Enhanced photo- and thermo stability of Au nanorods conjugated with small thiols

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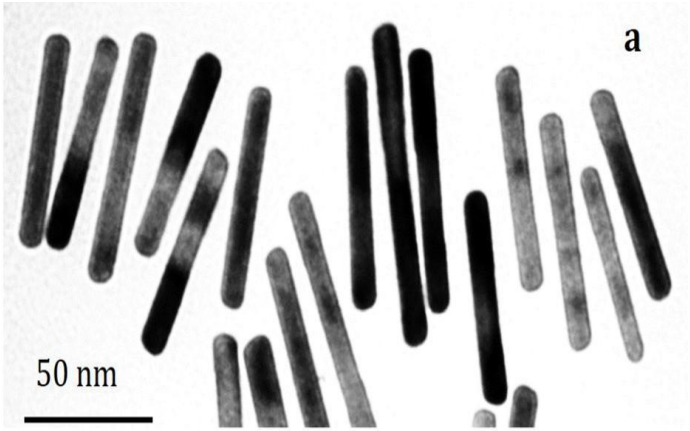
Motivation

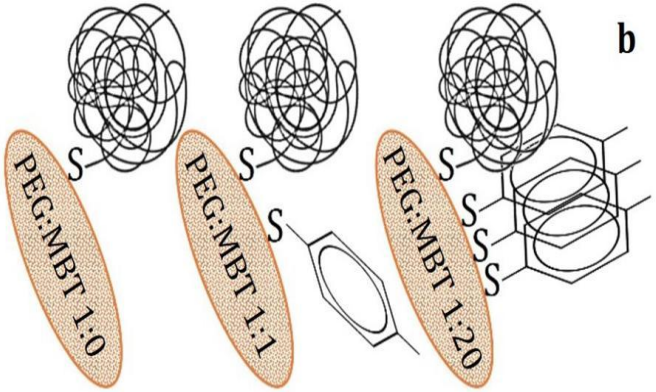
The optimization of Au nanorods photostability is an important issue because, relevant optical energy thresholds fall well below maximum permissible exposure boundaries needed for many (for example photoacoustic) applications and so represent a limiting factor.

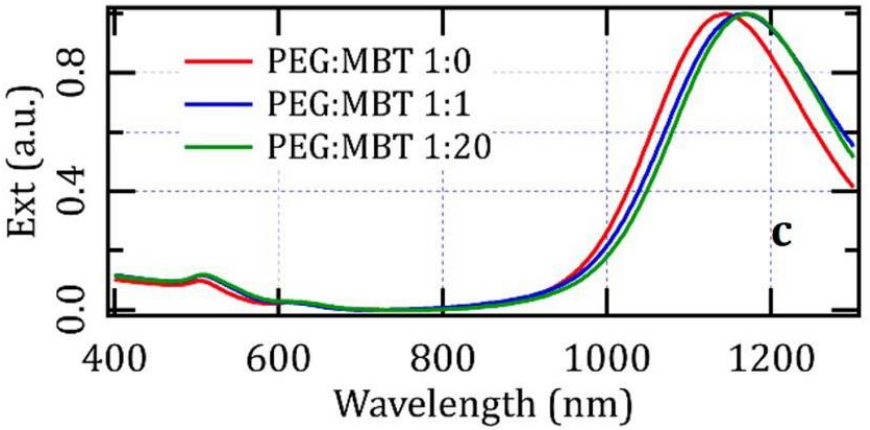
Here, we present a protocol that makes use of thiolated aromatic molecules to affect the kinetics of melting and reshaping of gold nanorods, and we assess its performance under conditions of practical relevance for photoacoustic applications.

Particles under study

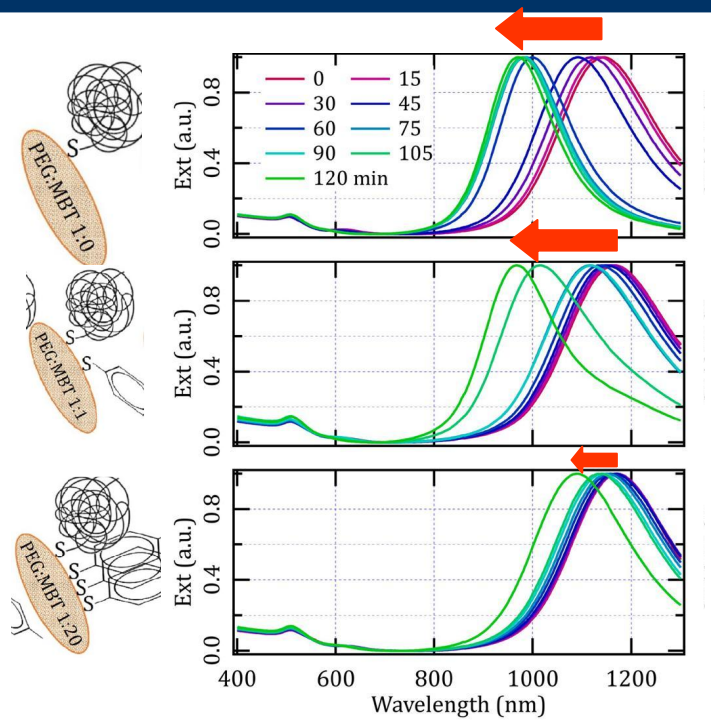


AuNRs with aspect ratio of 7.7 , plasmon resonance 1170 nm.
AuNRs were functionalized with thiolated PEG and mixtures of thiolated PEG with methylbenzene thiol (MBT). Final molar ratio PEG/MBT were 1:0, 1:1 and 1:20

