Biomimetic synthesis of erbium doped silver/peptide/silica chiral core-shell nanoparticles (ESPN)

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Supporting information

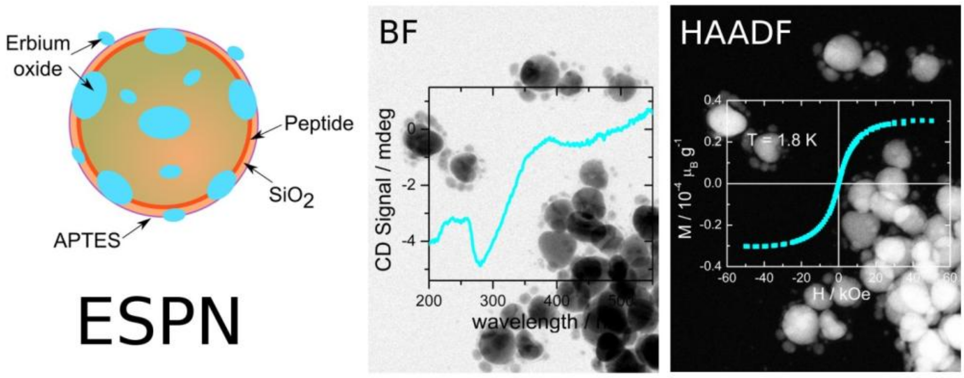

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Figure S1 shows representative TEM images of the silver nanoparticles used in this study and their size distribution as determined by counting more than 1000 particles. The picture shows that the nanoparticles are well dispersed on the TEM grid, and have a diameter of around 20 nm with a moderate polydispersity of around 20%, which is similar to our previous report.[1] Upon silicification, and already after 24 hours, there is a layer of silica forming around the nanoparticle, and the layer increases with further reaction time.[2]

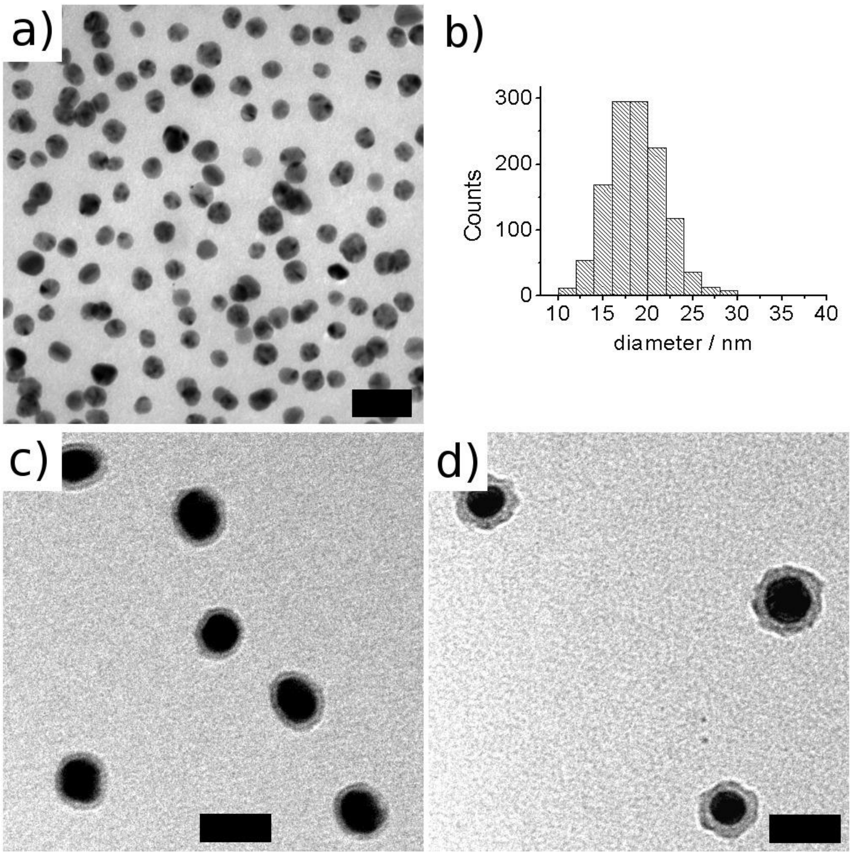

Figure S1: TEM of the different nanoparticles: (a) neat nanoparticles, that is, before any coating, (b) size distribution as determined from counting statistics (N = 1226, average = 18.7 nm diameter, σ = 3.2 nm), neat nanoparticles treated with TEOS for (c) 24 hours and (d) 48 hours. Scale bar is 50 nm.

Figure S2 shows high resolution scanning electron microscopy (HR-SEM) images of the ESPN grown in the presence of erbium and after coating with APTES. The particles are spherical and relatively monodisperse, with a diameter of *ca*. 30 nm, and show essentially no aggregation. In agreement with TEM, HR-SEM of nanoparticles prepared with 0.3 mol% erbium does not show a high contrast, electron-rich and an electron-poor region. TEM and HR-SEM thus suggest that small amounts of erbium are taken as dopant in the precipitating silica, as shown by TEM, see **Figure 1**, inset in panel c. This, in turn, increases the average electron density of the Er-doped silica shell, which makes it hard to observe it in electron microscopy. In contrast, with 3 mol% of erbium, the smaller nanoparticles are again clearly visible *in* and *on* the silica shell.

