Electronic supporting information for:

The effect of hyperbranched poly(acrylic acid)s on the morphology and size of precipitated nanoscale (fluor)hydroxyapatite

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Contents

Diffusion-ordered NMR spectroscopy 2

Quantities for (F)HA synthesis 4

Additional TEM Images 5

Diffusion-ordered NMR spectroscopy

DOSY measurements were carried out using Bruker ledbpbgp2s_compensated program, modified to have 32 gradient steps. The pulse, delay sequence is shown below in Fig. S1.

It is worth considering that DOSY can be affected by convection internally within the NMR tubes.[1] Studies have shown that this is less problematic for samples in deuterium oxide than for organic solvents such as chloroform or methanol.[1] As such all measurements carried out in deuterated solvents used thin NMR tubes (0.2 mm diameter) to reduce this issue. Gradient strengths were calibrated to provide a diffusion coefficient of 1.91 x 10^{-9} m^{-2} s^{-1} at 298.15 K (gradients operated from 95% to 5% using 16 points with a quadratic decay). The same bipolar LED sequence as for the sample measurements was used, with sine shaped gradient pulses and gradient strengths incremented between 0.28 and 5.19 G mm^{-1} in 16 steps equally spaced in gradient squared.

NMR tubes were filled with 0.8 ml solution to a constant volume. One dimensional 1H experiments were recorded using 16 scans. ^{1}H diffusion measurements were recorded using an LED sequence with bipolar gradients, with sine shaped gradient strength incremented between 0.28 and 5.19 G mm^{-1} in 32 steps equally spaced linearly. Data analyses were performed using TopSpin software version 3.5 (patch level 5).

In order to ensure the accuracy of using the Stokes Einstein equation to get the hydrodynamic radius of the polymer within the NMR tube a correction factor was used regarding the solvent diffusion peak. A blank sample of D_2O was scanned and gave a diffusion value of 1.914 x 10^{-9} m^2 S^{-1}. This measurement was repeated several times (n = 3) to ensure accuracy and found to vary by less than 1%. The value is close to the previously measured values for D_2O / H_2O mixtures. The number was used to gauge both the diffusion and viscosity of the pure solvent, and then when the diffusion of the solvent with polymer was analysed the viscosity of the sample was determined thus:

$$D_1\eta_1 = D_2\eta_2$$

This correction ensured that all hydrodynamic radii calculated using Stokes-Einstein would be accurate. The diffusion values of these polymers were recorded and the hydrodynamic radius calculated (Figure S2 and Table S1).

