Biomass Components to H_2 and Value Added Products by Sunlight Driven Photocatalysis with Electronically Integrated $Au^{\delta-}$-TiO_2: Concurrent Utilisation of Electrons and Holes

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Electronic Supplementary Information (ESI)

Figure S1: Digital photographs to show an uniform dispersion of the catalyst during reaction under direct sunlight.

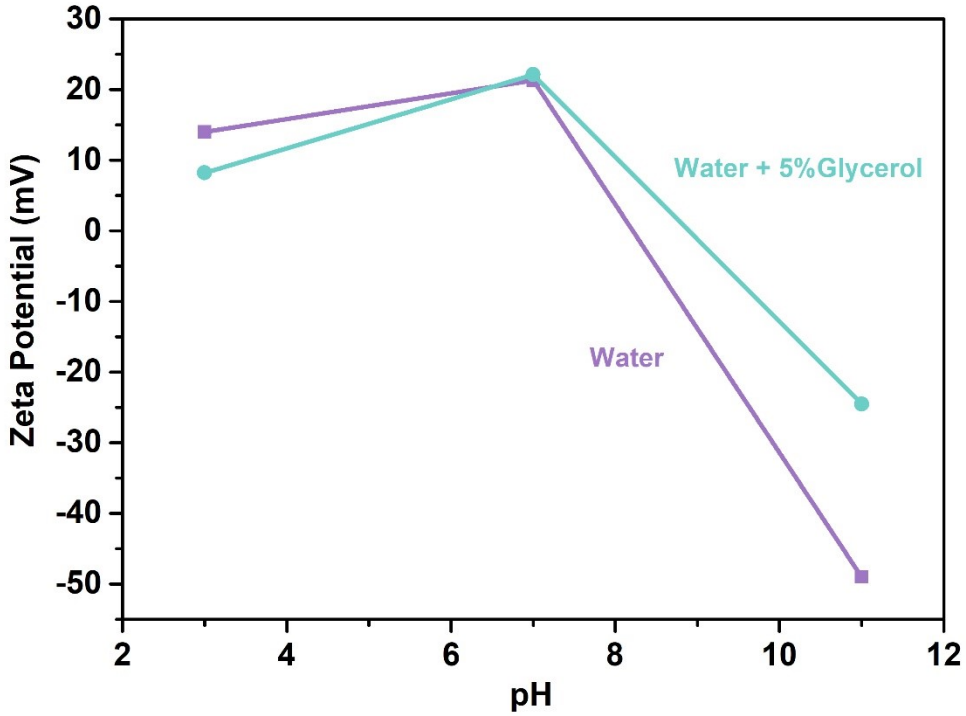


Figure S2: Zeta potential of 0.5Au@TiO_2 in water and water +glycerol solution at different pH. Zeta potential at acidic pH is closer to zero compared to neutral, which is more positive and also in agreement with the high photocatalytic activity reported in the main manuscript at neutral pH, than acidic or basic pH. Highly hydroxylated surface under basic conditions makes the zeta potential to be highly negative.

