Supporting Information

C-C Cleaving by Au/TiO_2 during Ethanol Oxidation: Understanding Bandgap Photo-Excitation and Plasmon Mediated Charge Transfer via Quantitative In-Situ DRIFTS

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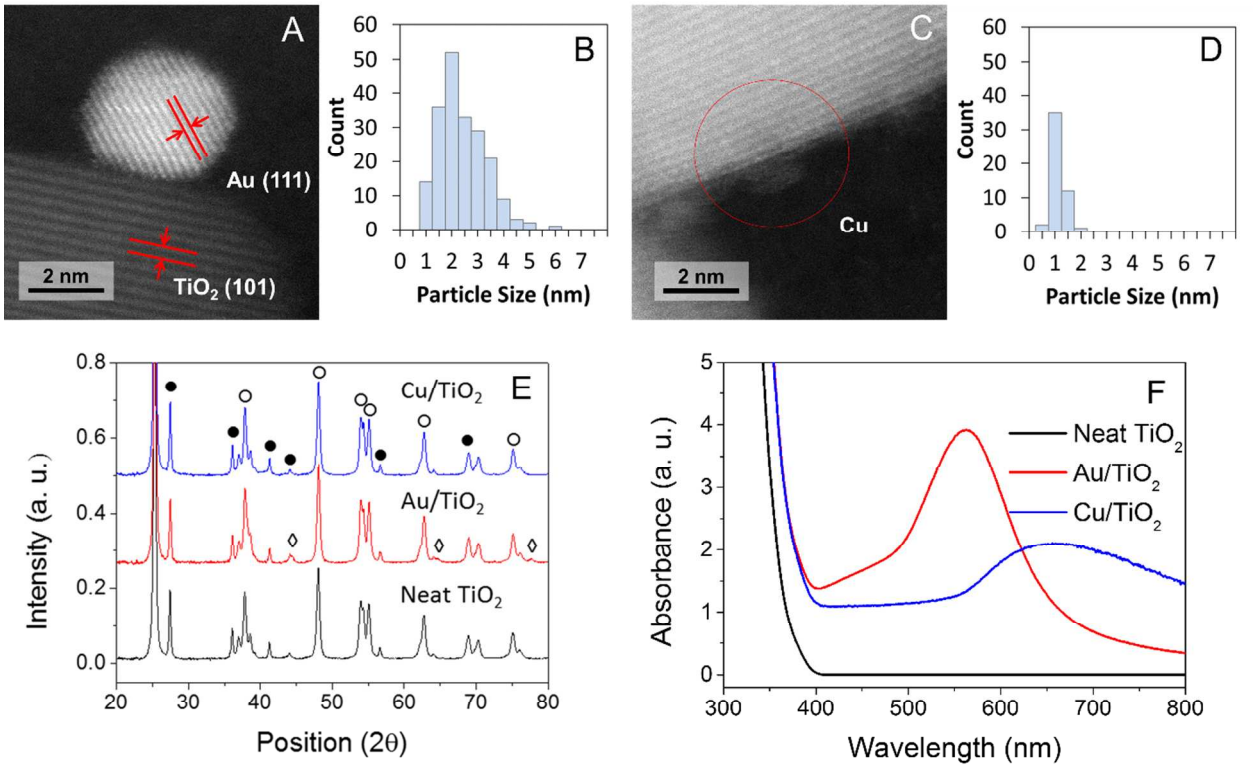

Figure S1 HAADF-STEM images and corresponding particle size distributions of Au/TiO_2 (A, B) and Cu/TiO_2 (C, D); XRD spectra of Cu/TiO_2, Au/TiO_2 and neat TiO_2 identifying peaks corresponding to the planes of Au (marked by ◊) in addition to distinct TiO_2 peaks (marked by, ● (rutile) and ○ (anatase) (E); Diffuse reflectance UV-vis spectra of Cu/TiO_2, Au/TiO_2 and neat TiO_2 showing a distinctive LSPR peak corresponding to Au (550 nm) and Cu (660 nm) (F). Adapted from Tan et al.[1] Copyright 2016 American Chemical Society.

