INL/MIS-22-66283-Revision-0



# Gamma Radiolysis of FTO and nITO Electrodes (Group Meeting 03-09-2022)

March 2022

Jeffrey R McLachlan

Changing the World's Energy Future

Idaho National Laboratory

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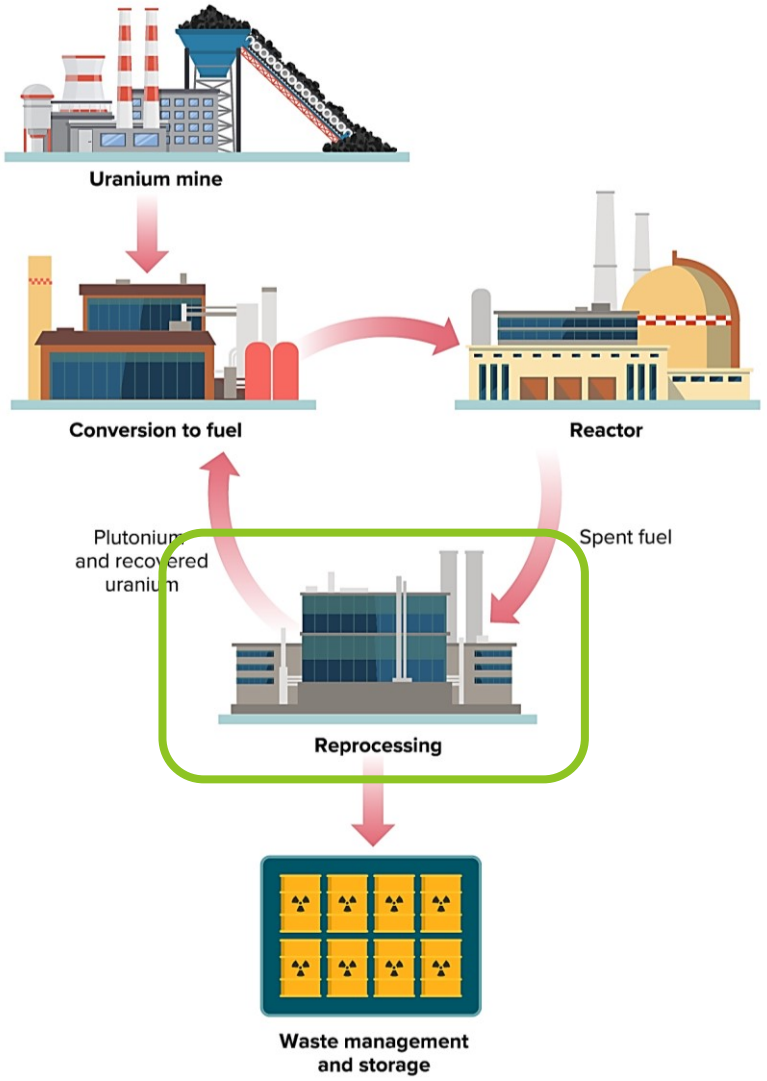
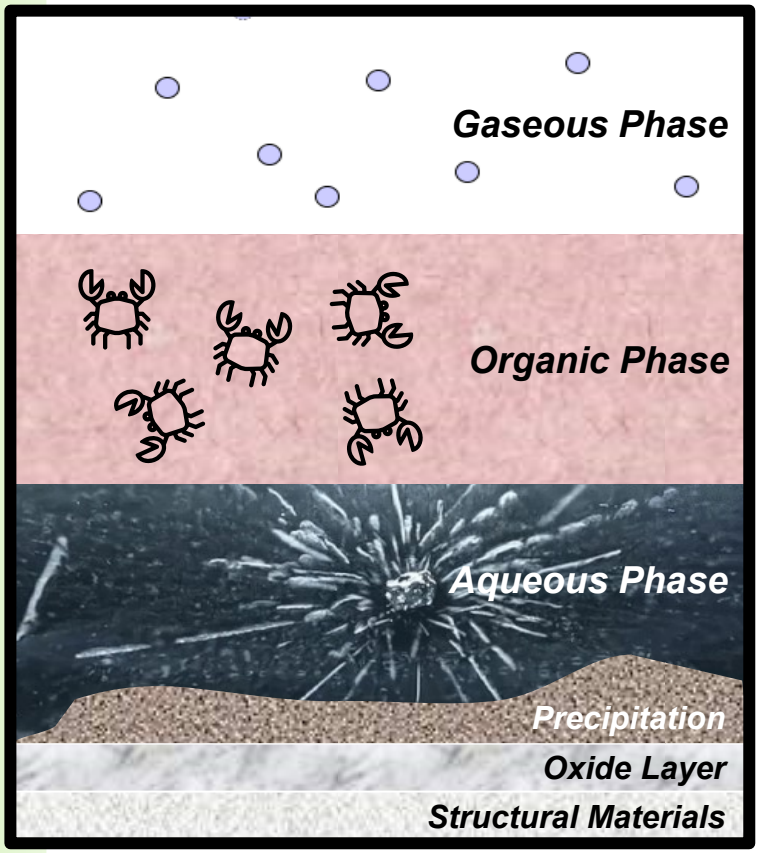
# Gamma Radiolysis of FTO and nITO Electrodes

# Reprocessing Used Nuclear Fuel




**Solvent Extraction Reprocessing**
**Ligands/organic diluent:$HNO_3$/$H_2O$**
**(± additives)**




- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop, August 30-September 1, 2021. Report for the US Department of Energy, Office of Nuclear Energy Workshop on Innovative Separations R&D Needs for Advanced Fuel Cycles, **2022**, under review.

