A Step Toward Control of the Surface Structure of Biomimetic Hydroxyapatite Nanoparticles: Effect of Carboxylates on the {010} P-rich/Ca-rich Facets Ratio

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SUPPORTING INFORMATION

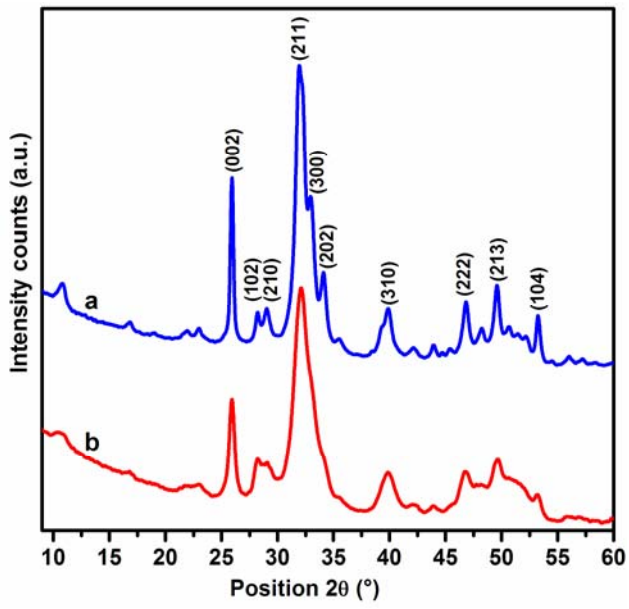

Figure S1. XRD patterns of: a) HA-1, b) HA-2 after outgassing at 573 K. Diffraction peaks assigned on the basis of JCPDS 9-432.

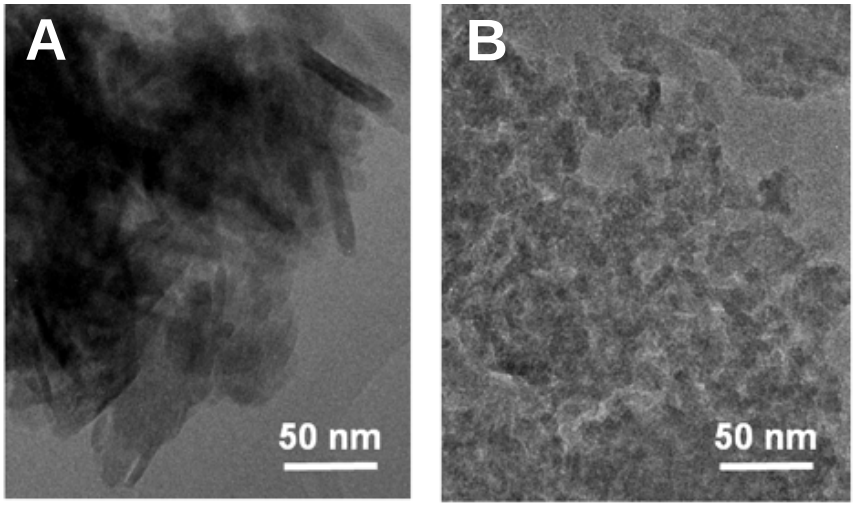

Figure S2. TEM images representative of the size and morphology of: A) HA-1 and B) HA-2 both after outgassing at 573 K.

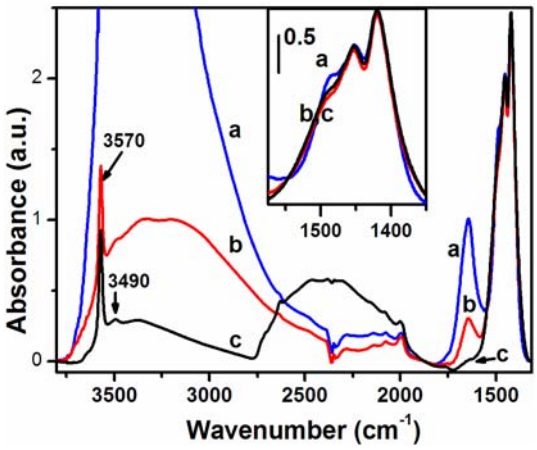

Figure S3. IR spectra of HA-1: (a) in the presence of 20 mbar of H_2O, (b) after 60 min outgassing at b.t., (c) after exchange with D_2O and subsequent 60 min outgassing at b.t.. Inset: zoom of the carbonate ν_{CO} region.

