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ESRF	**Experiment title:** Monitoring the photodeposition of Pt and Cu nanoparticles on TiO_2 for photocatalytic hydrogen production by operando XAS	**Experiment number**: CH-6630
Beamline: BM31	**Date of experiment**: from: 18.07.2023 to: 25.07.2023	**Date of report**: 25.09.2023
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Report:

The proposal was aimed on the understanding of the formation process and evolution of the local structure of Pt and Cu active sites in TiO_2 supported photocatalysts for hydrogen evolution reactions. This knowledge is important to highlight the role of different reaction components and reaction conditions on the catalytic performance. During the beamtime we have collected Pt L_3- and Cu *K*-edge X-ray absorption spectra in operando regime with simultaneous monitoring of the hydrogen production by mass spectroscopy.

The experiment at both Pt L_3- and Cu *K*-edges was performed in fluorescence mode with the collection of transmission signal to simultaneously measure Pt and Cu foils for energy alignment. The samples of TiO_2 powders with and without metals were prepared as inks and deposited on the windows of the self-made cell for photocatalytic studies (Figure 1). The cell was filled with deionized water with a small addition of a hole scavenger (formic acid or methanol) and continuously flushed by He. The outlet of the cell was connected to the mass spectrometer to monitor formation of hydrogen and carbon dioxide. The window with the catalyst was irradiated by UV-light and X-ray fluorescence signal was measured from the same side.

The first experimental procedure was the photodeposition of active metal on TiO_2 support. The metal precursors were dissolved in water and the window with TiO_2 later was irradiated by UV light. The irradiation times were set to 10 s, 30 s, 1 min, 5 min, 15 min, and 30 min, followed by XAS data collection with the light off. XANES spectra show a gradual reduction of metal.

In the case of platinum (Figure 2) it is reduced from Pt^{4+}, as in the precursor, to metallic Pt^0 state. This process was studied as a function of metal loading, type of hole scavenger and power of UV light.

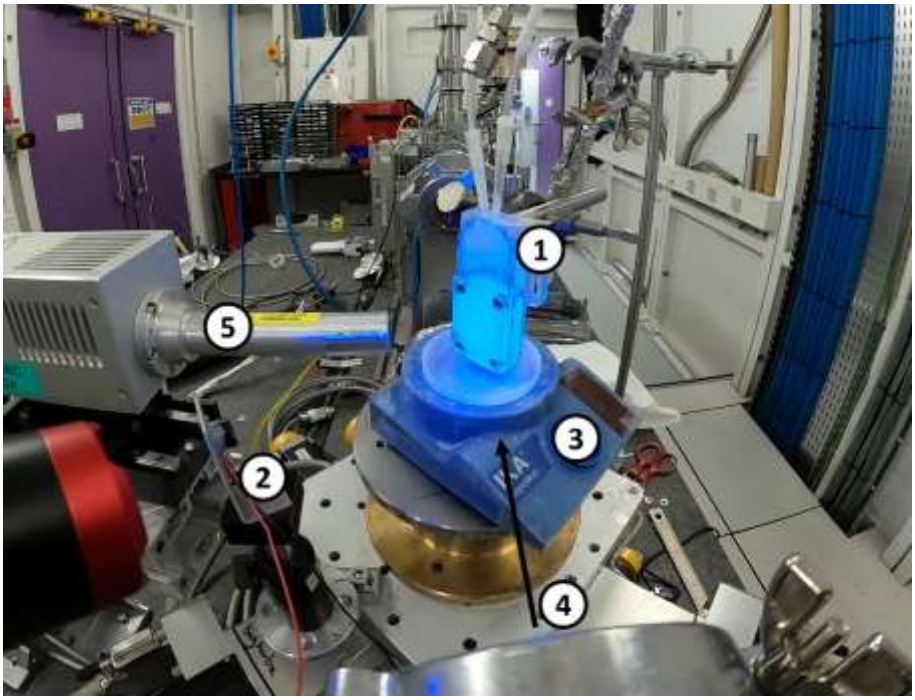

Figure 1. Experimental setup for operando photocatalytic studies. (1) Self-made photocatalytic cell, (2) UV light source, (3) magnetic stirrer, (4) incoming X-ray beam, (5) X-ray fluorescence detector

