

## **Supporting information**

**for**

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

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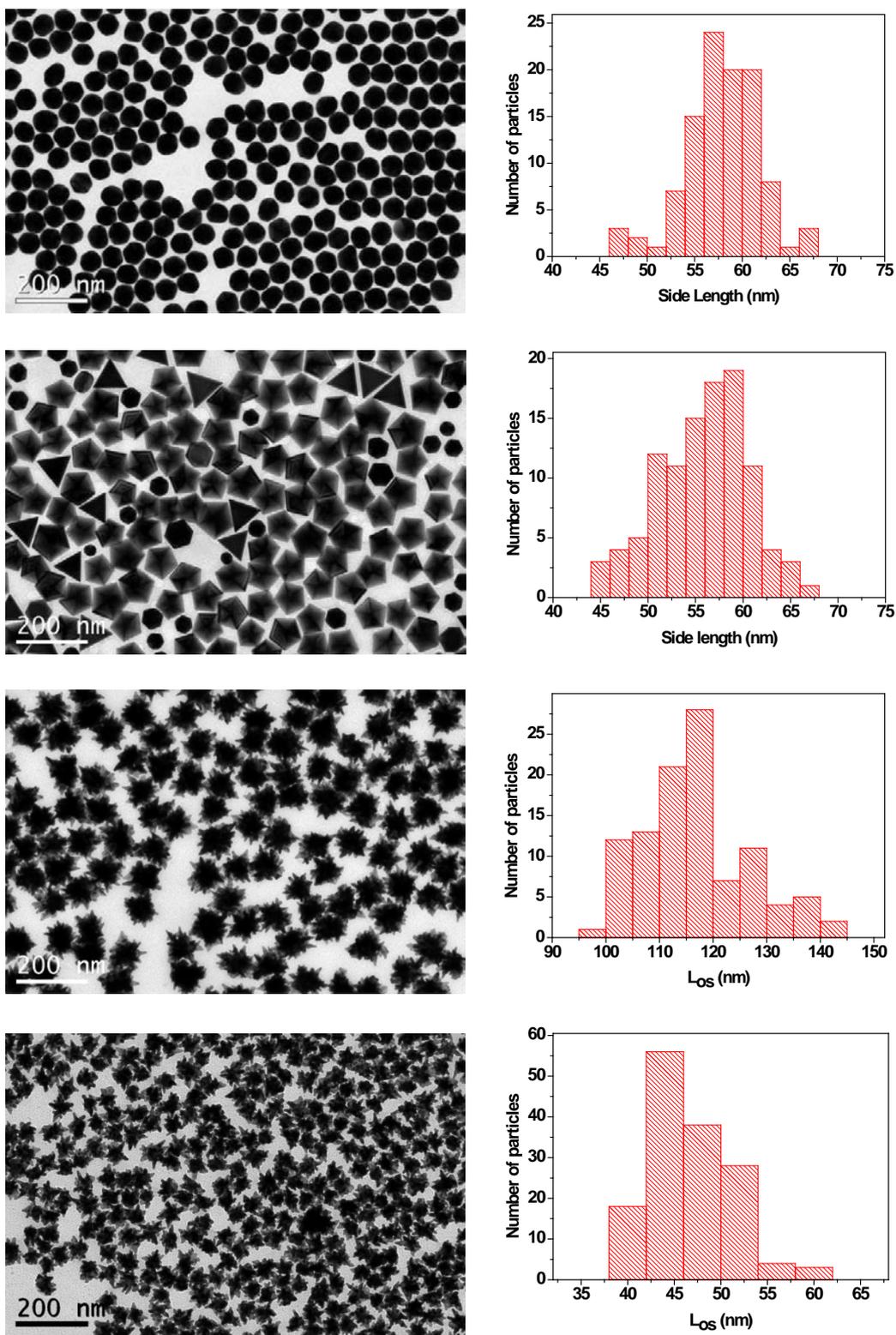
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### Calculation of degree of functionalization ( $\alpha$ ).

