

Supporting Information

Plasmonic Au/TiO₂ nanostructures for glycerol oxidation

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Calculation of conversion, selectivity and carbon mass balance for (photo-)catalytic glycerol oxidation

Glycerol conversion X in % at time t

$$X_{glycerol}(t) = \frac{c_{glycerol}^0 - c_{glycerol}(t)}{c_{glycerol}^0} \cdot 100 \quad \text{Eq. 1}$$

Selectivity S to product i in % at time t

$$S_i(t) = \frac{c_i(t)}{c_{glycerol}^0 - c_{glycerol}(t)} \cdot 100 \quad \text{Eq. 2}$$

Carbon mass balance in % at time t

$$CMB(t) = \frac{3 \cdot c_{glycerol}(t) + \sum_i n_i \cdot c_i(t)}{3 \cdot c_{glycerol}^0} \cdot 100 \quad \text{Eq. 3}$$

where

$c_{glycerol}^0$ – initial molar concentration of glycerol in mol L⁻¹,

$c_{glycerol}(t)$ – molar concentration of glycerol at time t ,

$c_i(t)$ – molar concentration of product i at time t ,

n_i - number of carbon atoms in product i.

Table S1. Theoretical amounts of deposited Au on TiO₂ (P25) compared with determined amounts via EDX analysis. Additionally, the mean particle sizes of Au NPs are reported (determined by TEM studies; at least 400 counts per sample).

Theoretical amount / wt%	EDX analysis / wt%	Mean particle size/ nm
1	0.9	$3.1 \pm 0.8^*$
5	5.4	3.5 ± 1.0
7.5	7.8	3.0 ± 1.0
10	10.2	3.2 ± 0.8
12.5	13.3	3.0 ± 1.1
15	15.8	3.8 ± 1.5

*100 counts per sample.

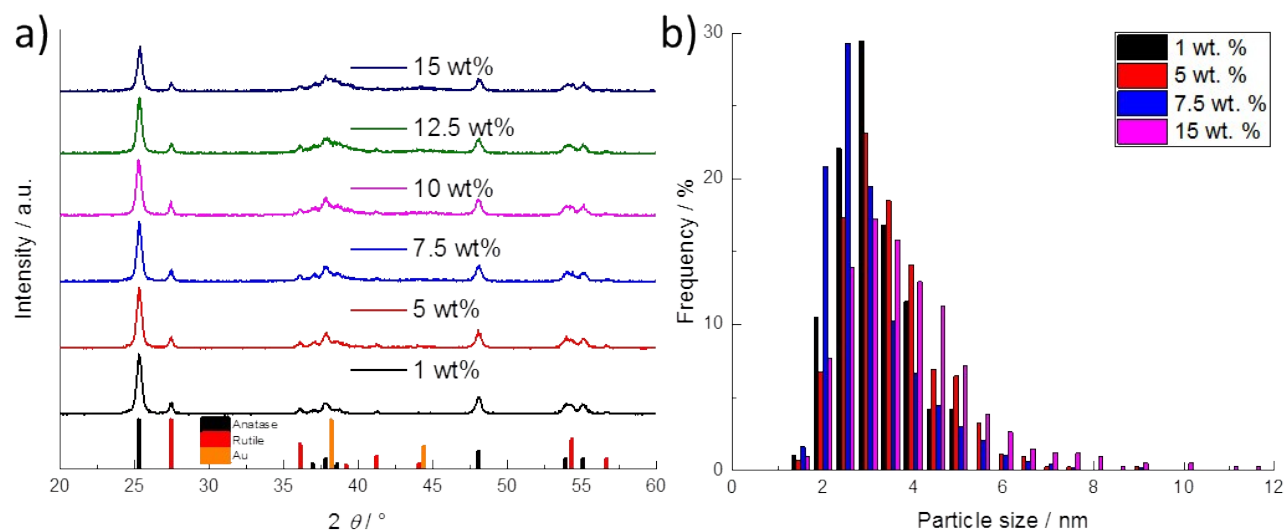


Figure S1. a) XRD patterns of prepared Au/TiO₂ with different Au loading amounts. The diffraction peak associated with [111] Au signal at ca. 38.2° is superimposed with the signal of TiO₂ anatase. Hence, only with high Au loading amounts signals can be observed for Au NPs. b) Au NP size

distribution for Au/TiO₂ with depicted Au loading amounts. More than 400 counts per sample, except for 1 wt% where 100 counts were performed.

