

Electronic Supplementary Information (ESI)

Pressure Sensor Based on the Orientational Dependence of Plasmonic Properties of Gold Nanorods

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Experimental Section

Chemicals. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), polyvinyl alcohol (PVA, 88% hydrolyzed, Mw 88000) were purchased from Acros Organics. Silver nitrate (AgNO_3 , 99.9%) was purchased from Fisher Scientific. L-ascorbic acid (BioXtra, $\geq 99.0\%$), hexadecyltrimethylammonium bromide (CTAB, $\geq 99\%$), sodium borohydride (NaBH_4 , 99%), polyethylene glycol (PEG, Mw 400) were purchased from Sigma-Aldrich. All chemicals were used as received without further treatment.

Synthesis of gold nanorods (AuNRs). CTAB-capped AuNRs were fabricated using a process similar to a previous report.¹ The seed solution for AuNRs was prepared as follows: 1 mL of 0.5 mM HAuCl_4 was mixed with 1 mL of 0.2 M CTAB solution, followed by injection of 0.12 mL fresh 0.01 M NaBH_4 under vigorous stirring. The stirring of seed solution was continued for 2 min and the color of solution changed from yellow to brownish yellow. The seed solution was aged for 30 min at room temperature before use.

To prepare the growth solution, 40 mL of 0.2 M CTAB was added a certain quantity (0.32, 0.48, 0.64 mL) of 0.01M AgNO₃, followed by addition of 40 mL of 1 mM HAuCl₄. Then 0.56 mL of 0.0788 M ascorbic acid was added after gentle mixing of the solution. The color of growth solution changed from dark yellow to colorless as ascorbic acid is a mild reducing agent. Finally, 96 μL of seed solution was injected into the growth solution. The resultant mixture was stirred for 2min and left undisturbed at 30 °C for 45 min for AuNR growth. The final products were isolated by centrifugation at 7000 rpm for 20 min followed by removal of the supernatant.

Fabrication of AuNR-polymer composite films. To obtain 10 wt.% PVA solution, 6.0 g PVA was dissolved in 54 mL distilled water under 90 °C and mechanical stirring for 6 h till complete dissolution of PVA. The solution was allowed to cool down to room temperature.

Typically, 10 wt.% PVA solution was diluted with distilled water and added a desired amount of PEG with careful mixing, as detailed in Table S1 (total volume of PVA/PEG polymer is fixed). Then the solution was added 0.35 ml of AuNRs (4 mg/mL) to form a homogenous mixture. The mixture was casted into glass beaker (10mL, KIMAX) and left in room temperature to allow the evaporation of water. Solid films were then peeled off from glass beaker and cut into small circular pieces with diameter of 3 mm using a homemade puncher.

Compression tests. Composite films were loaded into sapphire anvil cell (SAC) which is used for transferring external constant force. The pressure applied on the sample was then calculated by dividing the force by the area of SAC whose area is same as initial sample area.

Characterization. The morphology of products was observed on a s transmission electron microscope (TEM, Tecnai T12). A probe-type Ocean Optics HR2000CG-UV-NIR spectrometer was used to measure the UV-Vis spectra of the composite

films to get the *in-situ* real-time spectra during compression tests. The thickness of composite films was measured using optical microscope.

DDA simulations. The extinction profiles of AuNRs with different orientations were calculated by the discrete dipole approximation (DDA) method using software developed by Draine and Flatau (DDSCAT 7.3).^{2, 3} DDA is a general method to calculate the optical properties of metal nanostructures of arbitrary geometry and composition. In this approximation, the metal nanostructure, usually called target, is replaced by an array of N point dipoles. In this work, the target consisted in a cylinder with hemispherical end-caps, with a main axis of 42 nm (including two hemispherical caps) and a minor axis of 16 nm. We used 7584 dipoles for the target, corresponding to an interdipole spacing of 0.99 nm. To obtain the extinction profiles in different orientations, the target was rotated through the angle θ which specify the direction of \mathbf{a}_1 (corresponding to the main axis of Au rods) with respect to the incident wave vector \mathbf{k} . The wave vector was taken to be along the x-axis, and the polarization was considered to be along both y-axis and z-axis. The effect of solvent has been accounted for through the refractive index of ambient environment, that is $n=1.333$ for water. The Au dielectric constants from Johnson and Christy were used.⁴

Derivation details of the relationship between the change of azimuthal angle of the nanorod and the cumulative deformation (Equation 1 in the manuscript).