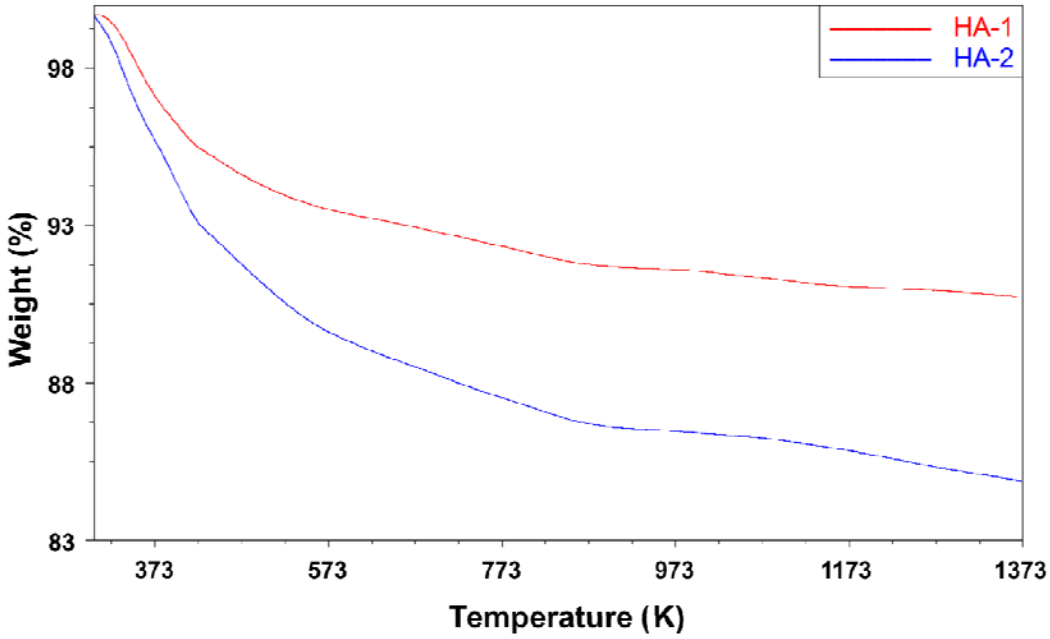

Figure S4: TGA curves HA–1 and HA–2

Comment to the figure

TGA analysis of HA-1 and HA-2 mainly showed three weight losses: (i) from room temperature to about 200 °C due to the adsorbed water, (ii) from about 473 to about 873 K related to structural and "lattice" water and "non-apatitic" HPO_4 ions, (iii) from 873 to 1373 K corresponding to the carbonate ions (Tõnsuaadu, K.; Gross, K. A.; Plūduma, L.; Veiderma, V. A Review on the Thermal Stability of Calcium Apatites. *J. Therm. Anal. Calorim.* **2011**, *110*, 647-659, quoted as ref. 46 in the Main Text.). The different weight loss of HA-1 and HA-2 in the range from room temperature to 473 K can be due to the higher SSA_{BET} of HA-2 that makes it able to adsorb a higher quantity of water. Similarly, the higher weight loss of HA-2 than HA-1 in the range from 473 to 873 K can be due to the greater amount of structural water and disordered "non-apatitic" $(HPO_4)^{2-}$ ions caused by the lower degree of crystallinity. The last thermal degradation (from 873 to 1373 K) was associated to the decomposition of carbonate ions and it was used to evaluate the content of carbonate in the samples.

