ESRF	**Experiment title:** Time-resolved XAFS and XRD study on the mechanisms of photo-induced Pd nanoparticle formation in the presence of Mo	**Experiment number**: ME–1406
Beamline: BM26A	**Date of experiment**: from: July 27, 2016 to: July 30, 2016	**Date of report**: October 26, 2016
Shifts: 9	**Local contact(s)**: Dr. Dipanjan Banerjee	*Received at ESRF:*

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Report:

Separation of platinum group metals such as Ru, Rh, and Pd from high level radioactive liquid waste is important process in reducing overall amount of nuclear waste. In this regard, we are developing new technique which allows wet separation of these elements from acidic media. In this proposal we focused exclusively on Pd wet separation. Quick XANES and extended XAFS measurements were performed on the system Pd/Mo/EtOH/HNO_3 mixture under *in situ* UV light illumination. Predicted initial speciation of Pd and Mo are Pd^{2+} and $Mo_7O_{24}^{6-}$, respectively. Upon illumination, we visually observed formation of black particle which partially aggregated and eventually started to precipitate. The original idea of the experiments was to track Pd(II) reduction *via* XANES and a growing Pd–Pd peak *via* XAFS. The experiments were in principle successful although the samples could have better been otpmized in order to get much higher reaction efficiency and more drastic spectral change.

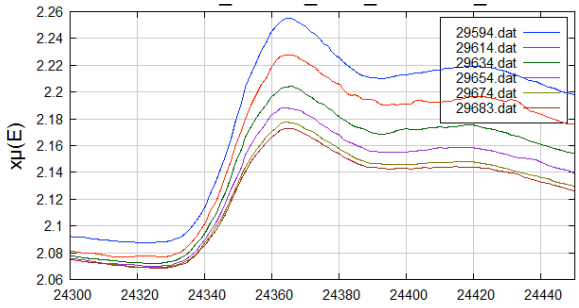

Fig.1 Stepwise XANES spectral change upon illumination of 4 mM Pd^{2+}/2 mM $Mo_7O_{24}^{6-}$/25 % EtOH/0.5 M HNO_3 mixture (blue: 1st scan, brown: 90th)

XANES spectral change upon illumination is given in **Fig.1**. Upon illumination there is slight shift of Pd edge presumably due to Pd(II) to Pd(0) reduction. Detailed analysis of the spectra shows two–step reaction taking place although origin of this is unclear at the moment. These spectra change do not occur in the absense of $Mo_7O_{24}^{6-}$ or ethanol. Our initial interpretation was that Pd(II) is reduced to Pd(0) upon illumination and ethanol acts as electron donor whereas $Mo_7O_{24}^{6-}$ plays only catalytic role.

In order to get deeper insights into this, we analyzed XAFS spectra of the sample before and after illumination. Both Pd and Mo K–edges were analyzed and Pd XAFS spectra are given in **Fig.2**. Upon illumination there is slight decrease of the Pd–O peak (at the distance of ~1.5 Å without phase correction) and increasing Pd–Pd peak (~2.4 Å without phase correction). Meanwhile there was no spectral change at all in Mo XAFS spectra (figure not shown). Taking together with data of Fig.1, there is photoreduction of Pd(II) to Pd(0) which result in formation of elemental Pd nano particle. Ethanol acts as electron donor and is consumed by the reaction whereas $Mo_7O_{24}^{6-}$ plays only catalytic role and remains basically intact. Our initial hypothesis on reaction schemes was proved to be positive through the measurements. However, upon starting of illumination, the solution instantly turned dark and intransparent which hampered further light penetration and the overall reaction efficiency remained small. Our initial idea to observe particle growth turned out to be difficult.

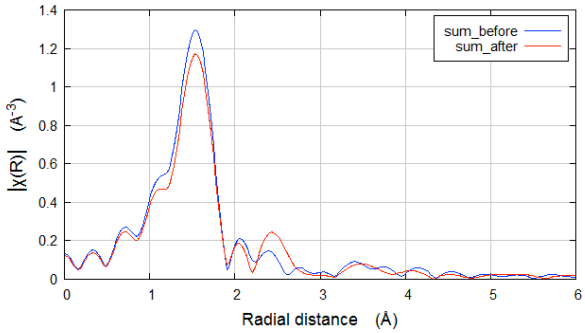

Fig.2 Pd K–edge EXAFS spectra of non-illuminated (blue) and illuminated (red) 4 mM Pd/ 1 mM $Mo_7O_{24}^{6-}$/5 % EtOH/0.5 M HNO_3 mixture

We were therefore led to change our strategy to focus on the measurements of precipitate. The illuminated solution was filtered through a membrane of 500 nm pore size and the collected black particles were analyzed by Pd K–edge XAFS spectra measurements. In **Fig.3**, we show four different XAFS spectra; solution before illumination (green), solution after illumination (purple), recovered precipitate (blue), and reference Pd foil (red). Comparison of these four spectra clearly show evolution of Pd–Pd peak upon illumination. The peak becomes more apparent in the precipitate and shows distinct features of that of Pd foil. Formation of elemental and metalic nanoparticle of Pd was confirmed.

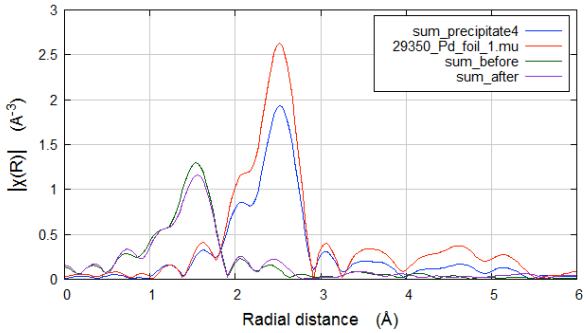

Fig.3 Pd K–edge EXAFS spectra of illuminated (purple) and non-illuminated (green) solution and that of the precipitate (blue). The spectra of Pd foil (red) is shown for reference.