Wavelength Dependence of Plasmon-Driven Catalysis on Nanoporous Au-Ag Shells

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Table S1. Reaction rate constants of different substrates at various excitation wavelengths and laser powers

Substrate	Power (mW)	λ (nm)	k_{1141} (s^{-1})	k_{1391} (s^{-1})	k_{1440} (s^{-1})
NPASs	0.17	532	0.0073	0.0044	0.0105
		633	0.0027	0.0021	0.0023
NPASs	0.42	532	0.0330	0.0215	0.0433
		633	0.0198	0.0170	0.0206
Ag NPs	0.42	532	0.0170	0.0163	0.0168
		633	0.0079	0.0078	0.0062
Au NPs	0.42	532	0.0029	0.0029	0.0016
		633	1.6×10^{-4}	1.4×10^{-4}	2.6×10^{-4}

Table S2. Wavelength dependence factor R (k_{532}/k_{633}) of different substrates at 0.42 mW

Substrate	R_{1141}	R_{1391}	R_{1440}	R_{avg}
NPASs	1.7	1.3	2.1	1.7
Ag NPs	2.2	2.1	2.7	2.3
Au NPs	18.1	20.7	6.2	15.0

Calculation details for AQY:

The estimated apparent AQY is defined as the ratio between the initial reaction-event rate R_0 and the incident photon flux N_{photon}:

$$\mathrm{AQY}(\%) = \frac{R_0}{N_{photon}} \times 100\%$$

The incident photon flux was calculated as:

$$N_{photon} = \frac{P\lambda}{hc}$$

where h is Planck's constant, and c is the speed of light. The illuminated projected area was estimated as $A = \pi (d/2)^2$ with $d \approx 2\mu m$. The number of surface molecules in the illuminated region was estimated as $N_0 = \sigma A$, using σ = 4–6 molecules·nm^{-2} as a conservative surface-density range supported by reference-free RF-GIXRF quantification of thiol SAMs on planar Au[1]. In Ref.[1], surface densities of ~4.1 molecules nm^{-2} are reported for aromatic thiols, whereas small linear alkanethiols can reach ~7.6 molecules nm^{-2}; therefore, σ = 4–6 molecules nm^{-2} was adopted to bracket uncertainty for our aromatic thiolate probe. Here, R_0 is defined as the initial DMAB formation rate, approximated as $R_0 = k_{avg} N_0$.

$$k_{avg} = \frac{k_{1141} + k_{1391} + k_{1440}}{3}$$

where k_{avg} is the arithmetic mean obtained from three DMAB bands (1141, 1391, 1440 cm^{-1}).

This is an estimated apparent AQY based on incident photons and an estimated surface density. The absolute AQY may be affected by differences in real surface area (roughness factor) among substrates; however, wavelength-dependent comparisons on the same substrate are less sensitive to the assumed σ.

1. Cara, E.; Hönicke, P.; Kayser, Y.; et al. Molecular surface coverage standards by reference-free GIXRF supporting SERS and SEIRA substrate benchmarking. *Nanophotonics* **2024**, *13*, 4605-4614.

Table S3. Estimated apparent AQY at P=0.42 mW

Substrate	λ (nm)	k_{avg} (s^{-1})	AQY (%) at σ=5	AQY (%) range （σ=4-6）
NPASs	532	0.0326	4.55×10^{-8}	$(3.64–5.46)\times10^{-8}$
NPASs	633	0.0191	2.25×10^{-8}	$(1.80–2.70)\times10^{-8}$
Ag NPs	532	0.0167	2.33×10^{-8}	$(1.87–2.80)\times10^{-8}$
Ag NPs	633	0.0073	8.57×10^{-9}	$(6.85–10.3)\times10^{-9}$
Au NPs	532	0.00247	3.45×10^{-9}	$(2.76–4.13)\times10^{-9}$
Au NPs	633	0.000187	2.19×10^{-10}	$(1.75–2.63)\times10^{-10}$

Note: N_{photon} was calculated to be 1.12×10^{15} photons/s at 532 nm and 1.34×10^{15} photons/s at 633 nm (P = 0.42 mW).

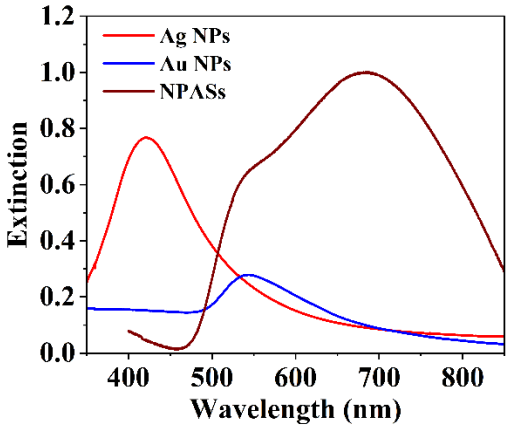


Figure S1. Raw (non-normalized) UV-Vis extinction spectra of Ag NPs, Au NPs, and NPASs.