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Supplementary Information

Mechanistic study of the role of Au, Pd and Au-Pd on surface reactions of TiO_2 in the dark and under photo-excitation.

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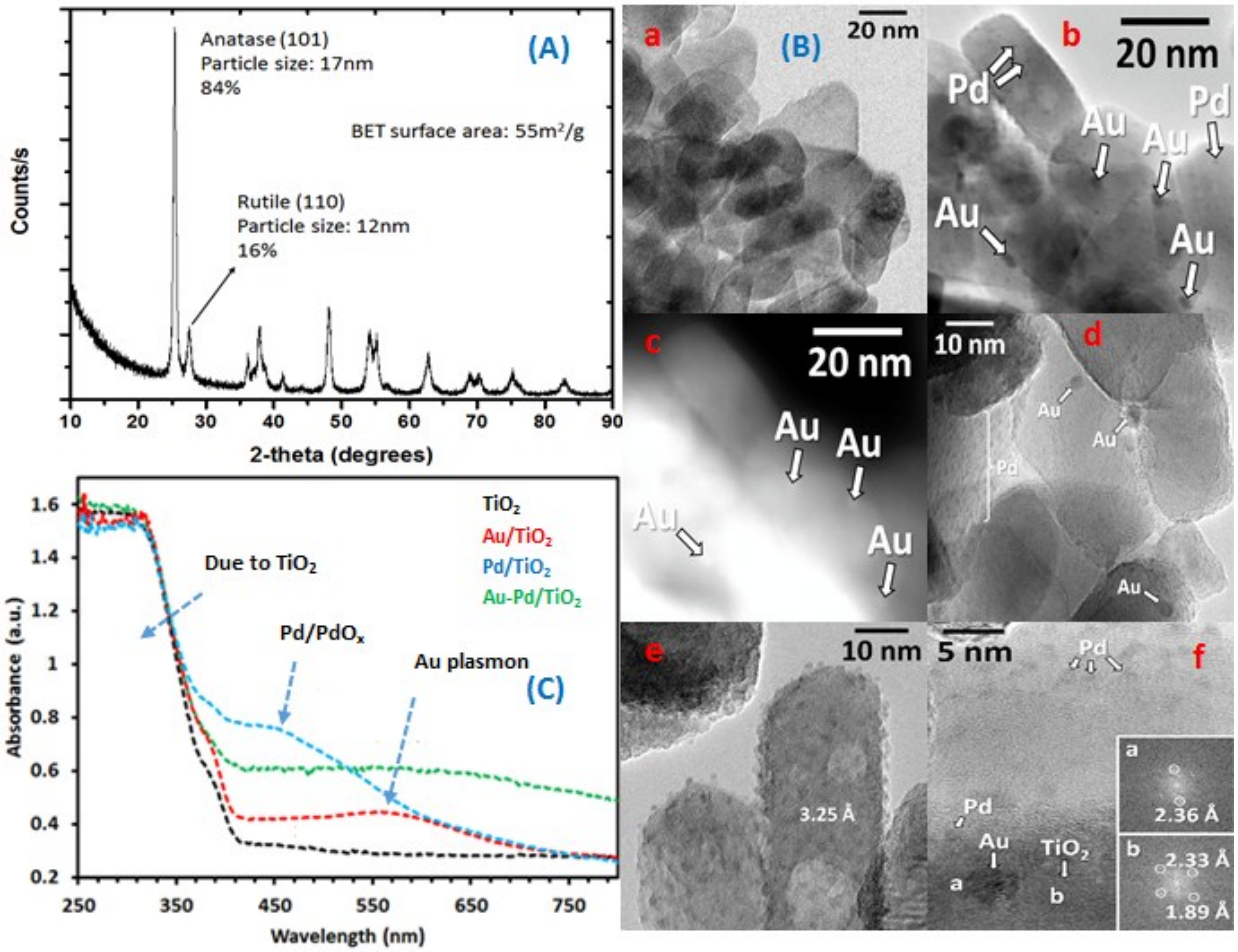

Figure SI-1:

(A) (a) Low Resolution TEM image of TiO_2 (A+R) particles (b) TEM image of 0.13 wt.% Au- 0.2 wt.% Pd/TiO_2 particle (c) combined BF and HAADF images in STEM mode of Au-Pd/TiO_2 (d, e and f) HRTEM images of Au-Pd/TiO_2 (inset show FT of Au and Pd).

(B) XRD pattern of TiO_2 (A+R) powder.

