Individual tubular J-aggregates stabilized and stiffened by silica encapsulation

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Supporting Information

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1. Comparison of EDX spectra for SiO_2 coating vs. SiO_2 standard

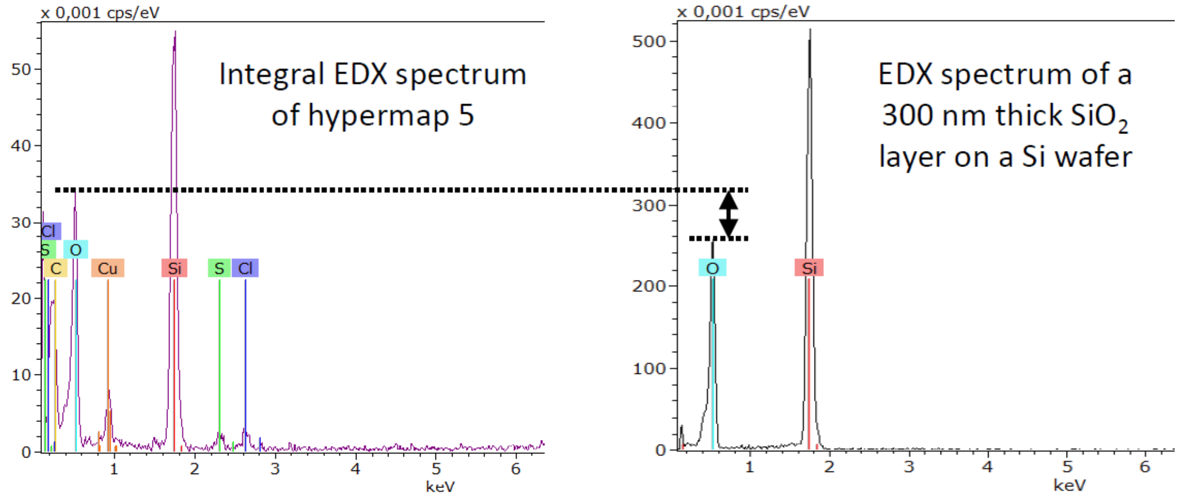

Figure S 1: The EDX spectrum of a silica covered aggregate (left) is compared to the EDX spectrum of a 300 nm thick SiO_2 *layer on a silicon wafer. The spectra are scaled such that the maxima of the Si peak is identical. As one can see, the ratio of O/Si intensity is higher for the aggregates than for the* SiO_2 *layer. This is most likely caused by the oxygen content of the dye molecules. The sulfur (S) and chlorine (Cl) signals also result from the dyes.*

