Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


## Supporting information:

# TiO2-supported Pt single atoms by surface organometallic chemistry for photocatalytic hydrogen evolution

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**Supplementary figures:**

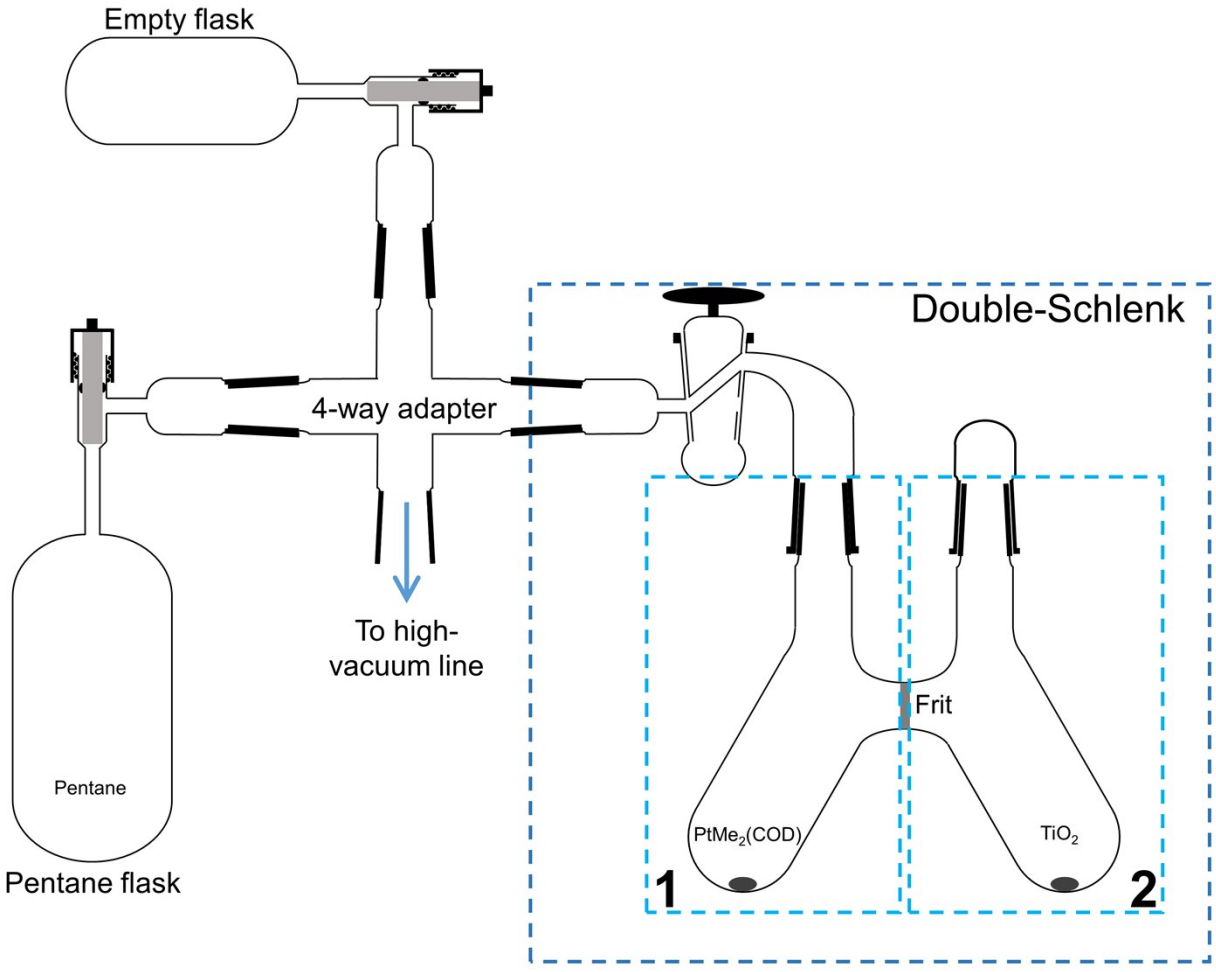



**Fig. S1** Setup used for grafting reactions

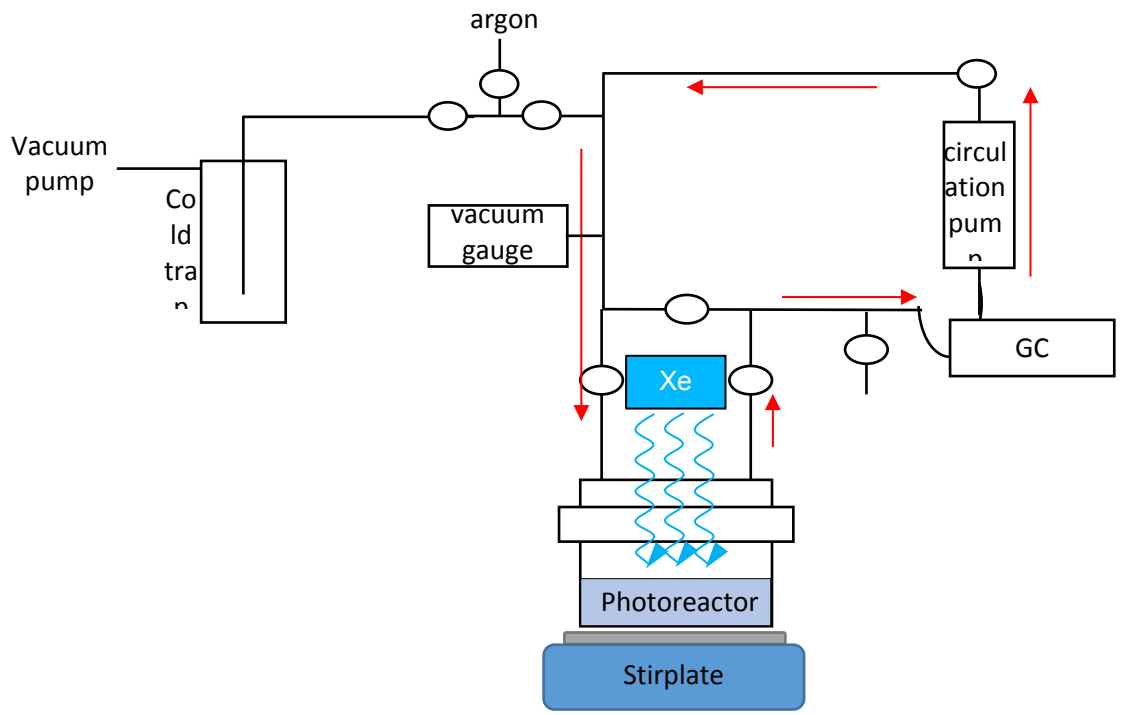



**Fig. S2** Photocatalysis setup

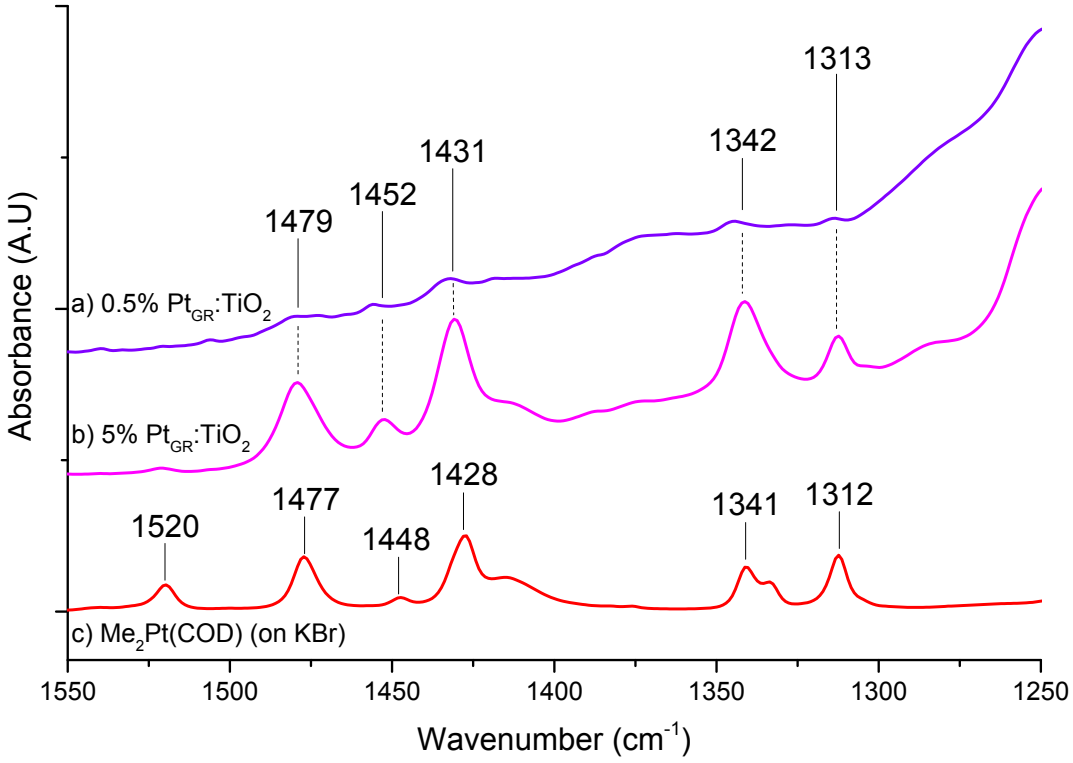



**Fig. S3** Infrared spectroscopy (DRIFTS) of a) 0.5%Pt$_{GR}$:TiO$_2$ ; b) 5% Pt$_{GR}$:TiO$_2$ ; c) Me$_2$Pt(COD) on KBr.

| Material | Band positions | | | | |
|---|---|---|---|---|---|
| $Pt_{GR}$:$TiO_2$ (this work) | 1479 | 1452 | 1431 | 1342 | 1313 |
| $Me_2Pt(COD)$ (this work) | 1477 | 1448 | 1428 | 1341 | 1313 |
| $Cl_2Pt(COD)$ | 1479[1], 1476[2] | 1446,[3] 1451[2] | 1432[1], 1427[3], 1426[2] | 1339[1,3], 1340[2] | 1310[1], 1312[3] |
| 1,5-cyclooctadiene | **1487[4,5], 1483[3]** | 1448[5], 1447[4], 1443[3] | 1426[5], 1425[4], 1423[3] | **1357[5], 1356[4], 1352[3]** | **1320[5], 1321[4]** |

**Table S1** Comparative table of the infrared absorption bands of the grafted materials, Pt(COD) complexes ($Me_2Pt(COD)$ ; $Cl_2Pt(COD)$) and "free" 1,5-cyclooctadiene.

