Supporting Information

Gold nanoparticles shape dependence of colloidal stability domains

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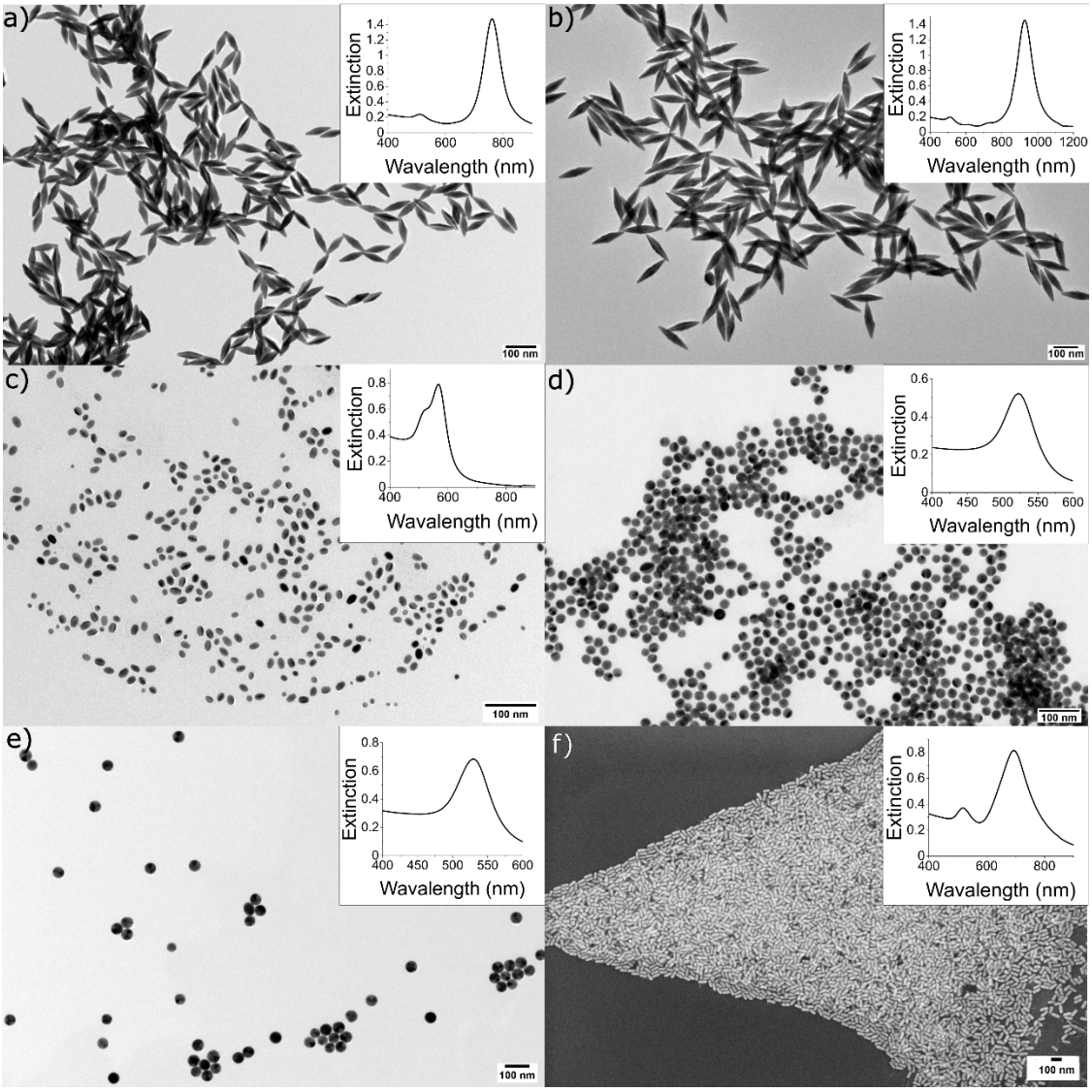

Figure S1 - Electron microscopy images of the synthesized nanoparticle along with their extinction spectra. (a-e) TEM image of (a,b) gold bipyramids samples (a) AuBP-83 and (b) AuBP-147; (c) Gold nanoellipsoids AuNE-18; (d,e) gold nanospheres, (d) AuNS-24 and (c) AuNS-45. (f) SEM image of gold nanorods sample AuNR-65.

Table S1 - Molar extinction coefficients at 400 nm (ε_{400}) for different the AuNPs used. Au_0 concentration was obtained by ICP and correlated to extinction at 400 nm to obtain ε_{400} using Lambert-Beer law. *For AuNS-24 the same experimental value of AuNS-45 is used. **Value determined by Z.J. Hu *et al.* [1]

Sample	ε_{400} ($L \cdot mg^{-1} \cdot cm^{-1}$)	Extinction at 400 nm	$[Au^0]$ ($mg \cdot L^{-1}$)
AuNS-45	0.01059434	0.3369	31.8
AuNS-24	0.01059434*	-	-
AuBP-83	0.014120155	0.3643	25.8
AuBP-147	0.014965116	0.5148	34.4
AuNE-18	0.010924078	0.5036	46.1
AuNR-65	0,01096**	-	-

