Electronic Supplementary Material (ESI) for Nanoscale.

## Supporting information for:

# Gold nanorods as a high-pressure sensor of phase transitions and refractive-index gauge

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## METHODS

### Synthesis of Au nanorods

The synthesis of Au nanorods was following: Firstly, the CTAB-capped Au seeds were synthesized by mixing 0.25 mL of 0.005 M aqueous $HAuCl_4$ with 4.45 mL of water and 171 mg of CTAB. Then, to the vigorously, magnetically stirred solution, 0.3 mL of freshly prepared, cold (refrigerated) 0.01 M aqueous solution of $NaBH_4$ was injected. Subsequently, after 30 s, the stirring was slowed down and the systems was heated over 15 minutes up to 30 $^{o}$C. The formed colloidal solution of Au seeds (≈2 nm diameter) was fair brown. Note: the Au seeds should be freshly prepared, and can be used within 2-3 h from their formation. They cannot be stored, as aggregate into larger NPs, and the color of their solution changes from brown to pink (SPR shifts from ≈400 to 530 nm).

In order to prepare the growth solution, 1.75 g of CTAB and 0.309 g of sodium oleate were dissolved in 62.5 mL of hot water (~50 °C). The solution was cooled down to 30 °C and 4.5 mL of 4 mM $AgNO_3$ aqueous solution, was added. The mixture was kept undisturbed at 30 °C for about 5 minutes. Subsequently, 50 mL of water and 12.5 mL of 0.005 M $HAuCl_4$

solution were added. The solution became colorless after 30-60 min of gentle stirring. In the next step, 0.375 mL of concentrated HCl was added to adjust the pH. After another 5 min of gentle stirring, 0.313 mL of 0.064 M ascorbic acid was injected and the solution was vigorously stirred for 30 s. Afterwards, 0.1 mL of the freshly (simultaneously) prepared Au seed solution was injected into the growth solution. The obtained mixture was manually stirred for 30 s and left undisturbed at 30°C, overnight. The final products were purified by 2-times centrifugation in water, at 7.000 rpm for 30 minutes. Then, the as-prepared Au nanorods were redispersed in water ($C \approx 0.1$ mg/mL).

## Materials

The following reagents were purchased from Sigma Aldrich: $NaBH_4$ (98%), $HAuCl_4 \times 3\,H_2O$ (≥99.9%), $AgNO_3$ (99.998%), hexadecyltrimethylammonium bromide – CTAB (BioXtra, ≥99%), sodium oleate (≥82%), The remaining compounds, i.e. L(+)-ascorbic acid (pure p.a., ACS, Ph.Eur.) and HCl (pure p.a., 37%), were purchased from POCh S.A. Deionized water (Milli-Q®) was used for all experiments.

## Characterization

Transmission electron microscopy (TEM) measurements were performed with a Hitachi HT7700 microscope, operating at 100 kV. The absorption spectra were measured using a UV-VIS-NIR JASCO V-770 spectrophotometer. Single-crystal diffractometer Xcalibur EOS CCD with Mo Kα X-ray source was used for diffraction measurements. The normal distribution curves in Figures 1 and S3 were matched using the curve fitting and data analysis program fityk 0.7.7.[1]

## DAC preparation

High-pressure X-ray diffraction and absorption measurements have been performed in a Merrill–Bassett diamond-anvil cell (DAC),[2] modified by mounting the diamond anvils directly on the steel supports with conical windows.[3] Pressure was determined from the ruby R1 fluorescence line shifts[4] by using a Photon Control spectrometer affording an accuracy of 0.03 GPa. The gaskets of 0.3 mm tungsten carbide (WC) foil with spark-eroded holes 0.5 mm in diameter were used.

### Pressure calibration

Before each measurement the value of the pressure in the DAC was determined on the basis of the spectral shift of ruby fluorescence (R1 ruby line), as its emission bands exhibit red-shift with increasing pressure. The source of excitation was continuous wave, 532 nm, diode-pumped solid-state laser (8 mW). The measurements were performed at ambient conditions, using a standard ruby calibration curve.[5]

### Structural measurements - XRD

The powder data were collected at 0.0001, 0.38, 0.96, 1.21, 1.62, 2.03, 2.47 and 3.18 GPa upon compression, and at 1.92, 0.88 and 0.0001 GPa upon decompression. The CrysAlisPro program suite was used for initial analysis of the diffraction data.[6] The DAC chamber was filled with dried (powder) Au nanorods and glycerol to ensure hydrostaticity.

### Setup for high-pressure absorption spectroscopy

High-pressure VIS spectra were measured with a JASCO spectrometer operated at the 1 nm resolution, with the probing-beam condenser focusing the beam at the DAC chamber and then expanding it back to the spectrometer pathway. DAC baseline were collected on loaded only with hydrostatic medium and ruby chip chamber and then used to prerecorded subtraction. After recording the baseline, to this same gasket, the as-prepared Au NRs (C ≈ 0.1 mg/mL) were prepared. Suspension of Au NRs (C ≈ 0.1 mg/mL) were centrifuged at 4000 rpm, for 6 minutes to concentrate them up to C ≈ 2 mg/mL. In order to ensure their stability under high-pressure compression, 30 μL of the concentrated aqueous solution of Au NRs was mixed with 70 μL of the aqueous solution of CTAB (freshly prepared by dissolving 7 mg of CTAB in 10 mL of water).