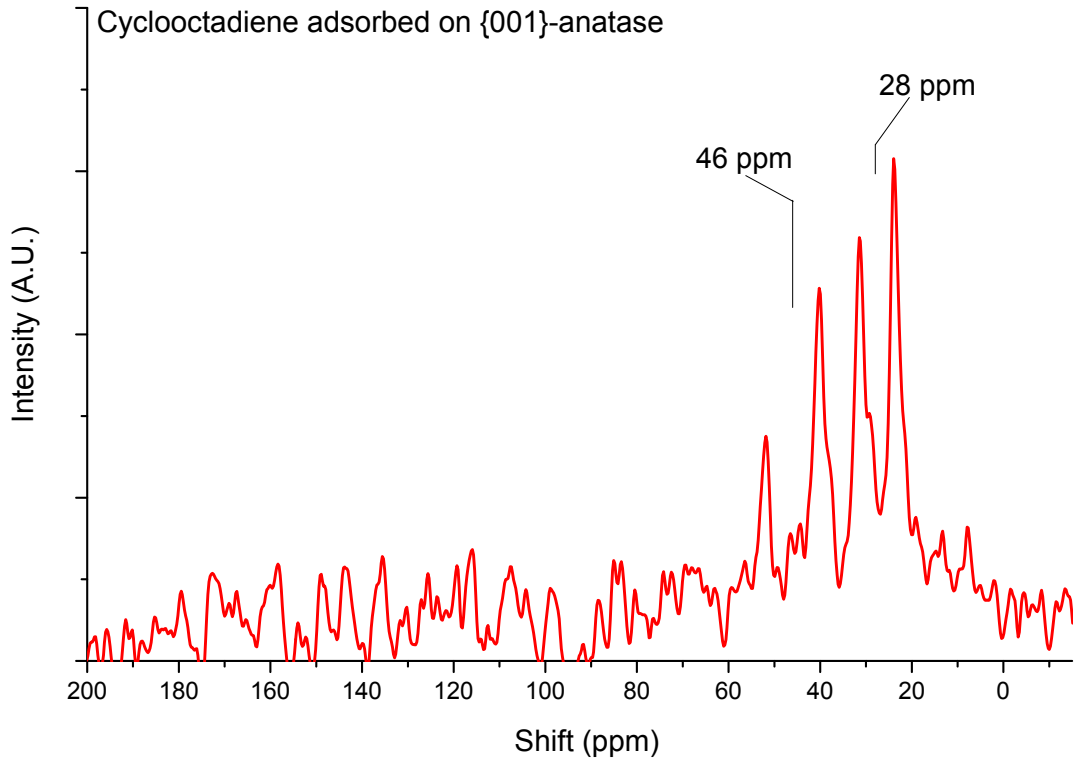



**Fig. S4** $^{13}C$ MAS SSNMR spectrum of cyclooctadiene adsorbed on {001}-anatase

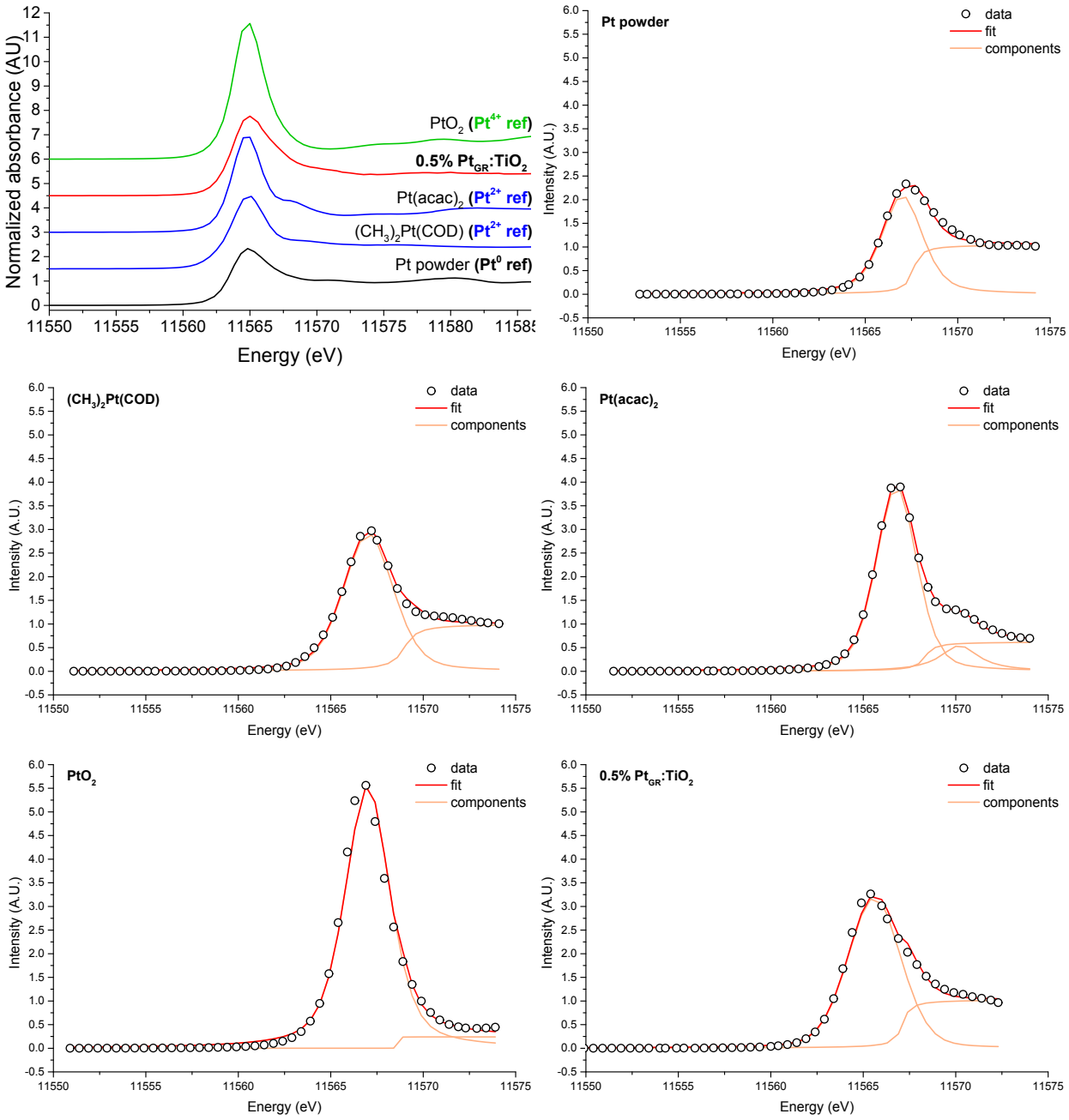



**Fig. S5** HERFD-XANES absorption spectra and fits using a pseudo-voigt function for the whiteline and arctangent function for the step. An additional lorentzian peak had to be included in the fitting model of the $Pt(acac)_2$ sample.

| Sample: | Oxidation number: | White line pseudo- | R-factor: | $\chi^2/v$: |
|---|---|---|---|---|

| | | Voigt area (arbitrary units): | | |
|---|---|---|---|---|
| Pt powder **(ref.)** | 0 | 7.1 | 0.002 | 0.004 |
| $(CH_3)_2$Pt(COD) **(ref.)** | +2 | 11.3 | 0.002 | 0.005 |
| Pt(acac)$_2$ **(ref.)** | +2 | 12.2 | 0.001 | 0.02 |
| $PtO_2$ **(ref.)** | +4 | 20.9 | 0.009 | 0.03 |
| 0.5% $Pt_{GR}$:$TiO_2$ | | 12.5 | 0.003 | 0.01 |

