Supporting Information

Shape-Controlled Self-Assembly of Colloidal Nanoparticles

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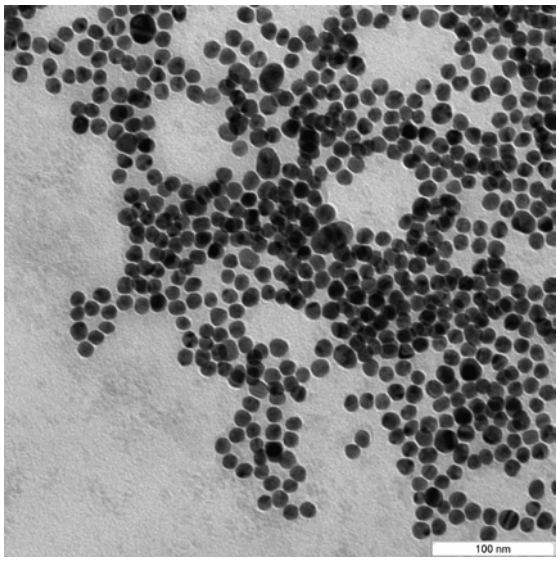

Figure S1. TEM image of monodisperse, quasi-spherical, 12 nm Au NPs obtained via citrate reduction of $HAuCl_4$ in water.

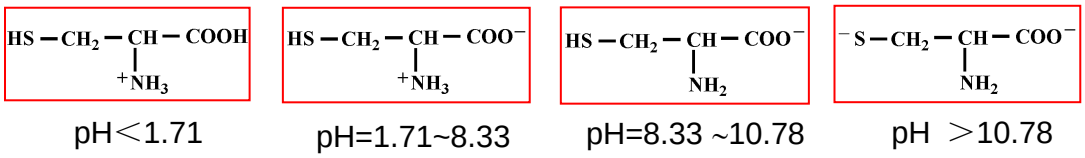

Figure S2-1. Schematic depiction of the four forms of L-cysteine depending on the pH in water (B. Monterroso-Marco, B. Löpez-Ruiz, *Talanta* **2003**, *61*, 733-741.)