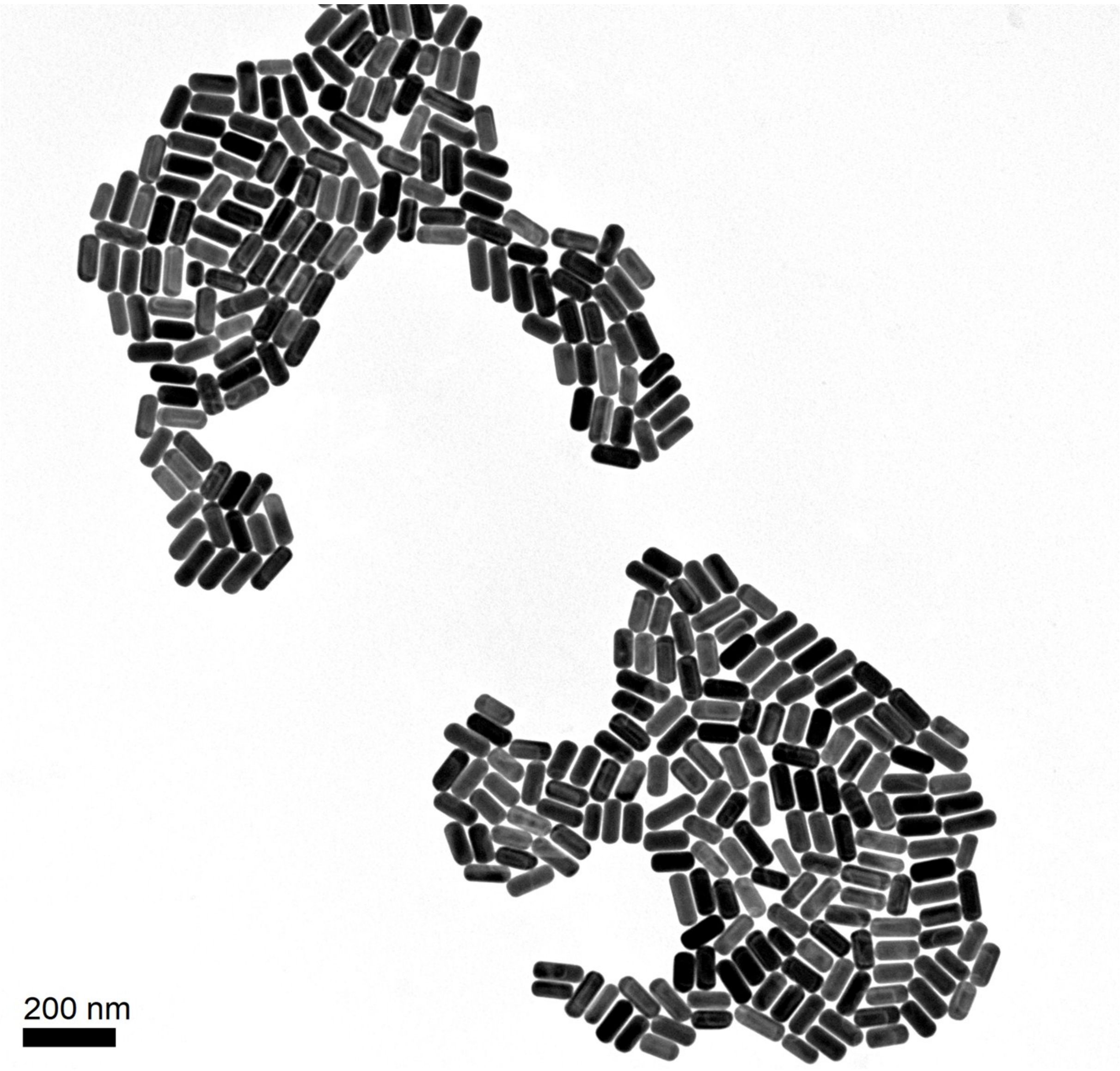

**Figure S1.** Transmission electron microscopy (TEM) image of the Au NRs synthesized in this project.

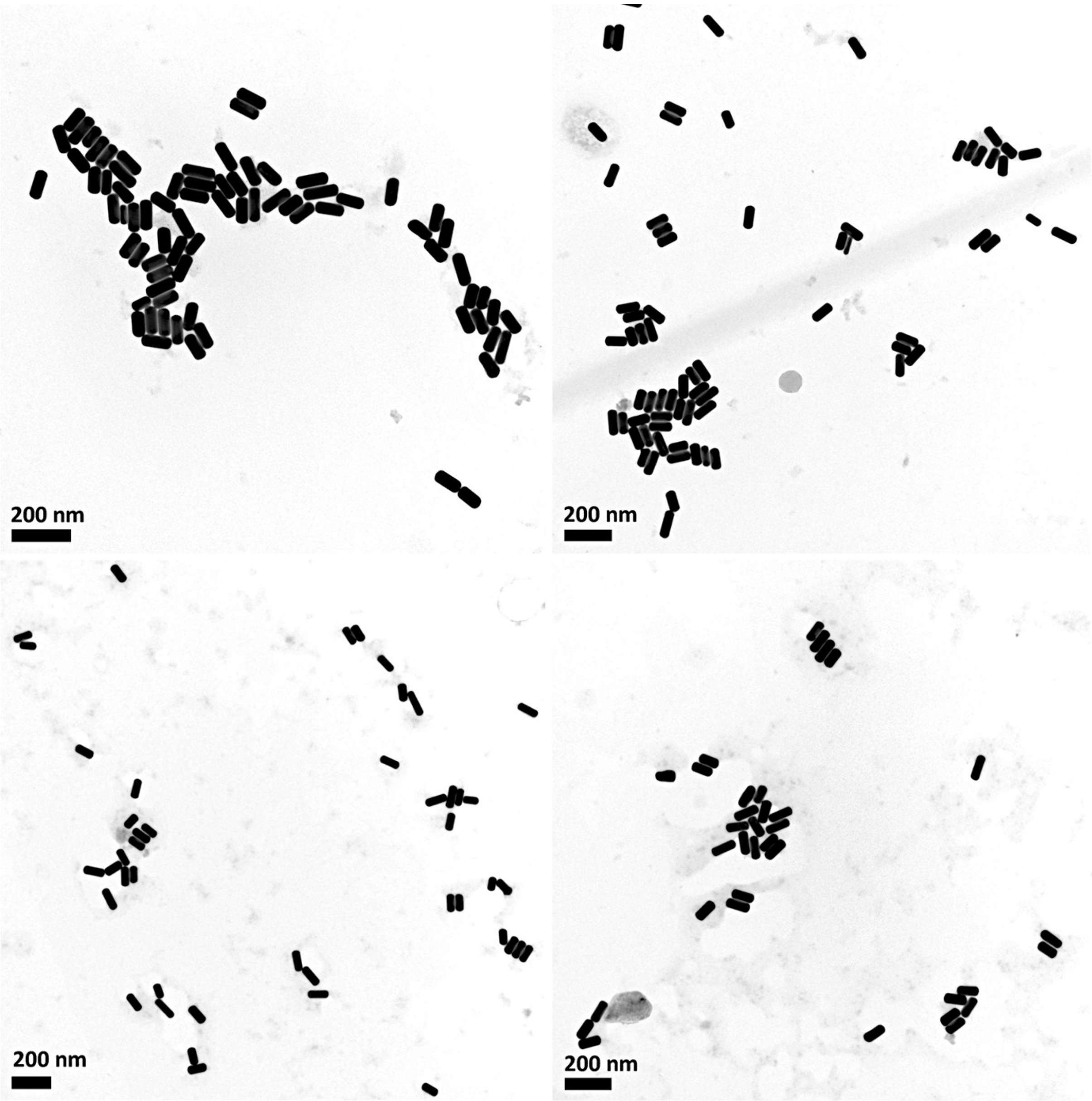

**Figure S2.** Tem images of synthesized Au NRs after squeezing up to 4 GPa.

