

Supporting Information

Nanobiocatalysts for cofactor-independent oxidoreductase catalysis in organic solvents

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Keywords: nanobiocatalysts • co-factor recycling • organic solvent • oxidoreductase • continuous flow

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Supporting Figures

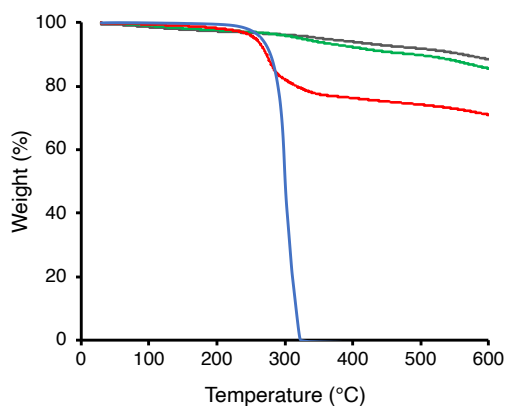


Figure S1. Thermogravimetric analyses of MSNs - measurements were carried out on MSNs before (green) and after work-up (green); control experiments were also carried out with neat CTAC (blue) and a physical mixture of CTAC and MSNs (red). CTAC displayed a consistent weight loss starting at *ca.* 255 °C (also in the mixture with MSNs); this loss can be safely attributed to molecular decomposition. No such mass loss is observed for MSNs in the range 200-300 °C (both before and after work-up) suggesting the absence of relevant quantities of CTAC in the MSNs. A slight weight loss is measured at temperatures above 350 °C; this can be safely attributed to the condensation and release of surface -OH functions from the silica surface.

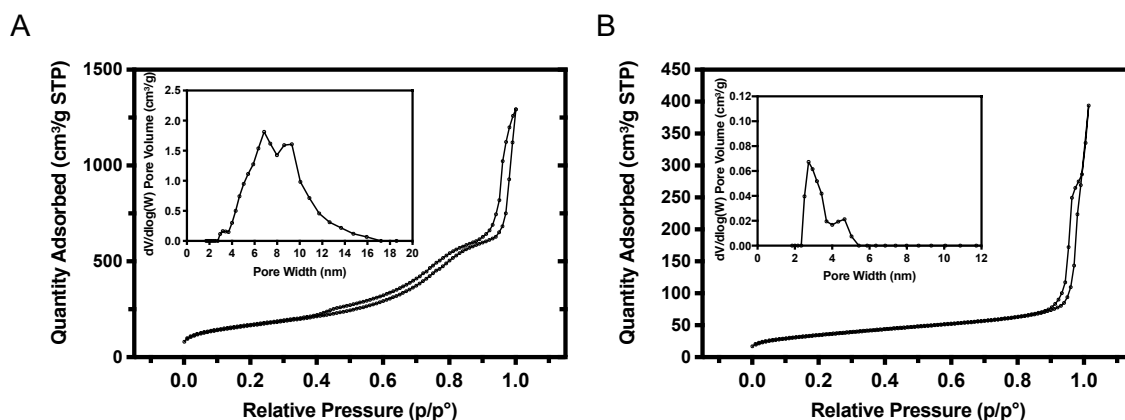


Figure S2. Nitrogen adsorption-desorption experiments - [A] core silica nanoparticles: the BET surface area was measured at $214 \text{ m}^2/\text{g}$, and the total pore volume was $0.87 \text{ cm}^3/\text{g}$. A capillary condensation step and hysteresis loop can be observed at the relative pressure around $0.4 < P/P_0 < 1.0$ in the N_2 sorption isotherm. Based on the density functional theory (DFT) method, the pore size distribution displays a complex shape centred on *ca.* 8 nm, as shown in the figure inset. While indicative of the pore size, this value needs to be considered carefully as the pores display a conical geometry. [B] MSNs: the BET surface area was measured at $120.8 \text{ m}^2/\text{g}$, and the total pore volume was $0.43 \text{ cm}^3/\text{g}$. A capillary condensation step and hysteresis loop can be observed at the relative pressure around $0.2 < P/P_0 < 1$ in the N_2 sorption isotherm. The pore size distribution is shown in the figure inset; it shows a bimodal distribution with two mean values of *ca.* 3 and 5 nm. The close connectivity and continuous pore channels between the first generation and the second generation are consistent with the results reported previously.¹ Measurements were carried out on MSNs before (green) and after the work-up (green); control experiments were also carried out with neat CTAC (blue) and a physical mixture of CTAC and MSNs (red). CTAC displayed a consistent weight loss starting at *ca.* $255 \text{ }^\circ\text{C}$ (also in the mixture with MSNs); this loss can be safely attributed to molecular decomposition.

