Comparison of oxidase activity of CeO_2 nanoparticles against laccase enzymes

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Nanozymes are defined as "nanomaterials with enzyme-like characteristics" [1]. The interest for them is growing as they present lower cost and higher stability in comparison with natural enzymes. Four types of redox enzymes had been mimicked by nanozymes: peroxidase, oxidase, catalase and superoxidedismutase (SOD) [2]. In biosensing applications catalases have been extensively characterized. However, as they need H_2O_2 as a substrate their application in point-of-care devices is not straight-forward. In this sense, oxidase – like nanozymes allows to think in a better solution simplicity as they can catalyze the oxidation of a substrate with the assistance of molecular oxygen dissolved in the solution. A lot of examples of this kind of activity in nanozymes has been reported, among them, ceria nanoparticles (CeO_2-NPs) is a particular interesting candidate that has proved to be able to operate in that mode. However, despite the numerous studies with CeO_2-NPs as oxidase published up to date, the comparison of the response between this nanozyme and natural oxidase-enzyme as laccase has been scarcely studied up to date.

In this work, a comparison of the oxidase activity both CeO_2-NPs and laccase is presented. Ferrocyanide ($K_4[Fe(CN)_6]$]) has been chosen as a mediator. We perform a steady-state kinetic assay at fix concentration of substrate and different concentrations of two different batches of Laccase (A and B) and CeO_2-NPs ranging from $5 \cdot 10^{-4}$ to 0.2 mg/mL. Absorbance measurements were done by recording the 420 nm peak increase in time corresponding to the oxidation of the mediator. Figure 1A shows the obtained results at different times (10 and 60 minutes). It can be seen that the amount of oxidized substrate in time depends on laccase batch. Under the same conditions, nanoceria showed a lower response than its living competitors. In order to compare the different catalytic performances, we characterized the enzymatic activity of the two different batches of laccases and the CeO_2-NPs. After that, we normalized the catalytic response of both laccases and CeO_2-NPs displayed in figure 1B to enzymatic units. It can be seen that both laccase batches and ceria align on the same response curve that follow the same behavior suggesting that under the given conditions, nanoceria perfectly mimics the behavior of a laccase enzyme.

References

[1] Hui Wei and E. Wang, Chem. Soc. Rev., 42 (2013) 6060-6093
[2] Yanyan Huang, Jinsong Ren and Ziaogang Qu, Chem. Rev., 119, 6 (2019) 4357-4412

Figures

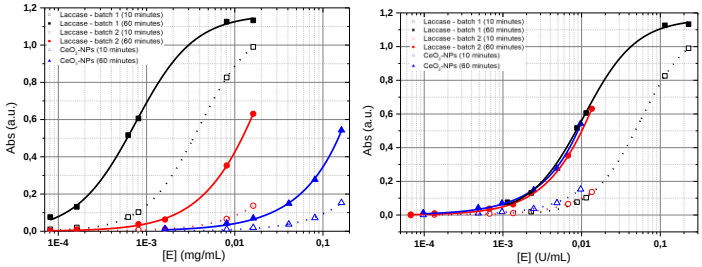

Figure 1: Effect of CeO_2-NPs or Laccase on the kinetics of ferrocyanide (420 nm) oxidation. A: Expressed in mg/mL. B: Expressed in (U/mL)