New biocatalytic composites assembled by metal ion coordination

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We report a new protocol for the synthesis of organic/inorganic protein nanohybrids that leads to highly stable catalytic composites. Our approach is based on the combination of three advanced protein-stabilization techniques, i.e. the encapsulation via single enzyme polyacrylamide nanogels (SEN) [1], the confinement inside metal organic frameworks (MOFs) [2], and the embedment into organic/inorganic hybrid nanoflower structures [3]. Using SEN methodology [4-5], we are able to wrap individual enzymes with a porous polymer that is fully decorated with imidazole motifs. In presence of a divalent cation, such as zinc or copper, as it happens in MOFs, the nanogels aggregate driven by the imidazole-cation coordination and create nanoflower-like structures. Fabricated hybrids show higher activity and stability than other nanoflowers synthesized by previously reported protocols. Moreover, we were able to overcome common issues related to the performance of the biocatalyst: protein recovery (SENs are homogeneous catalysts), substrate transfer and diffusion to the cavity of the hybrids (main issue in protein-MOFs), and stability at low pH and the restriction to limited number of divalent cations (inorganic biomineralization of nanoflowers). Also, our approach allows to extend the nature of cations used so far for the biomineralization, including silver and gold salts. On top of it, this is the first report in which Ni and Cd protein nanoflowers are successfully fabricated.
Finally, this work highlights the significant potential for transition metal ion coordination as a tool for directing the assembly of hybrid materials.

References

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Figures

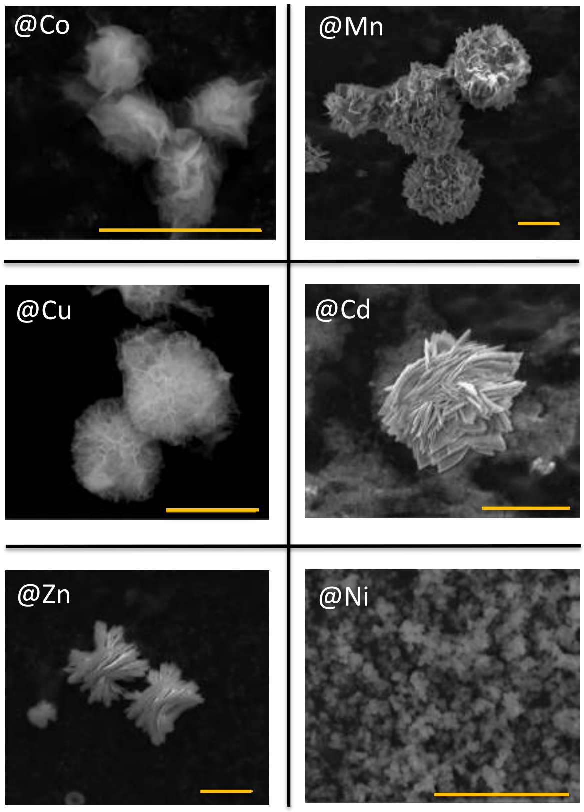

Figure 1: ESEM images of biocatalytic hybrids with peroxidase activity fabricated using an array of transition metal ions: Co(II), Mn(II), Cu(II), Cd(II), Zn(II), Ni(II). Bar: 5 µm