**Table S2** fitting results of Pt-$L_3$ edge HERFD–XANES of 0.5% Pt:{001}-anatase, along with four Pt references

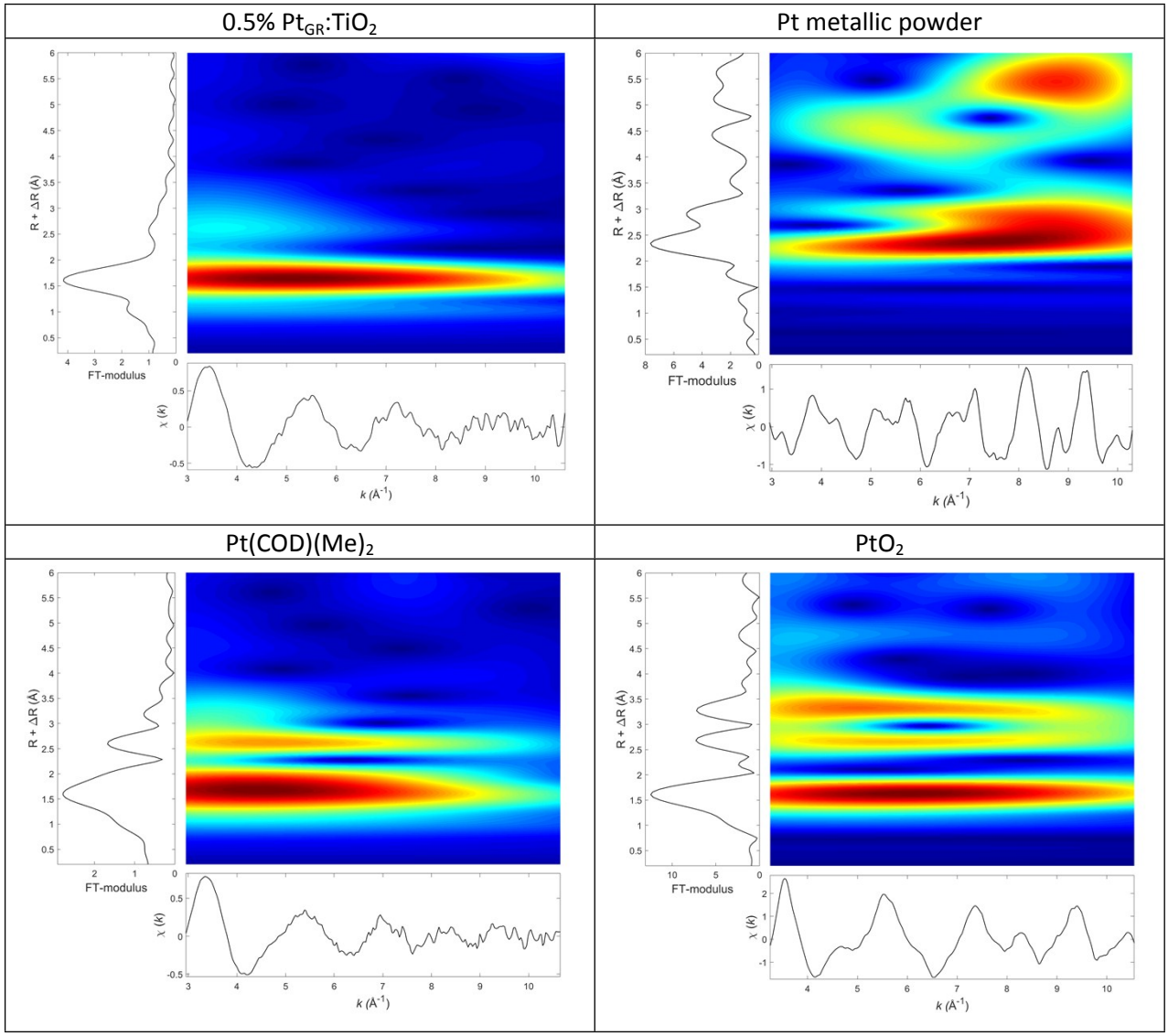
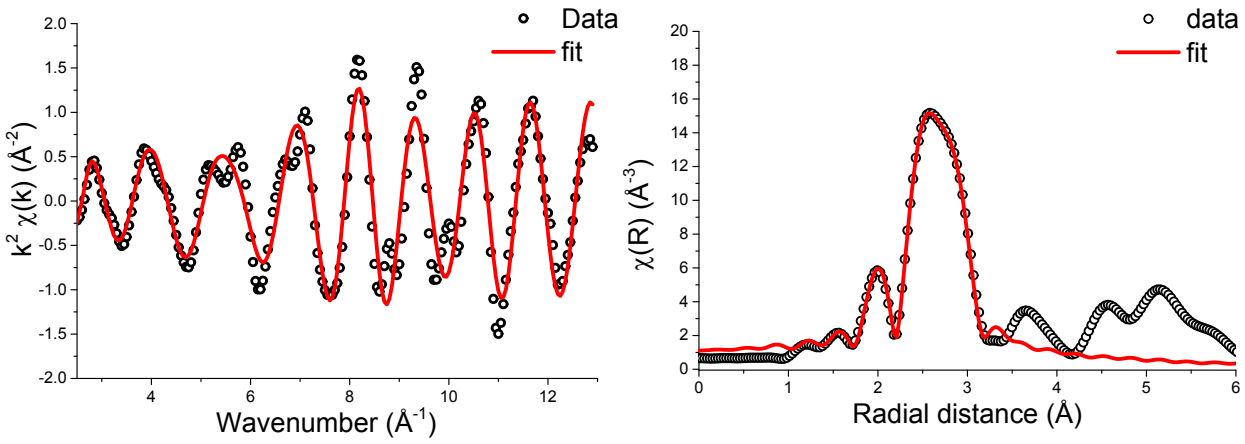



**Fig. S6** Contour plots of the wavelet transform magnitude showing the (k,R) localization of each FT-EXAFS contribution measured at the Pt $L_3$-edge for 0.5%$Pt_{GR}$:$TiO_2$, Pt metallic powder, Pt(COD)$(Me)_2$, and $PtO_2$




| Scatter | Coordination number | $S_0^2$ | R (Å) | $\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) |
|---|---|---|---|---|---|
| **Pt-Pt** | 12 (defined) | 0.77 ±0.04 | 2.763 ±0.002 | 0.0042 ±0.0003 | 7.6 ± 0.4 |

**Fig. S7** Platinum foil EXAFS fitting using only the first Pt-Pt scattering path to determine the amplitude reduction factor ($S_0^2$). k-range = 2.8 – 12 ; dk=1 ; R-range = 1.373 – 3.415 ; $\chi^2/\nu$ = 234.12 ; R-factor = 0.42 %

