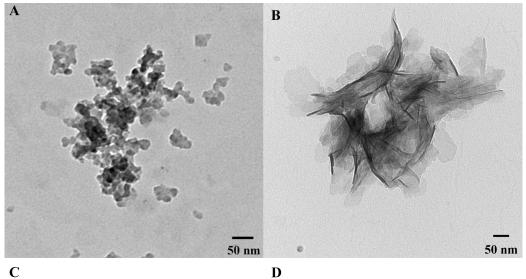
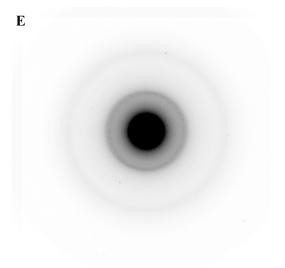
**Supplement Figure 1**. TEM micrographs of ACP (**A**) and LCCA (**B**), and their corresponding diffraction patterns (**C**) and (**D**), Diffraction pattern (C) is taken from a bare carbon coated grid.



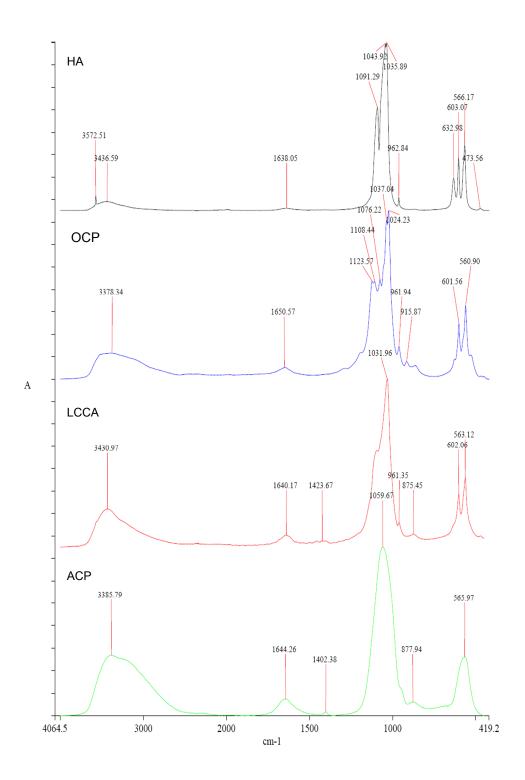








Supplement Figure 2. Absorbance FTIR spectra of HA (black), OCP (blue); LCCA (red) and ACP (green).



The FTIR spectrum of HA is characterized by a sharp peak at 3572.5 cm<sup>-1</sup>, corresponding the hydroxyl stretching band of structural OH<sup>-</sup> groups in the HA crystalline lattice, a doublet of phosphate  $v_4$  peaks at 603 and 566 cm<sup>-1</sup> and a split  $v_3$  phosphate absorbance band with two maxima around 1040 cm<sup>-1</sup> and 1090 cm<sup>-1</sup> (Lehr *et al.*, 1967; Ou-Yang *et al.*, 2000; Rehman and Bonfield, 1997). The highly crystalline stoichiometric HA is also characterized by a band at 633 cm<sup>-1</sup> arising from OH<sup>-</sup> libration (Ou-Yang *et al.*, 2000).

The spectrum of OCP lacks the sharp  $3572.5 \text{ cm}^{-1}$  band and has 2 well defined phosphate  $v_4$  peaks at 562 and 602 cm<sup>-1</sup>. Its  $v_3$  band is much broader than HA with the maximum at 1024 cm<sup>-1</sup> and with a number of smaller phosphate  $v_3$  peaks at 1076, 1008 and 1124 cm<sup>-1</sup>. It also contains a well distinguished HPO<sub>4</sub><sup>-2</sup> asymmetric stretching peak at 916 cm<sup>-1</sup> which is absent in HA spectra. All these features are characteristic of stoichiometric OCP mineral (Dekker *et al.*, 2005; Wang *et al.*, 2008).

The spectrum of low crystallinity carbonated apatite (LCCA) contains a  $v_3$  band with the maximum at 1032 cm<sup>-1</sup> and a shoulder around 1100 cm<sup>-1</sup> and doublet  $v_4$  band with maxima at 563 and 602 cm<sup>-1</sup>. (Gadaleta *et al.*, 1996; Ou-Yang *et al.*, 2000; Termine and Posner, 1966). An absorbance band in the 1400-1500 cm<sup>-1</sup> region indicates the presence of carbonate ions in the mineral. The carbonate content has been determined to be ~1.1% w/w using carbonate  $v_3$  to phosphate  $v_3$  intensity ratio as described elsewhere (Elangovan *et al.*, 2007; Ou-Yang *et al.*, 2001).

The ACP spectrum contains characteristic broad  $v_4$  and  $v_3$  phosphate bands with the maxima around 565 cm<sup>-1</sup> and 1056 cm<sup>-1</sup>, respectively, as reported elsewhere (Gadaleta *et al.*, 1996; Ou-Yang *et al.*, 2000; Termine and Posner, 1966). The strong broad bands with maxima at 1644 and 3380 cm<sup>-1</sup> indicate the presence of bound water. The absorbance peak in the 1400-1500 cm<sup>-1</sup> region suggests the presence of small amount of CO<sub>3</sub><sup>-2</sup> in the mineral, between 0.5 and 1% w/w based on the calculated carbonate/phosphate intensity ratio.

## **References:**

Dekker RJ, de Bruijn JD, Stigter M, Barrere F, Layrolle P, van Blitterswijk CA (2005). Bone tissue engineering on amorphous carbonated apatite and crystalline octacalcium phosphate-coated titanium discs. *Biomaterials* 26(25):5231-5239.

Elangovan S, Margolis HC, Oppenheim FG, Beniash E (2007). Conformational Changes in Salivary Proline-Rich Protein 1 upon Adsorption to Calcium Phosphate Crystals. *Langmuir* 23(22):11200-11205.

Gadaleta SJ, Paschalis EP, Betts F, Mendelsohn R, Boskey AL (1996). Fourier transform infrared spectroscopy of the solution- mediated conversion of amorphous calcium phosphate to hydroxyapatite: New correlations between X-ray diffraction and infrared data. *Calcif. Tissue Int.* 58(1):9-16.

Lehr JR, Brown EH, Fraizer AW, Smith JP, Thrasher RD (1967). Crystallographic Properties of Fertilizer Compounds Muscle Shoals: National Fertilizer Development Center.

Ou-Yang H, Paschalis EP, Boskey AL, Mendelsohn R (2000). Two-dimensional vibrational correlation spectroscopy of in vitro hydroxyapatite maturation. *Biopolymers* 57(3):129-139. Ou-Yang H, Paschalis EP, Mayo WE, Boskey AL, Mendelsohn R (2001). Infrared microscopic imaging of bone: Spatial distribution of CO32. *J. Bone Miner. Res.* 16(5):893-900.

Rehman I, Bonfield W (1997). Characterization of hydroxyapatite and carbonated apatite by photo acoustic FTIR spectroscopy. J. Mater. Sci.-Mater. Med. 8(1):1-4.

Termine JD, Posner AS (1966). Infra-Red Determination of Percentage of Crystallinity in Apatitic Calcium Phosphates. *Nature* 211(5046):268-270.

Wang H, Lin CJ, Hu R, Zhang F, Lin LW (2008). A novel nano-micro structured octacalcium phosphate/protein composite coating on titanium by using an electrochemically induced deposition. *J. Biomed. Mater. Res. Part A* 87A(3):698-705.