Electronic Supplementary Information

Plasmonic Behaviour of Poly(2-ethyl-2-oxazoline)-Coated

Gold Nanoparticles for Sensing and Temperature-Controlled

Applications

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1. Synthetic details and Characterization

Materials and Methods:

Chemicals. 2-Ethyl-2-oxazoline (EtOx, Sigma - Aldrich, >99%) was dried over calcium hydride and distilled under inert argon atmosphere. Methyl p-toluene sulfonate (MeOTs, 98%) potassium ethyl xanthogenate (97%) and calcium hydride (CaH₂, 93%) were acquired from Sigma - Aldrich and used without prior purification. Anhydrous acetonitrile was used without distillation (Acros Organics, extra dry 99.9%). Other solvents were purchased from Fisher Chemical (HPLC grade). Citrate buffer stabilized AuNPs 40 nm diameter, OD 1, PDI <0.2 from Sigma – Aldrich.

Nuclear magnetic resonance (NMR) ¹H spectrum was recorded on a Bruker 500 MHz spectrometer (500 MHz for ¹H) at room temperature. Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference (CDCl₃,¹H = 7.26 ppm).

Microwave System Biotage Initiator EXP with IR-sensor for temperature control was used.

Matrix adsorption laser desorption ionization time of flight (MALDI TOF) measurements were performed on a Bruker Daltonics Biflex III (SFR Matrix, University of Angers) mass spectrometer using a nitrogen laser delivering 2 ns pulses at 337 nm with positive ion ToF detection performed an accelerating voltage of 25 kV, and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile using (DCTB) as matrix.

Dynamic light scattering (DLS) studies of samples were performed using a NanoBrook Omni particle size analyzer (Brookhaven Instruments, USA) equipped with a 532 nm laser using quartz cell (pathlength of 1 cm). The scattered light was measured at an angle of 173° (backscattering). Measurements at each temperature point were performed at a stabilized temperature.

Zeta potential (ζ) of AuNPs and PEtOx-AuNPs were measured using a Zetasizer[®] Nano ZS (Malvern Panalytical, United Kingdom).

Light extinction (optical density) spectra were recorded on a Cary 60 spectrophotometer (Agilent, USA) using quartz cell (pathlength of 1 cm) equipped with Peltier unit for temperature measurements. Measurements at each temperature point were performed at a stabilized temperature.

Raman spectra were recorded by RM1000 μ -Raman spectrometer (Renishaw, UK) using 532 nm Raman laser at room 20 °C temperature.

Transmission electron microscopy (TEM) images were acquired using a Jeol JEM 1400 120 keV and equipped with a Gatan Orius digital camera. 3μ L of PEtOx-AuNPs or AuNPs solution were deposited on a formvar coated grid (formvar/cupper without a carbon film). The grid was allowed to dry for 4 hours at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on drop-cast PEtOx-AuNPs solutions on silicon wafers. The system utilized a monochromatic Al K α X-ray source with an energy of 1486.6 eV. Spectra were collected at a take-off angle of 90°, with a spot size of 0.7 × 0.3 mm2 under a vacuum pressure below 10–8 mbar. High-resolution scans targeting N 1s, S 2p, C 1s, O 1s and Au 4f regions were obtained with a 0.1 eV step size and a pass energy of 40 eV. All spectra were calibrated to the Au 4f reference binding energy of 83.96 eV, corresponding to the metallic gold state, without the use of an internal standard. Data analysis was performed with CASA XPS software, employing Shirley background subtraction followed by curve fitting using pseudo-Voigt functions, which combine Gaussian and Lorentzian profiles. Surface atomic ratios were calculated based on the normalized core-level spectral areas, adjusted for the number of scans and the element-specific sensitivity factors: O 1s (0.78), S 2p (0.668), N 1s (0.477), C 1s (0.278) and Au 4f (6.25).

Size exclusion chromatography (SEC). The number-average molar mass (M_n), weight-average molar mass (M_w) and dispersity (D) values of α -methyl- ω -ethylxanthato-poly(2-ethyl-2-oxazoline) (PEtOx) were measured by SEC using N,N-dimethyl formamide (DMF) with LiBr (1 g.L⁻¹) as an eluent and narrow linear poly(methyl methacrylate) was used as standards ranging in molar mass from 0.904 kg.mol⁻¹ to 304 kg.mol⁻¹.

Synthetic details:

 α -methyl- ω -ethylxanthato-poly(2-ethyl-2-oxazoline) (PEtOx)



Figure S1. Synthesis of PEtOx by cationic ring-opening polymerization.

