

Supporting information

Experimental details:

Synthesis of gold nanoworms. The synthesis of gold nanoworms was carried out in a standard Schlenk line under Ar gas, and the procedure was similar to that of gold nanotubes reported by Schwartzberg *et al.*^[1] In a typical synthesis, 100 μL of 0.4 M cobalt chloride hexahydrate (Fisher Scientific, 99.99%) and 100 μL of 0.1 M trisodium citrate dihydrate (Sigma-Aldrich, >99%) were added into 100 mL of deionized water and degassed several times. 1 mL of 0.1 M sodium borohydride (Fisher Scientific, 99%) was injected into the solution in the presence of an external magnetic field. This solution was allowed to react for 50 min, (under constant argon flow) until hydrogen evolution ceased, indicating complete hydrolysis of the reductant. The external magnetic field was then removed and 33 mL of 2.5×10^{-4} M chloroauric acid trihydrate (Fisher Scientific, ACS reagent grade) was injected under vigorous stirring. This mixture was reacted for a further 10 min under argon before being exposed to air until a colour change (from grey to light green) was observed. Finally, 500 μL of 0.1 M sodium citrate was added to stabilize the gold nanoworms.

After synthesis, the solution was filtered (Fisher Scientific qualitative filter paper) and concentrated through centrifugation ($3466 \times g$). The precipitate was redispersed into 10 mL of 0.6 mM sodium citrate solution. A TEM image of a typical nanoworm is shown in Figure S5.

Pre-functionalization of nanoworms. 2.5 mL of the concentrated gold nanoworm solution, 2.45 mL of deionized water and 50 μL of different concentrations (10^{-4} and 10^{-5}

M) of 4-mercaptobenzoic acid (in ethanol) were mixed together followed by 10 seconds of vortexing and left for 30 minutes before measurements were taken.

Fabrication of nanoworm membrane. 5 mL of pre-functionalized nanoworm solution was filtered using a polyvinylidene fluoride (PVDF) 13 mm diameter membrane with a pore size of 450 nm (Fisher Scientific FDR-272-010X). The membrane was then rinsed with deionized water and dried under nitrogen before measurements.

Post-functionalization of nanoworm membrane. 5 mL of non-functionalised nanoworm solution was immobilised onto a membrane and then immersed into 5 mL of 10^{-6} M of 4-MBA water solution for 30 minutes. It was then rinsed with deionised water and dried under nitrogen before measurements.

SEM characterisations. SEM characterisations were carried out on a Sirion 200 Schottky field-emission electron microscope operating at an accelerating voltage of 5 kV. The membrane samples required additional gold sputter coating before imaging.

SERS measurements. Solution SERS spectra were recorded on a Renishaw inVia microscope system, equipped with a 100x objective. Power at the sample was measured at approximately 150 mW and a 1200 groove diffraction grating was used. Samples were analysed using glass vials with 500 μ L of the nanoworm sample solution. Spectra were accumulated for 10 s, and 5 replicates were carried out at each sample point; the signals were normalized to a silica standard.

The SERS maps and dark-field images were performed on a WITec alpha300-R equipped with a MPLanFL N 100 $\times$ /NA 0.9 for SERS mapping and a ZEISS EC EPOPLAN dark-field 50 $\times$ /NA 0.7 for dark-field imaging. A 785 nm laser with a power of $\sim$ 750 μ W was

used as the excitation source. The integration time per point was 0.3 s. The geometry of the scanned areas was $25\ \mu\text{m} \times 25\ \mu\text{m}$ with a resolution of $0.5\ \mu\text{m}$.

