Supplementary Information

Photocatalytic Glycerol Oxidation on Au_xCu-CuS@TiO_2 Plasmonic Heterostructures

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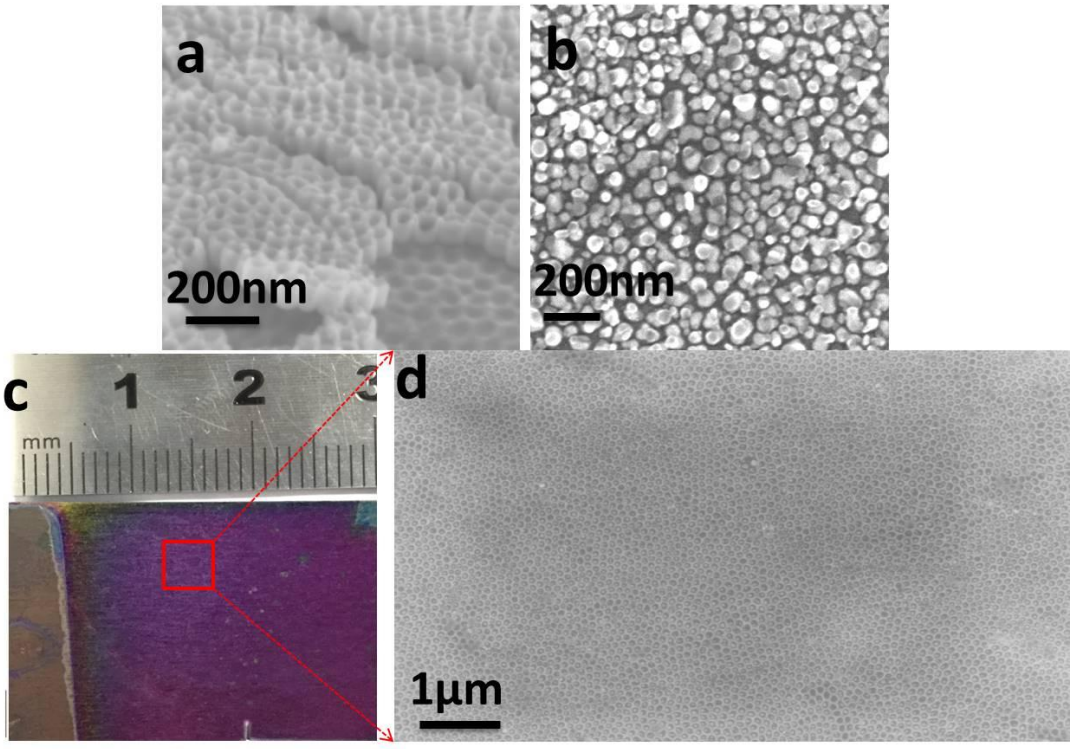

Figure S1. (a) SEM image of TiO_2 nanocavity arrays after e-Beam deposition of 10 nm Au/Cu; (b) 10 nm Au/Cu coating dewetted on a compact TiO_2 foil; (c) photo and (d) SEM image of the $AuCu_3$-CuS@TiO_2 film after sulfurization (sample size: 1×1 inch).

Table S1. Thermal properties of materials used in the heat transfer model.[1-3]

Materials	Specific heat capacity (J kg^{-1} K^{-1})	Density ($kg\ m^{-3}$)	Thermal conductivity (W m^{-1} K^{-1})
gold	129	19300	110 (40 nm)
water	4180	1000	0.6
Cu	390	8900	120 (40 nm)
TiO_2	710	4260	0.7

