

# Photocatalytic Methanol degradation on a TiO<sub>2</sub> Surface Monitored by IR-Vis Sum Frequency Generation through a Transparent Electrode Material

Contact paul.donaldson@stfc.ac.uk, acowan@liverpool.ac.uk

## K. Saeed

Department of Chemistry and Stephenson Institute for Renewable Energy,  
University of Liverpool, UK

## A. J. Cowan

Department of Chemistry and Stephenson Institute for Renewable Energy,  
University of Liverpool, UK

## A. Gardner

Department of Chemistry and Stephenson Institute for Renewable Energy,  
University of Liverpool, UK

## P. M. Donaldson

Central Laser Facility, Research Complex at Harwell,  
STFC Rutherford Appleton Laboratory, UK

## Introduction

Using sunlight to drive chemical reactions is a promising route to sustainably generating a large variety of chemicals and fuels. Earth-abundant metal oxides, such as iron, tungsten and titanium oxides, are well-suited for this purpose due to their high stability and low cost; titanium dioxide (TiO<sub>2</sub>) in particular has found a remarkable number of applications as both a photocatalyst and photoanode.<sup>1-4</sup> However, the widespread adoption of these materials for commercial processes is limited due to inefficiencies in light capture and electron-hole separation, as well as catalytic inefficiencies. Modifications in the design of these materials, such as nanostructuring of the surface,<sup>5</sup> addition of overlayers<sup>6</sup> or alloying,<sup>7</sup> can lead to significant improvements in performance. Understanding the mechanistic cause of inefficiencies of photoactive metal oxides such as TiO<sub>2</sub> is key to informing which design decisions are required for improved future materials.

Catalysis in most photocatalytic and photoelectrochemical systems occurs at a solid-liquid interface. The interface signal is often masked by inactive bulk material, making it difficult to study such catalytic mechanisms using conventional spectroscopies. IR-Vis vibrational sum frequency generation (VSFG) spectroscopy is a technique that allows rapid collection of highly surface-sensitive vibrational spectra, the mechanism of which has been described in detail elsewhere.<sup>8</sup> Briefly, the spatial and temporal overlap of short visible and infrared laser pulses results in a second order non-linear process, where light at the sum of the two incident frequencies is generated. In most systems, the magnitude of the SFG response is proportional to the square of the second order non-linear susceptibility ( $\chi^2$ ) of the material, although third order ( $\chi^3$ ) effects can start to dominate under greater electric field strengths.<sup>9</sup>  $\chi^2$  is only non-zero in media that lack inversion symmetry, such as interfaces, thus VSFG spectroscopy can be used as a surface specific vibrational probe.

A resonantly enhanced SFG signal is observed when the frequency of the IR pulse matches that of a vibrational mode for a surface species. Otherwise, a broad non-resonant signal is observed following the profile of the incident IR pulse. Unlike other surface-sensitive techniques, such as XPS and UPS, UHV conditions are not required in SFG experiments, allowing *in situ* photo- and electrocatalytic experiments to be carried out with relative ease.

Our aims are to develop an *in situ* photoelectrochemical SFG experiment for studying transparent metal oxide-based electrodes for use in the sustainable generation of chemicals and fuels. Such materials typically involve a layered structure, including a transparent support material (e.g. glass), a transparent conductive oxide (TCO) layer and a layer of the catalytically active material. A common problem in *in situ* electrochemical vibrational spectroscopy is attenuation of the IR light by the electrolyte,

leading to much weaker signals. The transparent nature of these materials presents an alternative experiment geometry where the IR (and/or Vis) light is passed through the back of the electrode instead of the electrolyte. However, this type of layered structure introduces many additional interfaces, at the boundary between each layer, leading to multiple potential sources of SFG light. It is therefore important to ensure the catalytically active interface is being probed, instead of the additional interfaces arising from the layered structure.

Previous SFG experiments have used methanol as a probe molecule for studying TiO<sub>2</sub> surfaces where the IR and Vis light was introduced onto the front of the material which was mounted on an electrochemically inactive substrate. In these studies surface bound methanol displayed strong resonant modes for C-H stretching vibrations.<sup>10</sup> This report describes our initial experiments, where the C-H stretch vibrations of methanol on TiO<sub>2</sub> are monitored to ensure the TiO<sub>2</sub> surface is being probed in our “through-electrode” experimental geometry. These initial experiments were carried out without an applying an external bias potential to avoid complicating spectra by introducing the possibility of third order contributions. Instead, we use a 355 nm LED to directly mineralize the methanol probe molecules from the TiO<sub>2</sub> surface. Nonetheless they demonstrate the capability of the ULTRA B SFG system to monitor a dynamic photocatalytic process in a novel experimental geometry.

