

Formation of helical superstructures from a semi-fluorinated alkoxy silane through a surface and solution self-assembly process†

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Helical superstructures were obtained through a surface and solution self-assembly process when a semi-fluorinated alkoxy silane modified silicon wafer was immersed in water of pH values ranging from 5.0 to 7.0 for more than one month.

Inspired by the unique functions of helical superstructures performed in biological systems,¹ many scientists have devoted themselves to generating synthetic helical assemblies. These investigations are important not only for the understanding of the origin of chirality and symmetry breaking of a system,² but also for the development of new functional helical architectures. Supramolecular helical structures have been created from the aggregation of chiral molecules³ and chiral polymers⁴ using non-covalent interactions. To the best of our knowledge, few reports have described the formation of an artificial helix from achiral molecules⁵ and achiral polymers.⁶ In these cases, only racemic products can be obtained if no optically active species was used as a guide. Here, we present another example of a helix and superhelix obtained from the achiral molecule 1H,1H,2H,2H-perfluorooctyltriethoxysilane ($C_6F_{13}(CH_2)_2Si(OEt)_3$) through surface and solution self-assembly processes.

Semi-fluorinated (SF) alkoxy silanes have been widely used for the formation of self-assembled monolayers (SAMs) on different substrates for the achievement of hydrophobic surfaces.⁷ In this study, interesting aggregates were obtained when SF alkoxy silane treated silicon wafers were immersed in water with pH values ranging from 5.0 to 7.0 for more than one month. The surface of the silicon wafers was treated with $C_6F_{13}(CH_2)_2Si(OEt)_3$ using a traditional method and were monitored by contact angle measurements. After the treatment, the contact angle increased from 27 to 122°. Then the silicon wafers were immersed in water of pH values ranging from 5.0 to 7.0 for more than one month. Helical and superhelical structures could be observed both in the aqueous phase and on the surface of the silicon wafers. Fig. 1 shows several typical TEM (transmission electron microscopy) images of the coil-like structures. In Fig. 1(a), left-handed helices with diameters of about 500 nm accompanied with coils with diameters of 80 nm can be seen. In Fig. 1(b), in addition to the left-handed helices ($\phi \approx 500$ nm), super-coils with diameters around 190 and 80 nm can also be seen. Superhelix structures can also be observed by SEM and AFM observation. From these topographic analysis, it can be seen that the mean diameters of the coils are

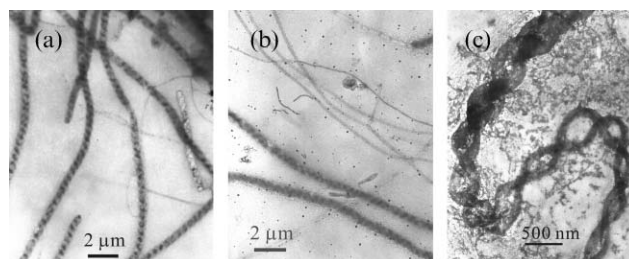
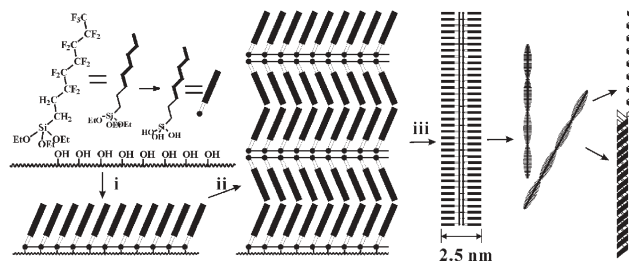


Fig. 1 TEM images of coils and supra-coils from an achiral semi-fluorinated alkoxy silane through a surface and solution self-assembly process. (a), (b) Typical images of coils and supra-coils. (c) Image of a loose double helix.

centered at 500, 190 and 80 nm. This discrete distribution of diameters revealed that the thicker one might have resulted from the thinner coil. Besides the left-handed helices, right-handed helices with the same dimensions and double helices can also be observed. TEM images of loose double helical structures were obtained occasionally, in which two coils with diameters of about 200 nm are twisted with each other to form a double helix (Fig. 1(c)).

