Supplementary Information

A mediator-free enzymatic carbonaceous cathode for bioelectrocatalysis reduction of furfural into furfuryl alcohol

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Assay

The ADH loading on the synthesized TpBD@ADH capsules were calculated by ICP-OES based on Zn mole ratios, according to the following equation:

$$ADH\ Loading = \frac{mole\ of\ ADH}{mole\ of\ TpBD} \times 100\% \quad (1)$$

As for the analysis of the electroenzymatic catalysis products, a high-performance liquid chromatography (HPLC) that was equipped with an ultraviolet (UV) detector (230 nm) was used to analyze the furfural and furfuryl alcohol concentrations in reactants. The mobile phase was consisted of 55 % (v/v) acetonitrile and 45 % (v/v) ultrapure water, and the flow rate of the mobile phase was 0.5 mL min^{-1}. The furfural conversion and selectivity can be calculated by the following equations:

$$Conversation\ (\%) = \frac{n_0 - n_{furfural}}{n_0} \times 100\% \quad (2)$$

$$Selectivity\ (\%) = \frac{n_{furfuryl\ alcohol}}{n_0 - n_{furfural}} \times 100\% \quad (3)$$

where n_0 refers to the initial concentration of furfural, $n_{furfural}$ is the furfural concentration after reaction, and $n_{furfuryl\ alcohol}$ stands for the furfuryl alcohol concentration.

Tables

Table S1. ADH immobilization rate determined by ICP-OES.

Sample name	ADH immobilization rate (%)
TpBD@ADH-1	2.32±0.14
TpBD@ADH-2	2.48±0.11
TpBD@ADH-3	3.42±0.06
TpBD@ADH-4	6.18±0.09
TpBD@ADH-5	9.07±0.03

Table S2. BET Surface areas and pore sizes of the nanoparticles.

Sample name	Surface Area ($m^2 g^{-1}$)	Pore size (nm)
TpBD Capsules	14.4239	7.4929
TpBD@ADH@$CaCO_3$	3.8834	2.3552
TpBD@ADH	30.4244	2.1398

Figures

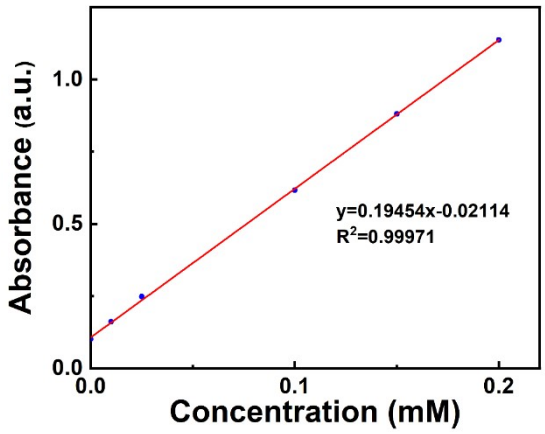

Fig.S1 UV-vis standard curve of NADH at 340 nm.

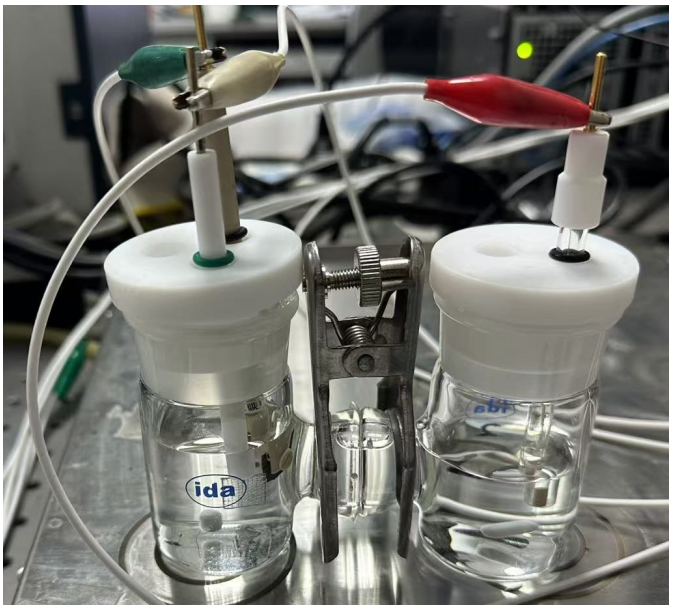

Fig.S2 H-cell used in the electroenzymatic furfural reduction.

