Silicification of Peptide-coated Silver Nanoparticles – a Biomimetic Soft Chemistry Approach towards Chiral Hybrid Core-shell Materials

Philipp Graf¹, Alexandre Mantion^{2,*}, Andrea Haase³, Andreas F. Thünemann², Admir Mašić⁴, Wolfgang Meier¹, Andreas Luch³, Andreas Taubert^{4,5}*

1 Department of Chemistry, Klingelbergstr. 80, University of Basel, CH-4056 Basel, Switzerland.

2 BAM - Federal Institute for Materials Research and Testing, Richard-Willstaetter-Str. 11, 12489 Berlin, Germany.

3 BFR - Federal Institute for Risk Assessment, Department of Product Safety, Thielallee 88-92, 14195 Berlin, Germany

4 Max-Planck-Institute of Colloids and Interfaces, 14476 Golm, Germany.

5 Institute of Chemistry, University of Potsdam, 14476 Golm, Germany.

* Corresponding author: A.T., Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, Building 26, D-14476 Golm, Germany, Tel.: ++49 (0)331 977 5773, Email: ataubert@uni-potsdam.de

* Corresponding author: A.M., BAM - Federal Institute for Materials Research and Testing, Richard-Willstaetter-Str. 11, D-12489 Berlin, Germany, Email: alexandre.mantion@bam.de

Supporting information

Complementary AFM investigations

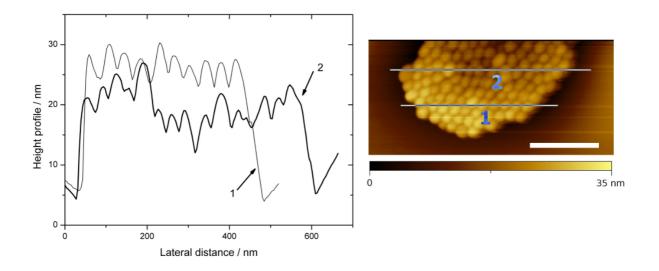


Figure S1: Height profiles extracted from a Ag/peptide@SiO₂ nanoparticle monolayer, with nanoparticles prepared after 2 days of reaction. Scale bar is 200 nm.

Figure S2 shows complementary atomic force microscopy (AFM) images of the shape and size evolution of the peptide-coated silver nanoparticles and the Ag/peptide@SiO₂ nanoparticles after silicification. During the process, the particle shape remains roundish, as shown in panel a) but the particle height (that is, the diameter) increases slightly more than 35 nm after 48 hours of reaction time. Panel b) clearly shows that the height increase induced by the formation of the by the core-shell structure is increasing smoothly with reaction time, and that already after 24 hours there is an inorganic shell on the silver nanoparticles. At higher concentration the nanoparticles form a uniform monolayer, see figure S1. In summary, AFM clearly shows that the nanoparticle thickness increases with reaction time and that the nanoparticles keep their round shape upon mineralization.

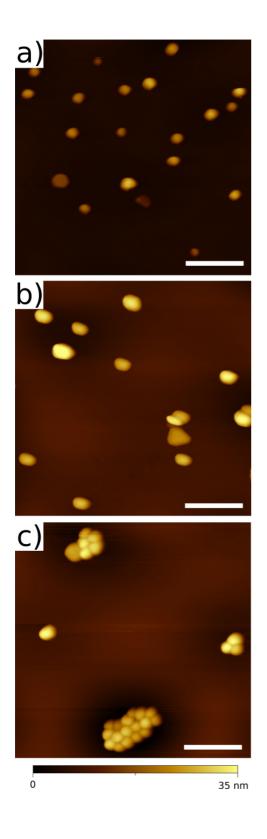


Figure S2: AFM images of a) peptide-coated silver nanoparticles, b) Ag/peptide@SiO₂ nanoparticles after 24 hours and c) 48 hours. Height scale is identical for all the images. Scale bar is 200 nm. .

Thermogravimetric analysis:

Figure S3 shows thermogravimetric analysis data of the particles before and after silicification for 48 hours. The Ag/peptide@SiO₂ core shell structure exhibits a larger weight loss than the peptide-coated Ag nanoparticles. The peptide-coated nanoparticles show a typical curve evolution for coated nanoparticles,¹ that is, there is one broad weight loss signal between ca. 100 and 340 °C. This weight loss can be separated in four strongly overlapping processes, which take place at approximately 129, 183, 275, and 335 °C. The silica coated particles exhibit three weight losses at roughly 129, 175, and 400 °C. Mass losses can be interpreted as dehydration and peptide decomposition in the first case. In the second case, the peptide decomposition is smeared out in the inorganic dehydration and reticulation processes. Overall, TGA confirms the high inorganic content of the material.