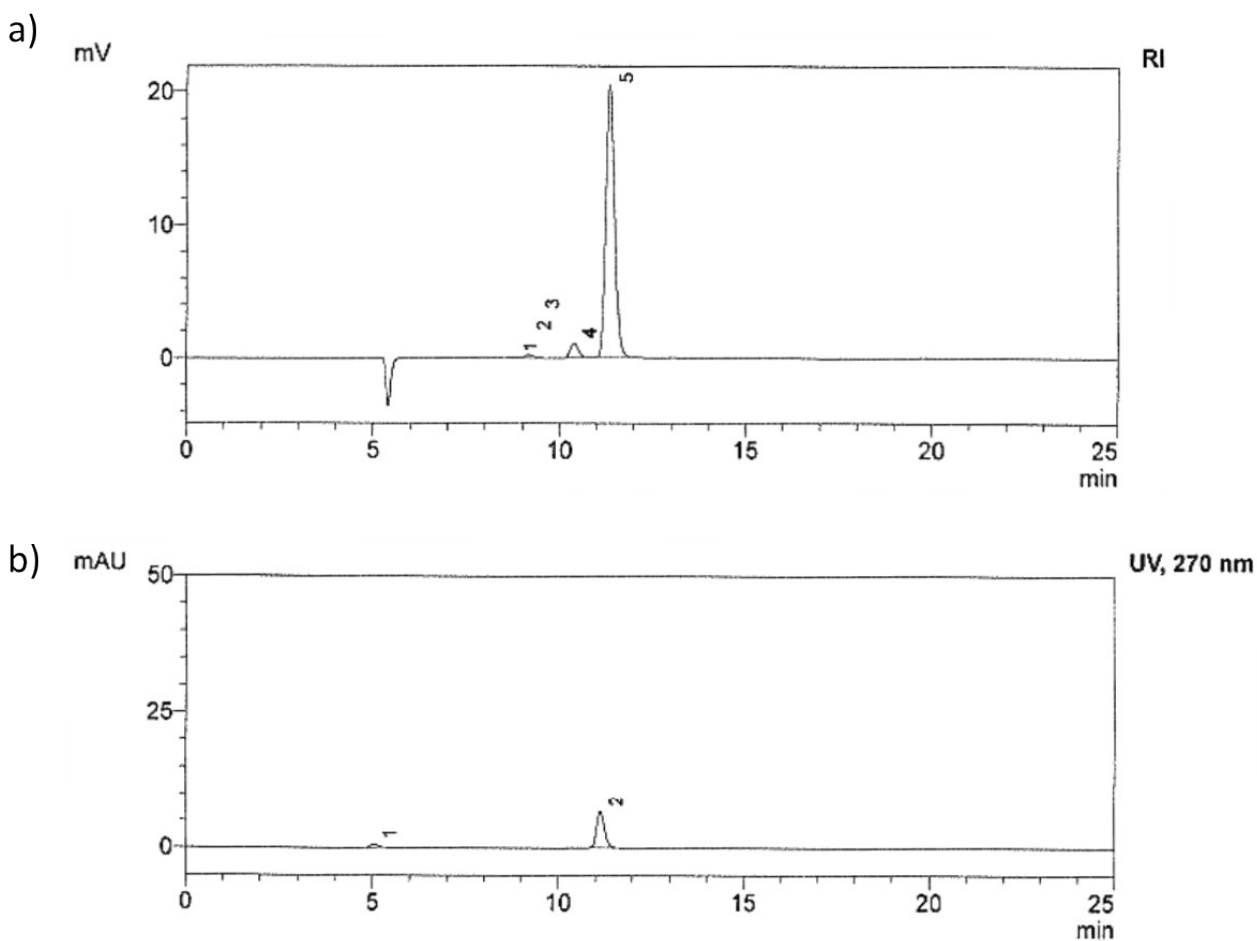


Figure S2. Typical chromatogram for product analysis of glycerol oxidation experiments. a) Detection via refractive index for products like glycolic acid (1), glyceric acid (4), and not converted glycerol (5). b) Detection via UV at 270 nm for dihydroxyacetone (2). The detection was performed *via* refractive index, whereas dihydroxyacetone was additionally detected *via* UV-vis at 270 nm. With this method, one can circumvent the problem of overlap between glycerol and dihydroxyacetone. Neither glycerol nor formic acid give a signal at 270 nm, which verifies that the observed signal can be assigned to dihydroxyacetone. The amount of dihydroxyacetone detected by UV analysis is then subtracted from the determined glycerol amount detected by refractive index. Hence, the true amount of glycerol can then be calculated.