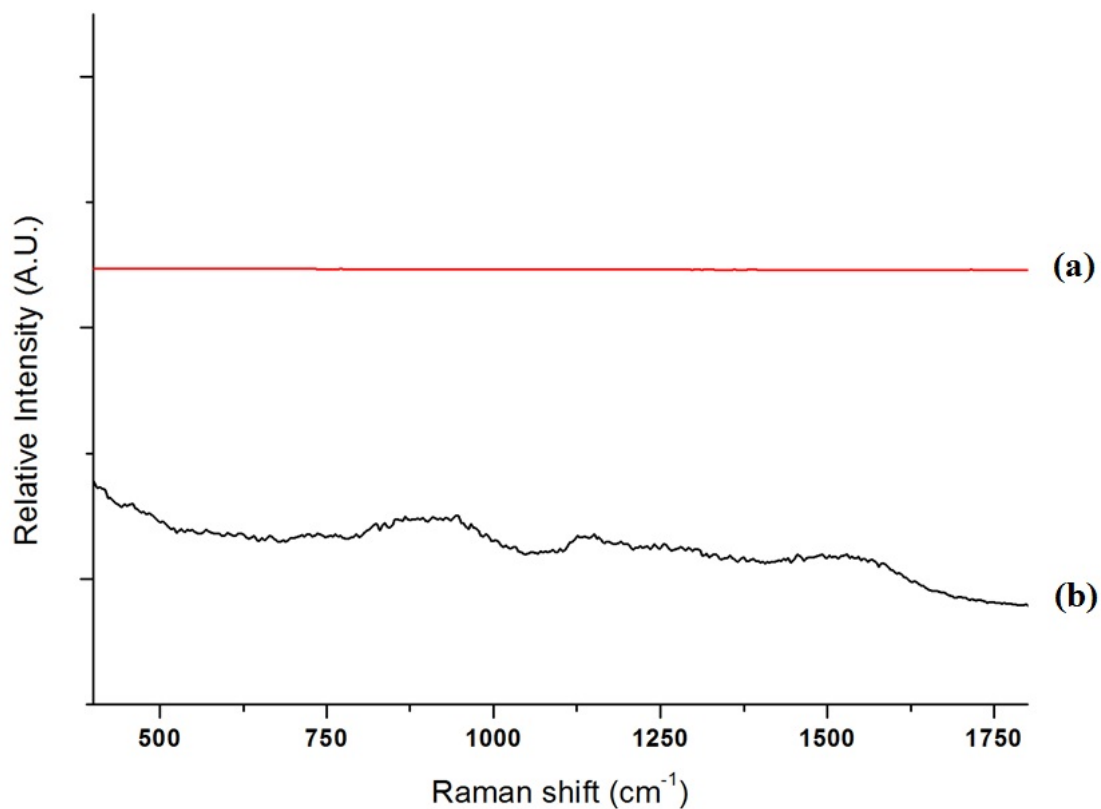


Figure S1. Average Raman backgrounds of a blank membrane (a) and a nanoworm membrane (b). They were averaged from the spectra of a whole SERS mapping area containing 625 individual spectra. They have been offset for clarity.