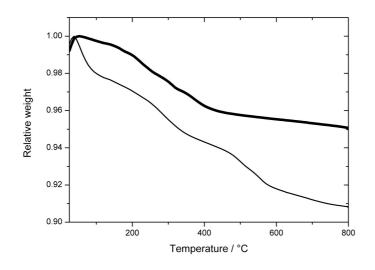


Figure S3. TGA curves of the peptide-coated silver nanoparticles (bold line) and the Ag/peptide@SiO₂ nanoparticles after 48 hours of reaction (thin line). Note that the small weight gain (smaller than 1%) before 50°C may be caused by some peptide oxidation or measurement instabilities.

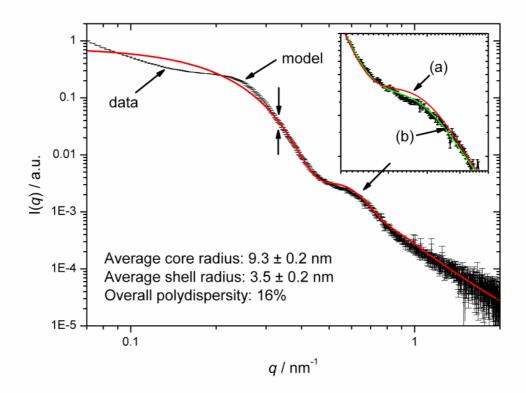


Figure S4. SAXS intensity curve of Ag/peptide@SiO₂ nanoparticles (thin line) and the corresponding modeling using a core-shell with a constant core radius / core + shell radii ratio and a common polydispersity (red line). Inset shows a comparison between two models: (a) constant core radius / core + shell radii ratio (red line) and (b) the polycore-shell model as described in text (green line). Both models lead to similar results, even so the fitting using model (b) is better, as in this case experimental data and fit are virtually undistinguishable.

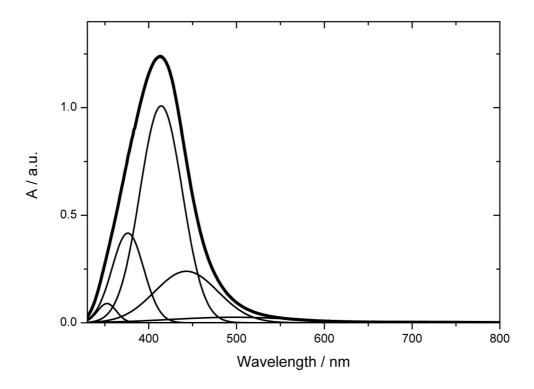


Figure S5. UV-Visible spectra deconvolution of the peptide-coated silver nanoparticles using Gaussian peaks. The differences between the fitting and the experimental data are barely visible.

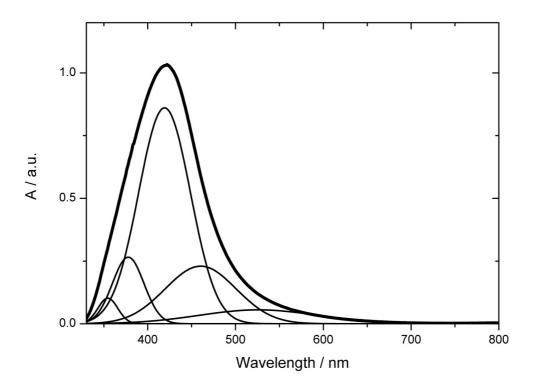


Figure S6. UV-Visible spectra deconvolution of the Ag/peptide@SiO₂ nanoparticles using Gaussian peaks. The differences between the fitting and the experimental data are barely visible.

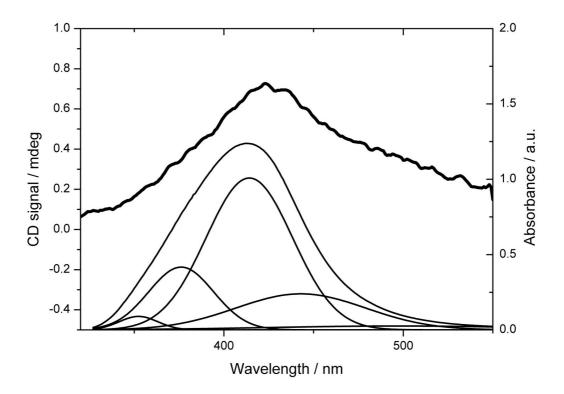


Figure S7. Peptide-coated silver nanoparticle CD spectra (bold line) superimposed with a deconvoluted UV-Visible spectrum of the peptide-coated silver nanoparticle.

