*Supporting Information*

# Visible light Photo-oxidation of Model Pollutants Using $CaCu_3Ti_4O_{12}$: An Experimental and Theoretical Study of Optical Properties, Electronic Structure and properties, electronic structure and selectivity

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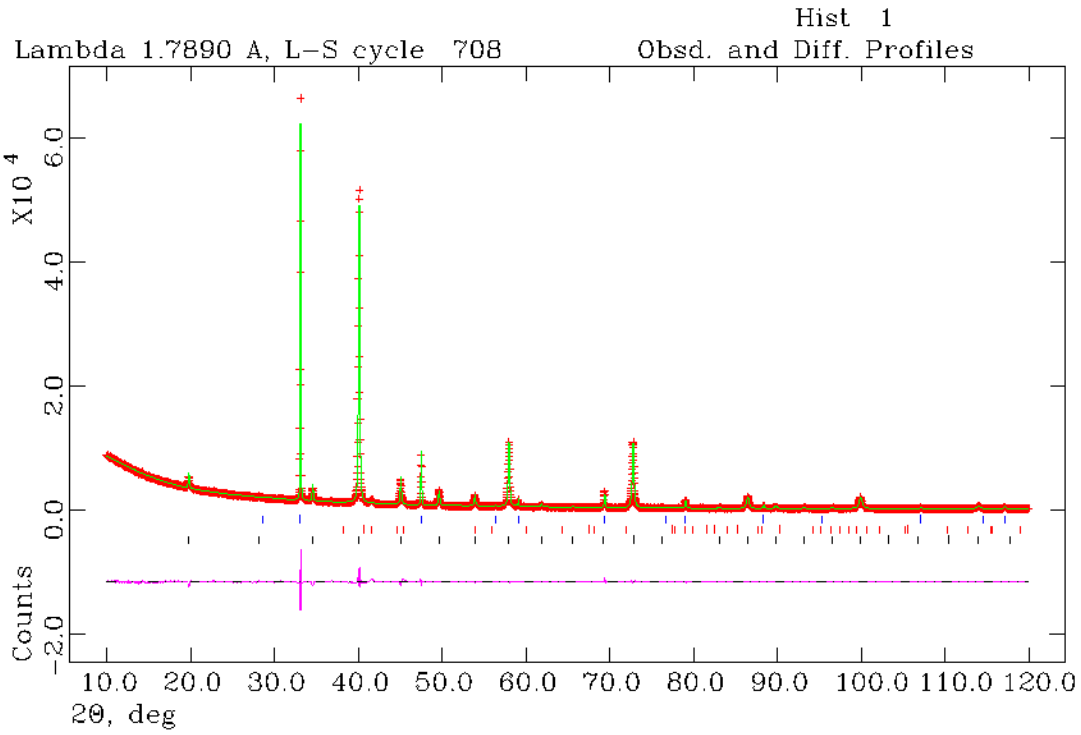


**Figure S1. Observed, calculated and difference plots for the 3 phase structural refinement of sol-gel derived $CaCu_3Ti_4O_{12}$ (OA 1:1:1) with CuO impurity (estimated at <2% of sample) and KCl as an internal standard. Im $\bar{3}$ *a*=7.39463Å. Final goodness-of-fit parameters: Rp=2.86%, wRp=4.50%, $\chi^2$=3.186.**