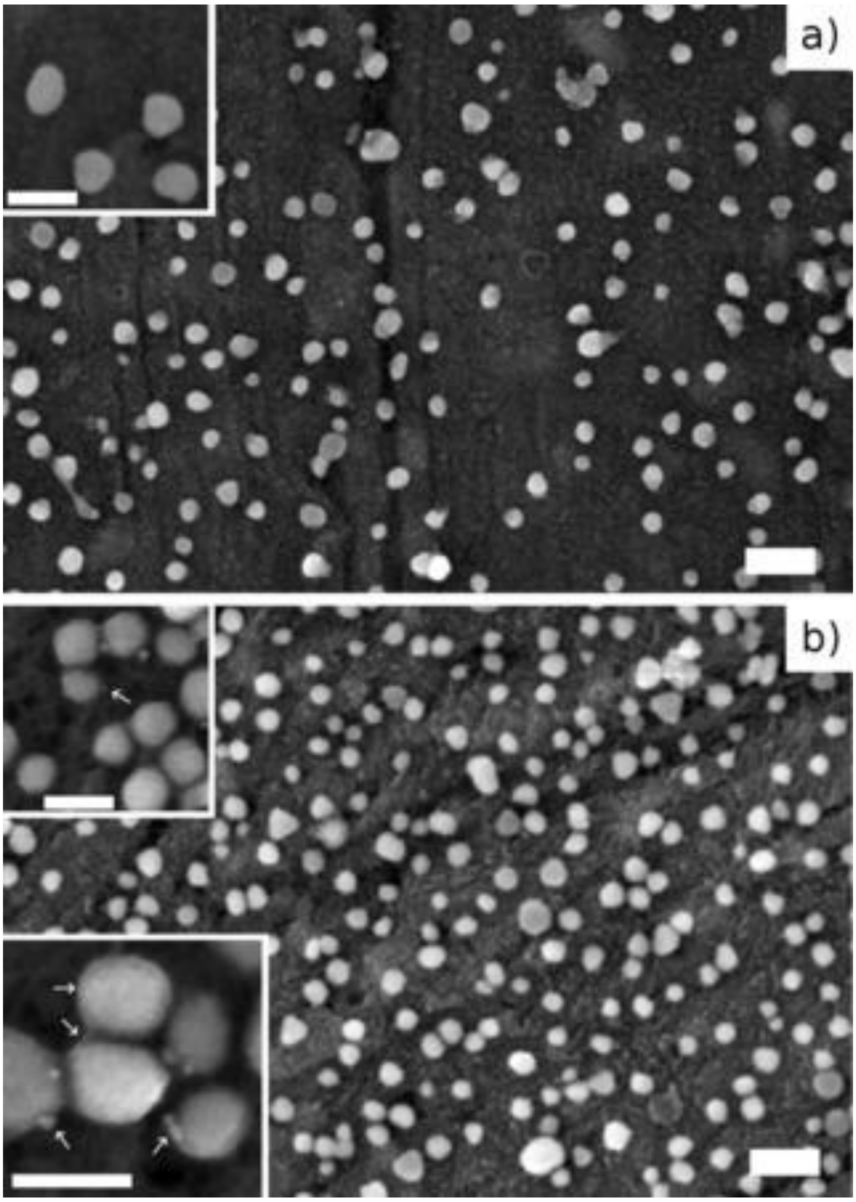

Figure S2: HR-SEM images of ESPN with (a) 0.3 mol% of erbium and (b) 3 mol% of erbium after 48 hours reaction and APTES coating. The texture and the small, *ca.* 4 nm, particles visible in the background are from the sample support and should no be confused with silver nanoparticles (see experimental part for details). Inset: details of the nanoparticle aggregates. The arrows point to small nanoparticles precipitated on the nanoparticle, and to the silica nanoparticle shell, see also **Figures 1 and 2.** Scale bars are 100 nm in the main images and 50 nm in the insets.

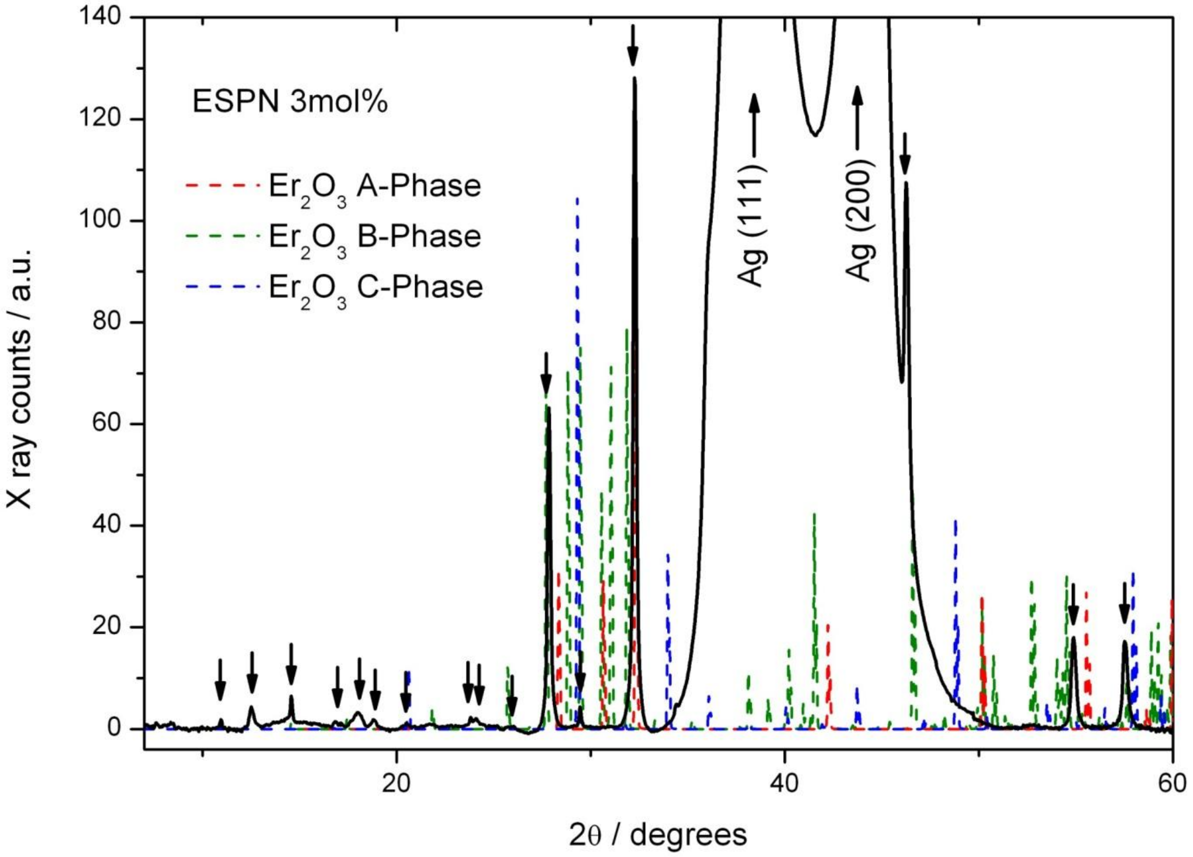

Figure S3: sXRD pattern of ESPN prepared with 3 mol% Er and overlay with calculated powder pattern using Fullprof[3] and literature data[4, 5]. Arrows point to the reflections arising from the erbium specie(s). Dashed lines refer to diffractrogram calculated from literature data. **Table S1** lists the peak positions and the corresponding d spacings. Wavelength was 1.5456 Å

Table S1: Reflection positions, intensities and corresponding d spacings for the ESPN prepared in the presence of 0.3 mol% and 3 mol% Er. Silver (111) and (200) were omitted for clarity. The Bragg equation was used to determine the d spacings. Wavelength was 1.5406 Å.