(C) UV-Vis spectra of TiO_2 and M/TiO_2 (M= 1.2 wt.% Au, 2.0 wt.% Pd and 3.2wt.% Au-Pd)

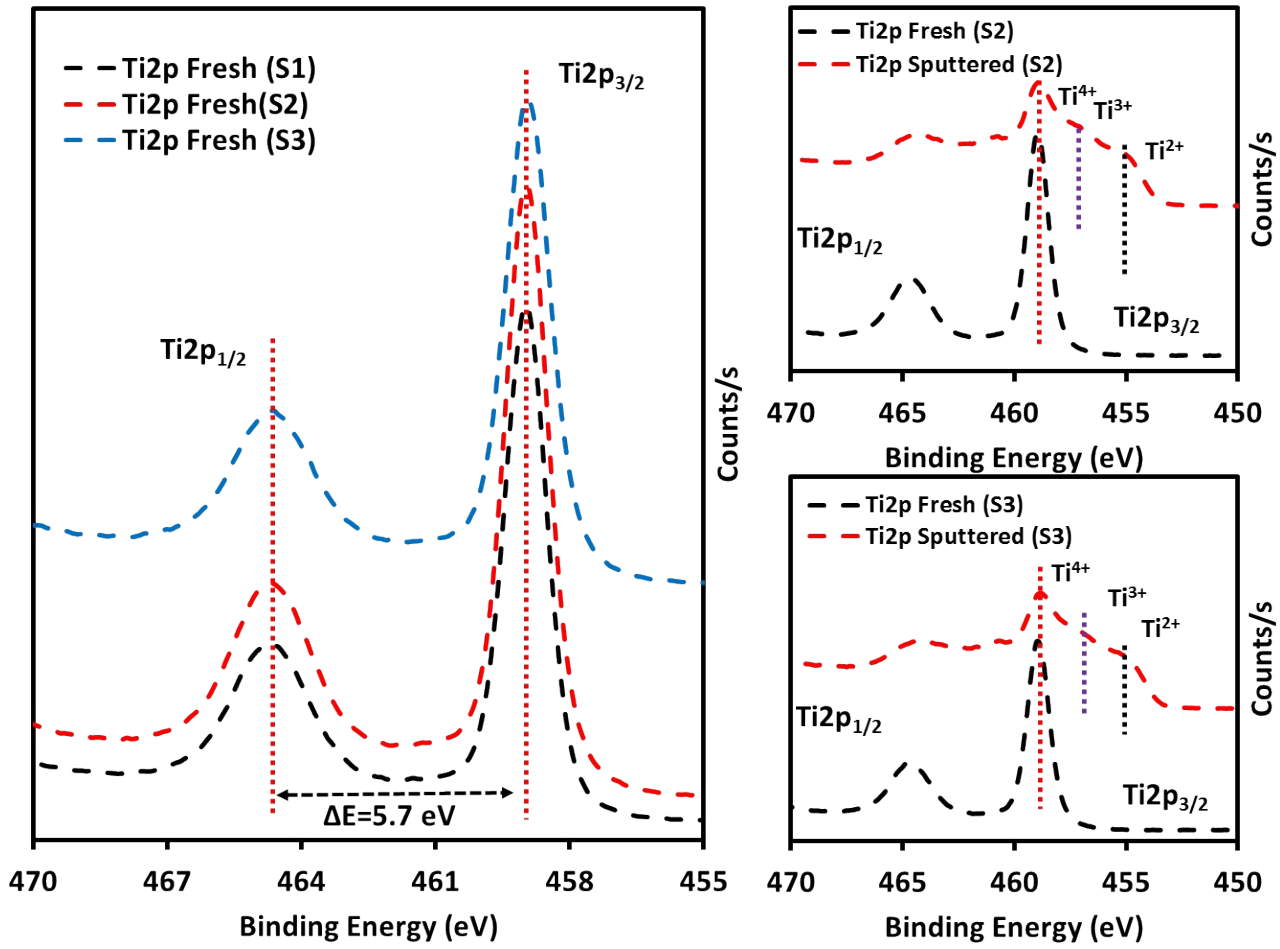

Figure SI-2:

XPS of Ti2p; before ion sputtering (fresh) and after 5 min Ar^+-sputtering of $Au-Pd/TiO_2$. Samples S1 (1.2 wt.% Au; 2.0 wt.% Pd), S2 (0.13 wt.% Au; 0.2 wt.% Pd) and S3 (0.06 wt.% Au; 0.1 wt.% Pd)

