Temperature triggered dynamic self-assembly of gold nanoparticles and -rods: The role of hysteresis

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The development of dynamic self-assembly systems is still a young research area.(1) An in-depth investigation of the assembly and disassembly processes is of great importance to gain insights into the intermediate assembly states. Here we show the detailed picture of temperature-driven reversible clustering of gold nanoparticles (gold nanospheres(2) and gold nanorods) functionalized with bis(p-sulfonatophenyl)phenylphosphine (BSPP). In-situ UV-VIS spectroscopy revealed the emergence of hysteresis during the cyclic temperature changes (Fig. 1). By varying nanoparticles diameter and their surface charge as well as the rate of applied stimulus we were able to describe qualitatively the contribution of thermodynamic and kinetic hysteresis in the whole process.
A particularly intriguing case is the reversible clustering of gold nanorods, that exhibits an asymmetric hysteretic response. Upon the clustering, gold nanorods adapt to transient mutual configurations, such as tip-to-tip or side-to-side, enriching the hysteretic response (Fig 1b). In addition, the large absorption cross-section of gold nanorods in the infrared spectral range allowed us for taking advantage of their efficient light to heat conversion. By using infrared light, instead of an external heating source, we were able to control locally the change of temperature which in turn altered the colloidal stability of the nanorods, revealing again hysteretic and oscillatory behaviour.
We foresee that the presented experimental framework offers an exciting playground to study the nature of meta-stable assemblies, and enables possible applications in spatiotemporal catalysis, thermo-mechanical nanotransducers, smart windows, among others.

REFERENCES

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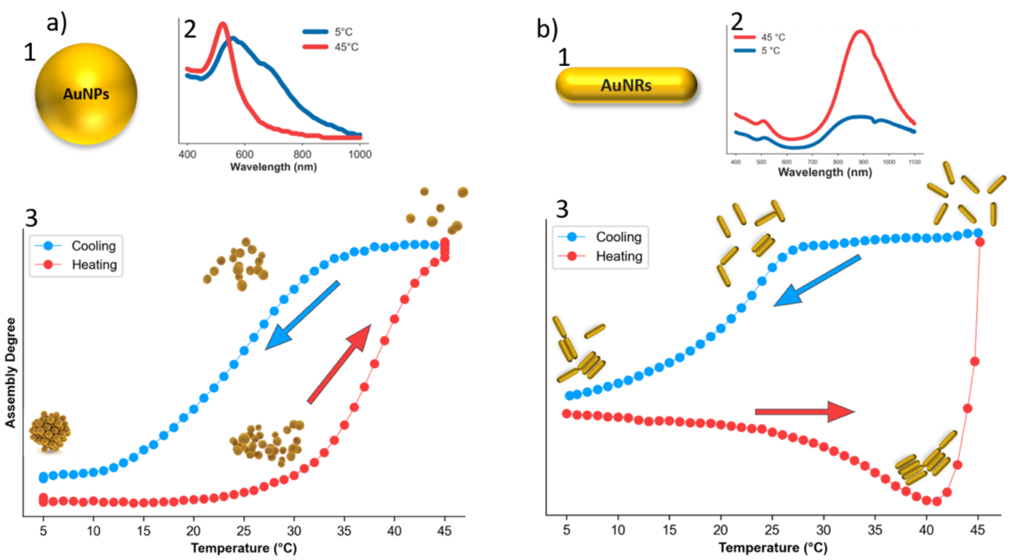

Figure 1 Temperature-induced reversible clustering of gold nanoparticles with hysteretic behavior. Upper panel demonstrates the change of optical properties for gold nanospheres (a) and nanorods (b). Lower panel shows the change of the aggregation degree over wide temperature range (5 - 45 °C). The nanoparticles can remain either in dispersed or aggregated states at the same temperature depending whether the sample is heated or cooled.