ESPN 0.3mol% Er			ESPN 3mol% Er		
2θ / degrees	Intensity / a.u	d spacing / Å	2θ / degrees	Intensity / a.u	d spacing / Å
12.47	4.16	7.0926	10.93	3.18	8.0882
14.57	5.51	6.0747	12.5	4.32	7.0756
17.91	3.2	4.9486	14.57	6.49	6.0747
18.63	1.42	4.7590	17.98	3.18	4.9295
24.77	3.72	3.5915	18.85	1.75	4.7039
25.18	3.88	3.5339	20.51	1.21	4.3268
27.81	152.21	3.2054	21.69	0.93	4.0940
29.44	6.13	3.0315	23.81	2.34	3.7341
32.22	308.36	2.7760	24.06	2.11	3.6958
46.21	36.12	1.9630	25.93	0.46	3.4334
54.81	46.55	1.6736	27.84	63.22	3.2020
57.47	46.31	1.6023	29.44	4.37	3.0315
			32.25	128.09	2.7735
			34.35	4.83	2.6086
			46.27	107.49	1.9606
			54.87	17.97	1.6719
			57.5	17.25	1.6015

Figure S4 shows a representative energy dispersive X-Ray (EDX) spectrum of the ESPN prepared in the presence of 3 mol% Er. The spectrum clearly indicates the presence of silver, carbon, oxygen, nitrogen, sulphur, and, importantly, erbium. This strongly supports the ESPN material structure in the sense that EDX provides evidence of a composite: the silver signal stems from the metal nanoparticle and the sulphur, nitrogen and a part of the carbon signals from the peptide. Moreover, silicon and a vast part of the signal attributed to oxygen (and a part of carbon, from TEOS) arises from the silica layer. Erbium signals arise from the Er-doped silica and/or the smaller nanoparticles. For samples prepared with 0.3 mol% Er (**Figure S5**), the erbium signal is below the limit of detection and cannot be detected. As a comparison, samples without erbium were prepared and subsequently analyzed, leading to the same observations as already reported,[2] see **Figure S6**.

In conclusion, EDX also support the presence of erbium in the structure for the 3 mol% case, even the amount is likely to be limited and the signals at higher energy get lost in the *Bremsstrahlung*.

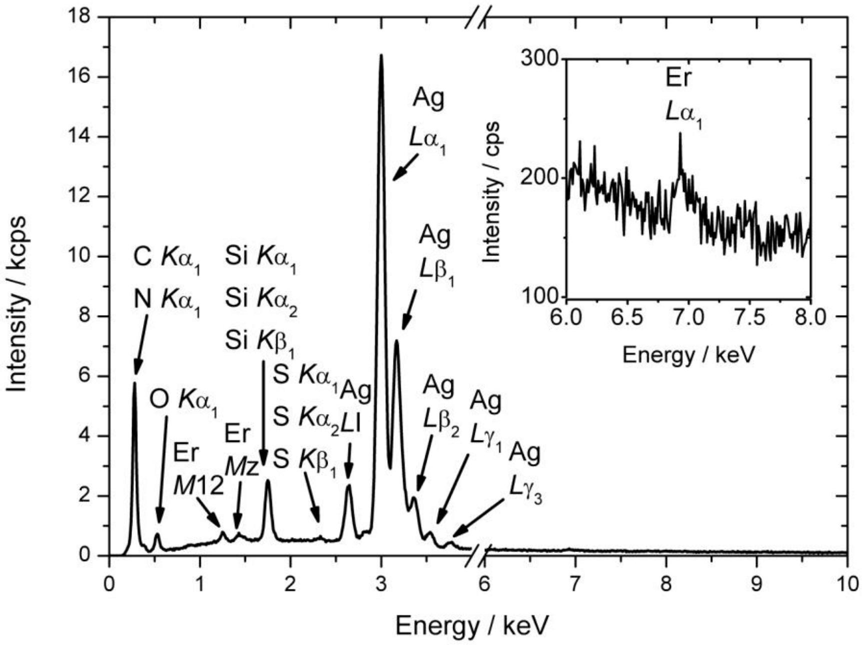

Figure S4: Energy-dispersive X ray spectrum from the ESPN prepared in the presence of 3 mol% of erbium, cast on a *carbon* sample holder and the respective energy signal assignment.[6] The carbon signal is over-estimated, as a part arises from the sample holder.

