In-situ study of photoelectron injection into electrolyte under stepwise coarsening of nanoporous gold (npAu)

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Aim

npAu with high surface to volume ratio:

examine the internal quantum efficiency of charge transfer from nanoporous gold (npAu) thin films with small ligament size (L)<10 nm.

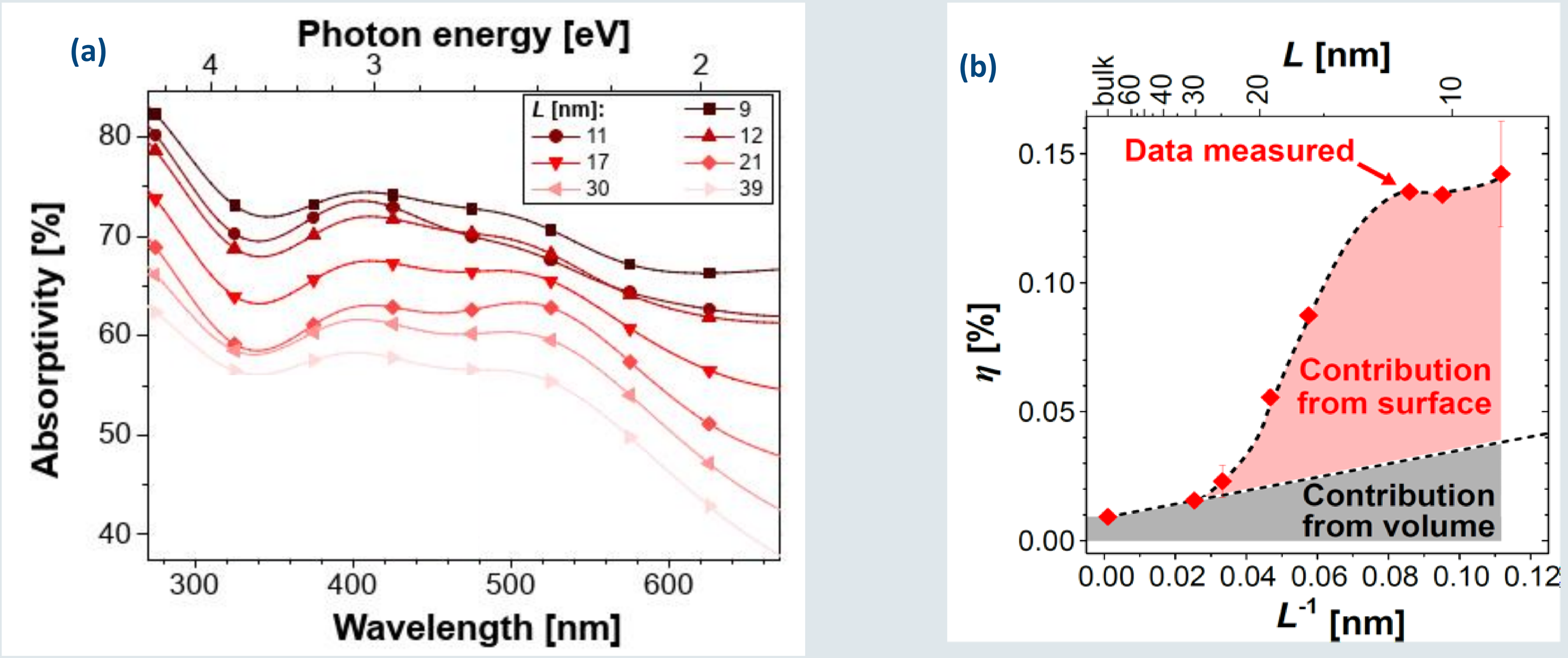
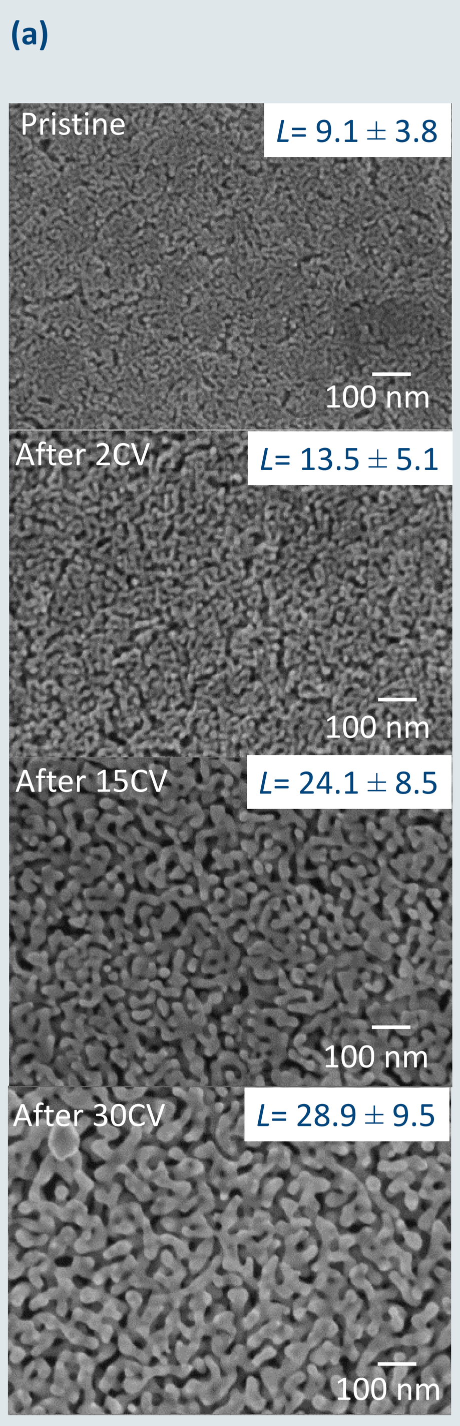