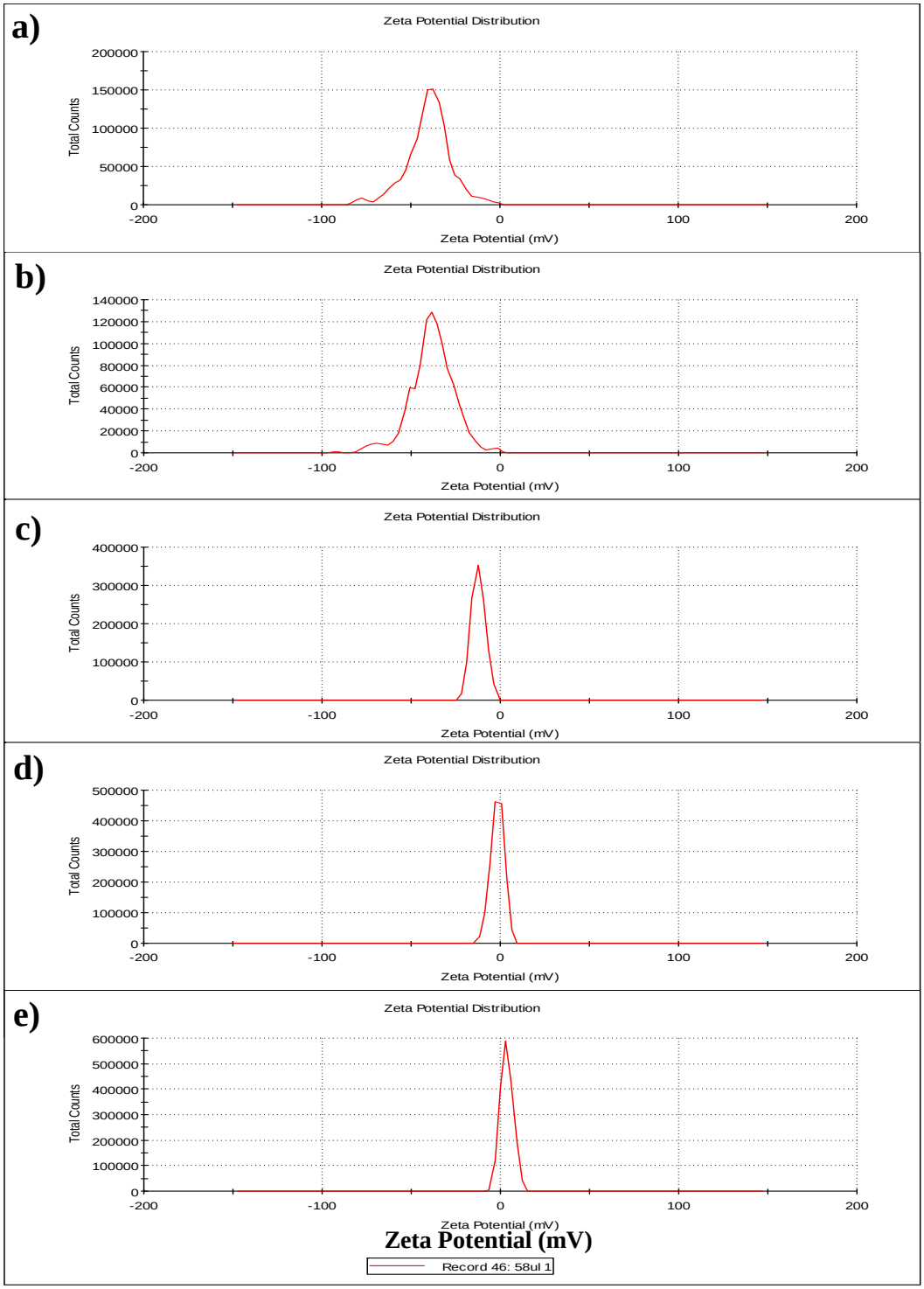

Figure S2-2. Zeta Potentials of Au@cysteine NPs at different pH: a) -39.1 mV at pH 9.7, b) -38.4 mV at pH 8.4, c) -12.2 mV at pH 5.5, d) -1.65 mV at pH = 5.1, e) +3.43 mV at pH = 4.8. The pH of the aqueous dispersions of the NPs has been carefully adjusted by dropwise addition of 1 M HCl. The NPs are negatively charged when the dispersion pH is higher than 5.02, the isoelectric point of L-cysteine (5.02), while they are positively charged when the dispersion pH is lower than 5.02.

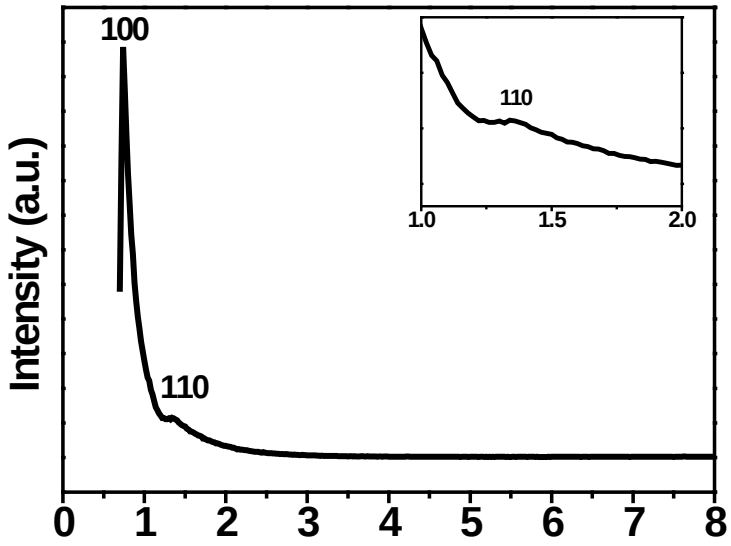

Figure S3. Small X-ray diffraction pattern of hexagonal microflakes of Au@cysteine NPs. Two peaks are associated with the *p6mm* hexagonal symmetry, indicating the presence of a long-range hexagonal ordering of the NPs within the microflakes.