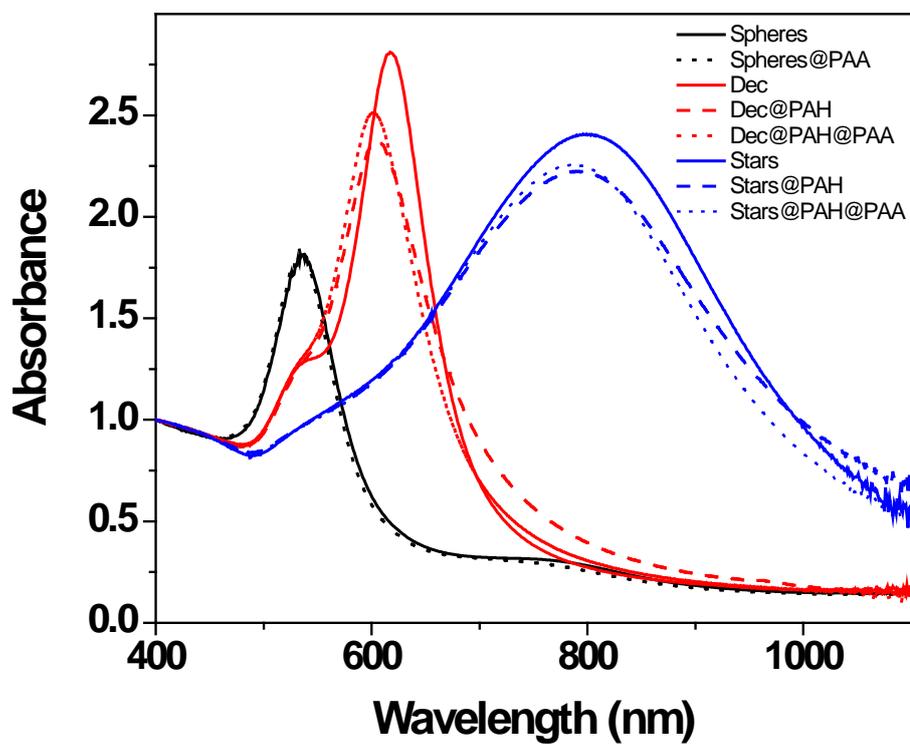
$\alpha$  has been calculated from the following equation:

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

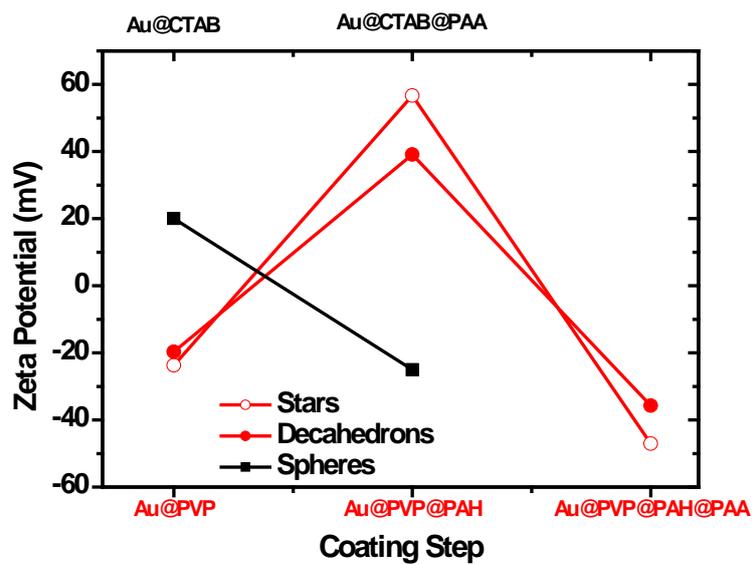
where  $N_N$  is number of nitrogens in a PAA chain (modified),  $M_N$  is the atomic weight of nitrogen,  $DP$  is the degree of polymerization,  $M_{AA^*}$  is the molecular weight of modified PAA repeating unit and  $M_{AA}$  is the molecular weight of PAA repeating unit.



