Experimental report

31/03/2017

Proposal: **9-12-463** **Council:** 4/2016

Title: Controlling Nanotube Formation in Amino Acid Amphiphiles – A Layer-by-Layer Approach

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C12KC12K + polyionic polymers

Instrument	Requested days	Allocated days	From	To
D33	2	2	08/11/2016	10/11/2016
D22	2	0		
D11	2	0		

Abstract:

Nanotubes with a well-defined radius can be formed by self-assembly of amino acid amphiphiles (AAAs). Recent experiments have shown that such AAA nanotubes, which are naturally charged, can be used as templates to form an oppositely charged polyelectrolyte layer around them, which then can also be used as basis for forming multi-layered nanotubes by stepwise addition of respectively oppositely charged polyelectrolytes, i.e. by applying the method of layer-by-layer (LbL) deposition. Accordingly the structural details of AAA nanotubes modified by the addition of different polyelectrolytes and for an increasing number of deposition steps need to be studied in detail. Polyelectrolyte modification leads to hybrid nanotubes with adjustable properties rendering these systems much more versatile for employing them in future applications, e.g. in delivery systems or as smart materials, focussing on the use of biofriendly materials (e.g. polysaccharides as polyions). The LbL technique also enables incorporating a variety of materials such as clays, ceramics, biomolecules or nanoparticles.

Controlling Nanotube Formation in Amino Acid Amphiphiles – A Layer-by-Layer Approach

Experiment number: 9-12-463 Beamline: D33
Date of experiment: 11/08/16-11/10/16
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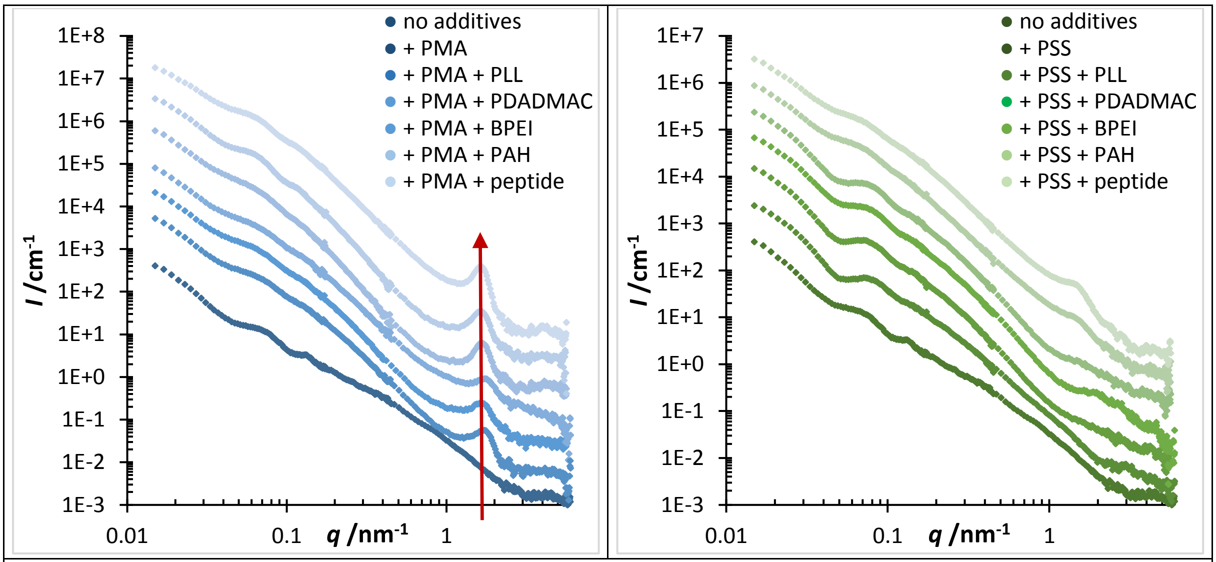
Introduction