Fig. 1: Previous results on ligament size dependence of **(a)** internal absoptivity **(b)** efficiency, η [1].

Rough electrochemical coarsening



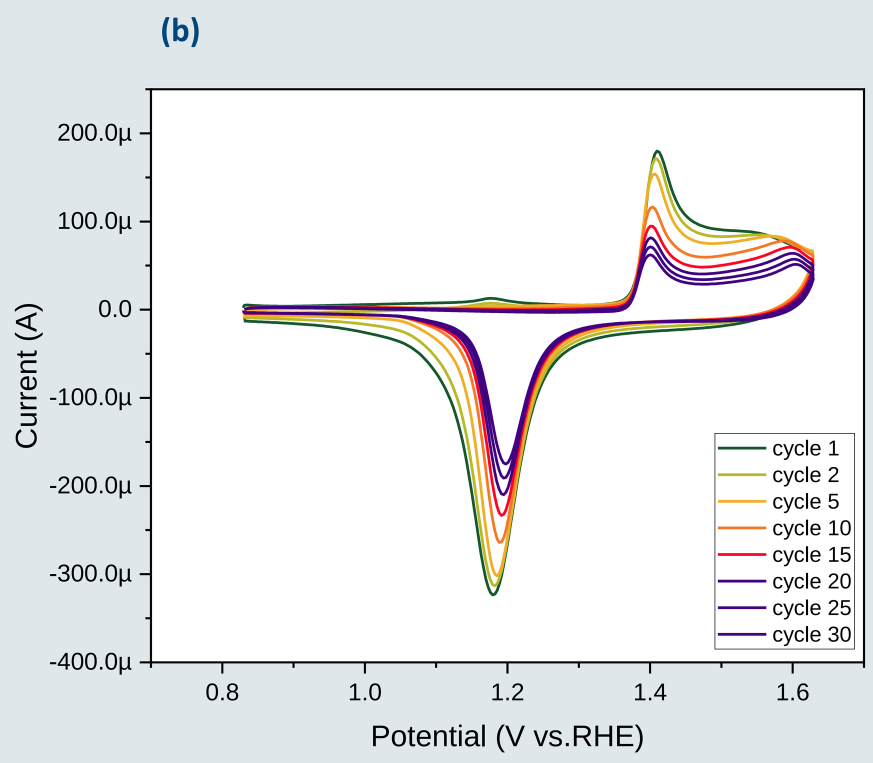


Fig. 2: (a) SEM micrographs of the pristine sample and after the specified numbers of cycles, **(b)** CV of the npAu in the potential window of 0.83 - 1.63 V vs. RHE; electrolyte: 0.5 M H_2SO_4, scan rate: 10 mV/s.

- The area under the current peaks decreases with the subsequent potential cycling
- Novel method to study charge transfer by in-situ changing the ligament size

Fine electrochemical coarsening

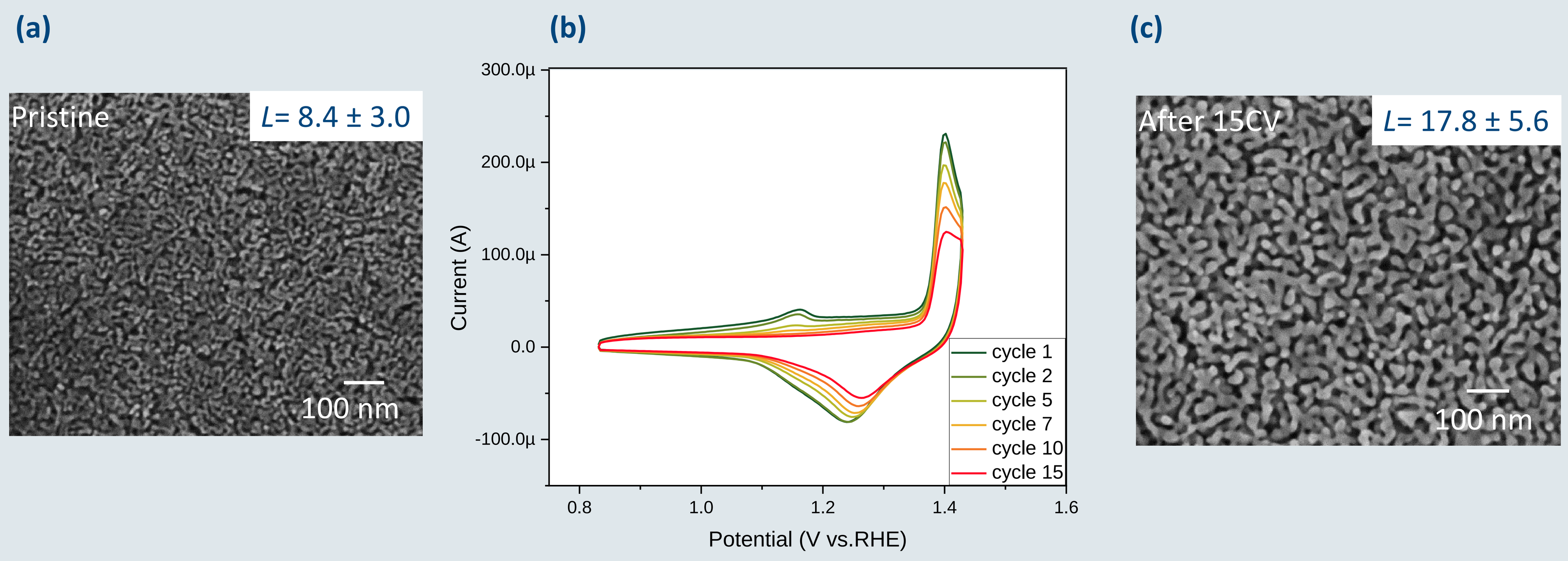


Fig. 3: (a) *SEM of the pristine npAu sample* **(b)** *CV of npAu in the potential window of 0.53 - 1.43 V vs. RHE; electrolyte: 0.5 M H_2SO_4, scan rate: 10 mV/s,* **(c)** *SEM after 15 CV scans.*