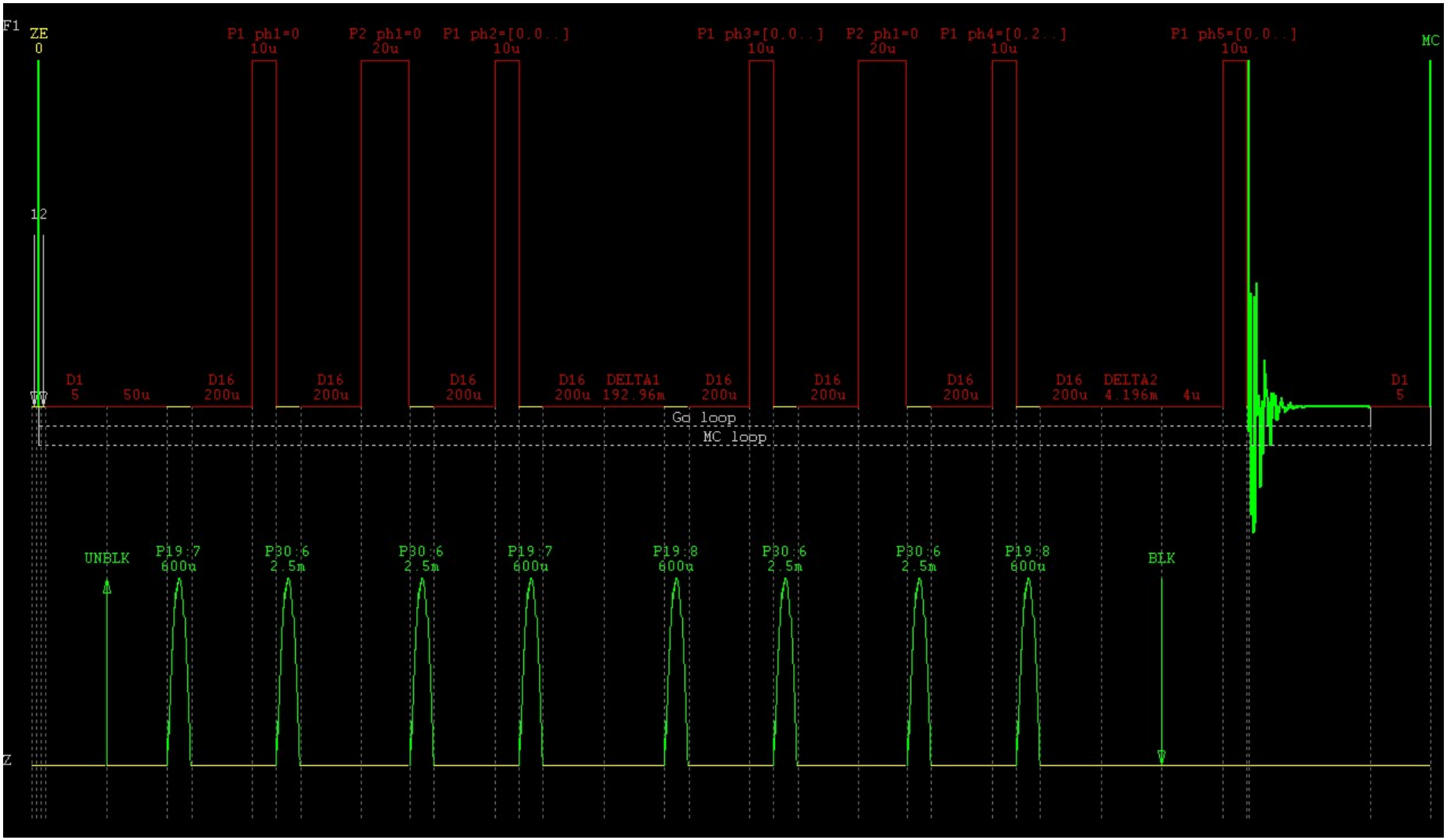


Figure S1. Pulse sequence used for DOSY measurements.

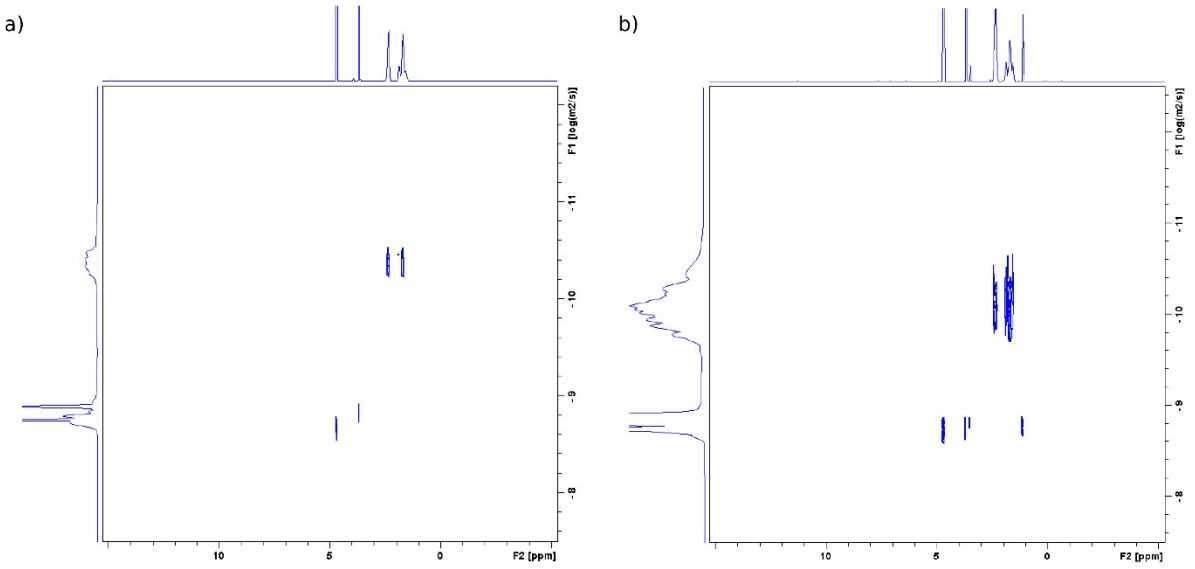


Figure S2. DOSY spectra for a) PAA-VBD and b) PAA-VPC.

Table S1. DOSY experiment raw data (–logD) and calculated hydrodynamic radii.

Sample	Solvent	Polymer	R_h / nm
D_2O	8.7180		
PAA-VDB	8.6850	10.3650	4.908
PAA-VPC	8.7460	10.1100	2.371