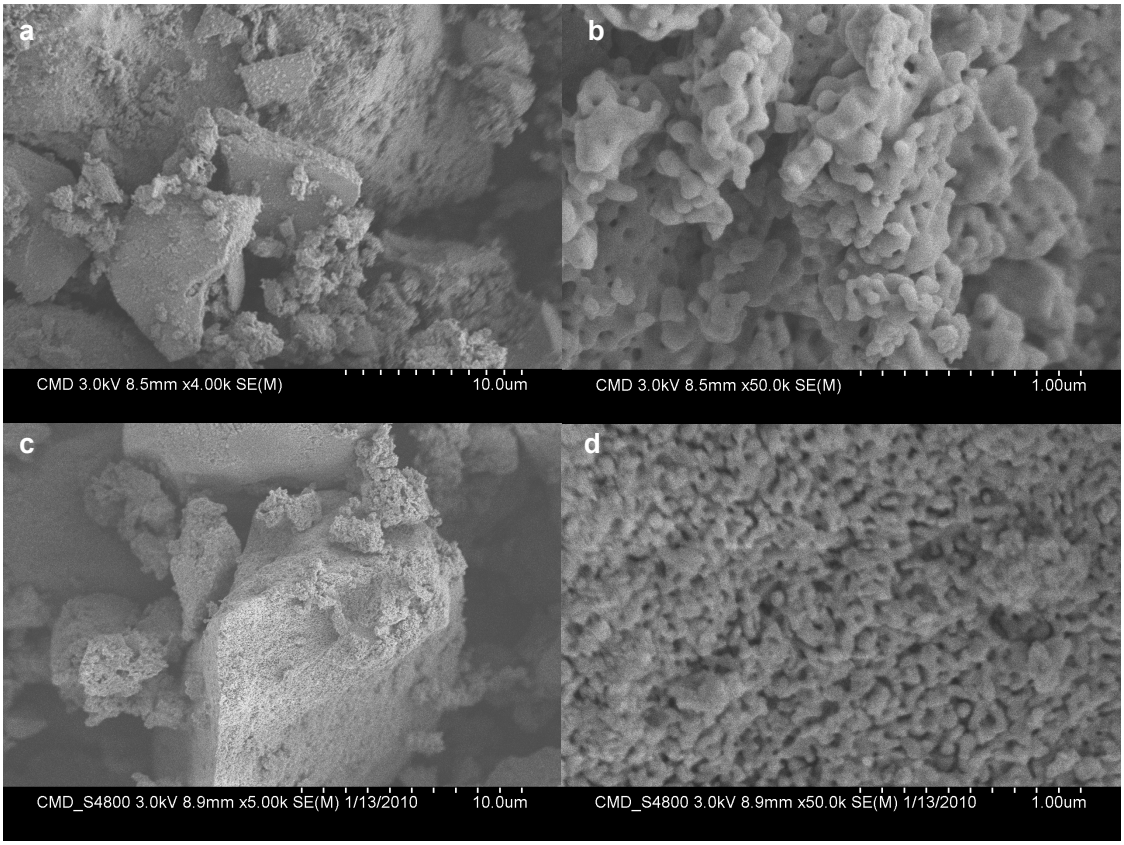


**Figure S2. SEM images of Pt-$CaCu_3Ti_4O_{12}$ (OA 1:1:1, pH1) before (a and b) and after (c and d) testing for activity toward photo-oxidation of MO**

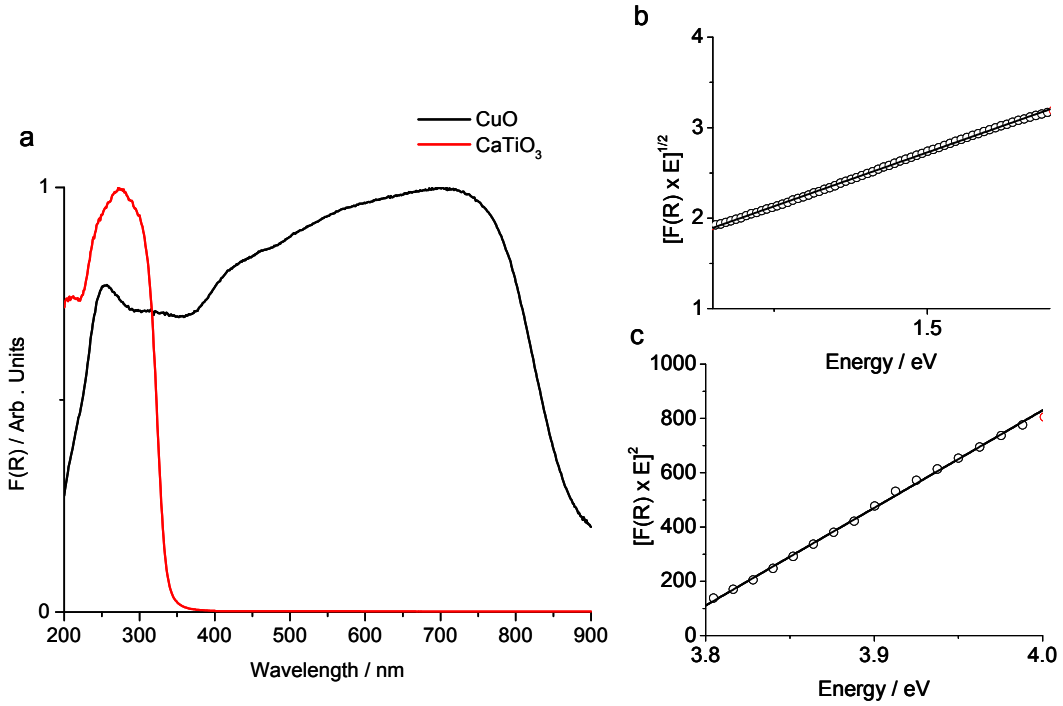


**Figure S3. Diffuse reflectance spectra of CuO and $CaTiO_3$, and linear fittings of absorption edges of b) CuO to an indirect transition of 1.27eV and c) $CaTiO_3$ to a direct transition of 3.76eV.**

