

Operando Laboratory X-ray Absorption Spectroscopy and UV-Vis Study of Pt/TiO₂ Photocatalyst During Photodeposition and Hydrogen Evolution Reaction

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1. Photocatalytic hydrogen evolution reaction (PHER)

Hydrogen production experiments were performed irradiating with UV light slurries containing 1.0 g·L⁻¹ of P25 TiO₂ powder of the materials and 2.0 mg·L⁻¹ of Pt photodeposited as Pt⁰ onto TiO₂ upon UV irradiation. The use of a co-catalyst increases the photogenerated carrier separation improving the kinetics of H₂O reduction, which would be very slow on the pristine TiO₂. The experiments were carried out at pH 3.7 using formate buffer 0.1 M. Formate acts also as hole scavenger. The irradiation experiments were carried out in magnetically stirred, cylindrical quartz cells containing 5 mL of slurry (therefore 5 mg of material). Before irradiation the cell containing the slurry was carefully purged with nitrogen to remove oxygen from the reaction environment. The removal of oxygen is fundamental in order to avoid the competitive oxygen reduction reaction. Hydrogen and CO₂ evolution was followed sampling periodically 2.5 mL of gas from the irradiation cell and replacing it with the same volume of N₂. The gas sample was analyzed with an Agilent 490 Micro GC gas chromatograph equipped with a Molsieve 5 Å column for H₂ analysis and a Poraplot U column for CO₂ quantitation. During the analysis the columns were kept at temperatures of 363 K and 313 K at a pressure of 200 kPa and 150 kPa, respectively. The carrier gases were argon and helium, respectively. The total amounts of H₂ and CO₂ produced as function of time were calculated from the concentration in the sampled gas, considering the total volume of gas in the irradiation cell and the previous samplings. The irradiation was carried out with a LED source centered at 365 nm with an irradiance of 40 W·m⁻². As highlighted in Figure S1, the H₂ photoproduction had a linear trend in a 60 min test. As expected, the evolution rate for H₂ and CO₂ is the nearly the same due to the stoichiometric ratio in the formic acid photoreformig reaction, the slight difference (~6%) falls well within experimental error of this kind of experiments.

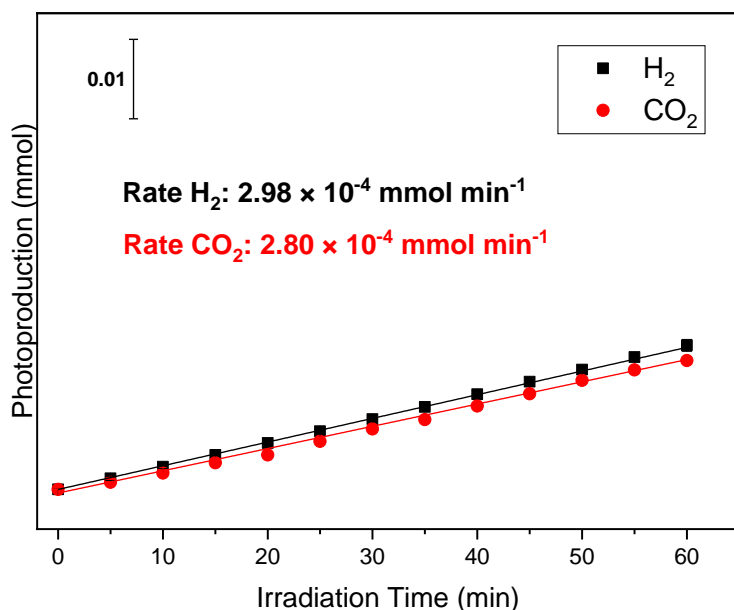


Figure S1. Formation of H₂ and CO₂ during PHER analyzed by GC.

2. Additional UV-Vis studies

To track the Pt photoreduction process in more detail we carried out an additional *in situ* UV-Vis experiments with better time-resolution (ca. 30 s per spectrum) without simultaneous XAS data collection. First, the photodeposition experiment was repeated with under similar experimental conditions as described in the main text, but to slow down the reduction of Pt⁴⁺ species and monitor a gradual decrease of the corresponding peak in the UV-Vis spectra, the Pt concentration was lowered by the factor of 5, and the UV lamp was placed at 0.3 m distance from the cell. The obtained results (Figure S2a) also demonstrate a rapid decrease of the Pt⁴⁺ signal already after 30 s of exposure (blue).