# Co-60 Gamma Irradiator – Foss Therapy Services Model 812


# Experimental Layout

| Samples | | dose (kGy) | | | |
|---|---|---|---|---|---|
| | | 0 (Soaked) | 25 | 50 | 100 |
| Water | pFTO | | | | |
| | pITO | | | | |
| | nITO | | | | |
| 0.1 M HNO3 | pFTO | | | | |
| | pITO | | | | |
| | nITO | | | | |
| Air | pFTO | | | | |
| | pITO | | | | |
| | nITO | | | | |
| n-dodecane | pFTO | | | | |
| | pITO | | | | |
| | nITO | | | | |

| Data | Technique | Samples | Samples |
|---|---|---|---|
| Surface Morphology | SEM | Soaked and 100 kGy "A" Samples | 24 |
| Elemental Analysis | EDS | Soaked and 100 kGy "A" Samples | 24 |
| Elemental Analysis and oxidation state sensitive | XPS | Soaked and Dose series from 0.1 M HNO3 and dodecane "C" Samples | 7 |
| Phase changes | Raman | Soaked and 100 kGy "C" Samples | 24 |
| Absorbance spectra and Optical Band Gap | UV-vis; Tauc Analysis | All samples in triplicate | 144 |
| Flat band potential | Chopped Illumination, Mott-Schottky, Illuminated OCP | All "B" samples in singlet | 48 |
| Surface Area | Loading RuP; Quantify via UV-vis + Echem | All "A" samples in Singlet | 48 |
| Quantify Dissolution | ICPMS of soaking solutions | Soaked and 100 kGy in triplicate | 54 |

Triplicate = 4*12*3 = 144 electrode samples

NOTE: I can only irradiate ~ 6 samples at a time

# Reprocessing Radiation Chemistry

## Water Radiolysis

$$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$$

## Indirect Radiation Effects

$$HNO_3 + {}^\bullet OH \rightarrow {}^\bullet NO_3 + H_2O$$

$$NO_3^- + e^- \rightarrow NO_3^{\bullet 2-}$$

$$NO_3^{\bullet 2-} + H_2O \rightarrow {}^\bullet NO_2 + 2OH^-$$

$$NO_3^- + H^\bullet \rightarrow HNO_3^- \rightarrow {}^\bullet NO_2 + OH^-$$

$${}^\bullet NO_2 + {}^\bullet NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 \rightarrow HNO_2 + HNO_3$$

## Direct Radiation Effects

$$NO_3^- \rightsquigarrow NO_3^{-*} \rightarrow NO_2^- + O$$

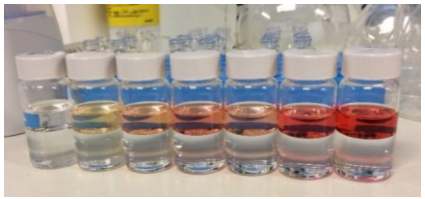
$$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$$

$$NO_3^- \rightsquigarrow {}^\bullet NO_3 + e^-$$

$$HNO_3 \rightsquigarrow {}^\bullet NO_3 + H^\bullet$$

## Alkane Radiolysis

$$R\text{-}CH_3 \rightsquigarrow e^-, R\text{-}CH_3^{\bullet +}, R\text{-}CH_2^\bullet, {}^\bullet CH_3, H^\bullet, H_2$$




- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

# Reprocessing Radiation Chemistry

## Water Radiolysis

## Direct Radiation Effects

**Radiolysis Products of Concern in Reprocessing**

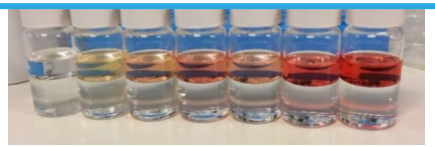
$H^{\bullet}$, $^{\bullet}OH$, and $H_2O_2$ from $H_2O$

$^{\bullet}NO_3$ and $HNO_2$ from $HNO_3$

$e^-$, $R\text{-}CH_3^{\bullet+}$, $R\text{-}CH_2^{\bullet}$, and $H^{\bullet}$ from **organic diluent**

