

Efficient MoS₂ Exfoliation by Cross-β-Amyloid Nanotubes for Multistimuli-Responsive and Biodegradable Aqueous Dispersions

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Abstract: Herein, we report the efficient exfoliation of MoS₂ in aqueous medium by short cationic peptide nanotubes featuring the nucleating core ¹⁷LVFFA²¹ of β-amyloid (Aβ 1–42), a sequence associated with Alzheimer's disease. The role of morphology, length, and nature of the amyloid surface on exfoliation/dispersions of MoS₂ were investigated through specific mutations of the amyloid sequences. Notably, owing to the properties of both the constituents, self-assembled soft nanostructures and MoS₂, the hybrid dispersions responded reversibly to various stimuli, including temperature, pH, and light. Addition of a protease resulted in loss of the dispersions, which are otherwise stable for months at ambient conditions. The design flexibility of the peptide sequences, along with the stimuli-responsiveness and biodegradability, can complement the applications of MoS₂ in diverse fields.

Molybdenum disulfide (MoS₂), belonging to the family of layered transition metal dichalcogenides (TMDs), have garnered immense attention in recent years, particularly after the great advancements witnessed in the applications of graphene.^[1] Exceptional layer-dependent properties of MoS₂ are observed when the size of the TMDs decrease from three dimensions to two dimensions.^[1a–d,2] Applications of these thin layers of MoS₂ have been realized in diverse fields, such as catalysis, solid lubrication, energy storage, photovoltaics, and thermoelectric materials.^[1a–d,2,3] The unique optical properties and large surface area of thin layers of MoS₂ have recently been exploited in elegant biomedical works.^[4] However, strong interlayer van der Waals interactions result in very poor solubility of these layered materials.^[5] Also, the high surface energy of MoS₂ in the range of 250 mJ m^{−2} limits the use of environmentally friendly aqueous media.^[5a] Many recent works have used reagents, such as oleum, H₂O₂, and ionic liquids, for assisting the exfoliation of MoS₂ in aqueous solvent.^[4a,d,6] On the other hand, Coleman et al. have extensively used commercial surfactants for large-scale aqueous exfoliation of layered materials where colloidal stability is achieved from the charge repulsion of the

surfactant coating.^[5a] Interestingly, intercalation of cationic species, such as lithium ions and even organic polycations based on pyrrole and aniline, have been used to inhibit the reaggregation of exfoliated MoS₂ layers.^[2c,4e,7] However, these procedures are time consuming, require harsh conditions, involve toxic reagents, and are sensitive to the environment. Therefore, it would be intriguing to find exfoliating agents for MoS₂ in aqueous medium that are purely derived from natural precursors and that are environmentally benign.

In this context, highly cationic surfaces of cross-β-amyloid nanostructures have been shown to bind diverse molecular architectures and surfaces, along with the capability to impart colloidal stability.^[1e,8] Additionally, these short peptide-based nanostructures can be designed to be acutely responsive to different physical and chemical environmental inputs.^[9] In an attempt to find an environmentally benign way of making MoS₂ dispersions which can be biodegradable and respond reversibly to external inputs, amyloid nanostructures created from ¹⁷LVFFA²¹ of β-amyloid (Aβ 1–42; Figure 1) were used to exfoliate MoS₂ in water.

To check the capability of amyloid nanostructures for MoS₂ exfoliation, we started with Ac-KLVFFAE-NH₂ from 16–22 residues of wildtype Aβ.^[8a,9c] Ac-KLVFFAE-NH₂ assembles to form classical amyloid fibrils with lengths of several microns and diameters of approximately 15 nm (Supporting Information, Figure S1). Briefly, powdered MoS₂ (6 mg) was added to an aqueous dispersion of Ac-KLVFFAE-NH₂ (3.5 mM, 2 mL) and sonicated (tip) for 30 min (Supporting Information). The resulting aqueous greenish black dispersion of MoS₂ remained stable for weeks (Figure 1C). The UV/Vis-NIR spectrum showed characteristic peaks at 448, 451, 610, and 672 nm, indicating efficient MoS₂ exfoliation (Figure 2B).^[1d,5b,10] As previously reported, the amount of dispersed MoS₂ was calculated by the filtration and weighing method (Supporting Information).^[4a,5a,6] The amount of dispersed MoS₂ was found to be 0.09 mg mL^{−1} (Figure 2A; Supporting Information, Table S1). To investigate the role of amyloid morphology on exfoliation, Ac-KLVFFAE-NH₂ was assembled at pH 2 (Supporting Information).