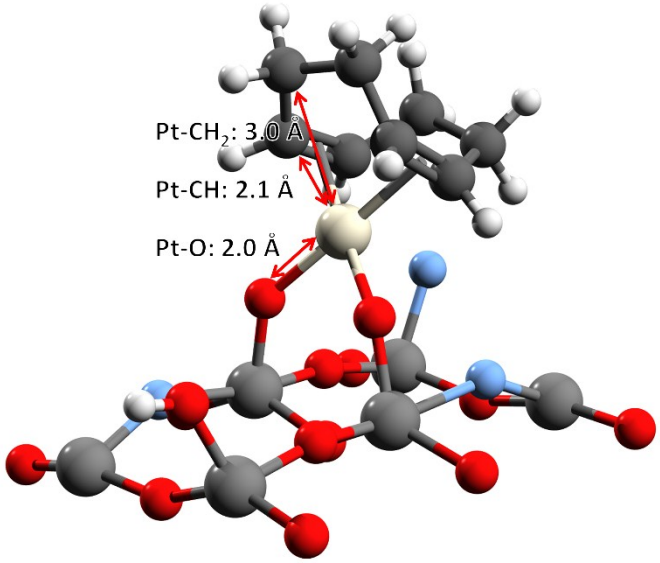



**Figure S8** O-Pt-O DFT-optimized structure

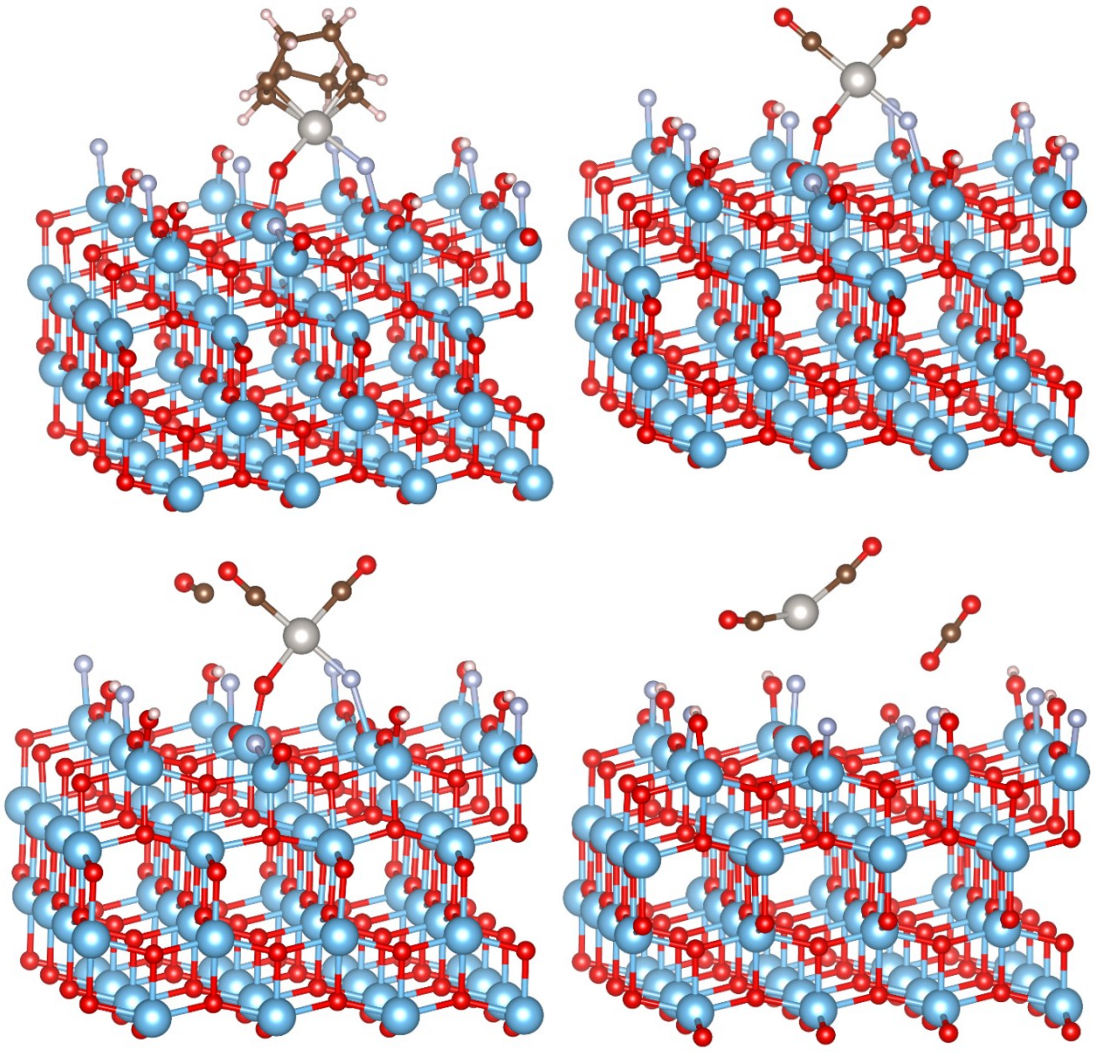


**Fig. S9** Complete DFT-optimized structures for the Pt reduction by CO reaction with the Ti-O-Pt(COD)-F-Ti structure.

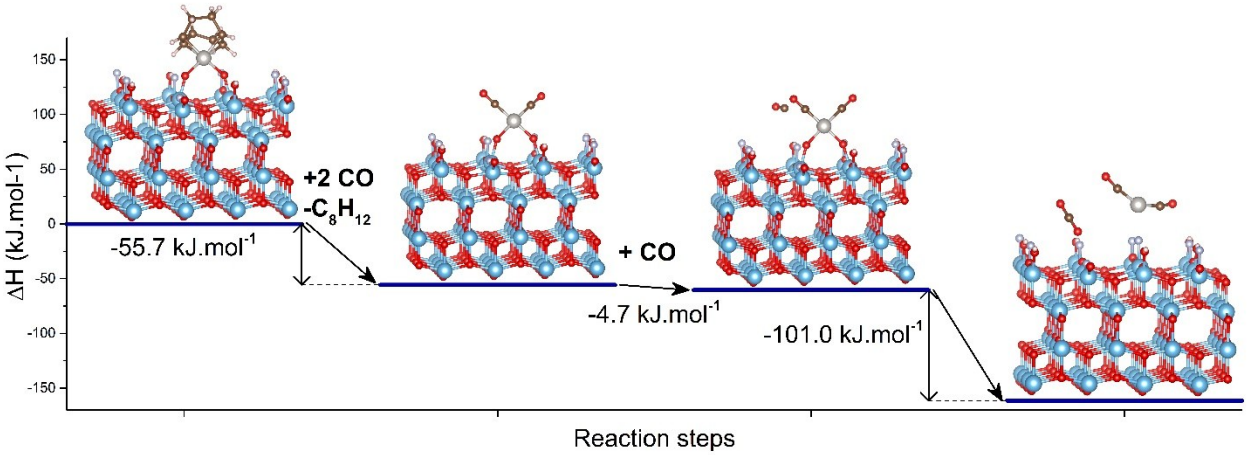