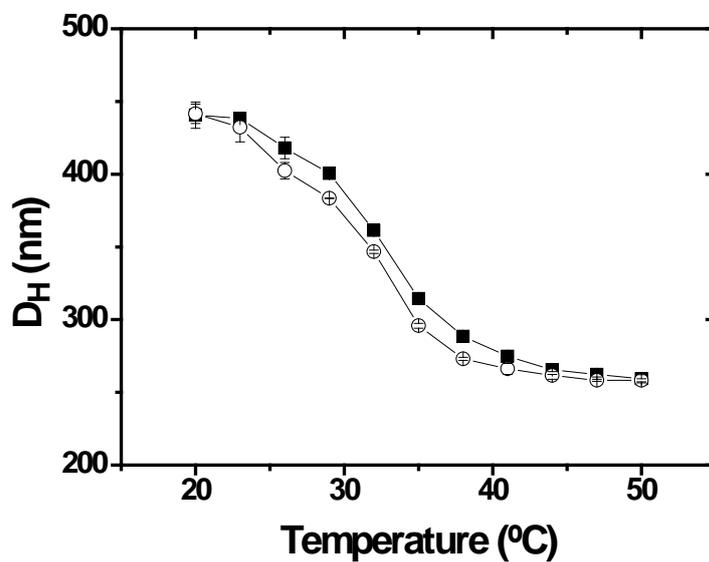
**Figure S1.** (Left) TEM images of Au spheres (top), decahedrons (center) and nanostars (bottom) used for the encapsulation within the pNIPAM microgels. (Right) Corresponding histograms displaying the size distribution of the colloids.



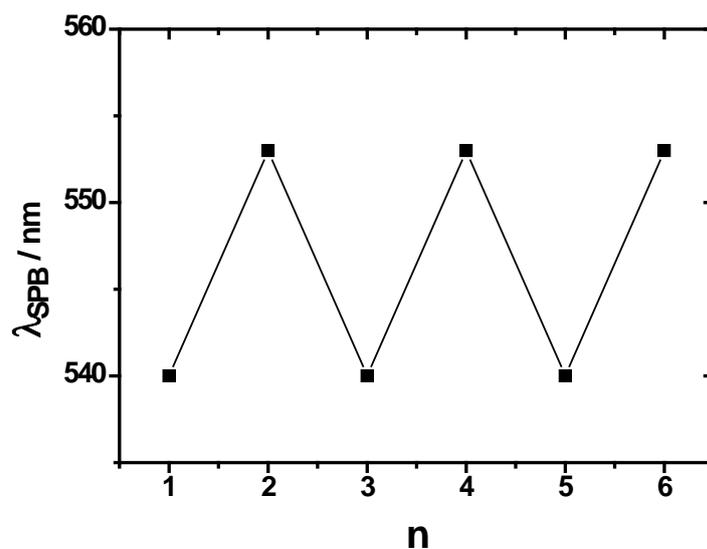
**Figure S2.** Visible-NIR spectra of dispersions of Au spheres (black), decahedrons (red), stars (blue) at different coating steps: as prepared (solid line), PAH coating (dashed line) PAA coating (dotted line). All spectra were normalized at 400 nm for better comparison.



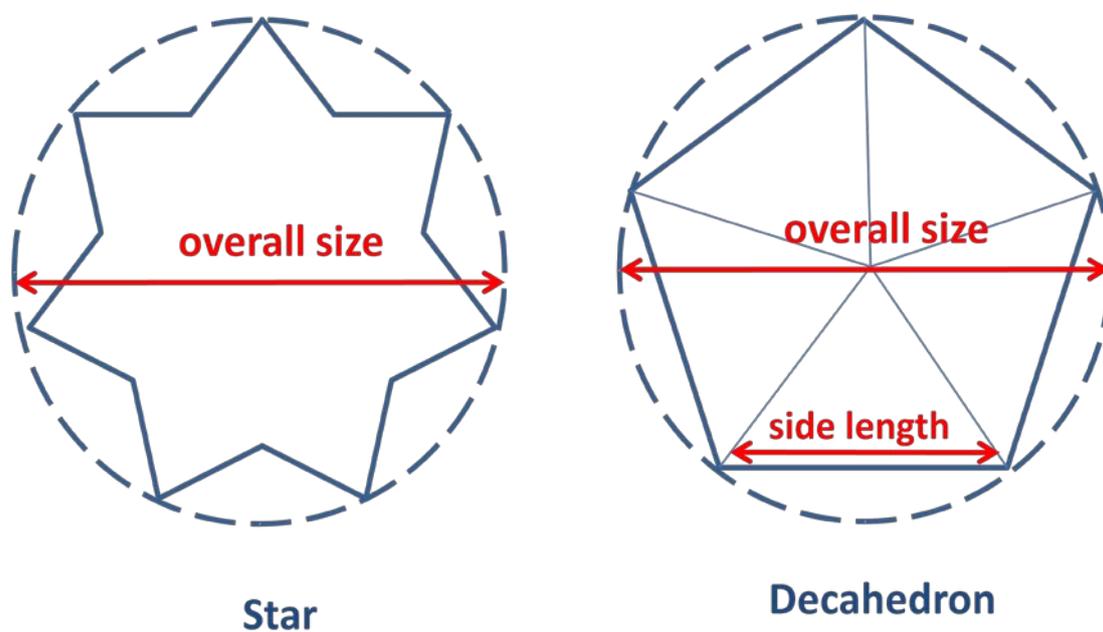
**Figure S3.** Zeta Potential (in mV) of dispersions of Au spheres (black) and decahedrons (red, full circles), stars (red, hollow circles) at different coating steps.