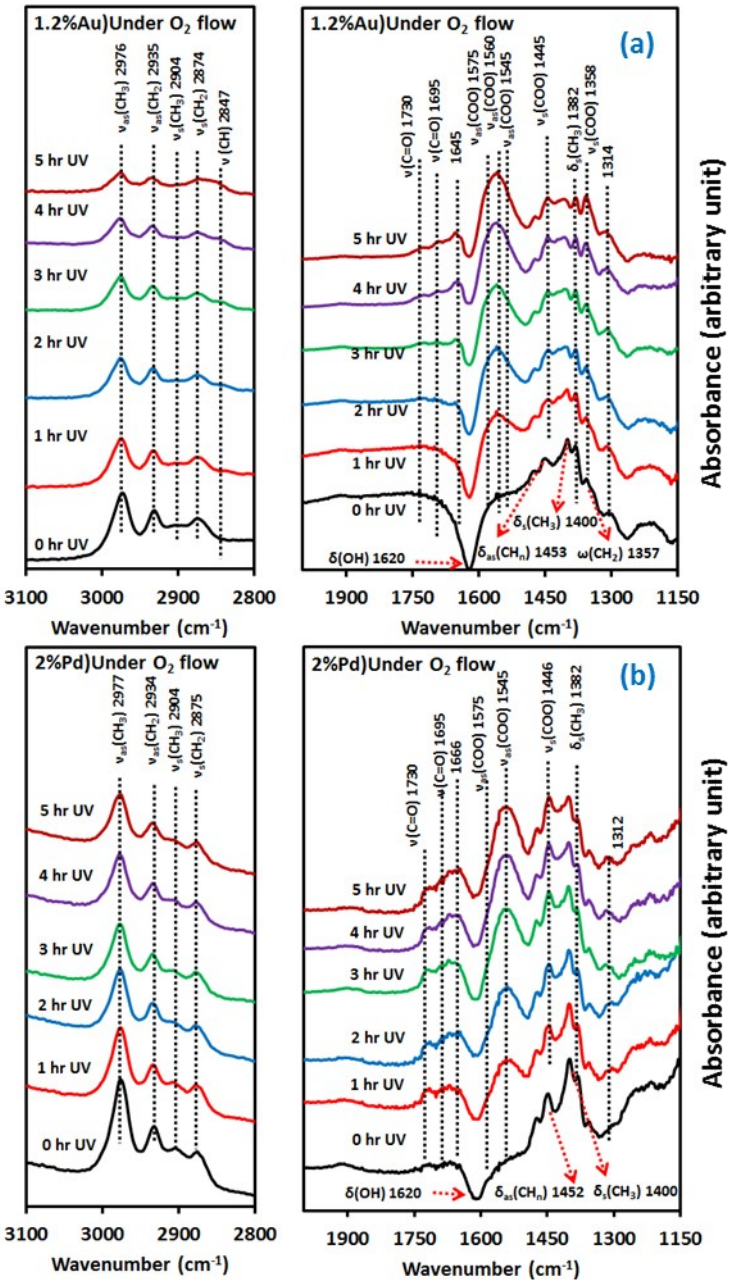

Figure SI-3:

FTIR spectra during the photo-reaction of ethanol in the presence of O_2 over (a) 1.2 wt.% Au/TiO_2 and (b) 2.0 wt.% Pd/TiO_2.

The surface was initially saturated with ethanol at 300 K, O_2 flow = 30 mL/min, P = 1 atm