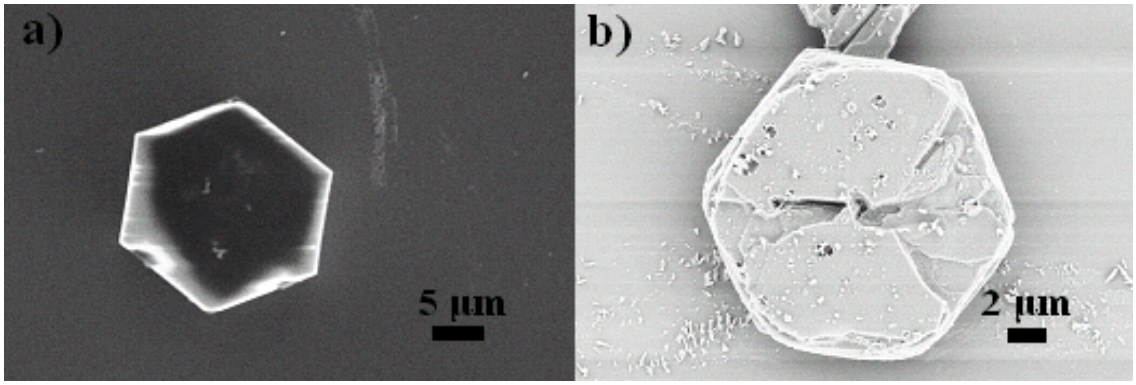

Figure S4. SEM images of hexagonal microflakes of Au@cysteine NPs before (a) and after (b) 50 min plasma etching. Plasma etching has been implemented in a Plasma Cleaner/Sterilizer PDC-32G (<0.21 mbar, 100W). After strong and long plasma etching, it is clearly found that the hexagonal flake-like shape remains little changed, indicating that the microflakes are composed dominantly of Au NPs rather than of L-cysteine.

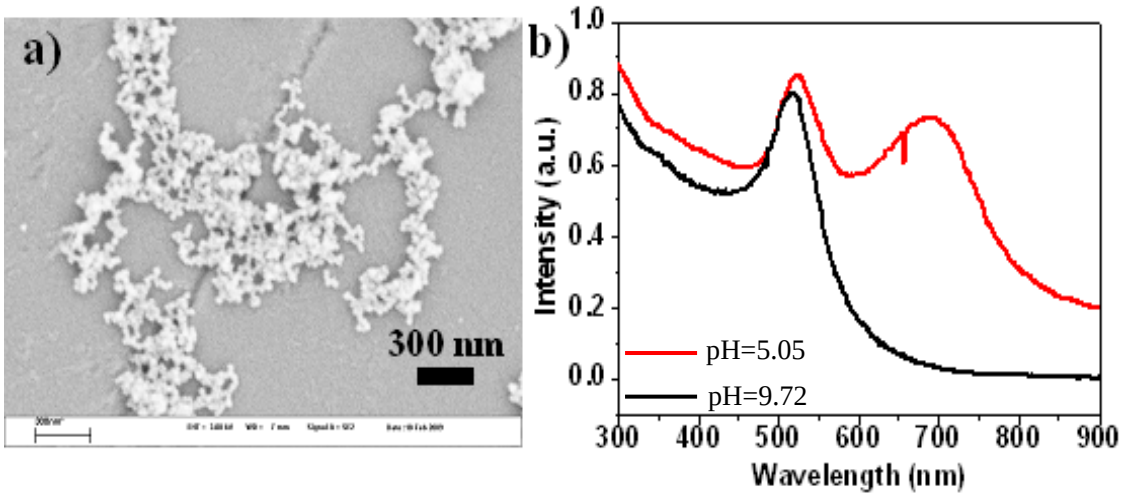

Figure S5. SEM image (a) and UV-Vis absorption spectra (b) of the aggregates of Au@cysteine chains prepared via NP self-assembly in the absence of excess of L-cysteine in the NP dispersions.

