Supplementary Information

Biomimetic Mineralization of Double-Stranded and Cylindrical Helical $BaCO_3$ Nanofibres

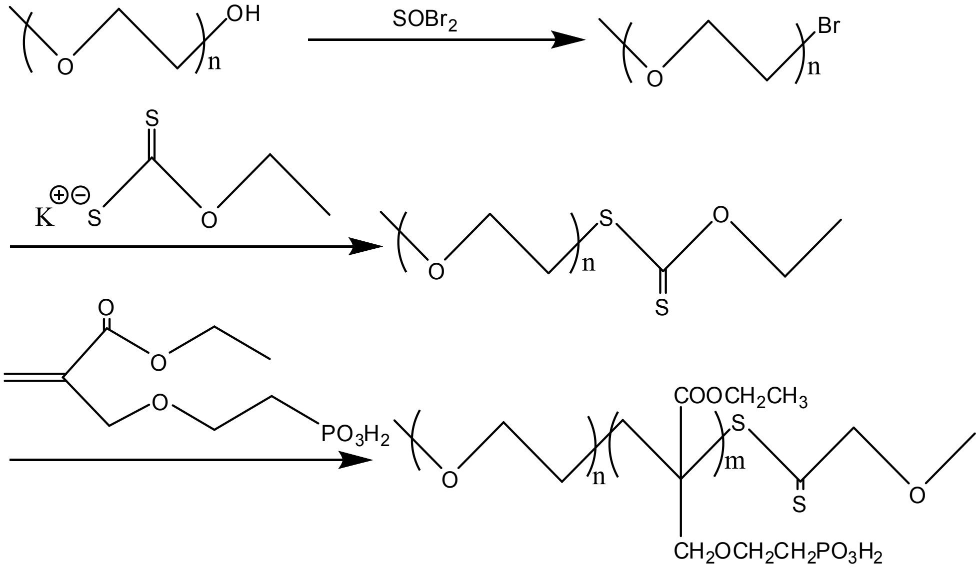
Jian-Hua Zhu[†], Shu-Hong Yu*[†], An-Wu Xu[†], Helmut Cölfen[‡]

Experimental sections:

[‡] Octadecyltrichlorosilane (OTS) (Aldrich, 97%wt), other reagents are analytic grade and used as received. Glass or silicon slides were modified with OTS molecules via dip-coating in an n-hexane solution (1 mM), and dried by N_2 for 1 min. Then the substrate was heated to 80 °C and maintained for 45 min. The precipitation of $BaCO_3$ was carried out in glass bottles with a volume of 10 mL, which were put into a closed desiccator at room temperature (20 ± 2°C). A stock aqueous solution of $BaCl_2$ (5 mM) was freshly prepared in boiled double distilled water and bubbled with N_2 for 2 h before usage. Polymer (0.5 g⋖L^{-1}) was dissolved in $BaCl_2$ solution under stirring. The initial pH was adjusted by HCl or NaOH. The Si or glass slides coated with OTS were put at the bottom of the bottles. The bottles were covered with Parafilm punched with three needle holes and placed in a desiccator. Finally, a glass bottle (10 mL) of crushed ammonium carbonate was also covered with Parafilm punched with three needle holes, which was put at the bottom of the desiccator. After different periods of reaction time, the glass slides with the crystals were taken out, and rinsed with doubly distilled water and ethanol and dried at room temperature.

X-ray diffraction was obtained on a (Philips X'Pert Pro Super) X-Ray powder diffractometer with Cu Kα radiation (λ = 1.541874 Å). The SEM images were taken on a field emission scanning electon microscope (JEOL JSM–6700F, 15 kV). High-resolution transmission electron microscope (HRTEM) photographs and selected area electron diffraction (SAED) patterns were performed on a JEOL JEM 2011 microscope at an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on the same HRTEM. FTIR spectra were measured on a Bruker Vector-22 FT-IR spectrometer from 4000 cm^{-1} to 400 cm^{-1} at room temperature. The optical images were taken on a microscope (Olympus B202) with a spot-enhanced charge-coupled device (CCD, Olympus DP70).