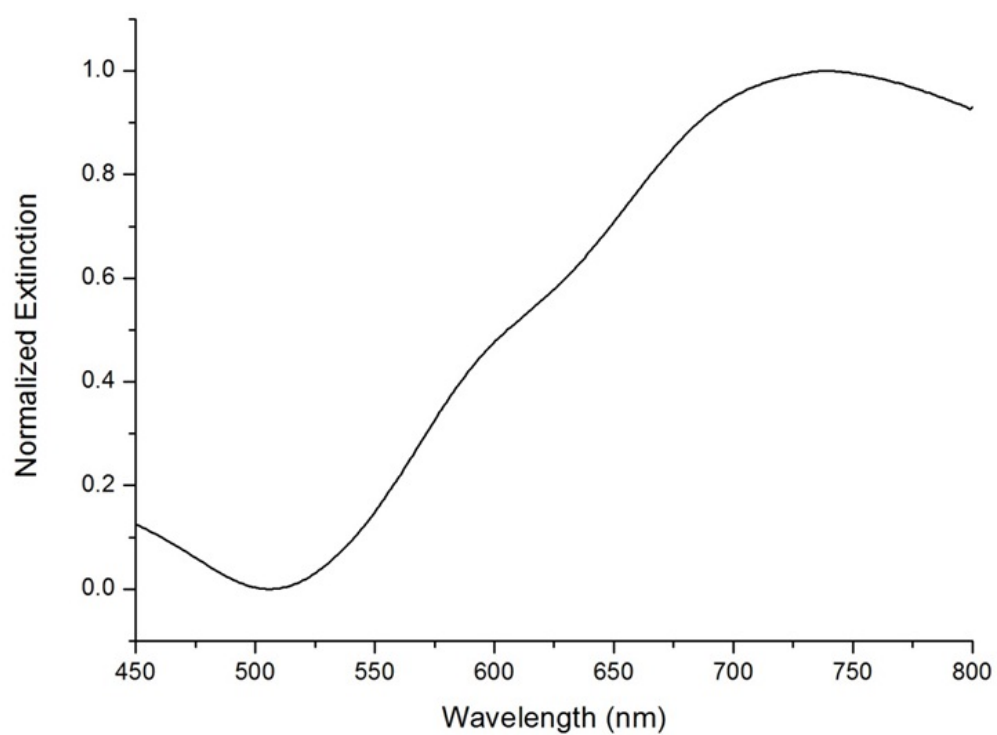


Figure S2. Extinction spectrum of the nanoworm solution with surface plasmon resonance around 745 nm.

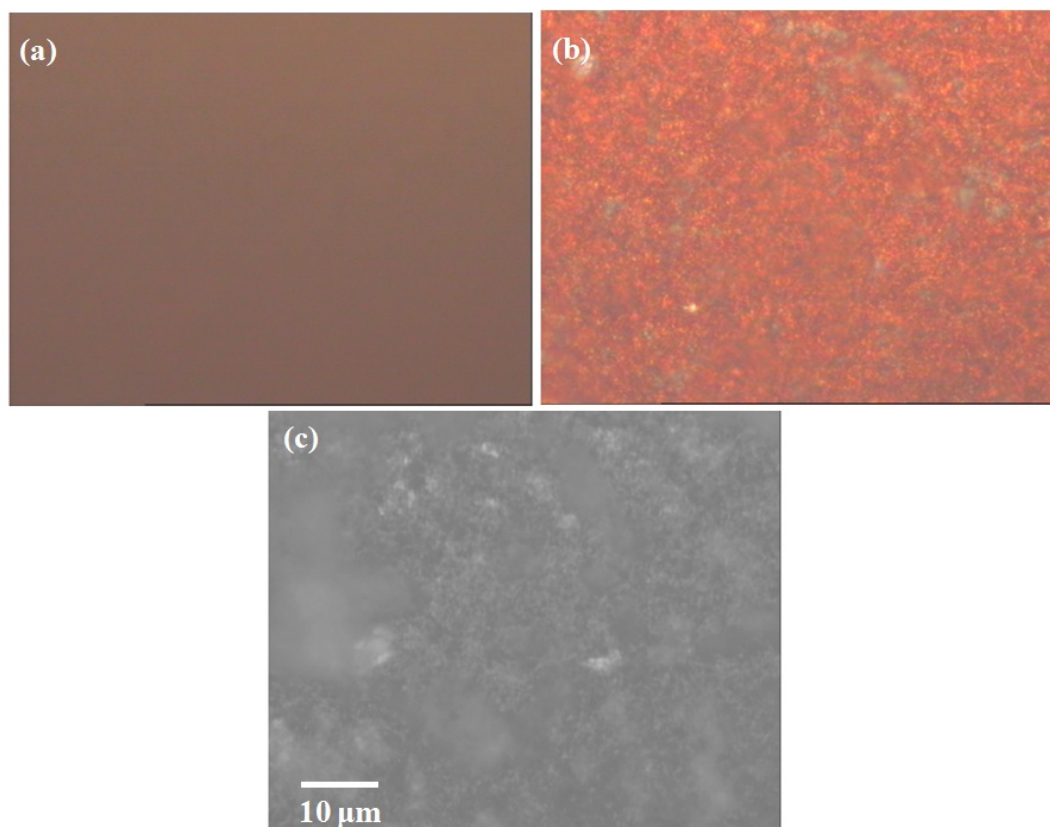


Figure S3. (a) Dark-field image of an empty membrane; (b) Dark-field image of a nanoworm coated membrane; (c) Bright-field image of a nanoworm coated membrane.