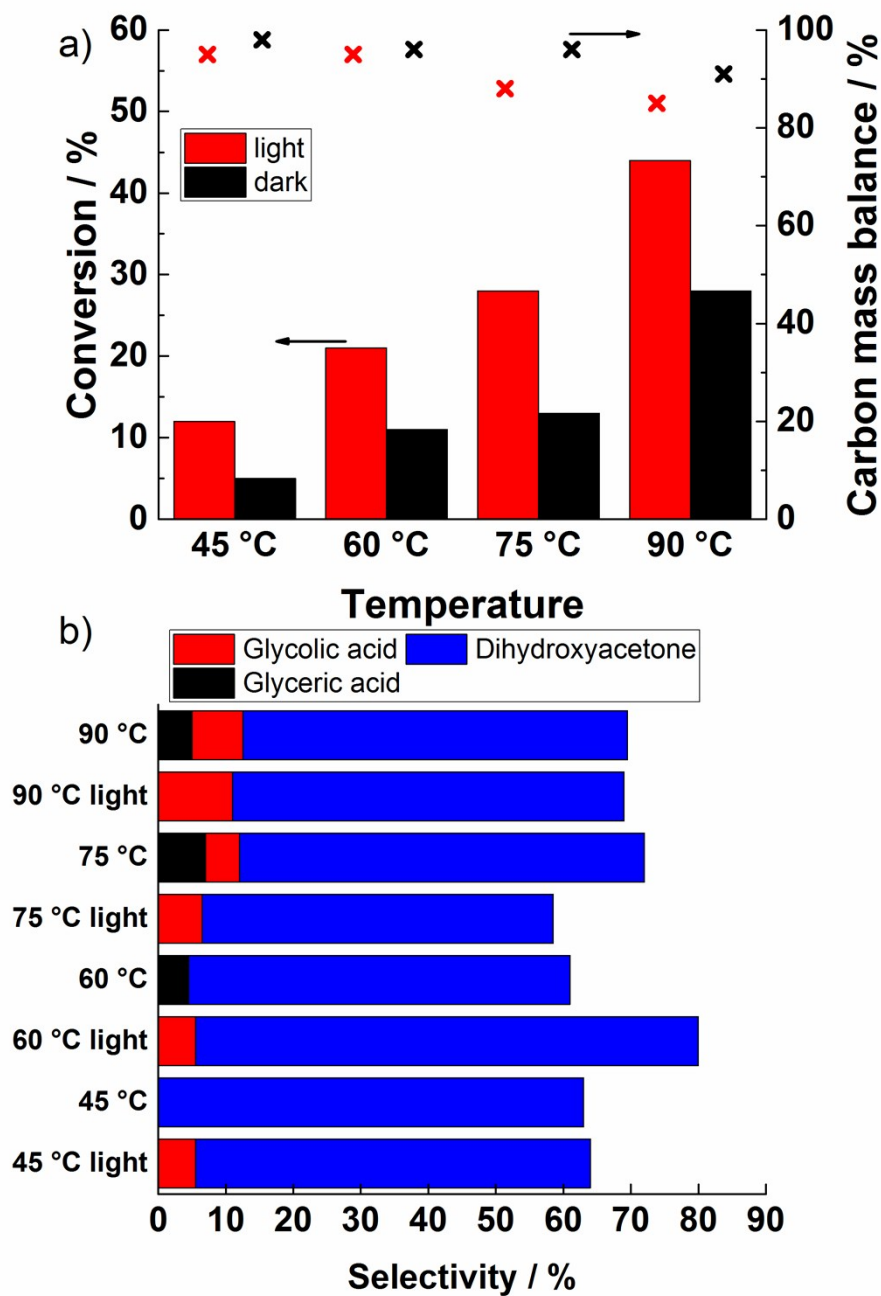


Figure S3. a), b) Conversions and selectivities for different reaction temperatures of (photo-)catalytic glycerol oxidation experiments for 7.5 wt% Au/TiO₂. Reaction conditions: 1 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 5 bar pure O₂, 5 h reaction time, visible light irradiation ($\lambda > 420$ nm) if denoted.

