## **Supporting Information**

pH-Sensitive "On-Off" Switching Behavior of
Layer-by-Layer Films Assembled by Concanavalin A
and Dextran toward Electroactive Probes and its
Application in Bioelectrocatalysis

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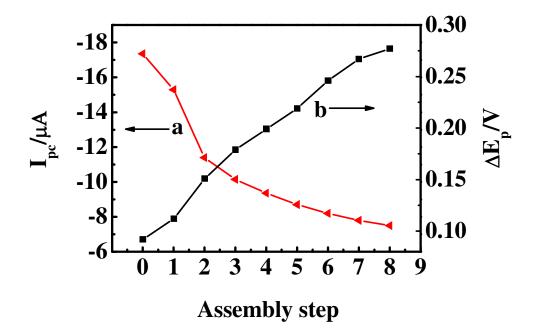
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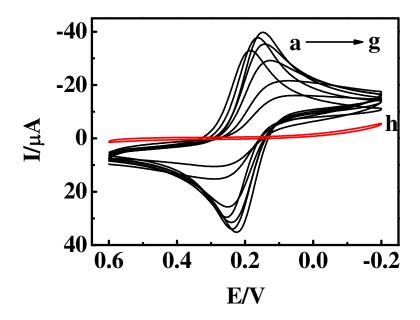
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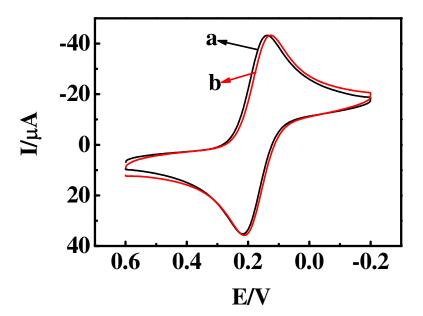
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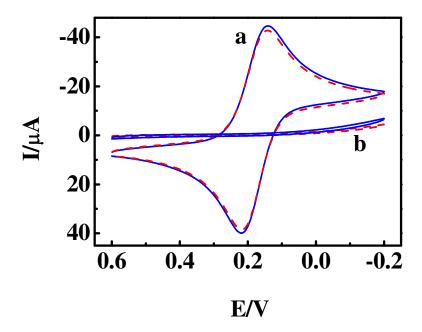
**Figure S1.** Dependence of CV reduction peak current  $(I_{pc})$  and CV peak separation  $(\Delta E_p)$  of  $Fe(CN)_6^{3-}$  on the assembly step of  $\{Con\ A/Dex\}_n$  films.



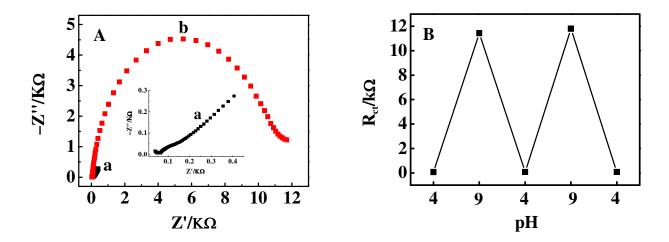
**Figure S2.** CVs of 1 mM  $K_3Fe(CN)_6$  for  $\{Con\ A/Dex\}_4$  films at 0.1 V s<sup>-1</sup> in buffers at pH (a) 2.0, (b) 3.0, (c) 4.0, (d) 5.0, (e) 6.0, (f) 7.0, (g) 8.0, and (h) 9.0.



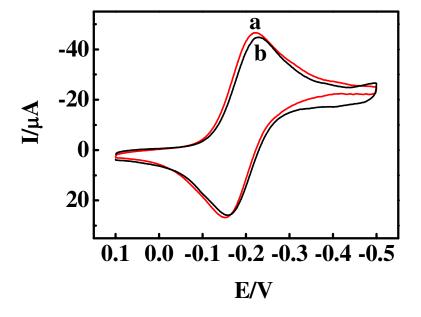
**Figure S3.** CVs of 1 mM  $K_3$ Fe(CN)<sub>6</sub> at 0.1 V s<sup>-1</sup> for bare PG electrodes in buffers at pH (a) 4.0 and (b) 9.0.