**Fig. S10** Proposed mechanism for Pt reduction by CO for the Ti-O-Pt(COD)-O-Ti structure

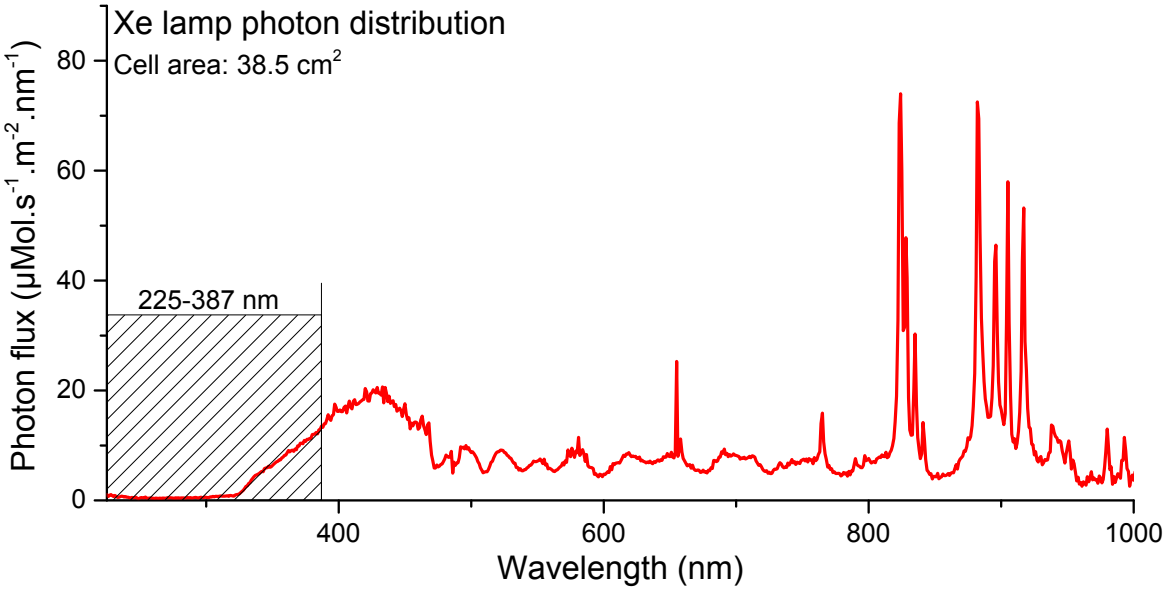



**Figure S11** Xenon lamp photon distribution.

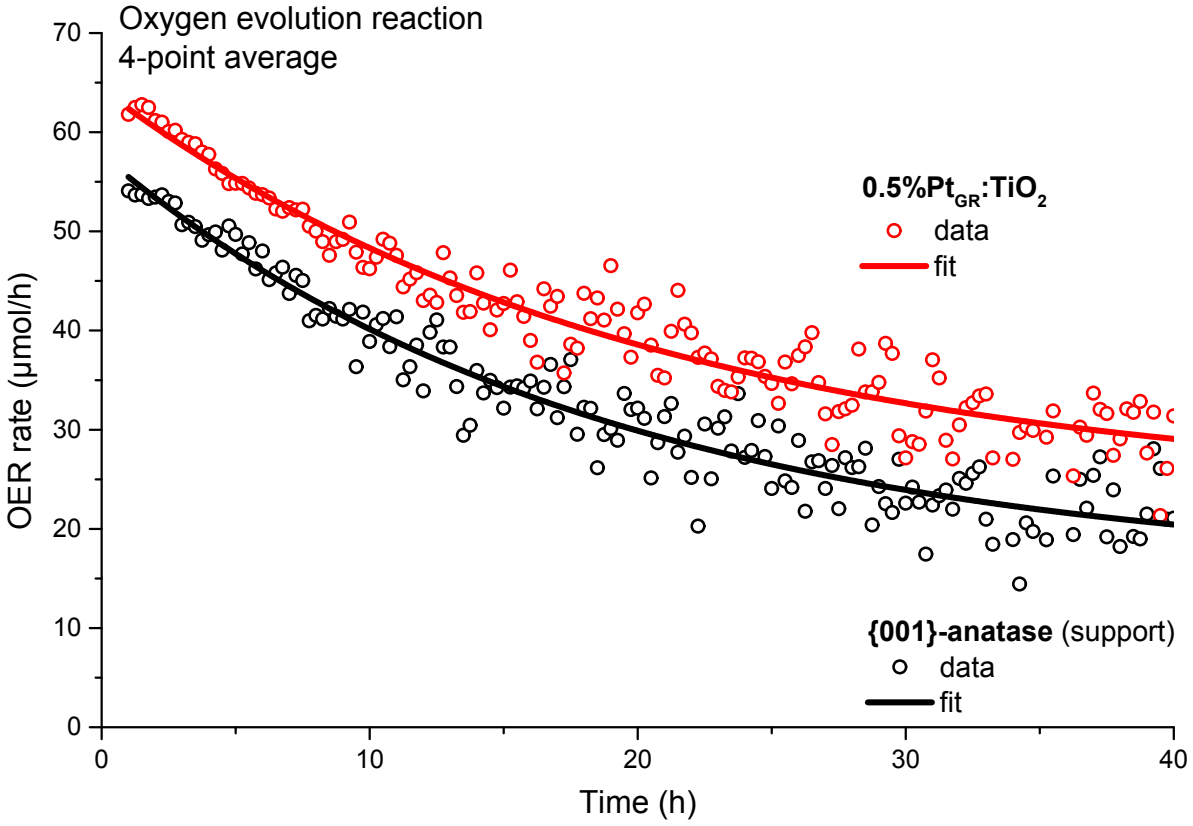



**Fig. S12** OER activity and exponential decay fits of {001}-anatase and 0.5%$Pt_{GR}$:$TiO_2$. First 30 minutes excluded due to gas mixing kinetics in the reactor