From the above investigation, it can be concluded that helix and double helix structures can be obtained after a self-assembly procedure. In order to study the mechanism of this aggregation process, the self-assembly of SF alkoxy silane on the surface of the silicone wafer was characterized by small-angle X-ray diffraction (SAXRD). A peak at 9.68° could be observed. This indicated that a multilayer structure rather than a monolayer structure, had been formed on the surface. As Allara and co-workers reported, *n*-alkyltrichlorosilanes could form layered, microcrystalline polymers through a simple hydrolytic polycondensation procedure.⁸ So we supposed that after the formation of a self-assembled monolayer on the surface of the silicon wafer, a multi-layer structure had been formed on this fluorinated surface (Scheme 1).



Scheme 1 The possible assembly process of helices and superhelices: (i), (ii) assembly process that takes place at the interface between ethanol and silicone wafers; (iii) assembly process occurring in water.

† Electronic supplementary information (ESI) available: Experimental details, other TEM images, XRD data, DLS spectrum and XPS, IR and AFM images. See [http://www.rsc.org/suppdata/cc/b4/b413599g/](http://www.rsc.org/suppdata/cc/b4/b413599g)
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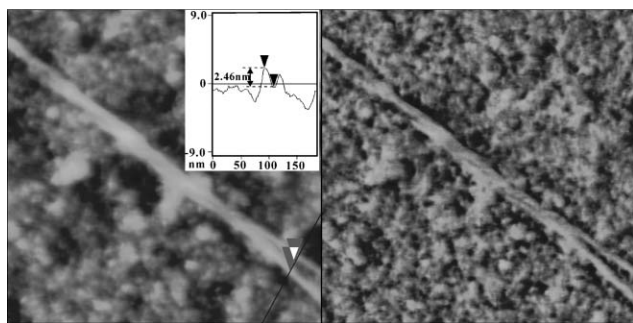


Fig. 2 AFM height images (left) and phase image (right) of the smallest assembly from a semi-fluorinated alkoxy silane through a self-assembly process. Data scale: 505 × 505 nm (the inset is a cross section profile of the smallest assembly from a semi-fluorinated alkoxy silane).

The SiOH species in the layered structure will be further polymerized through Si–O–Si cross-linking. According to previous reports, polymerization of alkylethoxysilanes and similar materials in a 2D restricted condition should result in linear polymers rather than network polymers.⁹ So, under our experimental conditions, a multilayer structure composed of bilayer stacks of linear polymerized SF siloxane was formed on the self-assembly monolayer. Additionally, adjacent SiOH groups in different polymer chains may cross link further to form a polymer with an inner siloxane backbone. When this surface is submerged in water for a long period, reconstruction of the multilayer structure will happen.¹⁰ The linear polymer will be removed from the surface and suspended in the aqueous phase. The higher cohesive energy of the fluorinated alkyl chains and amphiphilic interactions will make the silicone backbone twist to a filament-like helix. Furthermore, more filaments will be further assembled by interdigitation and intercalation of the fluorocarbon side chains to decrease the surface energy. Moreover, associations of the polymers may occur and form a helix (or coil aggregates to a helix) through amphiphilic interactions by the well-understood thermodynamics of amphiphilic aggregation.¹¹ Additionally, helicity may be transferred from filaments to supercoils. Although the precise mechanism behind the formation of these superstructures is still unclear, a hierarchical organization is evident.¹²

Besides the SAXRD data, further evidence has been obtained supporting the above hypothesis. Fig. 2 shows the smallest assembly that can be observed by AFM, where two filaments are coiled with each other to form a left-handedly twisted double helix. The height of these fibers was determined to be about 2.46 nm, which is very close to the calculated diameter of the above supposed siloxane polymer. The viscosity of the aqueous phase increased obviously after the silicon wafers were immersed in water for about one month. This is probably due to the presence of siloxane polymers in the water. The existence and aggregation of the siloxane polymers in water could also be observed by the dynamic light-scattering (DLS) spectrum of the solution. The size distribution of these aggregates calculated from the DLS data are mainly occurring in three regions as follows: $R_H = 192.6$ nm (3.55%), 1210 nm (21.68%) and 19 880 nm (74.46%) (R_H , the average apparent hydrodynamic radius). Because these aggregations do not have round shapes, the calculated sizes do not exactly

match those obtained from the TEM measurements. The composition of the aggregates was further confirmed by XPS and IR analysis.

In conclusion, helical superstructures were prepared from an achiral semi-fluorinated alkoxy silane through a convenient surface and solution self-assembly process. It was suggested that a multilayer structure had been formed during the surface assembly process, in which linear SF siloxane polymers were generated and further twisted and coiled into superhelices during the solution assembly process.

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