The synthesis of PEtOx *via* cationic ring-opening polymerization (CROP) is presented in Figure S1. In a 30 mL vial with a magnetic stirrer bar, MeOTs (0.14 g, 0.75 mmol, 1 equiv.) was dissolved in 7.6 mL of acetonitrile. The solution was purged under argon for 15 min before the addition of EtOx (3 mL, 0.03 mol, 40 equiv.), adjusting the total monomer concentration to 4 M. Polymerization was carried out in a microwave reactor at 140 °C and 600 W for 20 min.

After cooling to room temperature, an excess of potassium ethyl xanthogenate (0.144 g, 0.9 mmol, 1.2 equiv.) was added at 0 °C and the reaction mixture was stirred overnight at room temperature. The resulting solution was filtered, and the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform and washed twice with a saturated NaHCO₃ aqueous solution and once with brine to remove the excess of potassium ethyl xanthogenate. The organic phase was concentrated, and the polymer precipitated in ice cold diethyl ether. Characterization data for PEtOx are presented in Figures S2, and Table 1.

¹H NMR (CDCl₃), δ (ppm): 4.6 (CH₂ of ethyl xanthato group), 3.2 – 3.5 (CH₂ backbone of the polymer), 3.0 (CH₃ of the initiator), 2.1 – 2.3 (CH₂ of EtOx), 1.5 (CH₃ of ethyl xanthato group), 1.2 – 1.3 (CH₃ of EtOx).



Figure S2. Fragment of MALDI-TOF spectrum of PEtOx, DCTB pos. mode, M-H⁺.

Table S1. Characteristics of PEtOx synthesized by CROP.

Polymer	DP (theor.)	M _{nNMR} ^a (kg.mol⁻¹)	DF _{NMR} a (%)	M _{nMALDI-TOF} ^b (kg.mol ^{−1})	M _{nSEC} ^c (kg.mol ^{−1})	Ðc
PEtOx	40	3.97	97	3.2	3.9	1.25

^a M_n and degree of functionalization (DF) were determined by ¹H NMR in CDCl₃, ^b M_n was determined by MALDI-TOF, ^c M_n and D were determined by SEC in DMF.



Figure S3. TEM image of PEtOx -coated AuNPs and the corresponding size distribution ($40 \pm 2 \text{ nm}$, n = 100).

Commercial citrate-stabilized gold nanoparticles with a diameter of 40 nm, optical density of 1, and polydispersity index (PDI) < 0.2 were purchased from Sigma–Aldrich. These AuNPs were used directly in our experiments and also served as the core material for the preparation of PEtOx-coated AuNPs, given their identical gold core morphology and polydispersity (Fig. S3).



2. X-ray photoelectron spectroscopy

Figure S4. a - Survey spectrum of drop-casted PEtOx-AuNPs solutions on silicon wafers ; b - S 2p core level spectrum of the PEtOx-AuNPs. The signal recorded between 166 and 170 eV (fitted with two components at 167.5/168.7 eV) comes from traces of methyl p-toluene sulfonate used as polymerization initiator.

3. Extinction spectra of PEtOx-AuNPs



Figure S5. (a) – Extinction spectra of AuNPs and PEtOx-AuNPs with extinction peak of surface plasmon (SPR) and extinction peak of polymer (PEtOx) at 20 °C; (b) – SPR peak spectral range of extinction spectra.

4. LCST transition in PEtOx shell of AuNPs



Figure S6. Transformation of SPR peak of AuNPs (a, b) and PEtOx peak (c, d) in extinction spectrum of PEtOx-AuNPs during the heating – cooling cycle in the temperature range of $20 - 91 - 20^{\circ}$ C. The dashed arrow shows the direction of the temperature variation.

The PEtOx peak height is constant during heating within the temperature range of 20–78°C. Then a sharp decrease is observed between 78°C and 91°C, corresponding to a Lower Critical Solution Temperature (LCST) transition, (Fig. 3a). Obviously, the observed decrease is attributed to aggregation of the polymer molecules i.e. the transition to hydrophobic state, leading to precipitation and as a result, to decrease in optical density. During reverse cooling in the LCST transition range (91–76°C), the trend of decrease of the polymer peak height persists, which is obviously a consequence of the continued aggregation of polymer molecules. However, upon cooling in the range below the LCST transition region (76–20°C),