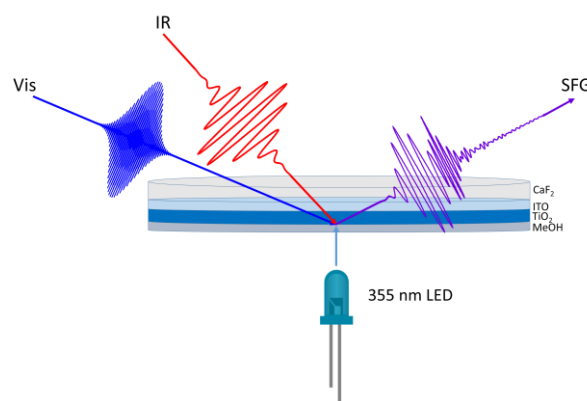


Figure 1: Diagram showing layered structure of transparent TiO<sub>2</sub> electrode and propagation of IR, vis and SFG light

## Experimental

ITO coated CaF<sub>2</sub> ( $\varnothing$ -25 mm, 2 mm thick) windows were prepared by magnetron sputtering of standard ITO (90:10 wt.) targets at 100 W power under 2 mTorr pressure with a substrate temperature of 400 °C for 4 minutes. These parameters give <100 nm thick films of the TCO materials (measured by profilometry) with a sheet resistance <1 k $\Omega$ /sq.

Spray pyrolysis of TiO<sub>2</sub> onto the conductive windows was carried out based on the procedure laid out elsewhere.<sup>11</sup>

Substrates were cleaned by sequential sonication (20 minutes) in acetone, ethanol and then water. Cleaned substrates were placed on a hot plate and heated to 400 °C. Titanium diisopropoxide bis(acetylacetonate) (0.2 M in ethanol) is sprayed for 100 coats using a glass spray nozzle and aspirator in a conical flask. The films are left to dry for an hour and then placed in a furnace ramping up to 450 °C over 1 hour and then holding at 450 °C for 1 hour to obtain the anatase phase of TiO<sub>2</sub>.

IR-Vis SFG experiments were carried out using 10 kHz ULTRA B. Full experimental details have been described elsewhere.<sup>12</sup> All experiments discussed below were carried out with s visible, p IR and uncontrolled SFG polarisations.

## Results & Discussion

Separation of the vibrationally resonant component of the SFG response from the nonresonant component is key for our purposes of identifying and monitoring catalytic intermediates at surfaces. This can be achieved by delaying the ps visible pulse by a few hundred fs, allowing the short-lived nonresonant response to decay, while the much longer-lived vibrationally resonant response still contributes to the SFG signal.<sup>13</sup> Figure 2 shows how varying the delay between the IR and visible pulses can result in complete suppression of the broad nonresonant feature, leaving two sharp resonant features at 2846 and 2951 cm<sup>-1</sup>. The position of the 2846 cm<sup>-1</sup> peak lies between the symmetric C-H stretches of a chemisorbed titanium-methoxy species (2828 cm<sup>-1</sup>) and a physisorbed molecular methanol species (2855 cm<sup>-1</sup>). The same is true for the peak at 2951 cm<sup>-1</sup> and the asymmetric C-H stretches of chemisorbed and physisorbed methanol at 2935 and 2968 cm<sup>-1</sup>, respectively. The resolution of the spectrometer may not be enough (~12 cm<sup>-1</sup>, determined by the nature of the fs derived time asymmetric ps 800 nm pulse) to resolve the methoxy and methanol species, but this initial study confirms that the correct interface is being probed.

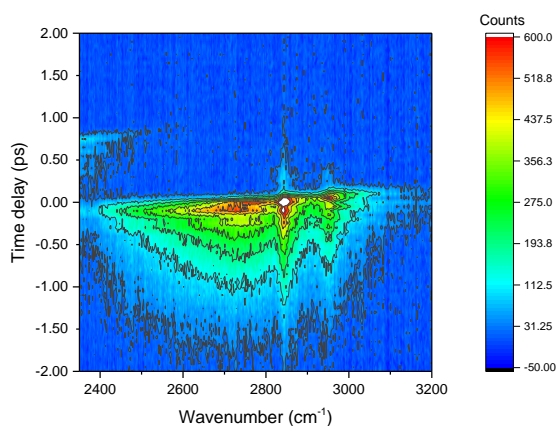


Figure 2: SFG spectra of MeOH on TiO<sub>2</sub> surface at varying time delays between IR and Vis pulses. Positive time delays indicate the visible pulse being delayed.