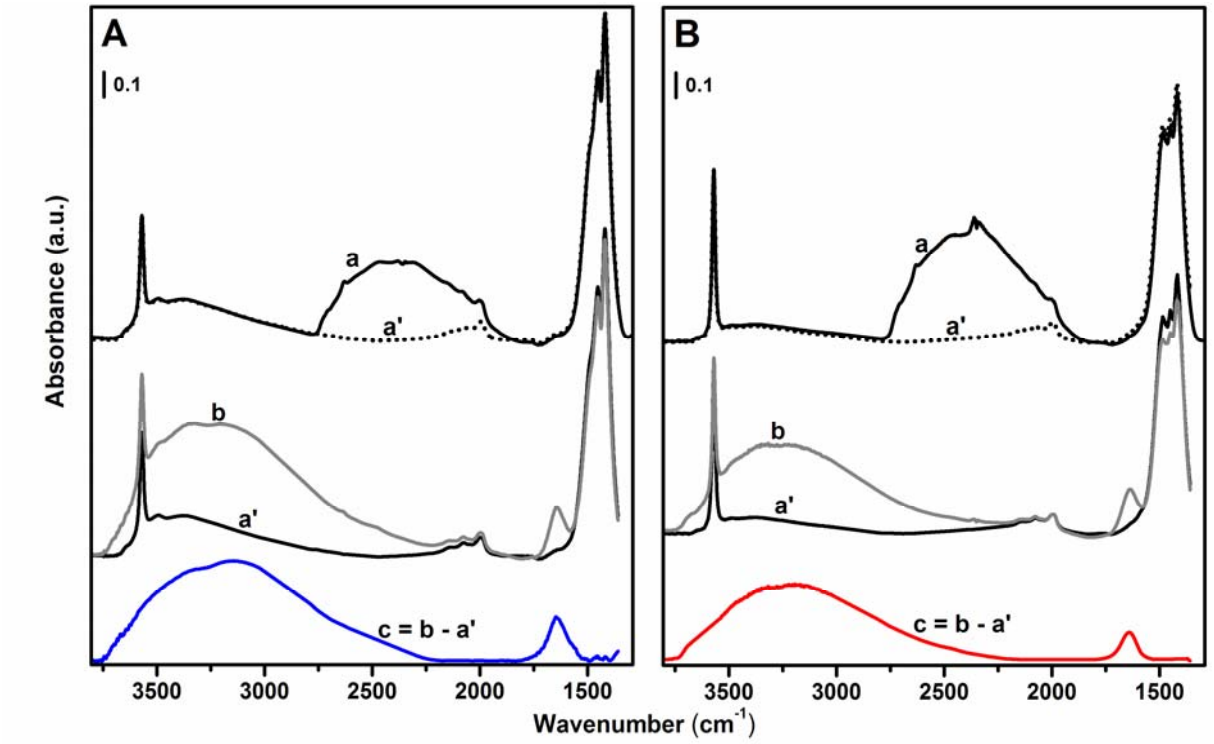

Figure S5. Example of data elaboration for the extraction of the signals related to adsorbed water molecules on HA-1section A and HA-2 section B: a) original spectrum of HA materials exchanged with D_2O and then outgassed at b.t. for 60 min; a') profile derived after compensation of the νD_2O band in the 2750-1800 cm^{-1} range, substituted by a reasonable baseline; b) original spectrum of HA materials outgassed for 60 min at b.t.; c) result of the subtraction of the simulated spectra (a') from spectra (b).

