Supporting information

Plasmonic Fabry-Pérot nanocavities produced via solution methods

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Materials:

Diethyl sulfide (DES, 98%), copper(I) thiocyanate (CuCSN, 99%), 4-methoxythiophenol (97%), tannic acid (99.5%), sodium citrate tribasic dihydrate (99%), were purchased from Merck (Sigma-Aldrich). Hydrogen tetrachloaurate(III) hydrate ($HAuCl_4$, Au wt.% ≥ 49%) was purchased from Thermo Fisher Scientific. All the chemicals and reagents were used as received.

Fabrication methods:

Gold nanoparticles (Au NPs) synthesis

As described elsewhere, Au NPs were prepared using a modified Turkevich method.[1] Briefly, a sodium citrate tribasic dihydrate (50 mL, 6.6 mM) water solution was put in a 100 mL round-bottom flask and stirred at 70 °C in an oil bath. Then, 0.1 mL (2.5 mM) tannic acid was added to the reaction mixture. Finally, 1 mL of (25 mM) $HAuCl_4$ was added instantly. After 5 min, the reaction mixture changed from dark blue to a wine colour, indicating the Au nanoparticle formation. The synthesised Au nanoparticles were stored in a fridge at 4 °C.

Characterization methods:

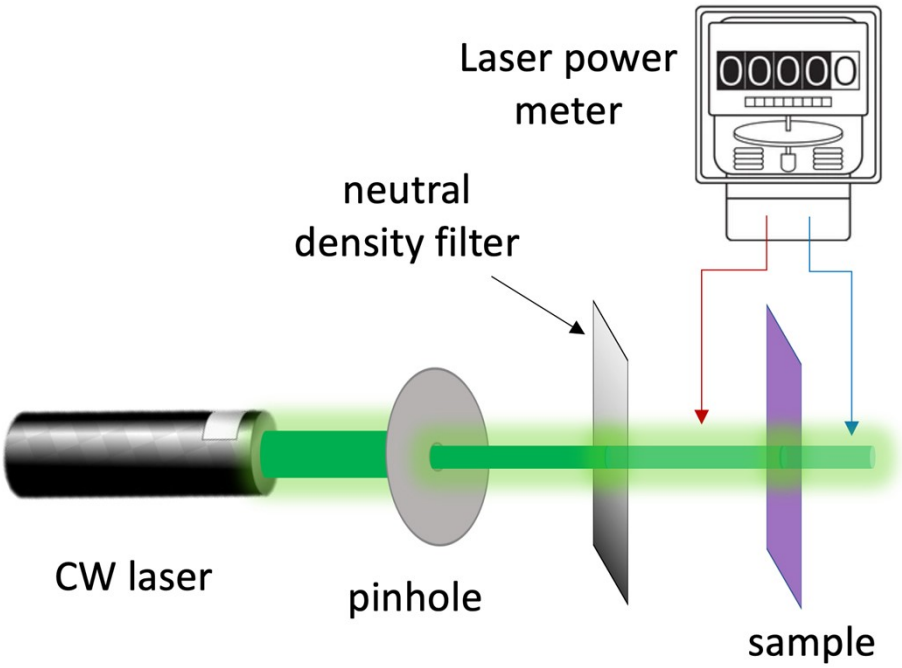
The Au NPs optical absorption was characterised via UV-vis spectra on a Cary 5000 UV-VIS-NIR (Agilent Technologies) spectrophotometer. Dynamic Light Scattering (DLS) in a Malvern Panalytical Zetasizer nanoS instrument estimated their average particle size and homogeneity. A total of 3 measurements comprised of 12 scans were done each time.

Scanning electron microscopy (SEM) was performed using a Zeiss Merlin microscope (Myfab, Ångström Laboratory). The acceleration voltage was 5 kV, and the working distance was 5-7 mm. The Au NPs were deposited on FTO glass. Cross-sections were measured from cleaved devices using a diamond-edge knife.

The films' surface topography was imaged by Atomic Force Microscopy (AFM) Nanosurf AG with a long Si cantilever in tapping mode with an Al reflex. The films' optical absorption was measured on a Cary 5000 UV-VIS-NIR (Agilent Technologies) spectrophotometer using an integrating sphere.