At pH 2, Ac-KLVFFAE-NH₂ formed nanotubes with diameters of 35–40 nm^[9c] and lengths up to 10 microns (Figure 1D). Nanotube morphology was found to be better for MoS₂ exfoliation as the amount of dispersed MoS₂ increased to 0.16 mg mL^{−1}. To remove the effect of pH, a glutamic acid residue was changed to leucine to form Ac-KLVFFAL-NH₂, which at neutral pH assembled to form homogenous nanotubes with diameters of 35–40 nm (Figure 1E).^[8a,b] The amount of dispersed MoS₂ increased further with Ac-KLVFFAL-NH₂ nanotubes to 0.18 mg mL^{−1}. Under

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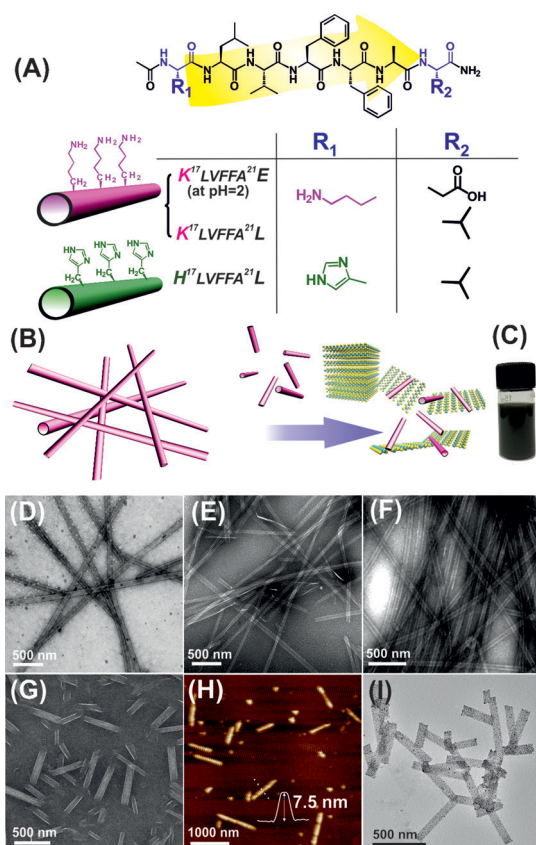


Figure 1. A) Structure of amyloid peptides. B) Representation of MoS₂ exfoliation by cationic amyloid nanotubes. C) Vial showing dispersion of MoS₂ by amyloid nanotubes. D–G) TEM images of nanotubes of D) Ac-KLVFFAE-NH₂ at pH 2, E) Ac-KLVFFAL-NH₂, F) Ac-HLVFFAL-NH₂, G) short Ac-KLVFFAL-NH₂ tubes formed after tip sonication (30 min). H) AFM image of short nanotubes of Ac-KLVFFAL-NH₂ with height profile. I) Anionic gold nanoparticles bound to short tubes without stain.

identical conditions, commercial surfactants like sodium cholate and sodium dodecyl benzene sulfonate (SDBS) could only disperse 0.05 and 0.04 mg mL⁻¹, respectively (Figure 2 A; Supporting Information, Table S1).

The exfoliated MoS₂ were characterized by TEM, which showed numerous thin flakes (Figure 3 A–C), indicating the presence of layers of MoS₂ nanosheets (Figure 3 B,C and HRTEM Figure 3 D). The lateral sizes of the flakes displayed a wide distribution from 65 nm to 1150 nm, with mean $\langle L \rangle = 328$ nm (Figure S2 C–2H, S3A TEM of precursor MoS₂ powder in Figure S2 A,B). The diffraction pattern (Figure 3 C inset) suggested an undistorted lattice with hexagonal symmetry.^[5a] In an attempt to visualize the nanotubes in the same TEM image frame, which was showing MoS₂ (Figure 3 E), the defocus values were changed during imaging. Nanotube morphology could be clearly seen in the background (Figure 3 E,F). Interestingly, the lengths of the nanotubes in the background were substantially shorter than the usual length. Consequently, we were curious about the state of the nanotubes after probe sonication. To this end, an aqueous solution of Ac-KLVFFAL-NH₂ (3.5 mM) nanotubes was separately sonicated (tip) for 30 and 60 min. Numerous short fragments of average length 400–550 nm were observed under TEM