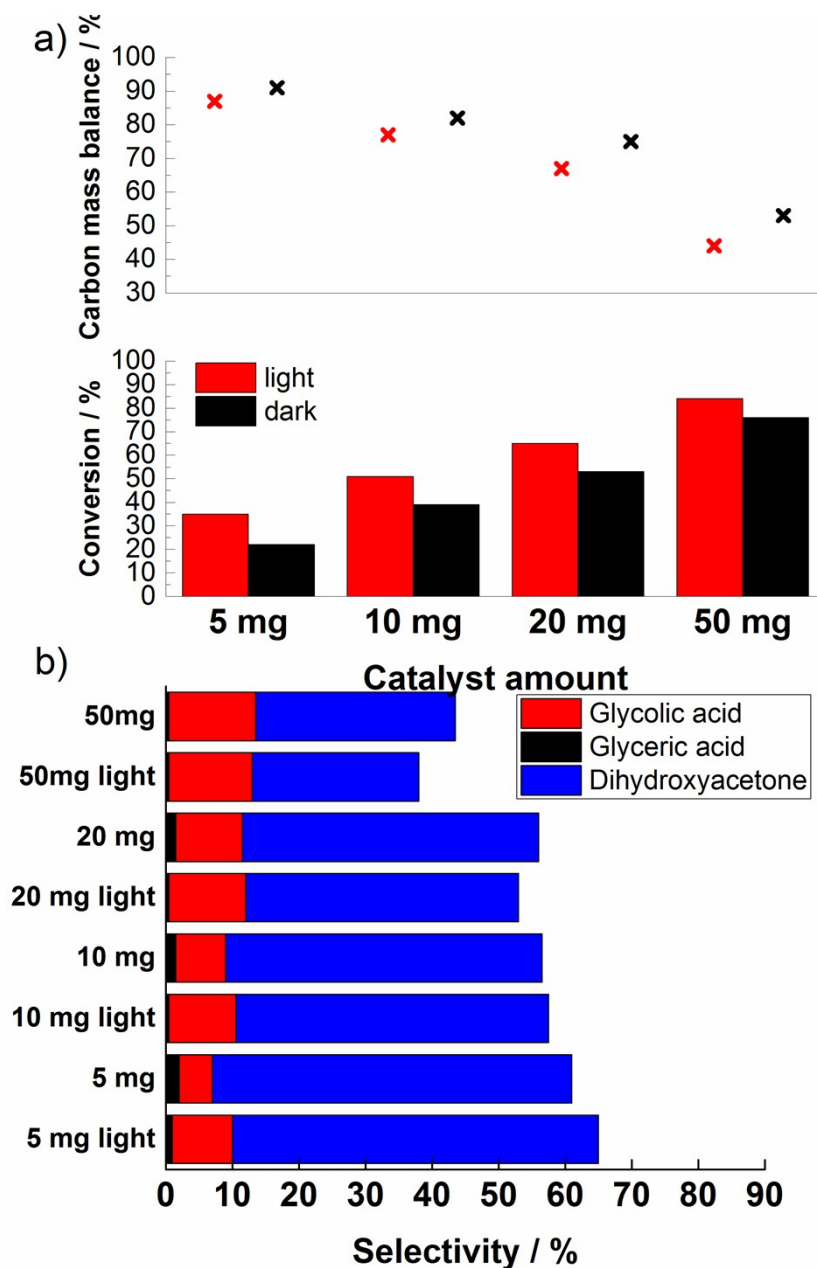


Figure S4. a), b) Conversions and selectivities for different catalyst amounts of (photo-)catalytic glycerol oxidation experiments for 7.5 wt% Au/TiO₂. Reaction conditions: 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 90 °C, 5 bar pure O₂, 3 h reaction time, visible light irradiation ($\lambda > 420$ nm) if denoted.