Under UV illumination TiO<sub>2</sub> can mineralize adsorbed alcohols,<sup>14</sup> which can be used a simple experiment to test the feasibility of monitoring dynamic processes using the ULTRA B system in this experimental geometry. Before attempting this type of experiment, the stability of MeOH on the TiO<sub>2</sub> surface needs to be tested. Figure 3 (red axis) shows that the amplitude of the asymmetric stretch remains relatively constant under the extreme visible laser intensities tested (40 and 70 mW, ~ 300 μm spot size); most SFG experiments were conducted at much lower visible intensities, typically ~20 mW. Interestingly, the ratio of the symmetric to asymmetric stretch (Figure 3, black axis) initially decreases significantly under illumination, but stabilises once it reaches unity, possibly indicating a photo-stimulated

change in orientation of the methanol species on the surface either due to the incident 800 nm light or through a thermal process. Experiments changing the incident angles and polarisation of the IR and vis could be used to further investigate this, providing information on the orientation of the adsorbed methanol on the surface.

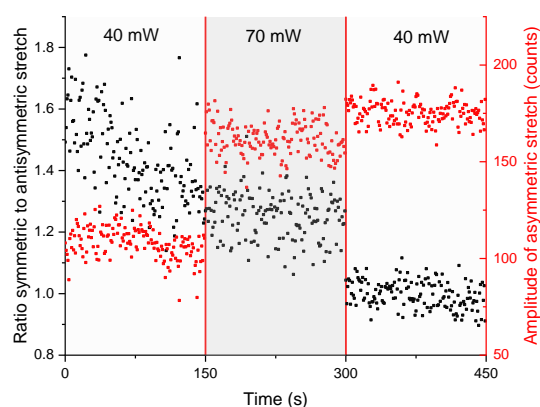


Figure 3: Change in ratio of symmetric (2846 cm<sup>-1</sup>) to antisymmetric stretch (2951 cm<sup>-1</sup>) of MeOH on TiO<sub>2</sub> surface over time. Red lines indicate a pause in the experiment to change the visible light intensity.

Methanol photolysis experiments were carried out by focusing a 355 nm LED through the front face of the electrode, while the IR and Vis were still incident through the back of the electrode. 450 nm longpass filters were placed before the spectrograph in an effort to remove residual UV light from entering the camera, however, a significant and randomly fluctuating baseline was present in spectra taken while the LED was on. Instead, spectra were recorded with the LED off, after 5 minutes of continuous illumination. Furthermore, experiments were conducted under a methanol atmosphere, so readsorption of bulk methanol on the timescale of the experiment (seconds) is possible and may have been suppressing any further changes occurring in the sum frequency spectrum. Despite this, Figure 4 shows a significant decrease in the intensity of both the symmetric and asymmetric stretches, in contrast to the minimal changes seen under the high visible laser power alone (Figure 3). This indicates that the methanol photolysis reaction is taking place and can be monitored *in situ* using IR-Vis SFG spectroscopy. Improvements in the experimental design are required to draw further conclusions, including the aforementioned polarisation and angular dependence studies. Replacing the LED with a fs visible pulse could also help in solving the problems with baseline rise, as well as allowing time-resolved experiments to be conducted.

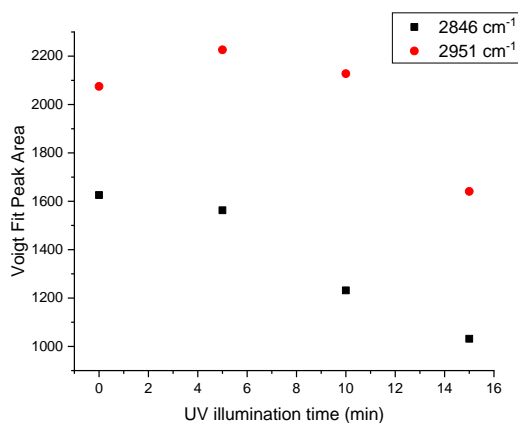


Figure 4: Change in peak area (Voigt fits) for the symmetric ( $2846\text{ cm}^{-1}$ ) and asymmetric ( $2951\text{ cm}^{-1}$ ) C-H stretches of methanol adsorbed on a  $\text{TiO}_2$  surface under 355 nm CW LED illumination

### Conclusions

This set of experiments demonstrate the application of IR-Vis SFG spectroscopy to the study of a transparent photocatalytic material under illumination. Combined with our previous experience of in situ electrochemical SFG spectroscopy, this study shows the feasibility of future in situ photoelectrochemical experiments, which is a promising area of research for the efficient generation of fuels from sunlight.

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