2. Fluorescence microscopy before and after vacuum drying

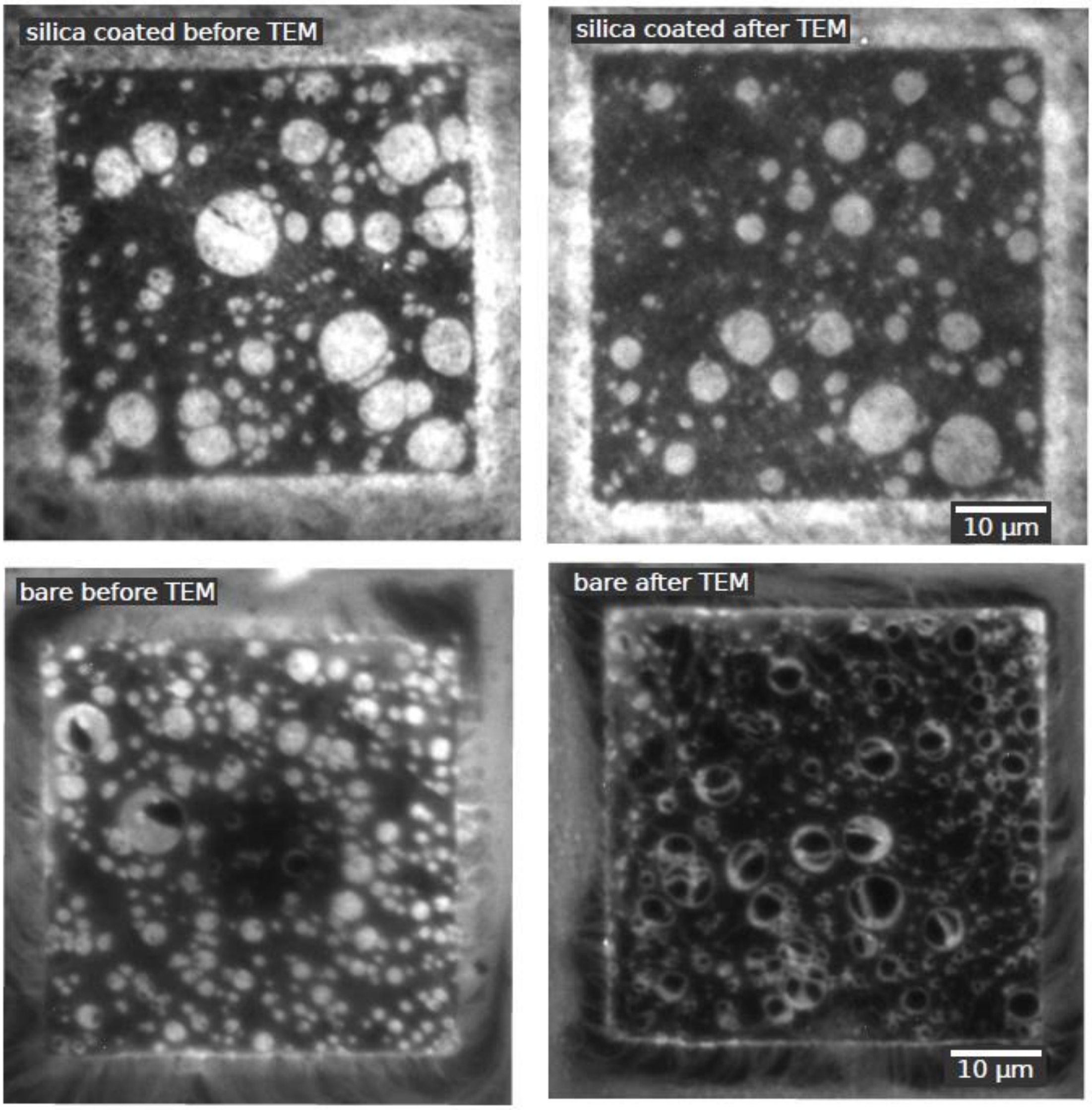

Figure S 2: Fluorescence microscopy image of TEM grid covered with carbon film and C8S3 aggregates on top. The TEM grid was inspected before (left column) and after (right column) inspection with TEM. Isolated aggregates could not be resolved by the microscope due to low resolution. However, it can clearly be seen that the silica covered aggregates (top row) are spanning the holes and the fluorescence is mostly unaffected by the vacuum treatment. The fluorescence of bare aggregates is also seen to span the holes prior to TEM inspection; however, through the drying the pull back to the edges of the holes and the total fluorescence significantly decays.