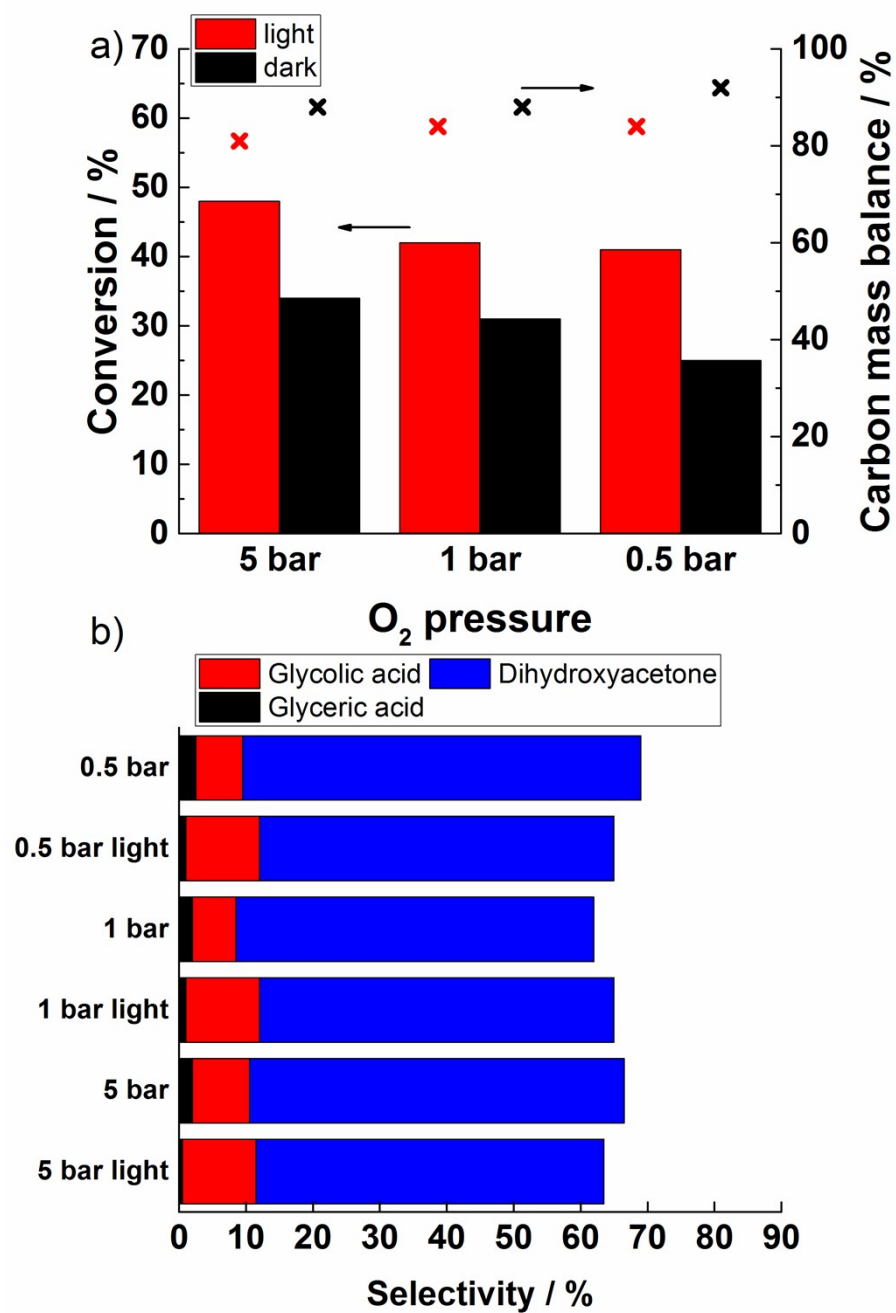


Figure S5. a), b) Conversions and selectivities for different O₂ pressures of (photo-)catalytic glycerol oxidation experiments for 7.5 wt% Au/TiO₂. Reaction conditions: 2 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 3 h reaction time, 90 °C, visible light irradiation ($\lambda > 420$ nm) if denoted.