Transient absorption spectroscopy (TAS) was used to determine plasmon relaxation dynamics. A 40-fs pulsed laser with a 3 kHz repetition rate was generated through the Libra Ultrafast Amplifier System designed by Coherent. An optical parametric oscillator (TOPAS- prime, Light Conversion) created the excitation beam. The signals were detected with a UV-NIR detector and a Newport MS260i spectrograph with interchangeable gratings. The fundamental laser (probe, 795 nm) passes through the delay stage (1-2 fs step size) and is focused in a Sapphire optical window to generate visible light from 400 to 750 nm. The instrument response function obtained for our system is ca. 95 fs. It should be emphasised that the TAS experiments were performed using exactly the same conditions for all devices regarding excitation fluency and illuminated area, enabling us to perform direct comparisons on lifetime and signal intensity.

Power-dependent light absorbance was performed following Scheme S1. The experiments used 532 nm and 630 nm CW lasers to evaluate the effect of exciting resonantly and non-resonantly, respectively.



Scheme S1. Power-dependent light absorbance experimental setup.

Additional data:

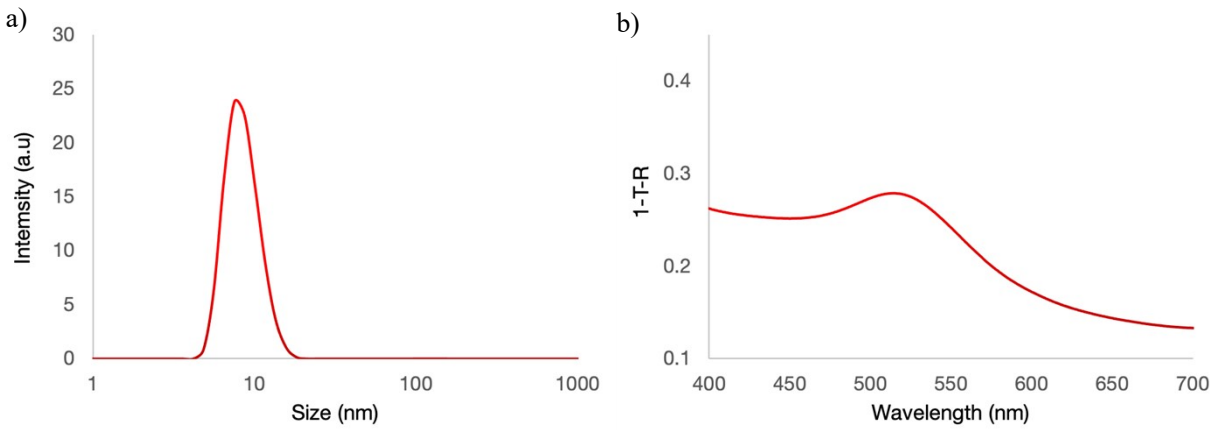


Figure S1. Au NPs solution characterisation. (a) DLS spectrum (b) UV-vis spectrum.

