Electronic supplementary information for "Resonant scattering enhanced interferometric scattering microscopy"

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1. Characterization of the gold NRs and PVA films

The gold NRs used in this study were prepared by a wet chemical method involving seed mediated growth in the presence of silver. [1] Figure S1a shows the UV–Vis extinction spectrum of the gold NRs in water solution. The spectrum is characterized by two bands. The shorter wavelength band (~515 nm) is attributed to the transverse surface plasmon resonance mode. The longer wavelength band (~702 nm) is attributed to the longitudinal surface plasmon resonance mode. Figure S1b shows the transmission electron microscope (TEM) image of the gold NRs. The diameters of the gold NRs are about 20 nm and the lengths are broadly distributed in the range of 30-70 nm (Fig. S1c and d).

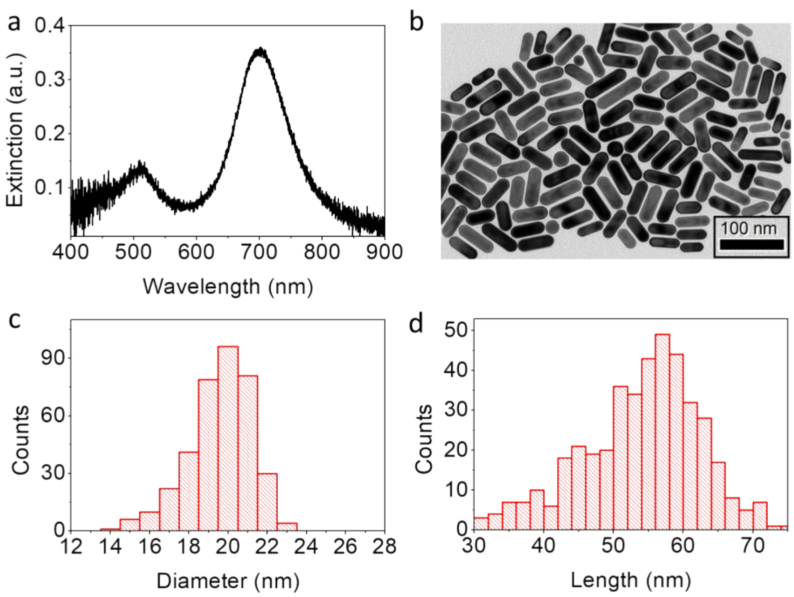

Fig. S1 (a) UV/Vis extinction spectrum of the gold NRs in water. (b) TEM image of the gold NRs. (c) Statistics of the diameter of the gold NRs. (d) Statistics of the length of the gold NRs.

The prepared gold NRs were firstly spin-coated on top of the piranha solution cleaned glass coverslips. Then PVA solutions with concentration of 2.1wt%, and 3.1wt% were spin-coated on top of three glass coverslips as the surrounding medium of the gold NRs with spin-coating speed of 1500, and 2800 r/min, respectively. In order to measure the thickness of the PVA film, the PVA films were scratched with a sharp stick and the step heights were measured using an atomic force microscope (AFM, NanoWizard 4, JPK Instruments AG). The roughness of the PVA film was found to be less than 5 nm. The measured thicknesses of the three PVA films are about 50, and 80 nm, respectively (Fig. S2).

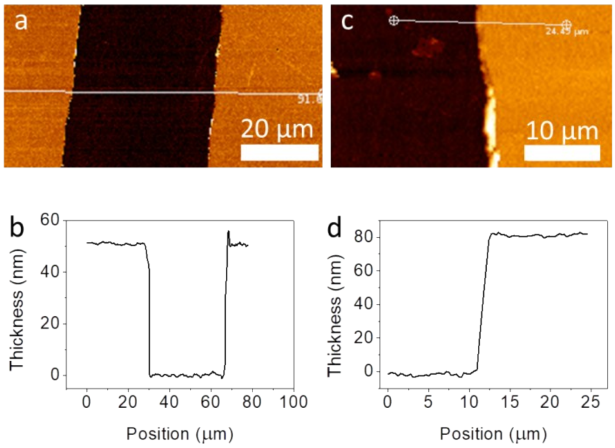

Fig. S2 (a,c) AFM images of the scratch borders on three glass coverslips. (b,d) Measured height profiles across the scratches. The measured thicknesses of the three PVA films are about 50 nm (a,b), and 80 nm (c,d), respectively.