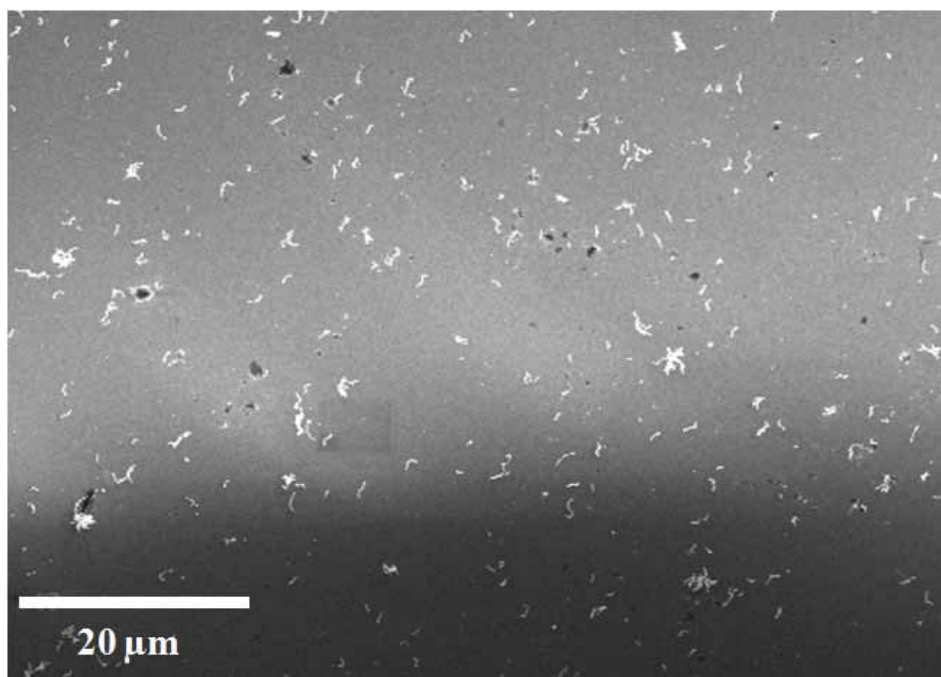


Figure S4. Illustration of the density of nanoworms on an ITO glass substrate.

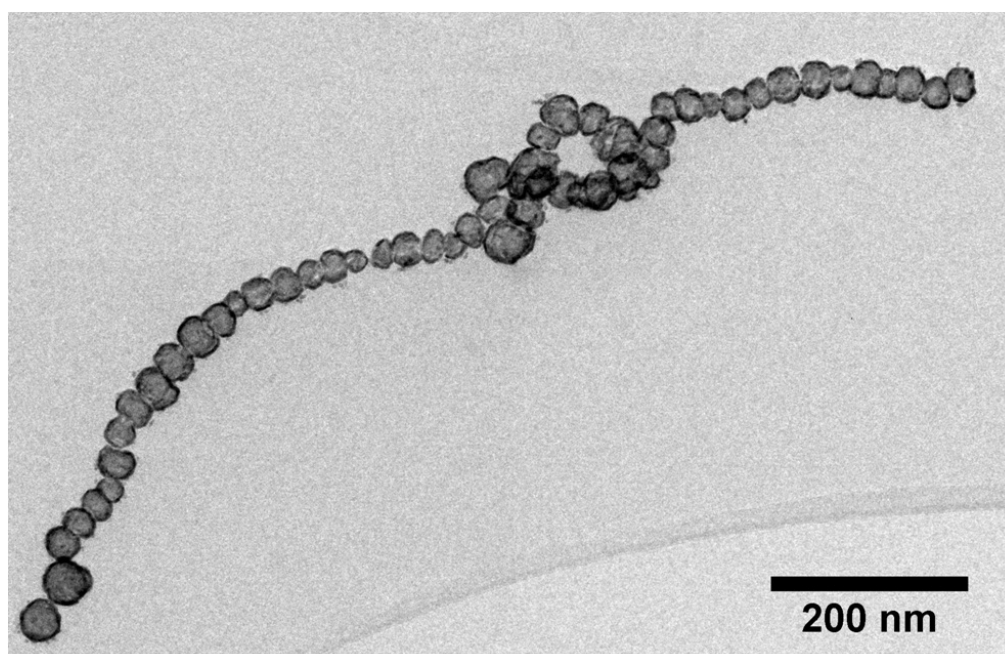


Figure S5. TEM image of a typical gold nanoworm.

References:

1. Schwartzberg, A. M.; T. Y. Olson; C. E. Talley; J. Z. Zhang. J. Phys. Chem. C 2007, 111, 16080-16082.