Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Functionalised Nanoclays as Microstructure Modifiers for Calcium and Magnesium Silicate Hydrates

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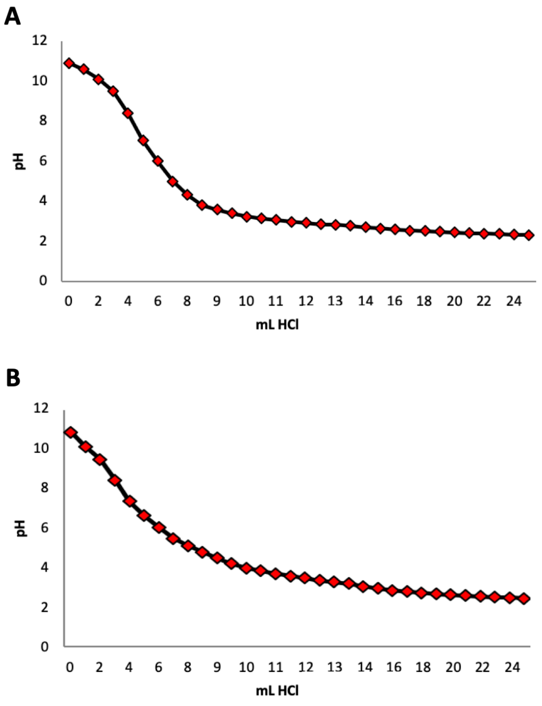
Modification of nanoclays surface

Functionalisation of HNT with carboxyl groups (-COOH)

Nanoclays functionalised with carboxyl groups (HNT-COOH) were prepared in two different steps. In the first step, the surface of the HNT was functionalised with NH_2 groups by mixing HNT with an excess of (3-aminopropyl)triethoxysilane (APTES) at pH 9 following the procedure proposed by Yuan et al.[1]. The reaction mixture was orbitally stirred for more than 24 hours and the product was washed by centrifugation with ethanol to remove the unreacted APTES. The obtained product was dried at 60 °C for 24 hours. Starting from the dry amino-derivate, HNT-COOH was prepared following the method proposed by Joo et al.[2]. Briefly, an ethanol dispersion of dry HNT-NH_2 was slowly added to an ethanol solution of succinic anhydride 0.1 M and the resulting dispersion was orbitally shaken for 24 hours. The product was washed by centrifugation with ethanol to remove the unreacted succinic anhydride and finally dried at 60 °C for 24 hours. The effective functionalisation of HNT with -COOH groups was assessed by means of a potentiometric titration. Two different dispersions of HNT and HNT-COOH halloysites (around 500 mg of solids in 15 mL of H_2O) were prepared and the pH was adjusted until the final value of 10.9 with NaOH 0.1 M. Subsequently, different amounts of HCl 0.01 M were used to titrate the solutions. The obtained curves for HNT and HNT-COOH are reported in Figure S1 together with their 1st derivative.



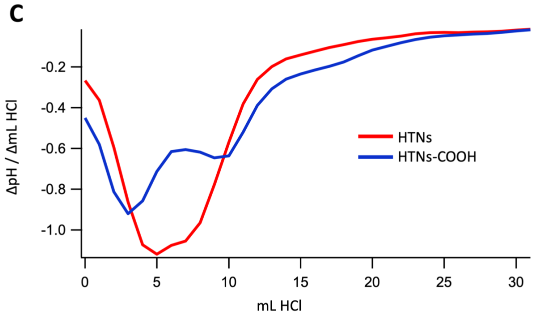


Fig. S1 Titration curves for HNT (panel A) and HNT-COOH (panel B) and first derivative of both curves (panel C).

The presence of two minima around pH 7-8 and pH 5 in the derivative of the HNT-COOH titration curve confirms the presence of two equivalent points that correspond to the neutralization of NaOH and the protonation of the carboxylate groups on the surface of the nanoclays, respectively. The derivative of HNT shows just one minimum that corresponds to the neutralization of NaOH.

A further confirmation of the presence of COOH groups on the surface of the halloysites comes from IR spectra (Figure S2) where the contribution ascribable to the carboxylate functionalisation at around 1650 cm^{-1} is clearly visible in the spectrum of the HNT-COOH sample.