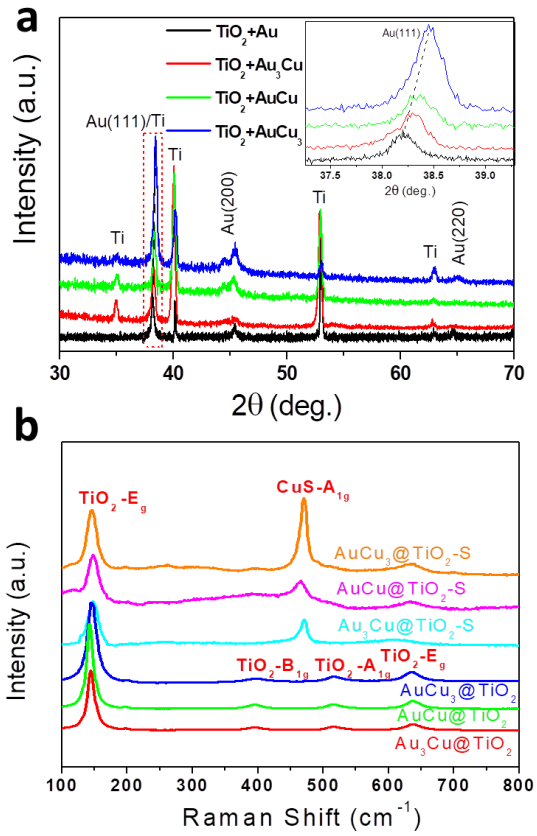

Figure S2. (a) XRD patterns of $Au@TiO_2$, $Au_xCu@TiO_2$ NPs arrays after dewetting at 400 ℃ for 1 h, and (b) corresponding Raman shift of the $Au_xCu@TiO_2$ NPs before and after sulfurization at 300 ℃ for 10 min.

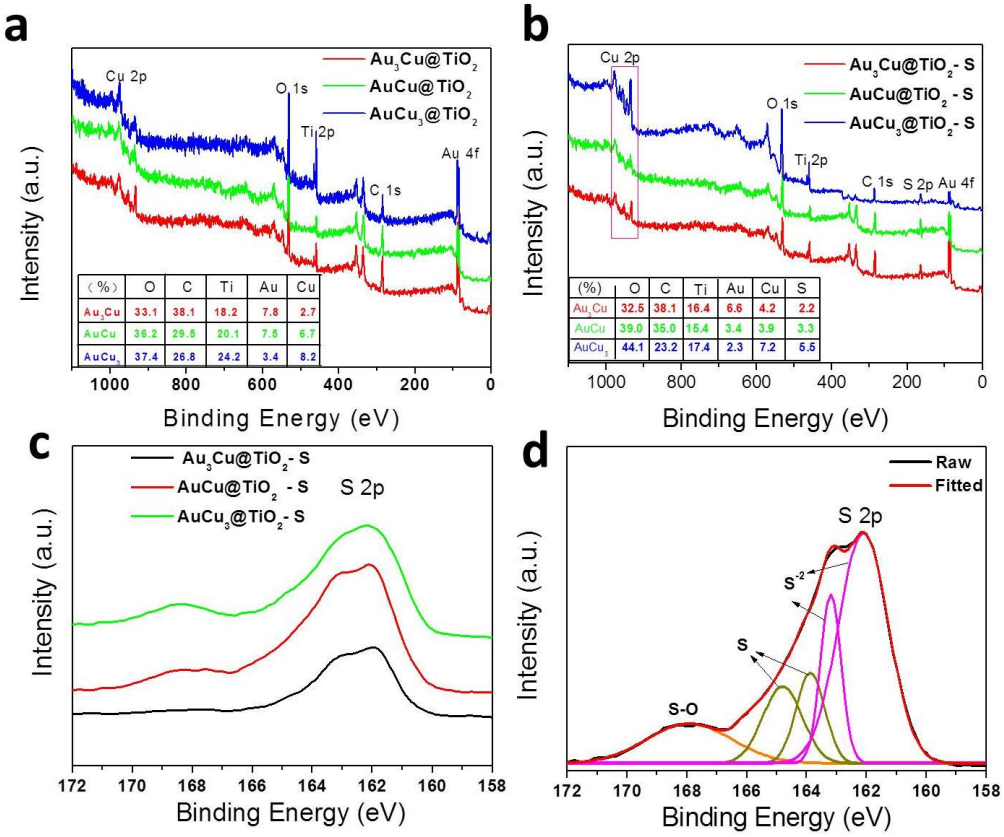

Figure S3. Survey scan of (a) $Au_xCu@TiO_2$ and (b) Au_xCu-$CuS@TiO_2$ heterostructures with elemental mole ratio inserted. (c) High-resolution XPS spectra of S 2p in the hybrids and (d) fitted binding energies from different chemical states of S.[4]