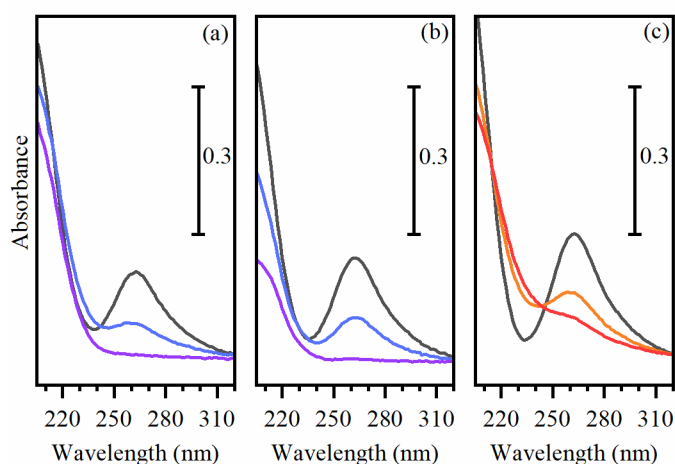


Figure S2. Evolution of UV-Vis spectra of the solution containing K₂PtCl₆ upon UV irradiation. The K₂PtCl₆ precursor was added to (a) a solution of water and formic acid (3:1) with TiO₂, (b) a solution of water and formic acid (3:1) without TiO₂, and (c) deionized water only. Initial states are shown by black lines, and the spectra taken after 30 s, 90 s, 5 min, and 15 min, are shown by blue, purple, orange, and red lines, respectively.

A second experiment was performed under similar conditions but omitting the addition of TiO₂. The results (Figure S2b) are very similar to those obtained in presence of TiO₂, indicating that the reduction of the K₂PtCl₆ precursor

occurred exclusively due to UV irradiation, and interaction with TiO₂ is not necessary at this stage. This finding also explained why the reduction of the Pt⁴⁺ precursor in solution, as monitored by UV-Vis spectroscopy, occurred before its deposition on TiO₂ as observed by XAS. However, we do not observe any evidence of the formation of Pt nanoparticles in the solution, which would give rise to a broad spectral feature in the UV-Vis spectra, arising from light scattering by the nanoparticles. Notably, although the reduction of Pt⁴⁺ was observed also in the absence of TiO₂, no signal of hydrogen production was observed for such sample. However, the CO₂ signal was observed in the beginning of the irradiation, indicating the oxidation of the formic acid (Figure S3).

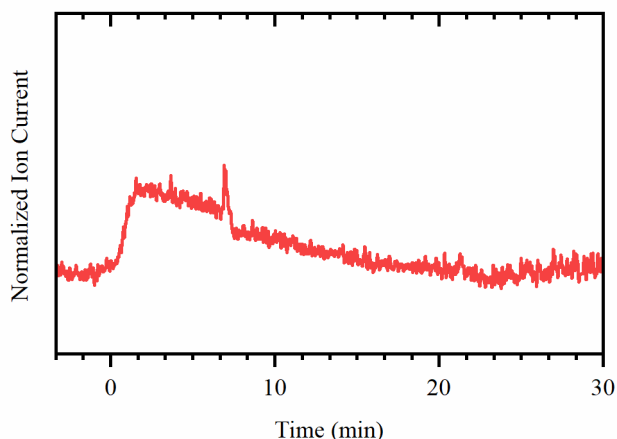


Figure S3. Normalized MS signal of $m/Z = 44$ recorded during the UV irradiation of K₂PtCl₆ dissolved in the solution of deionized water with formic acid (1:3) as in Figure 2d but without addition of TiO₂.

Finally, the third experiment was performed removing also the formic acid from the solution (i.e. only K₂PtCl₆ precursor in deionized water). The results shown in Figure S2c indicate that the reduction process was slowed down by an order of magnitude, which emphasizes the role of the hole scavenger in the photoreduction of Pt⁴⁺ to Pt⁰.

3. X-ray fluorescence (XRF) analysis

Pt content in TiO₂ after the photodeposition was determined by XRF spectroscopy on M4 Tornado spectrometer (Bruker, Billerica, MA, USA) with an XFlash 430 detector in the range from 0 to 25 keV. The signal was collected from 20 different points of the sample, and the averaged value together with the standard deviation were calculated. The wt.% of Pt was derived based on the fluorescence signal of platinum and titanium assuming that only Pt and TiO₂ are present in the samples. The solution of Pt precursor does not significantly penetrate to TiO₂ without UV irradiation, while after 1 h under UV, the samples with ca. 2 wt.% Pt were obtained (Table S1).

Table S1. Pt content from XRF elemental analysis.

Sample	Pt content, wt%
Without UV irradiation	0.39 ± 0.09
After 1 hour under UV	1.97 ± 0.47