

SUPPLEMENTARY INFORMATION

Methods

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-Ray diffractometer with a Cu K α anode ($\lambda = 0.1542$ nm) operating at 40 kV and 30 mA. The diffraction patterns were collected at 25 °C and over an angular range of 20 to 70° with a step size of 0.05° per step and a dwell time of 12 s per increment. The obtained pattern was matched to stoichiometric HAP (JCPDS, card number 01-072-1243) from the Powder Diffraction File-2 database of the International Centre for Diffraction Data.

Specific surface area analysis of HAP was determined by nitrogen adsorption/desorption isotherms at -196°C on a Micromeritics Tristar II 3020 system. The samples were outgassed at 80 °C overnight before analysis was performed. Nitrogen was used as the adsorbate gas, and the BET isotherm was determined with the ratio of the gas pressure to the saturated vapour pressure $z = P / P_0$ ranging from 0.1 to 0.35.

Transmission electron microscopy (TEM) was carried out on a JEOL 1010 TE microscope operating at an accelerating voltage of 100 kV. The specimens were prepared by taking 10 mg mL⁻¹ samples in water and evaporating them onto holey carbon coated copper grids.

Results

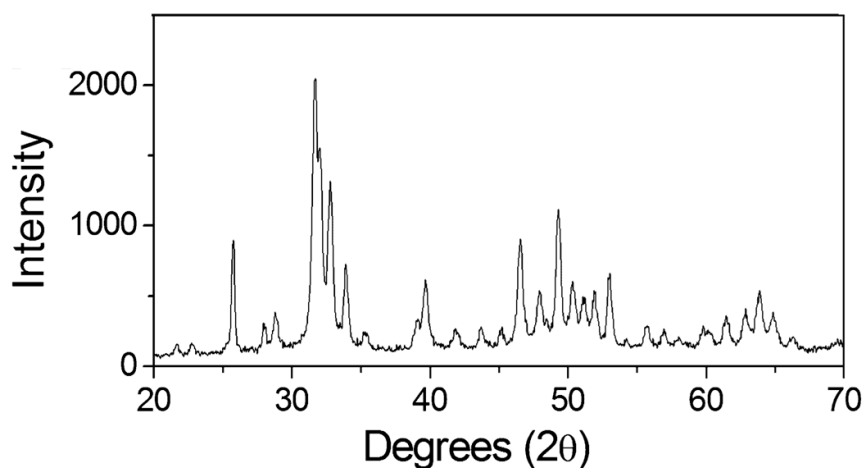


Figure S1. XRD pattern of synthesized HAP used for surface modification. This observed pattern matches that of the reference HAP synthesized in (Markovic, Fowler et al. 2004)

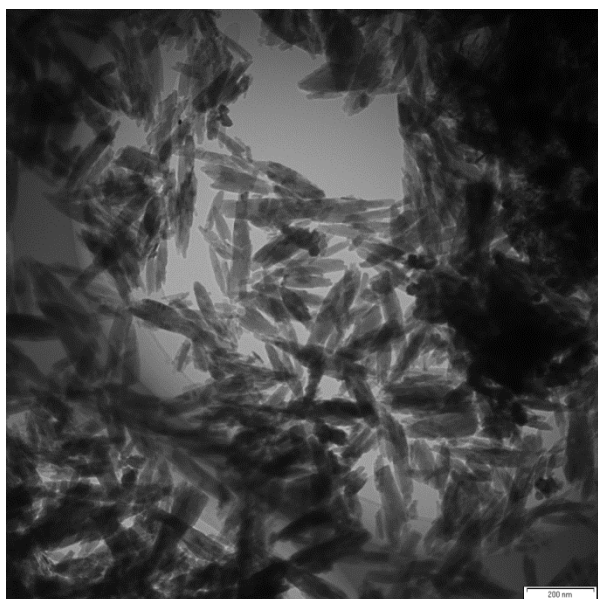


Figure S2. TEM image of HAP displaying the surface morphology and crystal size; the crystal lengths and widths ranged between 100-260 nm and 20-40 nm (scale bar is 200 nm) (see Table S1 for further details of crystal size)