2. The scattering spectra of gold NRs

The longitudinal surface plasmon resonance wavelength of the five gold NRs with negative signal contrast is 730, 749, 733, 733, and 739 nm for NR3, NR4, NR6, NR7 and NR8 respectively, which is longer than that of the three gold NRs with positive signal contrast (686, 701, and 712 for NR1, NR2, and NR5 respectively).

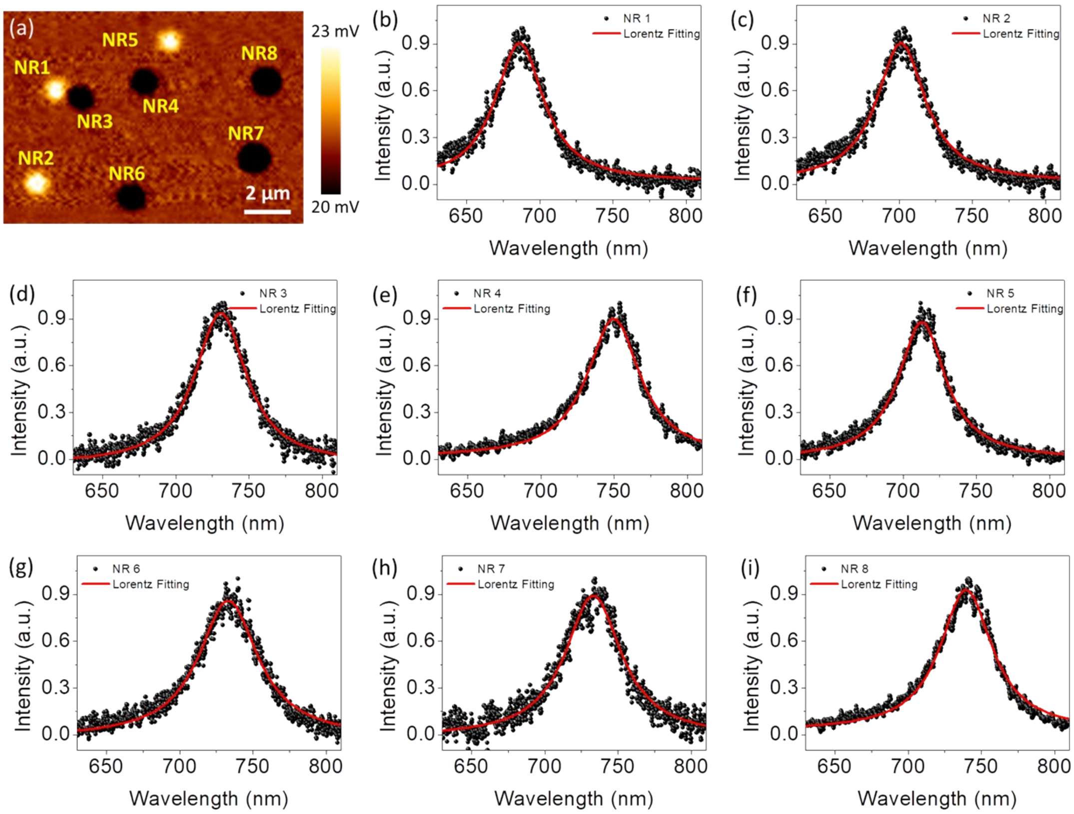

Fig. S3 (a) The iSCAT image shown in Fig. 2b of the main text. (b-i) The normalized scattering spectra of the eight gold NRs marked as NR1, NR2, NR3, NR4, NR5, NR6, NR7, and NR8, recorded with unpolarized white light in excitation and no analyzer in the detection path. Solid lines are Lorentzian fits, with resonance wavelength (width) 686 (40), 701 (40), 730 (43), 749 (44), 712 (39), 733 (49), 733 (46), 739 (43) nm, respectively.