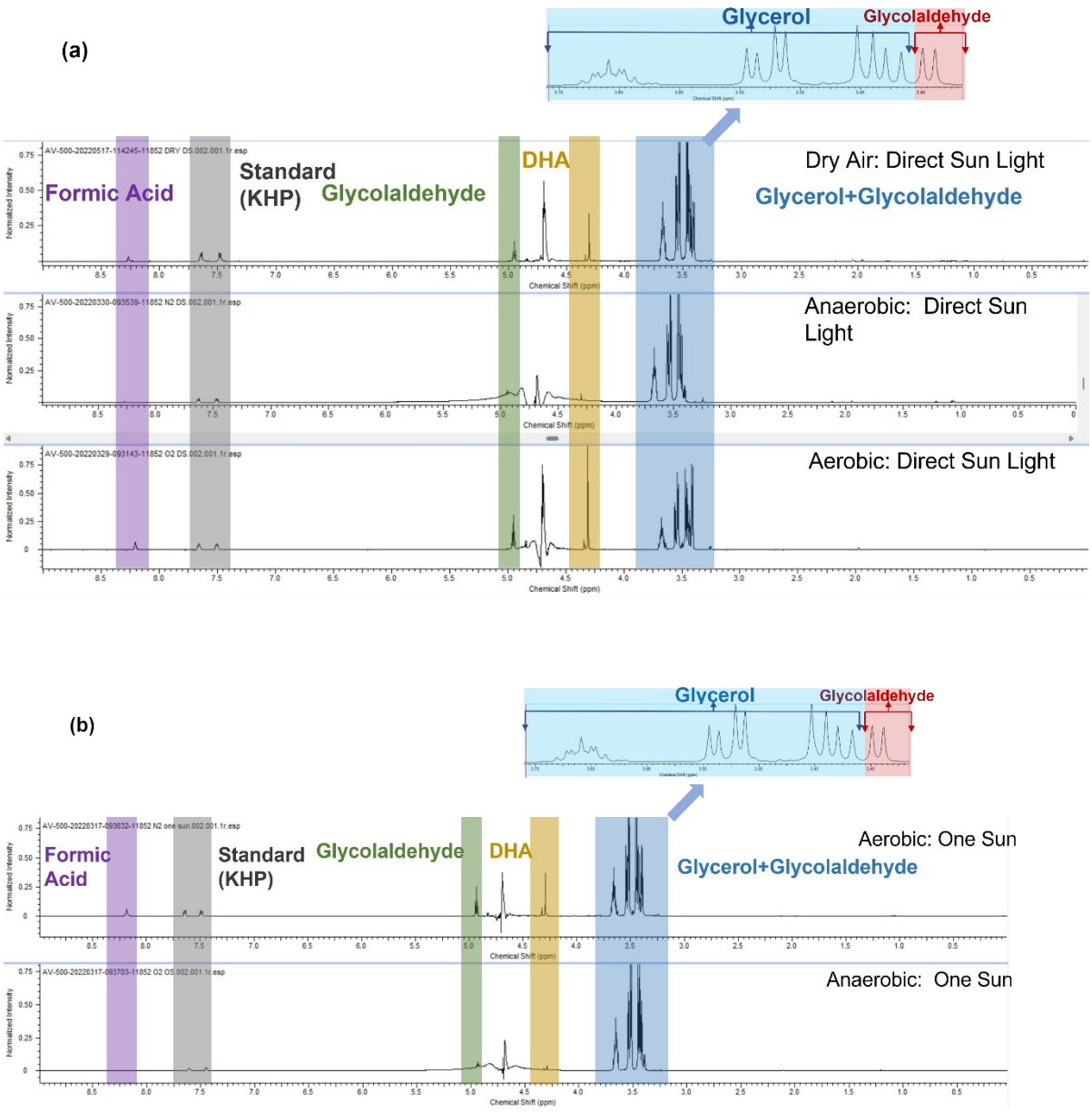


Figure S3: NMR spectra of the glycerol oxidation, a) With different condition under direct sunlight, b) under one sun. conditions: 5 mg catalyst in 5 ml glycerol solution, 5h reaction

Table S4: Product analysis of glycerol oxidation in **anaerobic** condition.

Product	Concentration (M/g. 5h)	Yield (mmol/g.5h)	Selectivity (%)[#]	Selectivity with respect to no of Carbon (%)	Conversion (%)	TON (Au loading)	TOF (Au loading)/h
Glycolaldehyde	0.32	1.6	52	54	6	64	12.8
Dihydroxyacetone	0.12	0.6	20	31		24	4.8
Formic Acid	0.17	0.85	28	15		34	6.8
CO_2	ND	ND	ND	ND		ND	ND
H_2	NA	32 mmol/g.	NA	NA		1280	256

[#]: Selectivity among the organic products

Table S5: Product analysis of glycerol oxidation in **aerobic** condition.