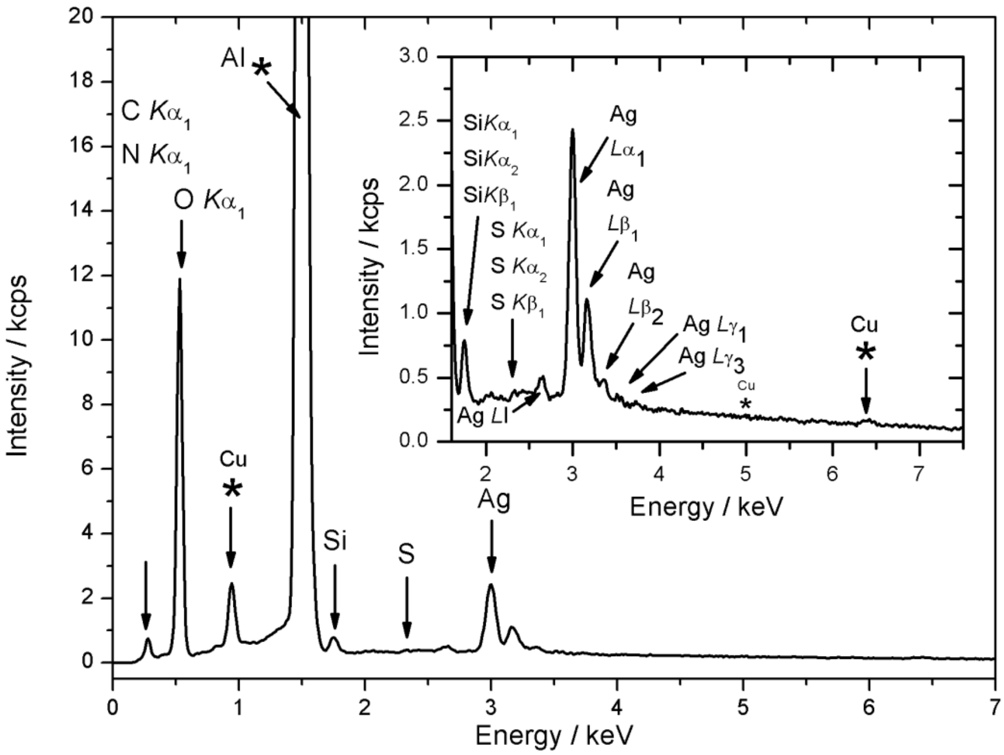

Figure S5: Energy-dispersive X ray spectrum from the ESPN prepared in the presence of 0.3 mol% of erbium, cast on an *aluminium* sample holder (the copper contamination arises from the sample holder) and the respective energy signal assignment.[6] The oxygen signal is over-estimated, as a part arises from the sample holder. The signal at around 6.4 keV in the inset should not be confused with an erbium signal. Asterisks denote the parasitic signals from copper and aluminium

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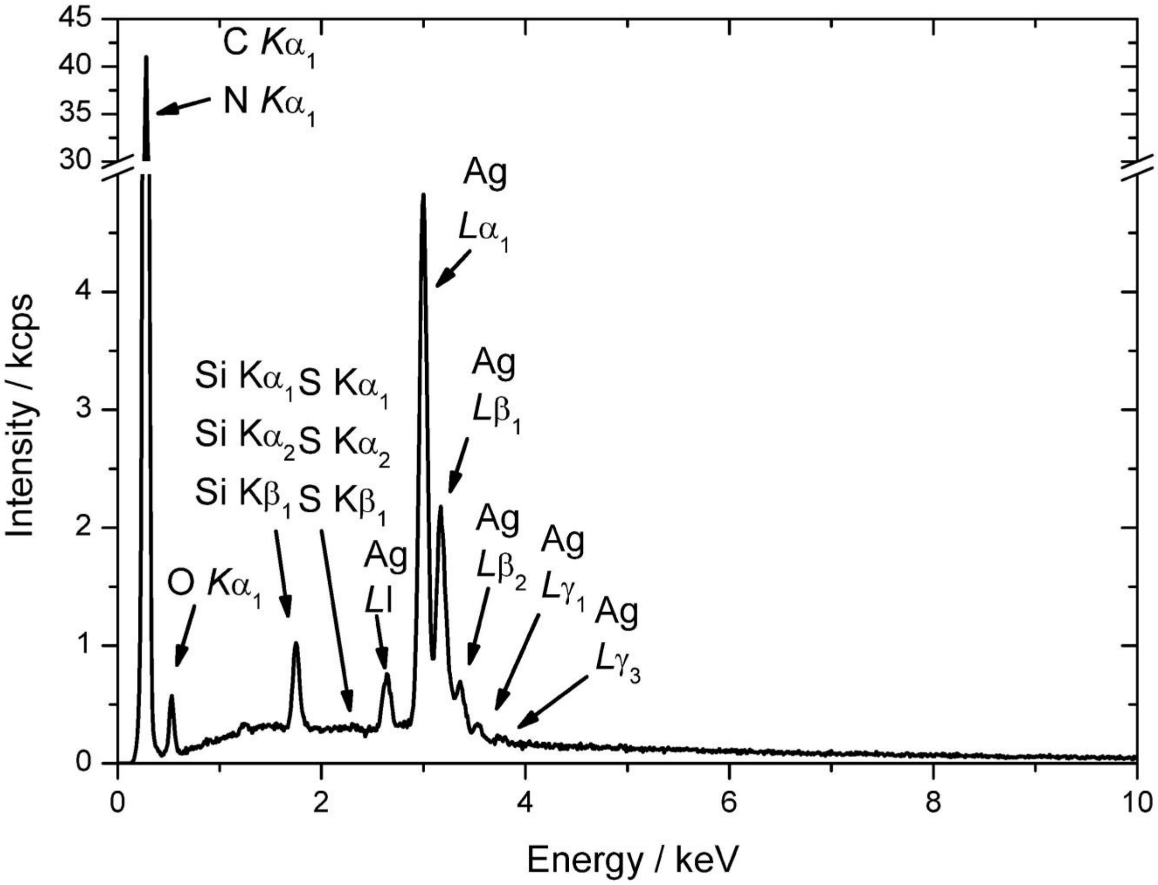

Figure S6: Energy-dispersive X-ray spectrum from the ESPN prepared in the absence of erbium, cast on a *carbon* sample holder and the respective energy signal assignment.[6] The carbon signal is over-estimated, as a part arises from the sample holder.

Table S2 shows the result of the deconvolution of the CD spectra using trained neural networks as implemented in CDNN[7] arising from the peptide set on the nanoparticle surface. Basically, the table confirms the *qualitative* observation that the peptide structure is conserved upon silicification on the surface even if the quantitative interpretation may be hampered by parasitic absorption from the metal nanoparticle, the erbium nanostructures *etc.*

Table S2: Result of the spectral deconvolution of the peptide-related signal using the CDNN software.[7] Predicted error[7] using a neural network in these wavelength range is around overall 6-7%. Data were normalized to 100%.