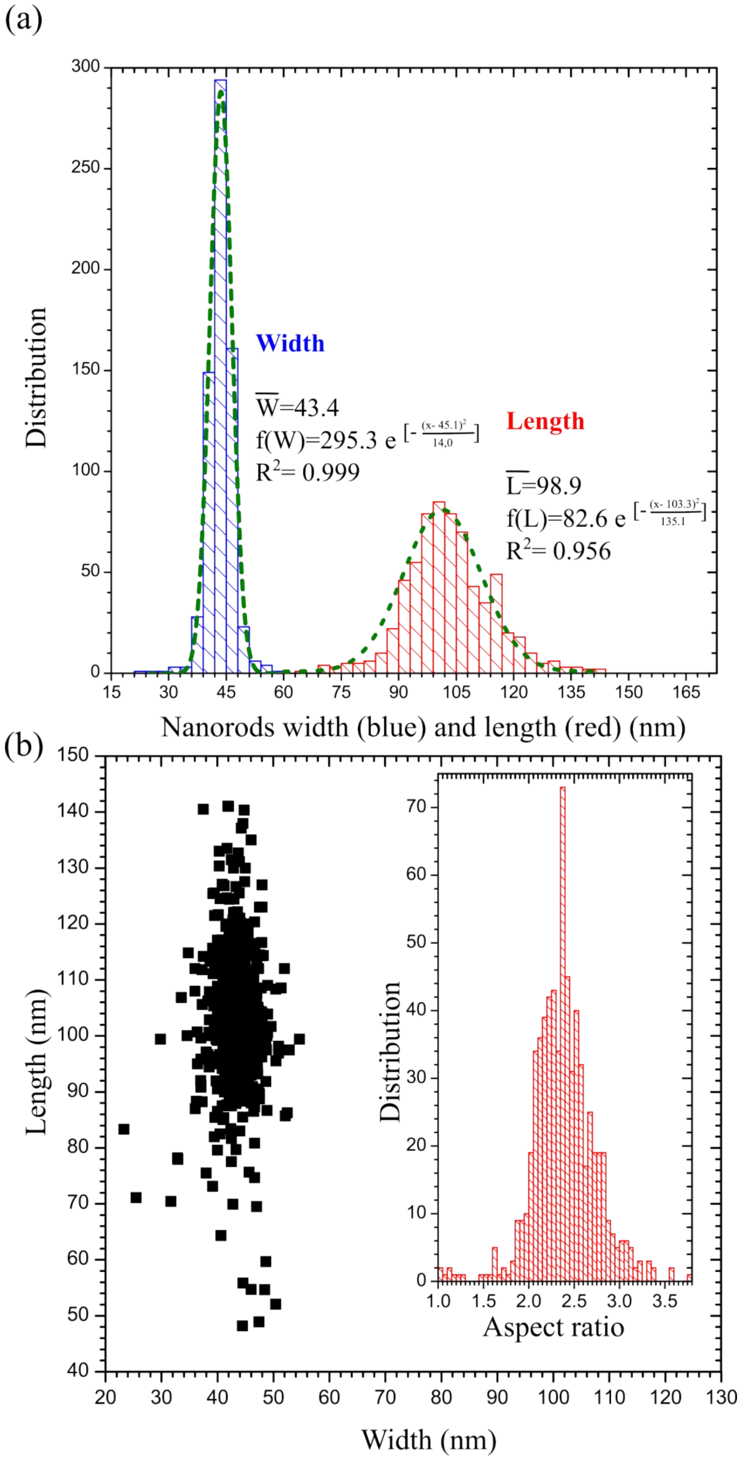

**Figure S3.** The distribution of widths and lengths of synthesized Au NRs after squeezing up to 4 GPa (a). The aspect ratio in the gold NR's as a scatter plot; the inset shows the distribution of the aspect ratio (b).