If a force is applied on the composite film, the thickness L will decrease ΔL and the radius of area R will increase ΔR . If we assume that the volume of the composite film is unchangeable during deformation, then

$$\Delta L \cdot \pi R^2 = 2\pi R \cdot L \cdot \Delta R$$

$$\frac{\Delta L}{L} = 2 \frac{\Delta R}{R} \quad (1)$$

So the deformation in thickness direction is two times the deformation in radius direction.

If we assume that the deformation in all radius directions is the same, we can analyze the deformation of AuNR-polymer composite film in one cross section. According to the relationship of deformation in thickness direction and radius direction, there should exist a simple planar extensional flow in the cross section as follows:

$$\begin{cases} \frac{\partial u}{\partial \rho} = \frac{1}{2} \dot{\gamma} \\ \frac{\partial u}{\partial z} = -\dot{\gamma} \end{cases} \quad (2)$$

where u is the fluid velocity, $\dot{\gamma}$ is the deformation rate in the thickness direction which changes with time, which can be obtained by differentiating cumulative deformation γ ($\dot{\gamma} = d\gamma / dt$).

The rotational motion for rigid cylindrical particles in a extensional flow can be described by Jeffery equations^{5, 6}:

$$\dot{\mathbf{P}} = \mathbf{\Omega} \cdot \mathbf{P} + \lambda \mathbf{E} \cdot \mathbf{P} - \lambda \mathbf{E} : \mathbf{P} \mathbf{P} \mathbf{P} \quad (3)$$

where \mathbf{P} is the unit vector along the axis of symmetry of cylindrical particles which is following the fluid, $\mathbf{\Omega}$ is the vorticity tensor which is zero in our system, \mathbf{E} is the rate of strain tensor which is divergence of the velocity field ∇u in our system, and the parameter $\lambda = \frac{r_e^2 - 1}{r_e^2 + 1}$ is a function of the ratio r_e between the length of the long and the short semi-axis of the ellipsoidal body (r_e is the ‘equivalent ellipsoidal’ axis ratio of the particle ($r_e = 1.14r^{0.844}$),⁷ where r is the aspect ratio of the rod).

So we can obtain

$$\mathbf{P} = \begin{bmatrix} \sin \theta \\ \cos \theta \end{bmatrix} \quad (4)$$

$$\mathbf{\Omega} = 0 \quad (5)$$

$$E = \dot{\gamma} \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -1 \end{bmatrix} \quad (6)$$

Then

$$\dot{P} = \begin{bmatrix} \cos \theta \frac{d\theta}{dt} \\ -\sin \theta \frac{d\theta}{dt} \end{bmatrix} \quad (7)$$

$$\lambda E \cdot P = \lambda E_{ij} P_j = \lambda \begin{bmatrix} E_{11} P_1 + E_{12} P_2 \\ E_{11} P_1 + E_{12} P_2 \end{bmatrix} = \frac{1}{2} \lambda k(t) \begin{bmatrix} \sin \theta \\ -2 \cos \theta \end{bmatrix} \quad (8)$$

$$\begin{aligned} \lambda E : PPP &= \lambda (P_k^T E_{kl} P_l) P_j = \lambda \begin{bmatrix} E_{11} P_1 P_1 + E_{12} P_1 P_2 \\ + E_{21} P_2 P_1 + E_{12} P_2 P_2 \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \end{bmatrix} \\ &= \frac{1}{2} \lambda \dot{\gamma} (\sin^2 \theta - 2 \cos^2 \theta) \begin{bmatrix} \sin \theta \\ \cos \theta \end{bmatrix} \end{aligned} \quad (9)$$