the dependence becomes constant, which indicates the reverse transition of PEtOx into the hydrophilic phase and, as a result, the termination of aggregation process. The LCST transition in the PEtOx shell of PEtOx-AuNPs is also clearly detected by the SPR peak (Fig. 3b–d). The peak height decreases smoothly and monotonously during heating in the temperature range of 20–76°C, then a sharp drop is observed between 76°C and 82°C, and with further heating in the range of 82-91°C, the height decrease slows down (Fig. 3b). A sharp decrease in the intensity of the SPR peak at 76-82°C indicates a LCST transition, having the same nature as a sharp drop in the polymer peak height, namely aggregation, which leads to the NPs precipitation. A gradual decrease of the SPR peak height at temperatures out of range of the LCST transition (20–76°C and 82–91°C) is characteristic for noble metal NPs (AuNPs in particular) and can be explained by an increase in the plasmon damping constant due to the intensification of electron-phonon scattering with increasing temperature.¹ During reverse cooling, the behavior of the height of the SPR peak is similar to the behavior of the height of the polymer peak described above and obviously has the same nature.

Meanwhile, heating in the region of the LCST transition (76–91°C) leads to a sharp red shift (Fig. 3c) and broadening (Fig. 3d) of the SPR peak. Obviously, the sharp red shift is caused by a sharp increase in the dielectric constant of the polymer shell during its shrinkage and densification at the transition, as well as by the aggregation of NPs. The substantial broadening of the SPR peak is likely a result of increased fluctuations in the dielectric constant of the NP environment during aggregation. This phenomenon arises from the statistical nature of aggregate formation, leading to the creation of aggregates with varying sizes and densities.

A sharp increase in the width of the SPR peak is probably a result of increased fluctuations in the dielectric constant of the surroundings of AuNPs during their aggregation. This phenomenon arises from the statistical nature of aggregate formation, leading to the creation of aggregates with different sizes and densities.

The slight monotonic red shift and broadening of the SPR peak upon heating in the temperature range below the LCST point (20–76°C) can be attributed to the increase in plasmon damping constant, which was discussed above. Similarly, to the behavior of the SPR peak height, during cooling within the LCST range (91–76°C), the trends for wavelength and width of the peak are maintained, i.e. the red shift and broadening are observed (Fig. 3c, d). During cooling in the range below the LCST point (76–20°C), the observed effects reverse, resulting in a blue shift and narrowing of the SPR peak. Moreover, initially in the range of 76–

55°C, the blue shift is quite sharp, which is caused by a sharp decrease in the dielectric constant of the polymeric environment of AuNPs, which occurs as a result of a decrease in the density of the shell during its transition to a hydrophilic state and partial destruction of aggregates. When cooling in the range of 55–20 °C, the blue shift becomes weakly pronounced. This weak blue shift and slight narrowing of the SPR peak is due to the decrease of the plasmon damping constant with decreasing temperature.



5. Raman spectra of PEtOx and PEtOx-AuNPs

Figure S7. Raman spectra of PEtOx and PEtOx-AuNPs deposited on Al substrate before (a) and after (b) heating-cooling 20–91–20°C cycle.

6. Z-scan photothermal lens spectroscopy

Thermal lens spectroscopy (TLS) provides a sensitive and quantitative method for measuring photothermal conversion in nanoparticles, molecular systems, and other light-absorbing materials with minimal sample perturbation. The excitation powers used are modest (in the milliwatt range), the resulting temperature increase in the solvent is minimal (well below $0.1 \,^{\circ}K$), and the response time is rapid (in the millisecond range). In addition to measuring photothermal conversion efficiency, TLS also enables quantitative determination of the thermal diffusivity of the medium. While TLS has been extensively and successfully applied to molecular systems in solution over the years,^{2,3,4} studies involving nanoparticle suspensions have only recently started to emerge. Building on the approach established in prior work,⁵ we employed a newly developed Z-scan thermal lens setup operating at 532 nm (Fig. S8), referred as Z-scan photothermal lens spectroscopy (ZsTLS).



Figure S8. Schematic of the Z-scan experimental setup. The sample cell, mounted on a motorized translation stage, is scanned along the beam propagation axis around the focal point (z = 0). The labeled components are: focusing lens (L1), optical chopper (Ch), circular aperture (Ap), photodiode detector (PD), digital storage oscilloscope (DSO), and computer (Cp).

A fused silica cell, 1 cm thick, containing PEtOx-AuNPs or AuNPs (40 nm Au core diameter), is mounted on a translation stage that scans along the z-axis (the optical axis), near the region defined by the depth of field (Rayleigh distance $Z_0 = 1.2 \text{ cm}$) of a focused Gaussian beam ($\omega = 45 \text{ }\mu\text{m}$). Heat generated in the sample induces a phase mask, which is observed at each position of the specimen by measuring the far-field diffraction intensity with a photodiode placed on the optical axis at a long distance from the cell, similar to the closed-aperture Z-scan method.⁶ This z-scanning technique is well established for characterizing third-order nonlinear optical indices and enables accurate measurement of the induced phase shift,⁷ which is thermal when using relatively low intensities in the continuous-wave (cw) regime.