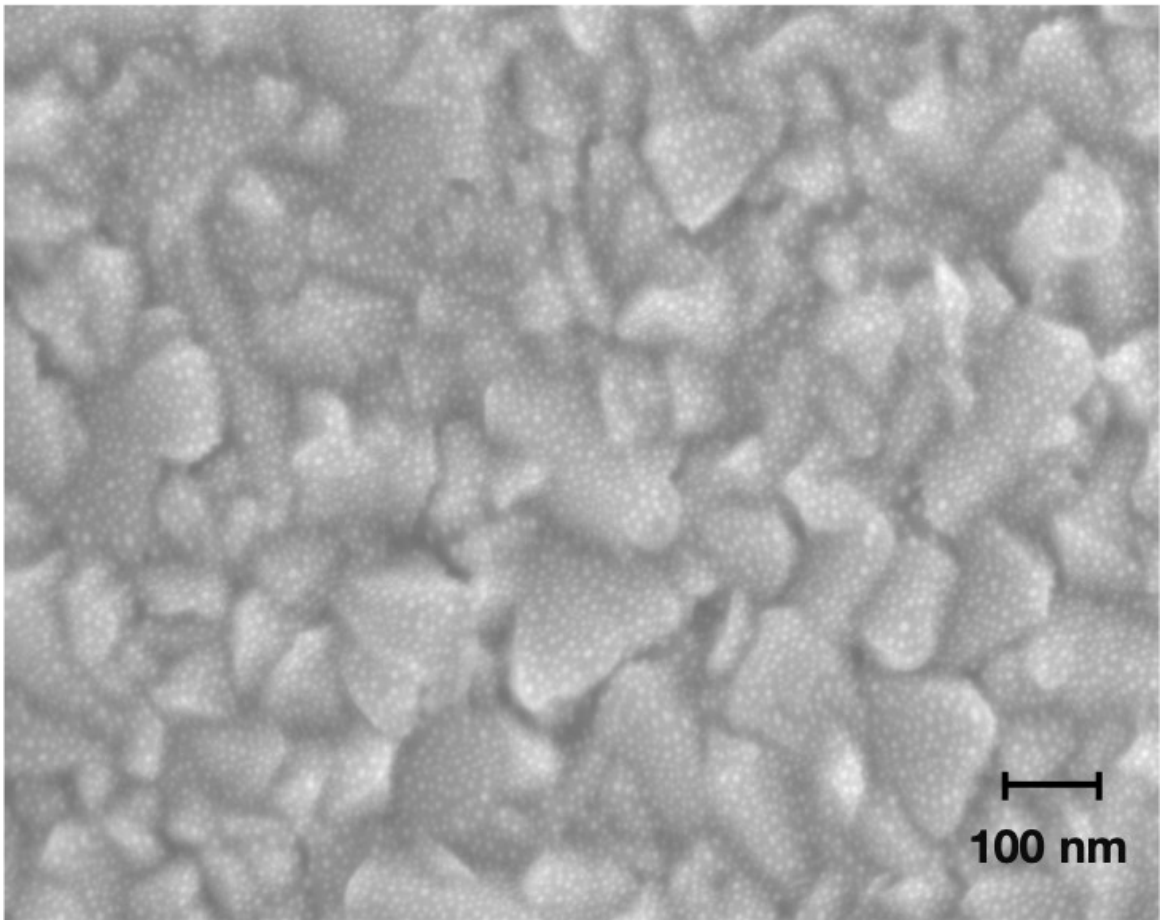


Figure S2. Scanning electron microscopy (SEM) of the Au NPs deposited on FTO glass in low magnification to establish Au NPs homogeneous distribution .