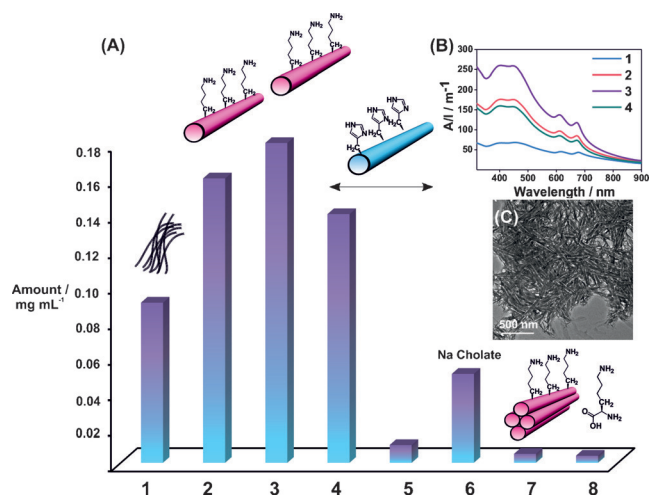


Figure 2. A) Amount of dispersed MoS₂ by Ac-KLVFFAE-NH₂ nanofibers (1) Ac-KLVFFAE-NH₂ nanotubes at pH 2 (2) Ac-KLVFFAL-NH₂ nanotubes (3) Ac-HLVFFAL-NH₂ nanotubes at pH 6.5 (4) and at pH 9 (5), sodium cholate (6), bundled Ac-KLVFFAL-NH₂ nanotubes (7), and lysine (8). B) Typical UV/Vis absorption spectra of exfoliated MoS₂ in Ac-KLVFFAE-NH₂ nanofibers (1), Ac-KLVFFAE-NH₂ nanotubes (2), Ac-KLVFFAL-NH₂ nanotubes (3), Ac-HLVFFAL-NH₂ nanotubes at pH 6.5 (4). C) TEM image of bundled short nanotubes treated with Na₂SO₄. Error ranged from 5–15% in triplicates.

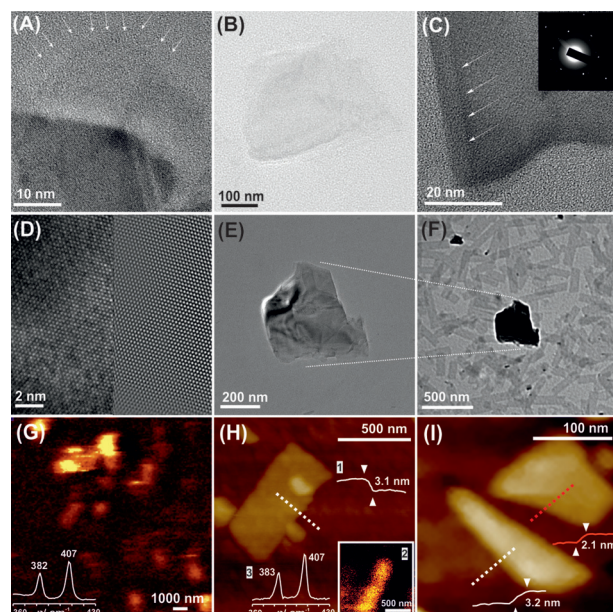


Figure 3. A–C) Bright field TEM images of MoS₂ showing thin layers of MoS₂. C) Zoomed image of MoS₂ indicating 2 layers. Inset in C shows typical electron diffraction pattern. D) Phase contrast and digitally filtered HRTEM of thin layer MoS₂ sheet. E) Thin layer MoS₂ sheet and F) nanotube morphology in the background. G) Raman mapping of MoS₂ deposited on silicon substrate. Inset showing typical Raman spectrum of exfoliated MoS₂. H) AFM image of MoS₂ sheet with insets 1) height profile of the sheet, 2) Raman map and 3) Raman spectra of the same region. I) AFM image of MoS₂ sheets with line profiles given in red and white.