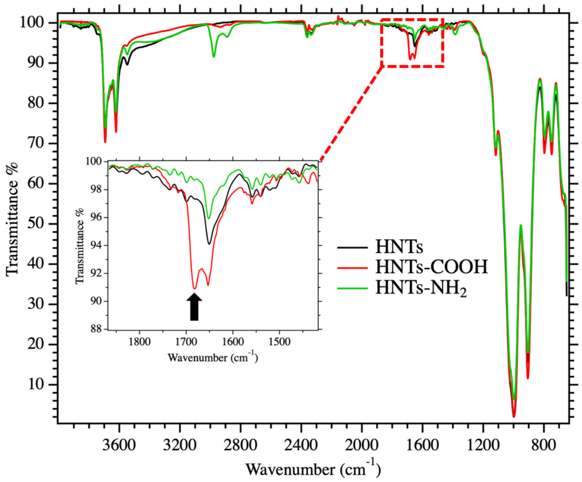


Fig. S2 FTIR spectra of the samples HNT (black line), HNT-NH_2 (green line) and HNT-COOH (red line).

Functionalisation of HNT with polycarboxylic groups (-PAA)

The functionalisation of HNT with polycarboxylic groups (HNT-PAA) was performed in two different steps. In the first step, the surface of HNT was functionalised with 3(trimethoxylsilyl)propylmethacrylate (MPS). Briefly, 60 mL of MPS were added to a dispersion containing 900 mL of ethanol and 3 g of HNT. After 72 hours under magnetic stirring, the product was centrifuged and washed three times with ethanol and MilliQ water to remove the unreacted MPS. Then, 1.5 g of the obtained product were polymerized with 3.5 g of acrylic acid (AA) in 300 mL of MilliQ water using 300 mg of $(NH_4)_2S_2O_8$ as radical initiator. The reaction was carried out at 80 °C for 60 minutes under nitrogen flow and magnetic stirring. Afterwards, the reaction temperature was changed to 70 °C and the reaction was completed in 6 hours. The final product was washed and centrifuged several times with MilliQ water to remove unreacted reagents and dried at 80°C until constant weight.

FTIR investigation (see Figure S3) of the different products and starting materials confirm the successful functionalisation of the HNT with -PAA moieties. In particular, the signal at 1720 cm^{-1} ascribable to the C=O of the acrylic acid in the spectrum of MPS is also visible in the spectrum of the sample HNT-PAA.

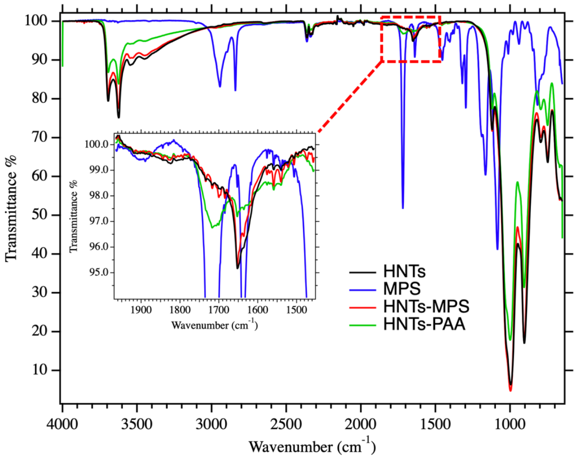


Fig. S3 FTIR spectra of HNT (black line), HNT-MPS (red line), MPS (blue line) and HNT-PAA (green line).

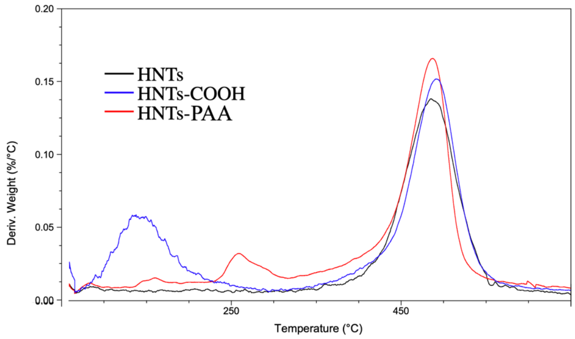


Fig. S4 Derivative weight % obtained from the thermograms acquired on the samples HNT (black line), HNT-COOH (blue line), and HNT-PAA (red line).

SEM micrographs

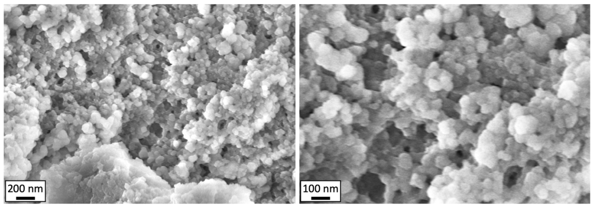


Fig. S5 SEM micrographs of M-S-H at two different magnifications, 100 kX (left) and 200 kX (right).