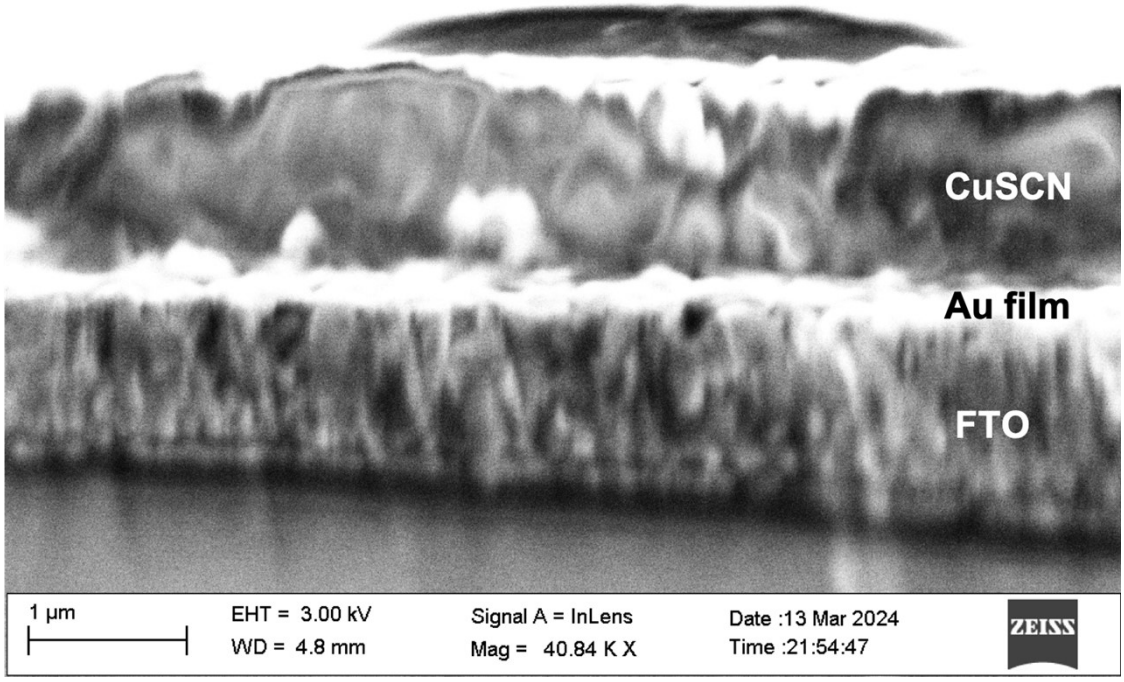


Figure S3. Scanning electron microscopy (SEM) of the nanocavity cross-section. The CuSCN layer is slightly thinner than FTO, which is known to be between 320 and 340 nm.

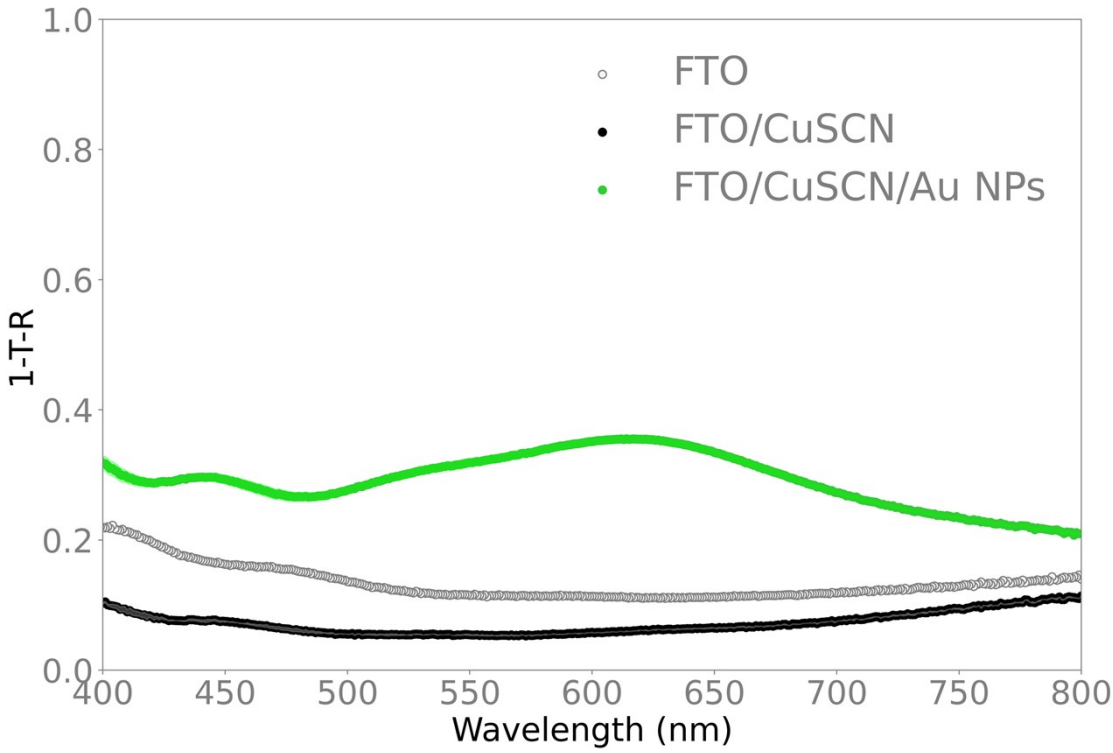


Figure S4. UV-vis spectra of the FTO (grey line), FTO/CuSCN (black line) and FTO/CuSCN/Au NPs (green line).