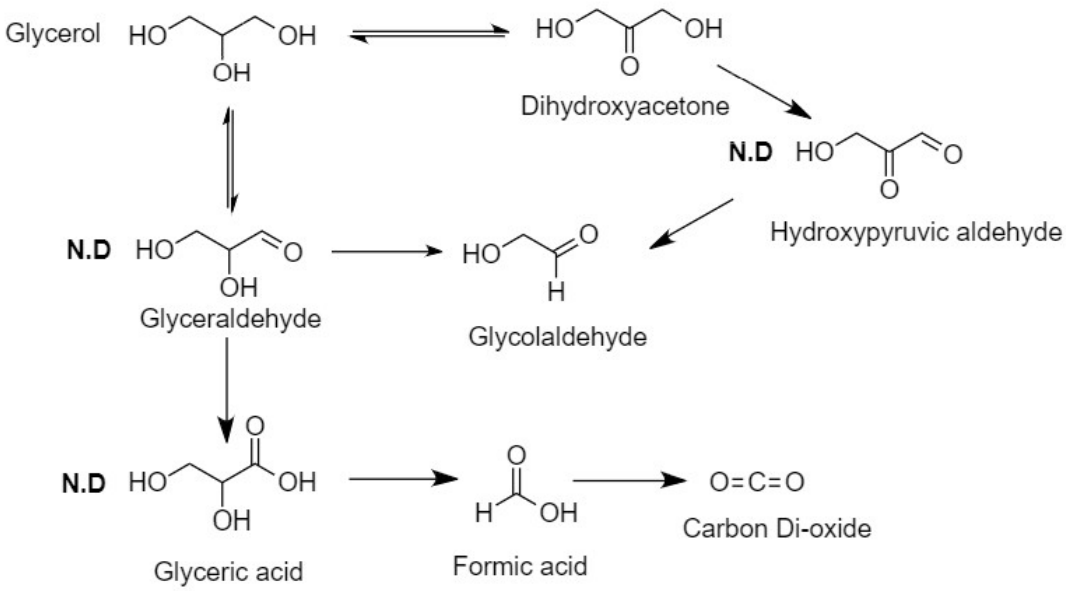
Product	Concentration (M/g. 5h)	Yield (mmol/g.5h)	Selectivity (%)[#]	Selectivity with respect to no of Carbon (%)	Conversion	TON (Au loading)	TOF (Au loading)/h
Glycolaldehyde	0.56	2.82	20	29	13	112.8	22.56
Dihydroxyacetone	0.34	1.7	13	26		68	13.6
Formic Acid	0.34	1.7	13	8		68	13.6
CO_2	NA	7.5	54	37		300	60
H_2	NA	1.9	NA	NA		76	15.2

[#]: Selectivity among the organic products

Table S6: Product analysis of glycerol oxidation by using **dry air**.

Product	Concentration (M/g. 5h)	Yield (mmol/g.5h)	Selectivity (%)[#]	Selectivity with respect to no of Carbon (%)	Conversion	TON (Au loading)	TOF (Au loading)/h
Glycolaldehyde	0.49	2.4	35	43	7	96	19.2
Dihydroxyacetone	0.19	0.95	14	26		38	7.6
Formic Acid	0.13	0.65	10	6		5.2	1
CO_2	NA	2.8	41	25		112	22.4
H_2	NA	23	NA	NA		920	184

[#]: Selectivity among the organic products



N.D: Not Detected

Figure S7: Plausible reaction pathway for glycerol oxidation to VAPs over Au@TiO_2 composites