Conformation	200-260 nm	205-260 nm	210-260 nm
	Pure nanoparticles (only peptide coating)		
α helix	5	3	4
β sheet antiparallel	39	42	42
β sheet parallel	5	5	5
β turn	17	18	17
Random Coil	33	33	32
Total Sum	100	100	100
	0 mol% Erbium (peptide + silica)		
α helix	6	4	4
β sheet antiparallel	38	40	41
β sheet parallel	5	5	5
β turn	18	18	18
Random Coil	33	33	33
Total Sum	100	100	100
	0.3 mol% Erbium (peptide + silica)		
α helix	5	4	4
β sheet antiparallel	38	41	42
β sheet parallel	5	5	5
β turn	18	18	18
Random Coil	33	33	32
Total Sum	100	100	100
	3 mol% Erbium (peptide + silica)		
α helix	5	4	4
β sheet antiparallel	38	41	42
β sheet parallel	5	5	5
β turn	18	18	17
Random Coil	33	32	32
Total Sum	100	100	100

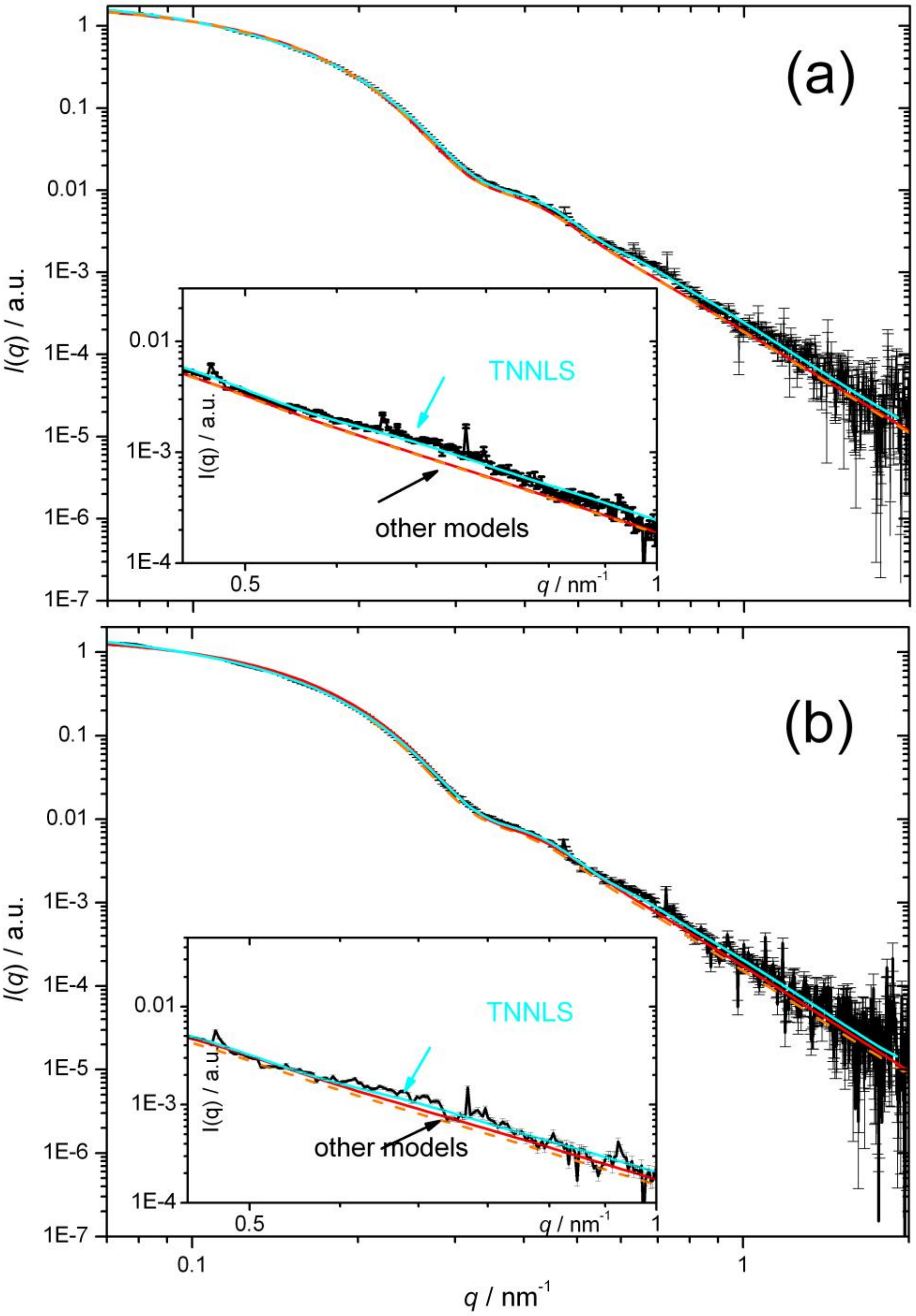

Figure S7: SAXS intensity curves of ESPN nanoparticles (black line) and the corresponding modeling. Panel (a) corresponds to ESPN prepared in the presence of 0.3 mol% Er and panel (b) corresponds to those prepared with 3 mol% Er. Modeling was performed using a TNNLS model (cyan line), or using a core-shell with a constant core radius / core + shell radii ratio and a common polydispersity (orange line) and finally with a polycore-shell model (red line). Insets show a comparison between the three models in the region where the TNNLS analysis better matches the experimental data. For the model description, please refer to the experimental part.

Figure S8 shows the difference in size distribution from the Ag/peptide@SiO_2 as previously described in our previous publication[2] and the current data as calculated from the TNNLS data analysis. Both curves are slightly shifted, but show similar polydispersities. Note the presence of populations of smaller nanoparticles. For details, see the manuscript.

