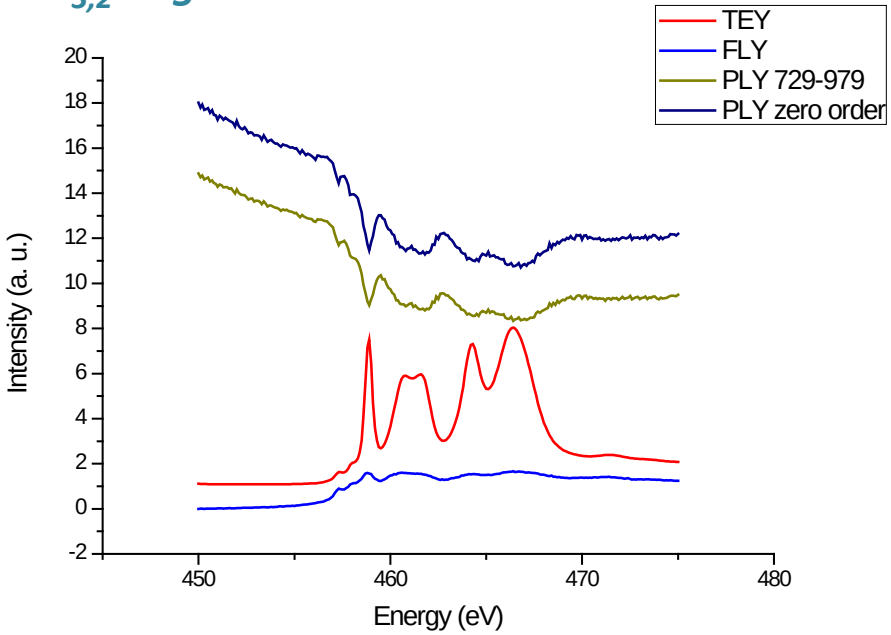


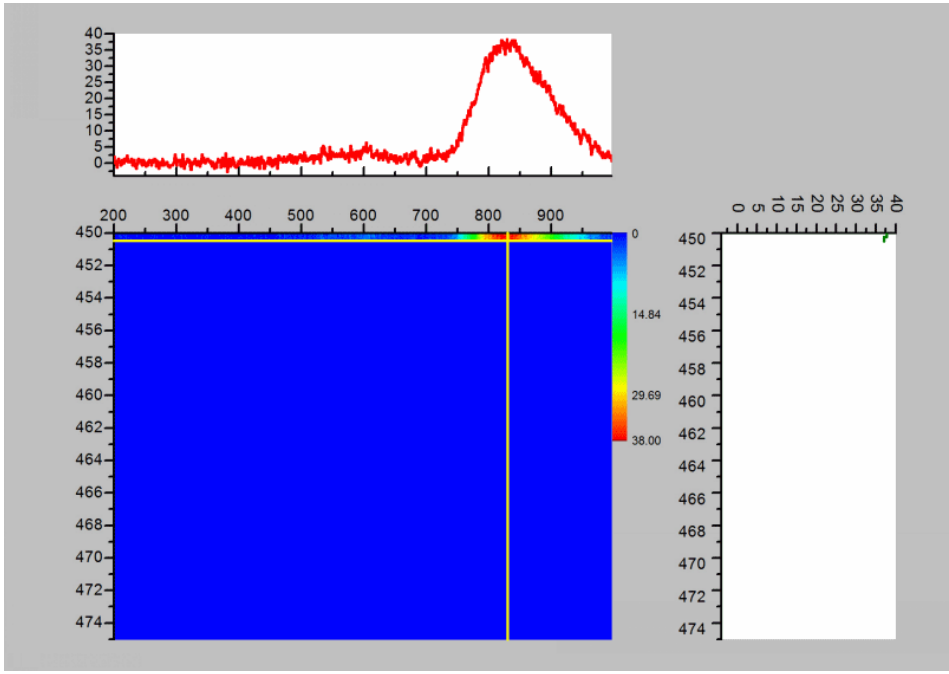
Ti-$L_{3,2}$ edge 900 ℃



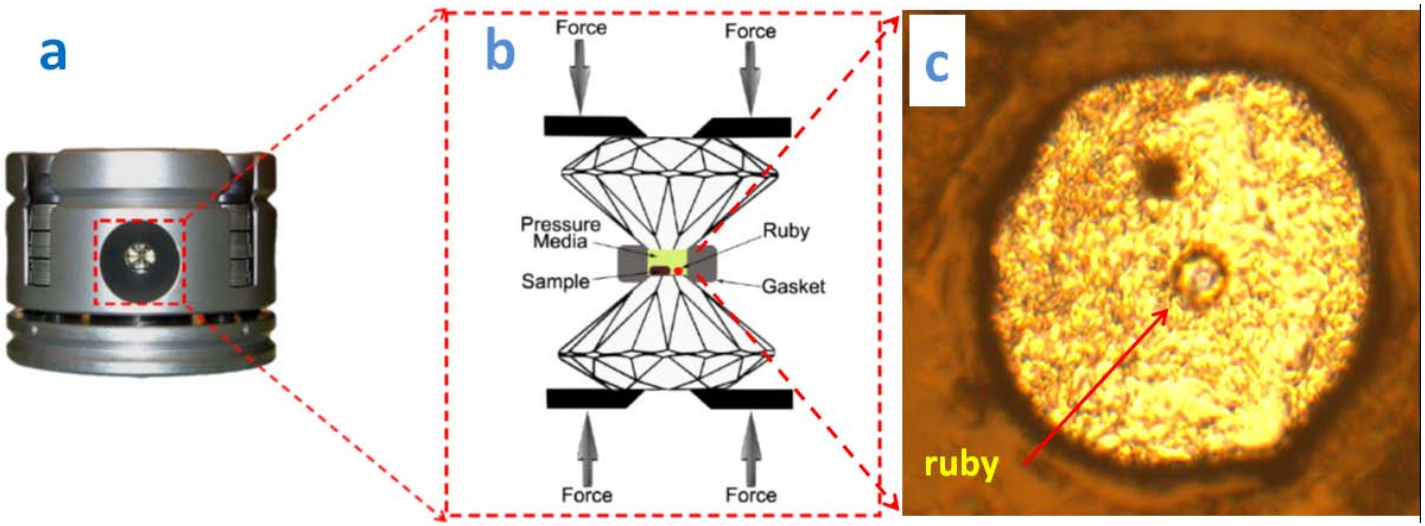


Ti-$L_{3,2}$ edge 1000 ℃



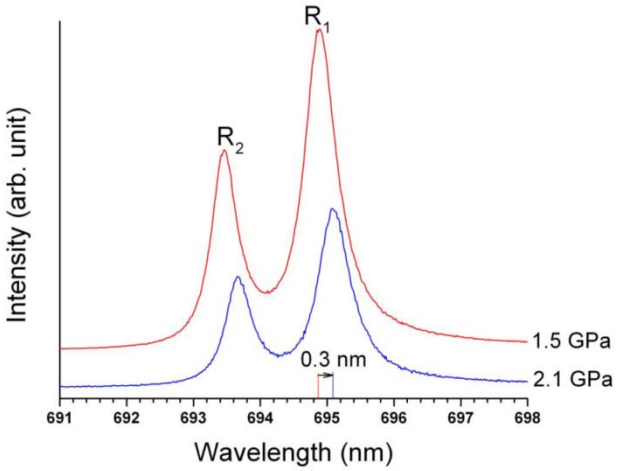


High Pressure XRD Study of TiO_2 Nanotubes



Diamond Anvil Cell (DAC)