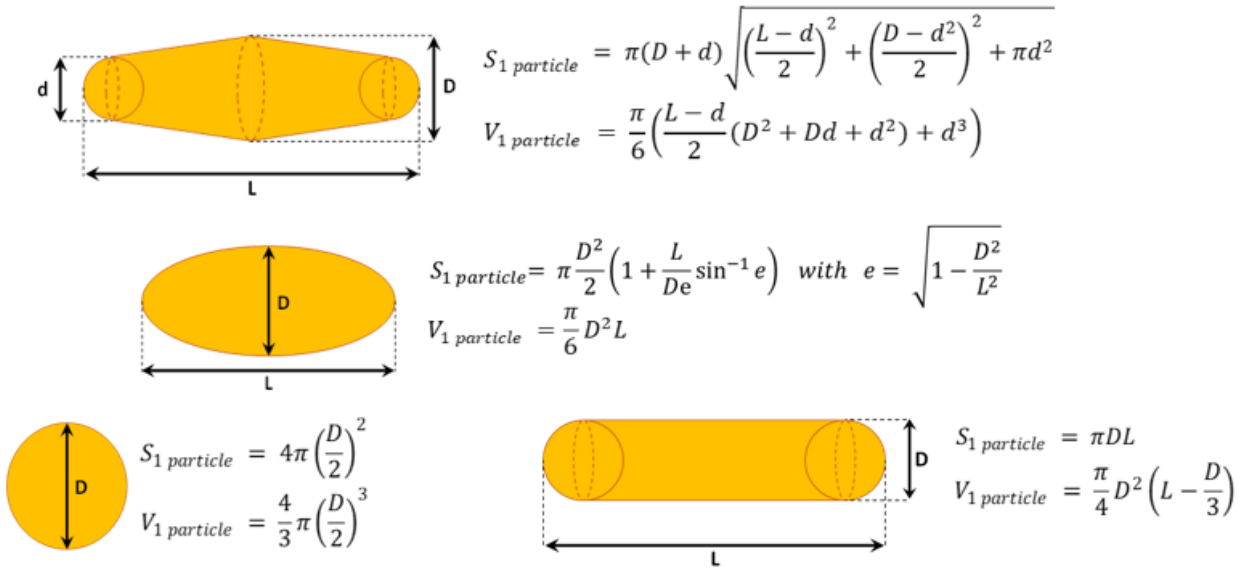

Figure S2 - Geometric models used to calculate the volume and surface of the single particles.

Table S2 - Volume and surface of the single particles calculated using the formulas reported in Figure S2.

Sample	$V_{1\,particle}$ ± st.dv (nm^3)	$S_{1\,particle}$ ± st.dv (nm^2)
AuNS-45	60804 ± 14686	7436 ± 1127
AuNS-24	7292 ± 2072	1803 ± 329
AuBP-83	20389 ± 2781	4538 ± 413
AuBP-147	63534 ± 9151	10340 ± 906
AuNE-18	1766 ± 703	706 ± 206
AuNR-65	29197 ± 5171	5242 ± 606

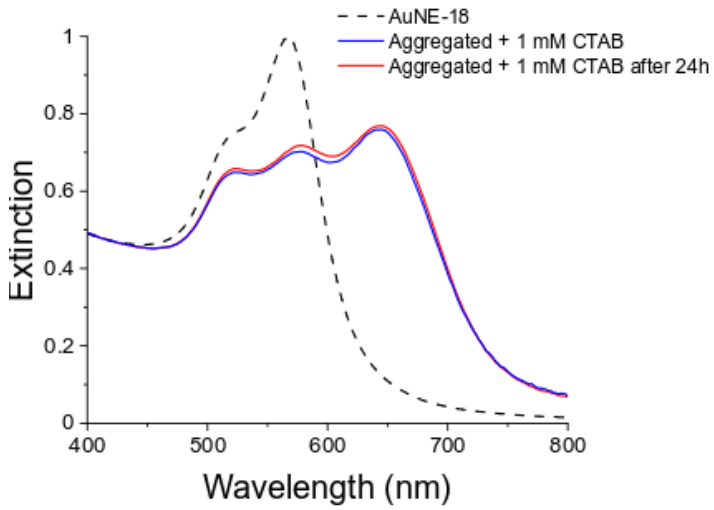

Figure S3 – Effect of increasing the CTAB concentration to 1 mM after the formation of AuNE-18 aggregates. The addition of CTAB was effective to freeze the aggregation process.

