XAS in the determination of the effect of biotemplating on the structure of TiO_2 nanoparticles

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Abstract:

Solar panels are amongst the most effective methods to harness renewable energy for home and commercial use. Currently solar photovoltaics cells are mostly based of silicon as it is an abundant, non-toxic, chemically stable semiconductor element that has been used for this purpose for more than 50 years. However, the stability of these cells is compromised by the sunlight-induced degradation over time of the silicon materials, which limits its potential. Recently, the incorporation of other semiconducting materials are being explored to improve the stability of the silicon cells. A particular nanomaterial, titanium dioxide (TiO_2), has been given consideration for being a highly biocompatible, inexpensive, non-toxic, corrosion resistant, highly chemical and optical stable inorganic semiconductor. TiO_2 nanoparticles would improve the stability and efficiency of the silicon-based solar photovoltaic cells preventing sunlight-induced degradation, thus prolonging optimal efficacy. Our goal is to analyze the outcome biotemplating has in the process of TiO_2 nanoparticles synthesis. This is possible using previously obtained experimental X-Ray Absorption Fine Structure (XAFS) data and comparing its X-ray Absorption Near Edge Structure (XANES) with a control sample.

Introduction:

Titanium dioxide (TiO_2) or titania, is a semiconductor material considered for this study due to its photocatalytic properties. It has been proven that TiO_2 occurs naturally in three polymorphs which are anatase, rutile and brookite. Anatase and rutile exhibit a tetragonal crystalline structure, unlike brookite which exhibits an orthorhombic crystalline structure. Furthermore, these three crystalline phases display separate photocatalytic activity performances from one another due to a difference in physical properties. The anatase phase is distinguished from the other phases for being meta-stable and having an optimal band gap of 3.2 eV. Anatase was obtained from the combined methods of biotemplating and sol-gel of TiO_2 nanoparticles. For the template, biomass from oregano (*Plectranthus amboinicus*) leaves was used for its affordability, ease of use and because natural materials as templates provide highly ordered structures. The synthesis using the sol-gel method yields highly pure samples efficiently, using neutral pH, at room temperature with no toxic alcohol byproduct.

X-ray Absorption Fine Structure (XAFS) data analysis was carried out using software tools such as *PyMca* and *MATLAB*. *PyMca* is a toolkit that permits its user analyze dataset imaging of XAS, XRF and powdered diffraction. It was used to determine if the samples prepared using biotemplating, present similar spectral features as the control. On the other hand, *MATLAB* is a programming platform that contains toolboxes useful for scientists and engineers. The toolbox of interest for this study is *BlueprintXAS*. This toolbox is designed for the processing and analysis of X-ray Absorption Near-Edge Structure (XANES) data assisting users find reasonable fit solutions while reducing user bias.

Data Analysis:

X-ray Absorption Fine Structure (XAFS) samples of TiO_2 anatase standard and biotemplated TiO_2 data were obtained at the Cornel High Energy Synchrotron Source (CHESS) PIPOXS beamline. Samples were run in triplicate. *(Processing and analysis were done according to Chris Pollock and Louise Debefve's XANES tutorial, May 2020)*

XAFS data of each sample group (anatase, biomass) were imported to *PyMca* were they were plotted. The individual data was normalized and compared amongst the same sample group.

After using the available tools provided by the software it was determined that the data for both groups did not suffer any damages at the moment the samples were taken. It was safe to create an average plot and proceed exporting the data for further analysis.

The exported data was then analyzed in *MATLAB*'s *BlueprintXAS* toolbox. To create the best fits on BlueprintXAS the unwanted regions were excluded, and a manual fit was done to resemble as close as possible the original graph. Then a hundred fits were programmed to run so the software can find the best fits. Once the run ended, the bad fits were manually removed, and we ended up with 7 good fits for TiO_2 Biomass samples and 22 good fits for Anatase Standard samples. With the best fits obtained, its safe to proceed exporting the data. The exported data was scatter plotted on *Microsoft Excel* with their corresponding background values subtracted and divided by their respective average intensity. Both graphs were combined to make a comparation between the samples.