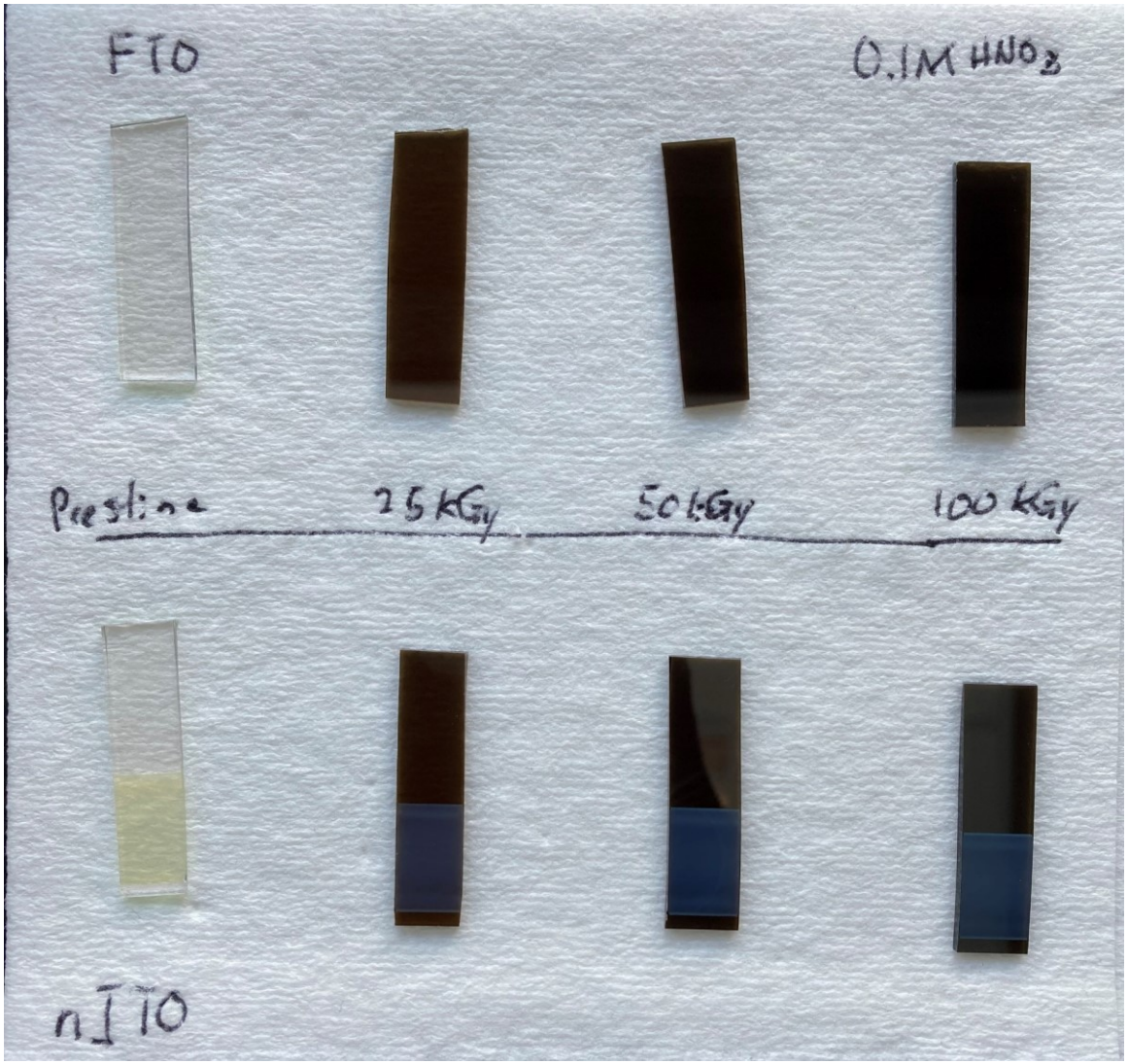
$H_3$, $H^{\bullet}$, $H_2$

$N_2O_4 \rightarrow HNO_2 + HNO_3$

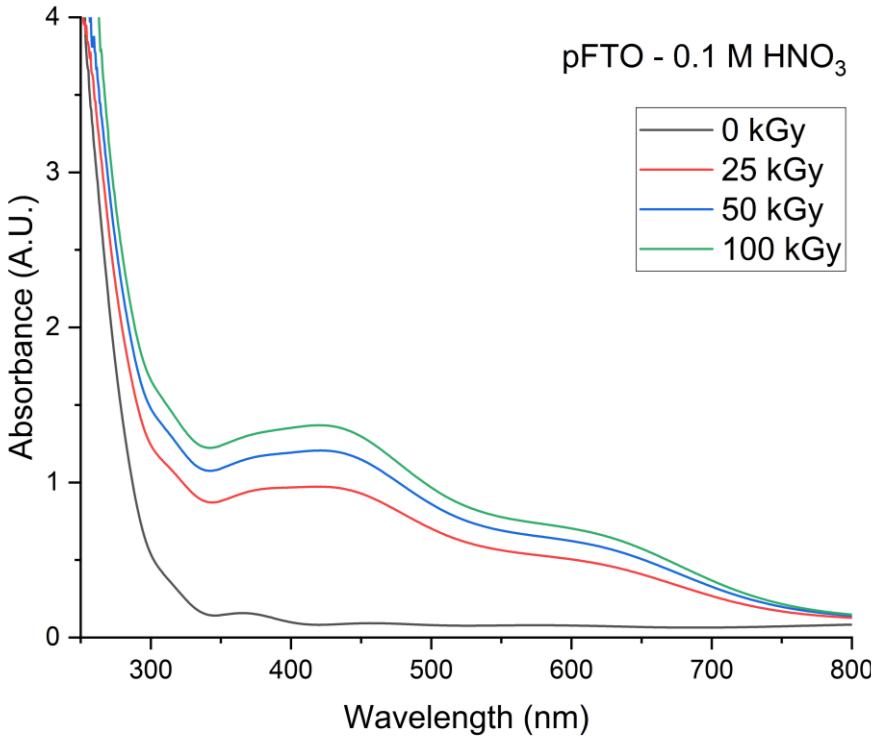


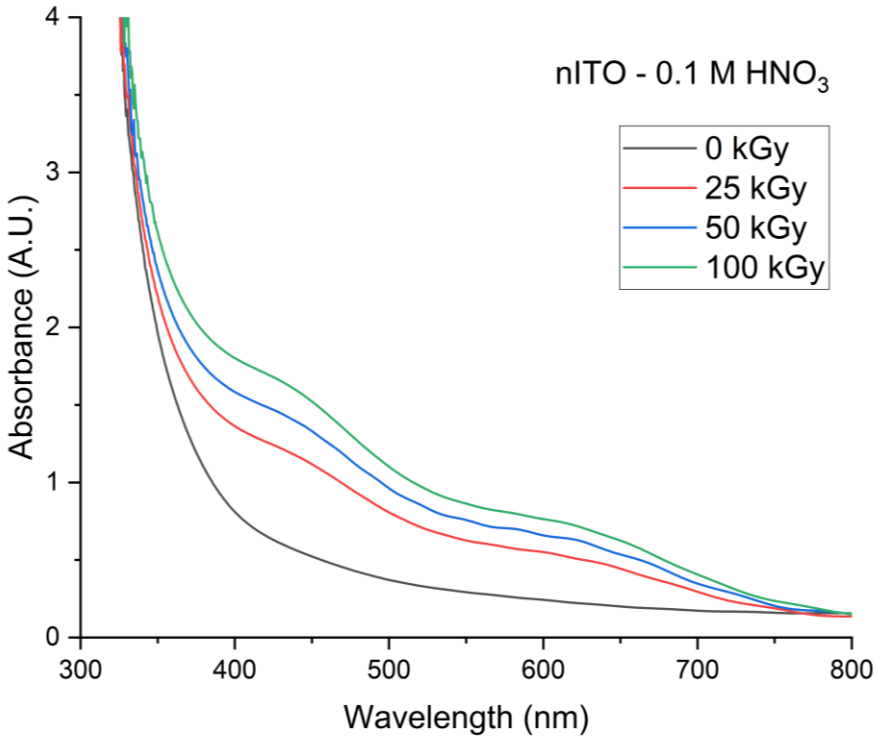
- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