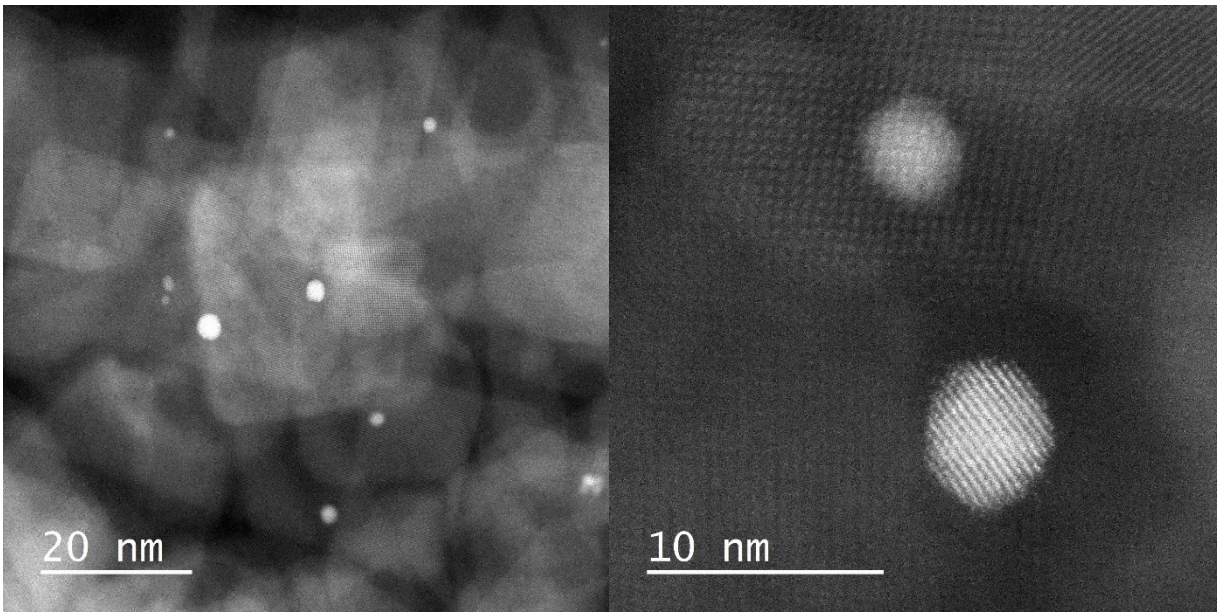



**Fig. S13** TEM micrographs of 0.5%$Pt_{GR}$:$TiO_2$ after photocatalysis with sacrificial methanol. Only nanoparticles are visible

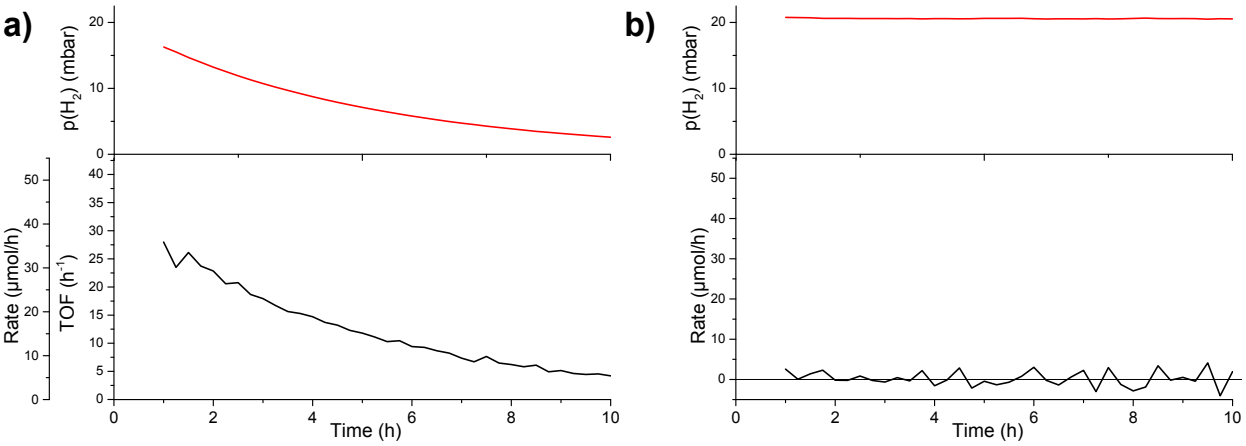



**Fig. S14** Backwards reaction rates measured on: a) impregnated 0.5%$Pt_{NP}$:$TiO_2$ and b) support blank ({001}-anatase) showing no noticeable activity.

**Bibliography:**

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