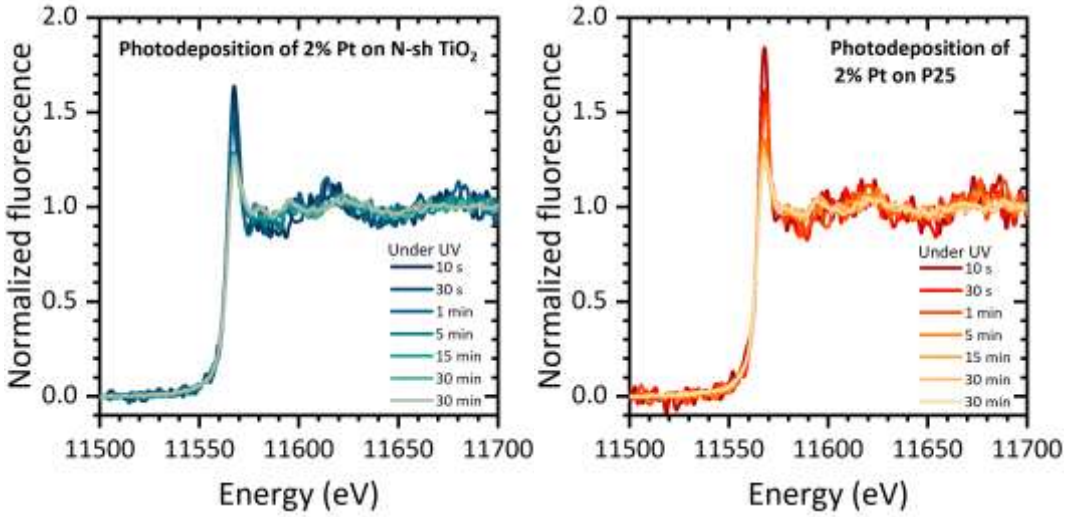

Figure 2. Evolution of XAS data upon photodeposition of the metal on different morphologies of TiO_2.

The second procedure was aimed to follow the process of hydrogen production on in situ made and pre-made catalyst. The premade catalysts were represented by both photo-deposited ones, and commercial Pt/TiO_2, synthesized using deposition-precipitation method. To highlight the differences, we periodically switched the light ON and OFF with continuous data collection. The evolution of H_2 signal is shown in **Figure 3**. The difference in XANES spectra are small but noticeable, especially for Cu K-edge (Figure 5). The average particle size was determined from EXAFS data for Pt species, being from 2.5 to 5 nm for different samples, which will be confirmed by TEM measurements planned for October 2023.

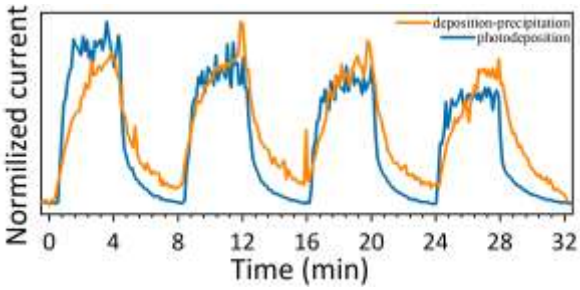

Figure 3. Mass spectroscopy data for hydrogen (m/Z = 2) normalized by the signal of helium (m/Z = 4) during hydrogen evolution experiment run over the samples made by photodeposition and deposition-precipitation techniques