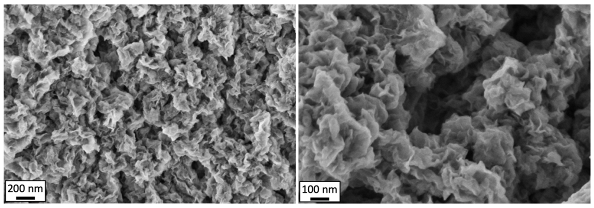


Fig. S6 SEM micrographs of C-S-H at two different magnifications, 100 kX (left) and 200 kX (right).

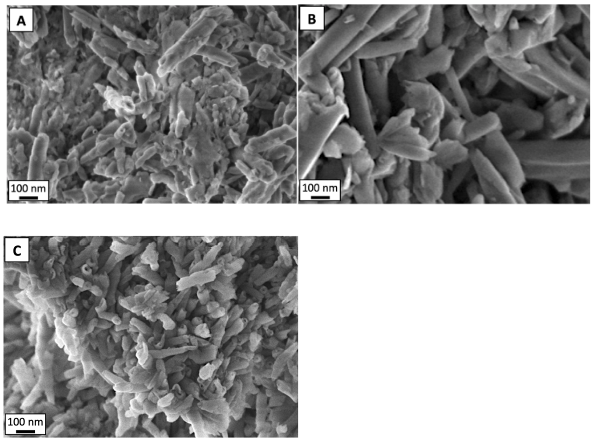


Fig. S7 SEM micrographs of: HNT (panel A), HNT-COOH (panel B), and HNT-PAA (panel C) at the same magnification (200 kX).

Table S1 EDX analysis

	Al/Mg or Ca
M-S-H @HNT-COOH	0.15 ± 0.01
M-S-H @HNT-PAA	0.14 ± 0.04
C-S-H @HNT-COOH	0.25 ± 0.02
C-S-H @HNT-PAA	0.05 ± 0.02

The Analytical SAXS Model for M-S-H

The intensity of a SAXS measurement of M-S-H can be expressed as Eq. S1:

$$I(Q) = N\langle\overline{P(Q)}\rangle S(Q)_c + bkg \qquad \text{(S1)}$$

where N is a scale factor related to number density, and electronic contrast; $S(Q)_c$ is the corrected inter-globule structure factor of the porous gel taking into account of the effect of polydispersity; $\langle\overline{P(Q)}\rangle$ denotes the normalized intra-particle structure factor averaged over the distribution of the size and for anisotropic shapes over all possible orientations of the base unit. Inter-globule structure factor $S(Q)_c$ is calculated by Eq. S2:

$$S(Q)_c = 1 + \beta(Q)[S(Q) - 1] \qquad \text{(S2)}$$

where

$$\beta(Q) = \frac{|\langle F(Q)\rangle|^2}{\langle |F(Q)|^2\rangle} \qquad \text{(S3)}$$

$\mathrm{F(Q)}$ is the particle form factor and

$$S(Q) = 1 + \left(\frac{\zeta}{R_e}\right)^D \Gamma(D+1)\frac{\sin[(D-1)\tan^{-1}(Q\zeta)]}{(D-1)[1+(Q\zeta)^2]^{\frac{D-1}{2}}(Q\zeta)} \qquad \text{(S4)}$$

where Γ is the Gamma function.

The essential parameters of the $S(Q)_c$ are the mass fractal dimension, D, the fractal cutoff dimension, ζ, and the equivalent radius, R_e.

The normalized intra-particle structure factor can be expressed as:

$$\langle\overline{P(Q)}\rangle = \langle |F(Q)|^2\rangle \qquad \text{(S5)}$$

P(Q) contains the structural information of the globules. This part is where M-S-H is different from C-S-H. In the case of C-S-H, the form factor reflects a multi-disk-like structure with water layers. However, such structure does not exist in M-S-H. Since the SAXS measurement of M-S-H is smooth in both low-Q and high-Q, a polydisperse spheres model for M-S-H globules was used in the modelling of the local geometrical arrangement of the base unit[3]. In this model the normalized intra-particle structure factor averaged over the radius of the polydisperse spheres as:

$$\langle\overline{P(Q)}\rangle = \int_0^{\infty} P(Q,R) f_s(R) dR \tag{S6}$$

where

$$P(Q,R) = \left\{\frac{3[\sin(QR)-(QR)\cos(QR)]}{(QR)^3}\right\}^2 \tag{S7}$$

the radius R is assumed to follow a Schulz distribution with

$$f_s(R) = \left(\frac{Z+1}{\bar{R}}\right)^{Z+1} R^z \exp\left[-\frac{Z+1}{\bar{R}}R\right] / \Gamma(Z+1) \tag{S8}$$

The fitting parameters of this polydisperse sphere model are the average radius of the spheres, $\bar{R}$, and the width parameter of the Schultz distribution of the sphere radius, Z. The equivalent radius R_e in $S(Q)$ is equivalent to $\bar{R}$.