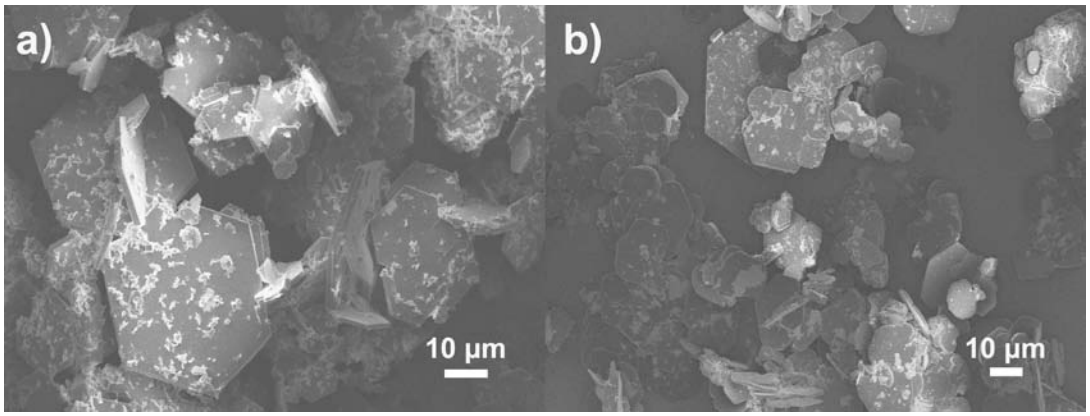

Figure S6. SEM images of the microflakes of Au@cysteine NPs obtained via NP self-assembly when 20% (a) and 50% (b) of cysteine are replaced by glycine.

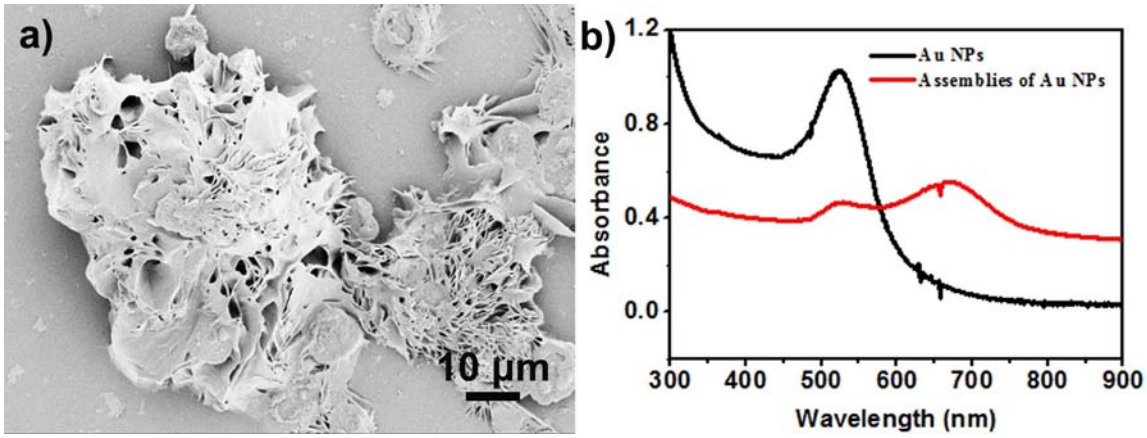

Figure S6. (a) SEM image and (b) UV-Vis absorption spectra of irregular flake-like assemblies.

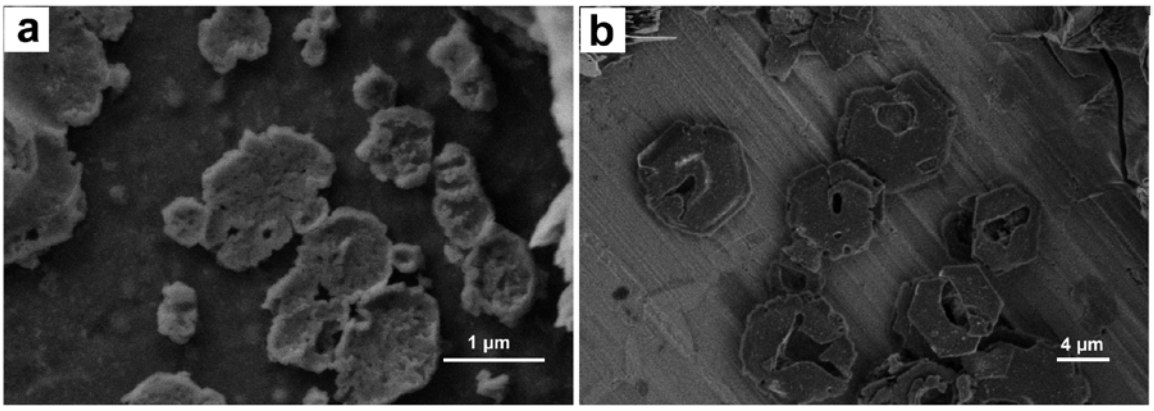

Figure S8. SEM images of the aggregates of Au@cysteine NPs obtained through drying of the NP dispersions at pH 7.8 (a) and 6.96 (b).

