**Supplementary Table 1.** Key characteristics of bionanocatalysts.

|  |  |  |
| --- | --- | --- |
| Property | Description | Ref. |
| Nanometric dimensions | Materials with sizes between 1 and 100 nm (nanoscale) exhibit fluctuations in averaged properties due to the motion and behavior of their individual particles (in contrast to what is observed in the bulk) that create ‘surface area effects’ (also referred to as quantum effects). These effects are due to the geometry of the material, which, in these low dimensions, can have a dramatic effect on the quantized states and thus the material properties. Bionanocatalysts have particle sizes in the order of 1-15 nm and 1-5 nm for cancer applications. | [84] |
| Catalysis | The intrinsic catalytic properties of the metals supported on inorganic oxide matrices of which the bionanocatalysts are composed allow them to carry out reactions that would otherwise not take place by decreasing the activation energy required for the processes to occur. In this way, bond cleavage (C-C, C-N) is possible and thus the destabilization of the desired molecule is possible. | [85] |
| High surface-area-to-volume ratio | An increase of the ratio by the miniaturization process allows to obtain a large number of active sites for the reactants, which results in a higher reactivity of the bionanocatalyst surface and, therefore, in an increase of the speed of the catalyzed reactions. Also, a large surface area allows the immobilization of metallic NPs. | [86] |
| Mesoporous architecture | Mesoporous materials have high surface area (800-1400 m2/g), large pore volumes, and tunable pore dimensions (2-50 nm), which are of great interest for heterogenous catalysis, as they facilitate mass transfer and allow a high concentration of active sites per mass. | [87] |
| Metal synergic effects | Metals exhibit intrinsic therapeutic properties related with their own characteristics. When incorporated into oxide matrices (such as bionanocatalysts), metals develop an increase in their functionalities through a synergistic interaction with the carrier; nonetheless, it is highly required to address compatibility and toxicity issues related to multiple metal species for biomedical applications. In this regard, bionanocatalysts increase their functionalities such that non-toxic concentrations are sufficient to obtain therapeutic effects attributed to higher concentrations. | [88] |
| Biocompatibility | The organic functionalization of bionanocatalysts endows them with physicochemical properties that mimic physiological ones, so that the organism does not activate labeling and elimination pathways as it does not recognize them as potential aggressors. | [89] |
| Selectivity | Appropriate modifications by ligands on nanocatalysts can dramatically improve the activity/selectivity of specific catalytic reactions. In general, the promoting effect of ligands in NPs can be classified into three categories: (1) their steric effects, (2) their electronic effects, and (3) the solubility effects. In the case of bionanocatalysts, organic functionalization allows them to interact only with damaged cells and catalyze bond cleavage only on nucleotides. | [90] |
| Stability | Bionanocatalysts are thermally stable and do not sinter or volatize at temperatures up to 450°C. | [91] |