



**Experiment title:** In situ PDF studies on the formation and the local structures of amorphous or partially amorphous Ti-based catalysts for the photoelectrolysis of water.

**Experiment number:**  
MA-3641

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|---------------------------|---|--------------------------------------|
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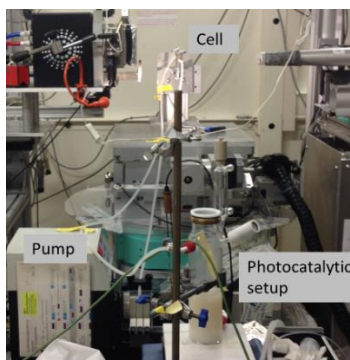
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**Report:**

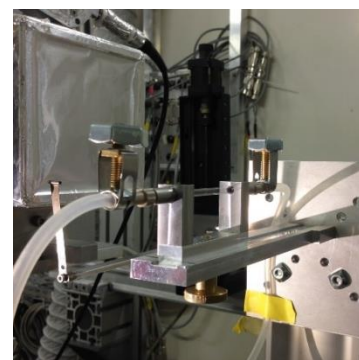
Ti-based photocatalysts have been used as water splitting materials since 1970's<sup>[1]</sup>. According to the recent research of our group, Ti and Ta based amorphous photocatalysts yielded better photocatalytic activity compared to the crystalline counterparts<sup>[2,3]</sup>. In order to understand the structural basis of the improved activity in amorphous materials, local structure analysis methods such as pair distribution function (PDF) analysis are required. For this purpose *in situ* scattering experiments using the photocatalytic setup used for catalytic testing were proposed to monitor the crystallization process in solution by *in situ* PDF analysis.

The photocatalysts were synthesized at room temperature in a photocatalytic cell using a method called 'direct injection' (Fig.1a). The photocatalytic cell is composed of two compartments. One compartment contains the UV source and the cooling parts. The other compartment is filled with a solution of water mixed with 10% methanol. Metal ethoxide is injected into this solution under UV illumination. Hydrogen and oxygen yields are measured during the formation of particles.

For the diffraction experiments the setup was put inside the hutch. The photocatalytic cell was attached to a borosilicate glass tube (100 mm long, 3.7 mm inner diameter with 0.05 mm wall thickness) where the X-ray beam will pass through the sample (Fig.1b.). A peristaltic pump was connected to circulate the solution between the vessel and the tube. The procedure started with the preparation of the solution mixture of 225 mL water and 25 mL methanol. Afterwards the different metal ethoxide precursors (Ti, Ta,



**Fig.1a.** The photocatalytic setup connected to the cell



**Fig.1b.** Borosilicate glass cell

Na/Ta mixed, Zr or Nb ethoxide) were injected to the prepared solution. Then the mixture was transferred to the photocatalytic cell. The photocatalytic cell was continuously stirred throughout the process. Before starting each measurement, the solution was purged with Ar for 20 min. Additionally, the UV lamp was cooled in order to keep the solution at room temperature. After each experiment the cell and all the components in contact with the solution were cleaned.

First the energy value was set to 87.4 keV corresponding to a wavelength of 0.14181 Å. Data analysis of the scattering experiments using Ti(OEt)<sub>4</sub> (injection volumes of 656 µL, 1.7, 3.4, 10.2 and 1.2 mL) and Ta(OEt)<sub>5</sub> (1.2 mL) precursors did not provide much structural information. It was decided to decrease the energy which could lead to less absorption and thus a better signal from the sample. Therefore, for the following experiments the energy was decreased from 87.4 keV to 69.7 keV corresponding to a wavelength of 0.17795 Å. Beam size was adjusted to 1 mm x 1 mm. The data were collected in the Q-range between 0.6 and 25.3 Å<sup>-1</sup>.

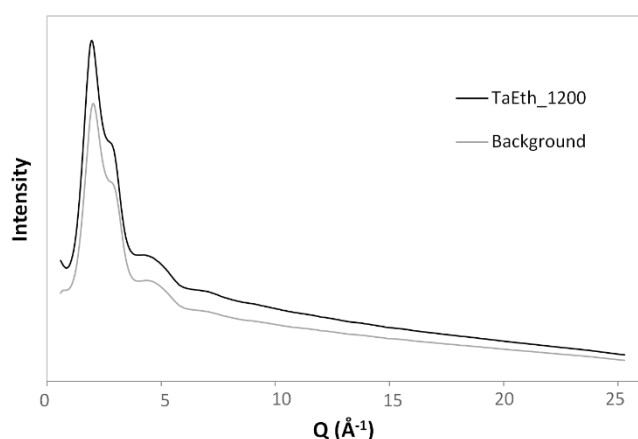
One measurement was carried out while only the water-methanol solution was flowing through the glass tube without any precursor injected. This measurement was used as background for the other measurements. The experiments started with the injection of 1.18 mL Ta(OEt)<sub>5</sub> as precursor. The diffraction patterns were collected first in the absence of UV light. After 1 h UV was turned on and data were collected for another 1 h. Afterwards all components of the photocatalytic setup and the glass tube were cleaned for the new experiment.

