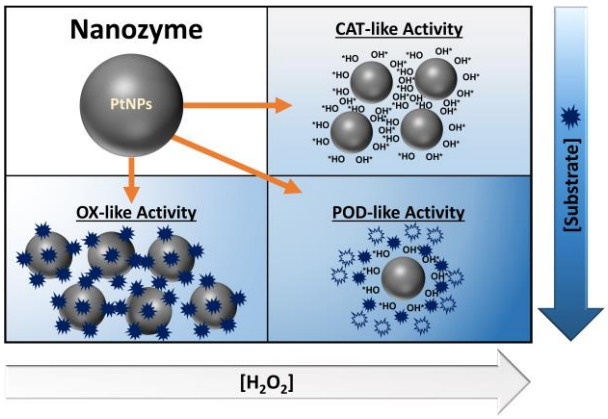
Unravelling the Multi-Enzymatic Activity of Platinum Nanoparticles

Lorenzo Cursi
Giulia Mirra, Luca Boselli* and Pier Paolo Pompa*
Nanobiointeractions&Nanodiagnostics, Istituto Italiano di Tecnologia, Genova, Italy
Lorenzo.cursi@iit.it

Nanozymes are a new class of nanomaterials exhibiting catalytic activities similar to natural enzymes.[1] Thanks to their versatility, robustness, low manufacturing costs, and long shelf life, they have been widely applied in diagnostics, environmental remediation, and nanomedicine.[2] However, the differences between the catalytic mechanisms of nanozymes and biological enzymes are often overlooked in literature, and some nanozymes have recently been questioned as catalysts due to their low activity and specificity.[3] Hence, studies aiming at clarifying the specific catalytic mechanisms and the advantages/drawbacks of nanozymes with respect to their natural counterparts are extremely important, especially for emerging nanomaterials. In this framework, platinum nanoparticles (PtNPs) possess multi-functional enzymatic activity, displaying oxidase- (OX), peroxidase- (POD), catalase- (CAT), and superoxide dismutase-like (SOD) activities, which attracted great interest for reactive oxygen species scavenging,[4] antioxidant detection,[5, 6] and antimicrobial activity.[7] Nevertheless, there is still much to disclose concerning the mechanisms underlying PtNP activities and their dependence on chemical/physical and environmental parameters. Such lack of knowledge hinders the development of new effective applications. Here, we systematically investigated the OX, POD, and CAT activities of citrate-capped PtNPs, as a function of pH, temperature, buffer media, and substrates. We observed that PtNPs are generally more active at acidic pH, and their activity increases with temperature. Different colorimetric assays, commonly used to test nanozymes' activities, were found to generate misleading results, due to the instability of the chromogenic probes and/or interference of the solvents, employed to solubilize the substrates even in commercial kits. The mechanisms underlying the PtNP catalytic properties were investigated using detection reagents with high selectivity for specific radicals. The three different enzyme-like activities resulted deeply interconnected: they occur simultaneously, but one can be favoured over the others tuning the relative concentration of reagents and catalyst. Eventually, the performances of the nanozyme were compared with three natural enzymes (one for each catalytic activity) proving that PtNPs are as active as their natural counterparts in physiological conditions and even more efficient in harsh conditions. In summary, the present study provides a comprehensive characterization of PtNP multi-enzyme functionalities and important insights on their catalytic mechanisms, which are of pivotal interest for the implementation of Pt-based nanozymes in sensing and nanomedicine applications.



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