ESRF	Experiment title: **In situ XAS study of the elaboration of core shell Cu_2O@Pt/TiO_2 for the valorisation of carbon dioxide by photocatalysis**	**Experiment number**: 20140298
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Report: The purpose of this study was to understand the mechanism of the reductive photodeposition of Cu(II) precursor on Pt/TiO2. Then, the analysis at both Pt LIII and Cu K edges of the formation of the interface between the noble metal and the Cu oxide during the reductive photodeposition is required to reach this objective. As mentioned above, the assistance of UV excitation appeared to be necessary to achieve a selective deposition of copper on Pt as well as the presence of a scavenger. Our objective is to study in situ the influence of these parameters (scavenger concentration and light power) in order to get a clear understanding of the local structure and oxidation state of deposited Cu oxide and the interface with surface Pt atoms. This can be achieved by using the recentlydeveloped in situ XAS cell combining an electrochemical cell and UV visible light excitation.

Results and the conclusions of the study :

Thanks to in-situ analysis of copper deposition on Pt/TiO_2, we studied the influence of different parameters.

First of all, the deposited copper nature was studied and reveals that majority of copper is deposited in metallic form. Cu(I) and Cu(II) seems to be intermediates. Putting the sample in oxygenic atmosphere leads to an oxidation process of Cu(0) into Cu(I) and Cu(II). When this new material is dispersed again in the solution, a part of the deposited copper (Cu(II)) is dissolved. This is an important observation for us to predict the behaviour of our catalysts during future catalytic tests. Inerting again the cell seems to stabilise deposited copper amount and irradiating again the sample reactivate the deposition process.

We also studied the influence of Pt on the copper deposition process by comparison with bare TiO_2. The results reveal that platinum has a beneficial impact on kinetic and nature of the copper deposition. On Pt/TiO_2, the deposition process is faster and leads to 53% of Cu(0), 45% of Cu(I) and only 2% of Cu(II). On bare TiO_2, Cu(II) is more present (23%), leading to less Cu(I) (13%) which is the future active specie. Moreover, in terms of dissolution process after material oxidation, the presence of platinum seems to stabilise copper deposition.

The ex-situ analysis of our materials lead us the selection of candidates for CO2 photocatalytic reduction test. By comparing this results with in-situ study, the major part of Cu(I), which is in oxide form Cu_2O, comes

from oxidation process of the catalysts surface after drying process. The following figure summarizes all the process.