(Figure 1 G; Supporting Information, Figure S4). Atomic force microscopy (AFM) also showed shorter nanotubes (Figure 1 H). To confirm that the surface of the short nano-

tubes is cationic, negatively charged citrate-coated gold nanoparticles (–AuNP) were added. TEM showed –AuNP specifically decorated the surfaces, strongly suggesting the presence of a cationic surface. Controls with positively charged gold nanoparticles (+AuNP) did not result in specific binding (Figure S5). At this point, we were curious to investigate whether the shorter length of amyloid nanotubes was playing a role in the efficient exfoliation. For this purpose, exfoliation was attempted with only mechanical stirring conditions and without any sonication (Figure S6). It is important to note here that strong interlayer forces present in MoS₂ necessitate large mechanical forces to overcome and hence sonication (tip) is used for prolonged time intervals.^[4,5] Interestingly, the short amyloid tubes were able to disperse MoS₂ even without probe sonication as, after centrifugation, a greenish supernatant was obtained and the UV/Vis spectra showed the characteristic peaks (Figure S6). The longer native tubes were less efficient at exfoliating MoS₂ (Figure S6, S7). Therefore, this experiment reinforced the importance of peptide nanotubes of shorter lengths which provided improved intercalation and colloidal stability to the exfoliated MoS₂.

To confirm the thin layers (Figure 3 A–D, Figure S2) were indeed MoS₂, Raman mapping of the samples (Figure 3 G) was done. Intense peaks at 382 and 407 cm^{–1} (inset of Figure 3 G) were observed, confirming the presence of undistorted structure of 2H MoS₂, a finding also supported from the diffraction pattern.^[5a,11] In contrast, harsh methods of ion intercalation often result in generation of distorted 2H structure of bulk MoS₂.^[5a] The layer thicknesses were monitored by AFM. However, samples prepared directly from MoS₂-Ac-KLVFFAL-NH₂ solutions showed densely populated short nanotubes (Figure S8). To image the sheets, the dispersions were diluted with water, before drop casting on silicon surface (Supporting Information). AFM showed numerous thin flakes (Figure 3 H–I; Supporting Information, Figure S2 I–L) which were confirmed to be MoS₂ from Raman Spectroscopy (Figure 3 H, inset). The height analyses showed a distribution with highest populations in the range from 2–3.5 nm, which correspond to 2 to 4 layers (Figure 3 H, I; Supporting Information, Figure S2 M–P, S3 B).^[2d,5b] Few thick flakes of heights more than 10 nm were also observed (Figure S3 C). It is important to note that the presence of peptide nanotubes is crucial for the stability of exfoliated MoS₂, and dilution results in rapid aggregation as flocculation is observed within 15 min. Also, aggregation phenomenon during deposition/drying in solvent exfoliated MoS₂ has been previously observed.^[5b] Removal of nanotubes through dilutions resulted in aggregation, as indicated from the few thick flakes. Despite the likelihood of aggregation, the presence of large numbers of thin layers indicates the efficient exfoliation by the nanotubes. Lateral lengths were found to be in the range from 78 nm to 1175 nm with a mean $\langle L \rangle = 374$ nm (Figure S3 C).

To explain the efficient exfoliation and interactions involved between MoS₂ and the peptide nanostructures, the role of the exposed surface was investigated. The solvent-exposed cationic lysine residue of Ac-KLVFFAL-NH₂ was mutated to histidine to form Ac-HLVFFAL-NH₂, which also

assembled to form homogenous nanotubes of 35–40 nm (Figure 1 F). According to pK_a and hydrophathy indices of the residues,^[12] lysine-exposed tubes should have higher cationic charge density than the histidines. Indeed, for histidine-exposed tubes (Ac-HLVFFAL-NH₂), the dispersed amount of MoS₂ was found to be 0.14 mg mL^{–1}, which was significantly less than the Ac-KLVFFAL-NH₂ nanotubes but was still higher than the Ac-KLVFFAE-NH₂ fibers. Expectedly, as the pH increased to 9, the histidine tubes were incapable of exfoliating MoS₂ owing to the loss of cationic surface. In addition to the charge, the colloidal stability of peptide nanotubes is expected to play a crucial role in the exfoliation. To investigate this, sodium sulfate was used to counterbalance the electrostatic repulsion of Ac-KLVFFAL-NH₂ nanotubes,^[13] as divalent sulfate ions are known to precipitate proteins and bundle amyloid nanotubes.^[8a] Indeed, TEM confirmed bundling (Figure 2 C) with addition of SO₄^{2–} ions, and the bundled tubes were unable to exfoliate MoS₂ (Figure 2 A; Supporting Information). The amino acid L-lysine was also unable to exfoliate MoS₂, which confirmed the importance of the nanotube morphology (Figure 2 A).