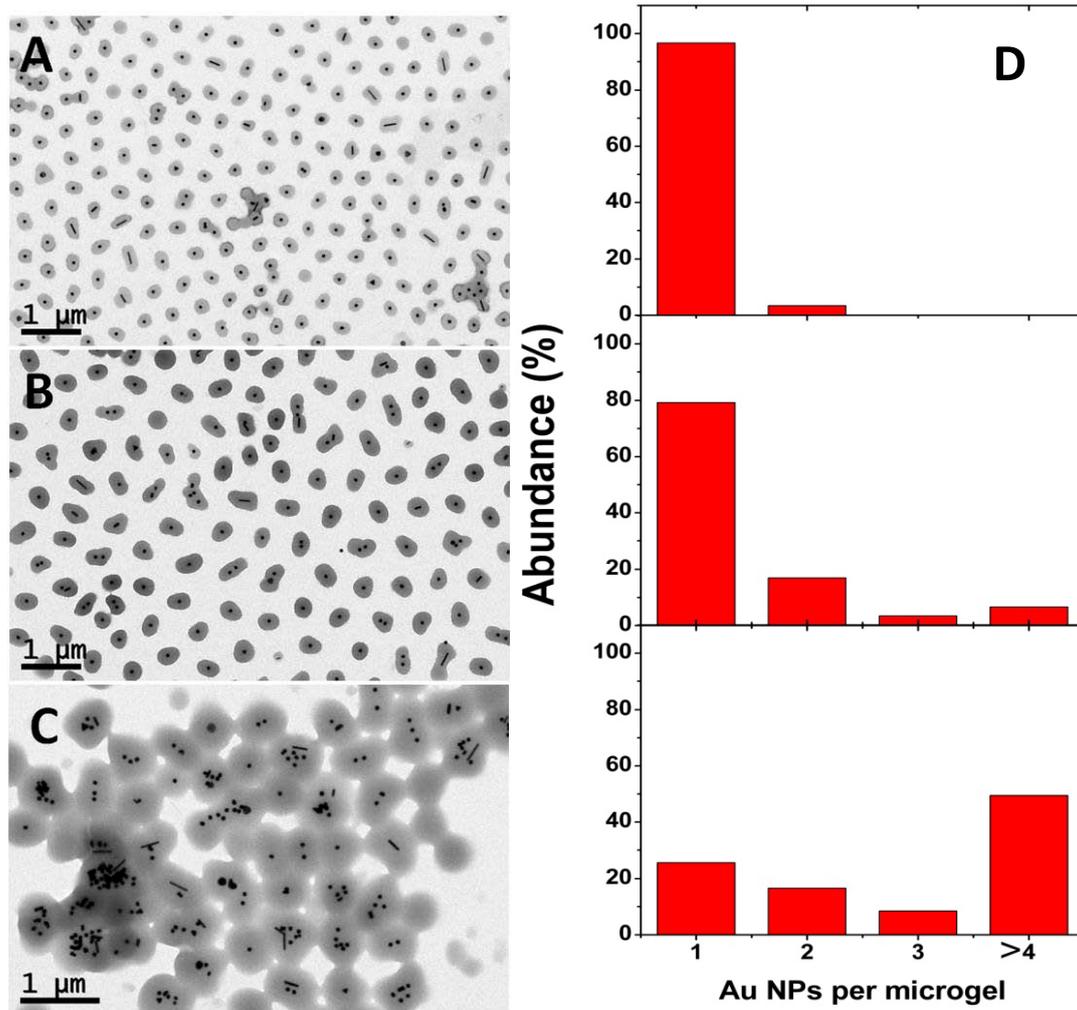
**Figure S4.** Variation of the hydrodynamic diameter of Au@pNIPAM composite particles with 58 nm gold nanoparticle cores, with temperature. Closed and open symbols denote the heating and cooling cycles, respectively.