# #CookThemBabiesUp



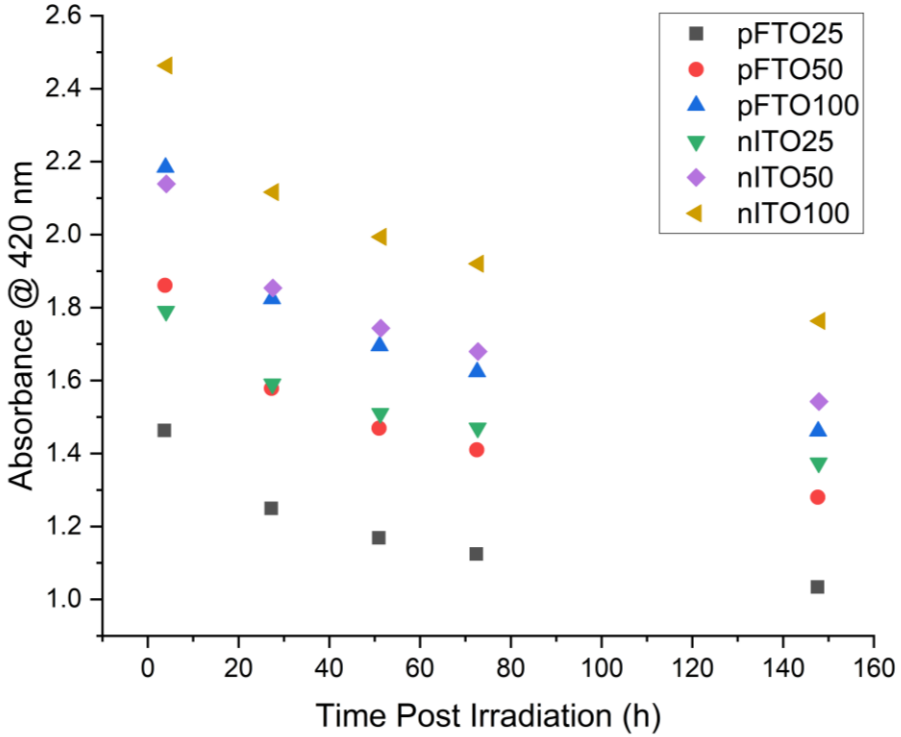
# UV-visible spectra



# UV-vis Time-Trial – Ambient Recovery

- We noticed that the spectra changed from day to day of the irradiated samples.
- We monitored 6 samples over the course of 150 hours and plotted changes in the Abs. at 420 nm