Synthesis of phosphonated block copolymer:[1] A mixture of A (5 g, ~ 1 mmol) and 4 g (~ 20 mmol) of the phosphonated monomer, 2-[4-dihydroxyphosphoryl]-2-oxabutyl acrylate ethyl ester (DHPOBAEE, a gift from Ivoclar Vivadent AG (Liechtenstein), 95.85%), in 40 mL dry THF was used as the starting solution. After slowly bubbling Ar into the solution for 1 hour, the reaction mixture was heated at 75°C overnight. After cooling down to room temperature, the precipitate was filtered and washed by THF, and the phosphonated block copolymer was obtained as white powder. The sedimentation coefficient distribution from sedimentation velocity was broad, and no indication of particle aggregation was found. The molar mass distribution from sedimentation velocity confirmed the molar mass average from sedimentation equilibrium and revealed the molar mass ranging between 2,000 and 160,000 g/mol.



Scheme S1 Chemicals and relevant reactions involved in the synthesis of phosphonated block copolymer (n = 200, m = 530). It has a weight average of 135,000 g/mol.

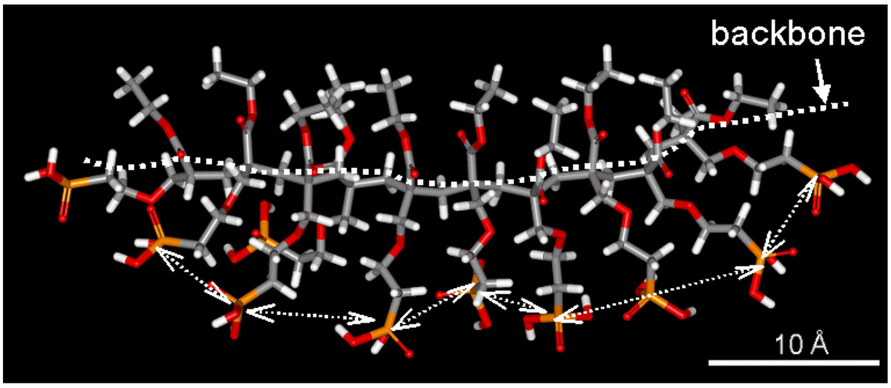


Fig. S1 Different magnifications of the computer modeling results of the vacuum energy minimum conformation of the functional block of PEG-*b*-[(2-[4-Dihydroxy phosphoryl] -2-oxabutyl) acrylate ethyl ester] in vacuum. Note the stiff structure as a result of steric constraints. The modeling was done with the *Cerius*^{2} software (Accelrys).

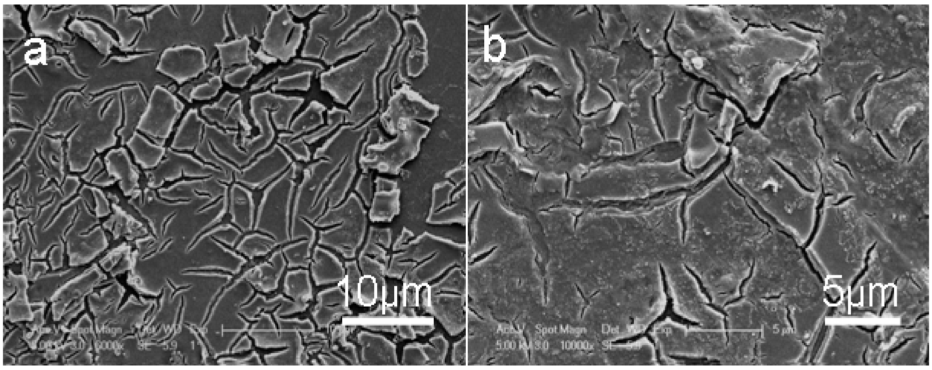


Fig. S2 SEM images of amorphous $BaCO_3$ mineral film formed on OTS-coated glass ([polymer] = 0.5 g⋖L^{-1}, [$BaCl_2$] = 5 mM, starting pH 3.5, for 1 day).