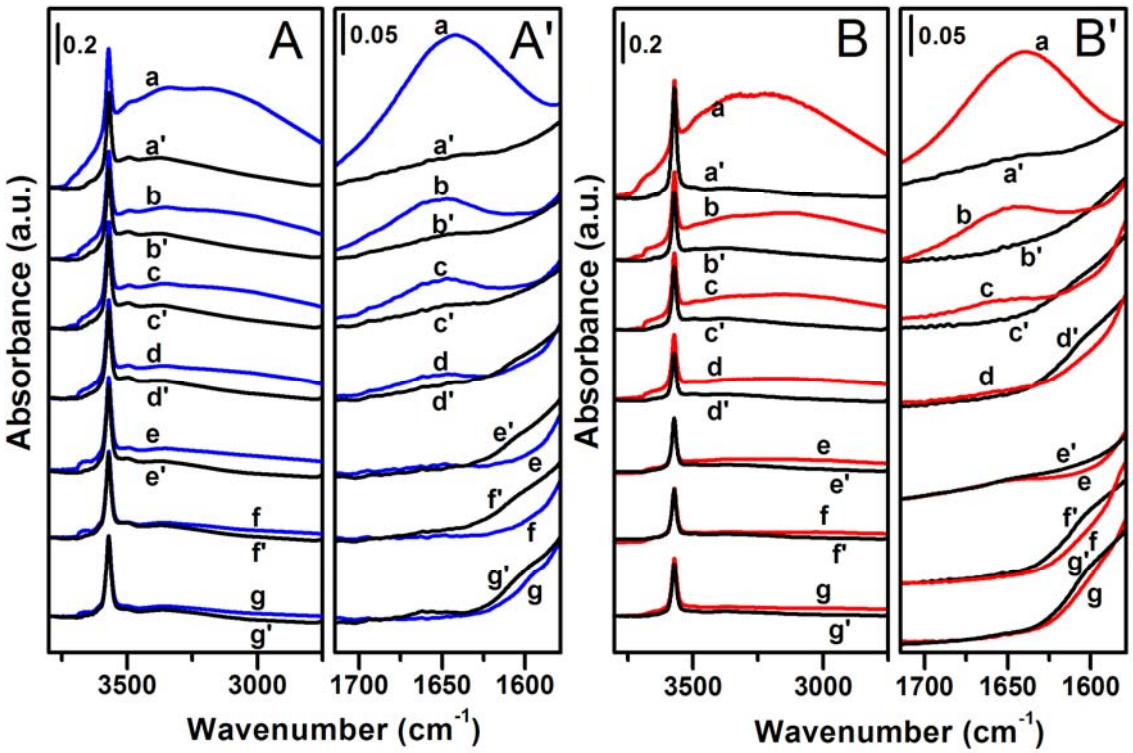

Figure S6. IR spectra of (A,A') HA–1 (B,B') HA–2 in the νOH (A,B) and δH_2O (A',B') regions. In all parts, the lettering is as follows: samples outgassed for 60 min at (a) 323 (b) 373, (c) 403, (d) 433, (e) 473, (f) 523, and (g) 573 K. Spectra a′-g′ were obtained by contacting the samples outgassed at the corresponding temperatures with D_2O vapour (20 mbar) and subsequent outgassing for 60 min at beam temperature.

