Supplementary information for

Amorphous or Nanocrystalline Calcium Phosphate as efficient nanocarriers of elicitors in vineyards

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S1. Rietveld analysis of the diffraction patterns

Diffraction patterns of nanocrystalline materials were analyzed using the Materials Analysis Using Diffraction (MAUD) software.[1] Instrumental line broadening was determined by measuring the pattern of the standard LaB_6, using the same conditions and collection parameters. A diffractogram of ACP was used as background. Scale factor and unit cell parameters (*a* and *c*) were refined. Other atomic thermal parameters, site occupancy factors and atomic position were maintained fixed. The anisotropic crystallite-size and microstrain contributions to line broadening were determined by the POPA model implemented in MAUD. Crystallite size of the 002 and 300 reflections were used as approximation of the length (L_{002}) and width (D_{300}) of the nanocrystals, respectively, and compared with the size measurements from TEM (Table S1).

S2. X-ray photoelectron spectroscopy

The surface of Ap and Ap-MeJ NPs has been analysed by X-ray photoelectron spectroscopy (XPS) to evaluate its composition before and after MeJ adsorption. XPS spectra were acquired on a Kratos Axis Ultra-DLD (CIC-UGR) using monochromatic Al-Kα radiation.

Figures

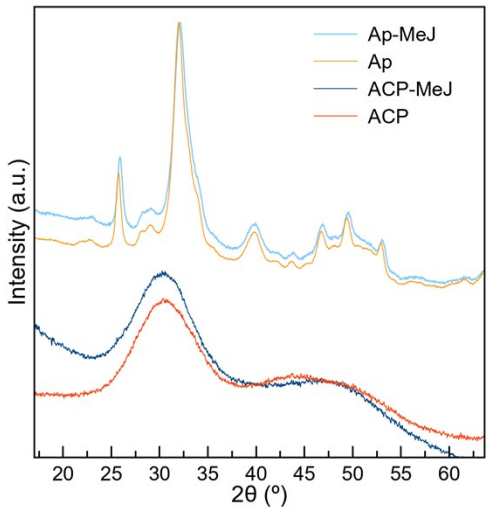

Figure S1. XRD patterns of ACP, ACP-MeJ, Ap and Ap-MeJ powdered samples.

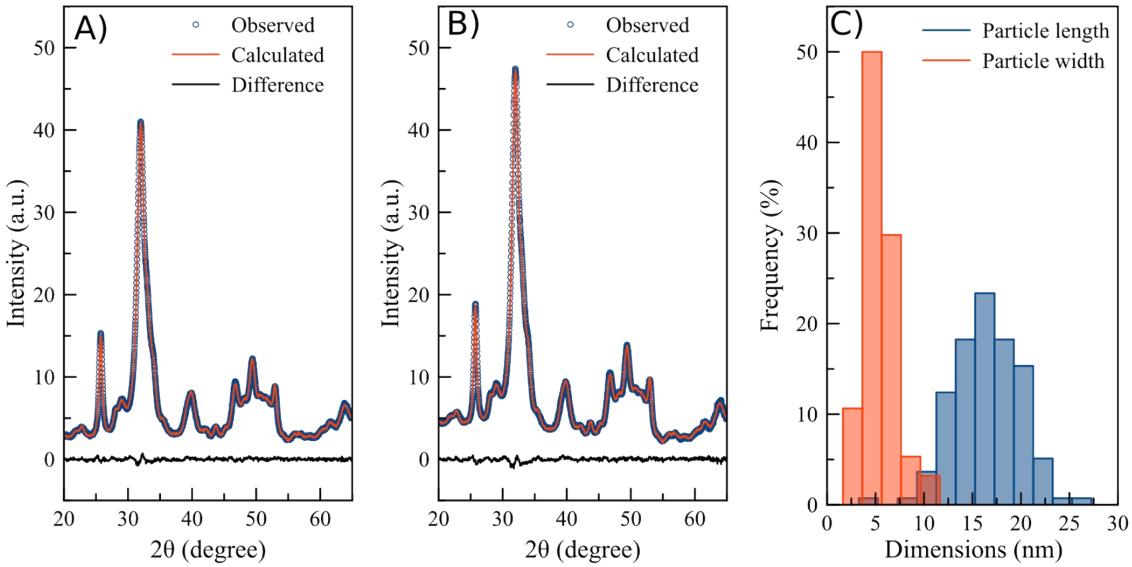

Figure S2. (A,B) Rietveld refinement of the diffraction patterns collected for Ap (A) and Ap-MeJ (B). (C) Histograms of the Ap-MeJ nanoparticles length and width as measured from TEM imaging (100 particles were measured).