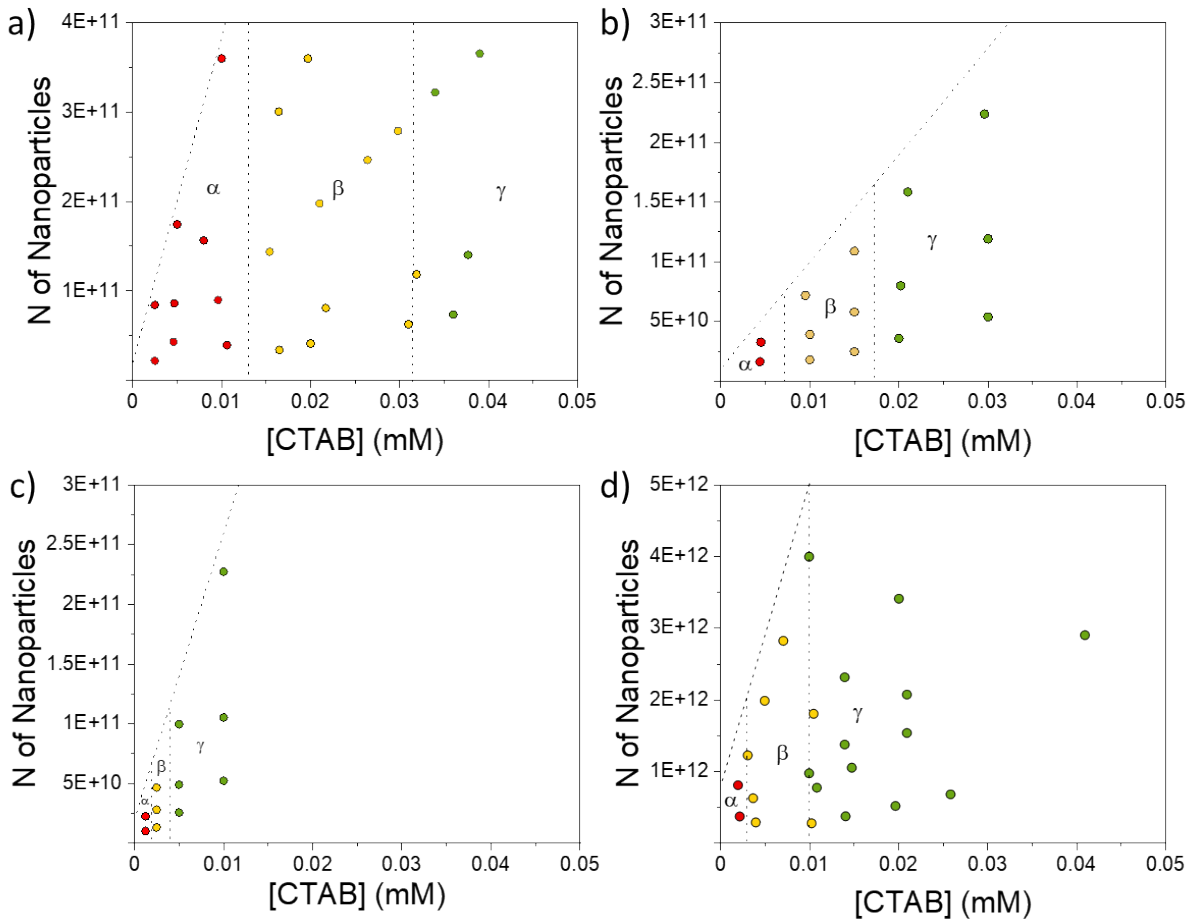

Figure S4 – Stability domains expressed in number of particles for (a) AuBP-83, (b) AuNR-65, (c) AuNE-18 and (d) AuNS-45.

Calculation of the CTAB coverage: The CTAB surface density used in the calculation is taken from literature and corresponds to 0.8 mol/nm^2 at 0.1 mM CTAB.[2] The higher specific surface reached in this work (around 28 cm^2 for AuNE-18) (Figure 2 in the main text) corresponds to $2 \cdot 10^{15}$ molecule of CTAB. For the lower limit, with a specific surface around 0.5 cm^2 (AuBP-147), the total number of CTAB molecules on the surface is $4 \cdot 10^{13}$. In comparison, a CTAB solution at 0.1 mM contains $6 \cdot 10^{16}$ molecules.