# Tauc Analysis – The "How To" Guide to Find Eg

Equation was derived making a handful of assumptions… and let's just say, porous thin films are at the edge of the assumptions

$$(\alpha * h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g)$$

$h$ is Planks constant: 6.62607015 x 10^-34 J*s

$\nu$ is the photon frequency in units s^-1

- Frequency relates to wavelength by the following:
- $v = c/\lambda$
- Where $c = 299792458$ m/s AND $\lambda$ is in units of meters

**B** is a constant

**γ** is a factor that depends on the nature of the electron transition and is equal to:

- ½ for a DIRECT band gap transition and,
- 2 for an INDIRECT band gap transition

**α** is Absorption coefficient

Convert wavelength in nm to energy in eV using:

$$eV = 1239.8/nm$$

For the *hv* term

How do we determine if it is direct or indirect?!?!?

# Converting Absorbance to α

If

$$Abs = \log\left(\frac{I_o}{I}\right)$$

And

$$I = I_o e^{-\alpha L} \quad OR \quad \alpha = \frac{2.303 \log\left(\frac{I_o}{I}\right)}{L}$$

Then

$$\alpha = \frac{2.303 * Abs}{L}$$

Where **L** = The path length of the solid absorber (aka thickness of the FTO or nITO film)

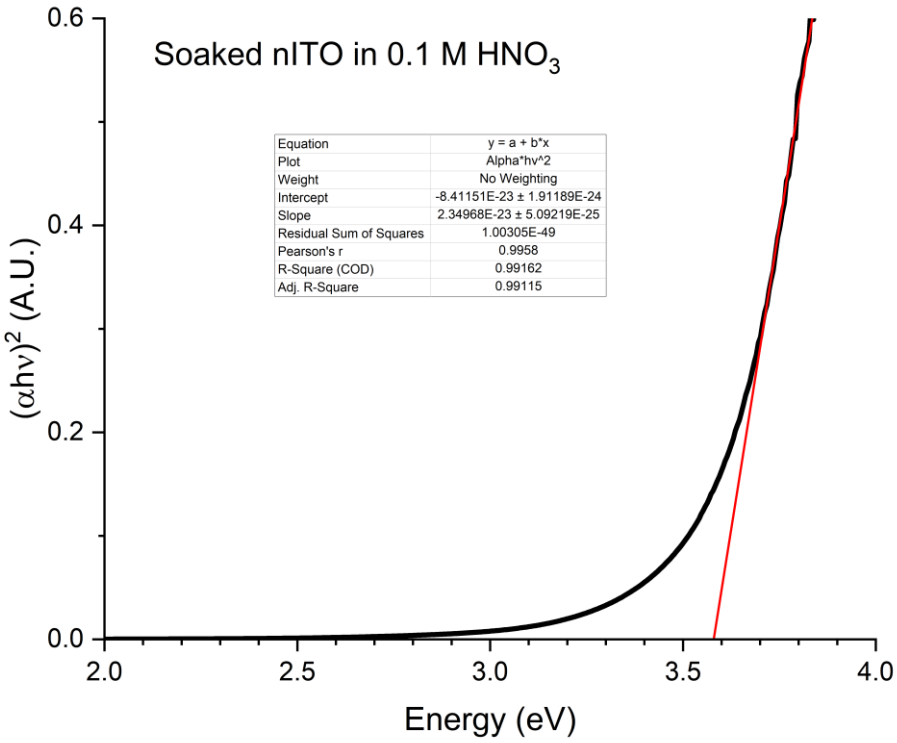
# Generate the Tauc Plot - $(\alpha * h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g)$

Plot $(\alpha * h\nu)^{\frac{1}{\gamma}}$ [y-axis] vs $h\nu$ (in eV) [x-axis]

