# Novel pathway for the preparation of a hybrid chemoenzymatic heterogeneous catalyst combining enzyme-polyelectrolyte complexes and zeolite nanocrystals

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Combining heterogeneous catalysis with biocatalysis is increasingly envisaged as a solution to exploit the respective advantages of each partner and to run effective chemoenzymatic reactions. The preparation of hybrid chemoenzymatic heterogeneous catalysts, however, still represents a major challenge [1]. The combination of glucose oxidase (GOx) and TS-1 zeolites was already proposed for the production of $H_2O_2$ cascaded with the epoxidation of allyl alcohol but, the performance (activity and stability) of the hybrid catalysts remained modest because enzyme grafting was ineffective [2]. Recently, we proposed the synthesis of hollow TS-1 microspheres used as cargos for GOx. The hybrid catalyst obtained via this two steps process was more active but poorly stable [3]. Moving further, leveraging on a spray drying technique and on the protection of the enzyme through the formation of enzyme-polyelectrolyte complexes (EPCs), we propose a novel one-step and continuous process for the preparation of a TS-1-GOx hybrid [4].

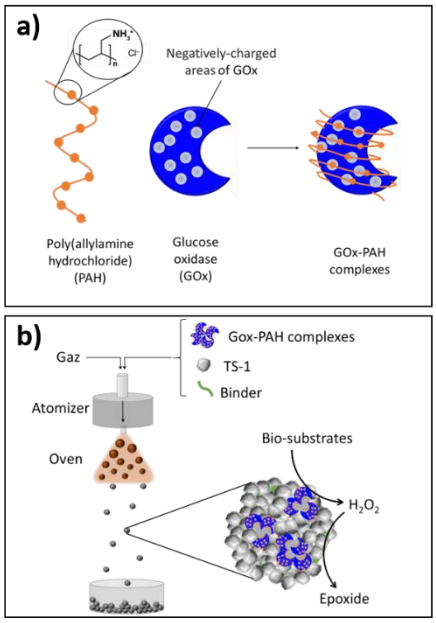


**Figure 2**: a) GOx-PAH complexes formation, b) Hybrid_EPCs synthesis by spray drying

When free GOx was mixed with a suspension of TS-1 nanocrystals and spray dried (50°C), the obtained hybrid material (Hybrid_GOx) was totally inactive (the enzyme – though effectively entrapped – was inactivated in the spray). This highlights the absolute need to protect the enzyme. Thus, EPCs were obtained by mixing poly(allylamine hydrochloride) (PAH), a positively charged polyelectrolyte, with GOx (Fig 1a). The formation of GOx-PAH EPCs led to a decrease of the enzymatic activity from 146 to 96 $\mu mol.min^{-1}.mg_{GOx}^{-1}$ (Fig 2a), but their stability toward pH and temperature was improved. The material obtained by spraying EPCs together with TS-1 zeolite nanocrystals (Hybrid_EPCs) (Fig 1b) was active for the cascade reaction (Fig 2b). In this solid, residual enzyme activity reached 33%, compared to the EPCs (Fig 2a). The strong interactions between GOx and PAH prevented enzyme leaching (<0.1%). The texture and activity of TS-1 was preserved.

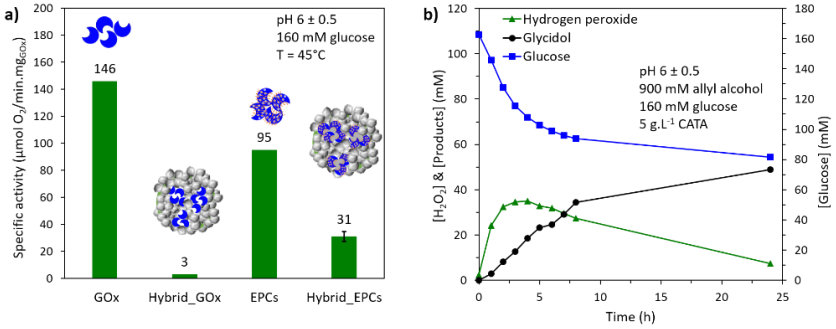


**Figure 1**: a) Enzymatic activity of free GOx, Hybrid_GOx, EPCs, and Hybrid_EPCs, b) chemoenzymatic epoxidation of allyl alcohol with Hybrid_EPCs

In conclusion, we disclose an effective strategy to synthesize active and stable hybrid chemoenzymatic heterogeneous catalysts using a one step, continuous, and scalable method. The application of EPCs as a protection for the enzyme and direct spray drying as a processing method could open up new avenues for the preparation of other other types of hybrid catalysts.

[1] D. P. Debecker; V. Smeets, M. Van der Verren, H. Meersseman Arango, M. Kinnaer and F. Devred,, *Current Opinion in Green and Sustainable Chemistry*, **2021**, 28, 100437; [2] P. N. R. Vennestrøm, E. Taarning, C. H. Christensen, S..Pedersen, J.-D. Grunwaldt and J. M. Woodley, *ChemCatChem*, **2010**, 2, 943-945. [3] V. Smeets, W. Baaziz, O. Ersen; E. M. Gaigneaux, C. Boissière, C. Sanchez and D. P. Debecker, *Chemical Science*, **2020**, *11*, 954-961. [4] M. Van der Verren, V. Smeets, A. vander Straeten, C. Dupont-Gillain and D. P. Debecker, *Nanoscale Adv.*, **2021**,*3*, 1646-1655.