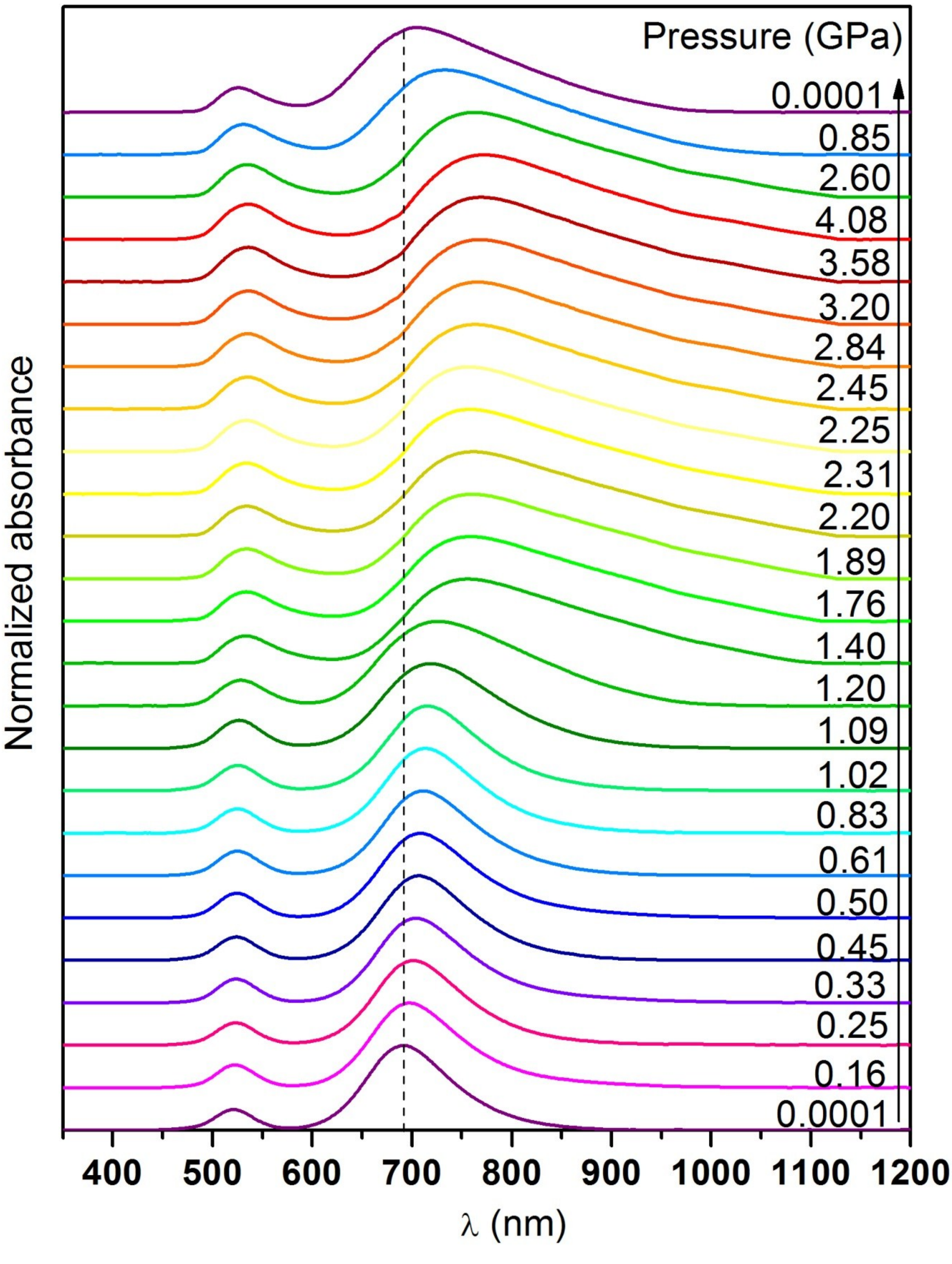

**Figure S4.** Absorption spectra of Au NRs in water in a compression-decompression cycle.

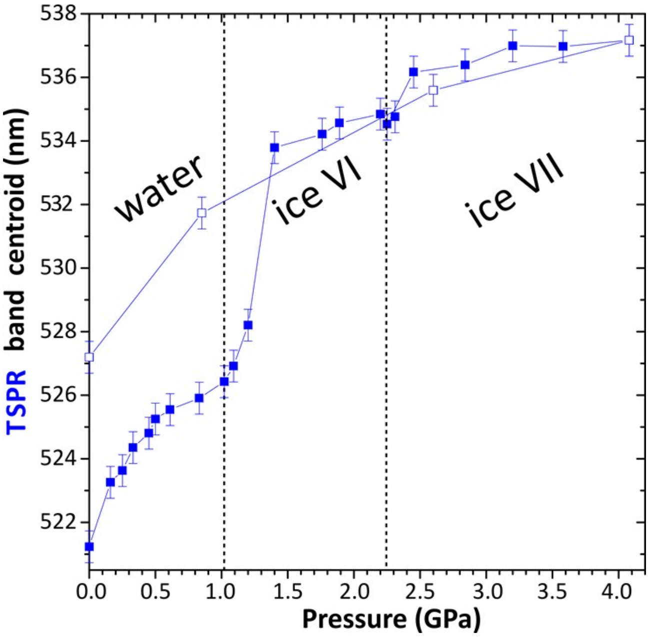

**Figure S5.** Spectral position (centroids) of the TSPR peak of Au NRs in compressed water and ices, measured in the pressure-increasing (full symbols) and pressure-reducing (open symbols) runs.

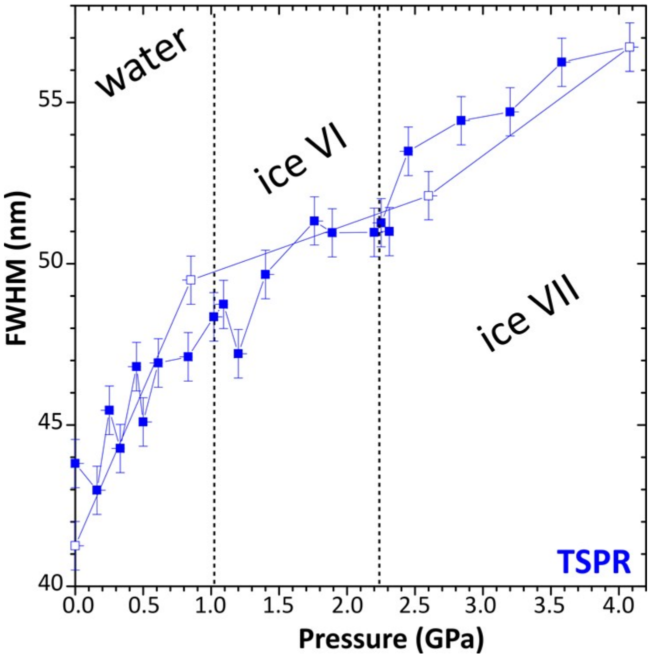