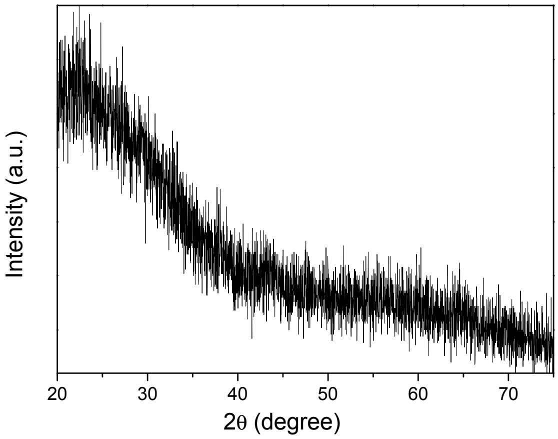


Fig. S3 XRD pattern of liquid mineral precursor grown for 1 day ([polymer] = 0.5 g⋖L^{-1} copolymer, [$BaCl_2$] = 5 mM, starting pH 3.5).

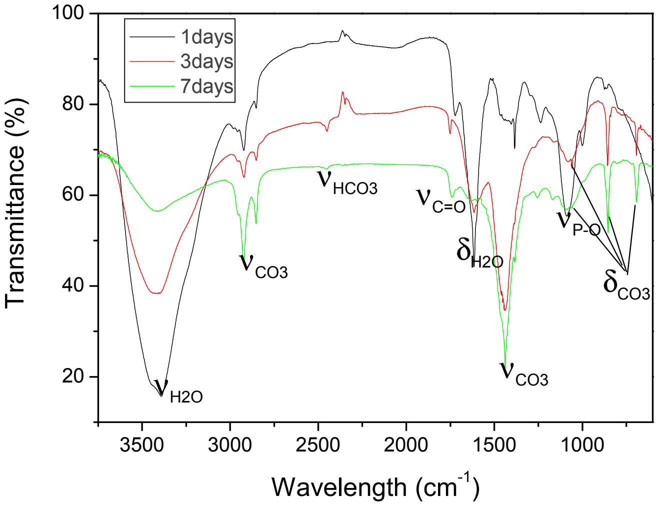


Fig. S4 FTIR spectrum of underlying crystal film at different reaction time. (a) 1days, (b) 3 days, (c) 7 days ([polymer] = 0.5 g∢L^{-1}, [$BaCl_2$] = 5 mM, starting pH 3.5).

Note for Fig. S4:

The FTIR spectrum shows a broad peak at 856 cm^{-1}, and splitting of the 1440 cm^{-1} peak, proving the amorphous nature of the mineral precursor [2] (Figure S4a). When the reaction time is prolonged for three and five days, the water absorption bands decease in intensity and υ_3 absorption bands of carbonate become more obvious (Figure S4b,c). Finally, the sample can turn into the pure orthorhombic phase, which is confirmed by the presence of 693 cm^{-1}, 854 cm^{-1}, and 1058 cm^{-1} signals.[3] With the reaction time increasing (7 days), the amorphous mineral film was transformed into a nanocrystalline $BaCO_3$ film.

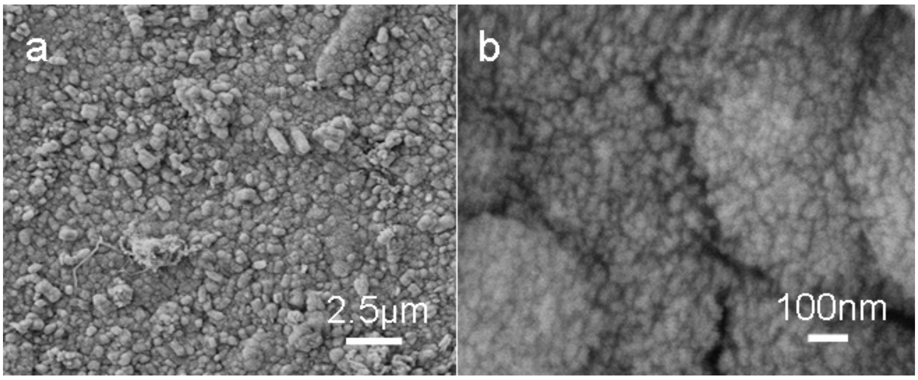


Fig. S5 SEM images of crystallized $BaCO_3$ mineral film on OTS-coated glass after mineralization for 7 days ([polymer] = 0.5 g∢L^{-1}, [$BaCl_2$] = 5 mM, starting pH 3.5).

