Supporting Information

Functionalized Ag nanoparticles with tunable optical properties for selective protein analysis

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Experimental details:

Nanoparticle synthesis: The synthesis of MUA functionalized AgNPs was carried out as follows: 1 mL of 1% $AgNO_3$ and 2.00 mL of 38.8 mM sodium citrate were added to 100 mL of Millipore water at ca. 0 ^oC.[3] After 1 min of stirring, 1.00 mL of fresh 0.01% $NaBH_4$ was slowly added dropwise under vigorous stirring. The resulting dark yellow colloidal solution was stirred for additional 30 min and stored in the dark at 4 °C.
For the Ag_{413}, Ag_{418} and Ag_{427} nm batches 50 mL of the above AgNP seed solution was mixed with 0.5, 0.8 or 1.5 mL of 1 mM AA respectively upon stirring.[6] After 2 min, 0.5 (0.8, 1.5) mL of 1 mM $AgNO_3$ was slowly added while vigorous stirring. The stirring was continued for 1 h. For all 4 batches 2 mL of 0.05 or 20 mM/L of MUA in 0.5 M KOH was then added. The solution was stirred overnight and subsequently centrifuged. The sedimented MUA-capped AgNPs were repeatedly washed with KOH and water to remove free MUA and KOH and stored at 4 °C.

SERR spectroscopic measurements: SERR spectra were measured using a confocal Raman microscope (LabRam HR-800, Jobin Yvon, lens 20x0.35) in backscattering mode or a conventional double-monochromator (U1000) in 90° scattering geometry (excitation lens f~200 mm, collection lens f~70 mm).

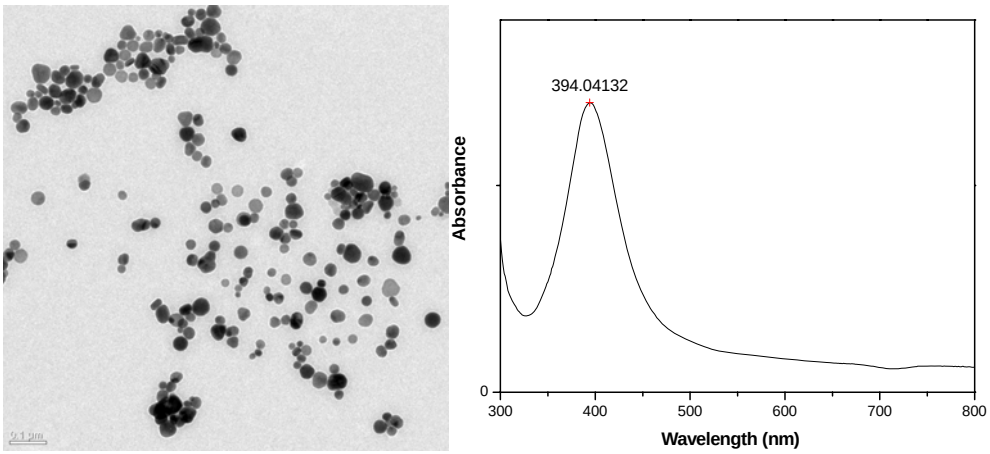

Figure S1. *TEM picture of citrate capped AgNps and corresponding UV-vis spectrum*