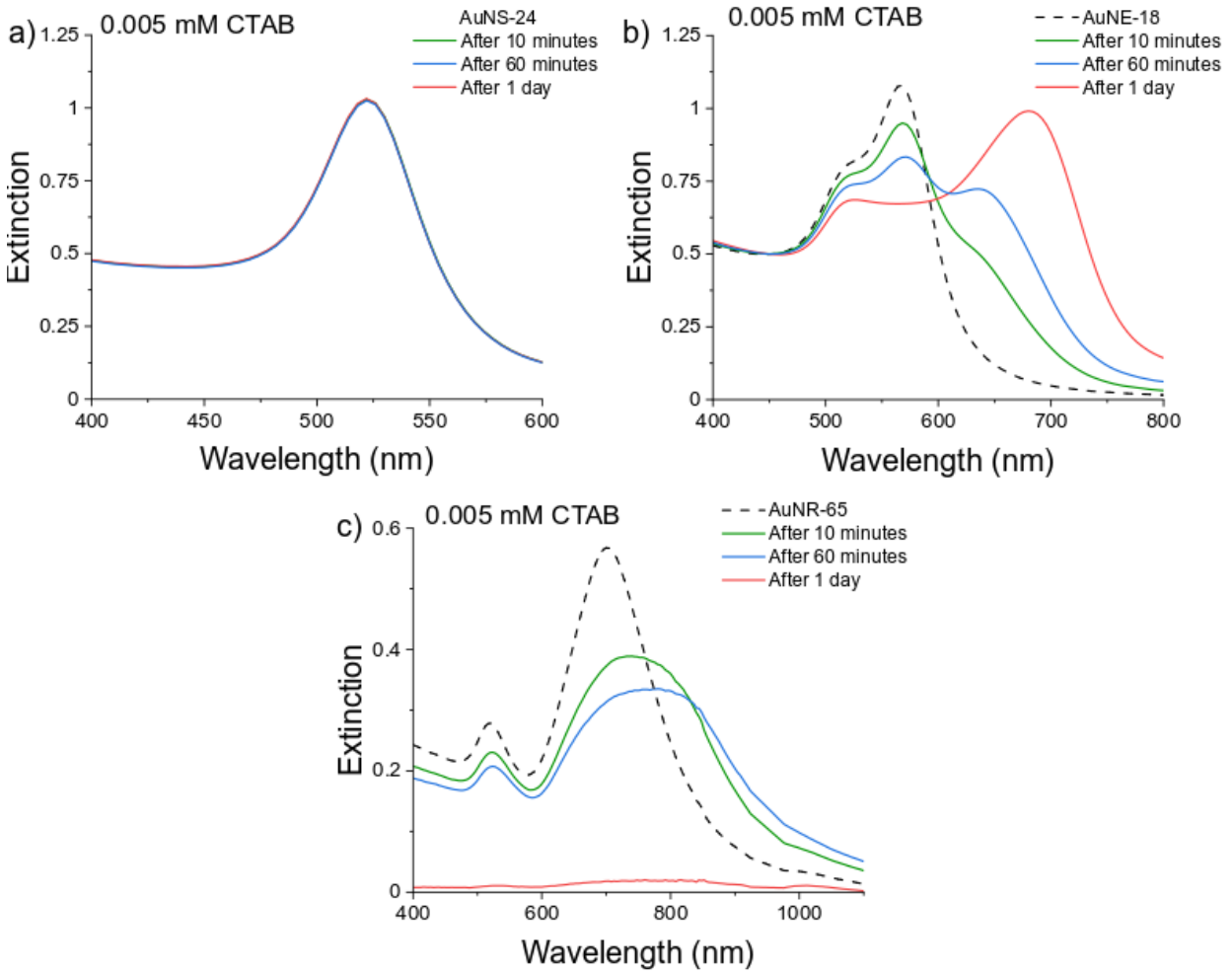

Figure S5 - Examples of criteria used to evaluate the colloidal stability. The different spectra were taken at 0.005 mM CTAB for different shapes. (a) Stable condition, no change in the spectrum was observed for AuNS-24 after 24 h. (b) In metastable conditions, aggregation of the monomer to bigger nanostructures was present for AuNE-18, evidenced by the apparition of a new band between 600-800 nm. No precipitation of the colloid was observed. (c) In unstable condition, aggregation, and precipitation was present for AuNR-65. Precipitation was associated with a progressively lower intensity at 400 nm, as well as the overall intensity of the spectrum.

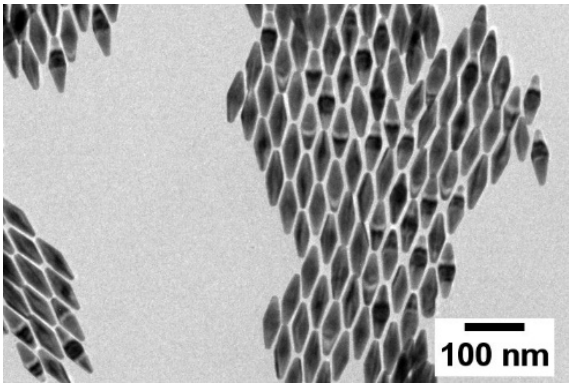

Figure S6 - TEM image of AuBPs deposited on a TEM grid. The particles were deposited taking care to have particles in stable conditions. The presence of CTAB both on the sides and the tips of the particles is evidenced by the presence of spacing between the particles.

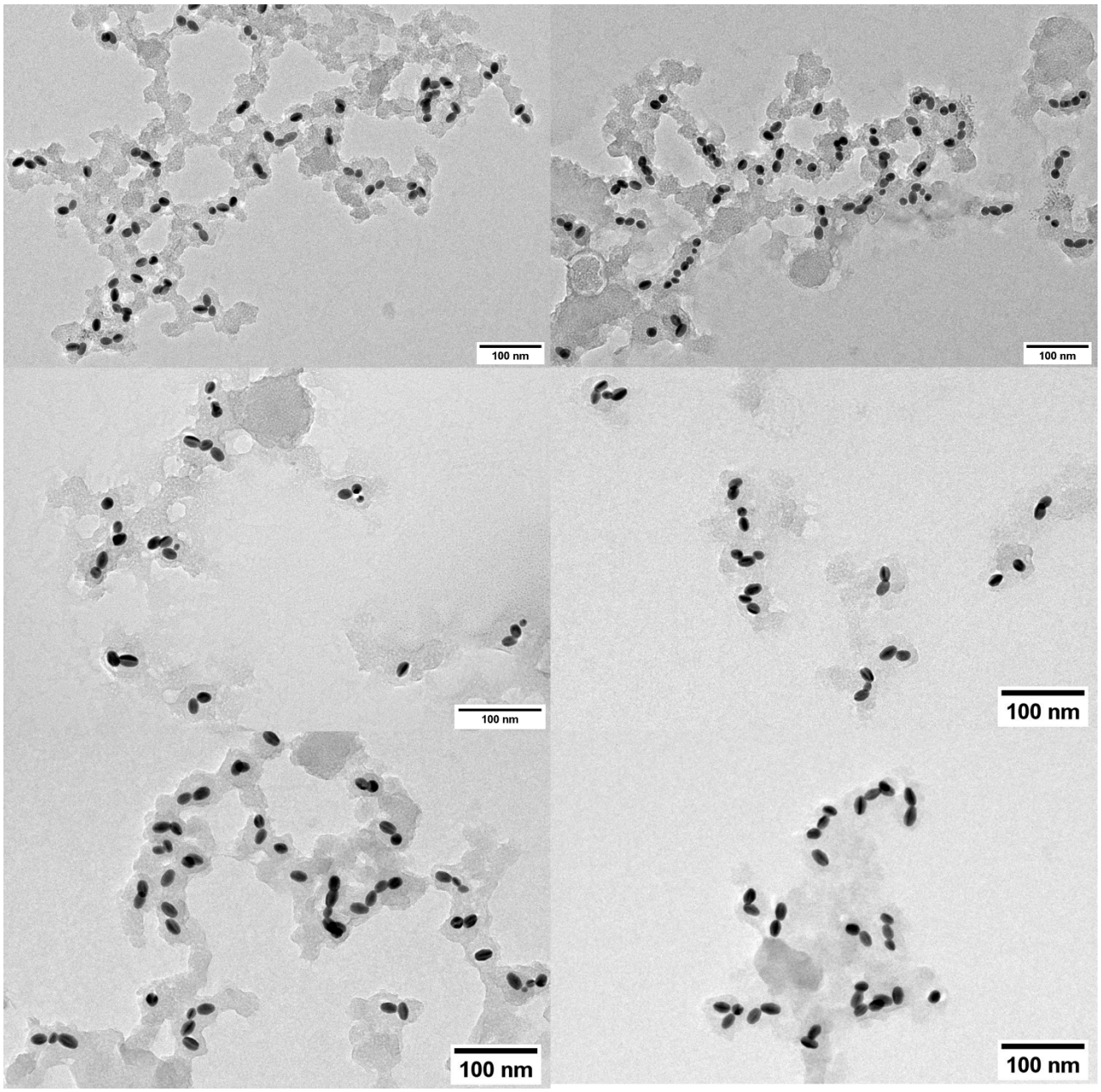

Figure S7 – Some of the TEM images of AuNE-18@Silicate assemblies used to calculate the statistics in Figure 6a in the main text. The statistics were made using 35 different images for a total of more than 500 cluster counted.