Sample Hole

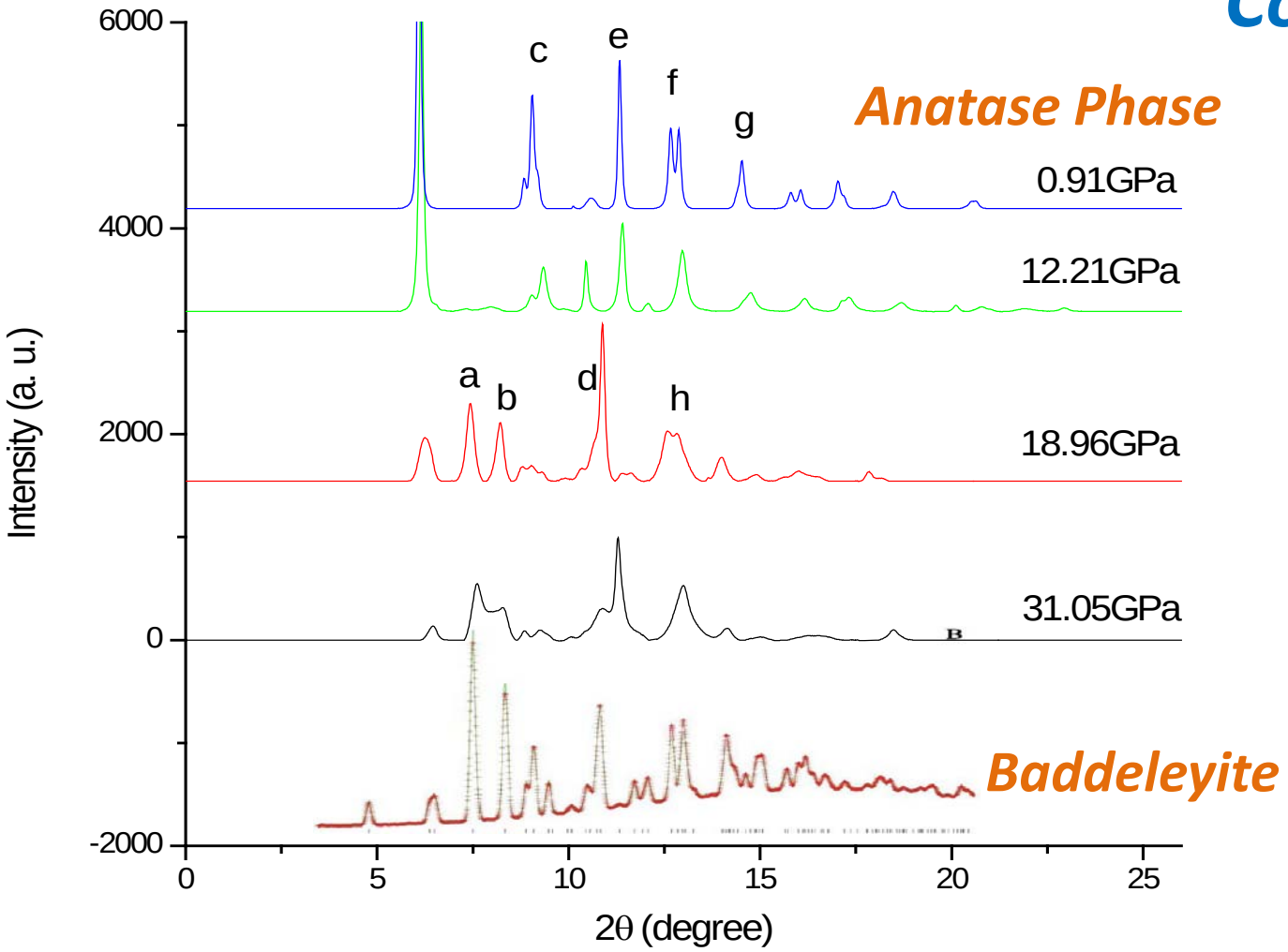


Pressure Calibration

$$P(GPa)=248.4\,[(\Delta\lambda/694.3+1)^{7.665}-1]$$

High Pressure XRD Study of TiO_2 Nanotubes

Compression



1. At 7.55 GPa, ***d*** shows up.

2. At 14.75 GPa, ***a*** & ***b*** show up.

3. At 18.96 GPa, ***c***, ***e***, ***g*** disappear and ***h*** shows up.

Gerward, L.; Olsen, J. S. *J. Appl. Crystallogr.* **1997**, *30*, 259.