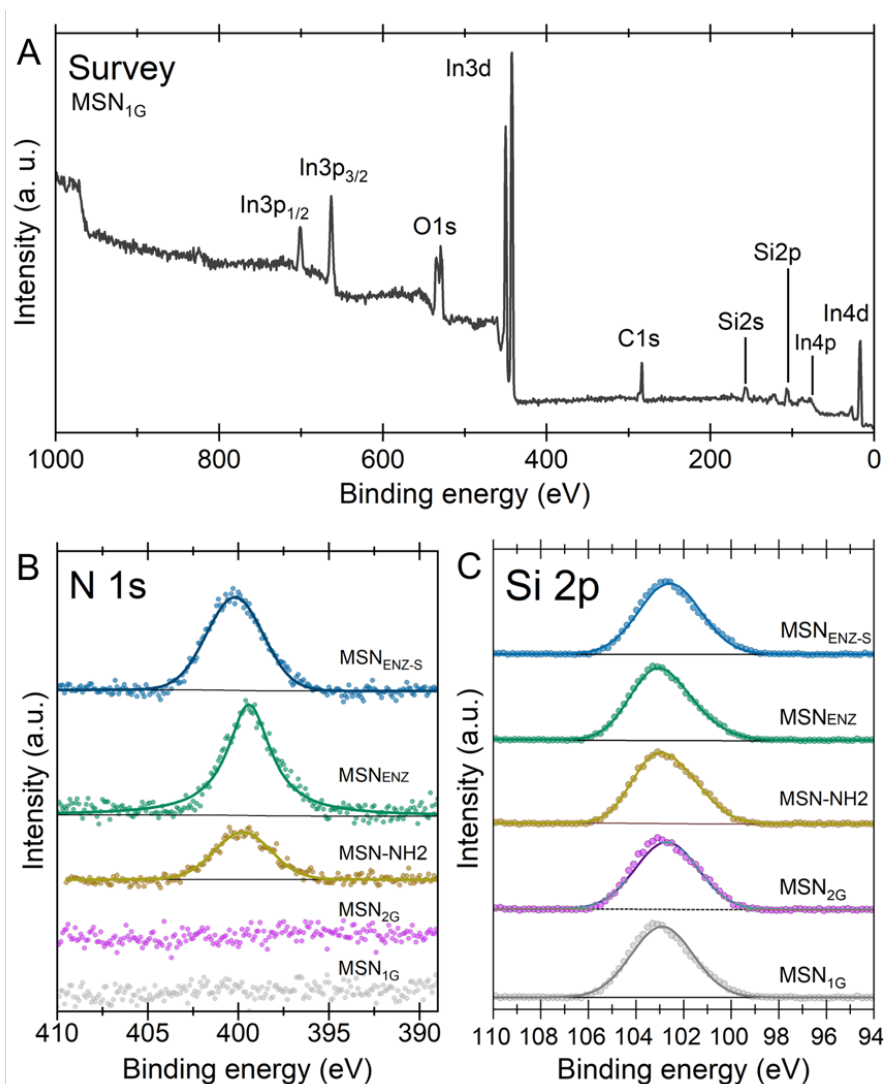


Figure S3. XPS measurements - Full survey XP spectra of MSN_{1G} (A); high-resolution spectrum of N1s (B) and Si2p taken at different stages of assembly of the core-shell MSN (C). Colour code: from the bottom to the top: MSN_{1G} (grey), MSN_{2G} (purple), amino-modified MSN_{2G} (yellow), MSN_{ENZ} (green) and MSN_{ENZ-S} (blue). Due to the insulating nature of the core-shell nanoparticles, all measurements have been performed using a flood gun to compensate for the charging effect.²

References

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2. D. R. Baer, M. H. Engelhard, D. J. Gaspar, A. S. Lea and C. F. Windisch Jr., *Surface and Interface Analysis*, 2002, **33**, 781-790.