**Figure S6.** FWHM of the TSPR peak of Au NRs in compressed water and ices, measured in the pressure-increasing (full symbols) and pressure-reducing (open symbols) runs.

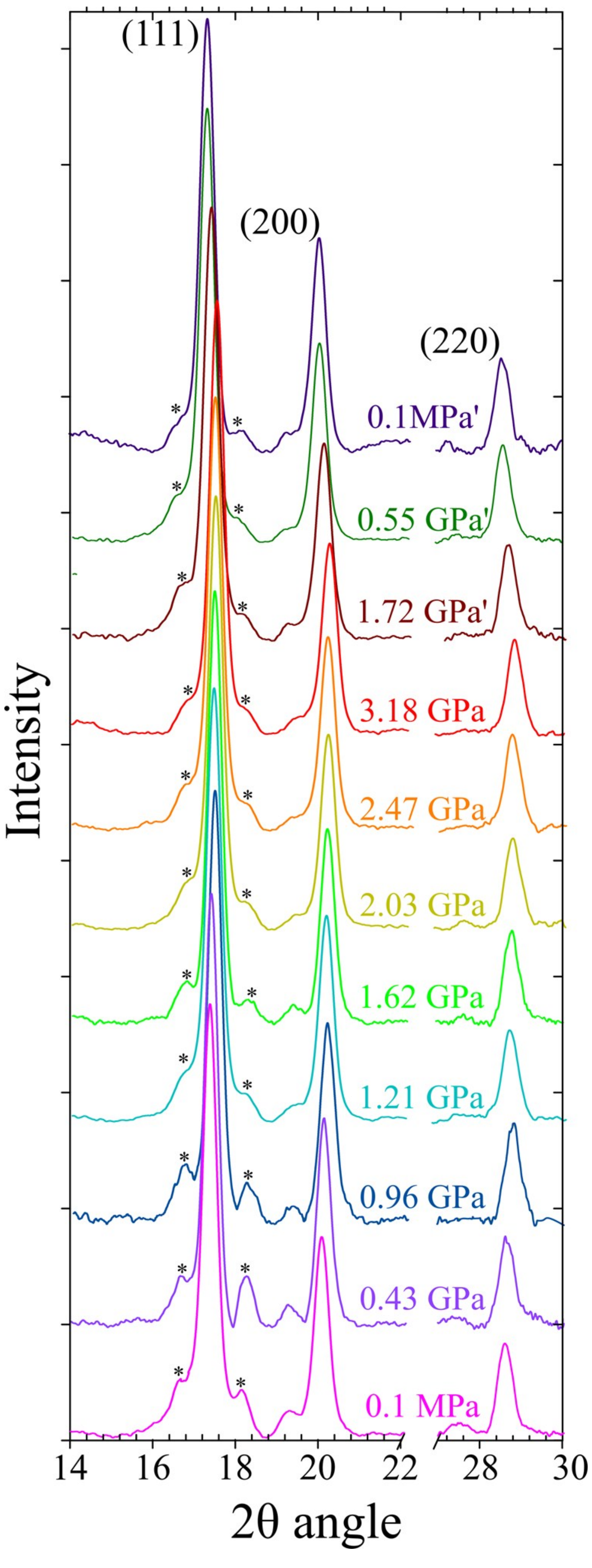
(111)
(200)
(220)
0.1MPa'
0.55 GPa'
1.72 GPa'
3.18 GPa
2.47 GPa
2.03 GPa
1.62 GPa
1.21 GPa
0.96 GPa
0.43 GPa
0.1 MPa
*
Intensity
14
16
18
20
22
28
30
2θ angle