Nanotubes with a well-defined radius can be formed by self-assembly of amino acid amphiphiles (AAAs). Recent experiments have shown that such AAA nanotubes, which are naturally charged, can be used as templates to form an oppositely charged polyelectrolyte layer around them, which then can also be used as basis for forming multi-layered nanotubes by stepwise addition of respectively oppositely charged polyelectrolytes, i.e. by applying the method of layer-by-layer (LbL) deposition. Accordingly the structure of AAA nanotubes modified by the addition of different polyelectrolytes and for an increasing number of deposition steps was studied in detail. Our SANS experiments yielded information regarding the nanotube wall and in particular how it becomes modified by using it as a template for polyelectrolyte layer deposition. This information was combined with cryo-TEM investigations, which deliver complementary information regarding the larger-size organization and the morphology of the self-assembled structures. Such polyelectrolyte modifications lead to hybrid nanotubes with adjustable properties rendering these systems much more versatile for employing them in future applications, e.g. in delivery systems or as smart materials. In the performed experiments we focused on the use of mostly biofriendly materials (e.g. polysaccharides as polyions) and it might be noted that the LbL technique also enables incorporating a variety of materials such as clays, ceramics, biomolecules or nanoparticles (and has been shown to be an effective technique to produce multicomponent layered materials on flat surfaces and carbon already).

In the experiments, the deposition of polyelectrolytes on self-assembled nanotubes from the AAA $C_{12}KC_{12}K\text{-}NH_2$ employing the method of layer-by-layer deposition was studied. Different pairs of polyelectrolytes were deposited in alternating steps on the already fully-formed cationic nanotubes. As polyanions poly(methacrylic acid) (PMA), poly(stryrene sulfonate) (PSS) and carboxymethyl cellulose (CMC) were used. Polycations employed were ε-poly(L-lysine) (PLL), branched poly(ethyleneimine) (BPEI), poly(diallyldimethylammonium chloride) (PDADMAC), poly(allylamine hydrochloride) (PAH) as well as $C_{12}KC_{12}K\text{-}NH_2$ itself as a non-polymeric short dication. Mixtures were prepared at 3 mM $C_{12}KC_{12}K\text{-}NH_2$ at pH8 and subsequently modified based on the number of charges z (with $Z = \frac{z(C12KC12K-NH2)}{z(polylectrolyte\ per\ layer)}$). LbL-solutions were used at twice the number of charges (defined as $Z=1:2$) present in the nanotube solution and kept constant for each deposition step. Additionally, the reduction of metal ions in or on nanotubes was studied. Therefore, solutions of $AgNO_3$ and $CuCl_2$ were added to the already fully-formed nanotubes at a constant charge ratio of $Z=1:40$. To facilitate reduction, the soft reducing agents ascorbic acid and citric acid were used at varying concentrations dependent on the molar amount (n) of metal ions present in the sample. Reducing agents were employed at $0.5n$, $1.2n$, $1.8n$ and $2.5n$.

SANS measurements were performed on D33@ILL and covered a wide q-range of 0.015 – 6 nm^{-1}. The three configurations used were 1) SD=1.2 m/2 m (front and side panel detector), Coll=5.3 m, λ=5 Å; 2) SD=12 m, Coll=12.8 m, λ=5 Å and 3) SD=12 m, Coll=12.8 m, λ=13 Å. Transmissions were measured for each sample for both wavelengths employed at SD=12 m and Coll=7.4 m.



Neutron scattering curves of 3 mM $C_{12}KC_{12}KNH_2$ in aqueous solution subsequently modified applying the layer-by-layer technique. All samples are at pH8 and have been aged for 50 d prior to analysis. Curves have been scaled to enhance clarity.