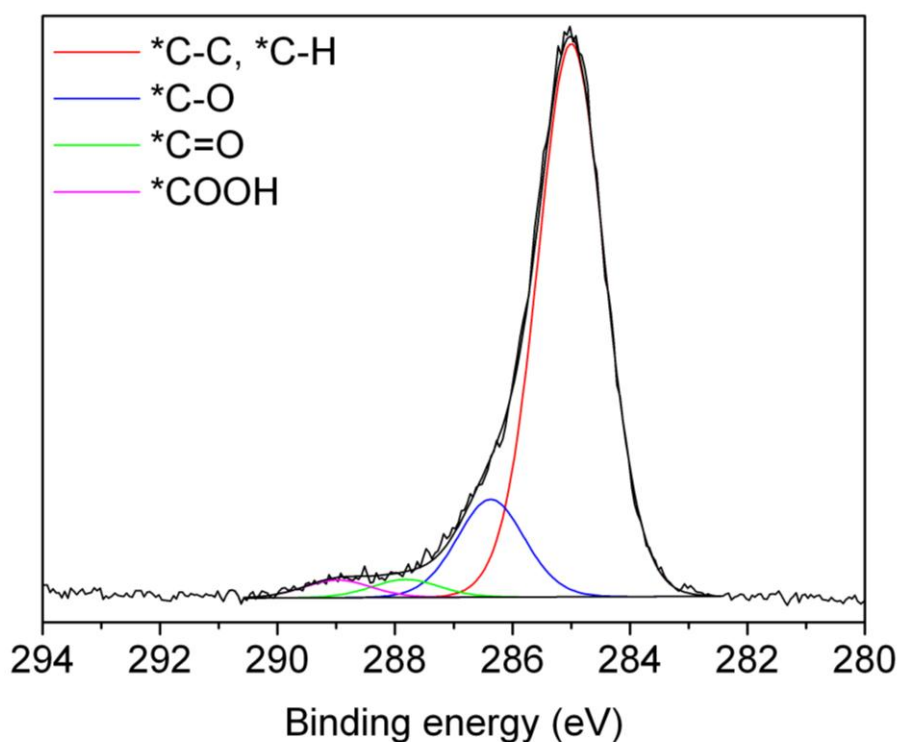


Figure S3. High resolution XPS spectrum of the C1s peak of HAP. The four fitted peaks appear at binding energies of 285.0 eV (*C-C, *C-H), *C-O (286.5 ± 0.2 eV), *C=O (288.0 ± 0.2 eV) and *COOH (289.0 ± 0.2 eV) (Beamson and Briggs 1992). The ratio of the hydrocarbon peak (C-C, C-H) to the cumulative oxidized carbon peaks (*C-O, *C=O and *COOH) is 0.2. This is in the range found for adventitious carbon in most literature. (Barr and Seal 1995)

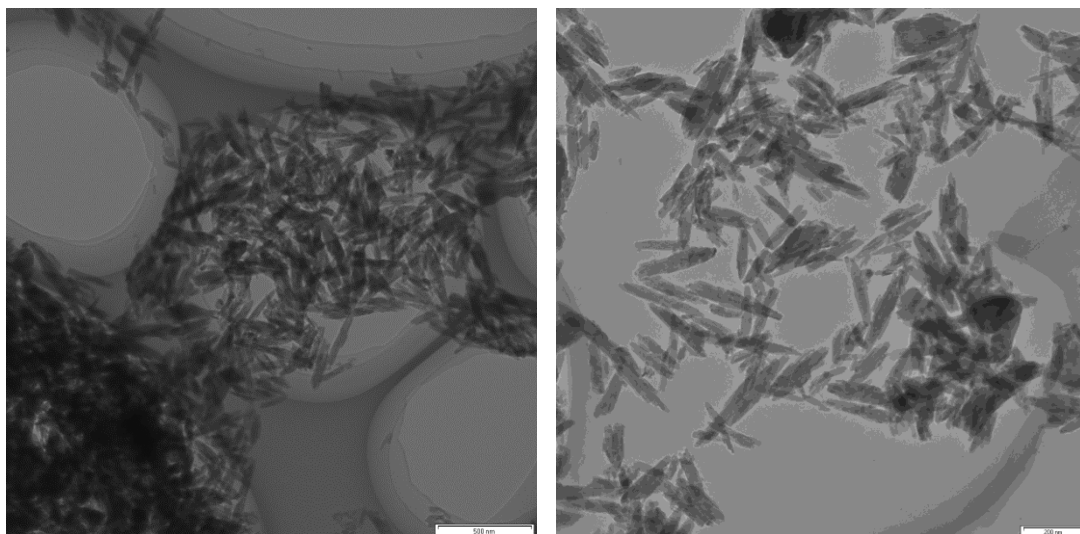


Figure S4. TEM image of samples A-HAP-3 (left, scale bar 500 nm) and A-HAP-3-150 (right, scale bar 200 nm) illustrating that only HAP crystals can be observed thereby confirming that separate silica particles do not form in the reaction.