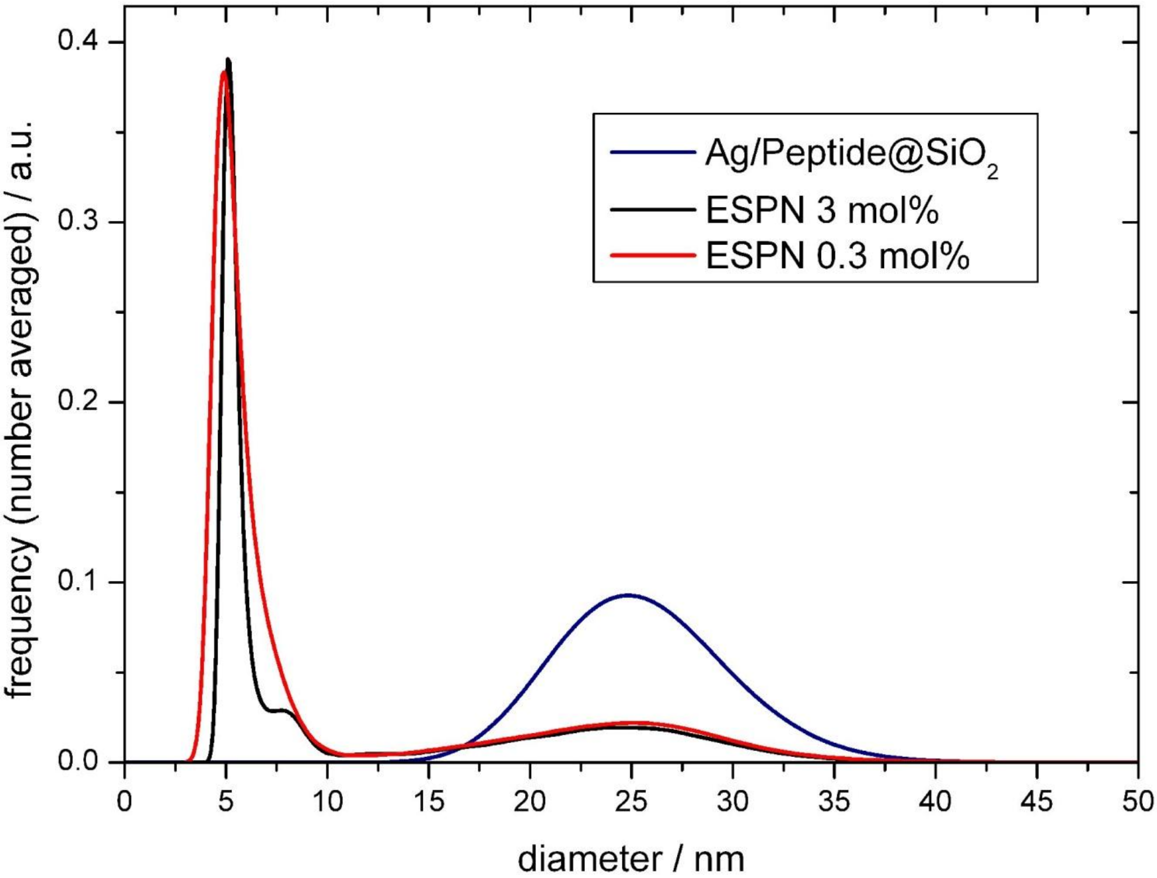

Figure S8 Comparison of the size distribution from Ag/peptide@SiO_2 (blue)[2] and ESPN synthesized in the presence of 0.3 mol% Er (red, from TNNLS analysis) and 3 mol% Er (black, from TNNLS analysis). Note that the data are number averaged.

Figure S9 shows the evolution of the UV/Vis spectra of the nanoparticles *vs.* the reaction time. As the reaction time increases, the absorption maximum red-shifts. This is not surprising, and can be related to a growing silica shell on the silver nanoparticle, as we recently reported.[2] This could be simply explained using the Mie theory. In short, the nanoparticles experience a different dielectric environment upon turning from water to silica, leading to a frequency shift in the plasmon polariton absorption band. Interestingly, there is no change upon addition of an APTES layer, which is probably due to the fact that the APTES layer is very thin, somewhat distant from the silver surface, and there is no aggregation of the particles, similar to our previous report.[2]

Figure S9 shows that after 24 hours all absorption spectra are similar. However, the absorption maxima are red shifted, from 412 nm with TEOS alone to 417 and 419 nm in the presence of 0.3 mol% and 3 mol% of erbium, respectively. This is not surprising, as TEOS can take up some erbium, which leads to a slightly different dielectric constant and thus to a shift in the absorption maximum. Moreover, the absorption bands are broader in the presence of erbium than without. A simple interpretation at that stage could not be furnished, as the later can be related to the appearance of an absorbing inorganic layer or to some interparticle interactions.[2] This is further supported by the data obtained for samples after 48 and 72 hours. Upon redispersion and coating with APTES, the nanoparticles are again dispersed and remains in this state.

