Standard Operating Procedure

(SOP)

UV-Visible Spectroscopy

Determination of Bandgap

Test ID # PEC-P-12

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Revision History

This page documents the revisions over time to the SOP. The most recent iteration should be listed in the row space, with consecutive versions following.

Date of Revision	Page(s)/Section(s) Revised	Revision Explanation

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3. Procedures

a. Scope and Applicability – This SOP details procedures for estimating the optical bandgap of photoelectrodes

b. Summary of Method – UV-vis spectra are taken of a reference photoelectrode. UV-vis spectra are taken of the working samples. Tauc plots are created from the spectra. Spectra are fitted to determine size and type of band gap.

c. Definitions – UV-Vis: Ultraviolet/visible
I – Intensity of light measured after interaction with the sample
I_0 – Incident light intensity
l – Path length of light through the sample
α – Absorption cross section
λ – Wavelength of light in nm
A – Absorbance
$A_{\%}$ – Absorptivity

d. Health & Safety Warning – Ultraviolet light can be damaging to skin and eyes. Appropriate measures to avoid exposure such as enclosure or ultraviolet blocking PPE should be utilized.

e. Cautions – Not applicable for this SOP.

f. Interferences – Reflection or scattering from the sample surfaces and/or interfaces can decrease the amount of light reaching the detector (I_0), creasting seemingly higher absorption values. To minimize reflection and refraction during transmission experiments, the sample should sit normal to the path of incident light. Scattering effects in transmission experiments should be minimized be placing the sample as close as possible to the detector. In highly scattering samples, an integrating sphere detector may be necessary.

Very thin samples may necessitate using diffuse reflectance or absorption configurations the true absorbance is measured.

Ensuring the source lamp has had adequate time to heat up and reach a stable spectrum prevents drift of the light source. Improper shielding of the apparatus from ambient lighting may also contribute to improper shielding. High order diffraction peaks arising from use of a monochromator can be avoided using appropriate long pass filters.

g. Personnel Qualifications / Responsibilities – Not applicable for this SOP.

h. Equipment and Supplies –

1. UV-Vis apparatus (commercial or consisting of the following:)
    a. Light source

b. Monochromator with long pass filters
c. Integrating sphere (for reflectance and absorption measurements)
d. Detector (such as a power meter)
e. Focusing optics

2. Reference sample
3. Working sample
4. Computer with data analysis software

i. Step by Step Procedure

- Instrument or Method Calibration and Standardization –
    1. Turn on lamp source and allow at least 15 minutes for the lamp temperature to stabilize.
    2. Place collect a baseline scan with no sample in the beam path.
    3. Place reference sample into beam path and collect transmission, reflectance, or absorption scan.
    4. Calculate absorption coefficient (if thickness is known) as a function of λ and create Tauc plots as detailed below.
    5. Fit the spectrum to determine size and type of band gap as detailed below.
    6. Ensure the results of the reference sample match known properties

- Sample Collection – Not applicable for this SOP.

- Sample Handling and Preservation –
    1. Never touch the front surface of the semiconductor, especially with bare hands.

- Sample Preparation and Analysis – Not applicable for this SOP

- Troubleshooting – Transmission should only be used for samples with a reasonable degree of transparency, typically thin films supported on transparent substrates. Opaque samples must utilize diffuse reflectance or absorbance measurements. Diffuse reflectance is optimal for particulate samples, to ensure that off axis scattering is accounted.

  In a transmission experiment, the instrument software may use Eq. (5.2) to directly calculate absorbance from the measured intensity. However, the measured intensity is affected not only by absorptance, but by reflectance and scattering as well (i.e., $A_{\%} \neq I_0 - T$). These effects are often related to the morphology of each sample (e.g., a sample with a rough surface will introduce significant light scattering that decreases the amount of light reaching the detector and consequently increases the perceived absorbance). These effects often manifest in the form of a nonzero baseline. One way to correct these effects is to shift all the data so that the

data point with the lowest absorbance value corresponds to zero absorbance. This method makes the assumption that any reflectance and scattering effects are wavelength independent. It is important to realize that this assumption is not always valid and can introduce error in the data analysis.

- Data Acquisition, Calculations & Data Reduction Requirements –

  Data Acquisition:
  1. Turn on lamp source and allow at least 15 minutes for the lamp temperature to stabilize.
  2. Place collect a baseline scan with no sample in the beam path.
  3. Place working sample into beam path and collect transmission, reflectance, or absorption scan.
  4. Calculate absorption coefficient (if thickness is known) as a function of λ and create Tauc plots.
  5. Fit the spectrum to determine size and type of band gap.
  6. Ensure the results of the reference sample match known properties

  Calculation of Absorption Coefficient
  1. For transmission experiments, output data in absorbance or convert *I* to absorbance using the formula $A = \varepsilon cl = -log_{10}\left(\frac{I}{I_0}\right)$
  2. A(λ) can then be converted to α using the equation $\alpha(cm^{-1}) = \frac{ln(10)\times A}{l(cm)}$

  Creation of Tauc Plots
  1. α(λ) should first be converted from a function of wavelength to a function of photon energy (α(*hν*)) using the equation $h\nu = \frac{1239.8\ (eV\times nm)}{\lambda\ (nm)}$
  2. $(\alpha h\nu)^n$ should then be plotted as a function of *hν* using values of 2, ½, 2/3, and 1/3 for *n*, as these represent the proportionalities of absorptivity to photon energy for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively.
  3. Least squares regressions of linear regions where $\alpha > 10^{-4}$ cm^{-1} within these plots should be performed. Intercepts of these transitions with the x-axis (*hν*) give estimations of the band gap for the material.

- Computer Hardware & Software – Computer for spectra collection and data analysis. Data analysis software capable of mathematical transformations, plotting, and linear regression.

j. Data and Records Management – Not applicable for this SOP.

4. Quality Control and Quality Assurance Section

5. Reference Section

(A) Z. Chen et al., Photoelectrochemical Water Splitting, Springer Briefs in Energy, DOI: 10.1007/978-1-4614-8298-7_5,