

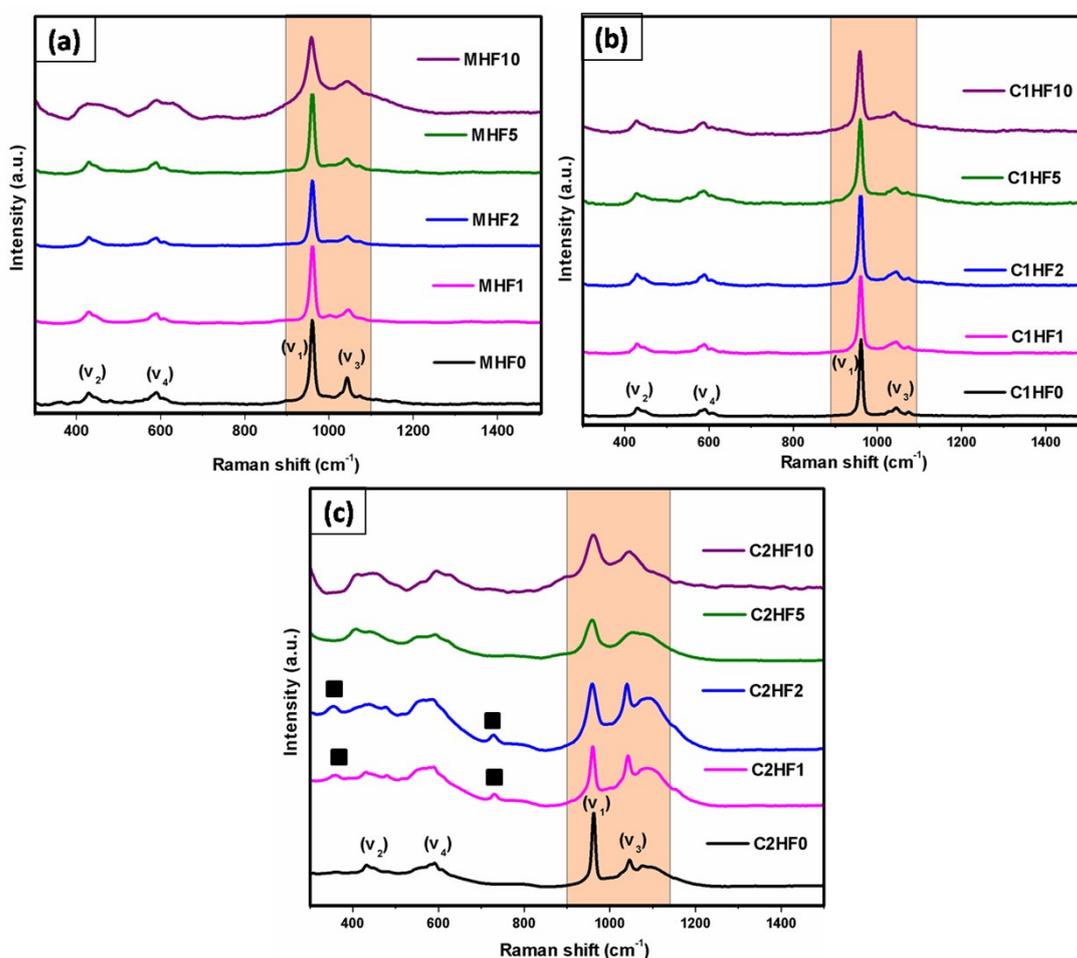
## Insights into Apatite Mineralization Potential of Thermally Processed Nanocrystalline $\text{Ca}_{10-x}\text{Fe}_x(\text{PO}_4)_6(\text{OH})_2$

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**Fig. S1** Raman spectra of pure and iron incorporated nHAp samples treated with (a) microwave, (b) 600°C and (c) 800°C temperatures. A highlighted region in spectra corresponds to changes in  $\text{PO}_4^{3-}$  ( $\nu_1$ ) mode.

Raman spectra of pure nHAp and iron-incorporated samples are displayed in Fig. S1(a-c). Pure nHAp exhibits a strong symmetric  $\text{PO}_4^{3-}$  ( $\nu_1$ ) stretching band around 960  $\text{cm}^{-1}$  at all thermal treatments. The band at 430  $\text{cm}^{-1}$  corresponds to bending ( $\nu_2$ ) vibrational mode of

P–O bond. The two bands resolved at 1040  $\text{cm}^{-1}$  and 1080  $\text{cm}^{-1}$  can be attributed to asymmetric  $\text{PO}_4^{3-}$  ( $\nu_3$ ) stretching modes. Another vibrational band 580  $\text{cm}^{-1}$  was observed due to bending vibrational character of the P–O ( $\nu_4$ ) bond [1, 2]. The spectra of Fe incorporated samples exhibits all the vibrational bands of pure nHAp as aforementioned. In addition, Fe incorporated nHAp revealed two additional small bands at 357  $\text{cm}^{-1}$  and 730  $\text{cm}^{-1}$  demonstrating the existence of iron by bonding with oxygen molecules [3, 4], which is more evident from 800 °C calcinated samples. Moreover, increased iron concentration showed peak broadening at 960  $\text{cm}^{-1}$  that can be attributed to the improved decomposition rate of nHAp structure, making it more calcium deficient [5] and corroborates with XRD result.

## References

- [1] C.S. Ciobanu, S.L. Iconaru, P. Le Coustumer, L.V. Constantin and D. Predoi, Antibacterial activity of silver-doped hydroxyapatite nanoparticles against gram-positive and gram-negative bacteria, *Nanoscale Res. Lett.*, 2012, 7(1), 324.
- [2] G.R. Sauer, W.B. Zunic, J.R. Durig and R.E. Wuthier, Fourier-transform Raman spectroscopy of synthetic and biological calcium phosphates, *Calcif. Tissue Int.*, 1994, 54(4), 414-420.
- [3] M. Hanesch, Raman spectroscopy of iron oxides and (oxy) hydroxides at low laser power and possible applications in environmental magnetic studies, *Geophys. J. Int.*, 2009, 177(3), 941-948.
- [4] A.M. Jubb and H.C. Allen, Vibrational spectroscopic characterization of hematite, maghemite and magnetite thin films produced by vapour deposition, *ACS Appl. Mater. Interfaces*, 2010, 2(10), 2804-2812.
- [5] S. Zou, J. Huang, S. Best and W. Bonfield, Crystal imperfection studied of pure and silicon substituted hydroxyapatite using Raman and XRD, *J. Mater. Sci. Mater. Med.*, 2005, 16(12), 1143-1148.