If we put the formula 7, 8 and 9 into equation 3, we can get

$$\begin{cases} \cos \theta \frac{d\theta}{dt} = \frac{1}{2} \lambda \dot{\gamma} [\sin \theta - (\sin^2 \theta - 2 \cos^2 \theta) \sin \theta] \\ -\sin \theta \frac{d\theta}{dt} = \frac{1}{2} \lambda \dot{\gamma} [-2 \cos \theta - (\sin^2 \theta - 2 \cos^2 \theta) \cos \theta] \end{cases} \quad (10)$$

From equation 12, we can get

$$\frac{d\theta}{dt} = \frac{3}{4} \lambda \dot{\gamma} \sin 2\theta \quad (11)$$

then

$$\frac{2d\theta}{\sin 2\theta} = \frac{3}{2} \lambda \dot{\gamma} dt$$

$$\ln|\tan \theta| = \frac{3}{2} \lambda \int \dot{\gamma} dt + T_0 = \frac{3}{2} \lambda \gamma + T_0$$

$$\tan \theta = T \cdot \exp\left(\frac{3}{2} \lambda \gamma\right)$$

When $t=0$, $\gamma=0$ then $\tan \theta_0 = T$

$$\text{So } \tan \theta = \tan \theta_0 \cdot \exp\left(\frac{3}{2} \lambda \gamma\right)$$

$$\tan \theta = \tan \theta_0 \cdot \exp\left(\frac{3}{2} \frac{r_e^2 - 1}{r_e^2 + 1} \gamma\right) \quad (11)$$

where θ is the azimuthal angle at time t , θ_0 is the azimuthal angle at initial stage (0 s).

Table S1. Fabrication conditions of AuNR-polymer composite films

PVA: PEG ratio	10wt.% PVA	PEG
4:6	1.186 g	158 μ l
5:5	1.500 g	133 μ l
6:4	1.822 g	108 μ l
7:3	2.151 g	82 μ l
8:2	2.488 g	55 μ l