Extrapolate the linear portion of the plot to the x-axis

When $(\alpha * h\nu)^{\frac{1}{\gamma}} = 0, \quad h\nu = E_g$

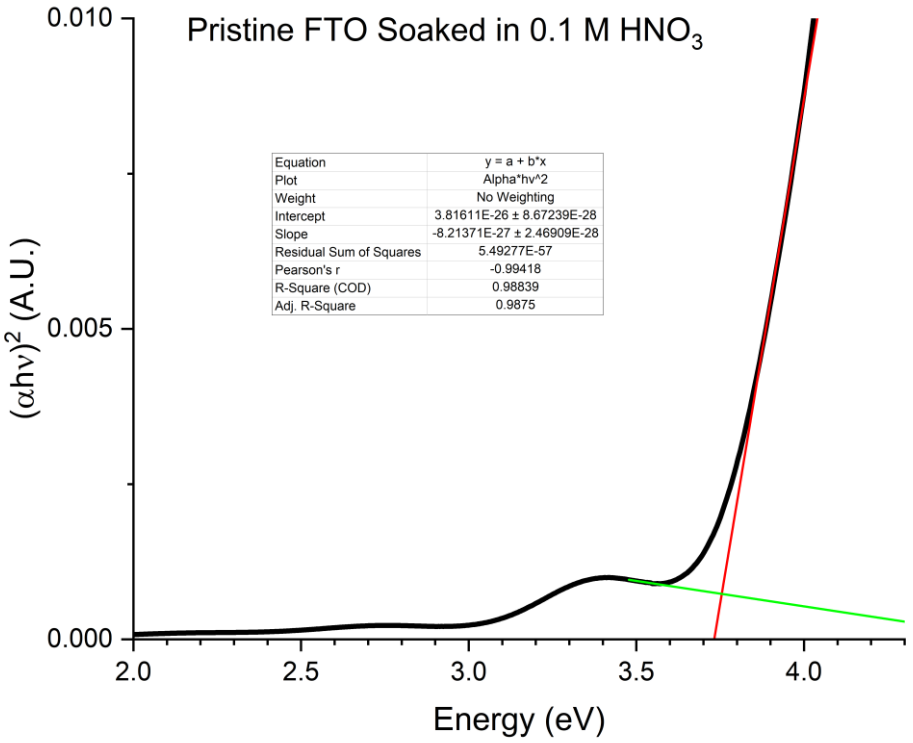
Therefore, the x-intercept of the extrapolated line is an estimation of your materials optical band gap



# What happens if it isn't so straight forward?

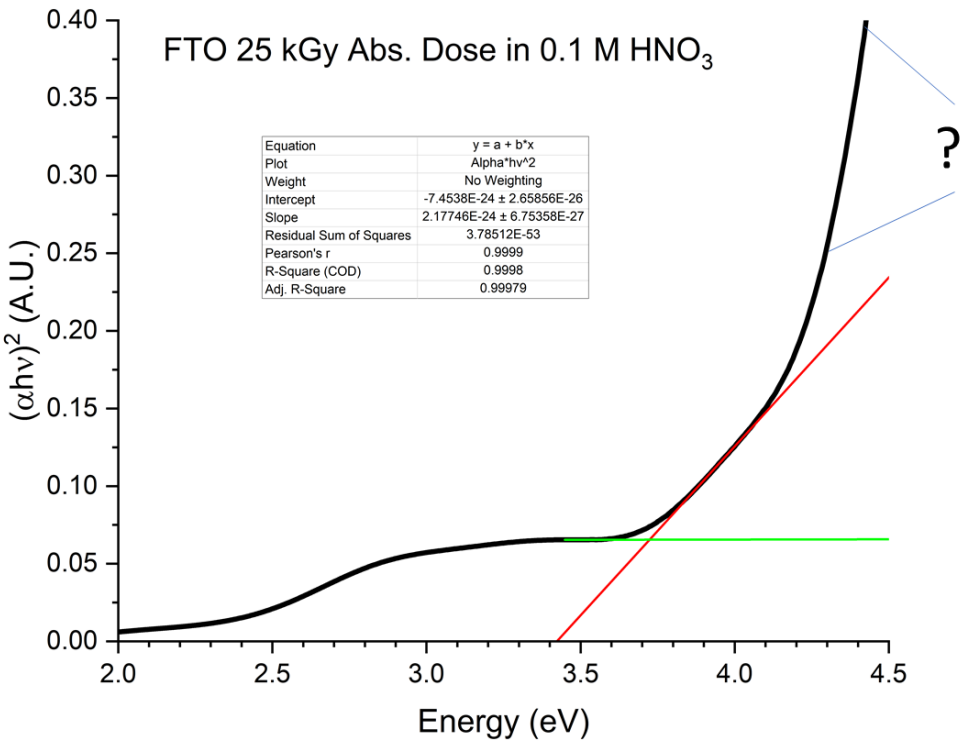
What happens if you have species in your sample which absorb light of lower energy than your materials band gap?

We utilize the fact that the net absorbance spectra is the linear sum of its components, therefore we can "subtract" the components that interfere with our extrapolation with a pseudo baseline correction.