The Analytical SAXS Model for C-S-H

The structure of the C-S-H globule can be modelled as a disk with layered sub-structure as proposed in our previous works[3–5]. We can describe the size distribution of the C-S-H globules as a Schultz distribution of the number of repeating layers *n* of the multi-layered disk.

$$\left\langle \overline{P(Q)} \right\rangle_{Orientation,n} = \int_0^{\infty} \left\langle \overline{P(Q,n)} \right\rangle_{Orientation} f_S(n)\, dn \tag{S9}$$

where

$$\left\langle \overline{P(Q,n)} \right\rangle_{Orientation} = \int_0^1 \overline{P(Q,\mu,n)}\, d\mu \tag{S10}$$

$$f_S(n) = \left(\frac{Z_n+1}{\bar{n}}\right)^{Z_n+1} n^{Z_n} \exp\left[-\left(\frac{Z_n+1}{\bar{n}}\right)n\right] / \Gamma(Z_n+1)$$

$$Z_n > -1 \tag{S11}$$

$$\overline{P(Q,\mu,n)} = \left|F(Q,\mu,n)\right|^2 = \left[\frac{2J_1\left(QR\sqrt{1-\mu^2}\right)}{QR\sqrt{1-\mu^2}}\right]^2 C^2\left(A^2+B^2\right) \tag{S12}$$

$$A = \chi \cos\left(\frac{Q\mu(nL-L_2)}{2}\right)\frac{\sin\left(\frac{Q\mu L_1}{2}\right)}{Q\mu} + \cos\left(\frac{Q\mu(nL+L_1)}{2}\right)\frac{\sin\left(\frac{Q\mu L_2}{2}\right)}{Q\mu} \tag{S13}$$

$$B = \chi \sin\left(\frac{Q\mu(nL-L_2)}{2}\right)\frac{\sin\left(\frac{Q\mu L_1}{2}\right)}{Q\mu} + \sin\left(\frac{Q\mu(nL+L_1)}{2}\right)\frac{\sin\left(\frac{Q\mu L_2}{2}\right)}{Q\mu} \tag{S14}$$

$$C = \frac{2}{n[\chi L_1 + L_2]}\frac{\sin\left(\frac{Q\mu nL}{2}\right)}{\sin\left(\frac{Q\mu L}{2}\right)} \tag{S15}$$

and

$$\chi = \frac{\rho_1-\rho_2}{\rho_2-\rho_s} \tag{S16}$$

where ρ_1, ρ_2, and ρ_s are scattering length densities (SLD) of water, calcium silicate, and solvent, respectively.

The fitting parameters of the intra-particle structure are the disk radius (*R*), the thickness of hydration water (*L₁*), the layer thickness of calcium silicate (*L₂*), the scattering length density contrast ratio (χ), the average number of repeating layers inside a globule ($\bar{n}$) and the width parameter (Z_n) of the number of layers described by a Schultz distribution. The equivalent radius R_e can be found as $R_e = (3\bar{n}R^2 L/4)^{1/3}$ where L is the interlayer distance ($L = L_1 + L_2$). The total thickness t can be calculated as $t = \bar{n}L$. More details on this model can be accessed in the literature[4].

Evaluation of additives scattering contribution in composites curves

The contribution of the additives to the SAXS profile was estimated considering the scattering profile of the composites as a linear combination of the pure phases:

$$y = x[1]*\mathrm{PHASE1}(Q) + x[2]*\mathrm{PHASE2}(Q) \qquad \text{(S17)}$$

where “PHASE1” is HNT-COOH or HNT-PAA and “PHASE2” is C-S-H or M-S-H.

The results are reported in Table S2.