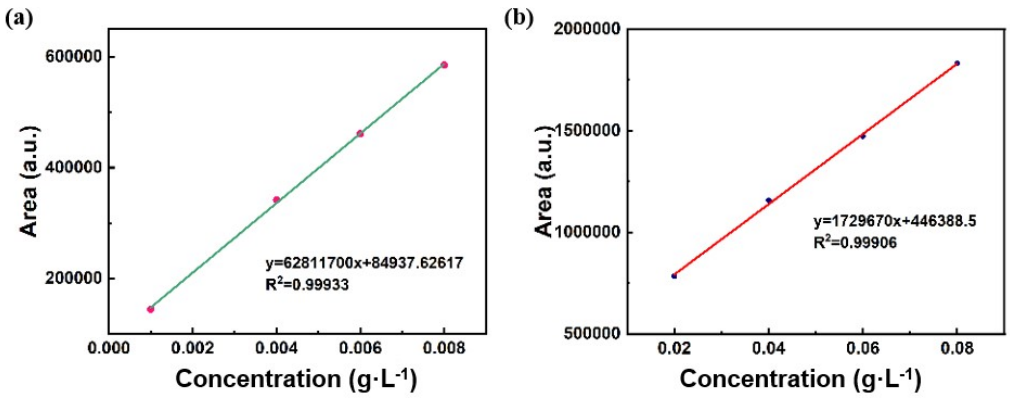

Fig.S3 HPLC standard curves of (a) furfuryl alcohol and (b) furfural.

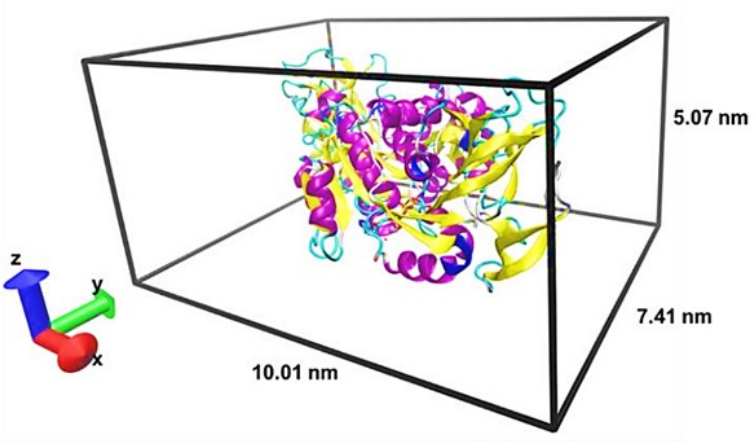

Fig.S4 Spatial size of ADH by molecular docking simulations.

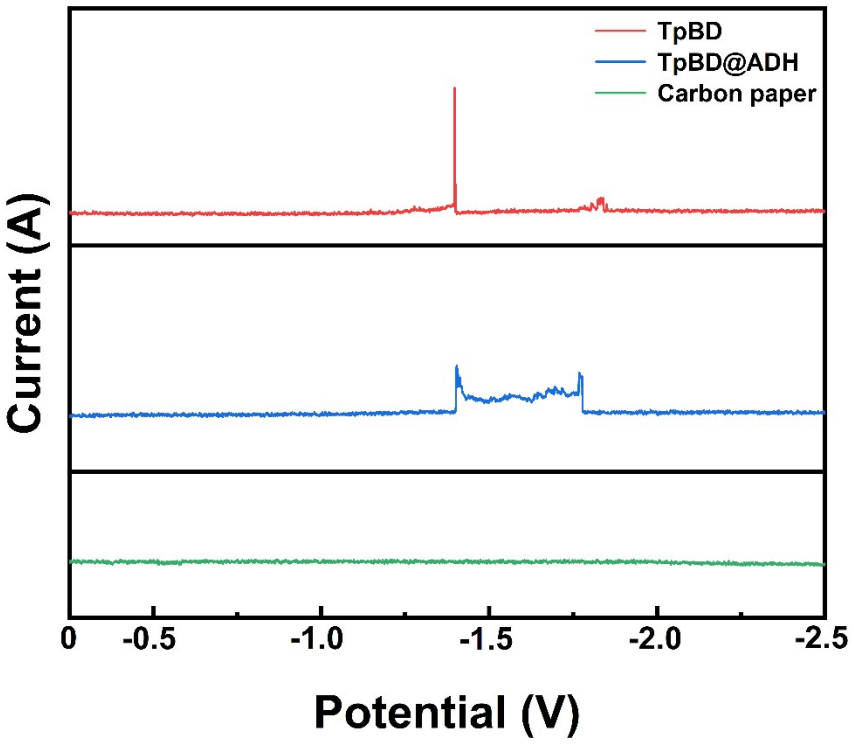

Fig.S5 LSV test of different electrode.

The LSV test of different electrode was performed in a cell. The reaction was conducted at room temperature (~25°C) with an external CHI760E workstation (CH Instruments, Shanghai, China). TpBD@ADH electrode (1.0 × 1.0 cm^2) was served as the working electrode. An Ag/AgCl (3.5 M KCl) electrode was used as the reference electrode, and a platinum mesh was equipped as the counter electrode. The electrolyte was 30 mL 0.1 M PBS buffer added 5 mM NAD^+ and 0.5 mM furfural. In the presence of NAD^+, linear sweep voltammetry (LSV) curves were obtained over a potential range of 0 V to -2.5 V vs. Ag/AgCl at a scan rate of 20 mV s^{-1}.