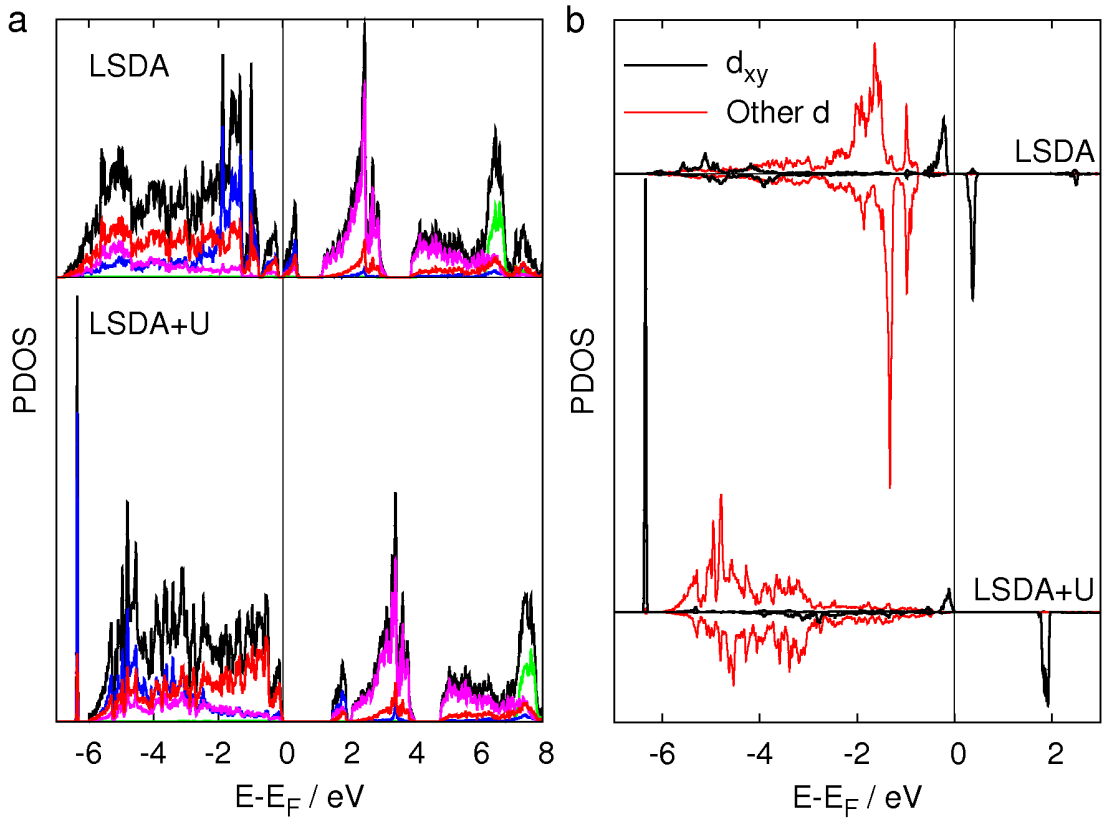


**Figure S4.a) Total and partial density of states (PDOS) calculated using LSDA and LSDA+U. The PDOS is projected onto the Ca, Cu, Ti and O atoms. b) PDOS projected onto the $d_{xy}$ orbital and the sum of the remaining $d_{xz}$, $d_{yz}$, $d_{z^2}$ and $d_{x^2-y^2}$ orbitals of the Cu atom coordinated to O atoms in the xy plane.**

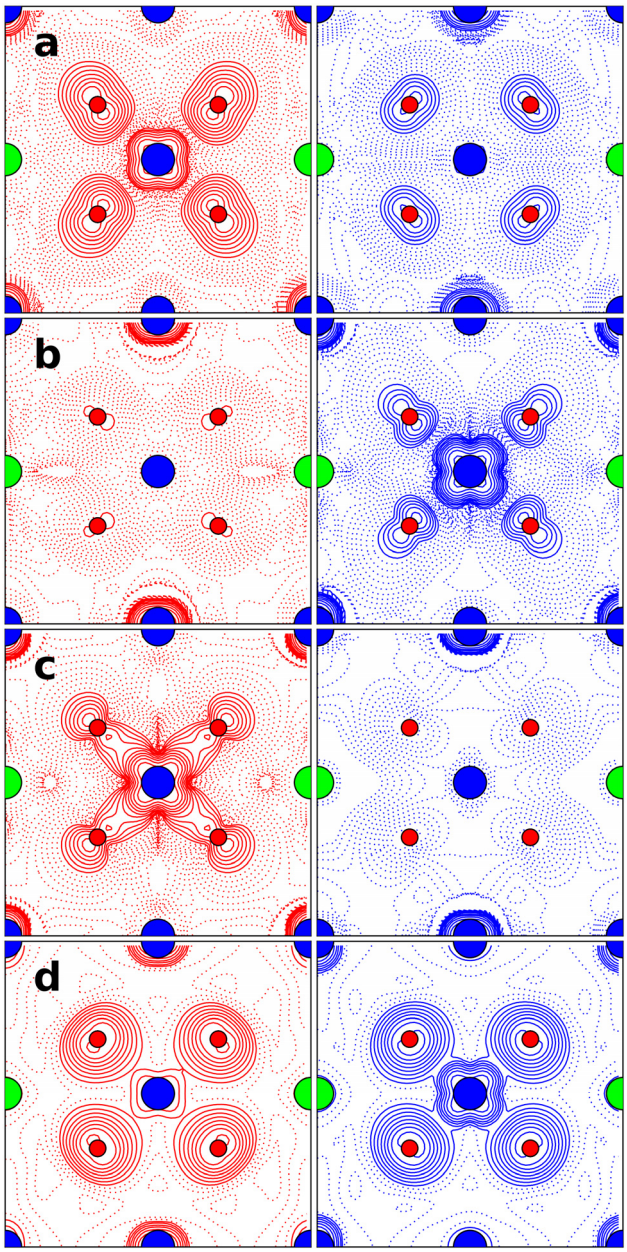


**Figure S5. Spin-up (left, red) and spin-down(right, blue) electron densities of a) the three occupied states at the top of the valence band and b) the three unoccupied states forming the narrow band above the valence band which are out-of-phase combinations of Cu 3d and O 2p orbitals, c) the three occupied states just below the valence band which are in-phase combinations of Cu 3d and O 2p orbitals, d) the conduction band showing the unoccupied in-phase combinations of Cu 3d and O 2p orbitals. Densities are plotted in the z = 0 plane with logarithmic contours. Contours below an**

**arbitrary threshold are shown dashed. The positions of the calcium (green), copper (blue) and oxygen (red) atoms are included in the plots.**