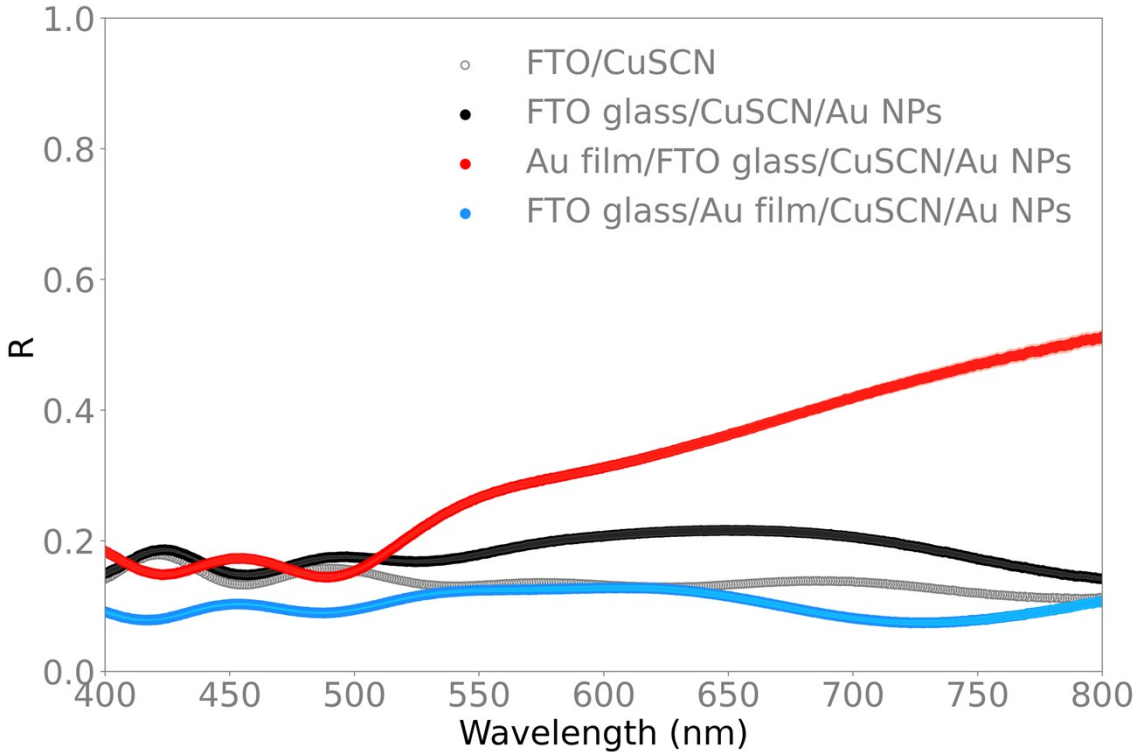


Figure S5: UV-vis reflectance spectra of the semitransparent samples: FTO/CuSCN (grey line), FTO/CuSCN/Au NPs (black line), Au film/FTO/CuSCN/Au NPs (red line) and FTO/Au film/CuSCN/Au NPs (blue line).