**Figure S7.** X-Ray powder diffraction patterns ($\lambda_{MoK\alpha}$ = 0.71073 Å) from Au NRs compressed at 298 K in water and ice. The patterns on decompression were recorded at 1.92 GPa, 0.85 GPa and atmospheric pressure. Three most intense reflections 111, 200 and 220 of Au RDs are indexed in brackets. Inconsistency connected with deformation of gasket have been marked with an asterisk.

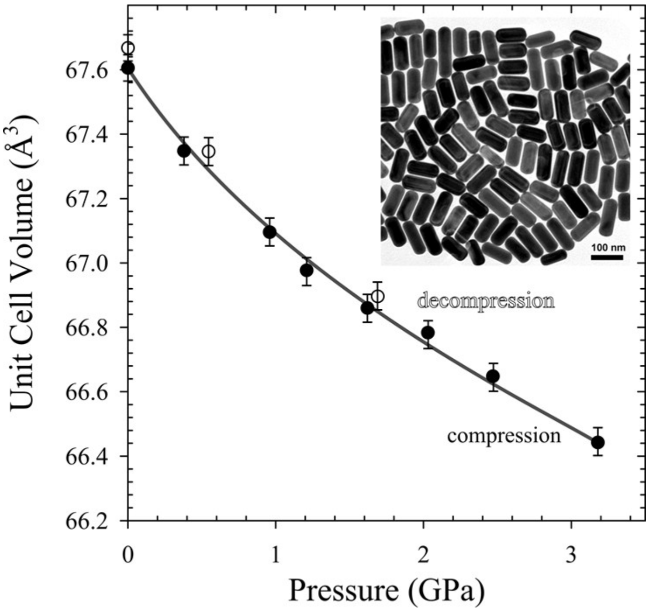

**Figure S8.** Au NRs unit cell volume changes with increasing (filled circles) and decreasing (empty circles) pressure. Au NRs foil was compressed isothermally to 3.18 GPa in glycerine without phase transition.

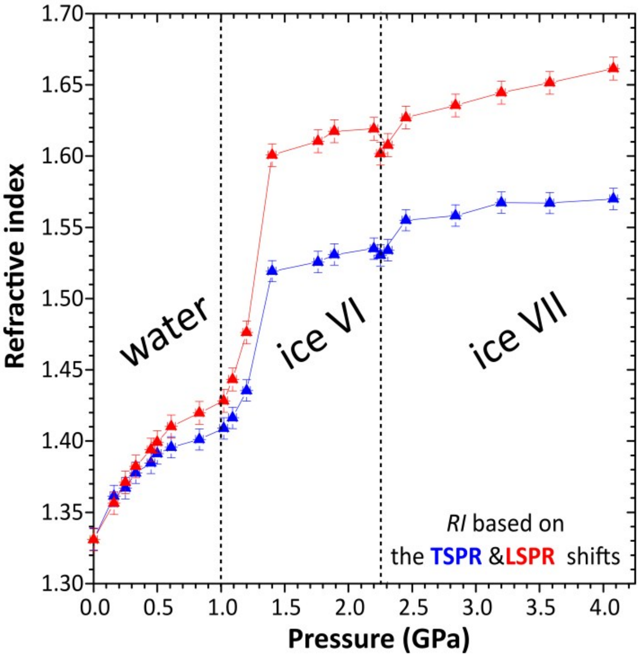

**Figure S9.** Refractive index of water compressed under high-pressure conditions, determined by TSPR and LSPR peak shifts as a function of pressure.