Table S1. Lengths and widths of crystals from TEM

| Sample | Length (nm) | Width (nm) |
|---------------------|--------------|-------------|
| HAP | 180 ± 80 | 30 ± 10 |
| A-HAP-3-150 | 200 ± 60 | 30 ± 10 |
| PAA-HAP | 170 ± 50 | 20 ± 10 |
| PAA-A-HAP-150 | 160 ± 60 | 30 ± 10 |
| PAA-A-HAP-200 | 160 ± 60 | 30 ± 10 |
| PAA-A-HAP-200-ionic | 170 ± 60 | 30 ± 10 |

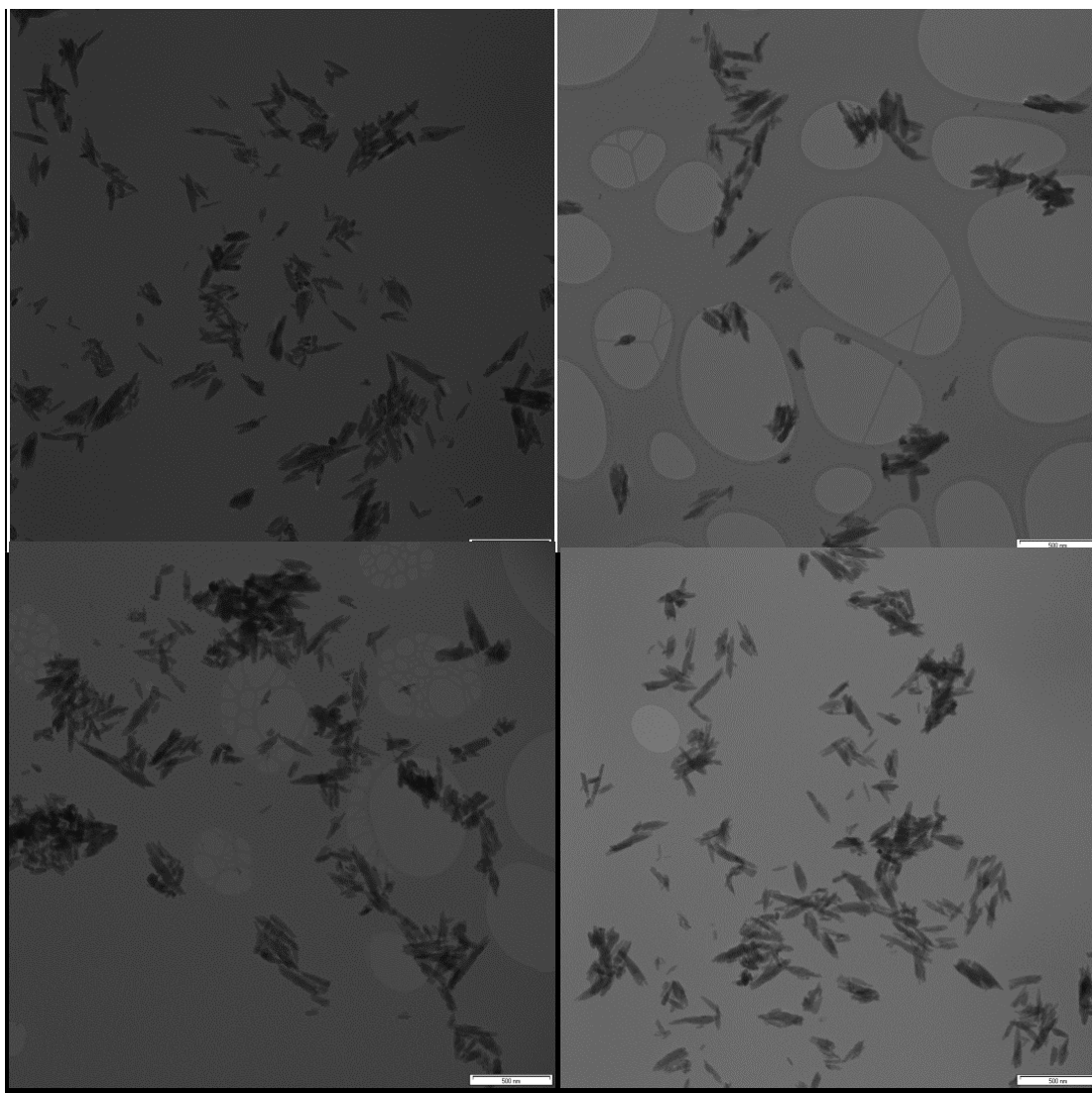


Figure S5. TEM images of PAA-HAP (top left), PAA-A-HAP-150 (top right), PAA-A-HAP-200 (bottom left) and PAA-A-HAP-200-ionic (bottom right) (scale bar in all images is 500 nm)