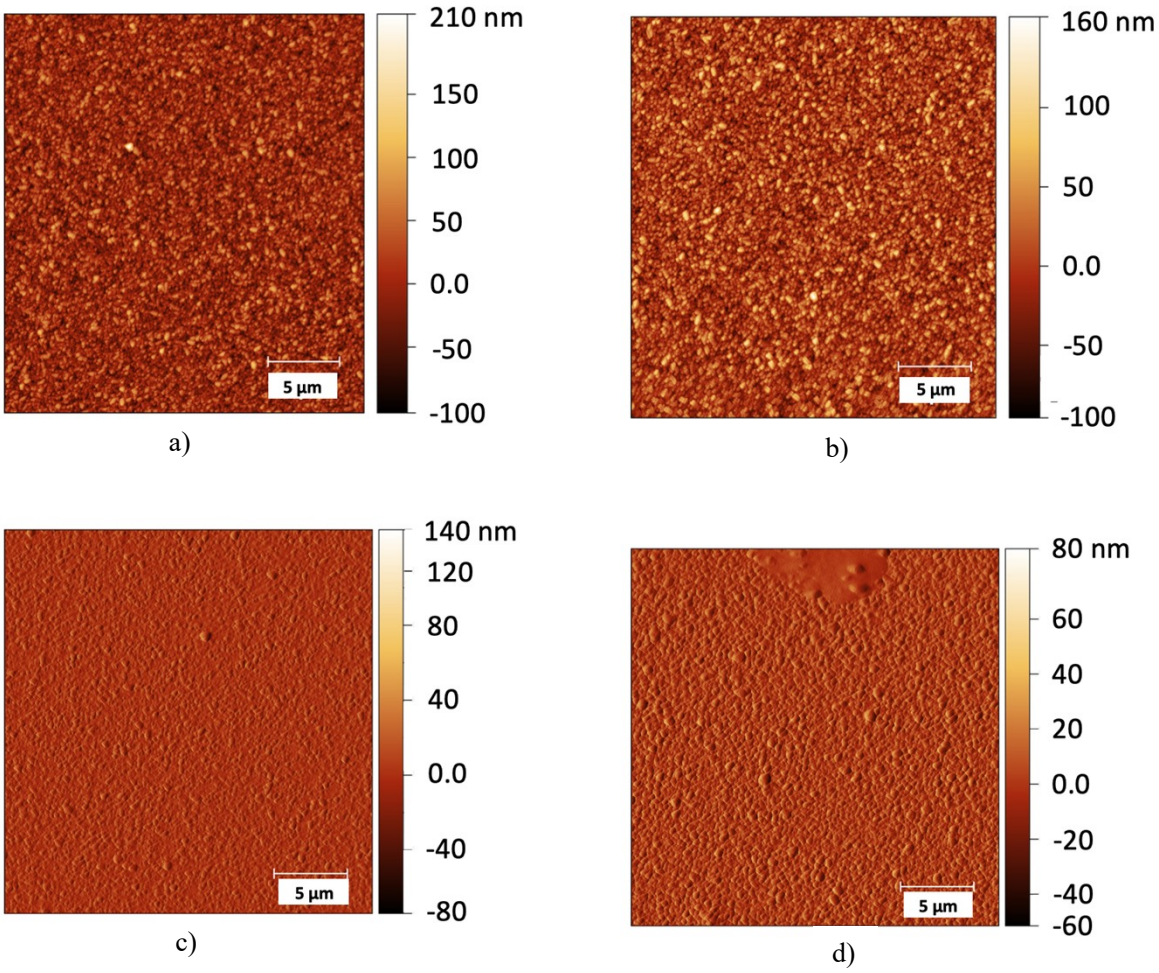


Figure S6. AFM images of the semitransparent electrodes with roughness root mean square (RMS) for each film. (a) FTO [RMS = 30.5 nm], (b) FTO/Au film [RMS = 29.5 nm], (c) FTO/Au film/CuSCN [RMS = 4.98 nm], and (d) FTO/Au film/CuSCN/Au NPs [RMS = 7.44 nm].

Table S1. Summary of the e-ph lifetimes extracted from the TAS kinetic traces.

Sample	Resonant excitation (ps)	Non-resonant excitation (ps)
FTO/Au NPs	4.0 ± 0.1	--[1]
FTO/Au film/CuSCN/Au NPs	2.2 ± 0.1	2.3 ± 0.1

[1] Too weak absorption at 650 nm, making it challenging to determine the value accurately.