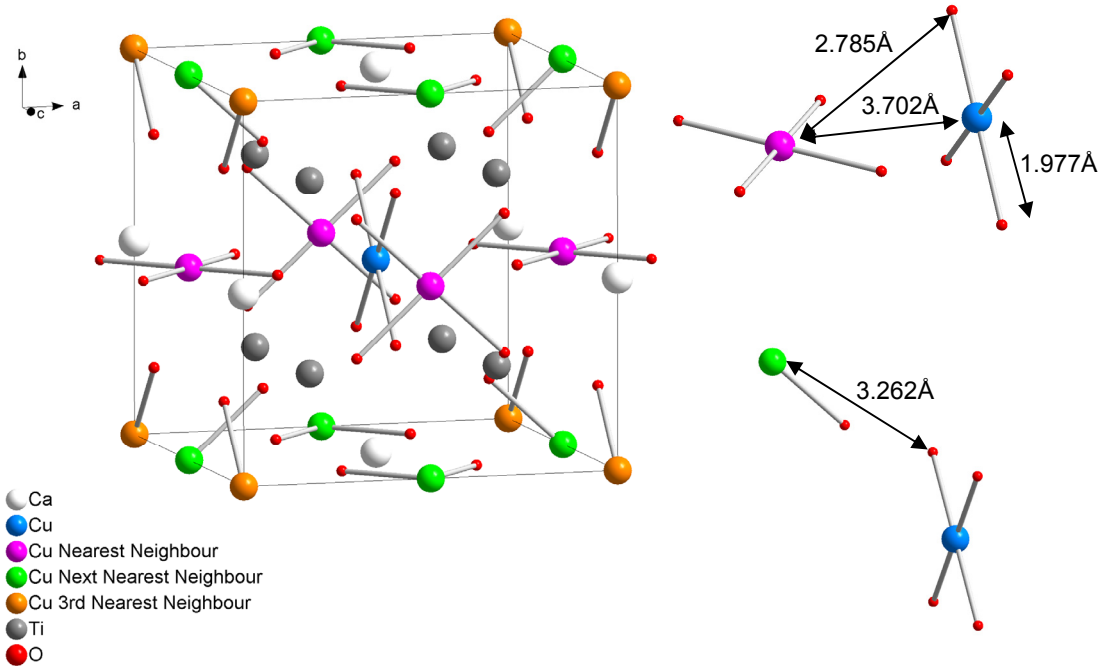


**Figure S6. Unit cell structure of $CaCu_3Ti_4O_{12}$ (left) and highlighted distances (right) showing coordination and isolation of $CuO_4$ units**