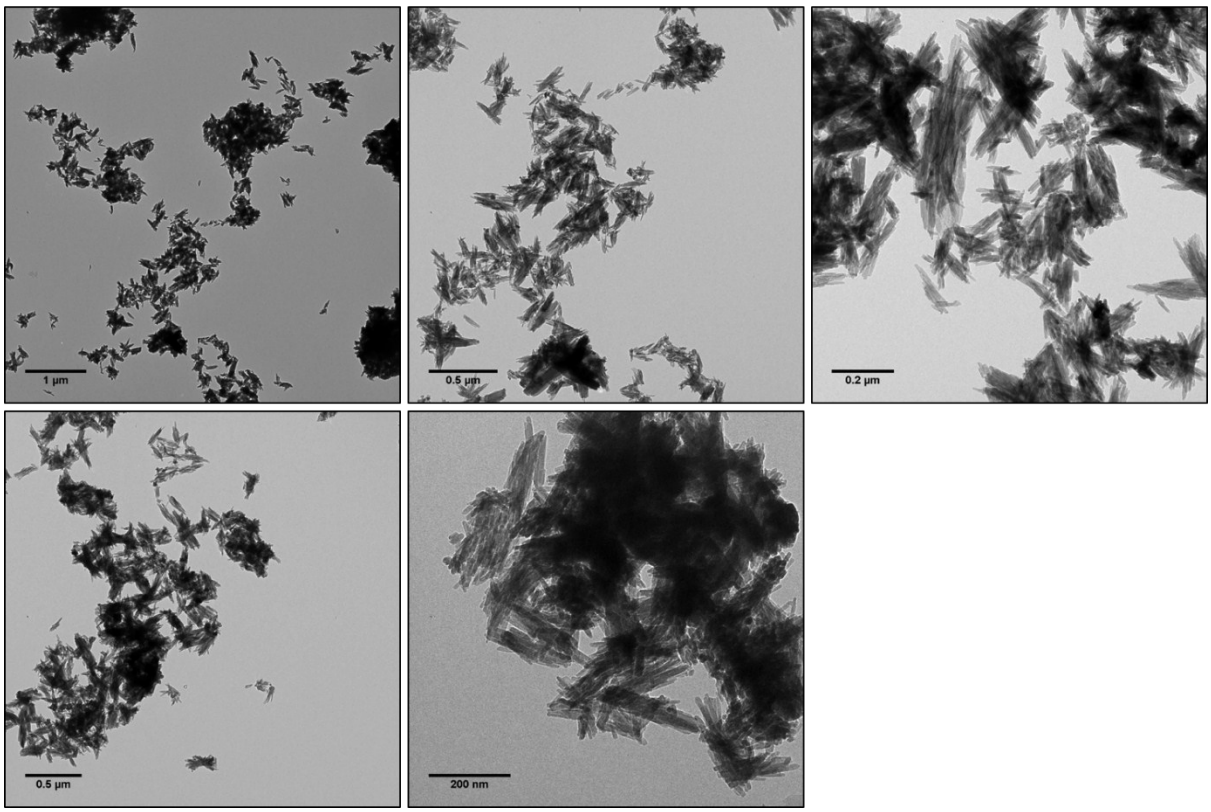
Quantities for (F)HA synthesis

Table S2. Masses of chemicals used in the synthesis of fluorhydroxyapatite and hydroxyapatite varying poly(acrylic acid) additive

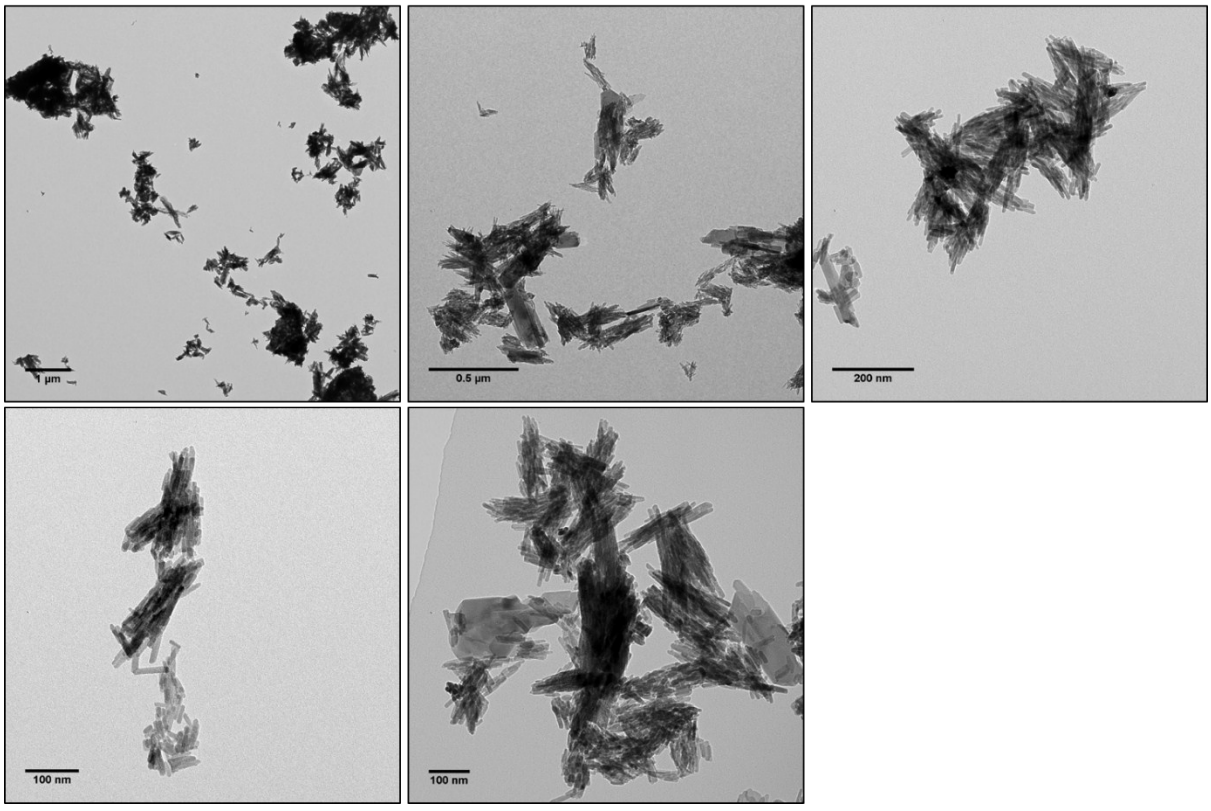
Sample	$CaCl_2$ / g	$(NH_4)_2HPO_4$ / g	NH_4F / g	E5 / g	E11 /g	PAA-VPC / g	PAA-VBD / g
FHA-E5	5.551	3.993	0.234	0.812	---	---	---
FHA-E11	5.556	4.012	0.235	---	0.813	---	---
FHA-NoP	5.553	4.003	0.231	---	---	---	---
FHA-PAA-VPC	5.561	3.992	0.234	---	---	0.202	---
FHA-PAA-VBD	5.546	4.031	0.232	---	---	---	0.207
HA-E5	5.552	3.997	---	0.804	---	---	---
HA-E11	5.557	4.011	---	---	0.811	---	---
HA-NoP	5.555	4.001	---	---	---	---	---
HA-PAA-VPC	5.543	3.999	---	---	---	0.203	---
HA-PAA-VBD	5.577	3.987	---	---	---	---	0.208