3. Nanomanipulation of silica covered aggregates by SFM

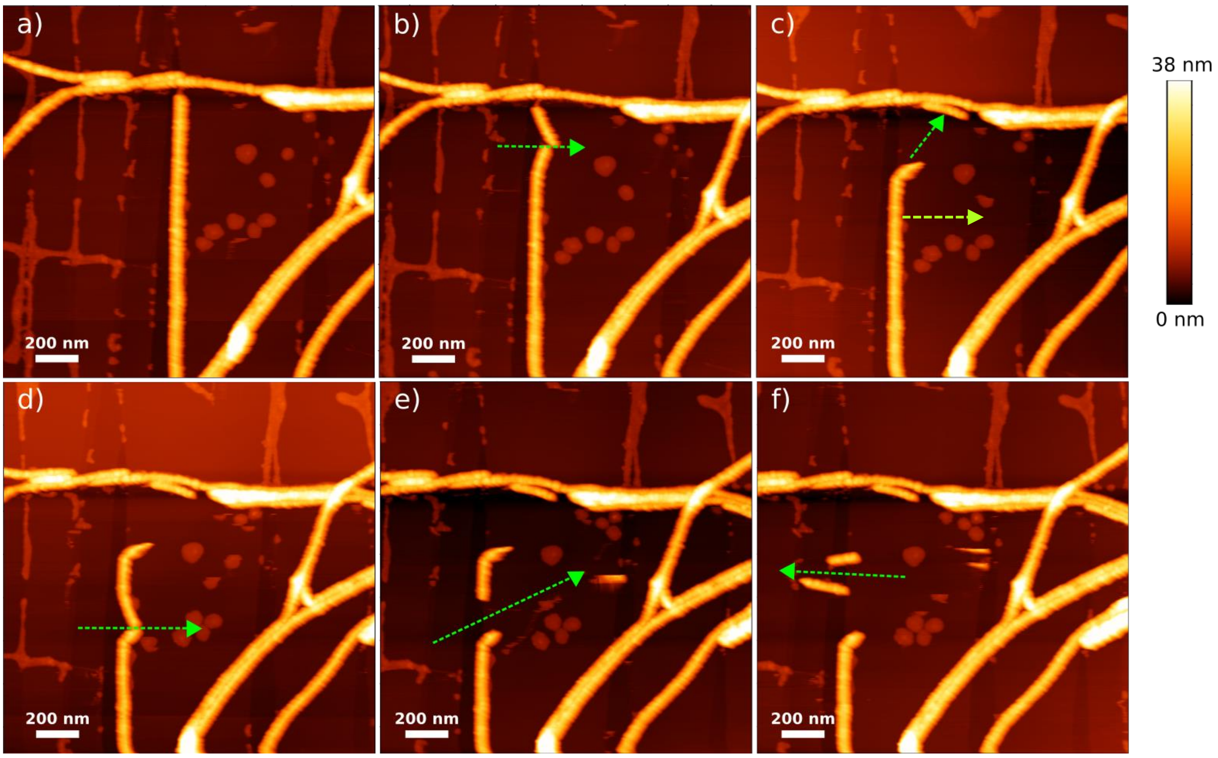

Figure S 3: SFM manipulation of silica covered aggregates of C8S3 dispersed on HOPG by spin coating. a) Image of coated aggregates taken in Tapping mode. b) to f) Images taken after dragging the tip along the surface in manipulation mode, i.e. in contact mode with increased lateral force. The manipulation path is indicated by the (green) dotted arrow. Parts can be broken of and moved to other places without noticeable deformation.

4. EELS measurement of the silicon and oxygen density profile

The measurement of Figure 10b in the text needs some further explanation. Since it mostly concerns technical issues but could be helpful also for others, we provide this information here.

For technical reason it was not possible to record the signals of the Silicon $L_{2,3}$ (99 eV) and Oxygen K (532 eV) EELS edges simultaneously, because the energy window that could be achieved with our detector was not wide enough to fit all the elemental signals. Instead of scanning repeatedly the same position, the position was slightly changed (few tenths of a nanometer) in order to avoid measuring over a contaminated area. It was observed that after imaging or during EELS scans the aggregates became blurred at the boundaries which was assigned to agglomeration of carbon from the substrate. In order to avoid this contamination effect, first low dose was used for the imaging, and second, no repetitive scans were performed at the same position.

The EELS spectrum line data were factorized using multivariate analysis. This analysis re-formulates the data into a short list of "factors" (that look like individual spectra) and their respective "abundance maps". These abundance maps can be interpreted as line profiles of element specific signals and are shown for silicon and oxygen in Fig. 10 of the publication.