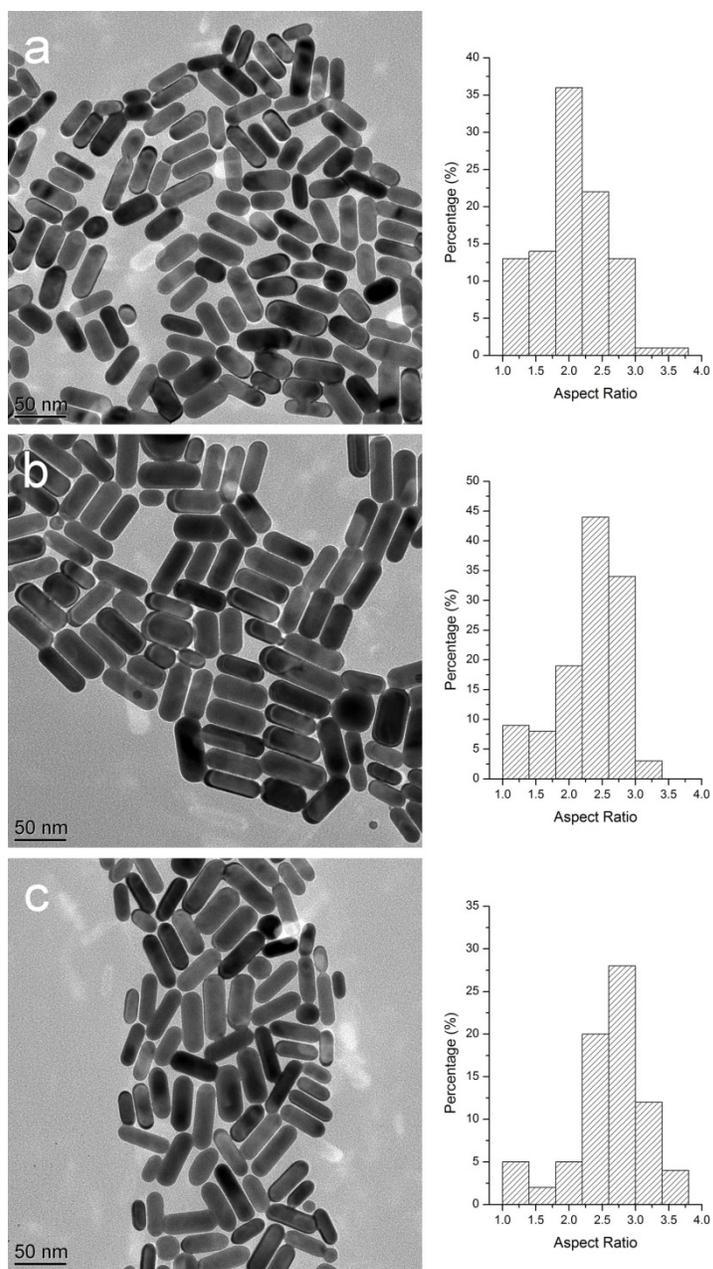


Figure S1. TEM images of AuNRs with different aspect ratios at the same magnification: (a) 2.06, (b) 2.31, (c) 2.60. To the right of the images are distributions of the aspect ratios of AuNRs.

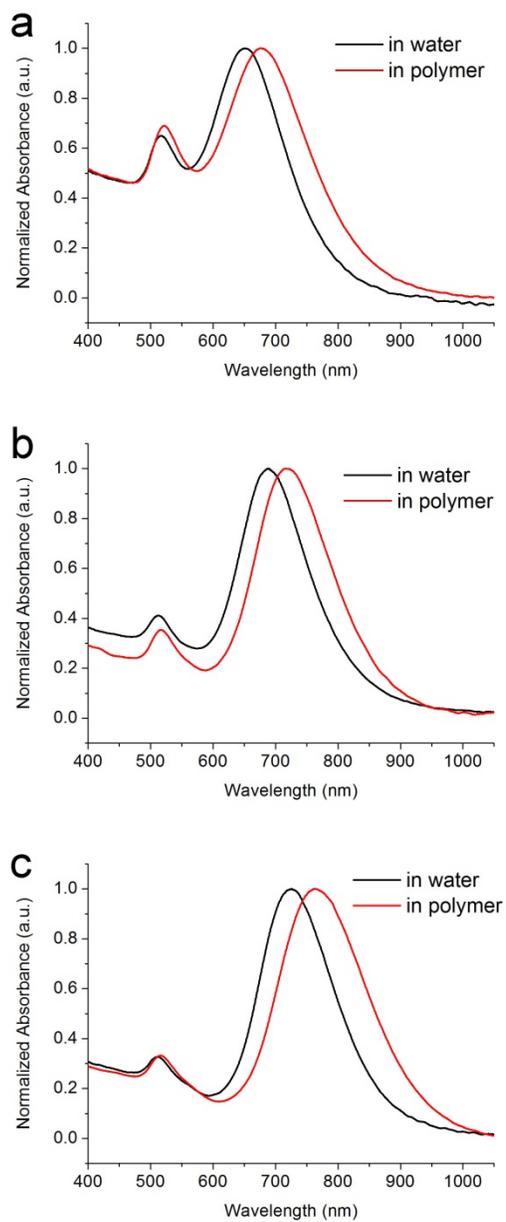


Figure S2. The absorbance spectra of AuNRs with different aspect ratios in water and in polymer: (a) 2.06, (b) 2.31, (c) 2.60.