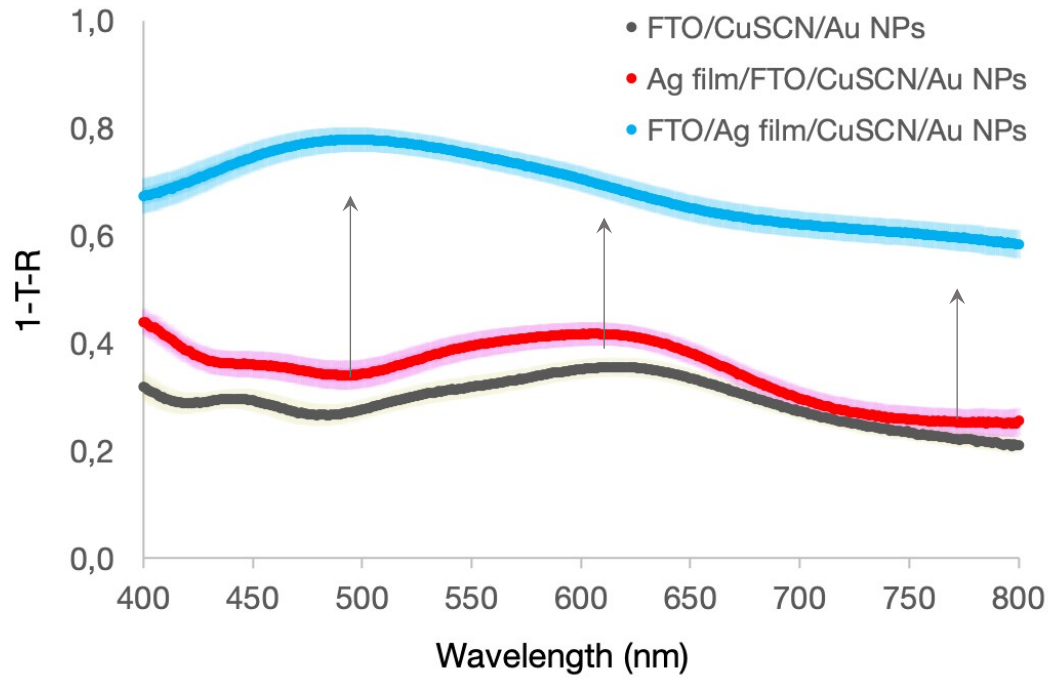


Figure S7. UV-vis spectra of the non-transparent samples with reflective metallic film (100 nm Ag). FTO/CuSCN/Au NPs (green line), Ag film/FTO/CuSCN/Au NPs (red line) and FTO/Ag film/CuSCN/Au NPs (blue line).

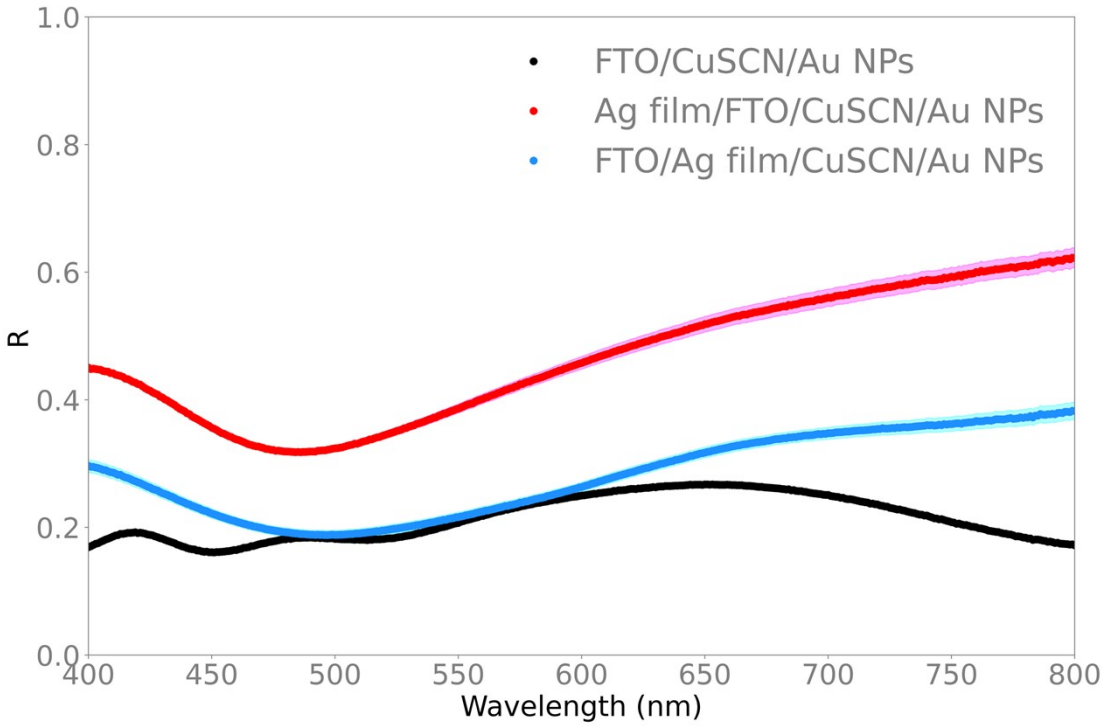


Figure S8. UV-vis reflectance spectra of the non-transparent samples with reflective metallic film (100 nm Ag). FTO/CuSCN/Au NPs (black line), Ag film/FTO/CuSCN/Au NPs (red line) and FTO/Ag film/CuSCN/Au NPs (blue line).

References:

1 Piella, J.; Bastús, N. G.; Puntes, V. Size-Controlled Synthesis of Sub-10-nanometer Citrate-Stabilized Gold Nanoparticles and Related Optical Properties. *Chem. Mater*. **2016**, *28*, 1066-5463.