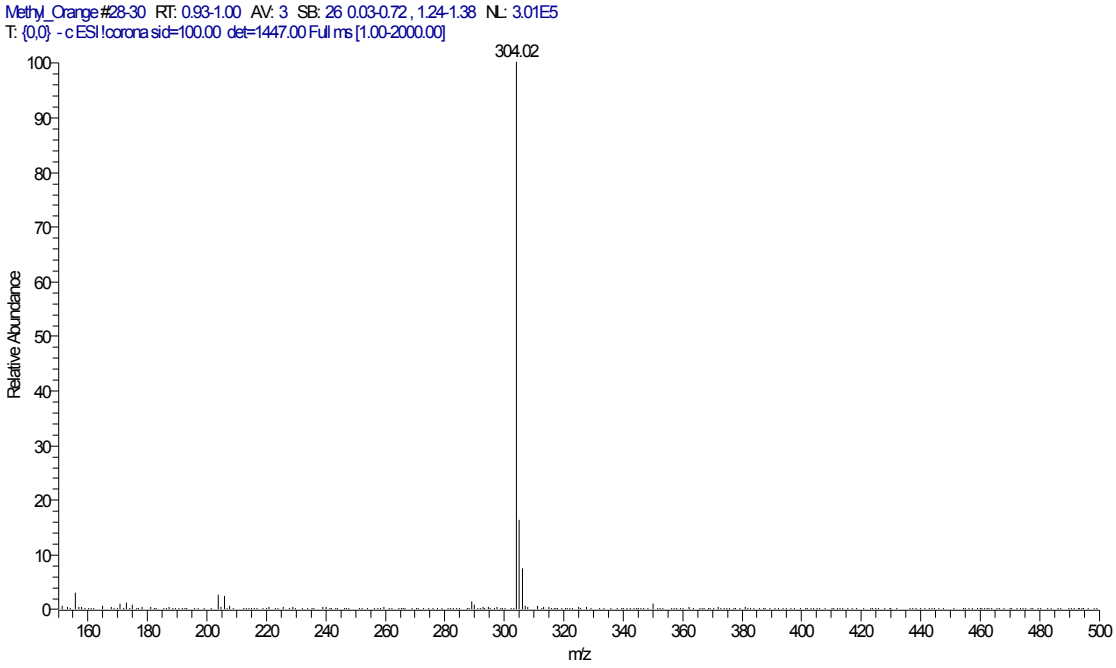


**Figure S7. MS data from MO in water.**

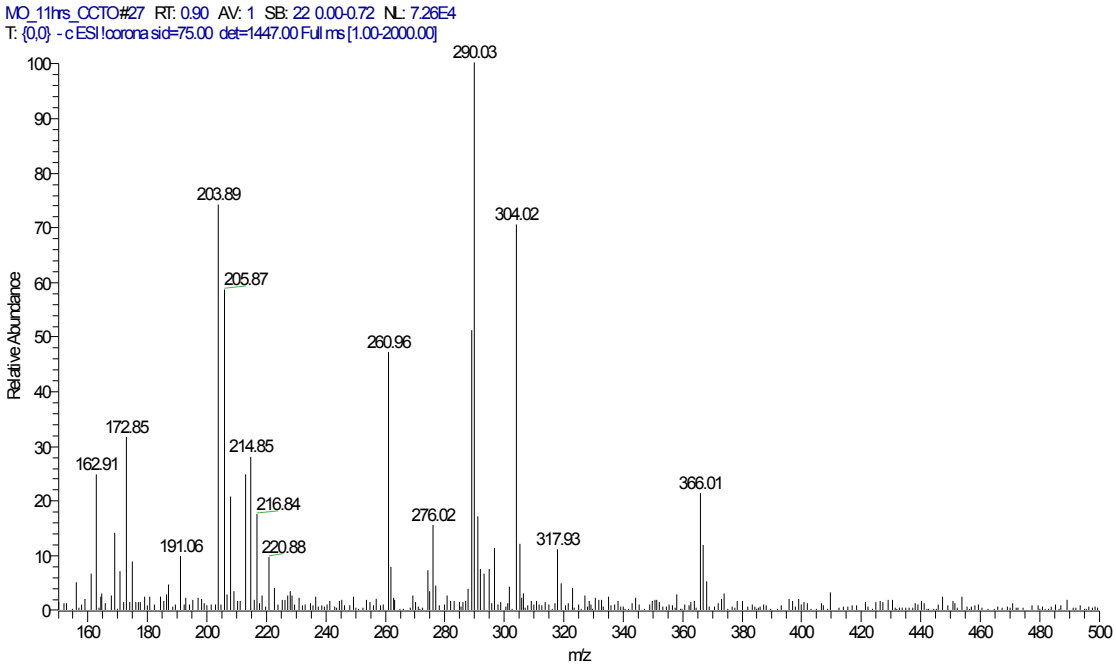


**Figure S8. MS data from MO after 11hrs under visible light irradiation in the presence of Pt-$CaCu_3Ti_4O_{12}$.**

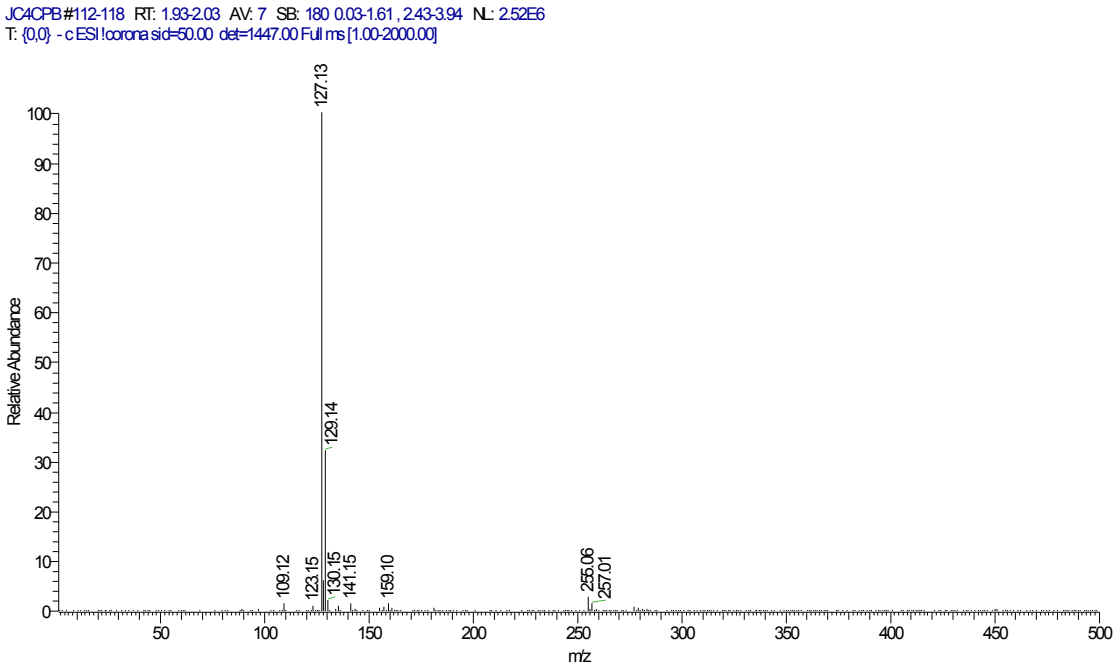


**Figure S9. MS data from 4CP in water.**

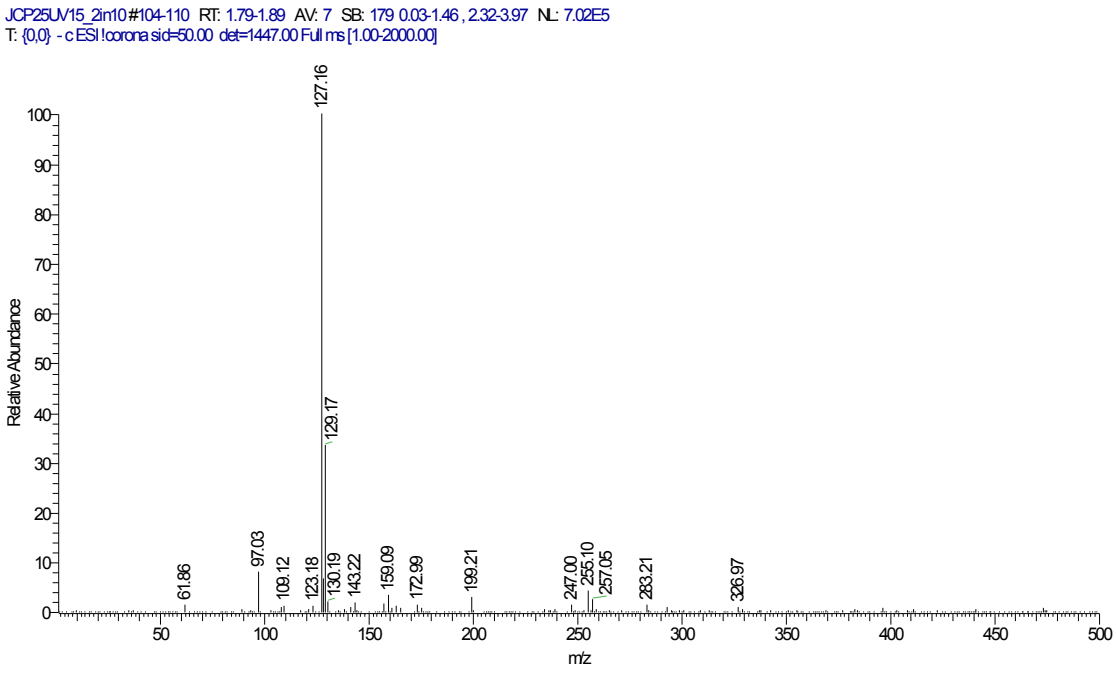


