Supporting information

for

A general LbL strategy for the growth of pNIPAM microgels on Au nanoparticles with arbitrary shapes

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Calculation of degree of functionalization (α).

α has been calculated from the following equation:

\[
\%N = \frac{N_N \times M_N}{\alpha \times DP \times M_{AA^*} + (1 - \alpha) \times DP \times M_{AA}} \times 100
\]

where \(N_N\) is number of nitrogens in a PAA chain (modified), \(M_N\) is the atomic weight of nitrogen, \(DP\) is the degree of polymerization, \(M_{AA^*}\) is the molecular weight of modified PAA repeating unit and \(M_{AA}\) is the molecular weight of PAA repeating unit.
Figure S1. (Left) TEM images of Au spheres (top), decahedrons (center) and nanostars (bottom) used for the encapsulation within the pNIPAM microgels. (Right) Corresponding histograms displaying the size distribution of the colloids.
Figure S2. Visible-NIR spectra of dispersions of Au spheres (black), decahedrons (red), stars (blue) at different coating steps: as prepared (solid line), PAH coating (dashed line) PAA coating (dotted line). All spectra were normalized at 400 nm for better comparison.
**Figure S3.** Zeta Potential (in mV) of dispersions of Au spheres (black) and decahedrons (red, full circles), stars (red, hollow circles) at different coating steps.

**Figure S4.** Variation of the hydrodynamic diameter of Au@pNIPAM composite particles with 58 nm gold nanoparticle cores, with temperature. Closed and open symbols denote the heating and cooling cycles, respectively.
**Figure S5.** Position of the maximum of the surface plasmon band of 58nm gold spheres coated with pNIPAM, as a function of a number of swelling and collapse events (alternating between 20°C and 40°C).

**Scheme S1.** Schematic representation of star shaped and decahedral nanoparticles where the overall size is defined.
Figure S6. Representative TEM images of Au@pNIPAM nanocomposites synthesized in the presence of different amounts of SDS: (A) 1mM, (B) 0.5mM and (C) 0.25mM. (D) Histograms showing the number of Au NPs per microgel for different SDS concentrations: (top) 1mM, (center) 0.5 mM, and (bottom) 0.25 mM.
**Figure S7.** (A) Representative TEM image of Au@pNIPAM nanocomposites with ca. 41 nm Au stars as core. (B) Histogram showing the number of Au NPs per microgel and (C) Variation of the hydrodynamic diameter with the temperature.