In Figure S Figure S 4, factors labeled 1 in panel c and labeled 0 in panel f, showed no specific spectral signature and their abundance maps look just like a slightly increasing slope (see panels b and e, respectively). Our interpretation is that this corresponds to a background signal, given by the carbon bulk plasmon (peak not visible at this range, at ~ 20 eV). The slight increase would be a signature of the carbon contamination as we measure. More information is given in the caption of the Figure S 4.

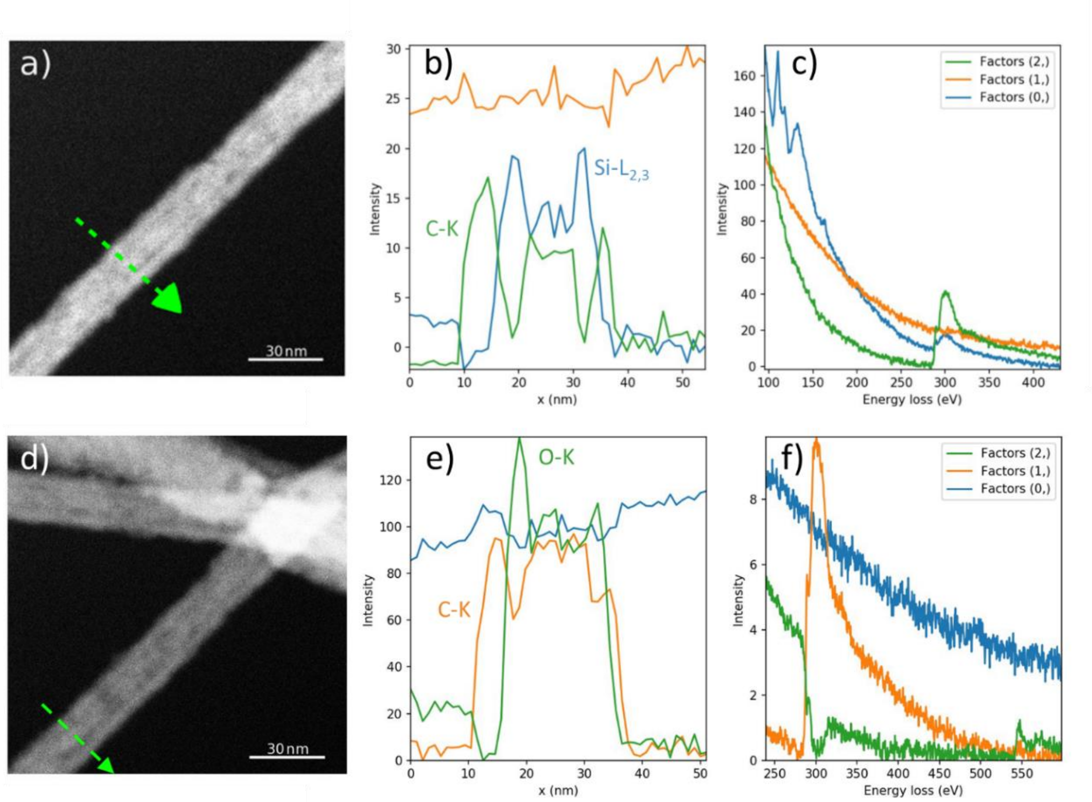

Figure S 4: Overview of the experimental procedure to obtain element specific cross-sectional profiles. a) and d): STEM-HAADF image of a single silica covered aggregate spanning a hole on a carbon covered TEM grid. Both images present the same aggregate but viewed from a different position. The EELS signal was detected while moving the electron beam along a line as indicated by the dotted (green) arrow. b) Line profiles obtained from the signals of the Silicon $L_{2,3}$ (99 eV) and Carbon K (284 eV) EELS edges of the spectra shown in c). The third signal represents a background signal which is not further specified. e) Line profiles obtained from the signals of the Carbon K (284eV) and Oxygen K (532 eV) EELS edges shown in f).