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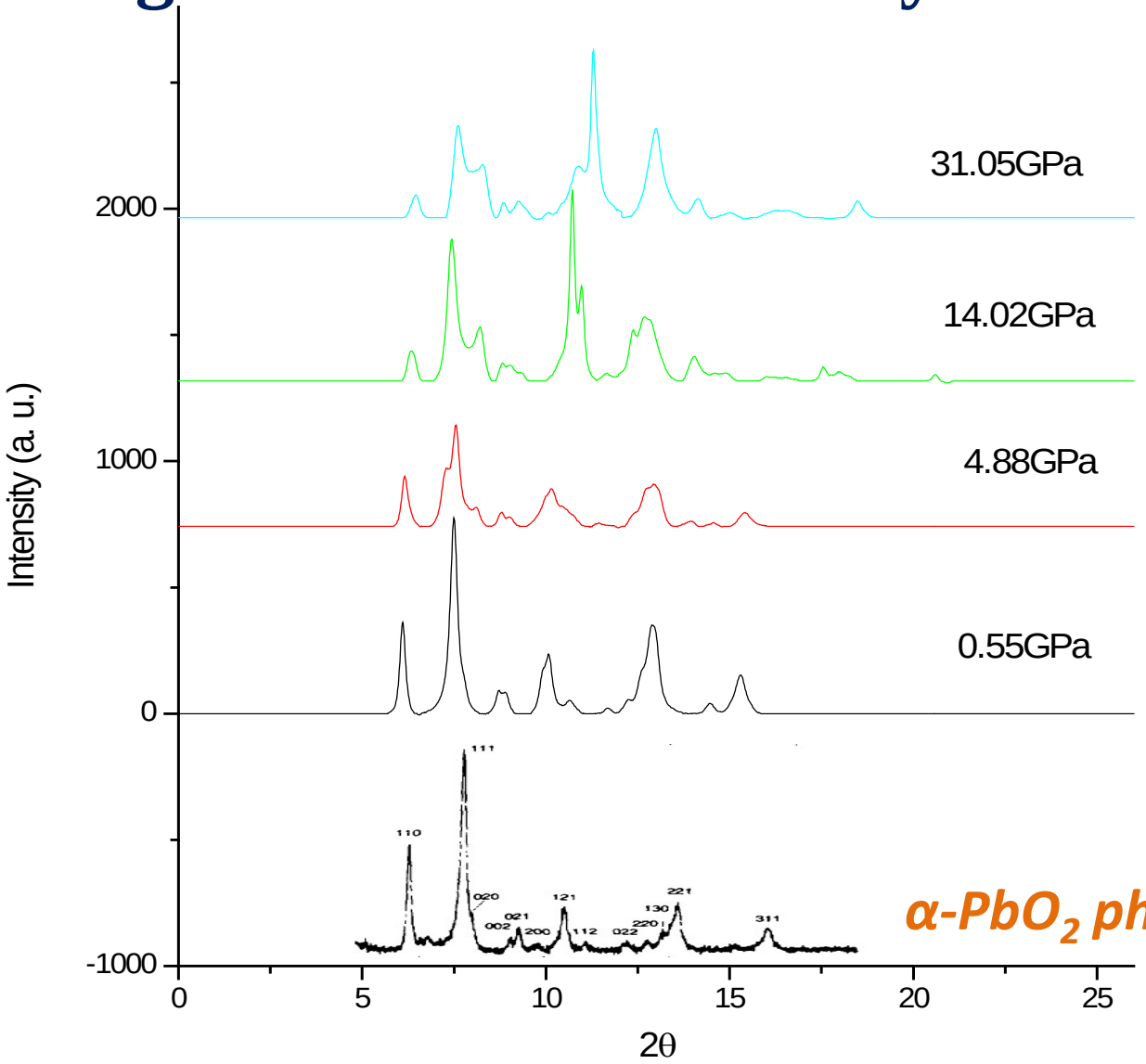

Decompression

1. At 31.05 GPa, ***g*** shows up.

2. At 4.88 GPa, ***b*** disappear.

α-PbO_2 phase

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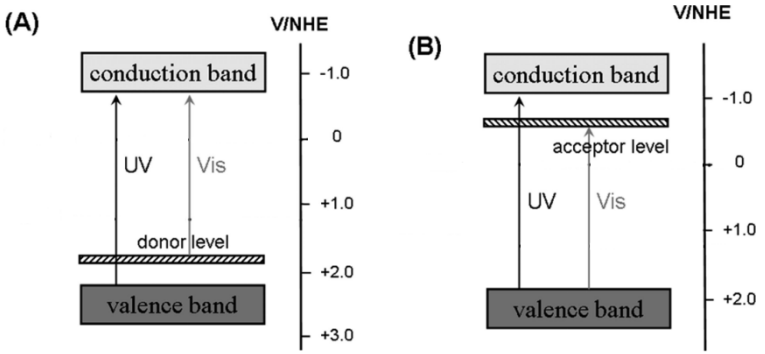
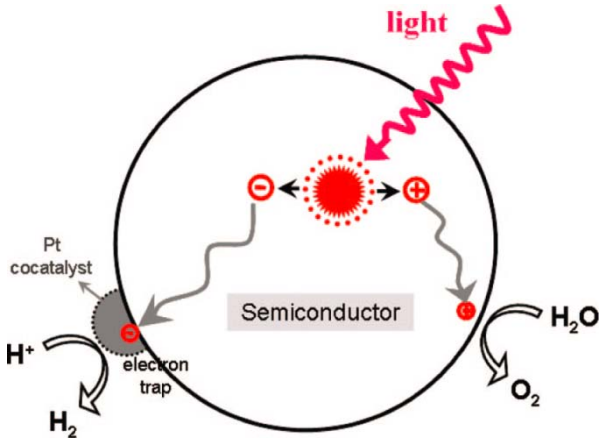
Prospects

- *Modifying the electronic band structure for visible light harvest* : e.g. metal ion doping, V-, Cr, Mn-, Fe-, Co- or Ni- doping.

- *Efficient photogenerated charge separation*: e.g. cocatalyst loading, Pt, Pd, Au and so on.





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Thank you!