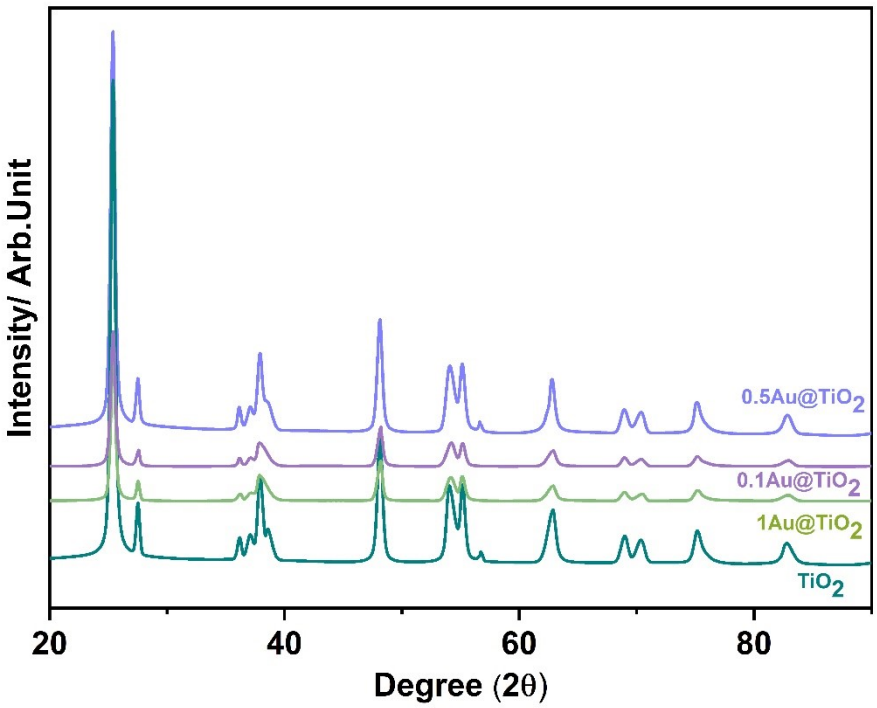


Figure S8: X-ray diffraction pattern of TiO_2 and $xAu@TiO_2$ (x = 0.1, 0.5 and 1). Same features are observed indicates with all of the catalysts underscore a possible fine-distribution of atom-like or very small size gold clusters. STEM results shown in Figure 5 fully support this conclusion.

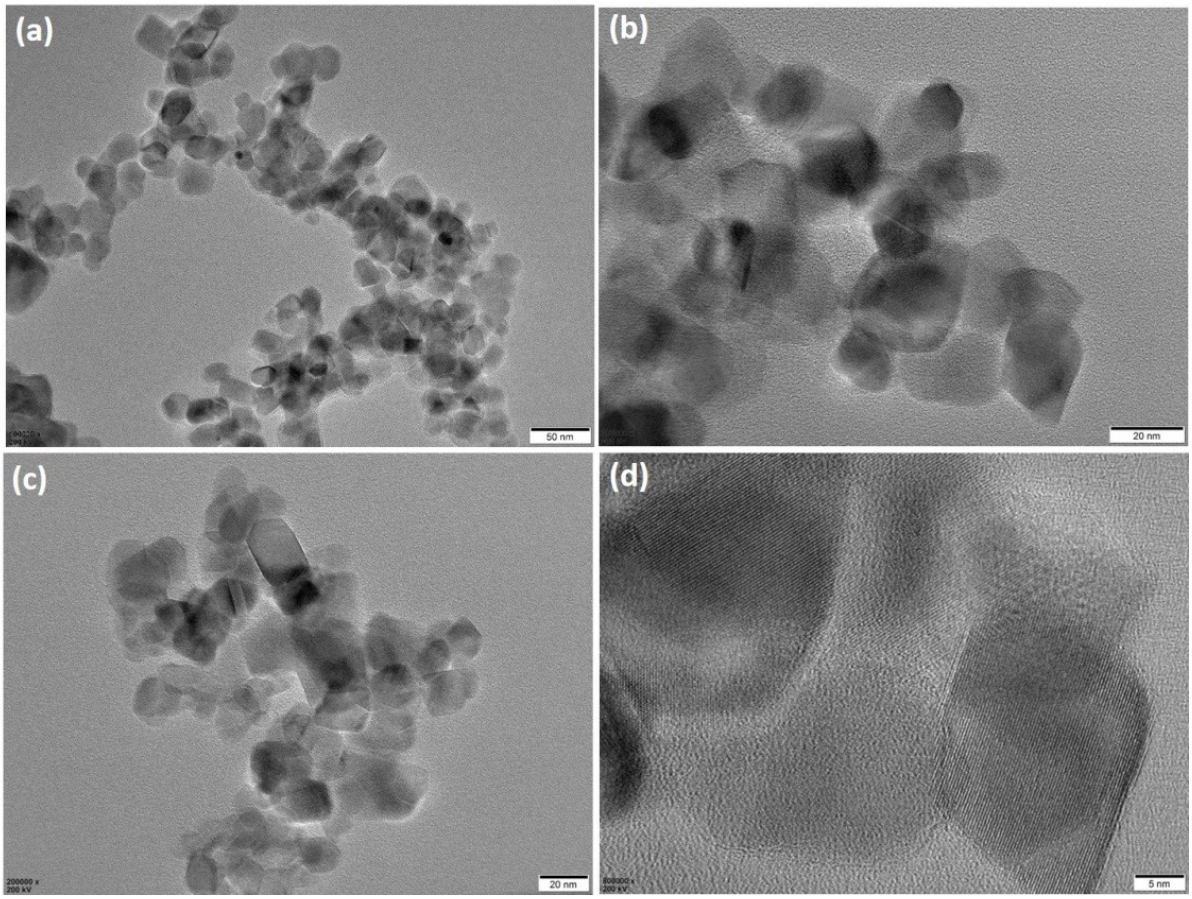


Figure S9: HRTEM images of 0.5Au@TiO_2. No gold feature was observed in HRTEM indicates the size of gold to be atom or atom-like clusters.