Additional TEM Images

FHA E5



FHA E11



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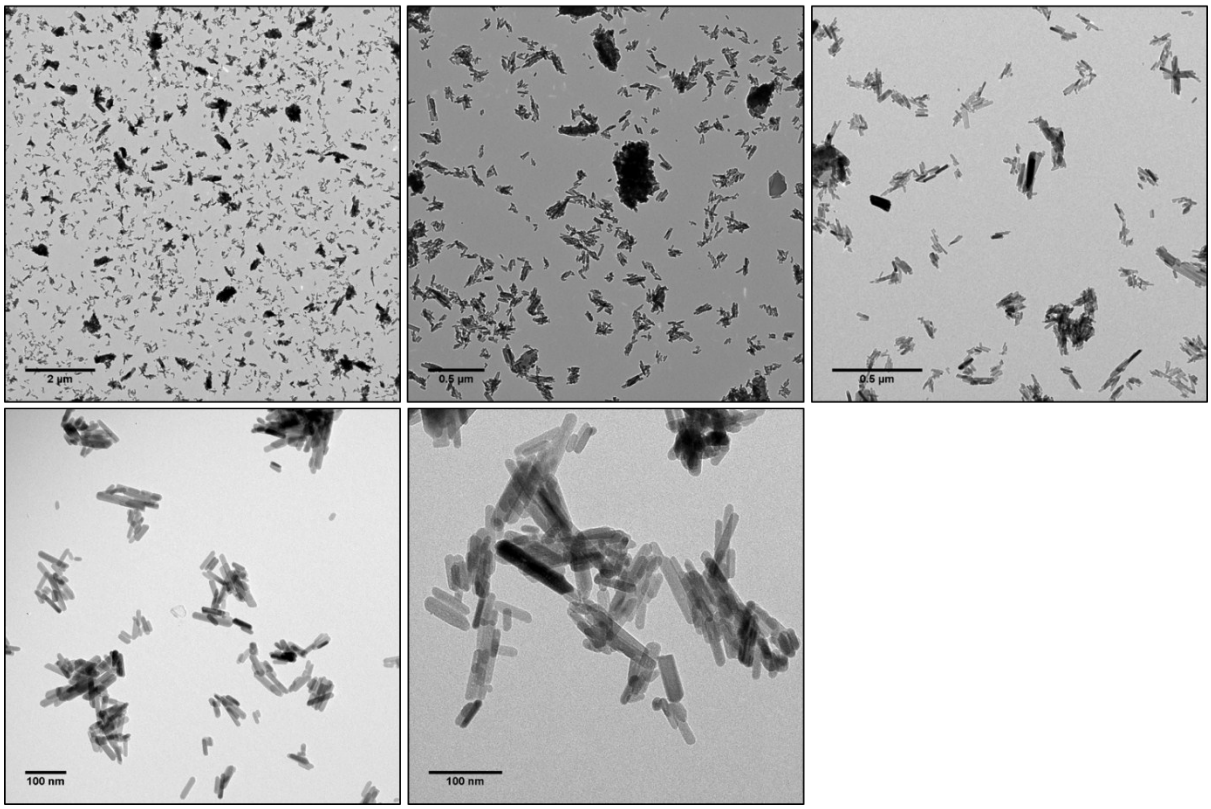
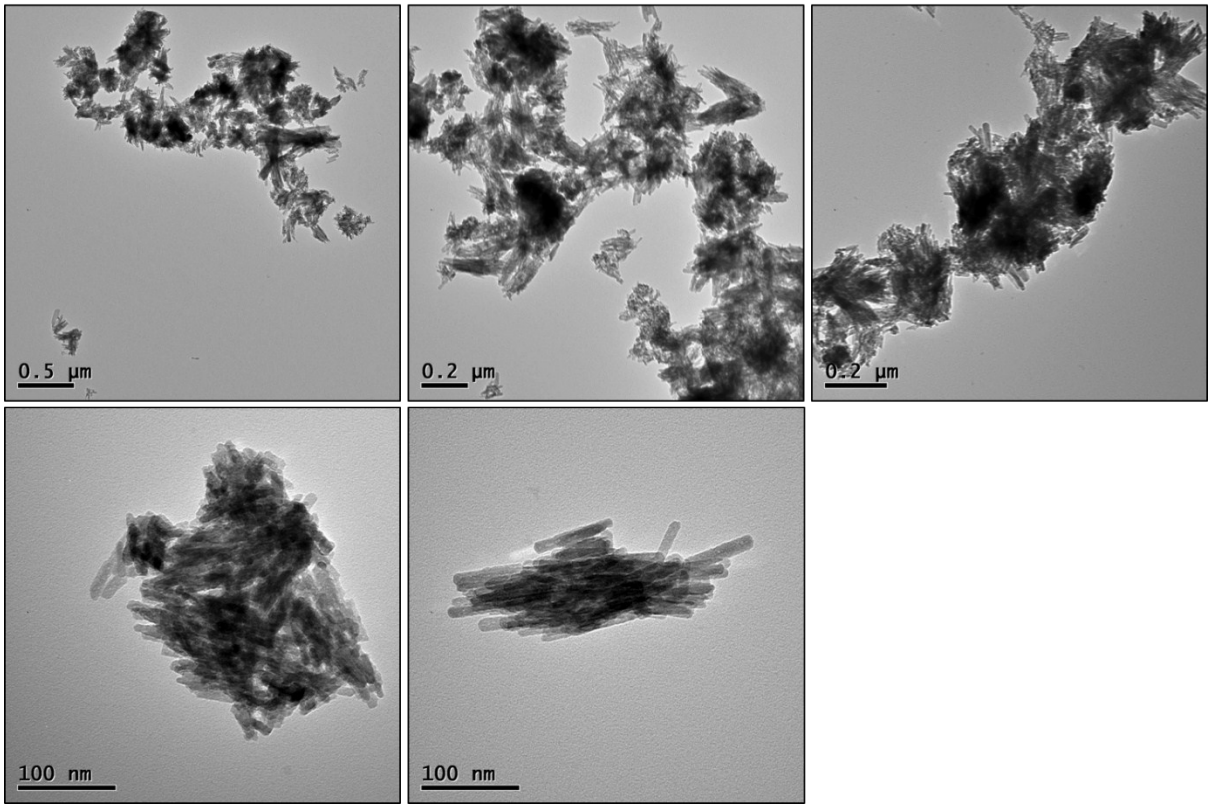
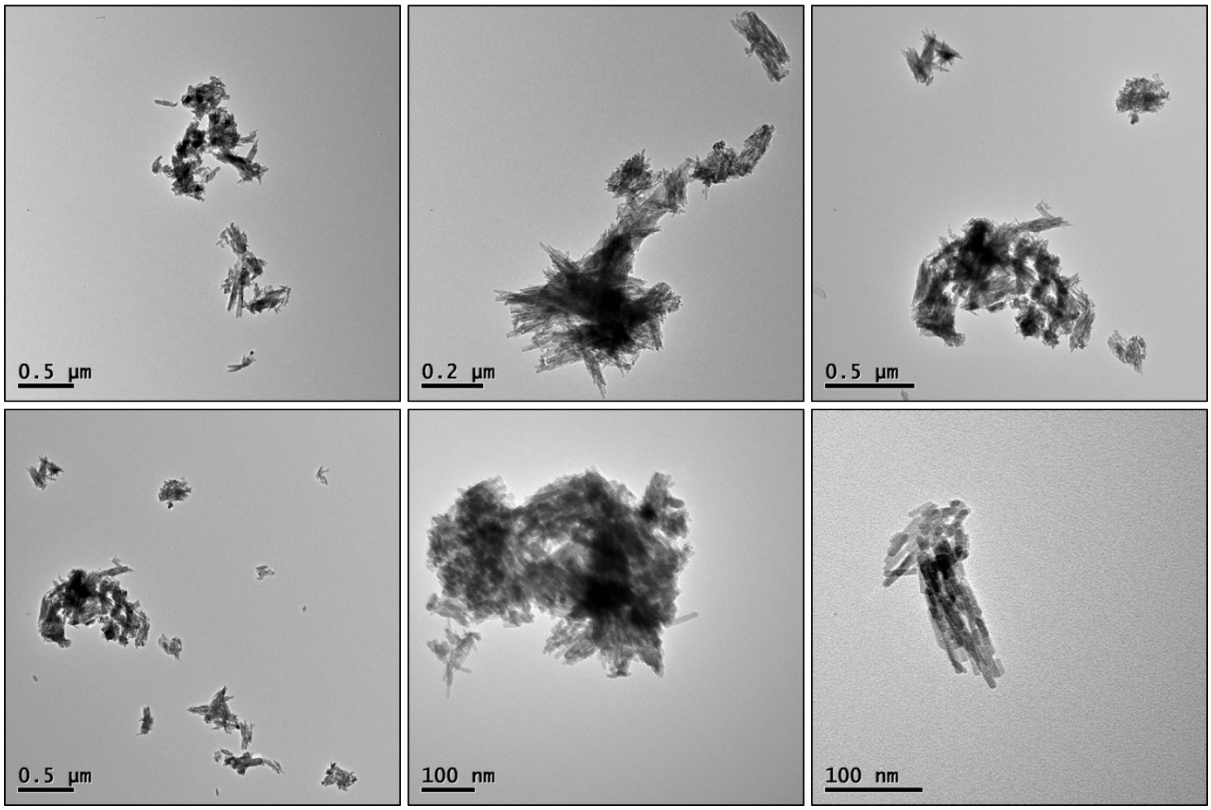