Limiting the upper part of the CV window makes smaller steps in the coarsening

Absorptivity of npAu

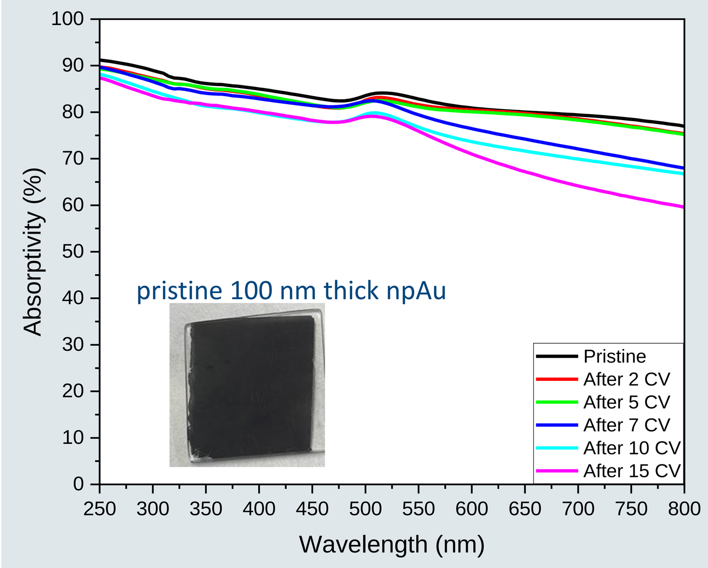


Fig. 4: Absorptivity of npAu films before and after CVs.

- Absorption is broadband due to the contribution of free electrons