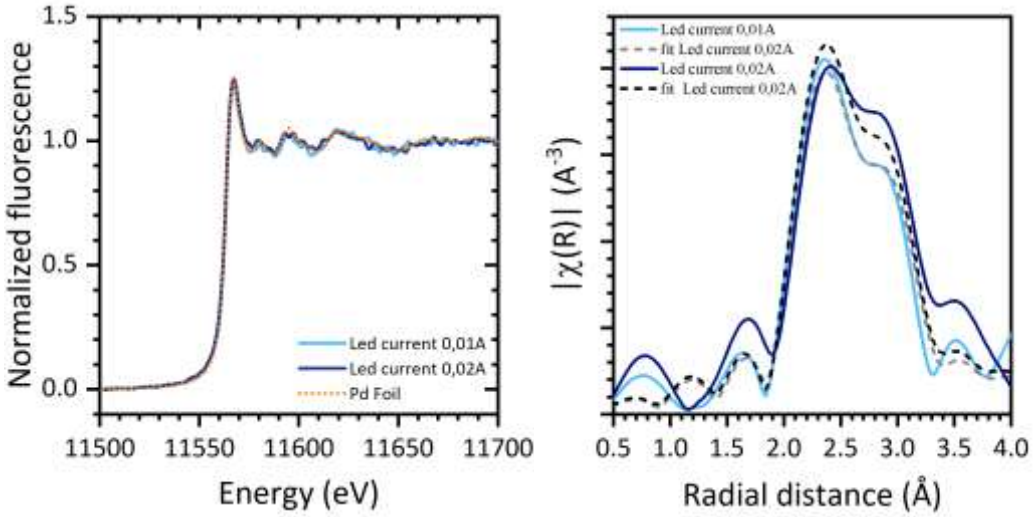

Figure 4. (a) XANES spectra after photodeposition of Pt on TiO_2 (a) with different current of LED UV in comparison with reference (dashed orange line). (b) Fourier-transformed EXAFS data of 2%Pt@TiO_2 with different current of LED UV activation

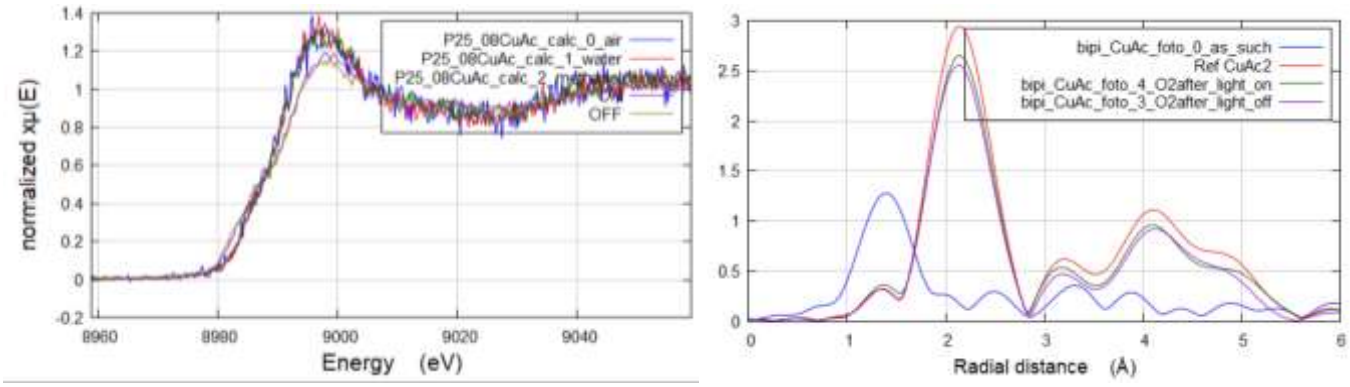

Figure 5. Cu *K*-edge XANES and EXAFS data at different statges of pre-treatment and photocatalytic reaction of Cu/TiO_2 sample.

In summary, we have successfully followed the photodeposition and photoreduction of Pt and Cu on TiO2-based photocatalyst for hydrogen evolution reactions by operando XAS. XANES spectra indicated the formation of metallic Pt and Cu species after photoreduction and during the catalytic reaction. EXAFS data will allow to estimate average particle size which will be correlated with the TEM measurements.