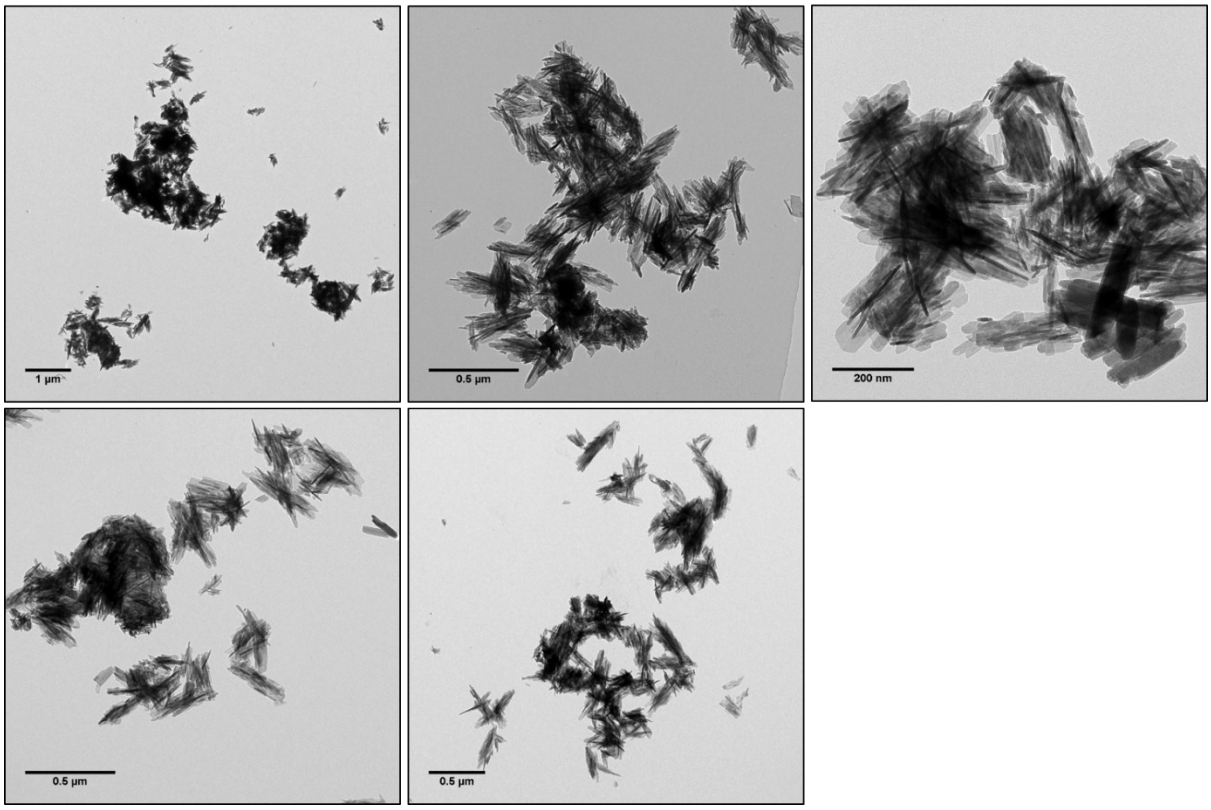
FHA PAA-VBD



FHA PAA-VPC



HA E5



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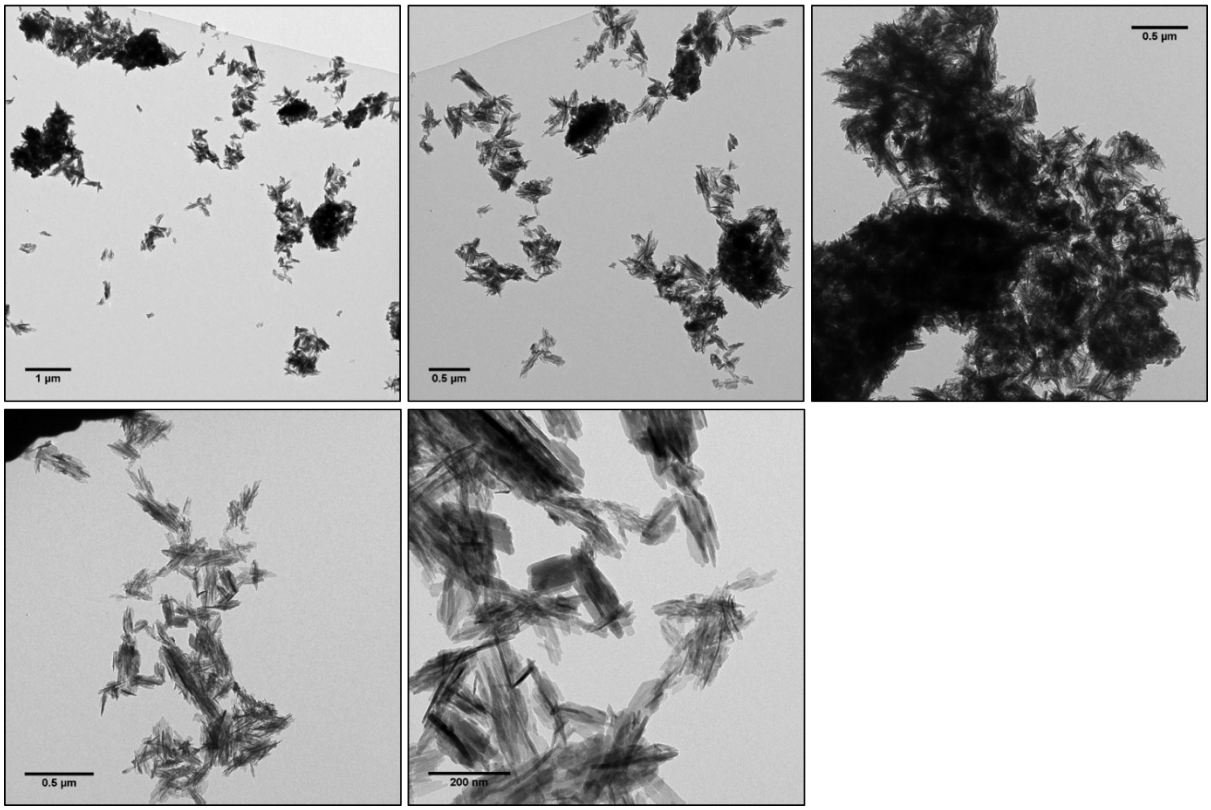