To further investigate the nature of interaction between the nanotubes and the sheets, thermogravimetric analysis (TGA) was performed on the MoS₂ film obtained after filtration and washing (Supporting Information).^[5a] TGA showed the MoS₂ residue was devoid of any bound peptides (Figure S9), and thus indicated the absence of any covalent interactions with the MoS₂ sheets. In this context, owing to the antiparallel out-of-register arrangement of β-amyloid ¹⁷LVFFA²¹ sequences,^[8a,b,9a,c] leucine residues generate hydrophobic regions on the nanotube surface, which presumably interact with the MoS₂ nanosheets through weak physical adsorption. The dual presence of hydrophobic regions and charged lysine residues on the amyloid surface has been shown to bind hydrophobic moieties of small molecules, hydrophobic 2D graphene sheets,^[8b,c] and also hydrophobic patches of cationic proteins.^[8a] In the present case, when strong forces are applied from tip sonication in presence of nanotubes, the van der Waals interactions between the layers of 2D nanosheets weaken^[2d] and the nanotubes interact with the sheets through hydrophobic interactions. AFM showed some MoS₂ sheets where nanotubular interaction could be observed (Figure S10). The charged lysines concurrently impart colloidal stability to the exfoliated sheets, which are also prevented from reaggregation owing to the presence of charged nanotubes in the surrounding solvent environment. Thus, for exfoliation it is important to have the self-assembled nanotube surface, which is lacking in the unassembled sequences. To check this, exfoliation was attempted in presence of HFIP pretreated disassembled Ac-KLVFFAL-NH₂ peptides (Supporting Information). Disassembled peptides (Figure S11) were unable to exfoliate MoS₂, thus indicating the importance of the nanotube surface to interact and exfoliate MoS₂ (Figure S12).

Clearly, the extent of MoS₂ exfoliation significantly depends on the surface properties of amyloid nanostructures, such as morphology, nature of exposed surface and colloidal stabilization through electrostatic repulsion. Intriguingly, these features of amyloid nanostructures are acutely respon-

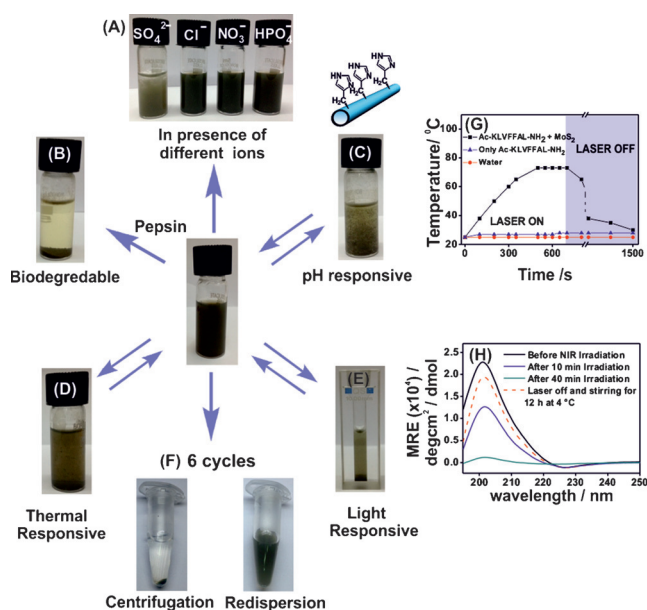


Figure 4. Responsiveness of MoS₂-amyloid peptide nanocomposites in the presence of different ions (A), biodegradability in presence of pepsin (B), pH (C), temperature (D), and light (E). F) Multiple centrifugation and redispersions cycles do not result in loss of dispersions. G) Change of temperature with time when MoS₂-amyloid peptide nanocomposites, control peptide, and only water was irradiated with a NIR laser (804 nm). H) CD spectra of MoS₂-Ac-KLVFFAL-NH₂ solutions before and after irradiation of NIR laser (804 nm).