Cu/TiO_2 was synthesised using the same DP method as for Au/TiO_2. The deposited Cu metal had an average size of ~1 nm based on the HAADF-HRSTEM images. The observed Cu deposit sizes were consistent with the lack of Cu peaks in the Cu/TiO_2 XRD spectra (i.e. the Cu deposit size is too small to be observed), which only showed the distinctive peaks of rutile and anatase TiO_2. Nonetheless, the LSPR peak of Cu at 660 nm indicates that the synthesised Cu deposits were present as metallic Cu.

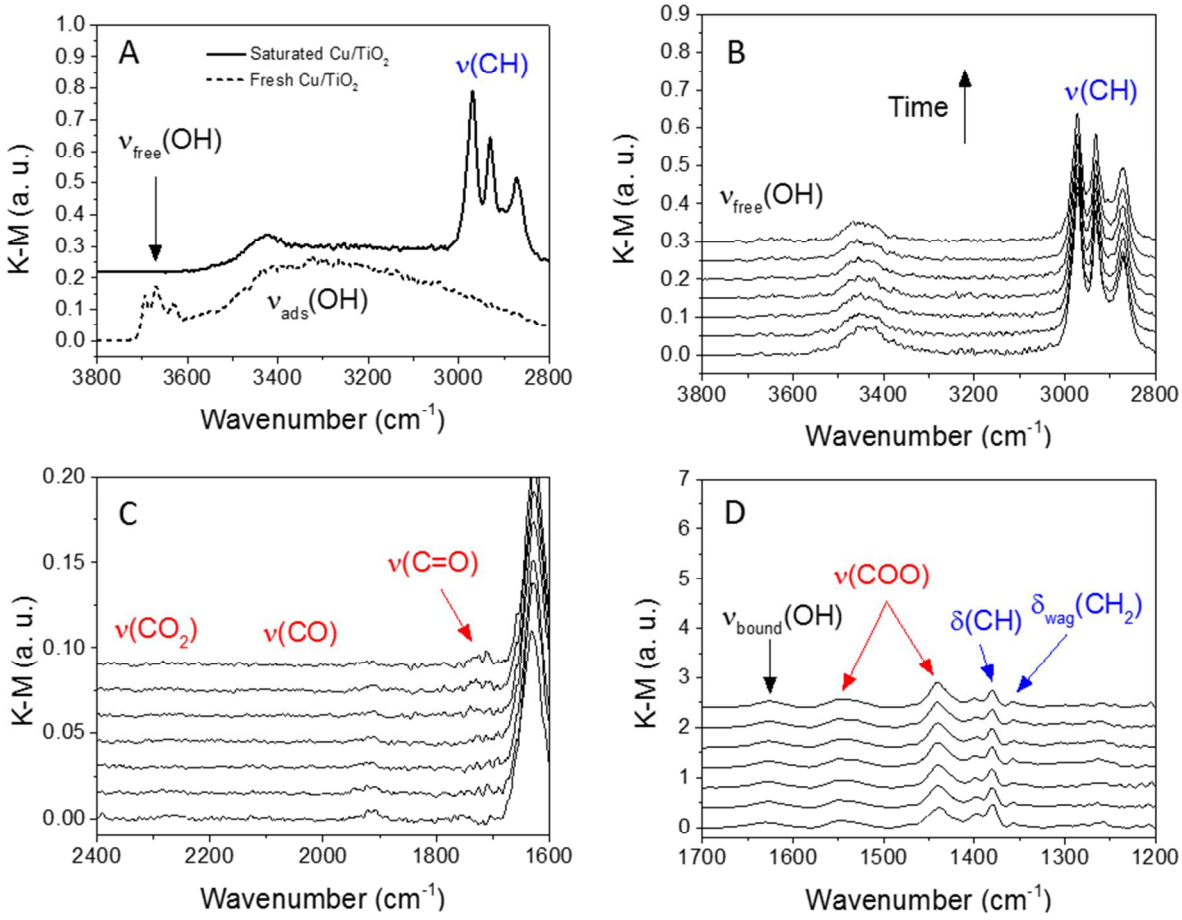

Figure S2 (A) In-situ DRIFTS spectra spanning (3800 – 3600 cm^{-1}) of Cu/TiO_2 before and after ethanol adsorption at 50 ^{o}C for 20 min. Ethanol feed concentration = 1000 ppm ethanol in N_2, gas flow rate = 20 mL/min, reaction performed at ambient pressure. In-situ DRIFTS spectra spanning: (B) 3800 – 3600 cm^{-1}; (C) 2400 – 1600 cm^{-1}; and (D) 1700 – 1200 cm^{-1} wavenumbers in ascending time steps (0 - 90 min, 15 min intervals) for Cu/TiO_2 during ethanol oxidation in air at 100 ^{o}C without illumination (i.e. in the dark). Air flow rate = 20 mL/min, reaction performed at ambient pressure.