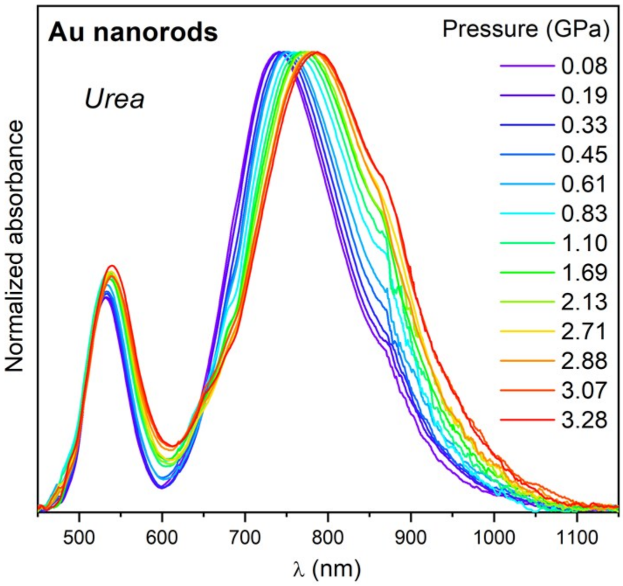

**Figure S10.** Absorption spectra of Au NRs in compressed urea crystals.

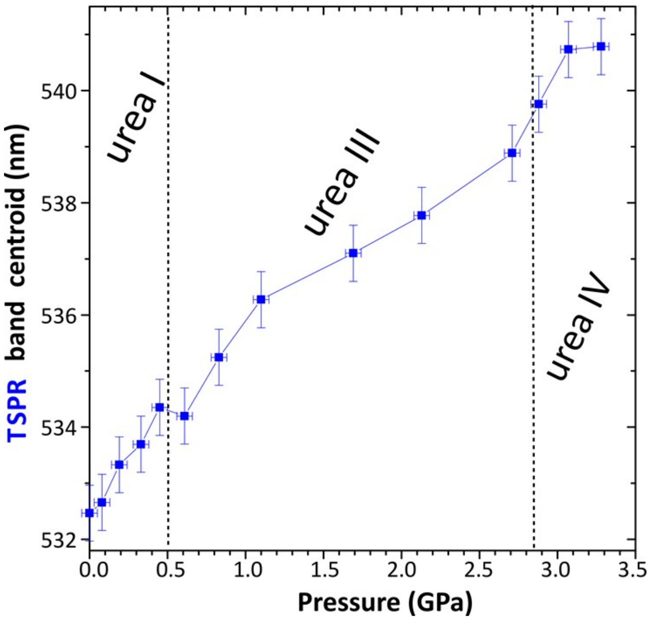

**Figure S11.** Spectral position (centroid) of the TSPR peak of Au NRs in compressed urea crystals as a function of pressure.

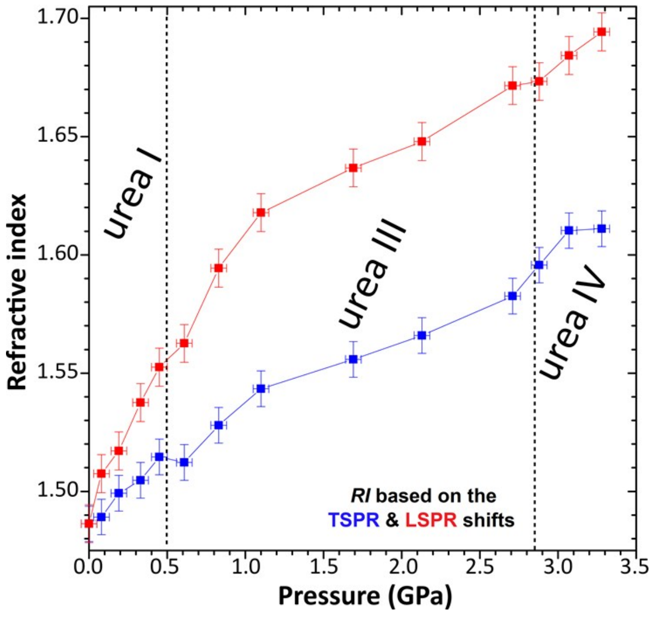

**Figure S12.** Refractive index of urea compressed under high-pressure conditions, determined by TSPR and LSPR peak shifts as a function of pressure.