**Figure S10. MS data from 4CP after 15mins under UV light irradiation in the presence of P25.**

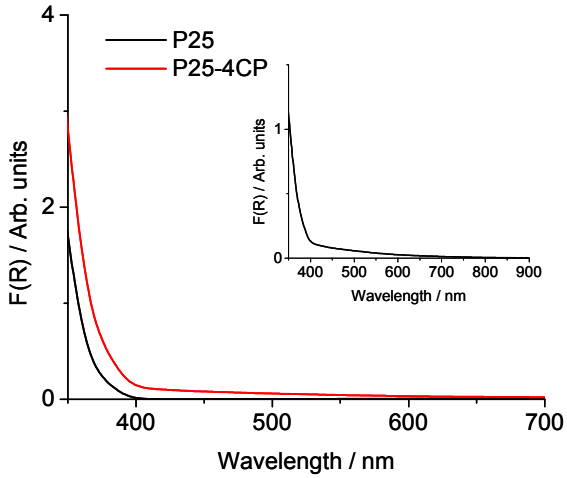


**Figure S11. Diffuse reflectance spectra of $TiO_2$ before and after visible light irradiation in the presence of 4CP, showing visible light absorption orginating from 4CP-Ti charge transfer surface complex. Inset shows difference diffuse reflectance spectrum.**