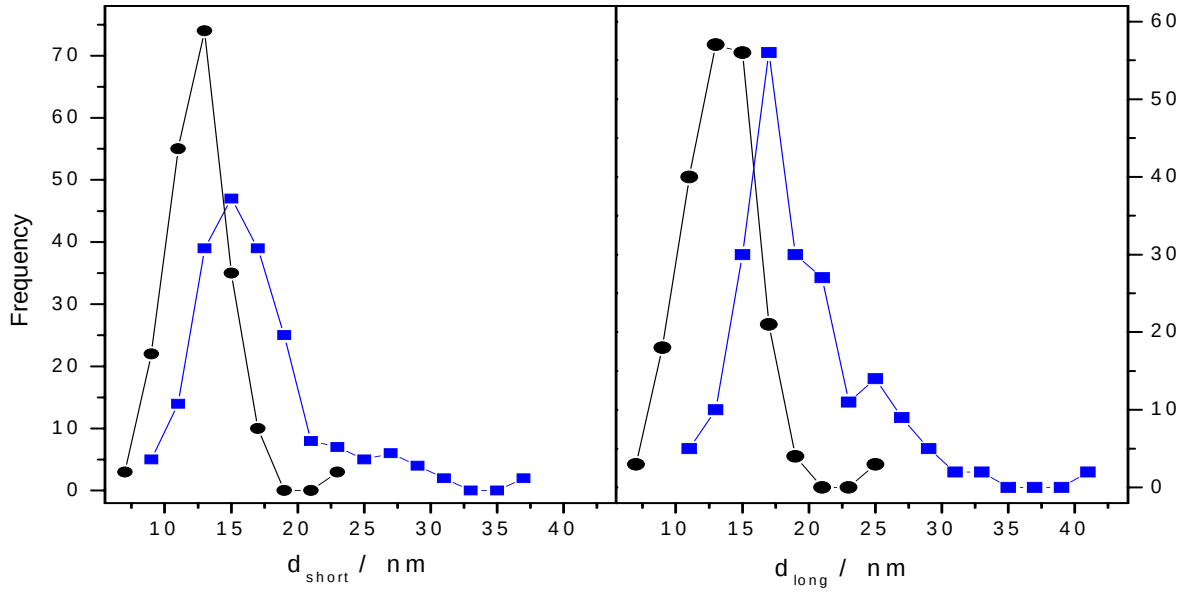

Figure S2: *Size distribution for the short (left) and long (right) axis for the 390 (black circles) and 413 (blue squares) nm batch.*

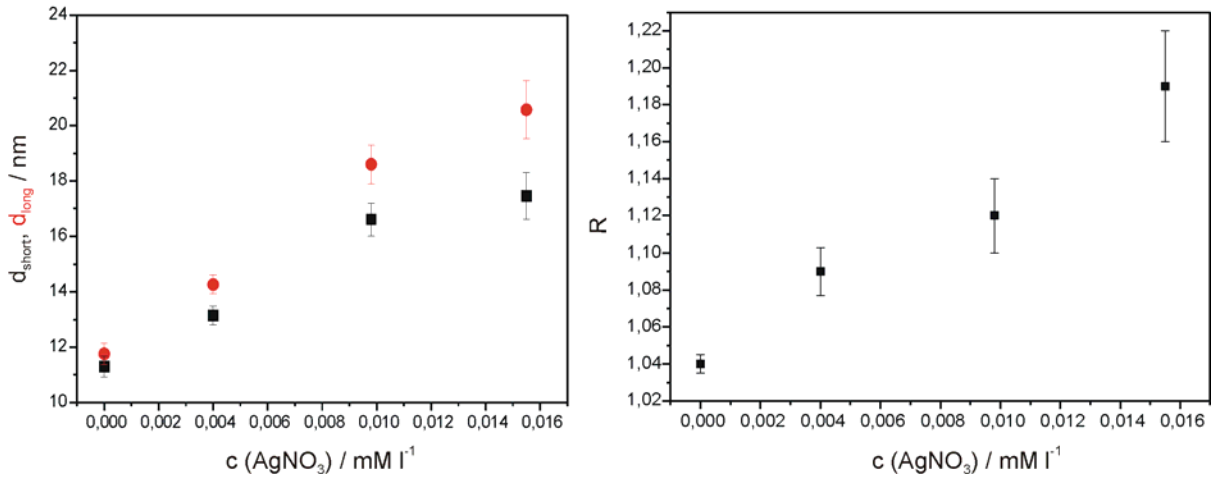

***Figure S3**: Mean diameter (left) of the shorter (black) and longer (red) axis of the nanoparticles and the respective aspect ratio (right) as a function of $AgNO_3$ growth solution concentration.*