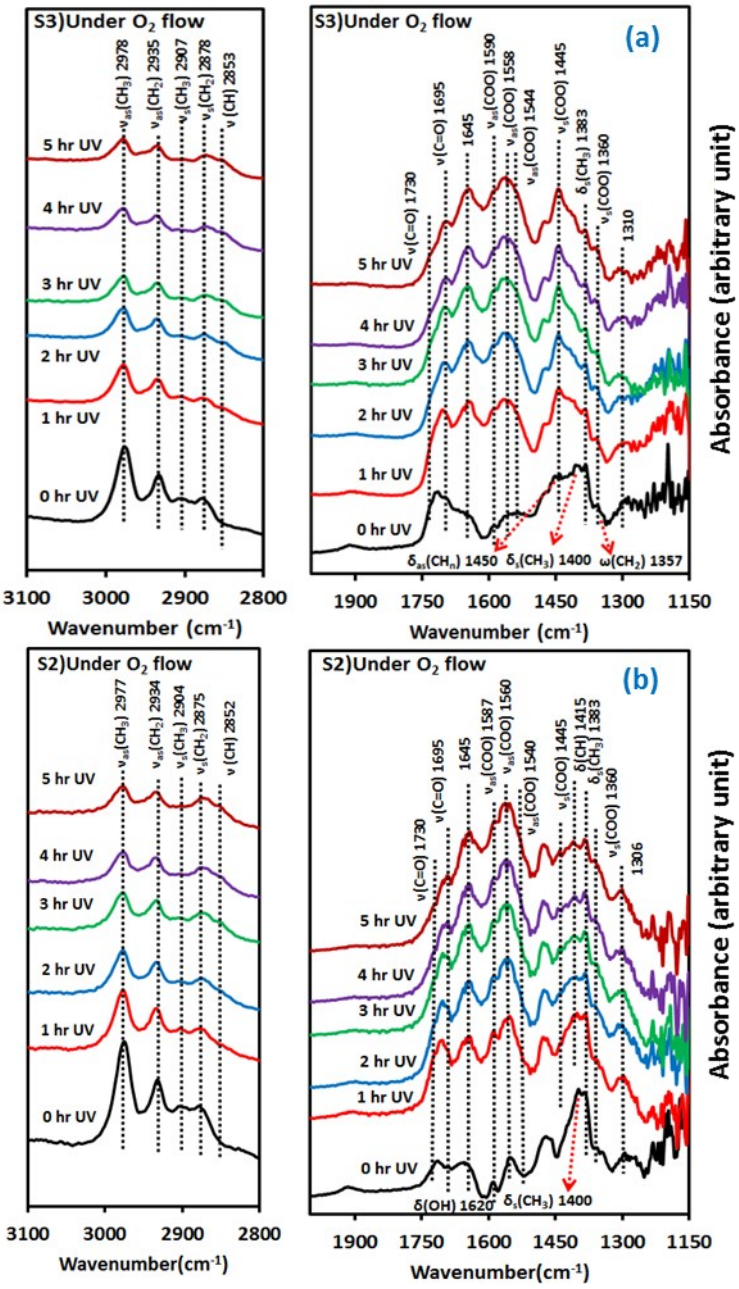

Figure SI-4:

FTIR spectra during the photo-reaction of ethanol in the presence of O_2 over (a) sample S2 (0.13 wt.% Au-0.2 wt.% Pd/TiO_2) and (c) sample S3(0.06 wt.% Au-0.10 wt.% Pd/TiO_2).

The surface was initially saturated with ethanol at 300 K, O_2 flow = 30 mL/min, P = 1 atm