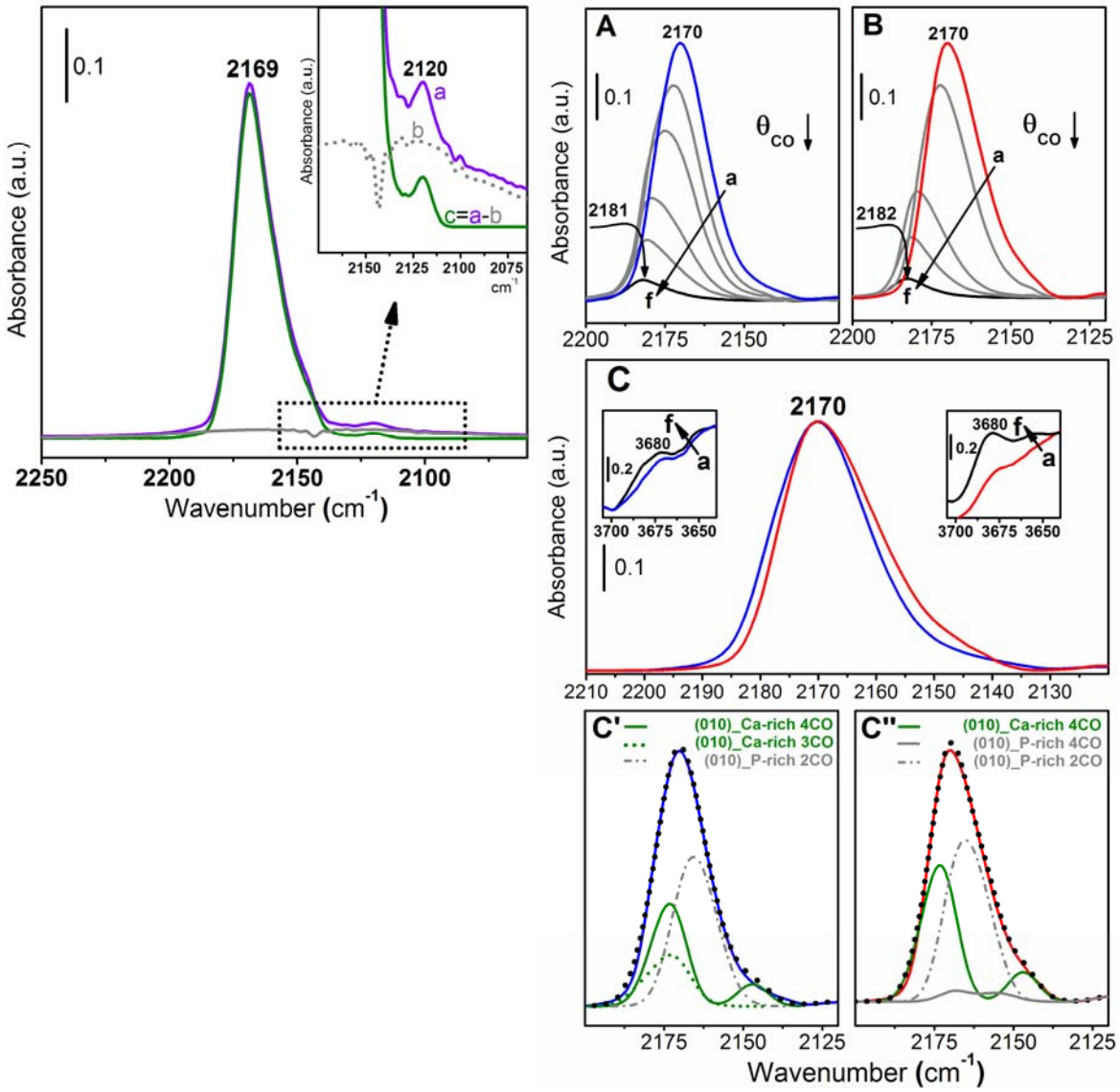

Figure S7. Left panel, example of spectral subtraction operated in order to remove the contribution of CO in gas phase from the spectra of HA samples in contact with CO: a) IR spectrum of 25 mbar CO adsorbed at ca. 100 K on HA–1 pre-outgassed at 433K; b) IR spectrum of 25 mbar CO in the empty cell; c) result of the subtraction between the two spectra in the order a-b. Insert: zoomed view of the 2175-2070 cm^{-1} range. The weak band at 2120 cm^{-1} is due to adsorbed ^{13}CO present in natural abundance. The same data elaboration was performed for all spectra collected in the presence of CO gas pressure down to 5 mbar. Right panel: IR spectra of CO adsorbed at ca. 100 K on A) HA–1 and B) HA–2, both pre-outgassed at 573 K. The lettering is in the sense of decreasing CO pressure, from (a) 25 mbar to (f) outgassing for 1 min. Spectra are reported after subtraction of the spectrum of the material before CO adsorption. Panel C: spectra at maximum CO coverage of HA–1 (blue curve) and HA–2 (red-curve), the same as curves (a) in both A and B panels. In the insets are the original spectra in the 3680-3625 cm^{-1} region (left: HA–1, right: HA–2) of: (a) in contact with 25 mbar CO and (f) after CO outgassing. Panels C',C'': blue and red solid lines are the experimental spectra (the same as in section C), while all the other curves represent B3LYP spectra calculated on the basis of the method reported in ref. [28]. Green solid curves: spectra of 4 CO molecules adsorbed on (010)_Ca-rich surface; green dotted curves: spectra of 3 CO molecules adsorbed on (010)_Ca-rich surface; grey dash-dotted curves: B3LYP spectra of 2 CO molecules adsorbed on (010)_P-rich; grey solid curve: B3LYP spectra of 4 CO molecules adsorbed on (010)_P-rich; in each panel, the sum of the B3LYP spectra resulted in the black-dotted spectrum.