3. Theoretical fitting of the iSCAT signal contrast

Let's consider the simple case of a gold spheroid embedded in PVA medium. The gold spheroid has two short axes of equal length (diameter) $a=b$ and long axis of length c. The aspect ratio is $R=c/a$. For polarization of incoming light parallel to the long axis of the gold spheroid, the polarizability is given as: [2]

$$\alpha = \frac{\varepsilon_0 V\left(\varepsilon-\varepsilon_\mathrm{m}\right)}{\varepsilon_\mathrm{m}+L\left(\varepsilon-\varepsilon_\mathrm{m}\right)} \quad \text{(S1)}$$

where $V=(4\pi/3)abc$ is the volume of the gold spheroid, and $\varepsilon=\varepsilon'+i\varepsilon''$ and ε_m are the permittivities of the gold spheroid and its surrounding PVA medium, respectively. The geometrical factor L is given by:

$$L = \frac{1-e^2}{e^2}(-1+\frac{1}{2e}\ln\frac{1+e}{1-e}),\quad e^2 = 1-\left(\frac{a}{c}\right)^2 \qquad \text{(S2)}$$

Figure S4a displays the calculated amplitude of polarizability $|\alpha|$ of gold spheroid with aspect ratio of 3 (the diameter is 20 nm) as a function of optical wavelength. The peak position of the polarizability, corresponding to the longitudinal surface plasmon resonance wavelength λ_{res}, is 717 nm.

The longitudinal surface plasmon resonance condition is roughly fulfilled when the denominator of eq S1 vanishes, or when [3]

$$\varepsilon' = \frac{L-1}{L}\varepsilon_{\text{m}} \qquad \text{(S3)}$$

A plot of ε' as a function of optical wavelength λ in the range between 640 and 810 nm is found to be nearly linear (Fig. S4b), and a fit gives the following values for the intercept and slope

$$\varepsilon' = 35.230 - 0.074\lambda \qquad \text{(S4)}$$

Similarly, plotting $(L-1)/L$ as a function of the aspect ratio R (Fig. S4c) and linearizing yields

$$\frac{L-1}{L} = 3.130 - 3.788R \qquad \text{(S5)}$$

Combining eqs S3-5 gives

$$\lambda_{\text{res}} = 476.08 - (42.30 - 51.19R)\varepsilon_{\text{m}} \qquad \text{(S6)}$$

Equation S6 is plotted in Fig. S4d as the green line, which shows very good agreement with the resonance wavelength calculated by using the full expression of eq S1 (black line in Fig. S4d).

The scattering field on detector is given by $\vec{E}_{\text{scat}} = s\vec{E}_{\text{i}} = \eta\alpha\vec{E}_{\text{i}}$, where η takes into account the detection efficiency and $\alpha = |\alpha| e^{i\phi_{\text{scat}}}$ is the complex polarizability of gold NR carrying information on amplitude $|\alpha|$ and phase difference ϕ_{scat} between the scattering field $\vec{E}_{\text{scat}}$ and the driving field $\vec{E}_{\text{i}}$. Thus the signal contrast of eq 2 in main text can be rewritten as:

$$\sigma = = 2\frac{\eta}{r}|\alpha|\cos\left(\phi_{\text{scat}} + \pi\left(1/2 - 4dn/\lambda\right)\right) \qquad \text{(S7)}$$

We fitted the data of iSCAT signal contrast shown in Fig. 4a and c by using the eqs S1, S6, and S7 with η/r and d left as free fitting parameters.