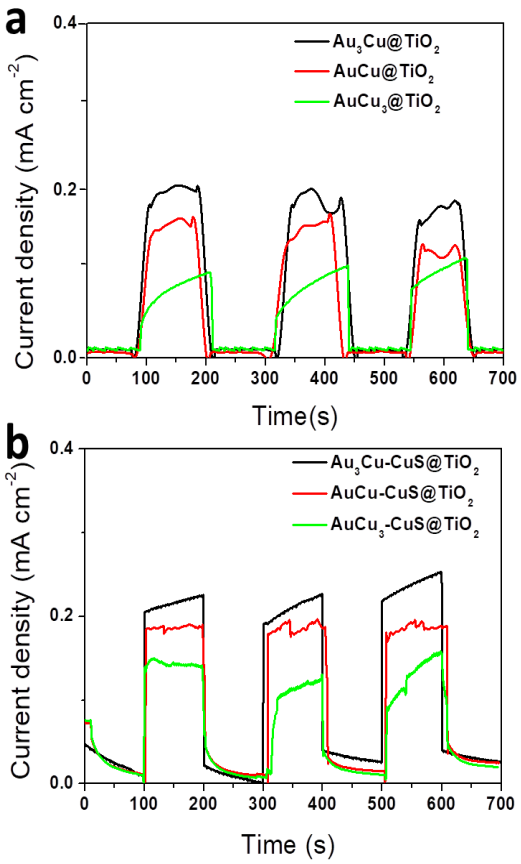

Figure S4. Photocurrent-time curves of (a) $Au_xCu@TiO_2$ and (b) Au_xCu-$CuS@TiO_2$ hybrid films upon solar light illumination on and off.

Table S2. Photocurrent density of different samples under simulated solar light

Samples	Photocurrent density ($mA\ cm^{-2}$)
$Au_3Cu@TiO_2$	0.2
$AuCu@TiO_2$	0.17
$AuCu_3@TiO_2$	0.09
Au_3Cu-$CuS@TiO_2$	0.22
$AuCu$-$CuS@TiO_2$	0.19
$AuCu_3$-$CuS@TiO_2$	0.11