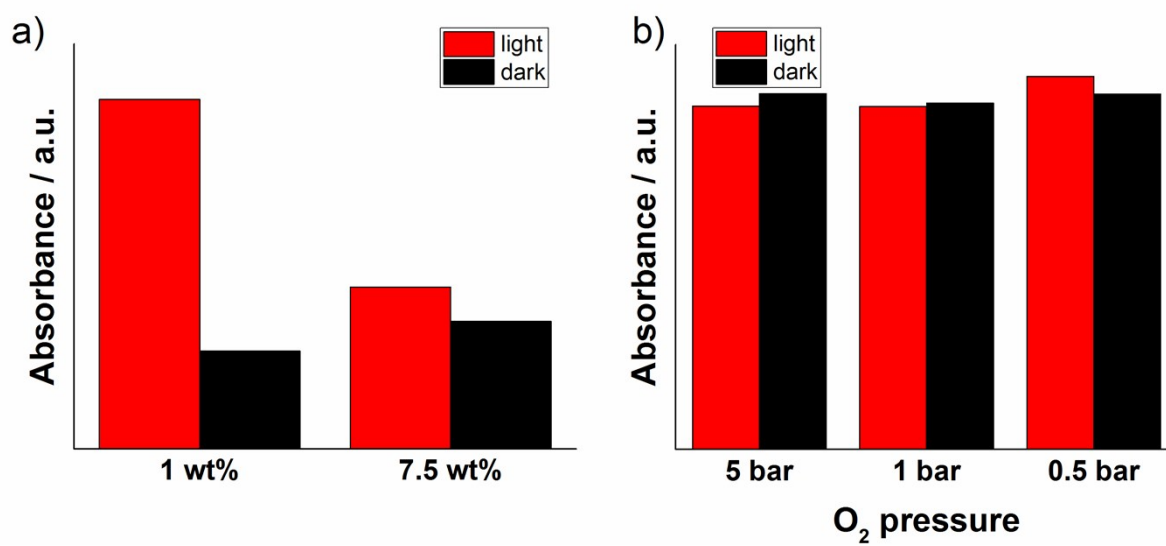


Figure S6. a) Tracking of H₂O₂ formation for Au/TiO₂ with different Au loading amounts via UV-vis spectroscopy after 3 h reaction. The absorbance is measured at 405 nm. For detailed procedure see Experimental Section. Reaction conditions: 1 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 3 h reaction time, 90 °C, 5 bar pure O₂, visible light irradiation ($\lambda > 420$ nm) if denoted. b) Tracking of H₂O₂ formation for 7.5 wt% Au/TiO₂ via UV-vis spectroscopy after 3 h reaction for different O₂ pressures. The absorbance is measured at 405 nm. Reaction conditions: 2 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 3 h reaction time, 90 °C, visible light irradiation ($\lambda > 420$ nm) if denoted.

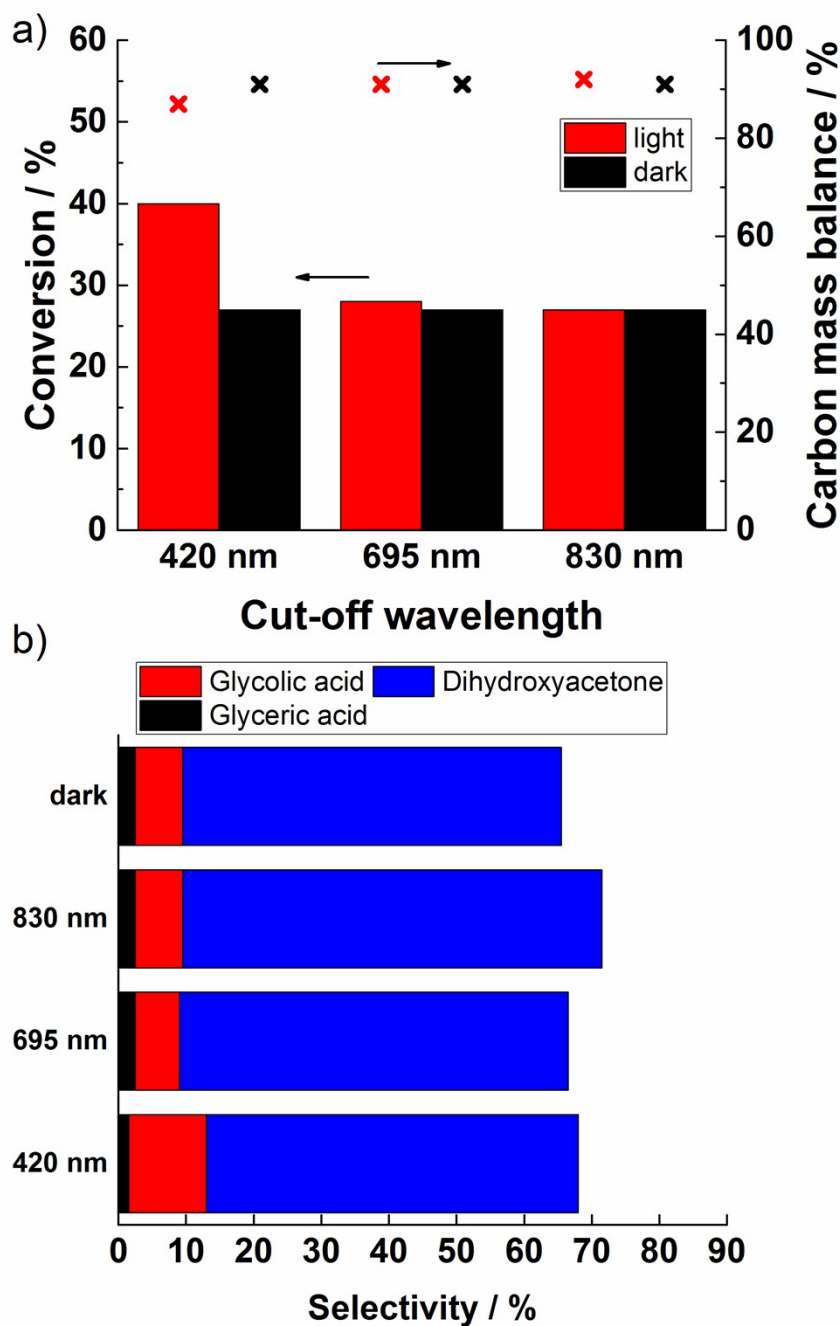


Figure S7. a), b) Conversions and selectivities for different cut-off wavelengths of (photo-)catalytic glycerol oxidation experiments for 7.5 wt% Au/TiO₂. Reaction conditions: 1 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 90 °C, 5 bar pure O₂, 5 h reaction time, visible light irradiation if denoted. Note that experiments under irradiation were performed with additional neutral density filter NG 5 (Schott, 70% transmission) in order to preserve the cut-off filter from high intensity. Hence, the reaction conducted with $\lambda > 420$ nm shows comparably lower conversion.