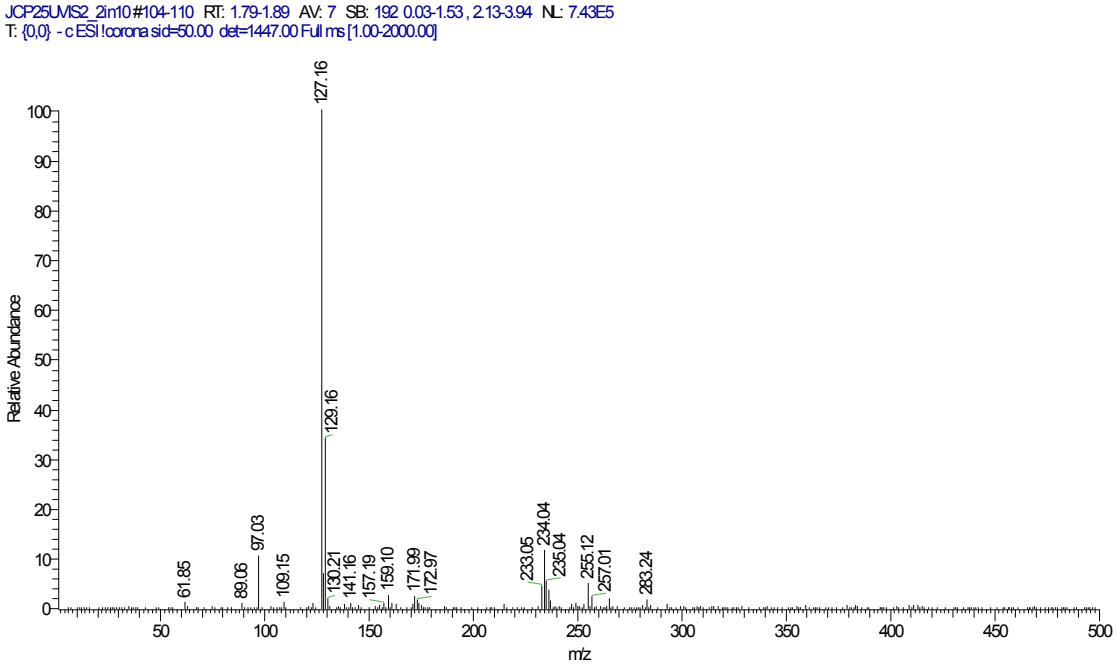

**Figure S12. MS data from 4CP after 2hrs under visible light irradiation in the presence of P25.**

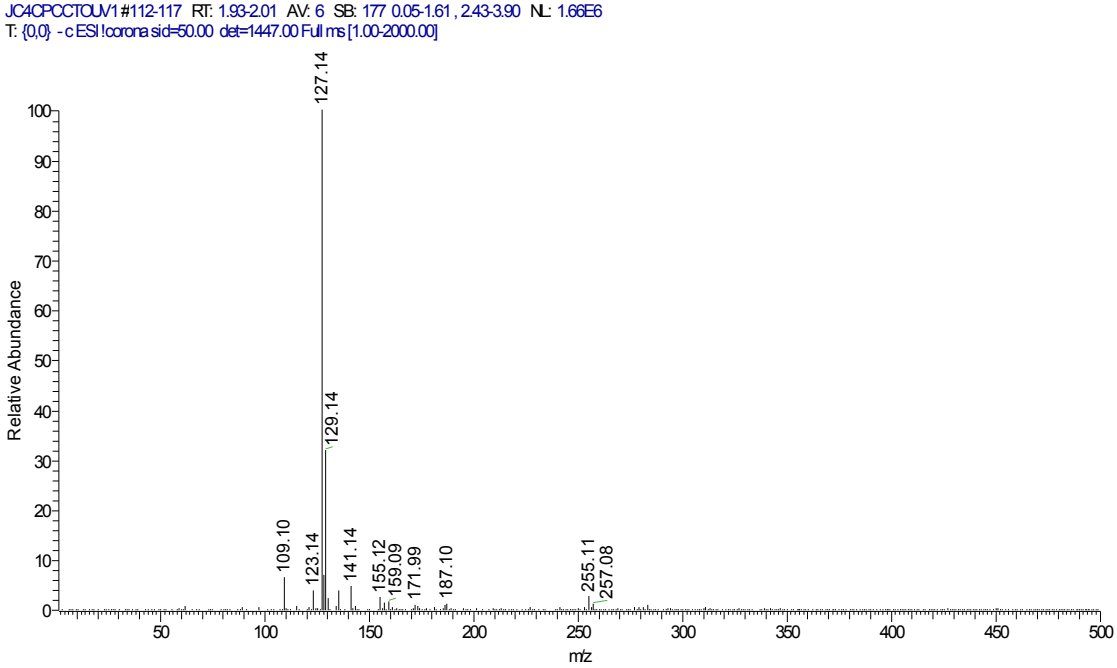


**Figure S13. MS data from 4CP after 1hr UV light irradiation in the presence of Pt-$CaCu_3Ti_4O_{12}$.**

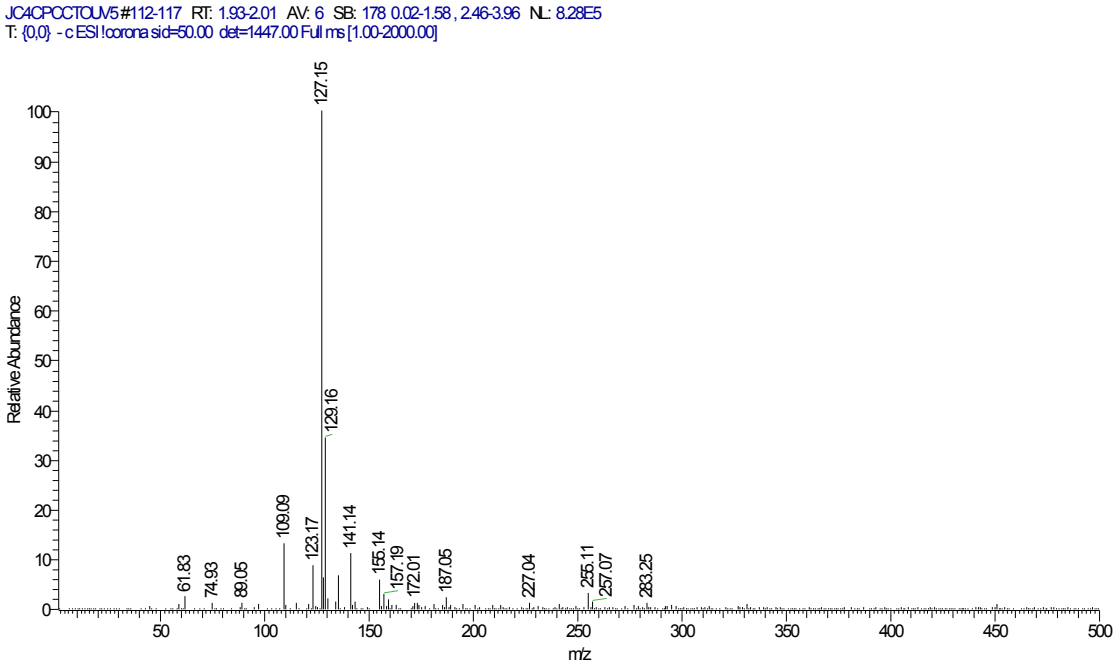


**Figure S14. MS data from 4CP after 5hrs UV light irradiation in the presence of Pt-$CaCu_3Ti_4O_{12}$.**

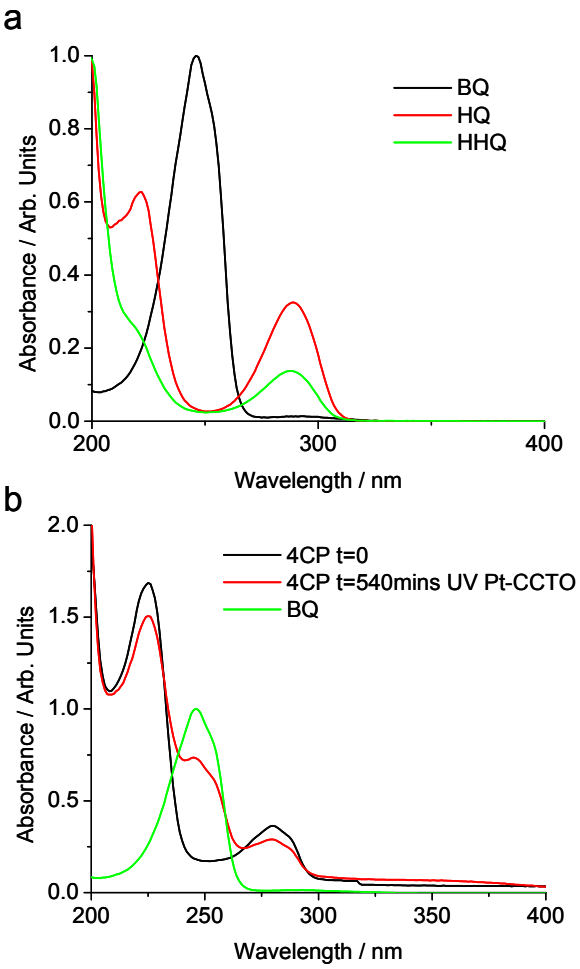


**Figure S15. a) UV/Vis absorbance spectra of some key intermediates in the photo-oxidation of 4CP under UV light; b) comparison between the spectra of BQ and 4CP that has been photo-oxidised in the presence of Pt-$CaCu_3Ti_4O_{12}$.**