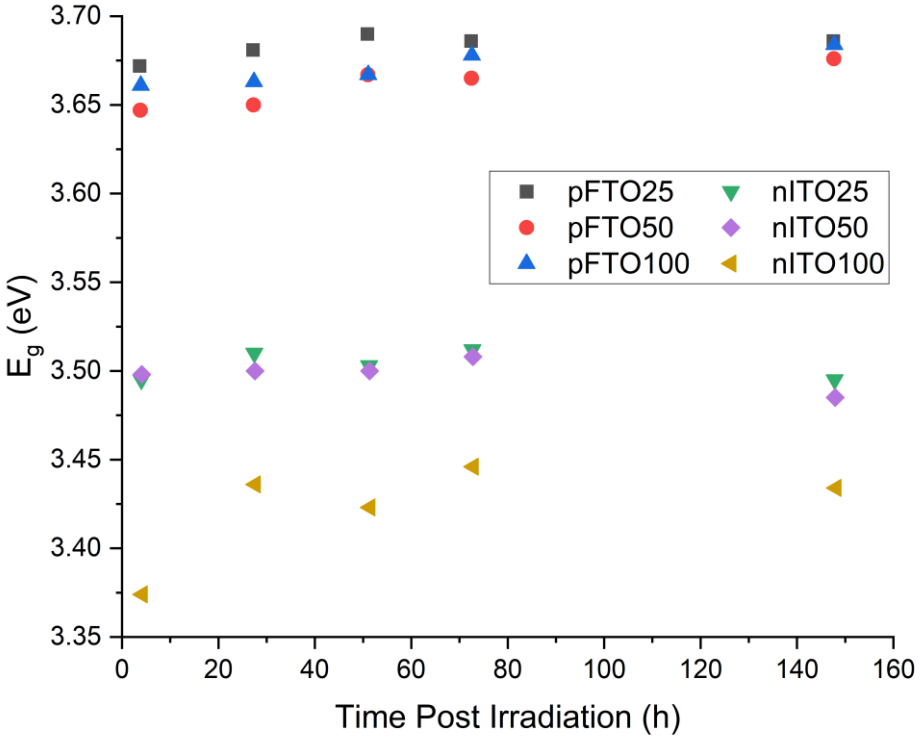
# What if there's multiple linear portions?

- Why don't we look at the linear region between 4.3 and 4.4 eV?
- This region corresponds to the glass substrate absorbing light!
- We must understand what absorbance events belong to or species of interest and examine that event



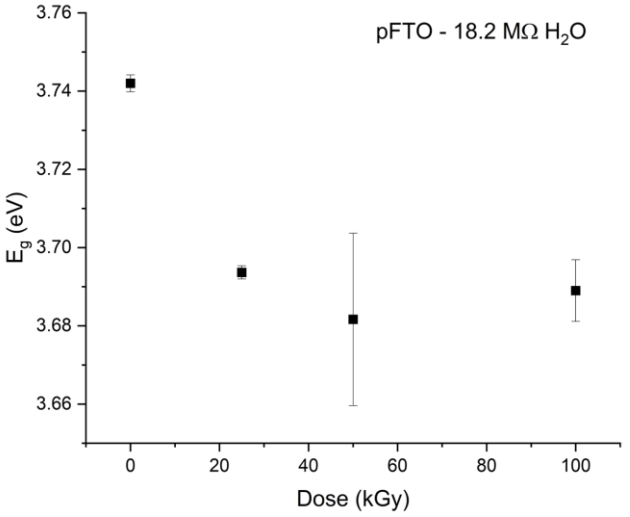
# $E_g$ time trial – Band gap stable with time

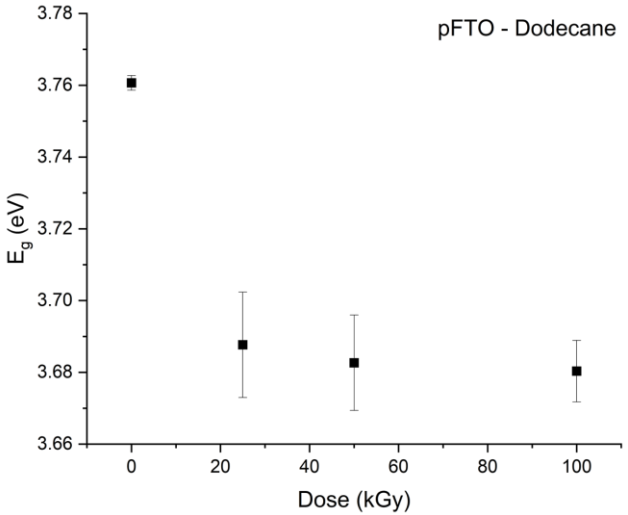
- Band gap remains stable over time.
- Proves that analysis days after irradiation are valid compared to instantly analyzed samples.
- Proves changes in Abs. spectra do not correlate to $E_g$ shifts.
- Note: determining $E_g$ of the nITO 100 kGy samples is difficult due to electrode darkening.