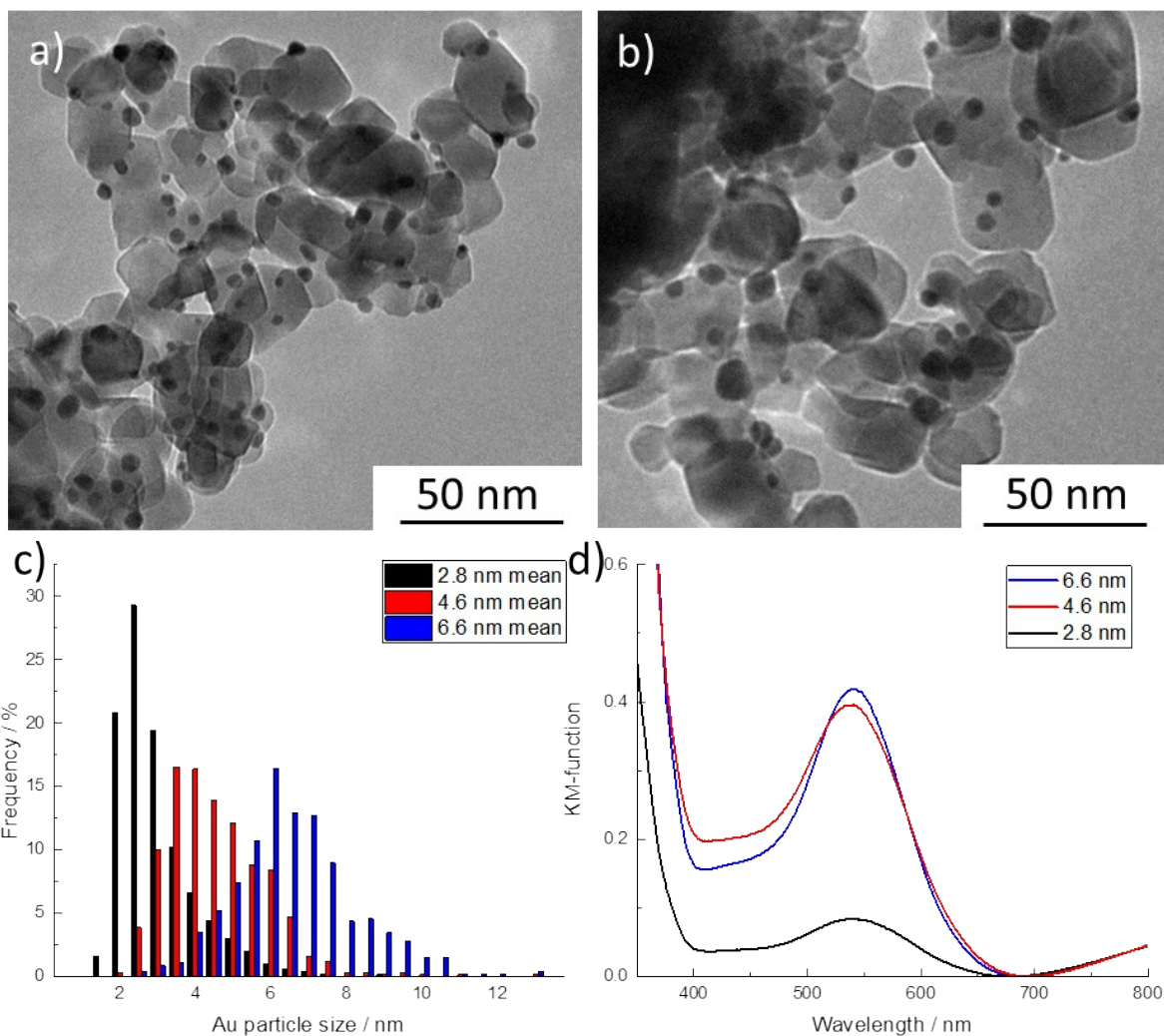


Figure S8. TEM micrographs of 7.5 wt% Au/TiO₂ for a) 4.6 nm mean Au particle size (567 counts) and b) 6.6 nm mean Au particle size (456 counts). c) Au particle size distributions for 7.5 wt% Au/TiO₂ with depicted Au mean particle sizes. d) Diffuse reflectance UV-vis spectra (Kubelka-Munk function vs. wavelength) of 7.5 wt% Au/TiO₂ for different mean Au particle sizes. All spectra are set to the same baseline at 800 nm. The samples are diluted with P25 with a weight ratio of 1:3 = sample:P25.