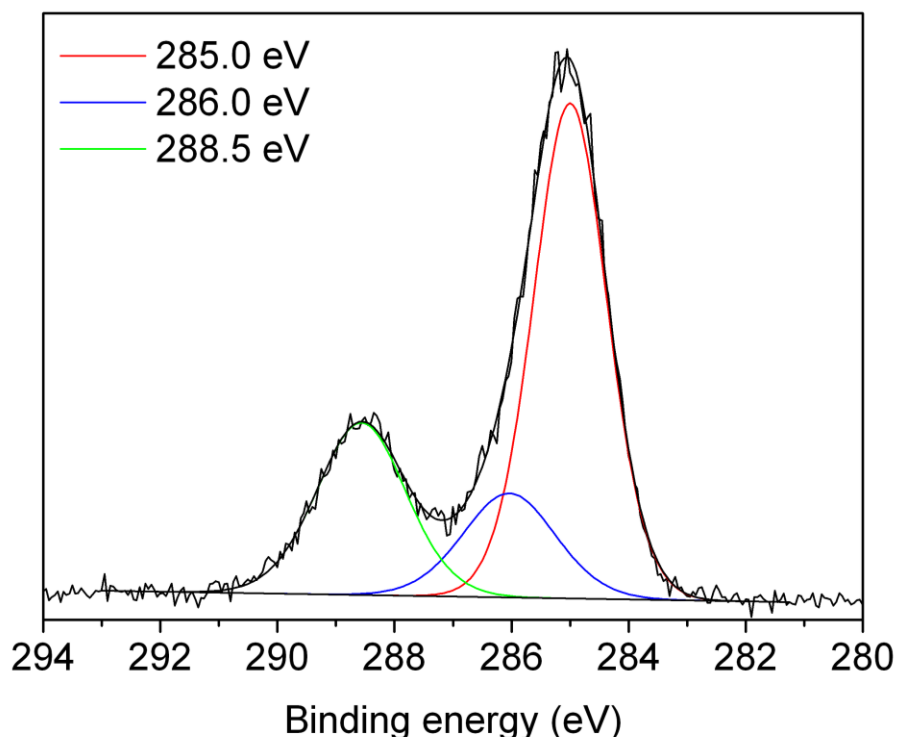


Figure S6. XPS C 1s narrow scan of PAA-A-HAP-150 with curve fit. The peak at 285.0 eV corresponds to *C-C,*C-H, *C-Si and *C-C=O, the peak at 286.0 eV to *C-N and *C-O, and the peak at 288.5 eV to N-*C=O, *COOH/*COO⁻ and CO₃²⁻. These positions for the curve fitted peaks are based on published values of *C-C,*C-H (285.0 eV), *C-Si (284.4±0.2 eV), *C-C=O (285.5±0.2 eV), *C-N (286.0±0.2 eV), *C-O (286.5±0.2 eV), N-*C=O (288.2±0.2 eV), *COOH (289.0±0.2 eV) and CO₃²⁻ (290.3±0.2 eV).(Beamson and Briggs 1992, Ratner and Castner 2009)

References:

Barr, T. L. and S. Seal (1995). "Nature of the use of adventitious carbon as a binding energy standard." *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **13**(3): 1239-1246.

Beamson, G. and D. Briggs (1992). *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, John Wiley and Sons.

Markovic, M., B. O. Fowler and M. S. Tung (2004). "Preparation and Comprehensive Characterization of a Calcium Hydroxyapatite Reference Material." *Journal of Research of the National Institute of Standards and Technology* **109**(6): 553-553-568.

Ratner, B. D. and D. G. Castner (2009). *Electron Spectroscopy for Chemical Analysis. Surface Analysis – The Principal Techniques*. J. C. Vickerman and I. S. Gilmore, John Wiley & Sons, Ltd: 47-112.