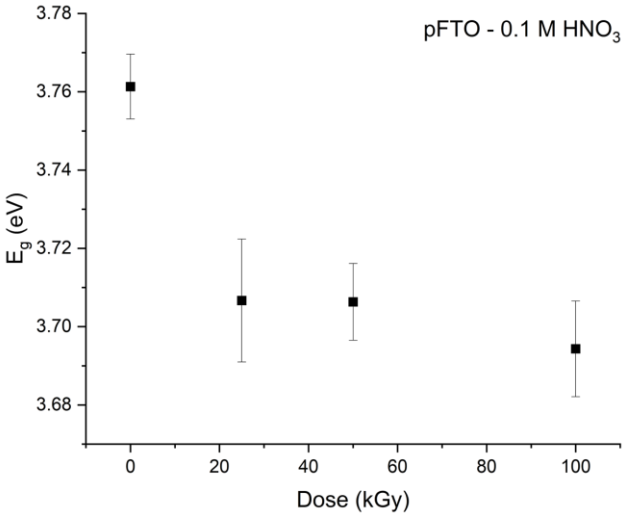


# Trends in $E_g$ vs Dose for FTO

- The initial application of radiation causes the band gap to decrease by about 0.06 eV.
- Increasing the dose does not heavily impact the band gap of FTO after initial exposure.
- Similar trends observed in pure water and 0.1 M $HNO_3$.

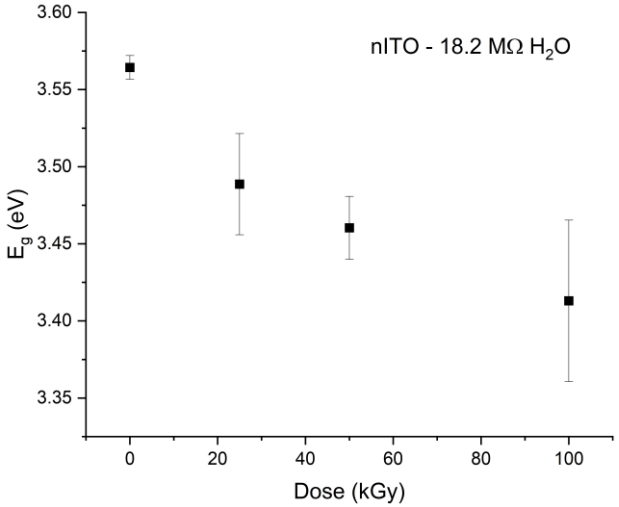


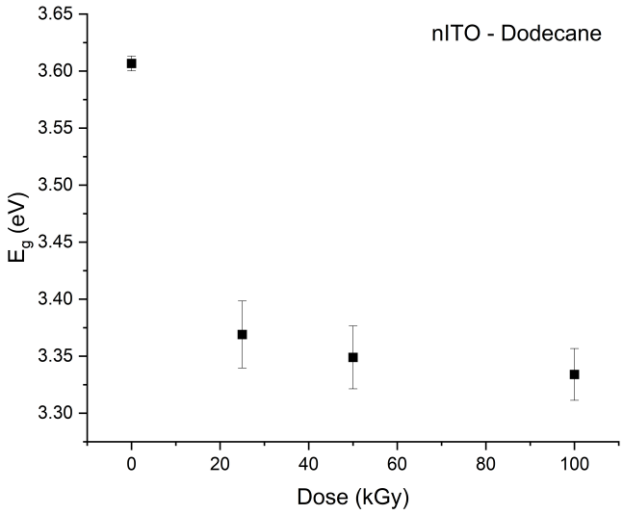



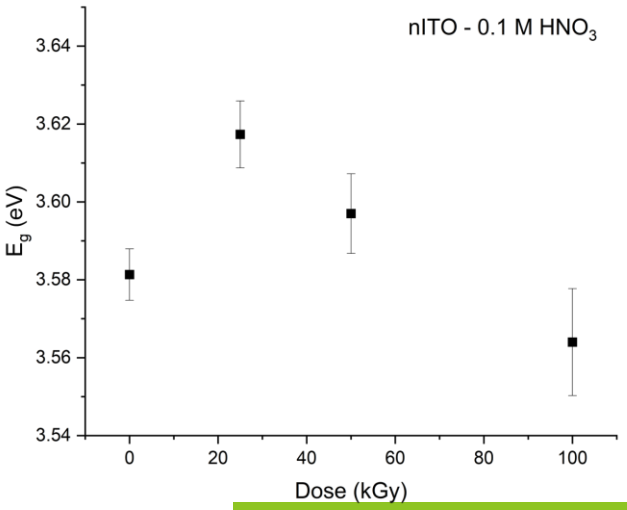



# Trends in $E_g$ vs Dose for nITO

- The band gap of nITO decreases as a function of applied dose in pure water.
- The initial 25 kGy dose caused the nITO band gap to increase by ~0.04 eV. Increasing absorbed dose there after caused the band gap of nITO to decrease as a function of dose.



# Preliminary Conclusions

- The band gap energies of pFTO and nITO electrodes are highly stable to the direct and indirect effects of gamma radiation.
- The transmission of light through these electrodes is severely compromised after irradiation.
- The darkened electrodes “recover” with time at ambient conditions, but do not fully return to their original transparency.
  - This suggests the formation of two types of irradiation induced color centers, one being much less stable than the other.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