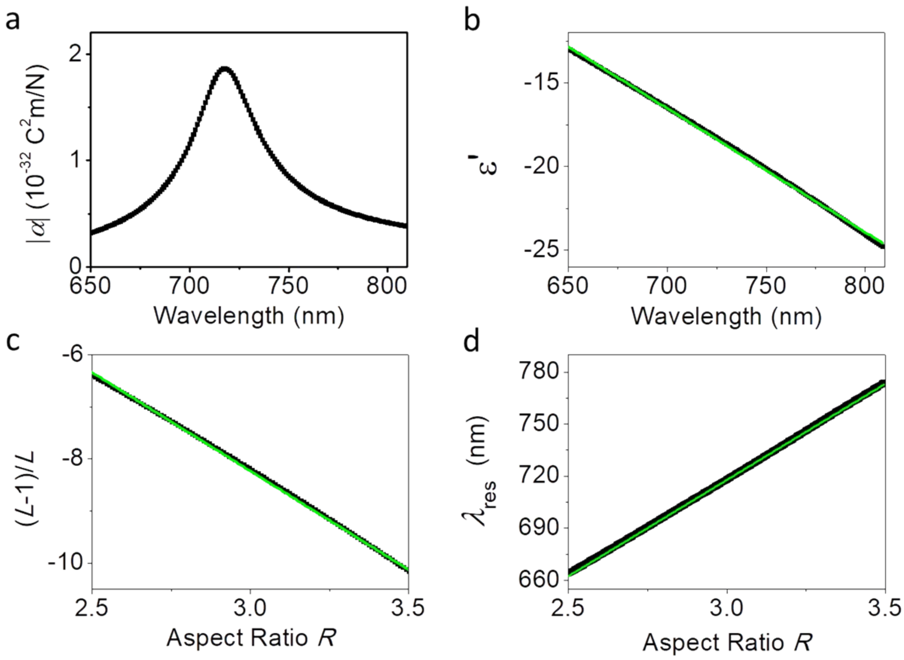

Fig. S4 (a) Amplitude of polarizability $|\alpha|$ for incoming light polarized parallel to the long axis of gold spheroid with aspect ratio of 3 (the diameter is 20 nm). (b) Real part of the permittivity of gold ε' as a function of the optical wavelength (black dot line). The green solid line represents the linear fitting of the data. (c) Value of $(L-1)/L$ as a function of the aspect ratio R (black dot line). The green solid line represents the linear fitting of the data. (d) Resonance wavelength λ_{res} of the gold spheroid as a function of its aspect ratio R obtained by using the full expression of eq S1 (black dot line). The green solid line is plotted according to eq S6.

4. The contribution of intensity of pure scattering light from gold NR to the iSCAT signal contrast

The iSCAT signal contrast with ($\sigma_{\mathrm{w/}}$) and without ($\sigma_{\mathrm{w/o}}$) the contribution of intensity of pure scattering light from gold NR can be expressed as:

$$\sigma_{\mathrm{w/}} = 2\frac{\eta}{r}|\alpha|\cos\phi + \left(\frac{\eta}{r}\right)^2 |\alpha|^2 \tag{S8}$$

and

$$\sigma_{\mathrm{w/o}} = 2\frac{\eta}{r}|\alpha|\cos\phi, \tag{S9}$$

respectively. Based on the fitted parameters of Fig. 3a in the main text, we plotted the iSCAT signal contrast with (red lines) and without (green lines) the contribution of intensity of pure scattering light from gold NR with different resonance wavelength (Fig. S5). Clearly, the difference between $\sigma_{w/}$ and $\sigma_{w/o}$ is so small that the term proportional to $(\eta/r)^2$ in eq S8 can be ignored, which indicates that the intensity of pure scatting light from gold NR is much smaller than that of the reference light.

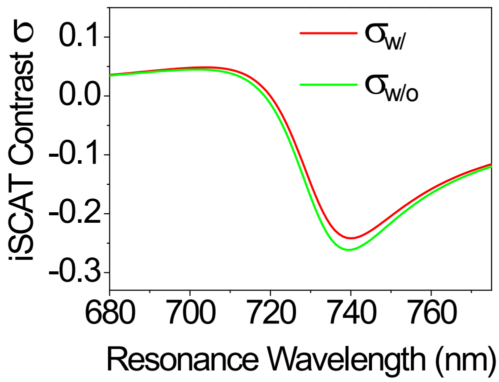

Fig. S5 The calculated iSCAT signal contrast with (red lines) and without (green lines) the contribution of intensity of pure scattering light from the gold NR with different resonance wavelength.

REFERENCES

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3. S. Link, M. B. Mohamed and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 3073-3077.