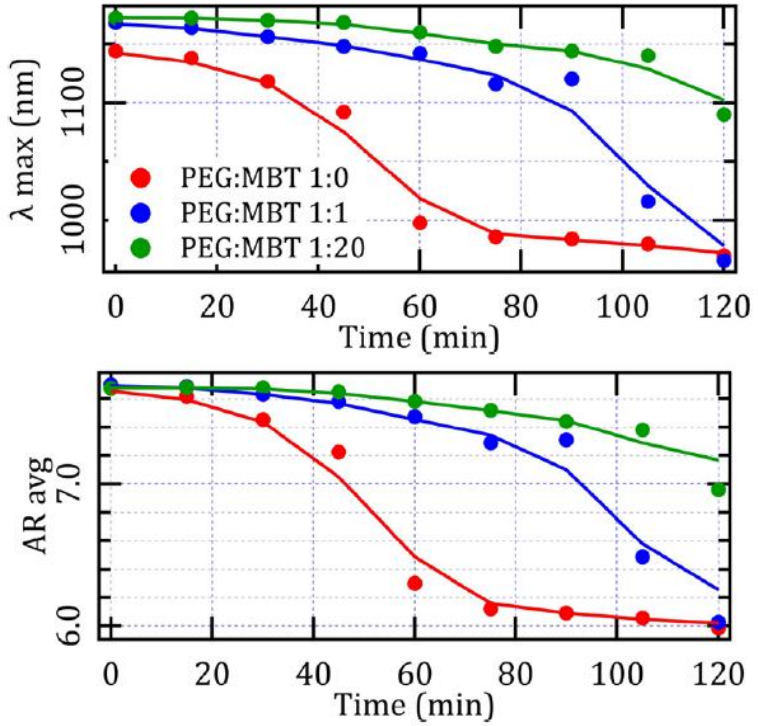




Thermal stability under 90 ^{O}C heating

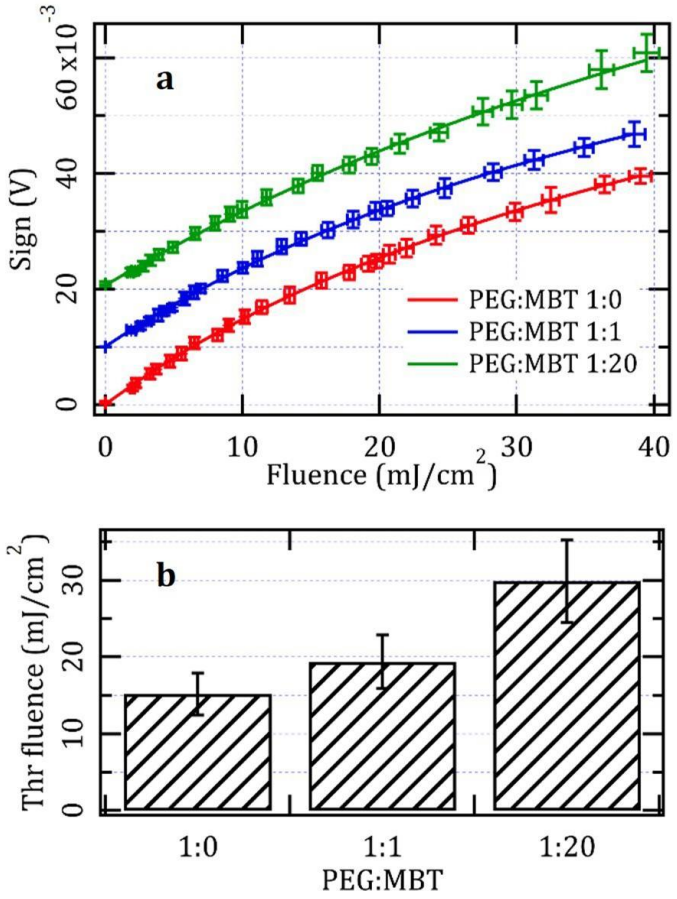


Normalized spectra of optical extinction for particles modified with the named mixtures of thiols and treated for the named intervals at 90 °C



The kinetics of evolution of peak position of the longitudinal band and average value of AR

Photostability under laser illumination 1064 nm, 4 ns, 40 mJ/cm^2



(a) Photoacoustic signal as a function of fluence of the optical trigger for particles prepared with the named mixtures of thiols: dots are experimental values; lines are a fit to an analytical model that accounts for a depletion of optical absorbance. (b) Threshold of fluence of the optical trigger corresponding to a loss of efficiency of photoacoustic conversion by 25%

Conclusion

We have investigated the effect of an aromatic thiol as MBT on the thermal and photostability of gold nanorods. We have treated colloidal suspensions of gold nanorods with mixtures of thiolated PEG and MBT with different molar ratios ranging from pure PEG to PEG/MBT 1:20. During annealing in an oven set at 90 °C, we found a sharp effect of MBT to delay the deformation of gold nanorods, for example, from 45 min to beyond 2 h. For instance, whereas after 1 h particles with PEG alone lost more than 70% of optical absorbance at their initial peak position, those saturated with MBT remained nearly unchanged. This result may enable the introduction of gold nanorods in biochemical processes as the polymerase chain reaction that require thermal annealing at temperatures approaching the boiling point of water over tens of minutes. In addition, we addressed the effect of MBT on the photostability of gold nanorods irradiated under conditions of interest for photo-acoustic imaging. Also, in this case we found a delay of relevant damage thresholds by about a factor of 2, that is, from 15 to 30 mJ/cm

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