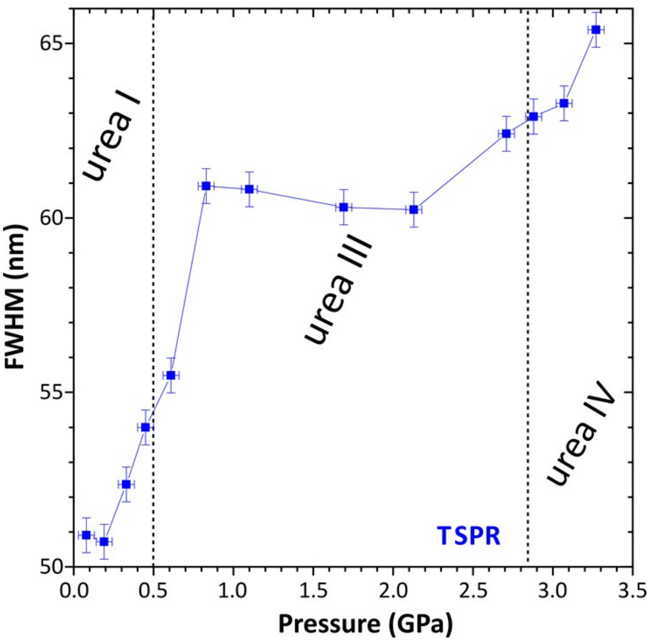

**Figure S13.** FWHM of the TSPR peak of Au NRs in compressed urea crystals as a function of pressure.

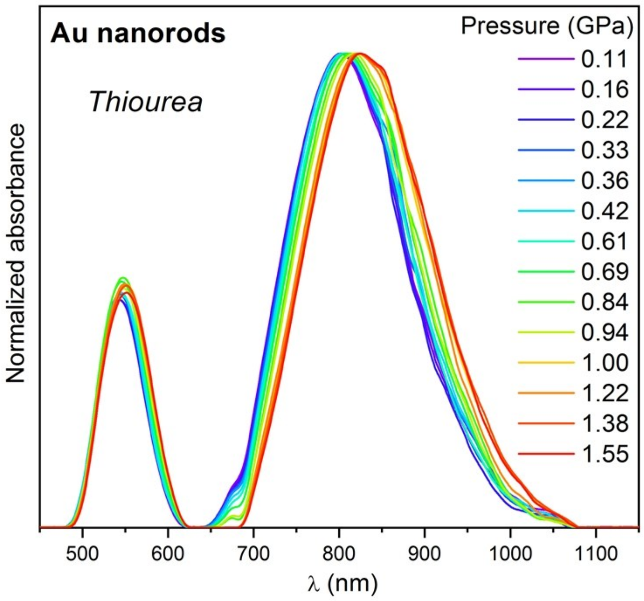

**Figure S14.** Absorption spectra of Au NRs in compressed thiourea crystals.

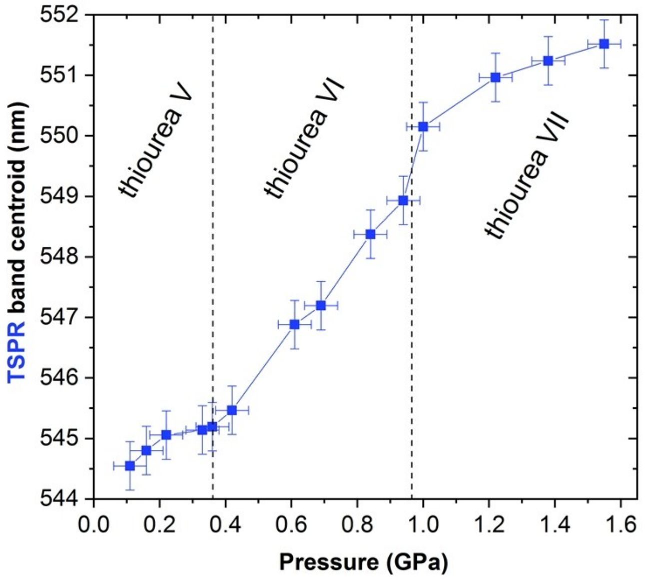

**Figure S15.** Spectral position (centroid) of the TSPR peak of Au NRs in compressed thiourea crystals as a function of pressure.

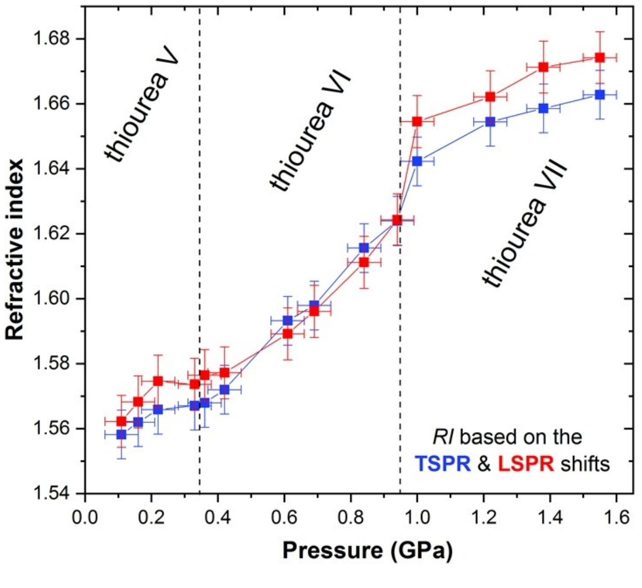

**Figure S16.** Refractive index of thiourea compressed under high-pressure conditions, determined by TSPR and LSPR peak shifts as a function of pressure.

**Table S1. List of the compression runs performed for absorption measurements, including the pressure values for each measurement.**

| water<br>run 1<br>P (GPa) | water<br>run 2<br>P (GPa) | urea<br>run 1<br>P (GPa) | urea<br>run 2<br>P (GPa) | thiourea<br>run 1<br>P (GPa) | thiourea<br>run 2<br>P (GPa) |
|---|---|---|---|---|---|
| 0.0001 | 0.16 | 0.19 | 0.08 | 0.11 | 0.16 |
| 0.25 | 0.33 | 0.45 | 0.33 | 0.22 | 0.36 |
| 0.50 | 0.45 | 0.83 | 0.61 | 0.33 | 0.61 |
| 0.83 | 0.61 | 1.69 | 1.10 | 0.42 | 0.84 |
| 1.09 | 1.02 | 2.71 | 2.13 | 0.69 | 1.00 |
| 1.40 | 1.20 | 3.07 | 2.88 | 0.94 | 1.38 |
| 1.89 | 1.76 |  | 3.28 | 1.22 |  |
| 2.31 | 2.20 |  |  | 1.55 |  |
| 2.25 | 2.84 |  |  |  |  |
| 2.45 | 3.58 |  |  |  |  |
| 3.20 |  |  |  |  |  |
| 4.08 |  |  |  |  |  |
| 2.60 |  |  |  |  |  |
| 0.85 |  |  |  |  |  |
| 0.0001 |  |  |  |  |  |

## References

(1) M. Wojdyr, Fityk: a general-purpose peak fitting programm, *J. Appl. Cryst.* **2010**, *43* 1126-1128.

(2) Merrill, L.; Bassett, W. A. Miniature diamond anvil pressure cell for single crystal x-ray diffraction studies. *Rev. Sci. Instrum.* **1974**, *45*, 290-294.

(3) Katrusiak, A. High-pressure crystallography. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2007**, *64*, 135–148.

(4) Piermarini, G. J.; Block, S.; Barnett J. D.; Forman, R. A. Calibration of the pressure dependence of the $R_1$ ruby fluorescence line to 195 kbar. *J. Appl. Phys.*, **1975**, *46*, 2774–2780.

(5) Mao, H. K.; Xu, J.; Bell, P. M. Calibration of the Ruby Pressure Gauge to 800 Kbar under Quasi-Hydrostatic Conditions. *J. Geophys. Res.* **1986**, *91*, 4673–4676.

(6) Xcalibur CCD System, CrysAlisPro Software System, **2014**.