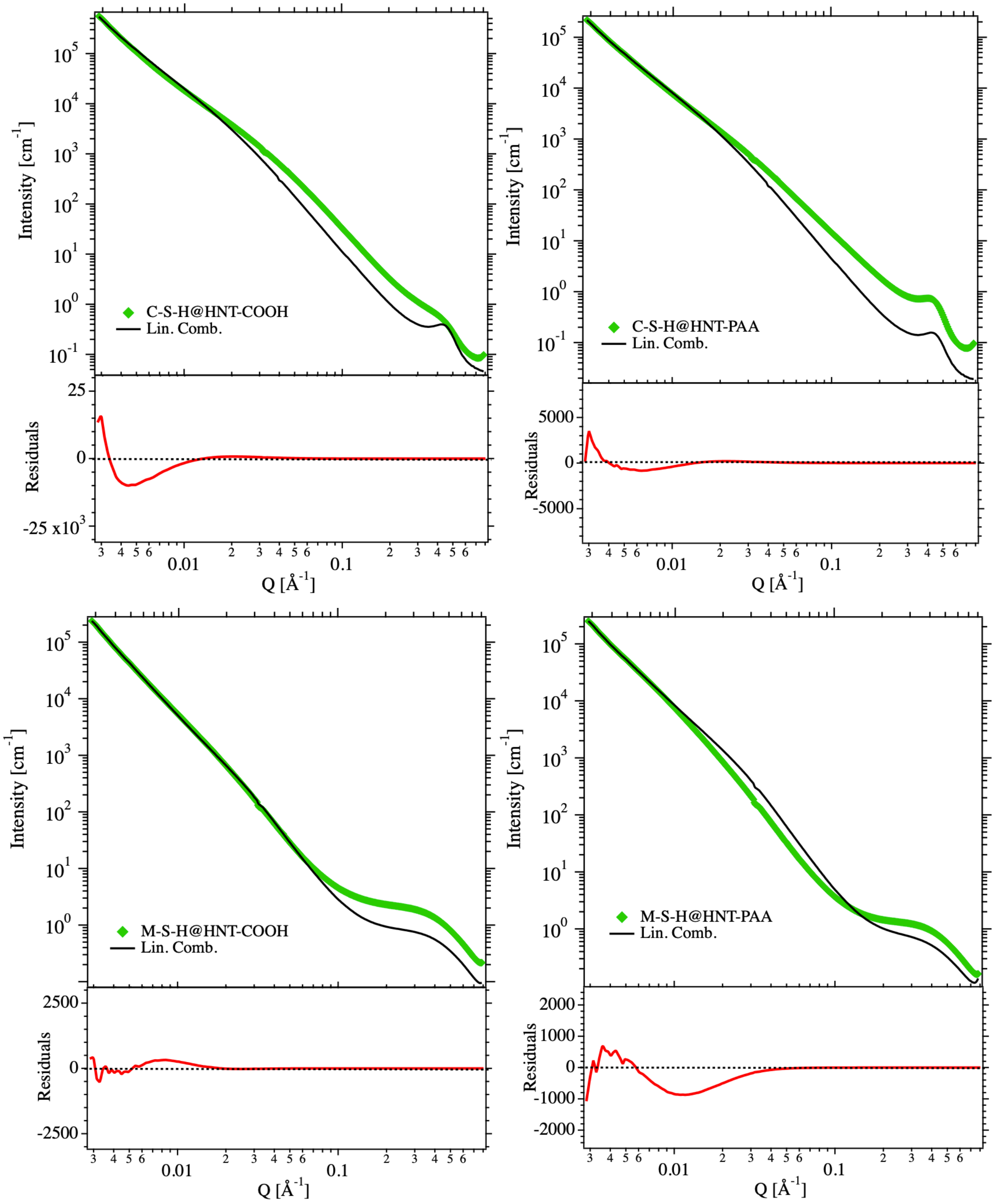


Fig. S8 SAXS curves of the composite samples (green markers) along with the linear combination of the corresponding pure phases (black lines) and residuals (red lines).

Table S2 Parameters extracted from the linear combination of the SAXS curves. Values in parentheses are standard deviations on the last significant figures.

	x[1]	x[2]
M-S-H@HNT-COOH	0.09(1)	0.58 (4)
M-S-H@HNT-PAA	0.16(3)	0.63(3)
C-S-H@HNT-COOH	0.004(2)	0.73 (12)
C-S-H@HNT-PAA	0.005(1)	0.30 (1)

It is worth noting that in this case the residuals are not strictly linked to the goodness of the final fit while represents the structural changes induced to the silicate phases by the HNTs. The scattering profile of the silicate phases in the composite could differ from that of the pure phases due to the heterogeneous nucleation taking place at the halloysites surface. Thus, the difference between the experimental data and the linear combination is attributed to the structural variations induced by the HNTs on the developing silicate phases.