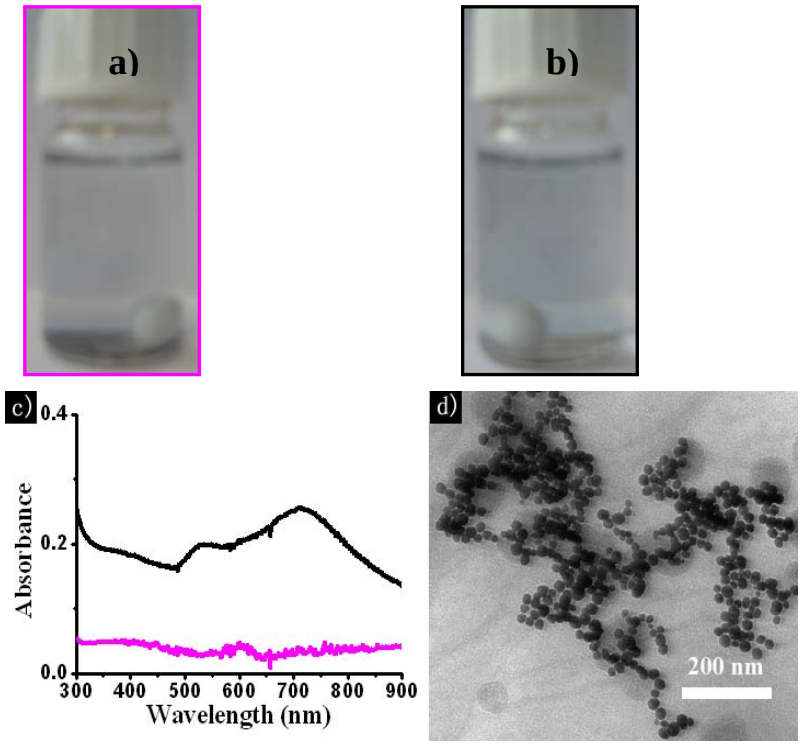

Figure S9. (a and b) Optical photos of the aqueous dispersions of hexagonal microflakes of Au@cysteine NPs before (a) and after use of 1 M NaOH to adjust the disperion pH to 10.5. It can be clearly seen that after the pH adjustment, the dispersions become blue, suggesting release of Au NPs and especially their aggregates from the microflakes to the surrounding media. (c) UV-Vis spectra of the microflake dispersions before (magenta curve) and after the pH adjustment to 10.5 (black curve). After the pH adjustment of the dispersions to 10.5, two pronounced absorption bands appear; one is centered at 520 nm and the other at 700 nm. This suggests presences of Au NP chains in the dispersions. (d) TEM image of the dispersions after adjusting their pH solution to 10.5. There are Au NPs and the NP chains clearly visible.