Results:

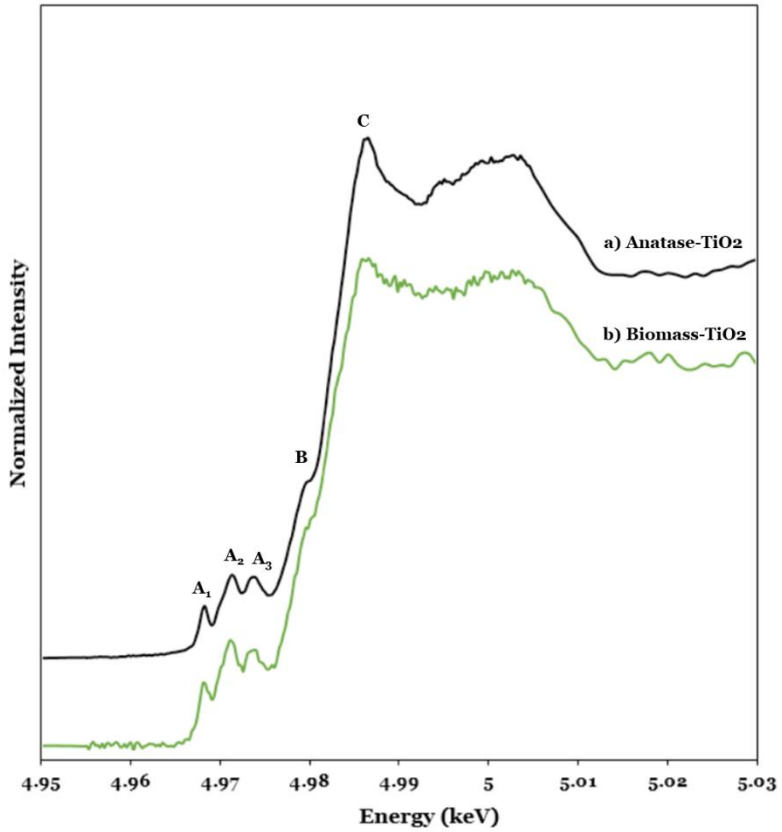

Figure 1. Measured Ti K-edges XANES of: a) Anatase-TiO_2 Standard (black) and b) Biomass-TiO_2 (green). There are three peaks featured in the Ti K-Edge structure from TiO_2: (A_1) represents $1s \rightarrow 1t_{1g}$ transition, (A_2) represents $1s \rightarrow 3d$ transition, and (A_3) represents $1s \rightarrow 3d$ transition [1]. Shoulder (B) is attributed to a $1s \rightarrow 4p$ transition [2]. Edge crest (C) is attributed to the bonding configuration (MS) of the ejected photoelectron wave from the central atom to the nearest and next-nearest neighbors [1] or Higher-lying p orbitals [3].

Conclusion:

A visual comparison after the analysis shows a similarity between the overall intensities of TiO_2 anatase standard and biotemplated TiO_2. This is noteworthy as it demonstrates that the biotemplated TiO_2 sample's features does not differentiate significatively from the Tio2 anatase standard. Therefore, suggests that biotemplating helps control particle size without affecting remarkably the structure and transitions of the obtained material. However, the spectra are not exactly the same. TiO_2 samples present a peculiar problem when obtaining data, they tend to generate self-absorbed spectra. Self-absorbed spectra usually have exaggerated and decreased intensities. Compared to fig. 1a, fig. 1b has higher intensity peaks in the pre-edge region ($A_{1,2,3}$) and in the shoulder (B), meanwhile it has a lower intensity peak on the edge crest (C), which means our Biomass-TiO2 sample is distorted due to self-absorption. This complicates the sample analysis. One way to deal

with this problem could be a correction for self-absorption, but this would make the analysis inaccurate. An adequate, better solution would be to opt for transmission instead of fluorescence spectra as they are less prone to distortion. Thus, further experiments will be performed to address this problem with the biotemplated sample.

References:

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