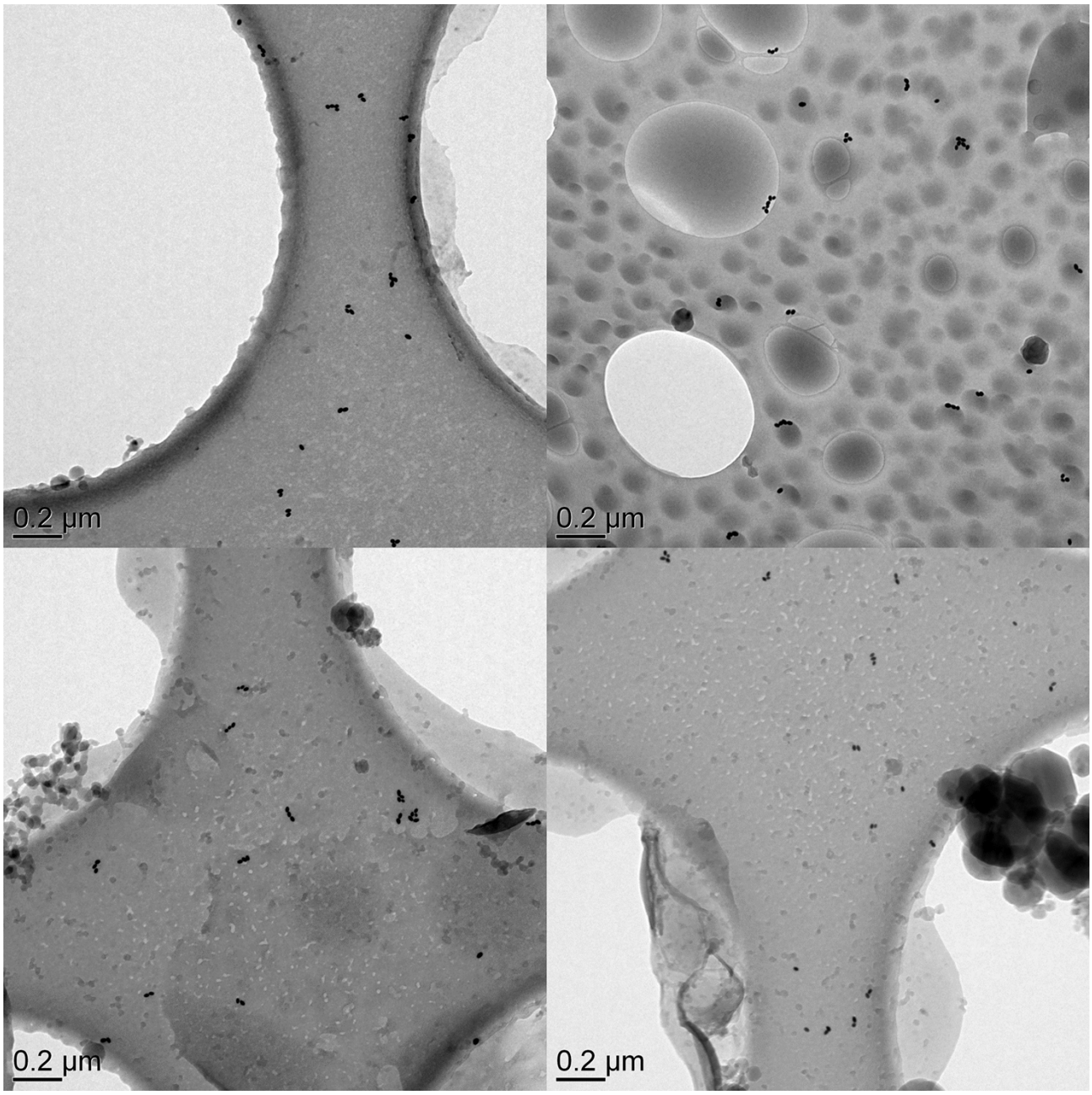

Figure S8 – Some of the CryoTEM images of AuNE-18 assemblies used to calculate the statistics in Figure 6a in the main text. The statistics were made using 43 different images for a total of more than 500 cluster counted.