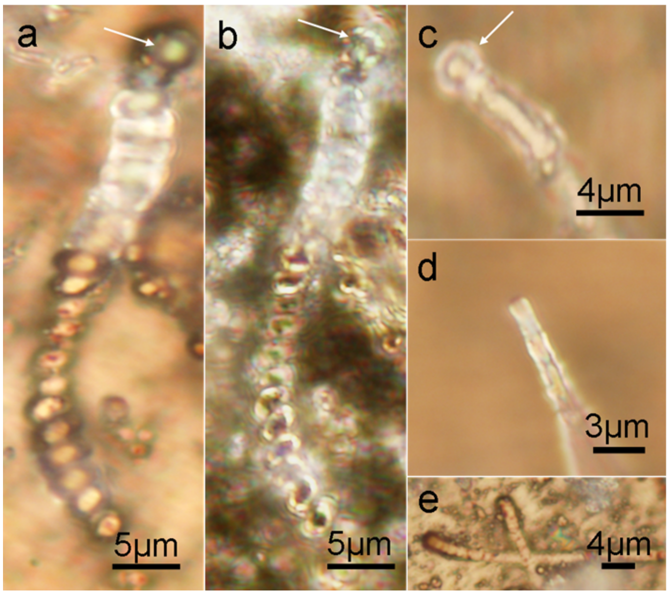


Fig. S6 Optical images of novel helices. (a), (b) Bright and dark field images of a double-stranded helix. (c), (d) bright field images of a cylindrical helix. (e) two helices growing across each other. Arrows points to the growth tips of the helical nanofibres.

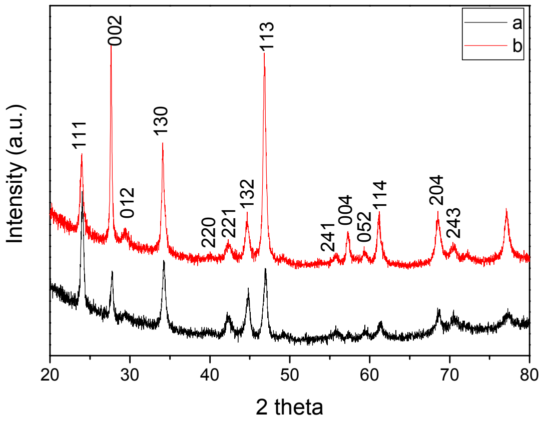
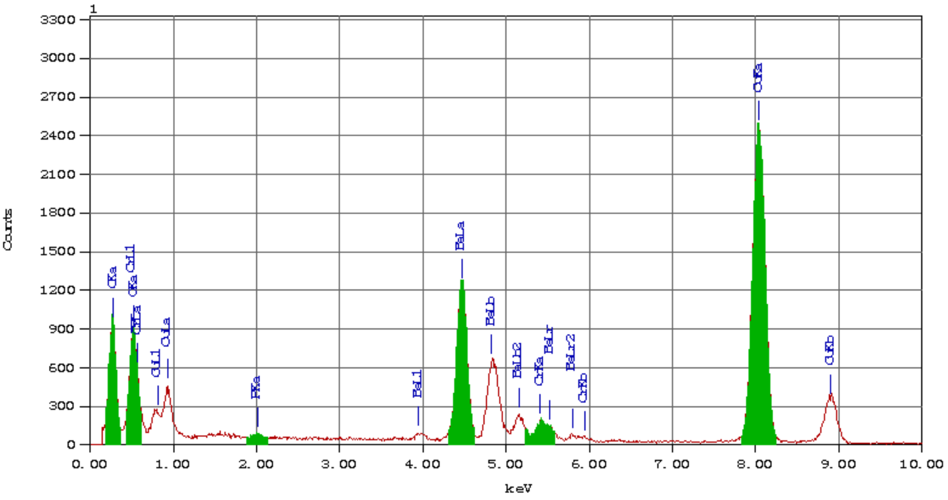


Fig. S7 (a) XRD pattern of $BaCO_3$ mineral films, after mineralization for a week. (b) XRD pattern of and $BaCO_3$ mineral films with helical nanofibres, after mineralization for two weeks.



Elements	Quality%	Counts	Error%	Atoms%
O	9.93	4002.68	0.01	48.14
P	0.51	342.14	0.33	1.27
Ba	89.57	15753.22	0.01	50.59

Fig. S8 EDX analysis of helical nanofibre surface.