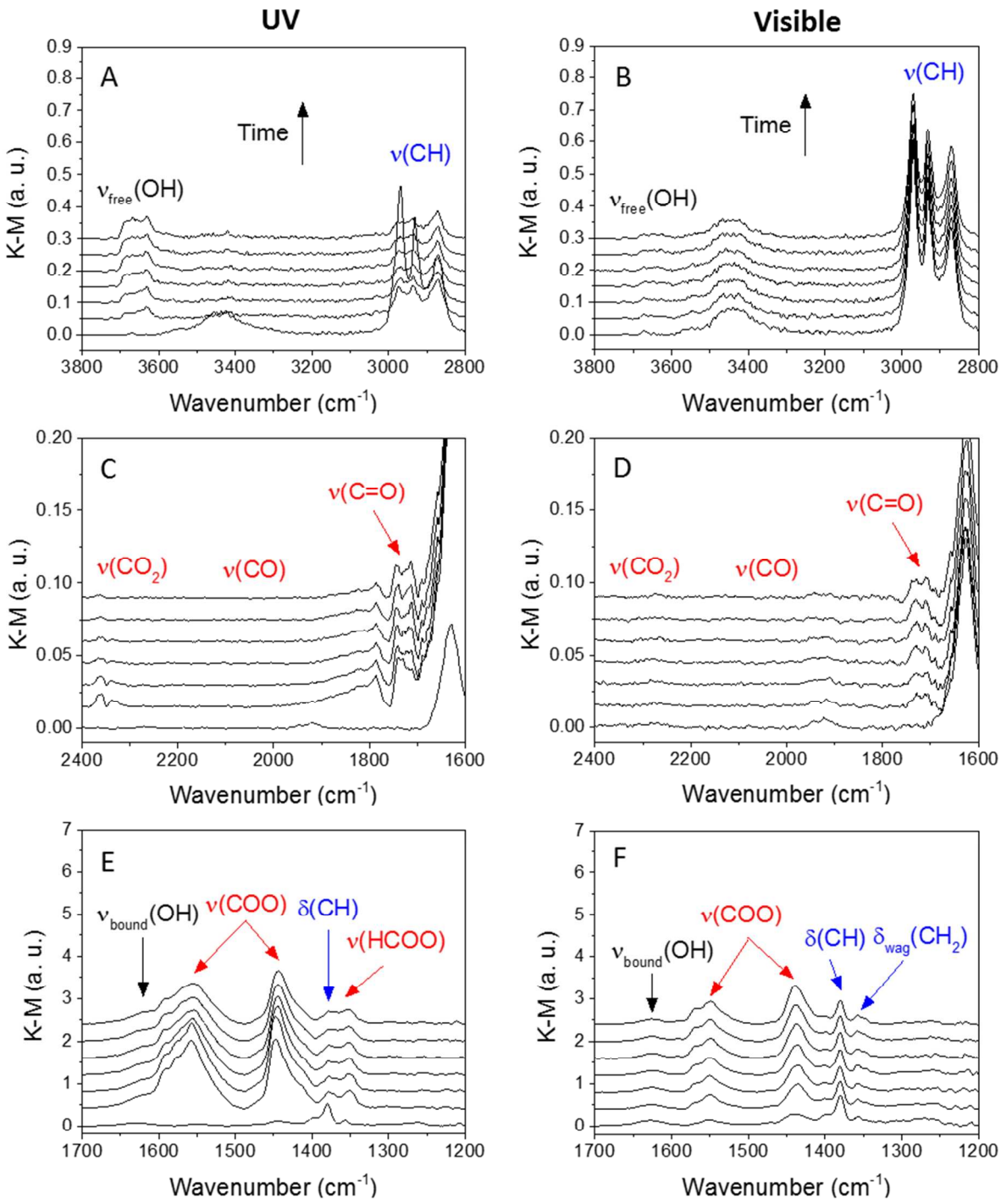

Figure S3 In-situ DRIFTS spectra spanning: (A, B) 3800 – 3600 cm^{-1}; (C, D) 2400 – 1600 cm^{-1}; and (E, F) 1700 – 1200 cm^{-1} in ascending time steps (0 - 90 min, 15 min intervals) for Cu/TiO_2 (during ethanol oxidation in air at 100 ^{o}C under UV (365 nm, 20 W/cm^2) and visible light (530 nm, 20 W/cm^2) illumination. Air flow rate = 20 mL/min, reaction performed at ambient pressure.

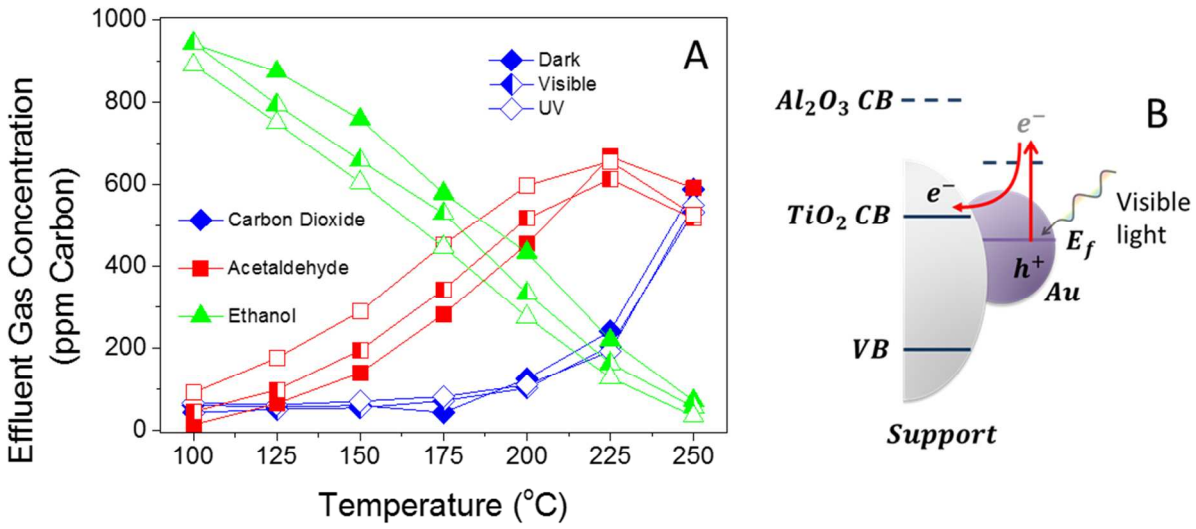

Figure S4 (A) Impact of temperature on the concentration of gases in the effluent stream during ethanol oxidation by Au/Al_2O_3 under (i) dark, (ii) visible light, and (iii) UV illumination. Temperature programmed oxidation study was carried out as detailed in our previous work.[1] Initial ethanol concentration = 1000 ppm carbon in air, gas flow rate = 100 mL/min, reactions performed at ambient pressure. (B) Potential plasmon mediated charge transfer pathway from an Au deposit to the neighbouring support under visible light illumination.

References

(1) Tan, T. H.; Scott, J.; Ng, Y. H.; Taylor, R. A.; Aguey-Zinsou, K.-F.; Amal, R. *ACS Catal.* **2016**, *6*, 1870–1879.