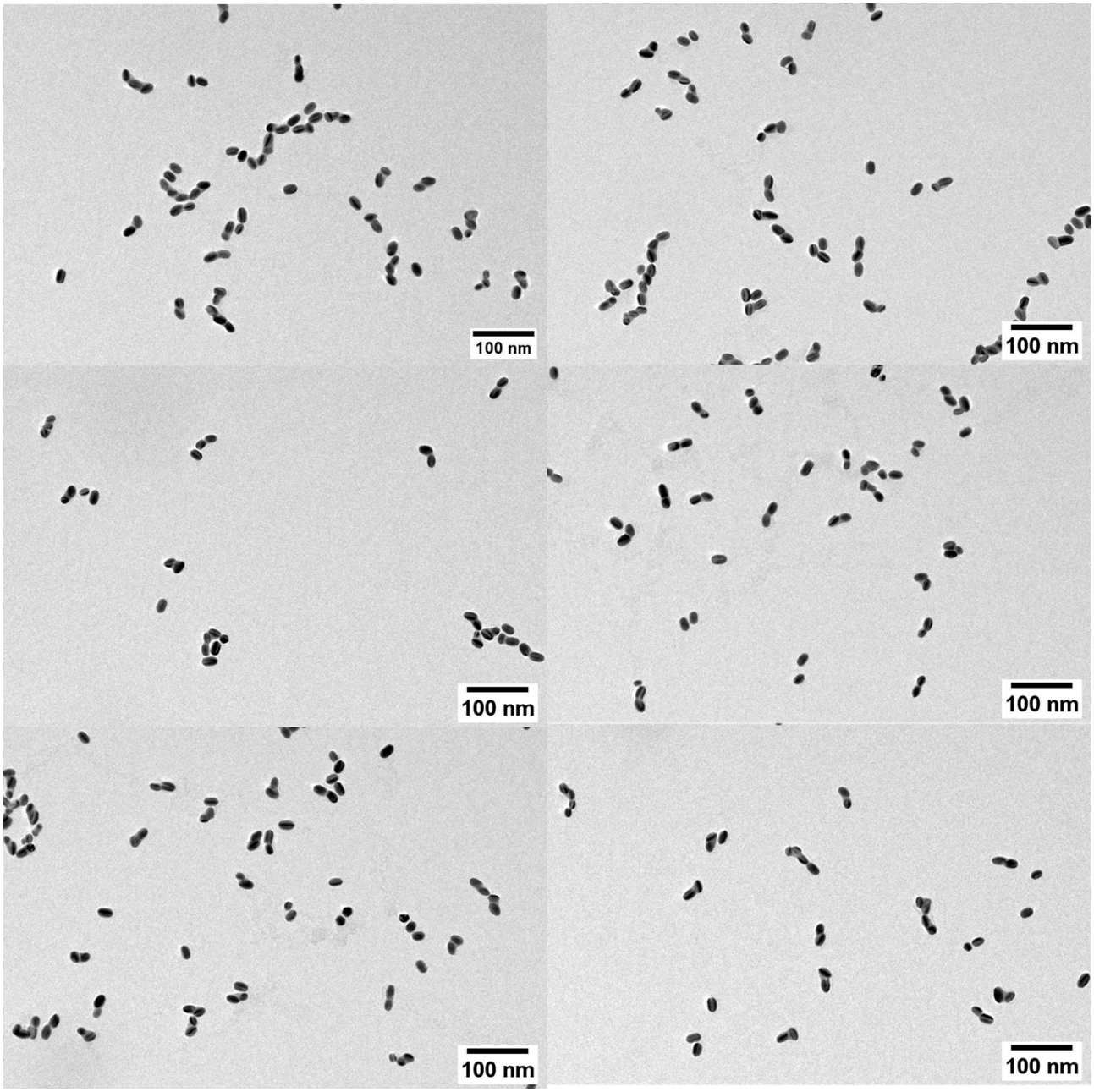

Figure S9 – Some of the TEM images of AuNE-18@Ag assemblies used to calculate the statistics in Figure 6a in the main text. The statistics were made using 19 different images for a total of more than 500 cluster counted.