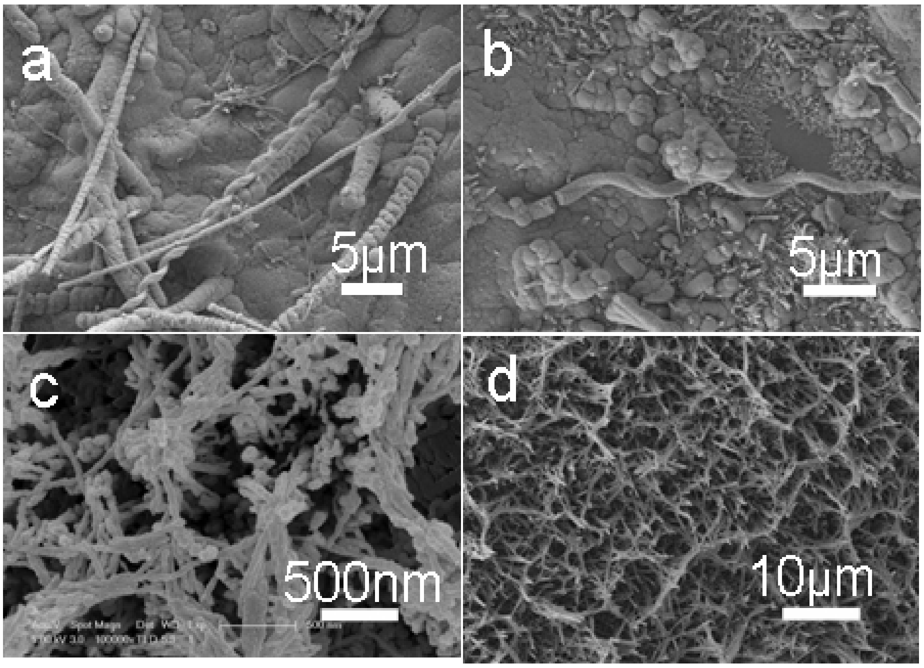


Fig. S9 SEM images of $BaCO_3$ synthesized at different starting pH. (a) 3.5, (b) 4.2, (c) 5.5, (d) 6.1. [polymer] = 0.5 g<L^{-1}, $[BaCl_2]$ = 5 mM, on OTS-coated glass substrate, for two weeks.

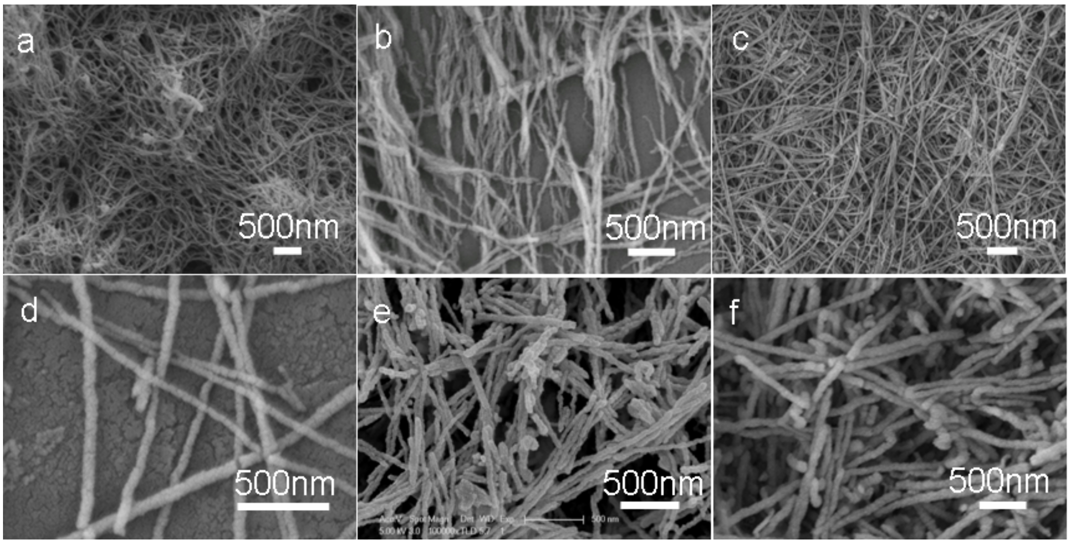


Fig. S10 SEM images of $BaCO_3$ fibres synthesized at different starting pH values. (a) 1.8; (b) 3.5; (c) 4.2; (d) 5; (e) pH 5.5; (f) pH 6.15. ([polymer] = 0.5 g⋖L^{-1} [$BaCl_2$] = 5 mM, on hydrophilic glass slices, for two weeks).