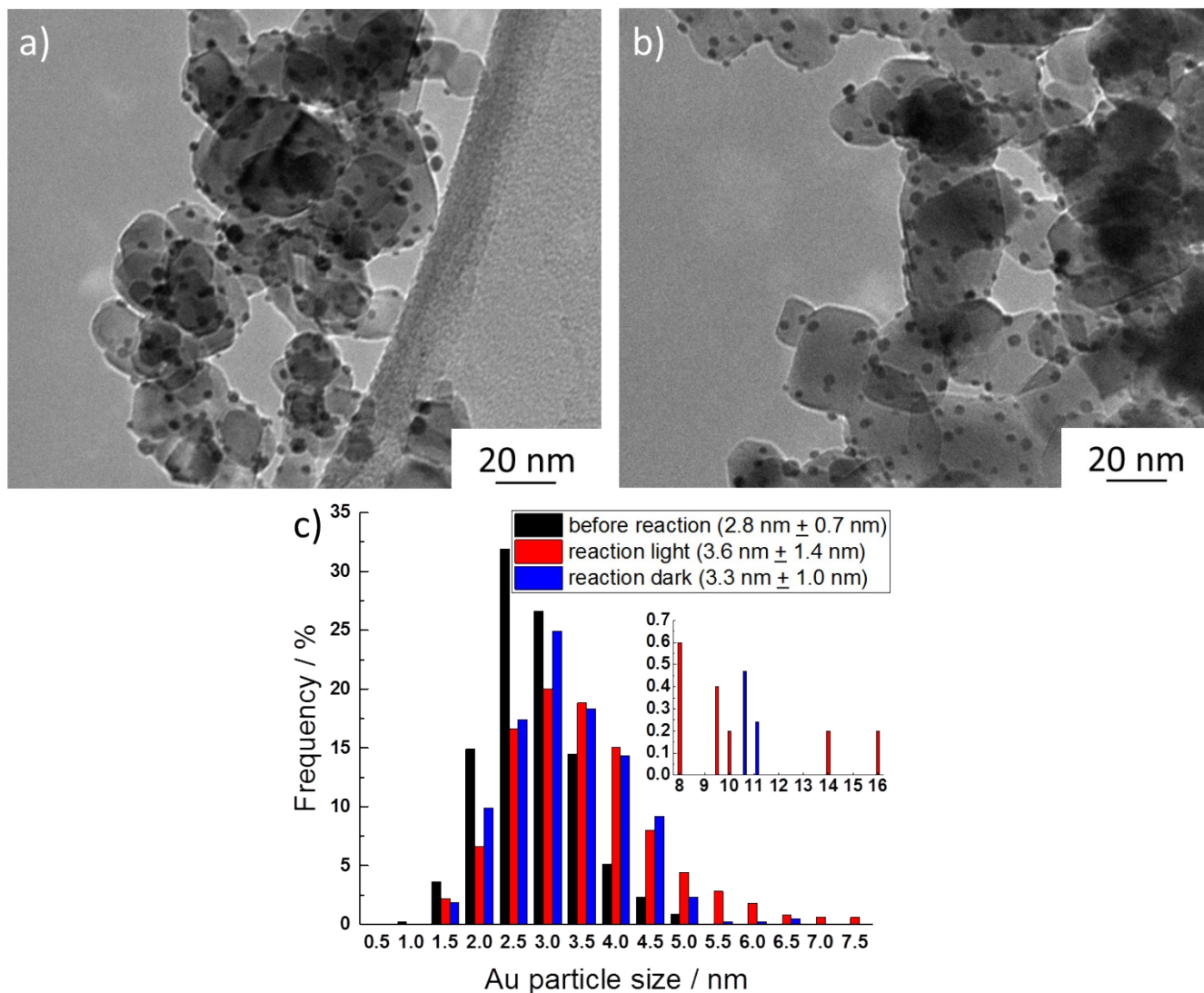


Figure S9. TEM micrographs of 7.5 wt% Au/TiO₂ after reaction with light irradiation (a) and under dark conditions (b). c) Au NP size distributions for 7.5 wt% Au/TiO₂ before and after reaction with light irradiation or under dark conditions. Au average particle sizes for the samples are given in parentheses (more than 400 counts per sample). Reaction conditions: 1 g L⁻¹ catalyst, 5 mL 0.05 M aqueous glycerol solution, initial pH = 7, 90 °C, 5 bar pure O₂, 5 h, visible light irradiation ($\lambda > 420$ nm) if denoted.