Experiments were continued with the Na/Ta mixtures. For this purpose 1.12 mL of Ta(OEt)<sub>5</sub> and 270 mg of NaOEt precursors were added separately to the water-methanol solution and then combined before injection. After 15 min of data collection, the UV light was turned on and data were collected under UV for 1 h.

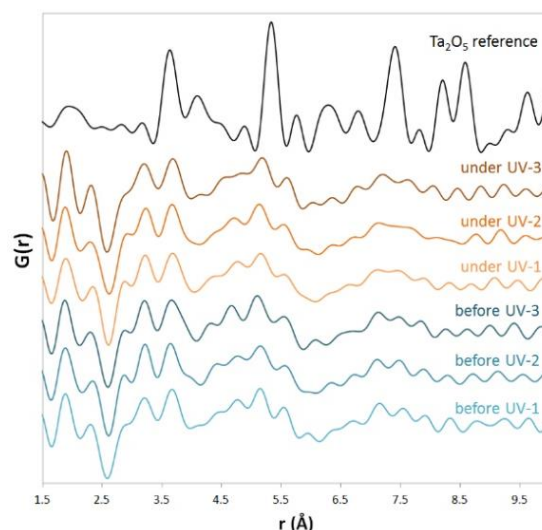
Experiments were continued with Nb(OEt)<sub>5</sub> as precursor. 1.89 mL of the precursor were injected and data were collected in the absence of UV light. The UV light was turned on for 1 h and then the cell was exposed to air for 15 min. Diffraction data were collected both during UV illumination and after exposure of the sample to air.

For the Zr system Zr(OEt)<sub>4</sub> was used as precursor. 1.014 mL of precursor were sonicated in a water-methanol solution before injecting it into the cell. Diffraction data were collected before and during UV irradiation.

As last experiment different amounts of Ti(OEt)<sub>4</sub> precursor, 0.656 and 2.63 mL, were injected in the water-methanol solution. The injection amounts were. For the first concentration the dilution was too high to obtain structural information. However, for the experiment with 2.63 mL of injected precursor data were collected before, during and after UV illumination.



**Fig. 2.** Intensities obtained from the measurement of the solution in the tube with (TaEth\_1200) and without the injected precursor (background).



**Fig.3.** dPDFs for *in situ* Ta(OEt)<sub>5</sub> experiments subtracting the PDF of flowing solution in the tube. Scans started before UV and continued under UV illumination (-# increases as proceeds) were compared to the reference Ta<sub>2</sub>O<sub>5</sub><sup>[5]</sup>.

The collected frames of each system were averaged in batches of 10 frames and then integrated separately. Then PDFs were generated using PDFgetX3<sup>[5]</sup> program. The program uses three input files to generate the PDF: the measured sample data, the background measurement and the configuration file which contains the parameters for the generation of the PDF data from the total scattering data. For the generation of the PDF data appropriate background treatment is most crucial. It should be mentioned that the solutions studied are highly diluted. In terms of catalytic purposes they may be considered as concentrated but with respect to diffraction experiments they are diluted. The intensities obtained for the blank solution and the solution containing the metal precursor are given in Fig. 2. The diffraction data are mainly determined by the scattering contribution of the water-methanol solution. The scattering differences obtained after background treatment are the basis for further PDF analysis. Therefore one of main issues encountered while generating PDFs is the choice of the correct background scale parameter.

As an example the PDFs generated from the Ta(OEt)<sub>5</sub> experiments are given in Fig.3. The generated PDFs were compared to the calculated PDF for Ta<sub>2</sub>O<sub>5</sub> structure. Even though the generated functions are very noisy, they show some similar features to Ta<sub>2</sub>O<sub>5</sub> structure. The peaks centred at 1.93 and 3.73 Å could be assigned to first Ta-O and the Ta-Ta distances respectively in the calculated PDF. The measured PDFs are generated using the differential pair distribution function (dPDF) method which is a method developed for diluted substances<sup>[6]</sup>. It should be mentioned that this method is highly sensitive to the chemical composition of the measured material. Therefore the compositions of the background and the background with samples were carefully calculated and inserted into the respective configuration files. The PDFs obtained for the water-methanol solution in the glass tube and the PDF of solution and sample were first generated separately and then subtracted.

The analysis of the obtained data continues with background treatment and generation of PDFs.

## References

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