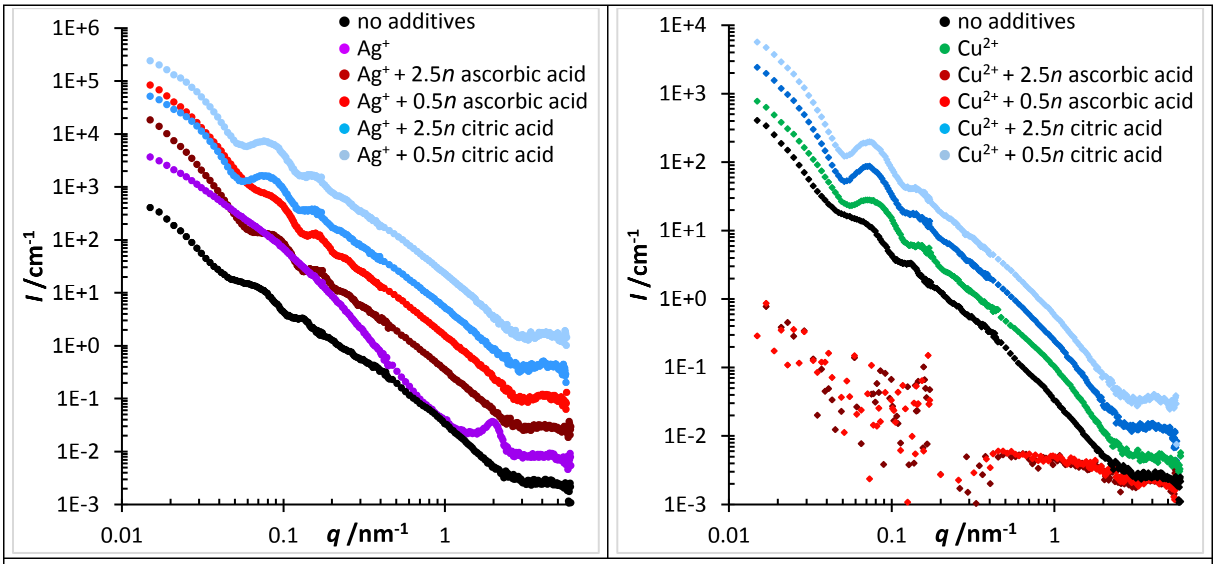
Fig. 1a. LbL-modification of self-assembled nanotubes with layer 1: poly(methacrylic acid) and layer 2: various polycations and $C_{12}KC_{12}KNH_2$ itself. The charge ratio was $Z=1:2$ for all modifications.

Fig. 1b. LbL-modification of self-assembled nanotubes with layer 1: poly(styrene sulfonate) and layer 2: various polycations and $C_{12}KC_{12}KNH_2$ itself. The charge ratio was $Z=1:2$ for all modifications.

Fig. 1a and b show exemplary results of LbL-modified nanotubes. The addition of polyionic compounds to solutions of $C_{12}KC_{12}KNH_2$ leads to a significant increase of intensity (i.e. more material scattering neutrons) compared to pure $C_{12}KC_{12}KNH_2$. There also appears to be slight a shift of oscillation minima as well as a steeper slope of the curves. All this indicates the formation of slightly bigger structures. Since the oscillation features become less pronounced but are still visible upon modification it is likely that the overall shape of the formed structures remains intact so that the changes can be interpreted as an increase in nanotube size and wall-thickness as would be the case for the formation of additional layers. The magnitude of these changes clearly depends on the compounds used as well as their respective mixtures.

In case of the tested polyanions forming one additional layer on $C_{12}KC_{12}KNH_2$, PMA shows the biggest increase in intensity (more than 220%), followed by PSS (about 140%, also compare fig. 1a and b) and then CMC (approx. 14%) despite the much smaller molecular weight per charge for PMA. When using PMA a strong structure peak emerges (at ~ 1.6 nm^{-1}, with minor variations in position, corresponding to a spacing of roughly 4 nm) which can be observed independent of the number of layers/modification steps. While its position is relatively fixed, the corresponding amplitude varies depending on the type of polycation employed in subsequent modifications, with $C_{12}KC_{12}KNH_2$ leading to the strongest peak, followed by PAH and BPEI (both similar); and PDADMAC and PLL with comparatively weak peaks. PSS also leads to the development of a structural feature. This, however, can only be clearly observed after a second LbL-step and is strongly dependent on the type of cation used. Its position ranges between approx. 1.4 – 2.1 nm^{-1}, corresponding to a spacing between 3 and 5 nm. A strongly diminished effect can also be observed when using CMC as a layering agent, the peak position being relatively constant at 1.5 nm^{-1}(corresponding to approx. 4 nm in real space). The presence of these peaks is interpreted as being indicative of the emergence of a regular and repeating spacing. Since it only is observed after LbL-modification, it most likely represents the thickness of the polyionic layer absorbed onto the nanotube surface.