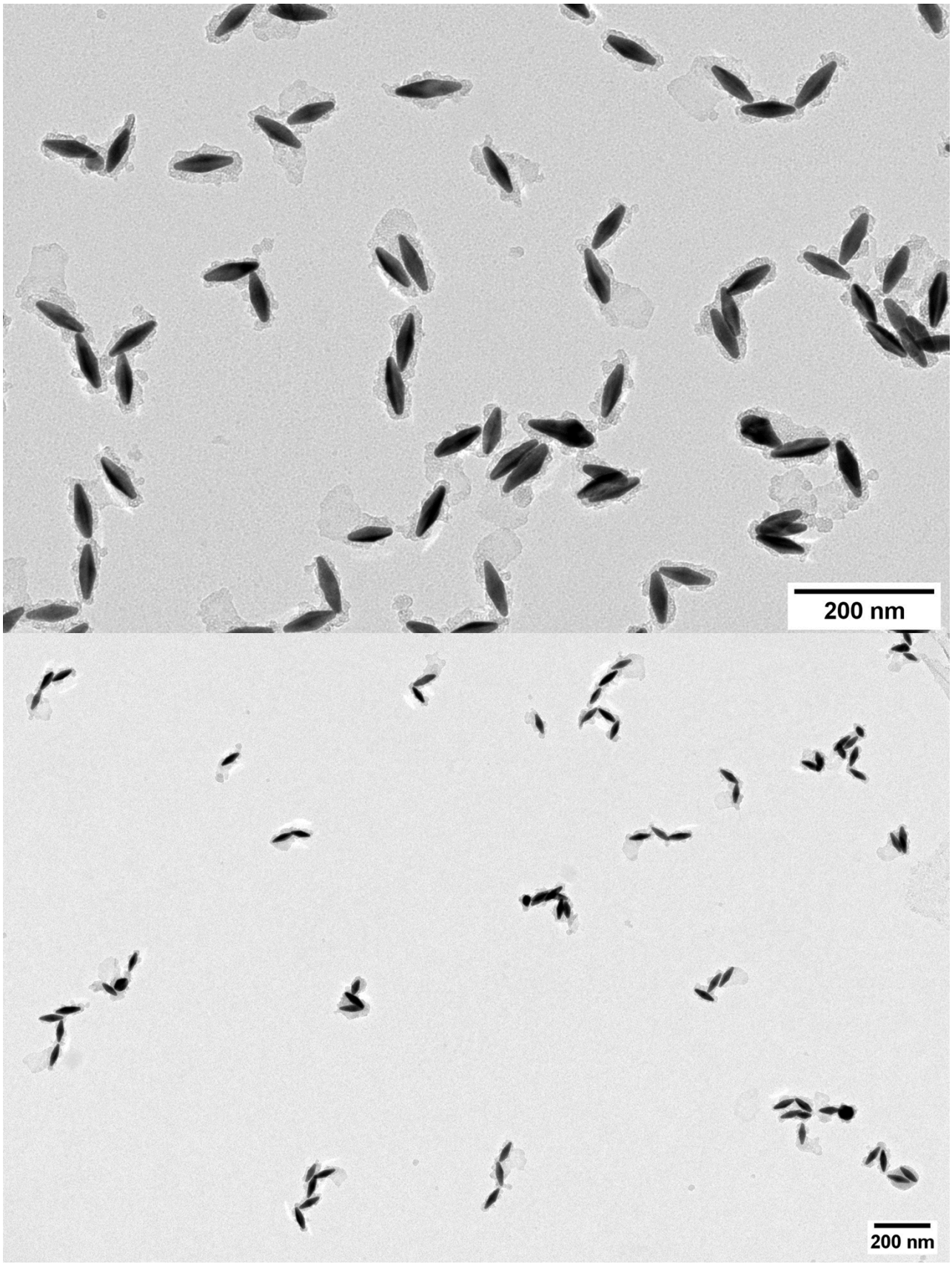

Figure S10 – Some of the TEM images of the AuBP-83@Silicate assemblies at 0.02 mM CTAB used to calculate the statistics in Figure 6c in the main text. The statistics were made using 11 different images for a total of more than 400 cluster counted.

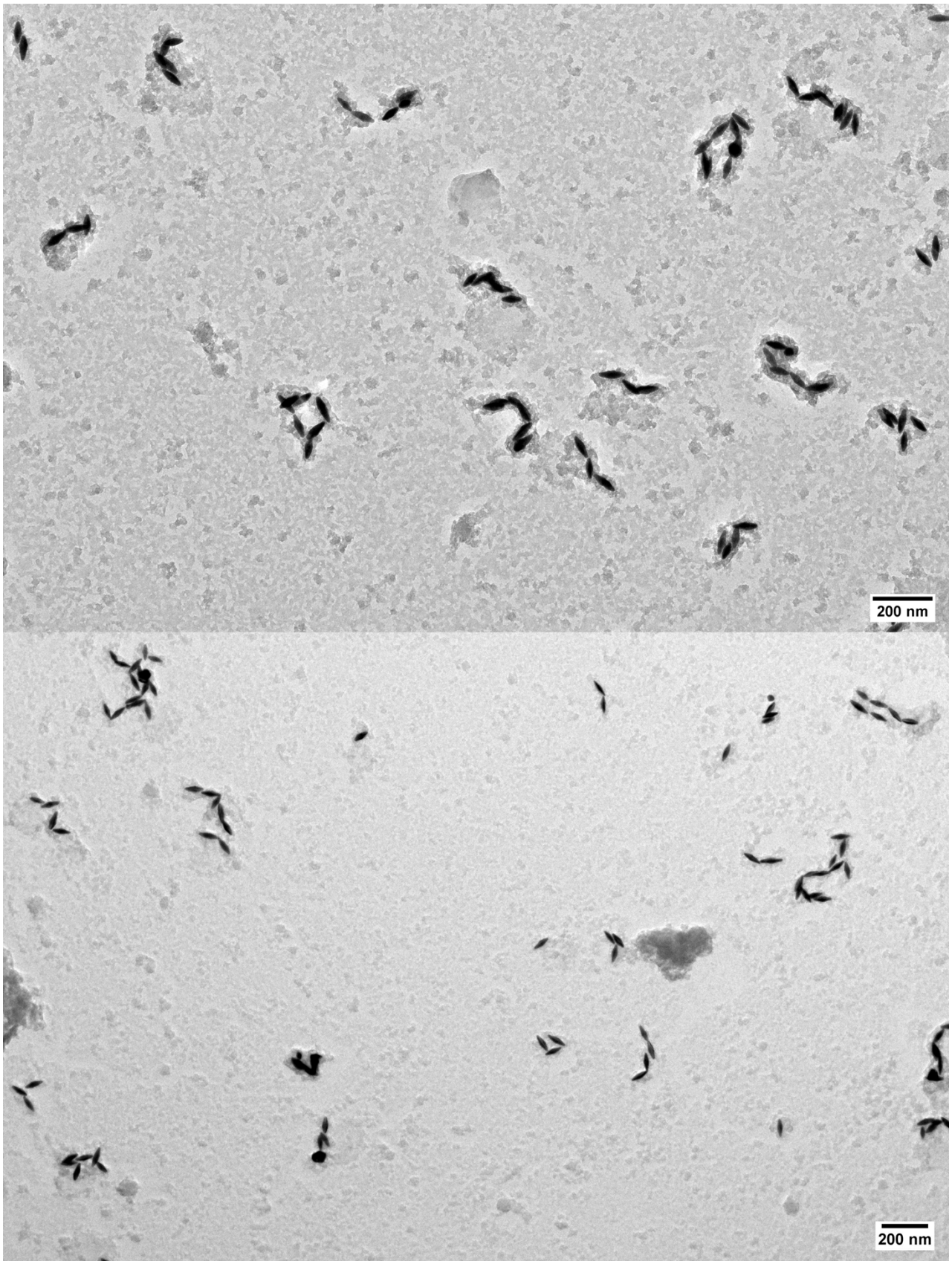

Figure S11 - Some of the TEM images of the AuBP-83@Silicate assemblies at 0.015 mM CTAB used to calculate the statistics in Figure 6c in the main text. The statistics were made using 9 different images for a total of more than 400 cluster counted.