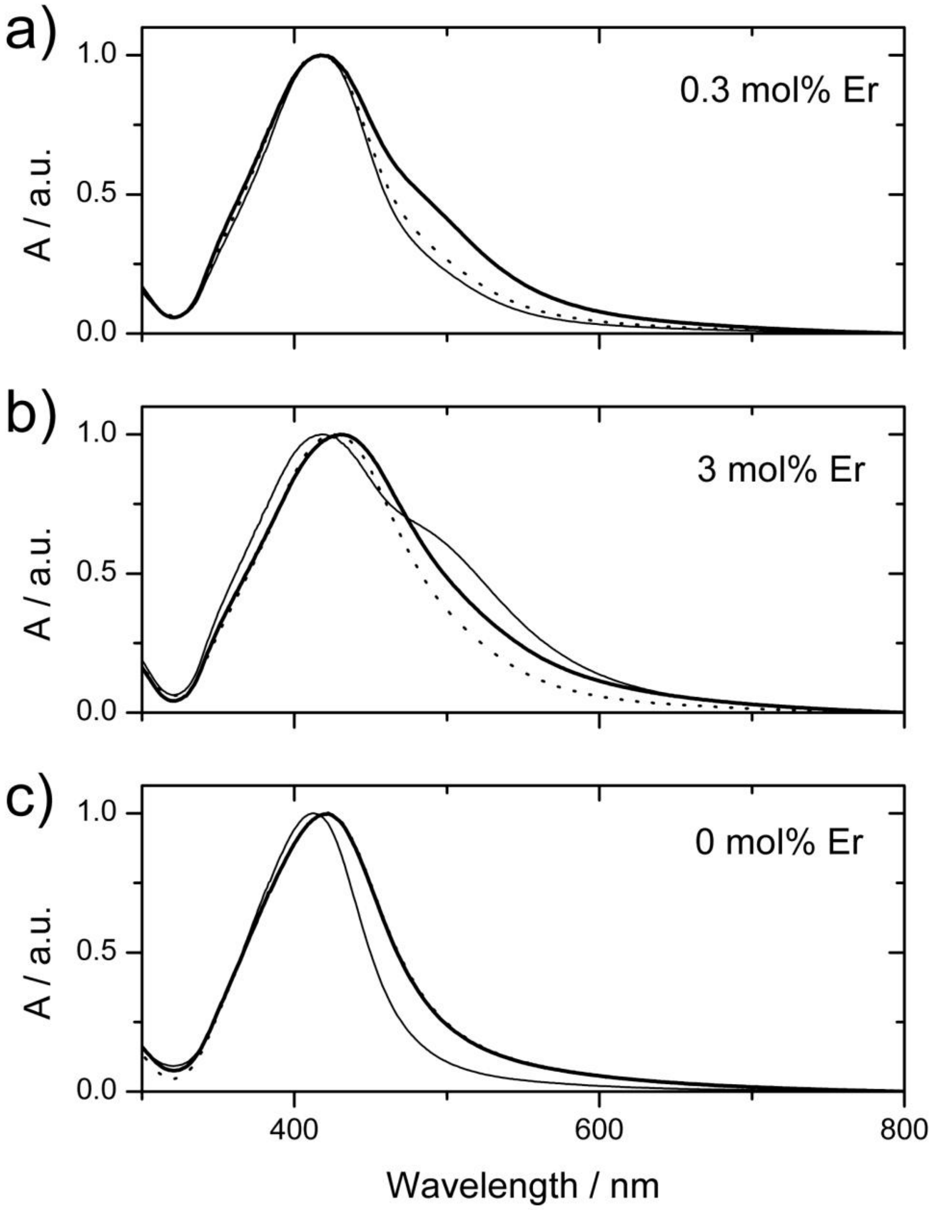

Figure S9: UV-Visible spectra of the ESPN grown in the presence of (a) 0.3 mol% of Er, (b) 3 mol% Er and (c) only TEOS. Thin line: after 24 hours, thick line: after 48 hours, and dotted line: after 72 hours and APTES coating. In panel (c), curves after 48 and 72 hours virtually superimpose. Data were normalized to 1 at wavelength maximum to simplify comparison.

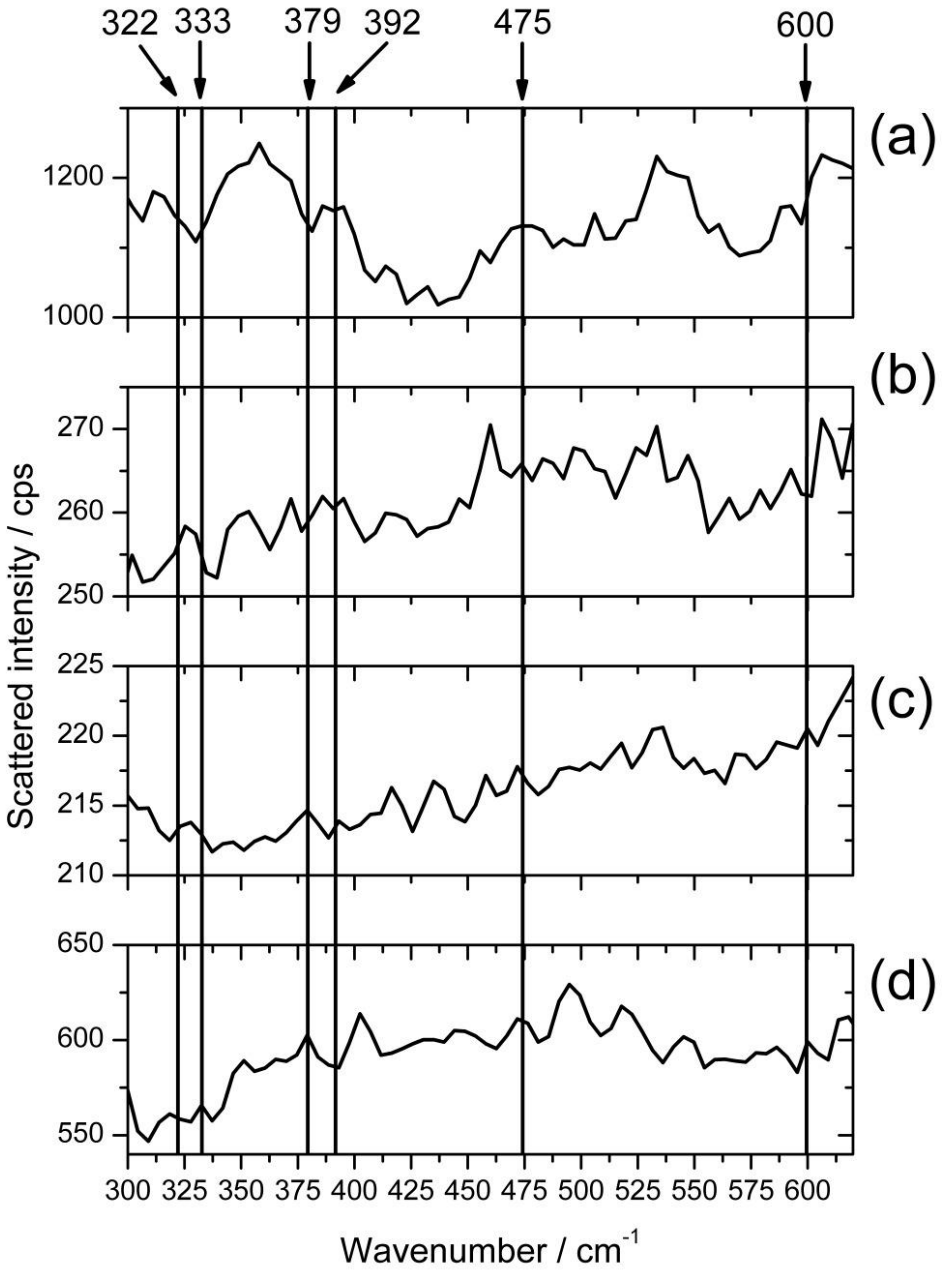

Figure S10: Raman spectra of (a) the pure nanoparticles, (b) ESPN prepared in the presence of 0 mol% Er, (c) 0.3 mol% Er and 3 mol% Er. Wavenumbers indicate the experimental values, compare with the published values[8] of 332, 338, 381, 390, 480 and 598 cm^{-1} for Er_2O_3. Note the spectral similarities between all the compounds. Resolution of the CCD camera is 4 cm^{-1}.