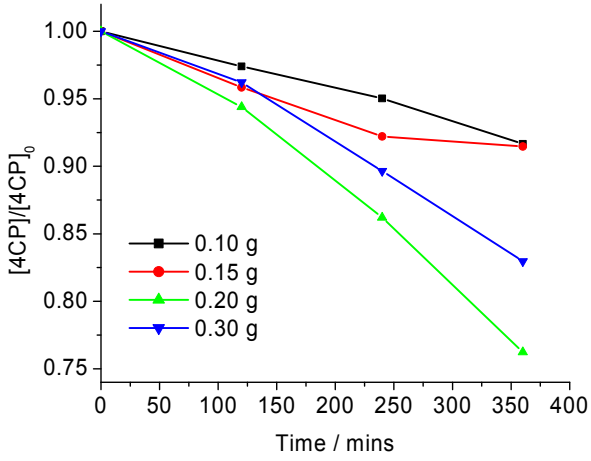


**Figure S16. Normalized change in [4CP] with respect to time for 4CP+Pt-$CaCu_3Ti_4O_{12}$+visible light ($\lambda$ > 420nm) with different amounts of catalyst present.**

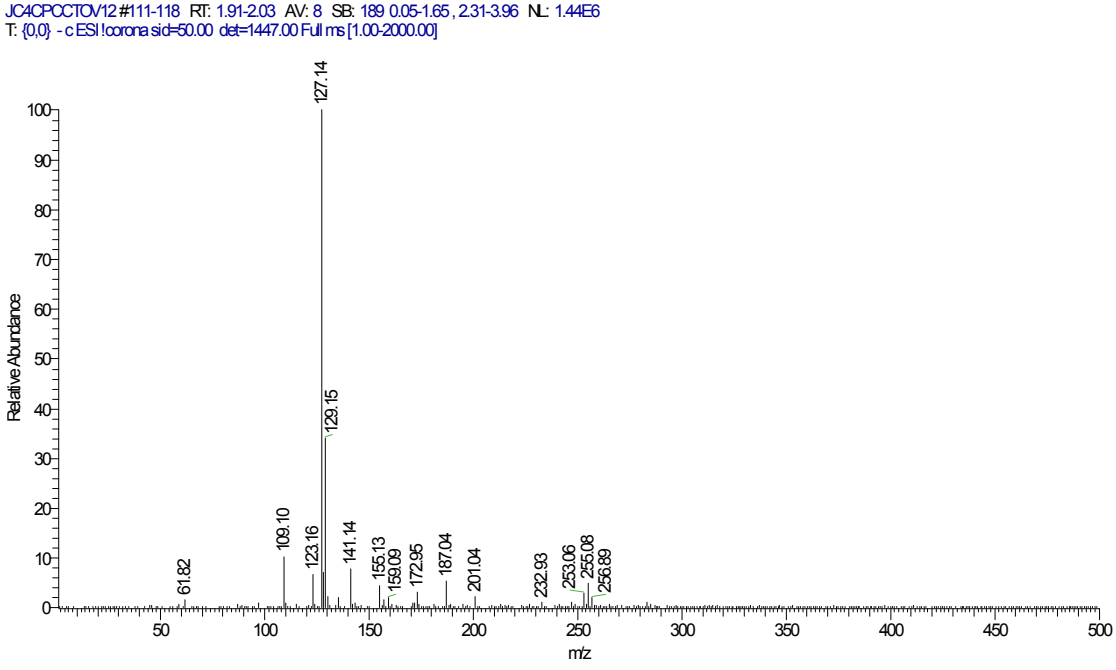


**Figure S17. MS data from 4CP after 12hrs visible light irradiation in the presence of Pt-$CaCu_3Ti_4O_{12}$.**

## Estimation of Active Sites for Turnover Number Calculations for 4CP Photo-oxidation over Pt-$CaCu_3Ti_4O_{12}$

0.1g 1wt%Pt-$CaCu_3Ti_4O_{12}$ => 0.099 x (0.1/614.184) = $1.611 \times 10^{-4}$ mols

BET Surface Area = $11.2 m^2 g^{-1}$

$CaCu_3Ti_4O_{12}$ unit cell parameter a=7.393Å=$7.393 \times 10^{-10}$m => face area=$5.46 \times 10^{-19} m^2$

Unit cells at surface of 1g = $11.2/5.46 \times 10^{19}$ => $3.40 \times 10^{-5}$ mols

=> unit cells at surface of 0.1g = $3.40 \times 10^{-6}$ mols

1 unit cell contains 2 $CaCu_3Ti_4O_{12}$ => $6.8 \times 10^{-6}$ mols at surface of 0.1g

[4CP]=$0.026 gL^{-1}$ => $1.02 \times 10^{-5}$ mols in 50ml

$6.8 \times 10^{-6}$ $CaCu_3Ti_4O_{12}$ mols at surface of 0.1g (as above)

1 turnover = $6.8 \times 10^{-6} / 1.02 \times 10^{-5}$ x100 = 66.66% 4CP degraded