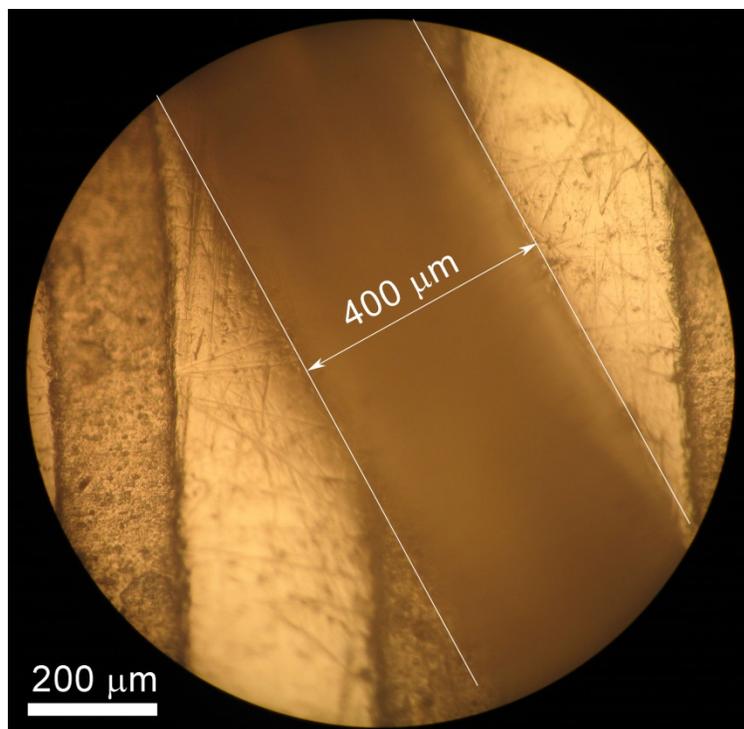


Figure S3. Dark field microscopy image of thickness section of one AuNR-polymer composite film.

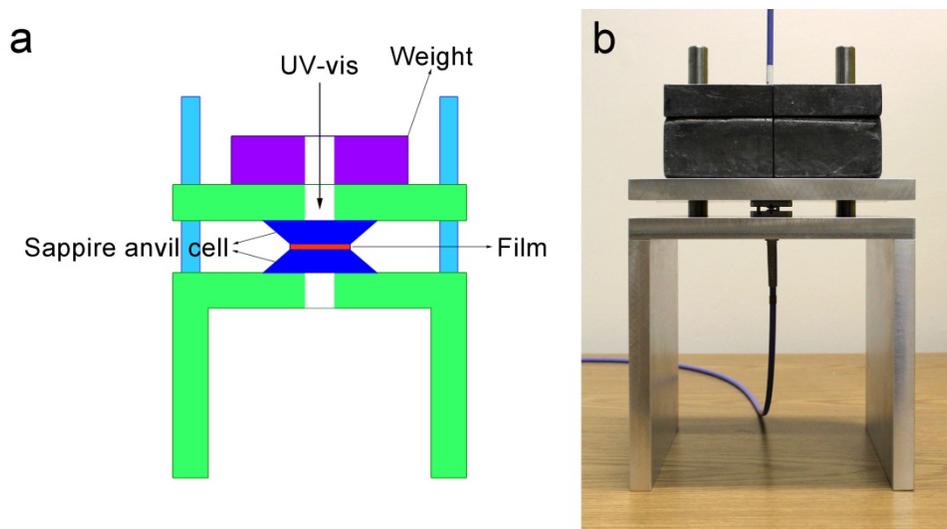


Figure S4. Illustration (a) and picture (b) of homemade equipment used for *in-situ* real-time UV-vis measurement.

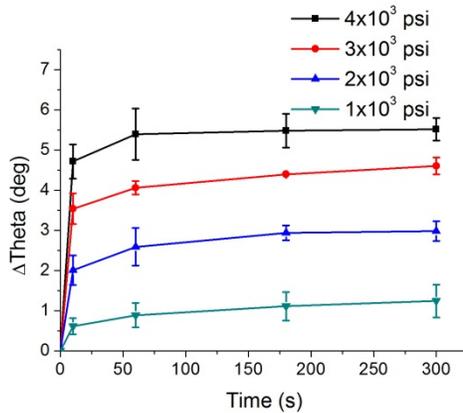


Figure S5. Plots of orientation change of AuNRs in the composite films experiencing different pressures for a series of application time. The initial angle between the AuNRs and incident light is set as 45° .

Reference

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