

Biomimetic calcium phosphate nanoparticles as promising nanocarriers for sustainable agriculture

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The application of conventional fertilizers, supplying the macronutrients as nitrogen (N), phosphorus (P) and potassium (K), is one of the current solutions to face the increase in global food demand.¹ However, only a small percentage of the NPK nutriens is assimilated by the plants, being the rest eventually washed into water bodies through leaching and surface run-off, or lost by volatilization under reduced conditions. Indeed, the low nutrient use efficiency (NUE) of convential treatments is causing serious environmental consequences, such as eutrophication.¹ Thus, the use of more efficient practices is crucial for ensuring increasing yields without compromising environmental integrity or public health.¹ Nanotechnology offers great promises as an innovative tool for a controlled and efficient delivering of active species in plants.² Biomimetic calcium phosphate (CaP) nanoparticles, similar to the mineral component of bone and teeth, have been widely explored in nanomedicine as bone-repair materials and multifunctional nanocarriers.³ In fact, CaPs exhibit excellent biocompatibility and biodegradability, can be easily doped or functionalized with active species (e.g., plant macronutrients) and show a pH-dependent solubility and thus, a pHresponsive release of the loaded species.⁴ Despite all these exceptional properties and the fact that they are intrinsically rich in P and Ca (important plant macronutrients), yery few reports can be found about the use of CaP nanoparticles in Agriculture.^{5,6} Nonetheless, the doping of CaP nanoparticles with essential macronutrients has not been yet explored. We will show a simple and easily scable protocol to obtain multinutrient nano-fertilizers based on the doping of calcium phosphate (CaP) nanoparticles. The nanofertilizers have been in-depth characterized in terms of composition, structure and particle size. We have demonstrated that the nanoparticles in aqueous media provide a slow and gradual release of the macroand micronutrients. Experiments on plants have been also performed to demonstrate the increase of NUE with the use of nanoparticles in comparison with conventional treatments. This work opens the possibility to engineer complex nanofertilizer (NPK) with multiple nutrient kinetic for targeted treatment in agriculture.

References

- [1] Tilman, D., Cassman, K. G., Matson, P. A., Naylor, R. & Polasky, S. Nature, 418 (2002) 671
- [2] DeRosa, M. C., Monreal, C., Schnitzer, M., Walsh, R. & Sultan, Y. Nat. Nanotechnol, 5 (2010) 91
- [3] Gómez-Morales, J., Iafisco, M., Delgado-López, J. M., Sarda, S. & Drouet, C. Prog. Cryst. Growth Charact. Mater. 59 (2013) 1–46
- [4] Dorozhkin, S. V & Epple, M. Angew. Chemie Int. Ed. 41, (2002) 3130–3146
- [5] Kottegoda, N., Munaweera, I., Madusanka, N. & Karunaratne, V. Curr. Sci. (2011) 73–78
- [6] Giroto, A. S., Guimarães, G. G. F., Foschini, M. & Ribeiro, C. Sci. Rep. 7 (2017) 46032