sive towards subtle changes of the environmental inputs. We thought this responsive behavior which stems from the reversible assembly/disassembly of amyloid nanostructures can be utilized to modulate the dispersion (Figure 4). We started by changing the temperature of MoS₂-Ac-KLVFFAL-NH₂ dispersions from 25 to 65 °C and further incubation for 60 min at 65 °C, which resulted in destabilization and flocculation (Figure 4D). Interestingly, when the same destabilized dispersion was stirred for 24 h at 4 °C, a homogenous greenish black dispersion of MoS₂ was retrieved. In this regard, MoS₂ has strong near infrared (NIR) absorbance, which can be used to photothermally heat the surrounding environment. Therefore, we used a NIR laser of wavelength 804 nm with power density of 1.5 Watt cm⁻² to irradiate an aqueous dispersion of MoS₂-Ac-KLVFFAL-NH₂ (Supporting Information). The temperature increased rapidly and resulted in boiling after irradiation for approximately 600 s (Figure 4G). The temperature decreased to room temperature within 10 min of turning off the laser. The secondary structures of cross- β -amyloid nanotubes after NIR laser irradiation were monitored by CD spectroscopy (Figure 4H).^[8b,9c] Indeed, NIR irradiation resulted in a substantial decrease of the characteristic β -sheet signature, which eventually showed complete melting of the nanotubes after 40 min (Figure 4H). Flocculation could be seen in the quartz cell after 60 minutes of irradiation (Figure 4E). The dispersion was retrieved after 12 h of stirring at 4 °C, with CD showing a strong β -sheet signature (Figure 4H), indicating the reassembly of the nanostructures. To demonstrate pH responsiveness, exfoliated MoS₂ in Ac-HLVFFAL-NH₂ nanotubes was used. The dispersions responded to subtle changes in pH from 6.0 (redispersed in

water) to 8, as flocculation and precipitation was observed (Figure 4C; Supporting Information, Figure S13). The dispersion was completely recoverable when the pH was adjusted back to 4.5 through addition of trifluoroacetic acid. This unique environmental input-dependent exfoliation of MoS₂ can have applications in diverse fields. The dimension of the amyloid nanotubes also allows easy separation from the medium. This attribute was exploited to isolate the exfoliated MoS₂ from aqueous dispersions through centrifugation at 17 000 rpm. This resulted in complete separation of the MoS₂-peptide composites as a black pellet (Figure 4F) and colorless supernatant. Removal of supernatant and addition of fresh aqueous solution and subsequent stirring for 30 min resulted in retrieval of the dispersed MoS₂, as evident from the UV/Vis spectra (Figure S14). Intriguingly, this process of centrifugation and redispersion could be done for at least six consecutive times, and thus may have potential applications in catalysis. The biodegradability of the dispersion was checked by addition of pepsin, a protease enzyme that resulted in flocculation after 2 days (Figure 4B). This happened due to digestion of Ac-KLVFFAL-NH₂, which concomitantly results in loss of dispersion (Figure 4B; Supporting Information, Figures S15–S18). The responsiveness of the dispersions, specifically towards divalent ions like SO₄²⁻, was also evident, as addition of different monovalent anions did not result in loss of dispersions (Figure 4A). Although the amyloid nanostructures used thus far were homogenous, to find the effect of polymorphism on stimuli-responsiveness, the temperature-responsiveness of 1:1 mixture of Ac-KLVFFAE-NH₂ fibers and Ac-KLVFFAL-NH₂ nanotubes was tested. Upon heat treatment, the incubation time required to destabilize the dispersion increased from 60 to 95 min, indicating the importance of homogeneity for responsiveness. Finally, the concentration of dispersed MoS₂ could be increased by varying the sonication time (Figure S18).^[5a]

In summary, we have found a unique and environmentally benign way of exfoliating MoS₂ in aqueous milieu. The simple procedure of creating MoS₂ aqueous dispersion, the design flexibility of the exfoliating agents, and the stimuli-responsiveness of the dispersions make developed MoS₂-peptide nanohybrids applicable in diverse fields.

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