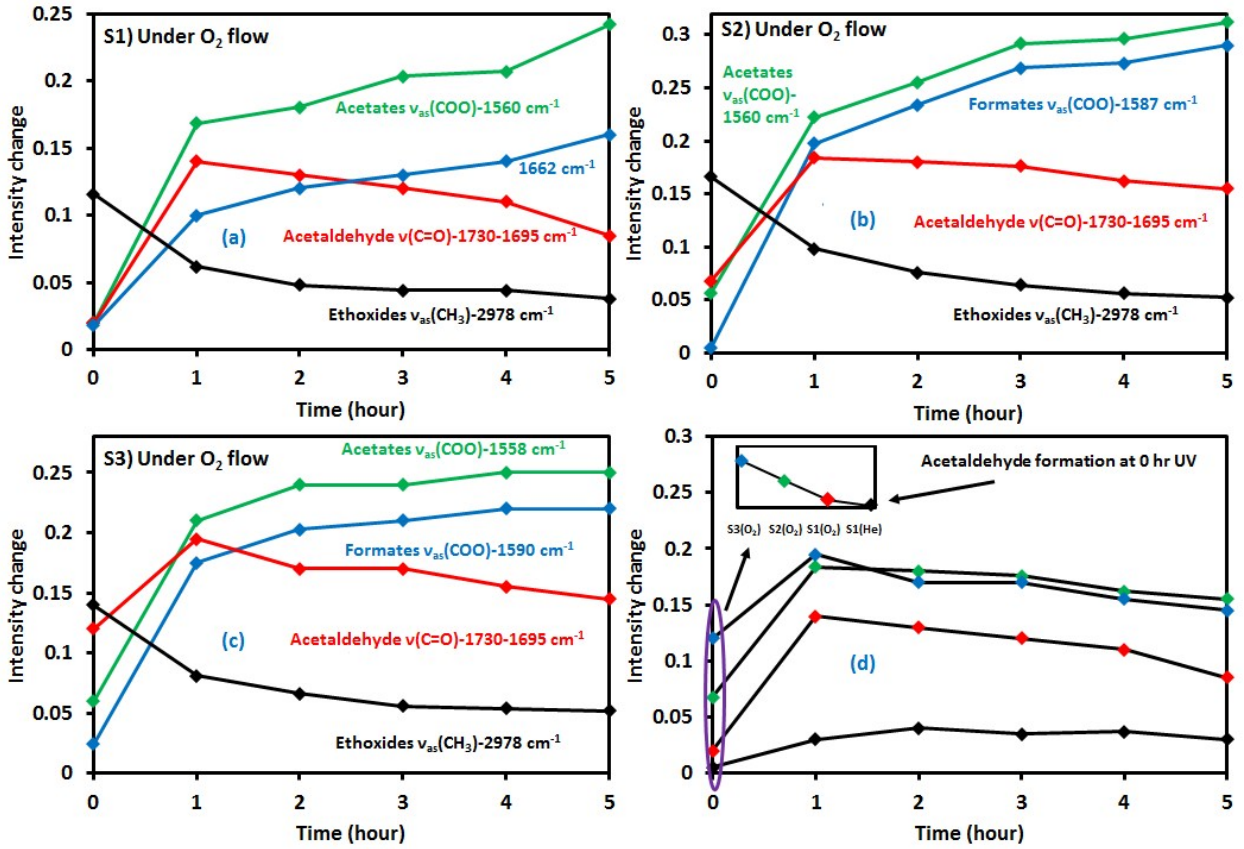

Figure SI-5:

Change in the IR intensity of species during the photo-reaction of ethanol in the presence of O_2 over Au-Pd/TiO_2 samples (a) S1, (b) S2 and (c) S3.

(d) Comparison of the acetaldehyde IR intensity change (v C=O) with time during photo-reaction of ethanol over samples S1(under He and O_2), S2 (under O_2) and S3 (under O_2). The inset shows the formation of acetaldehyde after dark reaction (before photo-excitation) at 300 K.

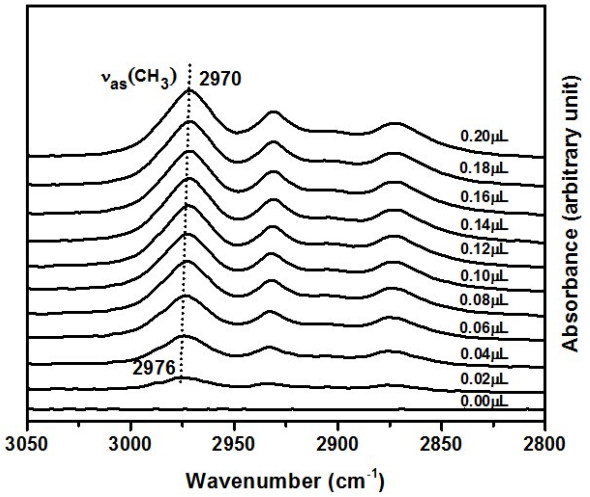

Figure SI-6:

IR spectra of different concentration of ethanol on TiO_2 (A+R) collected under vacuum (1 x 10^{-3} Torr).

Calculation of dissolved concentration of reaction products during photo-reforming of ethanol

The calculations are done using Dalton's law of partial pressure, Raoult's law and the Henry's law.

- According to Dalton's law of partial pressure

$P_T = P_{H2} + P_{CO2} + P_{CH3CHO} + P_{CH4} + P_{C2H5OH} + P_{H2O} + P_{N2}$

Where P_T = Total pressure of a mixture of gases; P_{H2}, P_{CO2}, P_{CH3CHO}, P_{CH4}, P_{C2H5OH}, P_{H2O} and P_{N2} are the partial pressures of components inside the reactor.

- According to Raoult's law

$P_T = P_{C2H5OH} + P_{H2O}$

$= x_e * VP_e + x_w * VP_w$

Where xe and xw are mole fractions of ethanol and water, VP_e and VP_w are the vapor pressures of ethanol and water at 300 K.

- According to Henry's law

$H^{cp} = C_a/P_i$ where H^{cp} = Henry's law constant ($mol.dm^{-3}.atm^{-1}$); C_a =Concentration of a species in the aqueous phase ($mol.dm^{-3}$) and P= Partial pressure of that species in the gas phase under equilibrium conditions (atm)[i].

[i] R. Sander, *Atmospheric Chemistry and Physics*, 2015, **15**, 4399-4981.