- Increasing ligament size leads to slight decrease of absorption due to increasing reflection from npAu

Photoemission

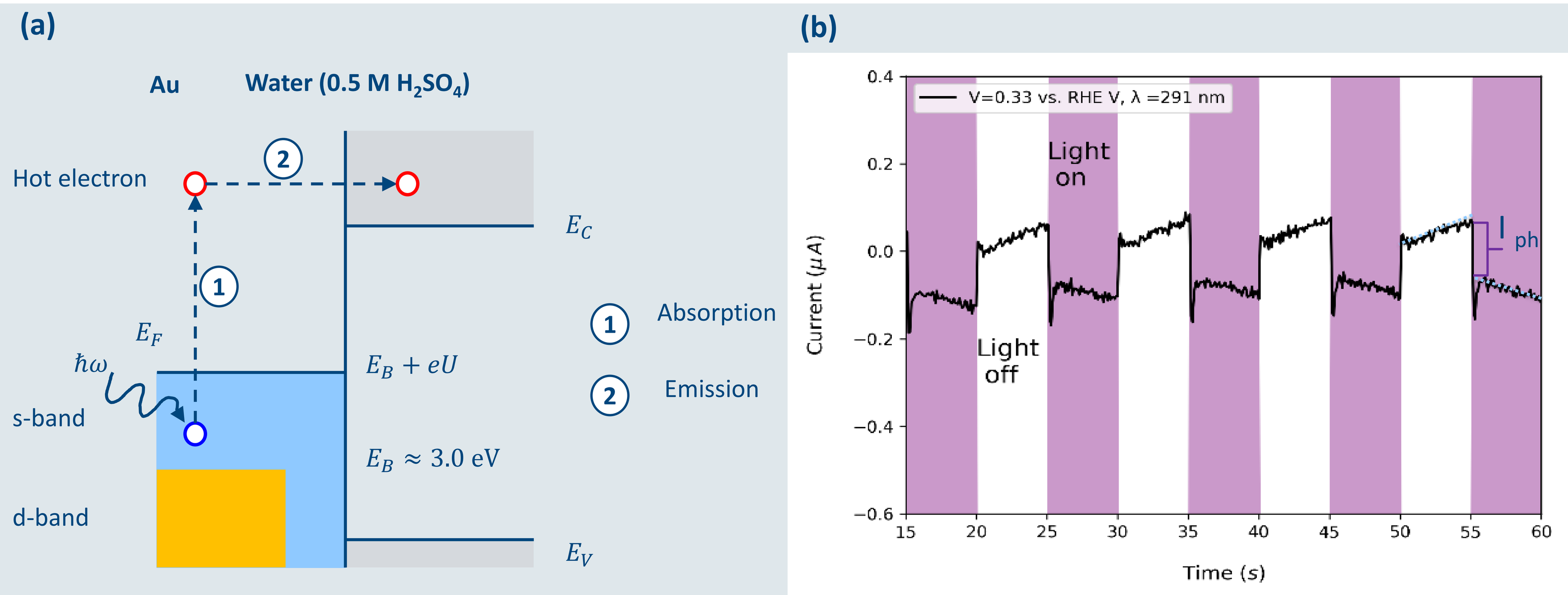
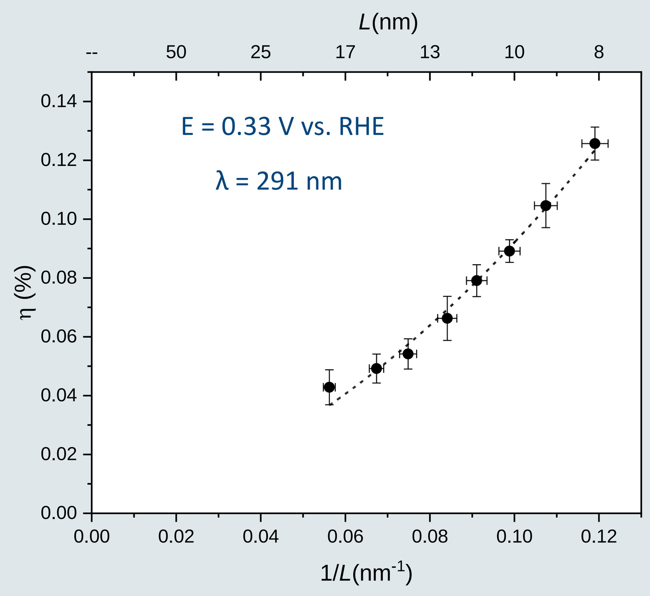