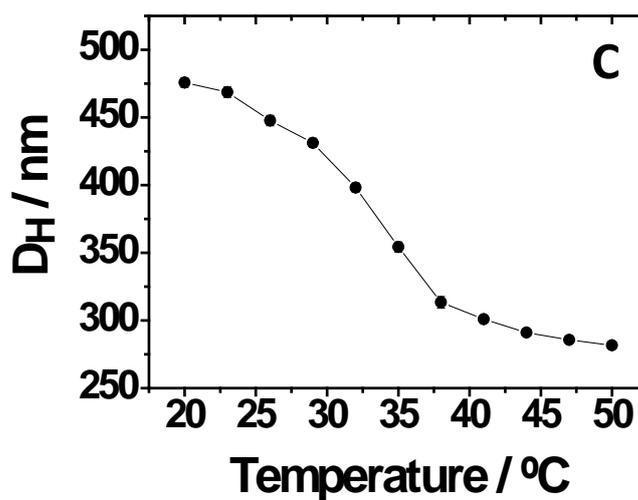
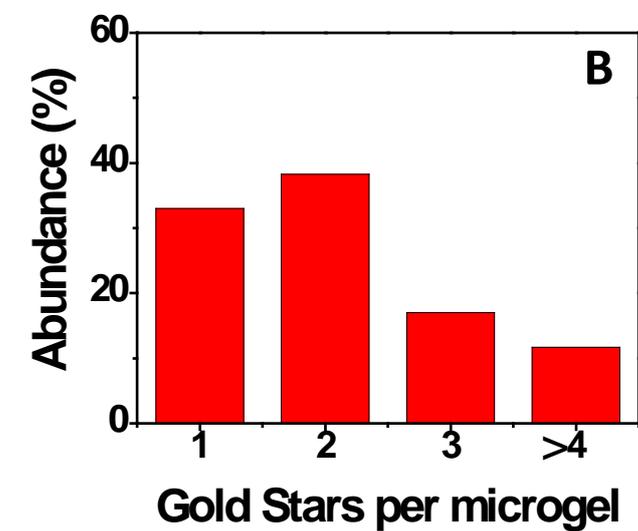
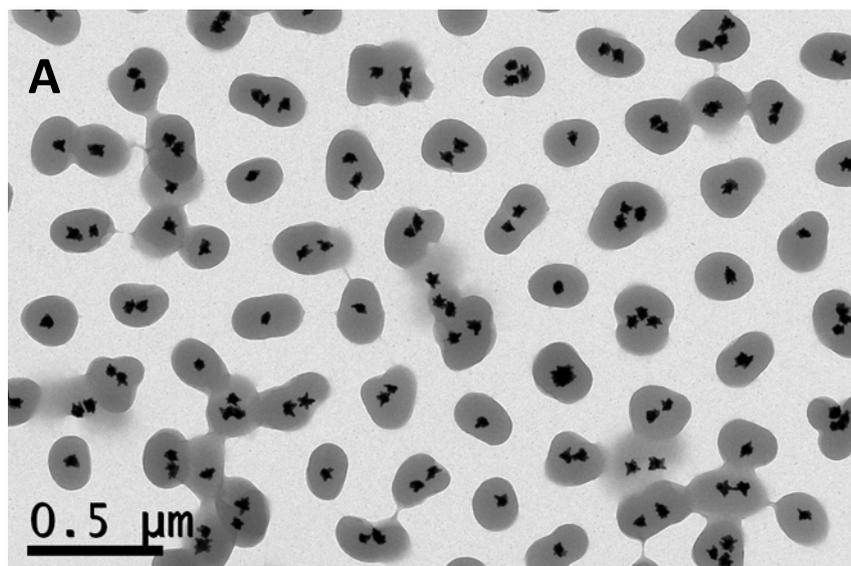
**Figure S5.** Position of the maximum of the surface plasmon band of 58nm gold spheres coated with pNIPAM, as a function of a number of swelling and collapse events (alternating between 20°C and 40°C).



**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.