On another note, all combinations of polyanions and (poly)cations resulted in multi-composite LbL-products, varying in stability. This is true for all polyanion/polycation-mixtures (two layers) as well as for polyanion/polycation/polyanion-samples (three layers).



Neutron scattering curves of 3 mM $C_{12}KC_{12}KNH_2$ in aqueous solution subsequently modified by addition of high concentrations of metal salts with or without reducing agents. All samples have been aged for 50 d prior to analysis. Curves have been scaled to enhance clarity.

Fig. 2a. Metallisation of self-assembled nanotubes with $AgNO_3$ and reducing agents (ascorbic acid or citric acid). The charge ratio was $Z=1:40$ for $C_{12}KC_{12}KNH_2$ and Ag^+ for all samples. Reducing agents were used as a multiple of the molar amount (n) of Ag^+ present.

Fig. 2b. Metallisation of self-assembled nanotubes with $CuCl_2$ and reducing agents (ascorbic acid or citric acid). The charge ratio was $Z=1:40$ for $C_{12}KC_{12}KNH_2$ and Cu^{2+} for all samples. Reducing agents were used as a multiple of the molar amount (n) of Cu^{2+} present.

Fig. 2a and b show the results of the attempted metallization of nanotubes with silver and copper. While the addition of silver ions lead to a complete change of the resulting scattering curve, this was not observed for copper: Upon the combination with Ag^+ a complete loss of oscillational features is visible as well as a change in slope and the emergence of a peak at 2 nm^{-1} (the corresponding real space size is ~ 3 nm). Adding Cu^{2+} lead to comparatively minor changes, most notable of which is the shift of oscillations to higher q, this being interpreted as a slight decrease in nanotube radius. This is attributed to a deposition of copper ions inside the nanotubes rather than on the outside as was observed for LbL-modifications with polymers. Adding copper also resulted in a slight enhancement of the “strength” of these oscillatory features, indicating an increase in monodispersity or of a change of the local contrast.

When adding reducing agents, the samples containing silver were able to retain their general structure. While the presence of ascorbic acid lead to a clear increase in scattering intensity, this was not the case for citric acid. Citric acid, however, had the clear effect of enhancing oscillations, showing an increase in monodispersity. Both reducing agents also resulted in a slight shift of oscillations to higher q, indicating a decrease of nanotube radius. Coupled with the increasing intensity for ascorbic acid addition, this interpretation makes sense whereas it is more difficult to understand the effect in citric acid-containing samples. Since these show no indication of the formation of a new layer on the nanotube surface, the observed q-shift might have to be attributed to a rearrangement of the self-assembled nanotubes. However, since the modification was done in solutions of fully (pre-)formed nanotubes which are essentially crystalline in their structure, it is doubtful whether they can freely rearrange their internal structure to adjust to the change in ionic strength and this effect has to be clarified further .

Upon the addition of reducing agents to samples modified with copper ions, ascorbic acid lead to complete precipitation of scattering material while citric acid did not. The effect of citric acid on samples containing copper or silver ions is virtually identical with an enhancement of oscillatory features while shifting these to higher q with no change in scattering intensity. The effect of the concentration of reducing agents is negligible or non-existent.

In summary, our experiments yielded valuable information regarding the modification of self-assembled AAA nanotubes.