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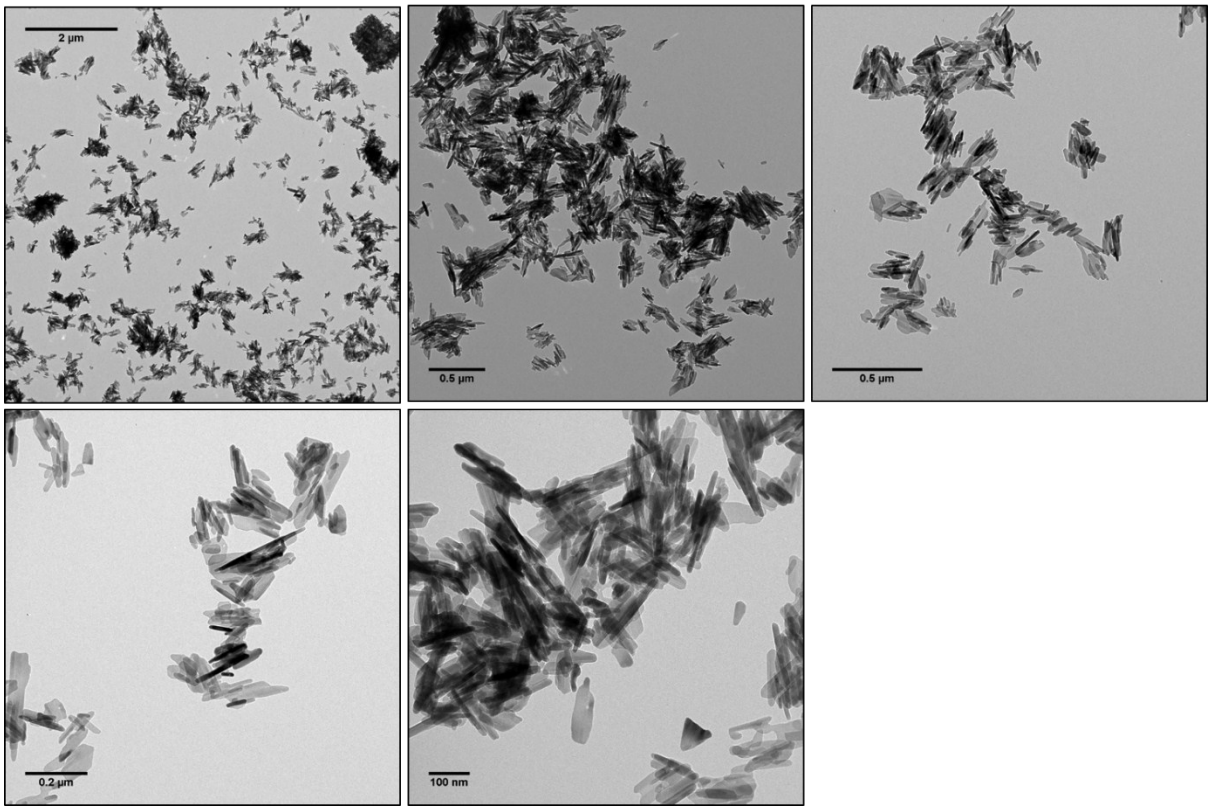
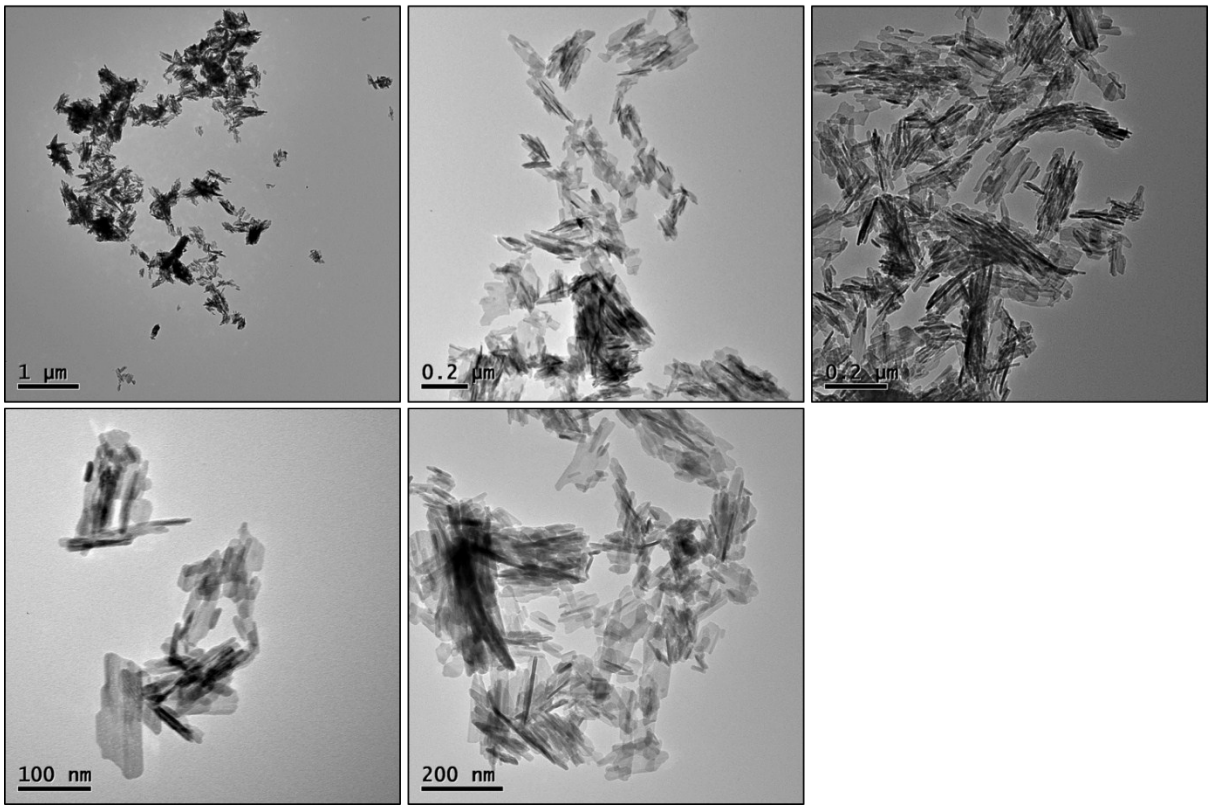


HA PAA-VBD



HA PAA-VPC