Photocatalytic in situ hydrogen peroxide production for biocatalysis based on peroxidases

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Motivation

The use of enzymes such as oxidoreductases in organic synthesis offers highly selective, efficient and therefore sustainable chemical processes. However, industrial utilization of oxidoreductases is often limited by their requirement of expensive cofactors. Peroxidases have the advantage that their cofactor, hydrogen peroxide, is economically priced and can be easily synthesized. The challenge for utilization of peroxidases is their poor stability against their own cofactor, hydrogen peroxide. This problem can be overcome by employing in situ generation techniques that guarantee a constant but low hydrogen peroxide concentration. However, the state of the art methods for achieving this all have certain disadvantages of their own, a satisfactory solution has yet to be found. Heterogeneous photocatalysis will be studied here as a possible alternative to previous methods that could overcome their drawbacks.

Aim

The aim of the project is to provide the peroxidase with ideal and therefore mild concentration of hydrogen peroxide to raise the stability of the enzyme and thereby TTN (total turnover number) of the reaction. For this purpose, the photocatalytic generation of hydrogen peroxide by titanium dioxide and other photocatalysts (e.g. Fe₂O₃, ZnO) will be explored and optimized under different conditions. Afterwards, this process will be combined with the peroxidase to form an integrated photobiocatalytic process (cf. Figure 1).

Advantages of this system are the homogeneous allocation of hydrogen peroxide within a set concentration regime and avoidance of detrimental concentration peaks. Also, no additional reagents are needed and separation of the catalyst by filtration is trivial. The only energy source needed is light, which is provided contactless from outside the reactor.

H₂O₂-build-up with TiO₂ photocatalysis

![Graph showing H₂O₂ build-up with TiO₂ photocatalysis](image)

Figure 2: Photocatalytic H₂O₂ production depending on the presence of phosphate and electron donors. (λ=320 nm, O₂-equilibrated, 0.5 g/l TiO₂, pH = 3.0, 0.1 M phosphate, 5 vol% 2-propanol or 0.5 mM benzoic acid) [5]

Preliminary results / proof of principle

![Graph showing reaction products before and after irradiation](image)

Figure 3: GC-MS-data of the reaction from Thymol to Chlorothymol without (A) and with (B) titanium dioxide. (4 U/ml chloroperoxidase, 100 mM acetate-buffer pH = 3.7, 50 mM phosphate, 25 mM, 0.5 g/l TiO₂ (only B), 300 min UVA-irradiation: 105W lamp with λₘₚₓ = 365 nm)

References