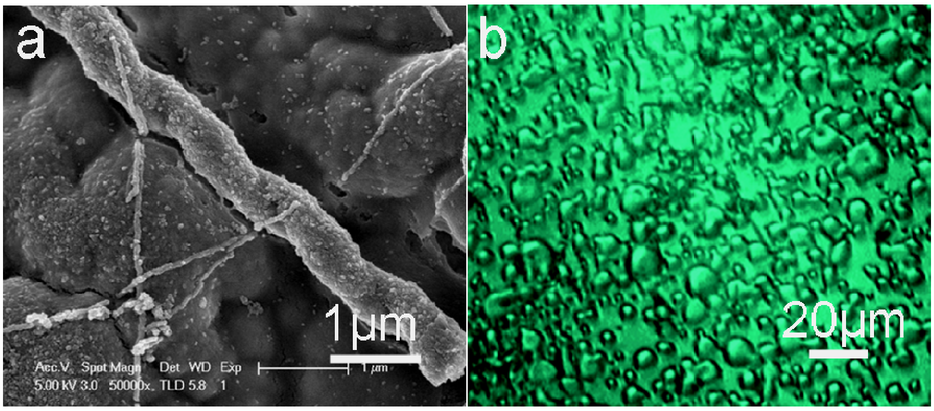


Fig. S11 (a) SEM image of gelatinous films deposited onto the former mineral films. (b) Optical images of liquid mineral precursor droplet deposit onto the glass substrate. After the deposition of mineral films on the OTS-coated substrate (5 days), the substrate was taken out. New substrate was put into the reaction system.

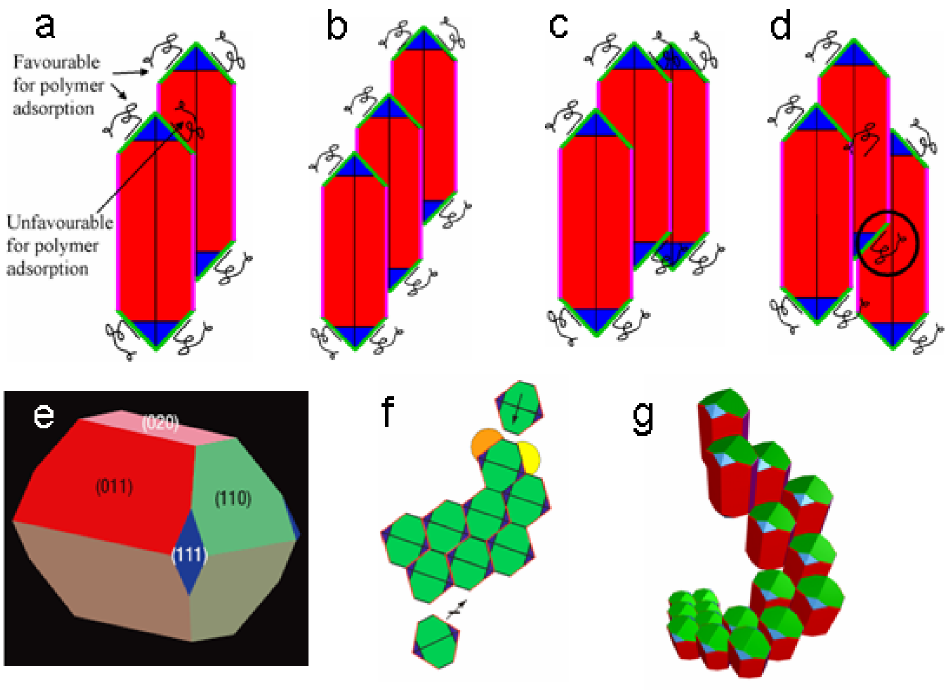


Fig. S12 Proposed mechanism leading to helix structure. Colors for the figure: (110) = green, (111) = blue, (011) = red and (020) = pink.[4]

References

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