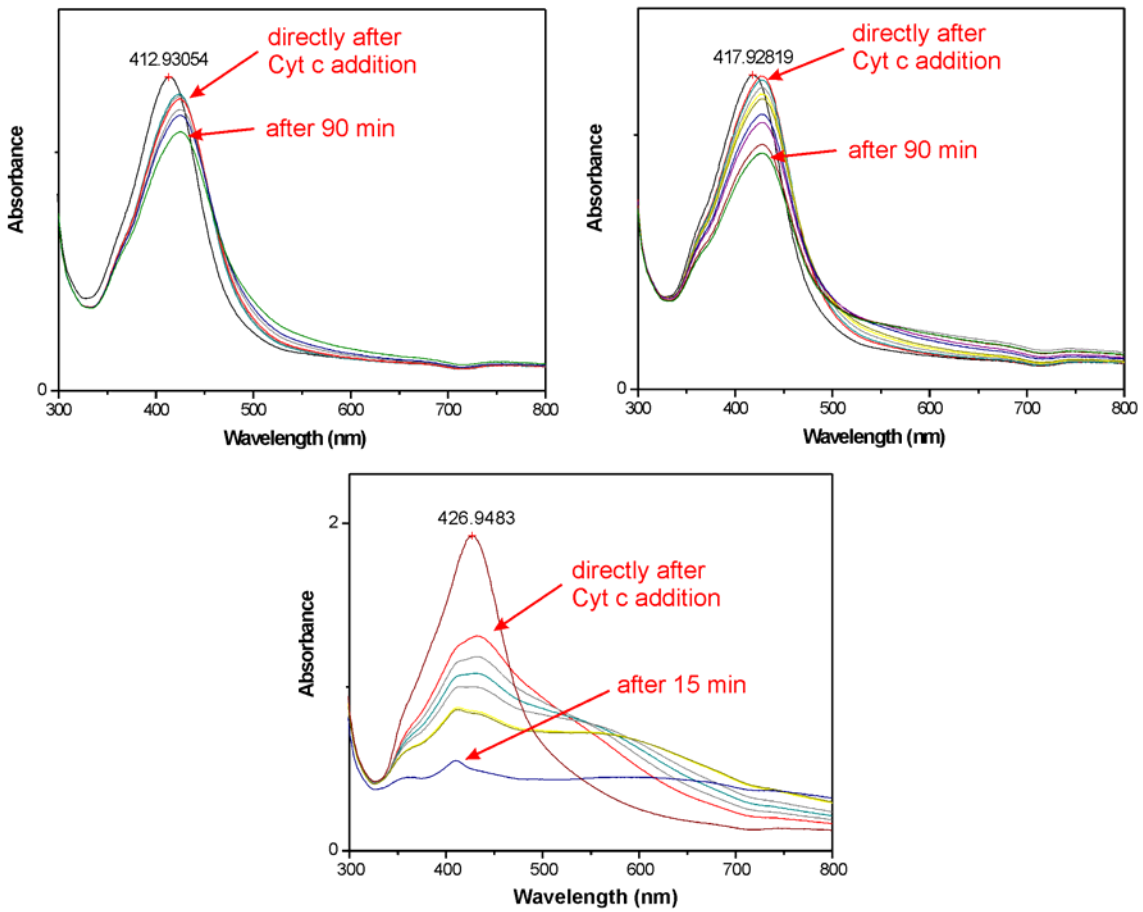

***Figure S4:** UV-vis spectra of MUA coated AgNps before and after Cyt c addition*

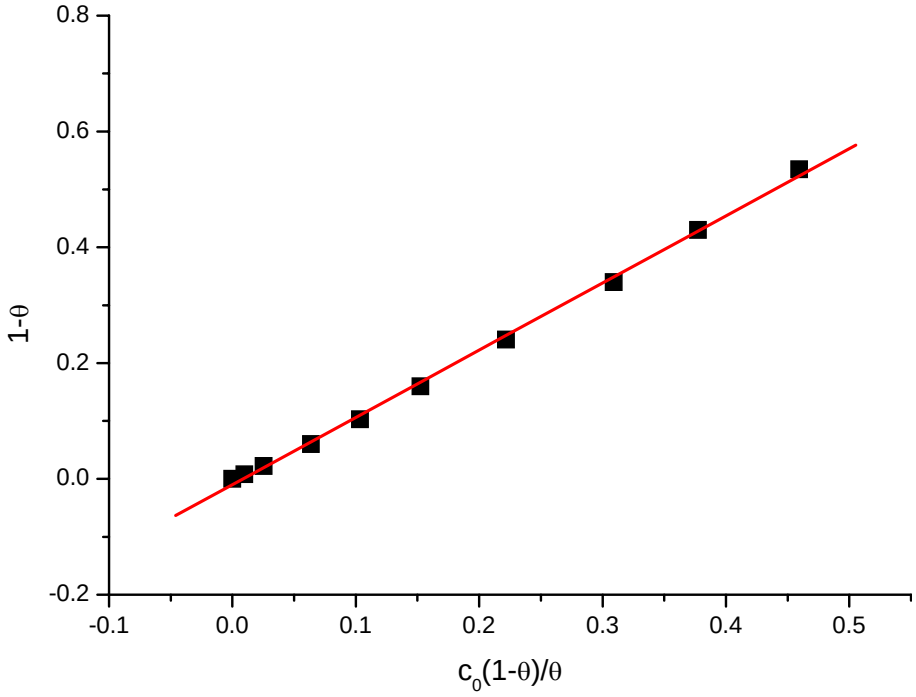

***Figure S5**: Determination of Γ_s and K from the Langmuir isotherm by plotting:*

$$1-\theta = \frac{1}{\Gamma_s}\cdot\frac{c_0(1-\theta)}{\theta} - \frac{1}{K\Gamma_s}$$

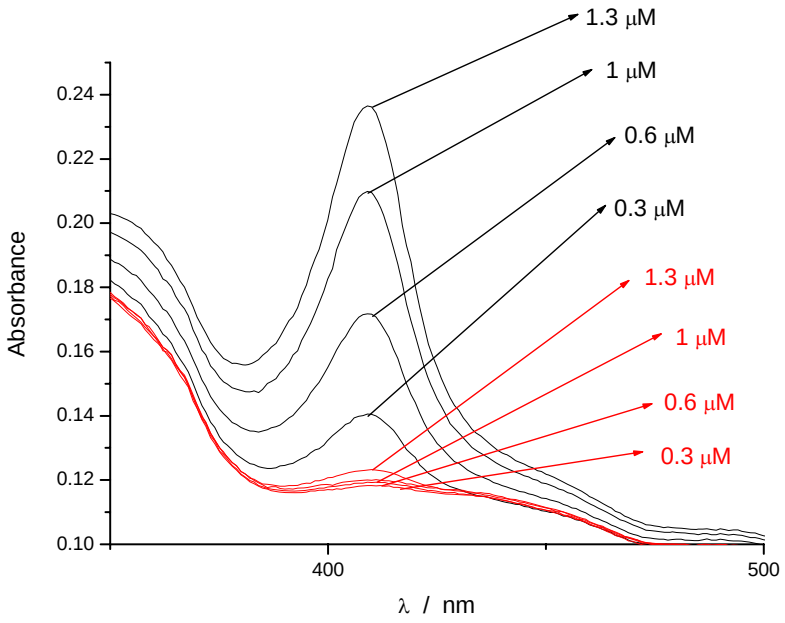

***Figure S6:** UV-Vis spectra of Cyt c in solution before (black) and after (red) MUA capped AgNp addition for different initial Cyt c concentrations. The AgNps were centrifuged before the second measurement.*