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Supporting Information

Glucose oxidation performance is improved by the use of a supramolecular self-assembly of glucose oxidase and catalase

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Methods

Preparation of 6-carboxyl-β-CD

(i) CD-OTs

β-CD (18 g, 16 mmol) was dissolved in 250 mL of water. 10 mL of a NaOH solution (8.2 mol/L) were added dropwise to the suspension over 5 min with stirring. A solution of p-toluenesulfonylchloride (4.37 g, 23 mmol) in 10 mL of acetonitrile was added dropwise to the mixture and white precipitates appeared immediately after the addition. The mixture was allowed to stir for a further 4 h at room temperature. The pH value of the mixture was adjusted to 6 using 3 mol/L HCl. The precipitates were collected by filtration to give CD-OTs. ^{1}H NMR (DMSO-d6): δ 7.77 (d, 2H), 7.43 (d, 2H), 5.83–5.63 (br, 14H), 4.85–4.77 (m, 7H), 4.51–4.20 (m, 9H), 3.7–3.22 (m, 40 H), 2.44 (s, 3H). For the wild CD, ^{1}H NMR (DMSO-d6): δ 5.75–5.6 (br, 14H), 4.85–4.8 (m, 7H), 4.5–4.4 (m, 9H), 3.7–3.3 (m, 40 H), 2.4 (s, 3H). By comparing the structure of CD and CD-OTs, ^{1}H NMR: δ 7.77 (d, 2H), 7.43 (d, 2H) proved that p-toluenesulfonyl was successfully grafted on CD.

(ii) ***6-carboxyl-β-CD***

CD-OTs (7 g, 5.4 mmol) and alanine (2 g, 22 mmol) were dissolved in 50 mL of a triethanolamine/water (2:3 w/w) solution, and the mixture was stirred at 130°C for 24 h. Solvent was removed by distillation under reduced pressure; ethanol was then added to the residue, and the system was cooled to room temperature. The precipitates were collected by filtration, and then dried in a vacuum oven at 70°C overnight. The product was purified by chromatography using Sephadex^{TM} G-25 (water) to give 6-carboxyl-β-

CD. ^{1}H NMR (400 MHz, D_2O): δ 4.99 (m, 7H), 4.04 (m, 1H), 3.89–3.48 (m, 42H), 3.33–3.21 (m, 1H), 3.21–3.08 (m, 1H), 2.49 (t, J = 6.4 Hz, 1H). ^{13}C NMR (400 MHz, D_2O): δ178.33, 101.81, 101.14, 81.38, 81.18, 80.40, 71.77, 67.50, 60.55, 57.42, 47.66, 44.97, 31.96. Thus, ^{1}H NMR: δ 7.77 (d, 2H), 7.43 (d, 2H) for CD-OTs and 3.89–3.48 (m, 42H) for 6-carboxyl-β-CD proved that p-toluenesulfonyl was successfully replaced by alanine.

Tables

Table S1. Kinetic parameters for the GOX/CAT SAME catalyzed preparation of gluconic acid at 35°C based on glucose concentration with different concentration of host to 1:1 GOX: CAT complex.

The addition of CD in GOX/CAT SAME	K_m (mM)	k_{cat} (s^{-1})	k_{cat}/K_m ($mM^{-1} \times s^{-1}$)
0	7.18	187.17	26.08
100	2.78	167.84	60.33
200	1.84	176.61	95.76
500	1.27	178.06	140.00
800	0.93	175.81	189.70
1000	1.30	170.57	131.20
2000	2.54	151.20	59.61
5000	2.23	134.10	60.22

Table S2. Kinetic parameters for different enzymes catalyzed formation of gluconic acid at 35°C based on glucose concentration (free GOX, GOX/CAT mixture, GOX/CAT mixture with 800% CD and the GOX/CAT SAME with 800% CD).

	K_m (mM)	k_{cat} (s^{-1})	k_{cat}/K_m ($mM^{-1} \times s^{-1}$)
Free GOX	1.01	60.13	59.53
GOX/CAT mixture	3.42	87.72	25.65
GOX/CAT mixture with 800% CD	3.53	82.13	25.33
GOX/CAT SAME 800% CD	0.93	175.81	189.70

Figures

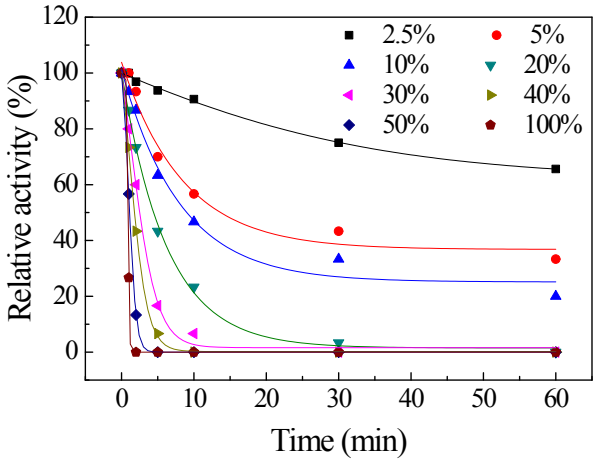

Figure S1. The effects of different hydrogen peroxide concentrations on GOX activity. The initial GOX activity was defined as 100%. The 15% (w/v) glucose generated H_2O_2 was defined as 100%.