Hollow cylinders form factor

This model considers the cylinder with an uniform SLD and the SLD inside and outside of the cylinder is the same[6]:

$$P(Q) = scale \cdot V_{shell} \cdot (\Delta\rho)^2 \int_0^1 \Psi^2\left[Q, R_{shell}(1-x^2)^{1/2}, R_{core}(1-x^2)^{1/2}\right]\left(\frac{\sin Qhx}{QHx}\right)^2 dx \qquad \text{(S18)}$$

where

$$\Psi(q,y,z) = \frac{1}{1-\gamma^2}\left[\Lambda(Qy) - \gamma^2\Lambda(Qy)\right] \qquad \text{(S19)}$$

$$\Lambda(w) = 2J_1(w)/w \qquad \text{(S20)}$$

$$\gamma = \frac{R_{core}}{R_{shell}} \qquad \text{(S21)}$$

$$V_{shell} = \pi\left(R_{shell}^2 - R_{core}^2\right)L \qquad \text{(S22)}$$

where J_1 is the first order Bessel function.

Residual values

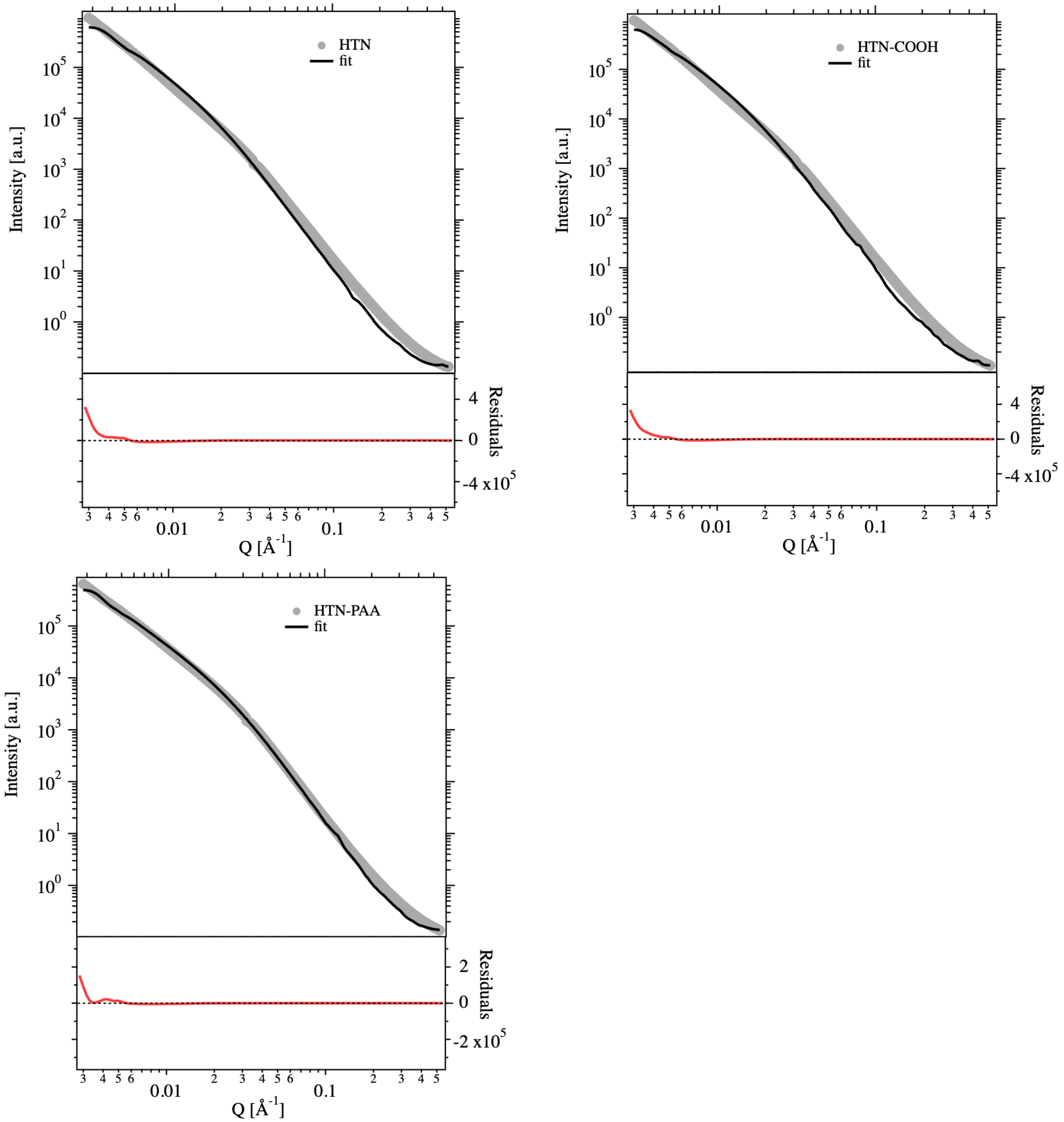


Fig. S9 SAXS curves (grey markers) of HNT, HNT-COOH and HNT-PAA along with the best fit (black lines) and residuals (red lines).

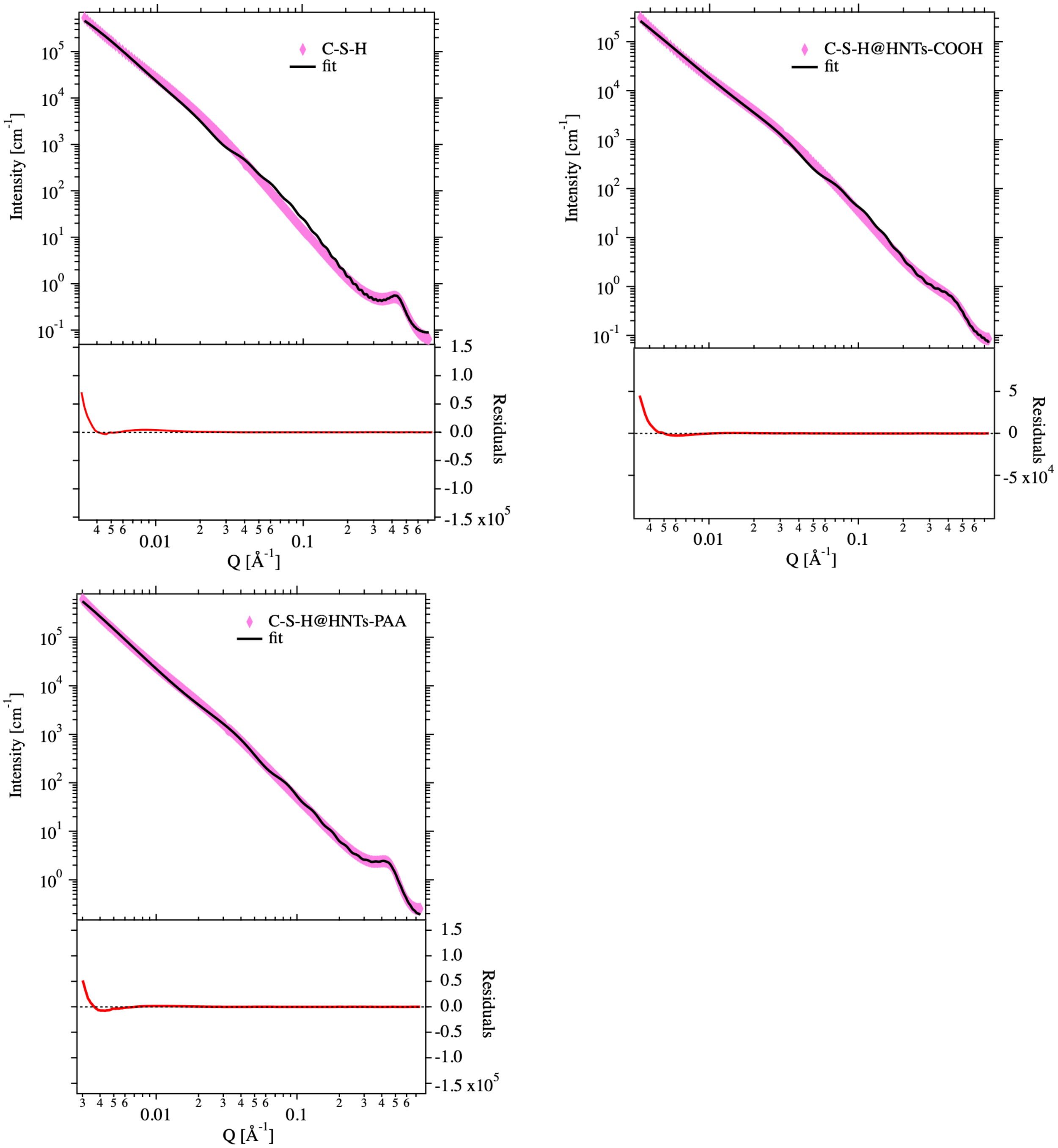


Fig. S10 SAXS curves (pink markers) of the pure C-S-H phase and composites containing HNT-COOH and HNT-PAA along with the best fit (black lines) and residuals (red lines).