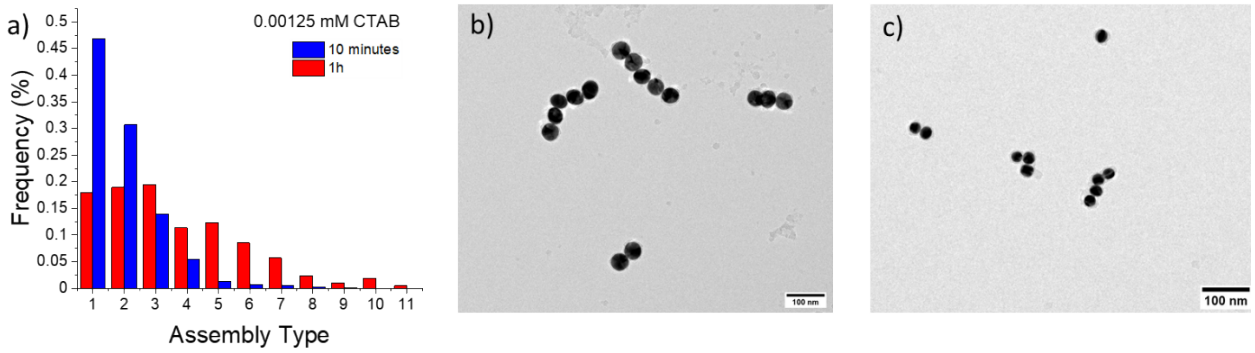

Figure S12 – Evolution of the assembly over time for gold nanospheres measured by TEM along with the silicate method. In both cases, the CTAB concentration was set at 0.00125 mM. (a) Statistics of the number of particles participating in the assemblies after 10 minutes and 1 h after mixing. (b) TEM image of AuNS-45 at 1 h after the mixing. (c) TEM image of AuNS-24 at 10 minutes after the mixing.

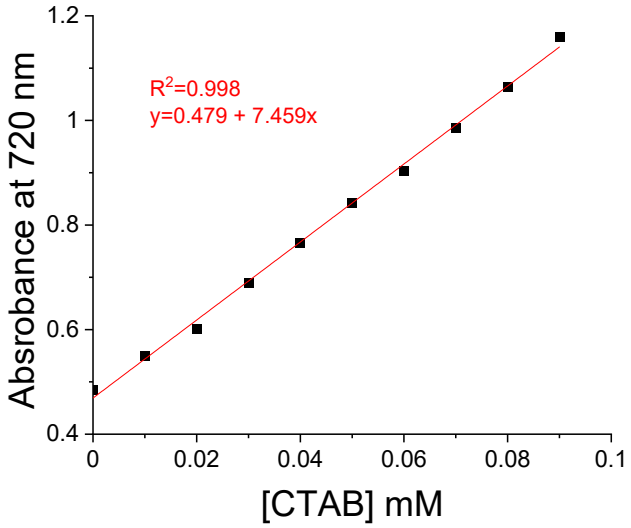

Figure S13 – Titration curve obtained measuring the absorbance of the spectra at 720 nm.

CTAB spectrophotometric titration procedure:

The method used in this work is presented in detail in a work of Ensafi *et al*.[3] The calibration curve was obtained in the range of 0 to 0.09 mM CTAB (Figure S8). Into a 5 mL volumetric flask, 1 mL of universal buffer pH 10.01 was introduced followed by 0.2 mL of ETB 2.7 mM. Later, different volumes (from 0 to 0.18 mL) of a 2.5 mM solution of CTAB were introduced in the flask and filled to the mark with water and mixed. After precisely 5 min, the absorbance of the solution at 720 nm was measured.

Table S3 - To evaluate if the dialysis was effective to remove the excess of CTAB and setting the desired concentration, both solutions inside and outside the membrane were titrated. The solution inside the membrane was centrifuged to avoid possible interference with the gold particles and the supernatant was collected and [CTAB] titrated. The table below shows the results obtained along with the relative experimental error (st.dv. over 3 measurements).

Sample	Measured [CTAB] (mM)
Dialysis solution	0.59 ± 0.04
Supernatant	0.54 ± 0.04

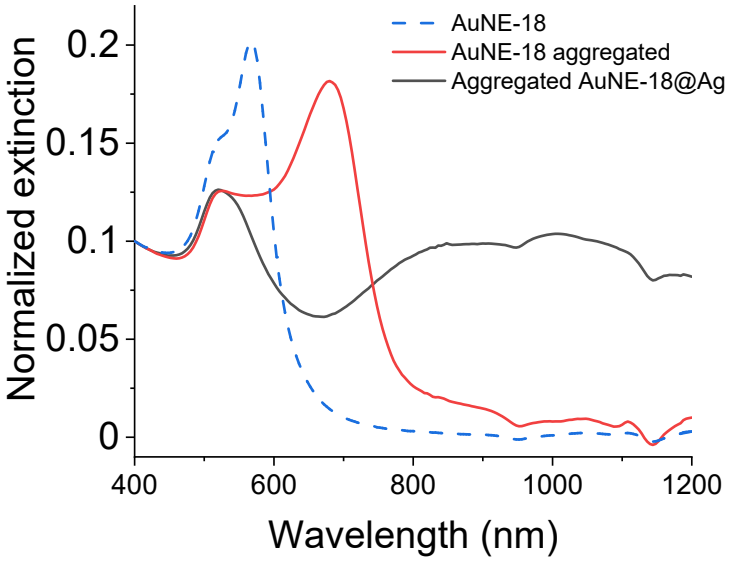

Figure 14 – Extinction spectra of AuNE-18 as isolated particles (dotted blue curve), after aggregation (red) and after silver treatment (black)

References

1 Z. J. Hu, S. Hou, Y. L. Ji, T. Wen, W. Q. Liu, H. Zhang, X. W. Shi, J. Yan and X. C. Wu, *AIP Advances*, **2014**, 4, 117137.

2 B. E. Janicek, J. G. Hinman, J. J. Hinman, S. hyun Bae, M. Wu, J. Turner, H.-H. Chang, E. Park, R. Lawless, K. S. Suslick, C. J. Murphy and P. Y. Huang, *Nano Letters*, **2019**, 19, 6308–6314.

3 A. A. Ensafi, B. Hemmateenejad and S. Barzegar, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2009**, 73, 794–798.