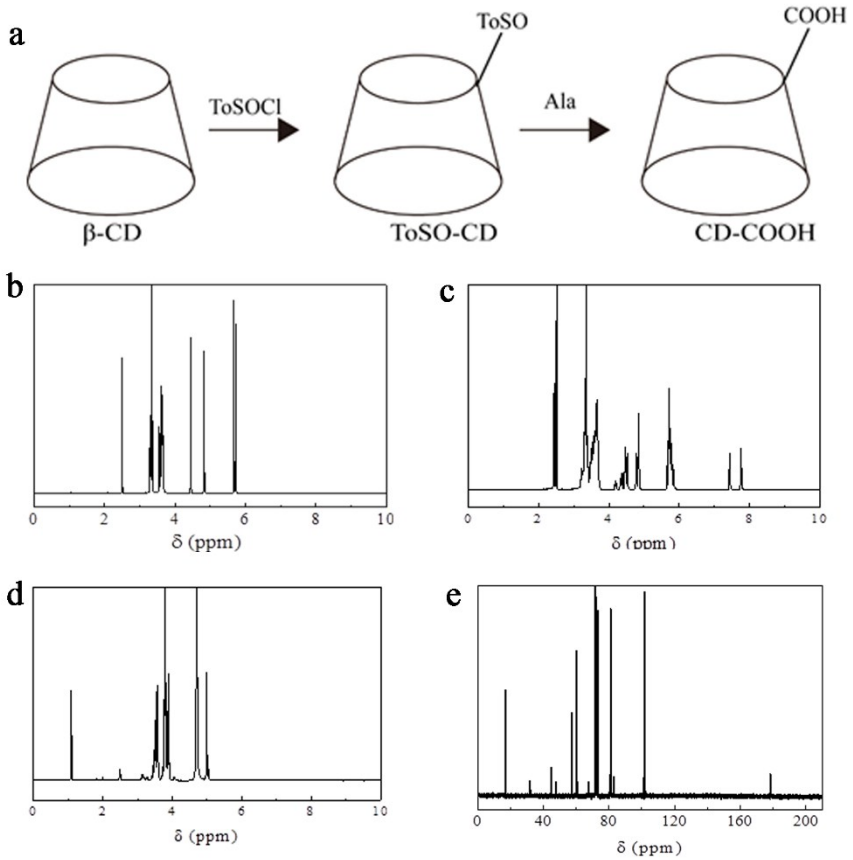

Figure S2. The synthesis of 6-carboxyl-β-CD. (a) Scheme for the synthesis of 6-carboxyl-β-CD. (b) ^{1}H NMR of CD. (c) ^{1}H NMR of CD-OTs. (d) ^{1}H NMR of 6-carboxyl-β-CD. (e) ^{13}C NMR of 6-carboxyl-β-CD.

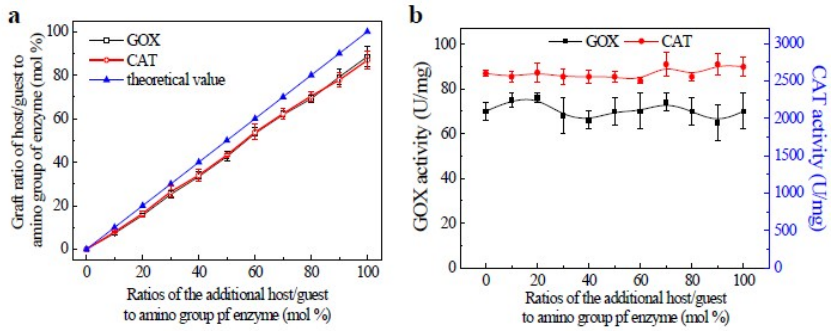

Figure S3. (a) Grafting efficiency of 6-carboxyl-β-CD and 1-adamantanecarboxylic acid to GOX and CAT, respectively. (b) Activity of GOX and CAT with different CD and AD grafted ratios.

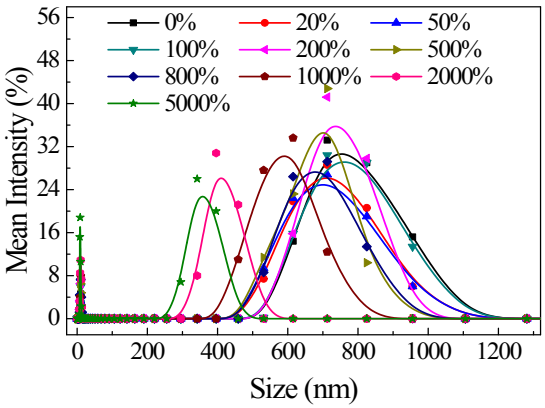

Figure S4. DLS analysis of GOX/CAT SAME with the additional of CD.

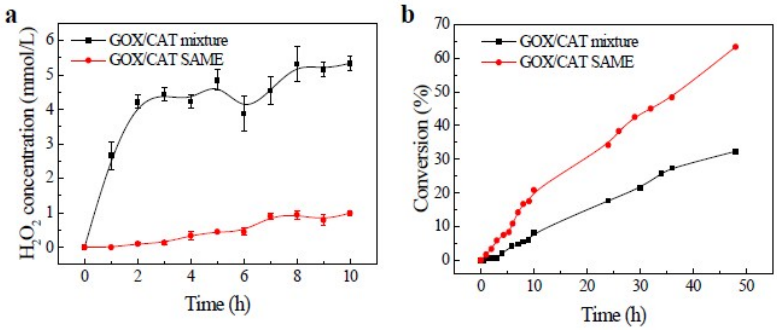

Figure S5. (a) Concentrations of H_2O_2 in GOX/CAT mixture and GOX/CAT SAME system. (b) Conversion of glucose to gluconic acid catalyzed by GOX/CAT mixture and GOX/CAT SAME without the addition of oxygen.