5. Silica encapsulation of tubular J-aggregates of C8O3/SDS

Silica coating were also prepared on aggregates of the dye 3,3'-bis(3-carboxypropyl)-5,5',6,6'-tetrachloro-1,1'-dioctylbenzimidacarbocyanine (C8O3) mixed with sodium dodecyl sulfate (SDS). These mixtures do form tubes with larger diameter than C8S3 and are able to form multilamellar tubes with diameters of several ten nanometers. [1] It was the purpose of this work to demonstrate the applicability of the protocol (with slight modifications) to grow silica shells as well. It opens the route to stabilize differently structured tubular aggregates including multilayered ones.

The dye C8O3 was obtained commercially (FEW Chemicals) and used as received. 0.2 mM stock solutions were prepared by dissolving the dye powder in either 10 mM aqueous NaOH or in water adjusted to pH 9 with ammonia. The solutions were mixed with a stir bar spinning at 200 rpm for 24 hours with avoidance of light. The stock solution was diluted by a factor of 10 for a final working dye concentration of $2 \cdot 10^{-5}$ M. A 2mM solution of SDS in water was added so that the molar ratio of dye to SDS was 1:1. The solution was briefly mixed by vortexing, stored in the dark, and used within 3 days of preparation.

Typical transmission electron microscope (TEM) images are shown in Figure S 5 for bare and silica covered aggregates.

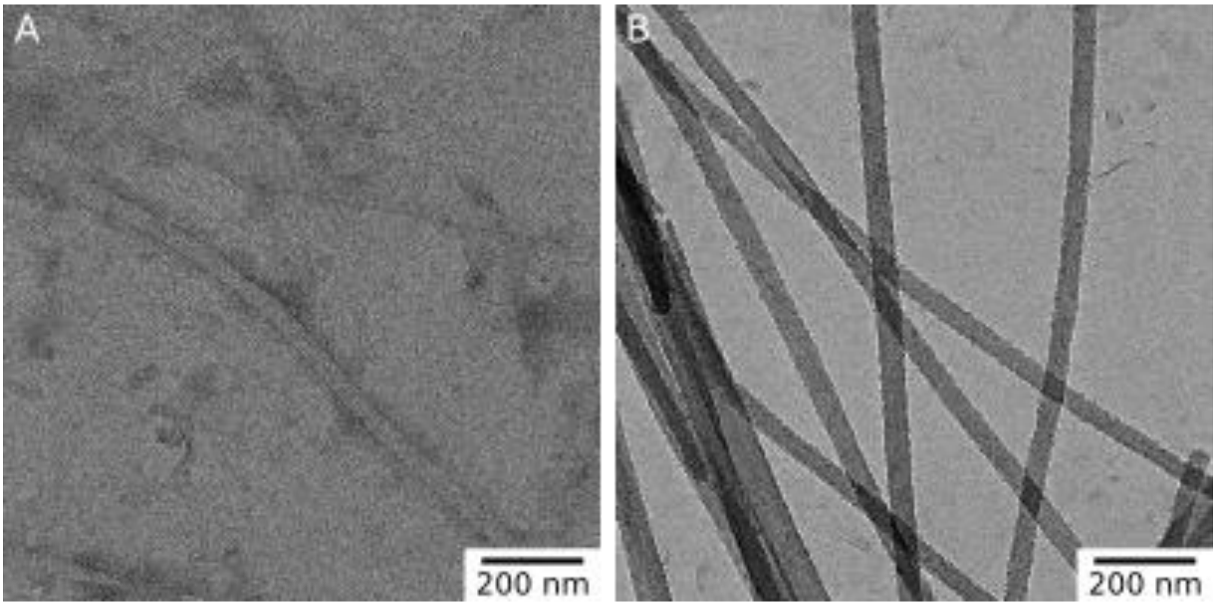

Figure S 5: Transmission electron microscope (TEM) image of C8O3/SDS aggregates. A) Bare aggregates with very low contrast. B) Silica covered aggregates with similar rough surface texture as observed for the C8S3 aggregates.

1. von Berlepsch, H., et al., *Surfactant-Induced Changes of Morphology of J-Aggregates: Superhelix-to-Tubule Transformation.* Langmuir, 2000. **16**(14): p. 5908-5916.