Figure S11 shows the infrared spectra of the different ESPN (0.3 mol% Er and 3 mol% Er), the nanoparticles coated with a layer of pure silica and the peptide, the nanoparticles coated with the peptide and finally the pure peptide alone. The spectra of the peptide, the peptide-coated, and silicified silver particles were already described somewhere else and are only shown for comparison.[1,2] In short, the spectrum of the peptide-coated silver nanoparticles is controlled by the special selection rules of objects adsorbed on a metallic surface, thus leading to the apparently poor infrared spectrum. Comparing curve (a) and (b) clearly shows that the nanoparticle surfaces are significantly different, that is, both of them show different structures, as could be inferred from both TEM and high resolution SEM investigation. Comparison of (a) with (c) suggests that the nanoparticle surface is lacking a layer of amorphous silica, or this one is too small or of peculiar structure to be detected. In contrast, the comparison of (b) with (c) clearly points out this presence, as attested by the presence of multiple, intense vibration bands arising from the amorphous silica layer, with broad bands at around 800 cm^{-1}, 950 cm^{-1}, 1044 cm^{-1} and 1188 cm^{-1}. These bands can be attributed to ν(Si-O), δ(Si-OH), ν(Si-O-Si), and δ(CH_2) from the residual TEOS present at the surface or included in the surface.[9, 10] In contrast, the peptide signals are barely visible. In summary, IR spectroscopy supports the presence of a layer of amorphous silica at the particle surface of the ESPN prepared with 3 mol% of erbium but with 0.3 mol% of erbium the results are less clear, pointing to a thinner silica layer.

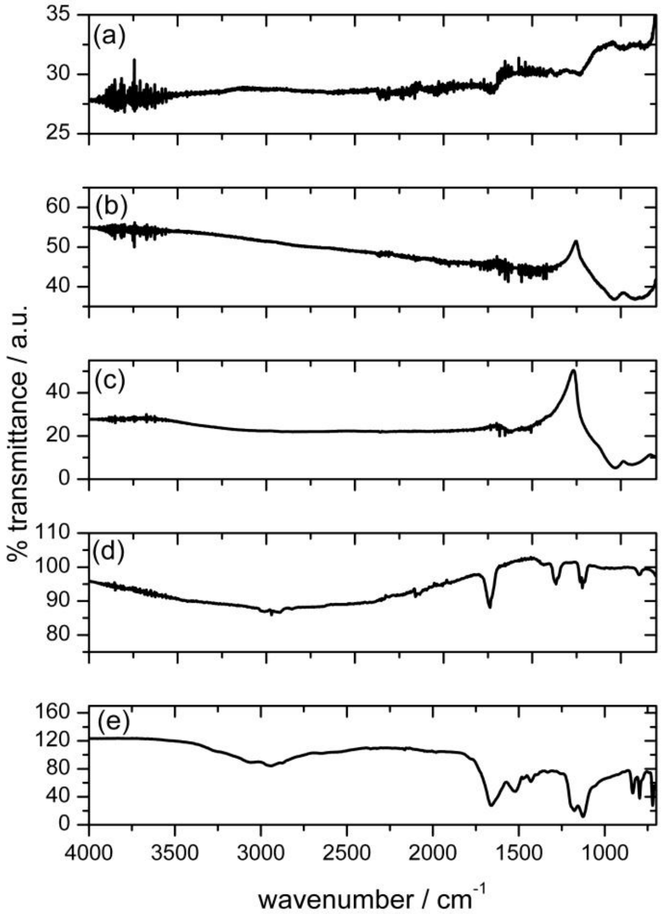

Figure S11: IR spectra of the ESPN: (a) prepared with 0.3 mol% Er, (b) 3 mol% Er, (c) 0 mol% Er, (d) pure peptide-coated silver nanoparticle[1] and (e) the peptide alone.[2]

Figure S12 shows the thermogravimetric analysis (TGA) data of the particles before and after mineralization for 48 hours. The silver@inorganic nanoparticles clearly exhibit a larger weight loss when compared to their peptide-coated counterparts.[1,2] Adding even a small amount of erbium leads to larger relative weight losses. The peptide-coated silver nanoparticles shows a typical decomposition curve for coated nanoparticles,[1] that is there is a 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°C, 175°C, and 400°C.[2]

Doping the silica with 0.3 or 3% mol erbium leads to the same thermal behaviour, but the transitions are more pronounced.

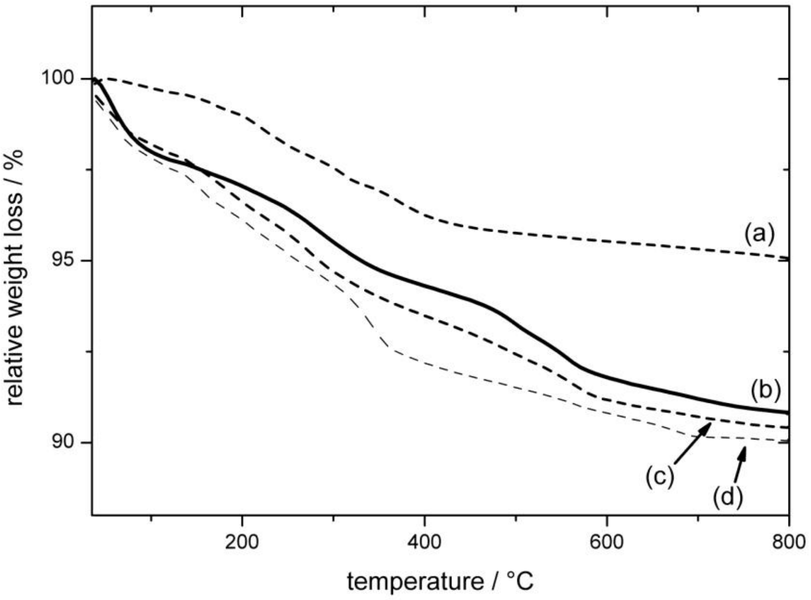

Figure S12: TGA curves of the (a) peptide-coated nanoparticle[1], (b) Ag/peptide@SiO_2 nanoparticles[2], (c) ESPN prepared in the presence of 3 mol% Er and (d) in the presence of 0.3 mol% Er.

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