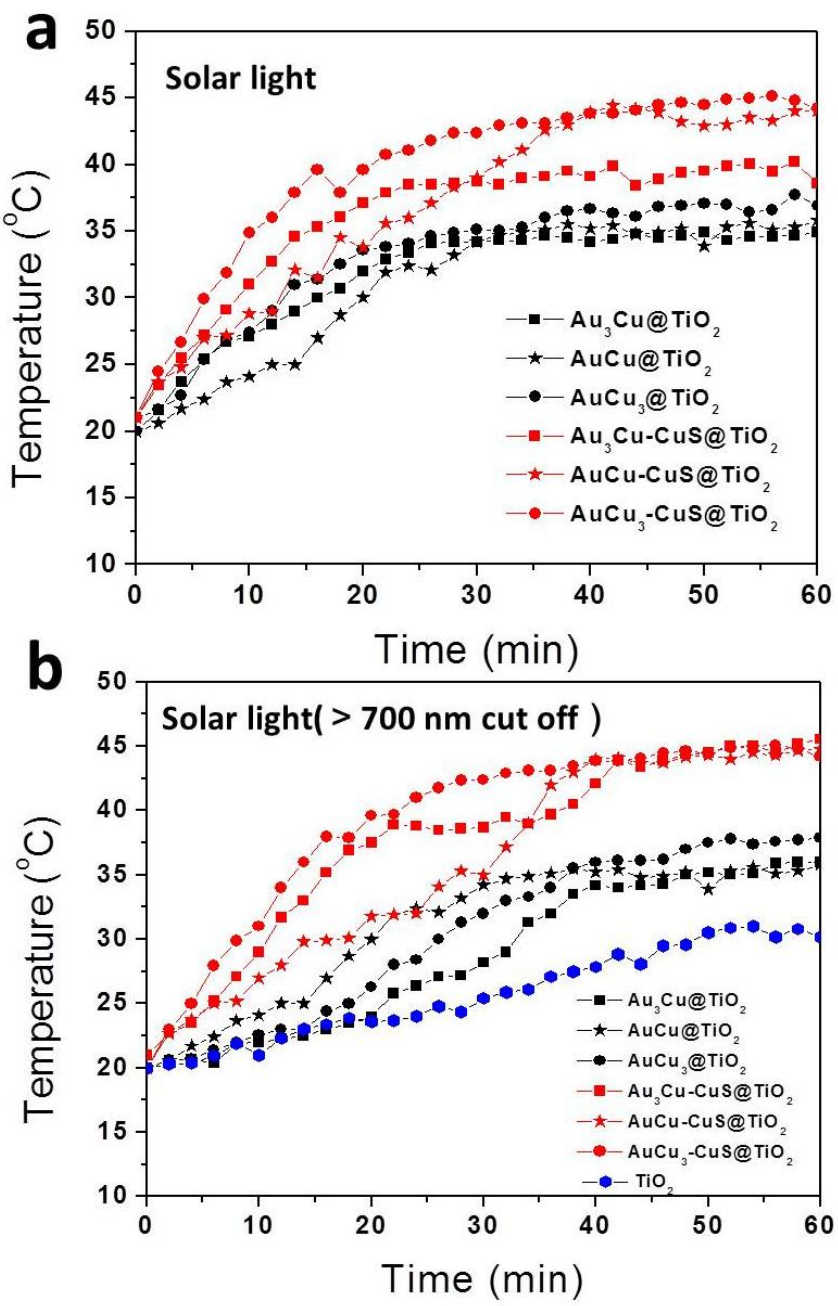

Figure S5. Temperature variation of $Au_xCu@TiO_2$ and Au_xCu-$CuS@TiO_2$ NP arrays in water over a period of 60 min upon exposure to (a) solar light and (b) solar light with NIR cutting-off.

Table S3. Selectivity of glycerol oxidation on the $Au_xCu@TiO_2$ and Au_xCu-$CuS@TiO_2$ NCAs.

Samples	DHA (%)	Glycolic acid (%)	Glyceric acid (%)	Glyceraldehyde (%)	Tartronic acid (%)
$Au_3Cu@TiO_2$	72	8	13	5	2
$AuCu@TiO_2$	69	11	14	3	3
$AuCu_3@TiO_2$	69	12	13	4	2
Au_3Cu-$CuS@TiO_2$	69	14	13	5	1
$AuCu$-$CuS@TiO_2$	66	17	13	4	0
$AuCu_3$-$CuS@TiO_2$	63	18	14	3	2

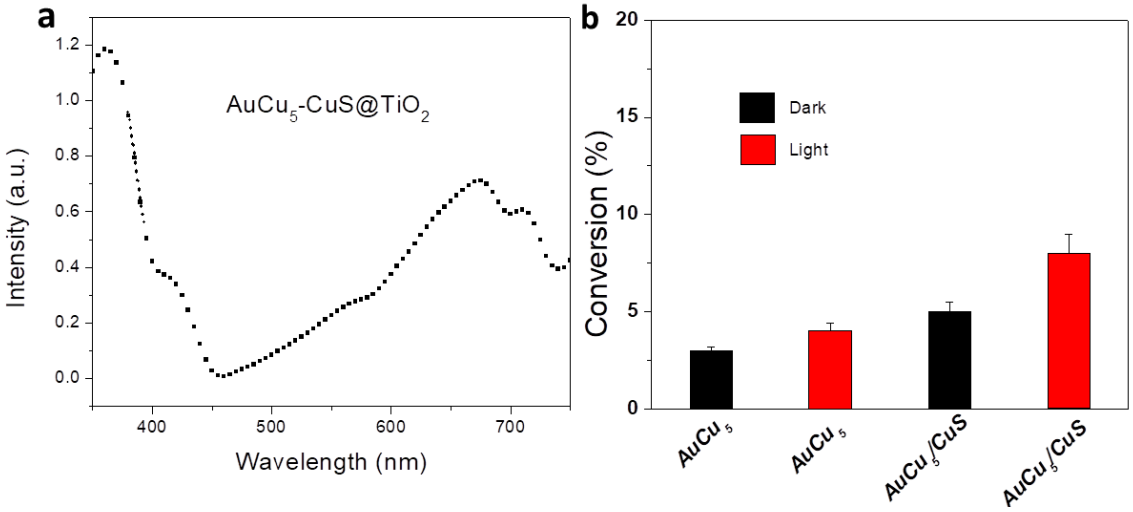

Figure S6. UV-vis diffuse reflectance spectrum of $AuCu_5$-$CuS@TiO_2$ heterostructure and glycerol conversion efficiency under dark and solar light.