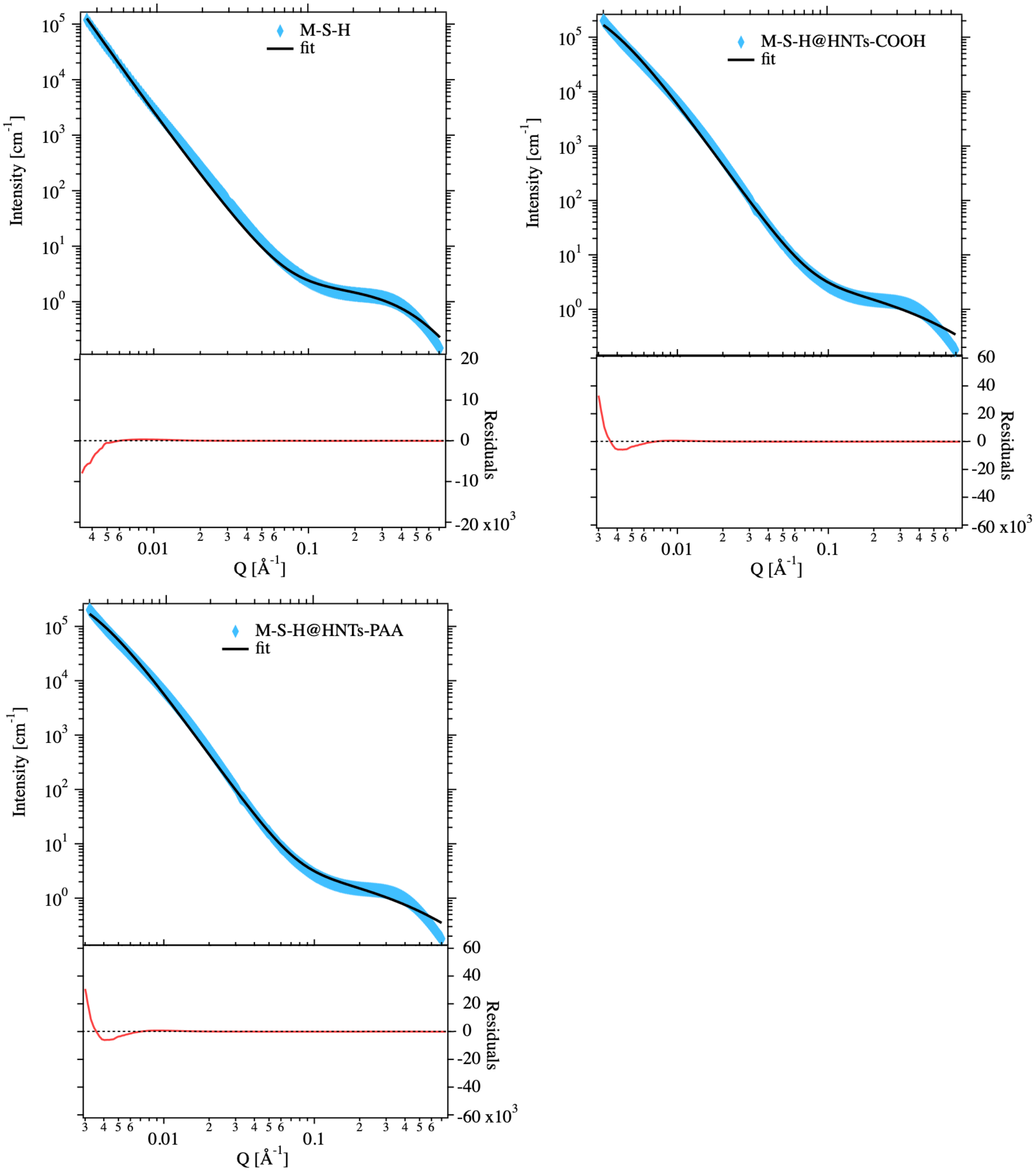


Fig. S11 SAXS curves (light blue markers) of the pure M-S-H phase and composites containing HNT-COOH and HNT-PAA along with the best fit (black lines) and residuals (red lines).

References

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