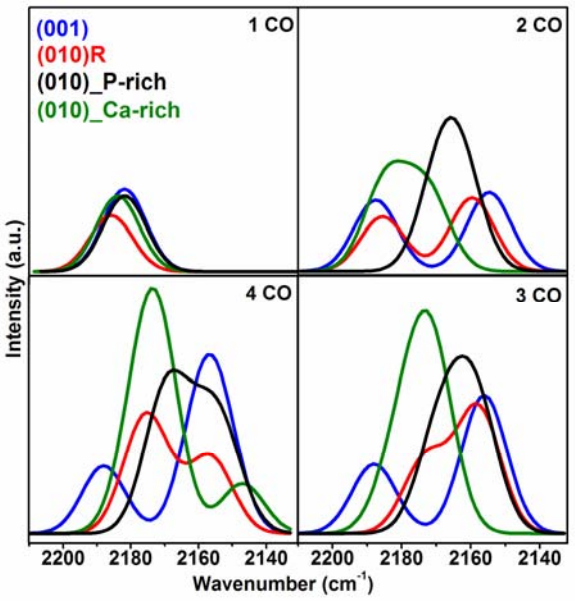

Figure S8. (from ref. 1) Scaled B3LYP harmonic infrared spectra computed resulting from previous work [1] assuming a bandwidth of 15 cm−1 for each component. In each panel are the spectra calculated for 1 (top-left), 2 (top-right), 3 (bottom-right), and 4 (bottom-left) CO molecules on the four HA surface termination considered. The colour code for the association spectrum surface is in the top-left panel.

Reference

[1] (the same as ref. 26 in the main text) Chiatti, F.; Corno, M.; Sakhno, Y.; Martra, G.; Ugliengo, P., Revealing Hydroxyapatite Nanoparticle Surface Structure by CO Adsorption: A Combined B3LYP and Infrared Study. *Journal of Physical Chemistry C* **2013,** 117, (48), 25526-25534

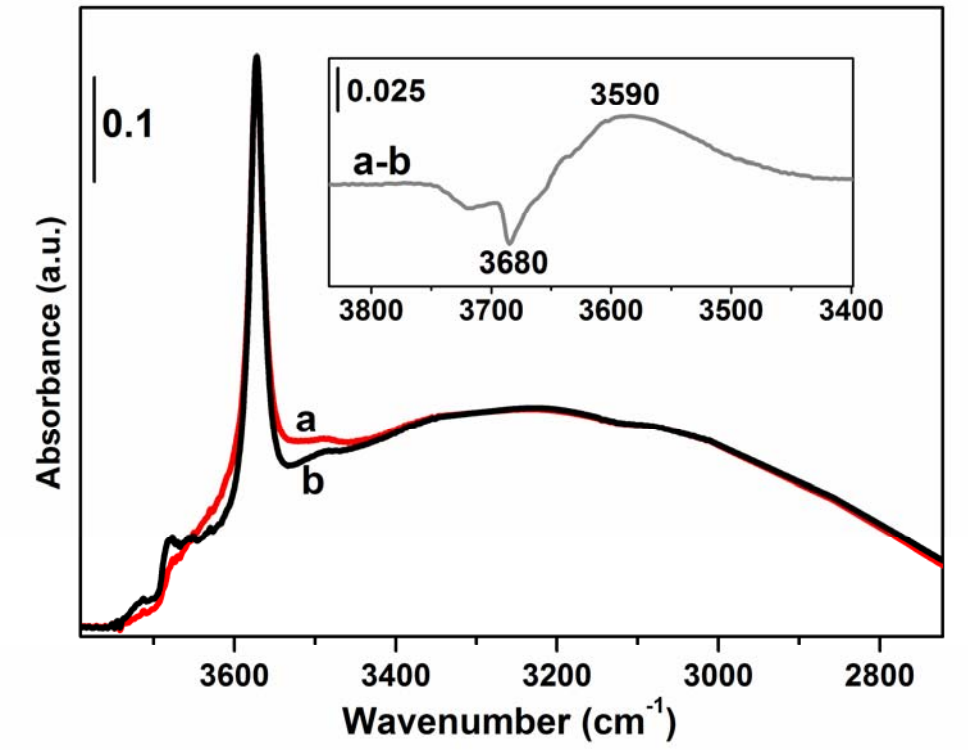

Figure S9. IR spectra, in the 3800-2700 cm^{-1} range of HA–2 preoutgassed at 433 K and then cooled down to 100 K and: a) contacted with 25 mbar CO; b) outgassed for 1 min. Inset: result, in the 3820-3400 cm^{-1} of the difference (spectrum a) – (spectrum b).