Fig. 5: (a) Scheme of electron photoemission from gold into water **(b)** current transients for 100 nm-thick npAu detected experimentally.



internal quantum efficiency:

$$\eta = \frac{N_e}{N_{ph}} = \frac{I_{ph}}{e}\frac{\hbar\omega}{AP}$$

N_e : no. of electrons
N_{ph} : no. of absorbed photons
I_{ph} : photocurrent
P : power
A : absorptivity

Fig. 6: Size-dependence of the internal quantum efficiency η. The dashed line is a parabolic fit with linear and quadratic terms versus L^{-1}.

	Excitation probability	Emission probability	Internal quantum efficieny
Volume effect	$P^{Ex}_{v} = \text{const}$	$P^{Em} \sim \frac{1}{L}$	$\eta_V \sim \frac{1}{L}$
Surface effect	$P^{Ex}_{s} \sim \frac{1}{L}$		$\eta_S \sim \frac{1}{L^2}$

- At a ligament diameter of 10 nm, the contribution from linear term 0.03% is smaller than from quadratic term 0.061 %.
- The photoemissionof npAu with small ligament size is 1-2 orders of magnitude larger than emission observed at similar wavelengths from flat gold electrodes.

Summary and outlook

- NpAu with ligament sizes below 10 nm for optical characterization achieved.
- Electrochemical annealing in aqueous electrolyte employed for in-situ fine coarsening of npAu in the photoelectrochemical setup.
- Strong contribution from surface photo effect at a ligament size of 10 nm was observed.
- OH adsorbates and organothiol molecules will be employed to tailor charge transfer mechanism.

References

[1] Graf, M. et al., ACS Catal. 9, 3366 (2019).
[2] Graf, M. et al., ACS Nano 15, 2 (2021).

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