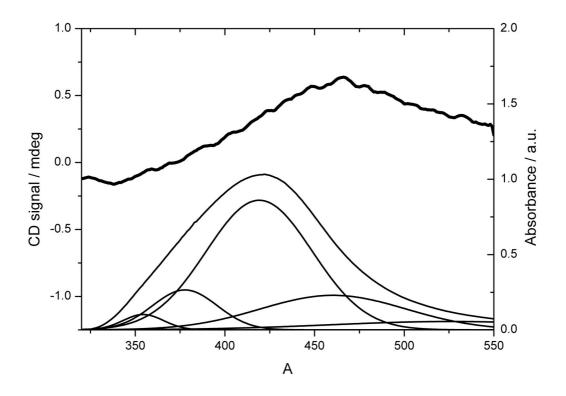


Figure S8. Ag/peptide@SiO₂ CD spectra (bold line) superimposed with a deconvoluted UV-Visible spectrum of the Ag/peptide@SiO₂ nanoparticles. Particles are investigated after 48 hours of reaction.

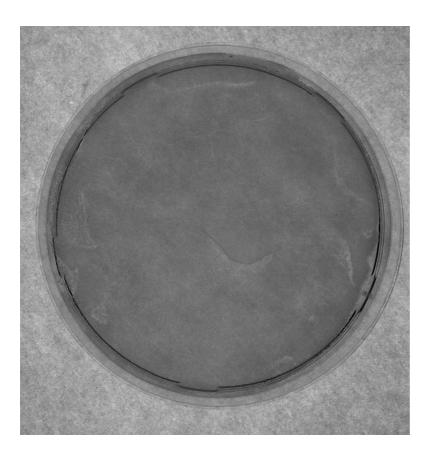


Figure S9. Agar plate incubated without nanoparticles. Bacteria concentration: 5.10^5 CFU. Incubation conditions: 37° C for 24 hours.

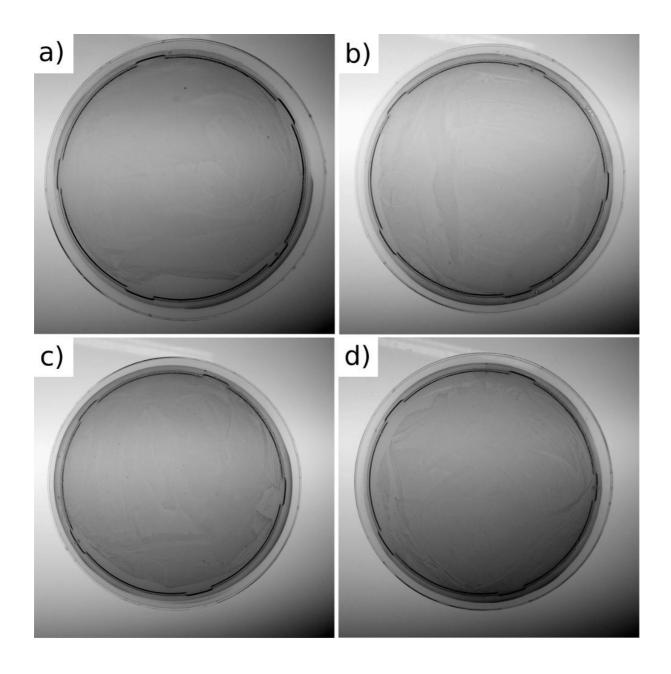


Figure S10. Peptide-coated gold nanoparticles at a concentration of a) 10 μ g/mL, b) 18 μ g/mL, c) 25 μ g/mL and d) 35 μ g/mL Bacteria concentration: 5.10⁵ CFU. Incubation time 24 h at 37°C. Note the bacteria layer.

Reference:

1. Graf, P.; Mantion, A.; Foelske, A.; Shkilnyy, A.; Masic, A.; Thunemann, A. F.; Taubert, A., Peptide-Coated Silver Nanoparticles: Synthesis, Surface Chemistry, and pH-Triggered, Reversible Assembly into Particle Assemblies. *Chemistry-a European Journal* **2009**, *15* (23), 5831-5844.