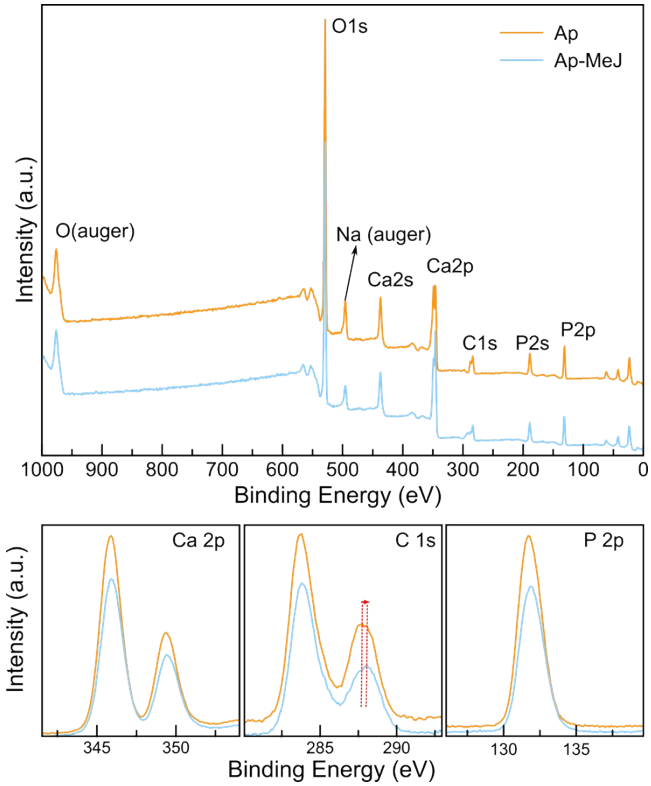

Figure S3. The XPS survey spectra of Ap and Ap-MeJ NPs. High-resolution XPS spectra of Ap and Ap-MeJ focusing on the P 2p, C 1s and Ca 2p peaks.

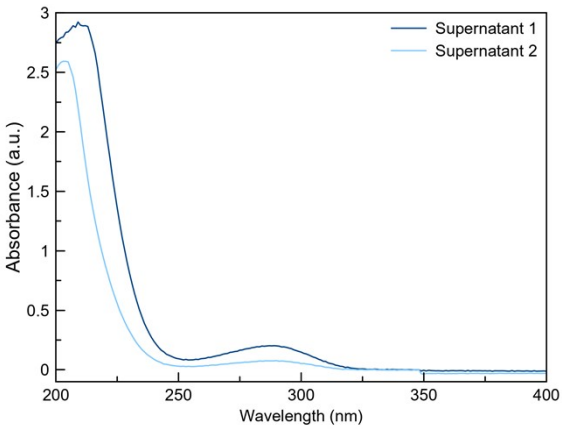

Figure S4. UV-Vis spectra of the supernantants collected after 72 hours of delivery in water (supernatant 1) and a second cycle of delivery in water (supernatant 2). The band centred at 291 nm is due to the absorption of MeJ.

Tables

Table S1. Crystallite size (from Rietveld refinements) and particle size (from TEM imaging) of Ap (before adsorption) and Ap-MeJ (after adsorption).

	Crystal Size (nm)		Particle size (nm)	
	Length (L_{002})	Width (D_{300})	Length	Width
Ap	20.5	7.8	17.6 ± 2.9	4.7 ± 0.9
Ap-MeJ	20.2	8.0	16.5 ± 3.3	5.5 ± 1.6

Table S2. Surface charge of ACP and Ap (Ap and Ap* with modified surface) before and after MeJ adsorption. MeJ loading capacity of ACP-MeJ, Ap-MeJ and Ap*-MeJ estimated by UV-Vis spectroscopy.

Sample	**ζ-potential (mV)**		**Loading (%wt)**
	Before	After	
ACP-MeJ	-10.53±0.08	-6.2±1.0	10.6±0.5
Ap-MeJ	-21.6±0.2	-16.4±2.2	4.5±1.1
Ap*-MeJ[(a)]	-0.7±0.2	-1.8±1.1	6.9±0.4

[(a)] Ap-NPs were immersed in a sodium hydroxide solution (1M) for 1 hour to remove citrate molecules from Ap surface and obtain Ap* NPs with less negative surface charge.

References

(1) Lutterotti, L. Total Pattern Fitting for the Combined Size–Strain–Stress–Texture Determination in Thin Film Diffraction. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **2010**, *268* (3), 334–340.