The refractive signal (Fig. S9) is defined as the fractional intensity change observed when the cell is positioned at a specific z location after reaching the stationary regime (the exact mathematical definition of S is provided in Eq. 10 of reference ⁸). A typical thermal lens signal curve comprises a peak and a valley, as illustrated in Fig. S8 with example data (blue circles) obtained for PEtOx-AuNPs. The incident power was P = 2.3 mW, corresponding to an intensity of $I_0 = 0.7 MW/m^2$, with a suspension characterized by an extinction coefficient $\alpha_e = 89.4 m^{-1}$. The characteristic rise time ($t_c(z)$) of the signal was measured to be a maximum of 5 ms. Consequently, the chopper frequency was set to allow a heating and extinction time of approximately 230 ms, significantly longer than t_c . This ensured the system reached a steady-state regime while allowing adequate cooling time between heating pulses.



Figure S8. Relative intensity variation *S* versus normalized position of the sample cell $V = z/Z_0$ obtained for PEtOx-AuNPs using 2.3 mW incident power. Experimental data in blue circles and numerical fit in red line.

It should be noted that the experimental measurements are clear, with S, the relative intensity value, tending to be less than zero for pre-focal positions (V < 0) and greater than zero for post-focal ones. This behavior indicates that the sample acts as a diverging lens. Most solvents exhibit a decrease in refractive index with increasing temperature, explaining why the induced thermal lens is divergent for water.

The solid red line in Figure S8 represents the fit of the experimental data (blue stars), yielding $\theta_{eff} = 311 \ mrad. \ \theta_{eff}$, is a coefficient that characterizes the thermally induced phase filter (see Eq. 7 in reference⁹). It is proportional to the incident power, the sample absorbance, and the thermal properties of the solvent. The absorption coefficient α_a can be calculated using Eq. (12) in reference⁹, giving $\alpha_a = 77.4 \ m^{-1}$.

These parameters are necessary to determine the quantum yield Φ , which represents the ratio of scattered photons to extinguished photons: $\Phi = [exp(-\alpha_a L) - exp(-\alpha_e L)]/[1 - exp(-\alpha_e L)]$. The photothermal efficiency $PTE = 1 - \Phi = [1 - exp(-\alpha_a L)]/[1 - exp(-\alpha_e L)]$. This term quantifies the fraction of light extinction not due to scattering but instead absorbed by the nanoparticles, leading to photothermal heating and the observation of the thermal lens signal.

To increase the reliability of the measurement, the experimental methodology involves the implementation of multiple measurements at varying laser power on a single sample, to plot θ_{eff} against the incident power (P, in W) as presented in Figure S9. This approach allows us to initially assess the linearity of the data, thereby ensuring the accuracy of the measurement. Secondly, it enables us to determine the slope coefficient of the linear regression line and to calculate the absorption of the sample, limiting the error due to statistical analysis.



Figure S9. Linear data fit of NPs suspension in water for the citrate stabilized gold nanoparticles AuNPs (in black) and α -methyl- ω -ethylxanthato-poly(2-ethyl-2-oxazoline) stabilized gold nanoparticles PEtOx-AuNPs (in red) with $\alpha_e(m^{-1}) = 89.4, 88.3$ obtaining $\alpha_a(m^{-1}) = 77.8, 69.0$, respectively at 532 nm.

Figure S9 presents the measurement data obtained for each sample in this study. The linear variation trend of the data indicates the good experimental behaviour following Eq. 7 in ⁹: $\theta_{eff} = P dn/dT [1 - exp(-\alpha_a L)]/\lambda k$. The absorption coefficient relative to the AuNPs and PEtOx-AuNPs was measured to be $\alpha_a(m^{-1}) = 77.8$, and 69.0, respectively. This was done using least squares regression analysis as developed in reference.⁸ For AuNPs the response is always weaker in terms of phase shift and therefore thermal efficiency. The red fit of the PEtOx-AuNPs shows a significant shift and therefore a much stronger response at the same power levels as the black curves, demonstrating the superior thermal efficiency of this compound.

Finally, combining the absorption coefficient α_a with the extinction coefficient α_e , which is measured precisely by classical transmission experiment (for details see ⁸), allows to obtain the photothermal efficiency (PTE) as shown in Table 2.

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