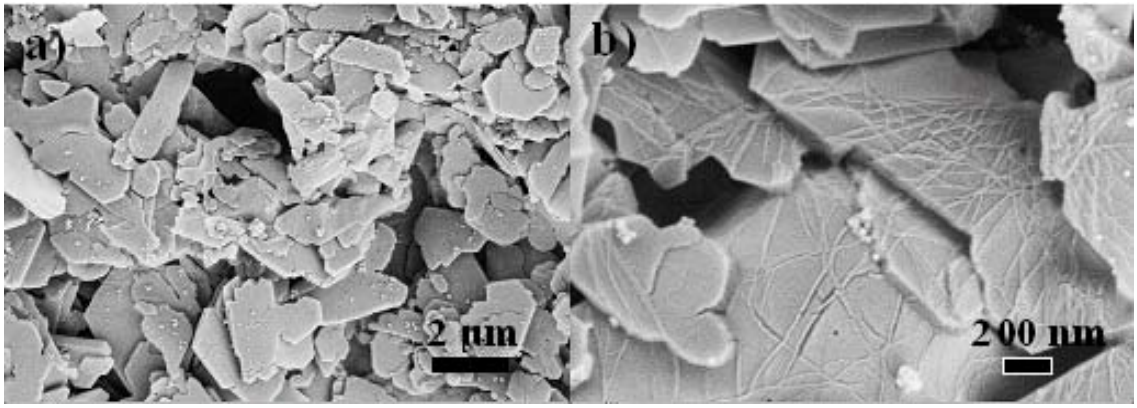

Figure S10. Low (a) and high (b) SEM images of microflakes obtained after 2 months incubation of ultralong microwires of Au@cysteine NPs, shown in Figures 2c and 2d, in water at room temperature.

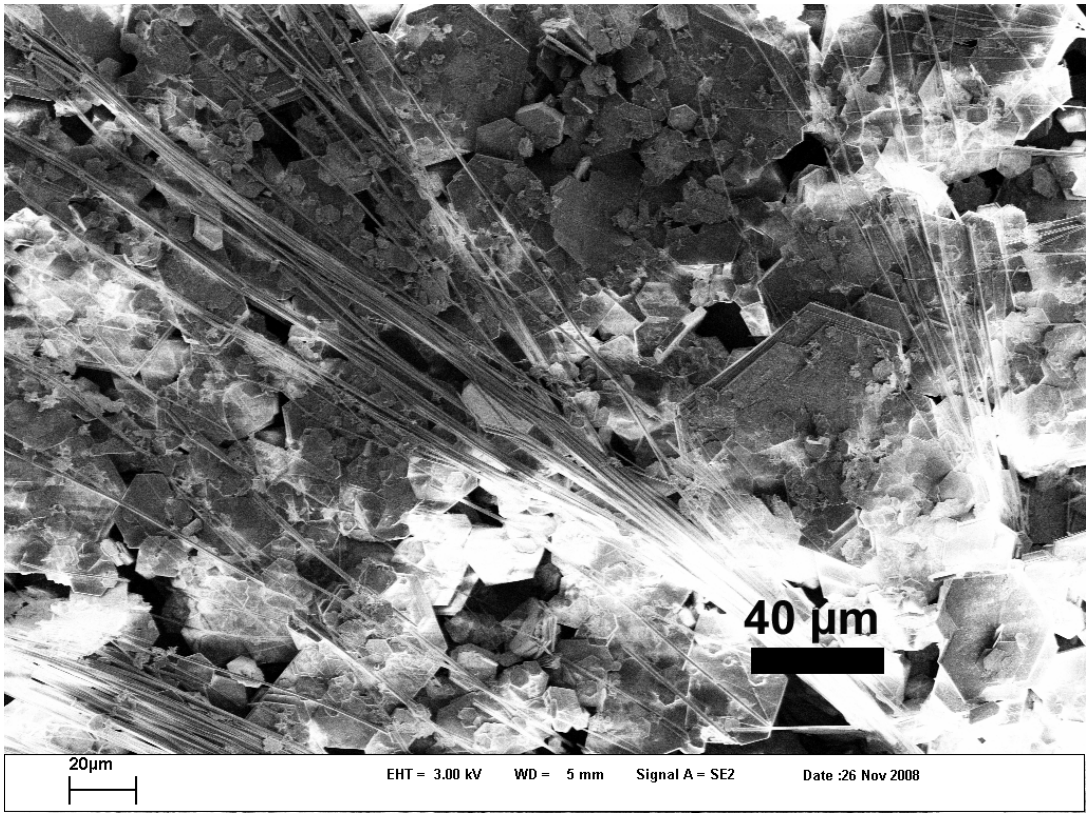

Figure S11. SEM image of the aggregates of Au@cysteine NPs obtained via self-assembly in the presence of 3 vol% acetonitrile in the NP dispersions upon stepwise reduction of the dispersion pH from 9.32 to 5.05. The dominant products are microflakes in coexistence with a small amount of ultralong microwires.