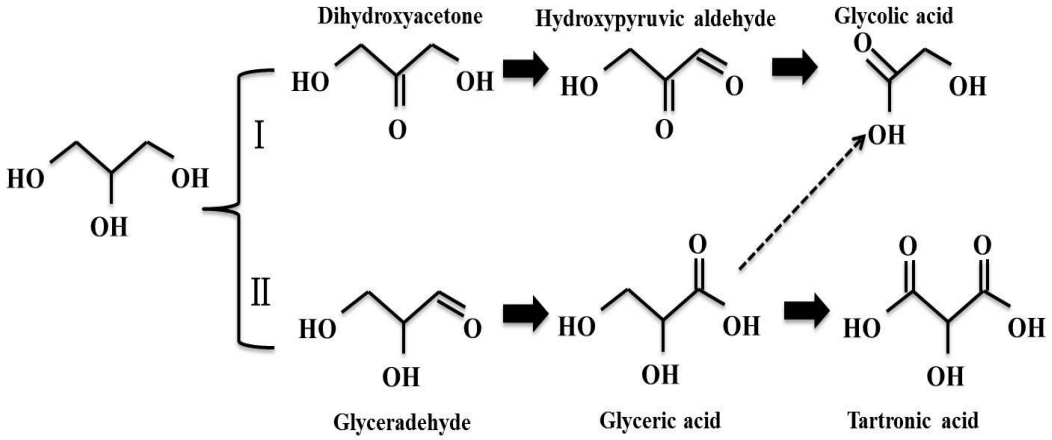

Figure S7. Two possible pathways of glycerol oxidation to different products.[5]

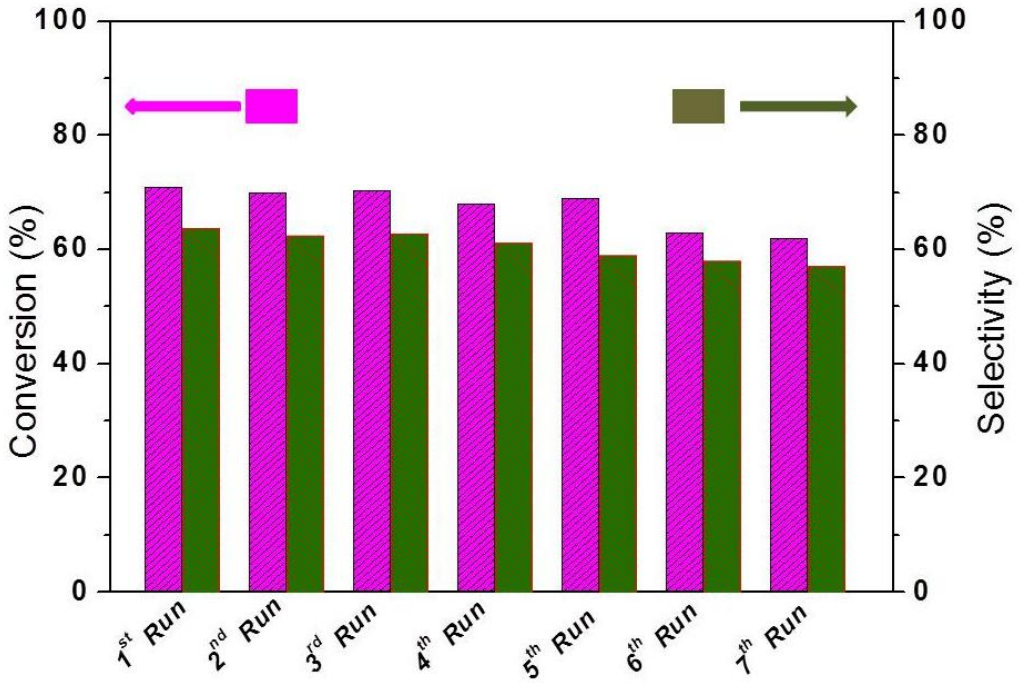

Figure S8. Recycling performance for glycerol oxidation under the simulated solar light on the AuCu-CuS@TiO_2 catalyst with selectivity toward dihydroxyacetone.

Reference:

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