Giant Hollow Fiber Formation through Self-Assembly of Oppositely Charged Polyelectrolytes Brushes and Gold Nanoparticles

Electronic Supplementary Information

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1 Characterization of the gold nanoparticles (AuNPs)

The synthesized AuNPs were characterized by transmission electron microscopy as shown in Fig. S1. The radius of the gold particle core was calculated from the TEM micrographs based on statistic over 100 particles (see histogram) was determined at 22.7 \pm 3.7 nm. The surfactant stabilization can be seen as a thin layer surrounding the gold core with a thickness between 5 and 8 nm. AuNPs were well-dispersed as confirmed by the hydrodynamic radius of $R_H = 27$ nm determined from the dynamic light scattering using the Zetasizer, in good agreement with the size determined by TEM, including the surfactant layer.

2 Dynamic light scattering analysis of AuNP-SPB association.

In the early stage of association, the size and distribution of the particles present in suspension were determined using dynamic light scattering (DLS). All measurements were performed approximately one week after the preparation of the samples. Fig. S2A displays the normalized field autocorrelation functions and Fig. S2B the decay times distribution determined from the CONTIN analysis at 90° as a function



Fig. S 1 Transmission electron micrograph of a 0.2 wt.% aqueous AuNP suspension. The number size distribution is indicated on the histogram. The higher magnification evidences the presence of the surfactant layer at the surface of the particles.

of c_{AuNP} . The distribution is binodal for AuNP-SPB mixtures having $c_{AuNP} \leq 4.9 \times 10^{-2} \text{ gL}^{-1}$ with a major contribution of the slow relaxation process. The resulting decay times distribution clearly indicated that AuNP addition did not result in the formation of large aggregates. On the contrary the decay times related to slow relaxation processes decreased, which implied faster relaxation processes and thus to a decrease of the average apparent size. Broadening of the peaks related to the increase of the polydispersity could be observed by adding AuNPs. The decay rate Γ corresponding to the inverse of the decaytime, was then plotted as function of the squared wave vector q^2 for angles ranging between 30 and 130° with an increment of 10°. As $\Gamma = q^2 D$, the diffusion coefficient D can be determined from the linear extrapolation as shown in Fig. S2C. An apparent hydrodynamic radius R_H has then been calculated from the Stockes-Einstein relation for different c_{AuNP} . This analysis was performed for the two contributions. First the decay rate Γ derived for fast relaxations processes was plotted as function of q^2 for the different mixtures in the inset of Fig. 3C. The same linear dependence was found for the

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Fig. S 2 Dynamic light scattering experiment of the AuNP-SPB association for the different concentrations presented in Fig. 2 in the manuscript (SPBs: hollow circles, mix 2: hollow squares, mix 3: down triangles, mix 4: full circles, mix 5: full squares and mix 6: up triangles). A) Normalized field autocorrelation functions for the different mixtures. B) CONTIN analysis at 90°. C) Dependence of decayrate Γ on the squared scattering vector q^2 for the slow relaxation processes. The inset considers fast relaxation processes related to the free AuNPs present in suspension.

different AuNP-SPB mixtures and an apparent hydrodynamic radius of 20.5 nm. As this value was in the same order as the size of the AuNPs derived from TEM and DLS analysis, we attribute this contribution to the presence of free AuNPs in the suspension. The same treatment was performed for slow relaxation processes. The linear dependence of Γ as function of q^2 is respected until $c_{AuNP} = 4.9 \times 10^{-2} \text{ gL}^{-1}$, afterwards the experimental data scattered particularly for the measurements performed above 90° . Fig. 2 in the article, summarized the evolution of the apparent hydrodynamic radius of the AuNP-SPB hybrid complexes derived from this analysis.

3 Structural analysis of the association.

In parallel to the UV vis spectroscopy, zetapotential and DLS experiments, different microscopy methods were employed to image the association of the two particles. Fig. S3 presents the micrographs obtained for different mixtures by TEM, SEM and SFM in the early stage of the association. AuNPs were found to get inhomogeneously adsorbed on SPBs and free AuNPs could be observed at the surface of the waiver. Aggregates of many particles were also present on the micrographs, which could be a consequence of the drying of the sample after preparation. Whereas the association was obvious for dipcoated samples, we observed that spin coated preparations were not showing any association due to the high shear and fast drying related to this preparation. We conclude that the interactions between AuNPS and SPBs are weak and can not fully maintain the structure of the association during the drying process. Thus this analysis confirms the apparent association between AuNPs and SPBs, and that AuNPs are not strongly absorbed on SPBs.



Fig. S 3 Micrographs of the association between AuNPs and SPBs investigated in the dried state by: A) Transmission electron microscopy (mix 4), B) SEM (mix 3) and C), D) SFM (mix 4, phase images).

4 Additional characterization of the fibers.

Fig. S4 presents bright field microscopy of the fibers for two different AuNP concentrations (mix 5 and 6). The aggregates appeared in the form of very long fibers with an average width below 2 μ m. The AuNPs presence in fibers could be clearly visualized from the red color. The fibers color did not strongly shift to the blue, which indicates that the AuNPs did not self-aggregate in the fiber and that no plasmon coupling took place. The same aggregates were observed in the others mixtures and



Fig. S 4 Optical microscopy of the fibers obtained for a AuNP-SPB mixture with $c_{AuNP} = 4.9 \times 10^{-2} \text{ gL}^{-1}$ (mix 6 A) and $4.0 \times 10^{-2} \text{ gL}^{-1}$ (mix 5 B).



Fig. S 5 Confocal laser-scanning microscopy (CLSM) of the fibers obtained for a AuNP-SPB mixture with $c_{AuNP} = 4.9 \times 10^{-2} gL^{-1}$ (mix 6). A) 3D reconstruction (61.5 × 58.2 × 20 µm) obtained from the projection of the maximum intensity values and B) from an isosurface values representation.

the amount of fibers present in suspension after one month was found to increase with c_{AuNP} . The fibrilar network was investigated in situ via confocal laser scanning microscopy (CLSM). For this purpose, the negatively charged PSS shells of the SPBs were stained by adding a cationic water-soluble dye (Rhodamine B). Two 3D reconstructions either considering the maximum intensity or the isosurface values are presented in Fig. S5. The fibers appeared hollow and relatively monodisperse with an average diameter equal to 1.3 μ m. Locally, the width also drastically varied and larger hollow excressences were observed.