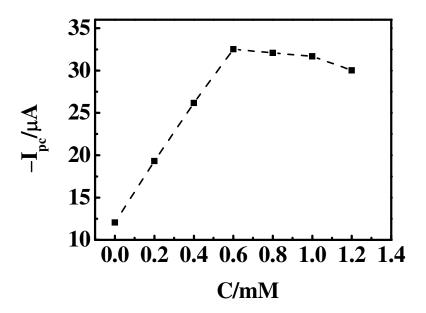
**Figure S4.** CVs of 1 mM  $K_3Fe(CN)_6$  at 0.1 V s<sup>-1</sup> for {Con A/Dex}<sub>3</sub>/Con A (blue and solid curves) and {Con A/Dex}<sub>4</sub> (red and dashed curves) films in buffers at pH (a) 4.0 and (b) 9.0, respectively.



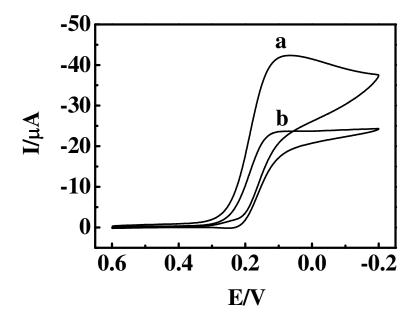
**Figure S5.** (A) EIS responses of 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> at 0.17 V in buffers at pH (a) 4.0 and (b) 9.0 for  $\{\text{Con A/Dex}\}_4$  films. Inset is a magnification of curve a. (B) Dependence of  $R_{ct}$  of 5 mM Fe(CN)<sub>6</sub><sup>3-/4-</sup> on solution pH switched between pH 4.0 and 9.0 for the same  $\{\text{Con A/Dex}\}_4$  films.



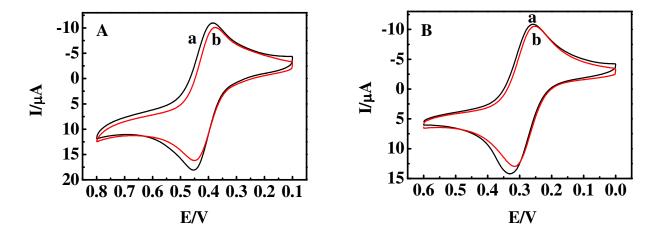
**Figure S6.** CVs of 1 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> at 0.1 V s<sup>-1</sup> for bare PG electrodes in buffers at pH (a) 4.0, (b) 9.0.



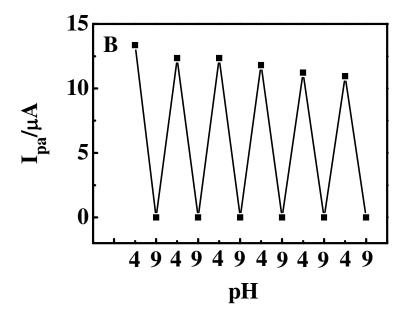
**Figure S7.** Dependence of CV electrocatalytic reduction peak/wave current ( $I_{pc}$ ) at 0.01 V s<sup>-1</sup> on concentration of  $H_2O_2$  at {Con A/Dex}<sub>4</sub> film electrodes in pH 4.0 solutions containing 1 mM  $K_3Fe(CN)_6$  and 0.5 mg mL<sup>-1</sup> HRP and  $H_2O_2$ .



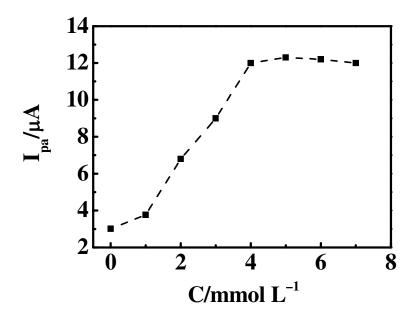
**Figure S8.** CVs at 0.01 V s<sup>-1</sup> for bare PG electrodes in pH (a) 4.0 and (b) 9.0 buffers containing 1 mM  $K_3Fe(CN)_6$ , 0.5 mg mL<sup>-1</sup> HRP and 0.5 mM  $H_2O_2$ .



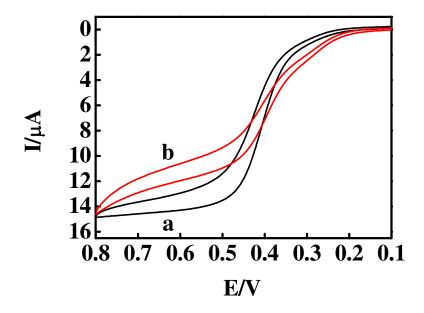
**Figure S9.** (A) CVs of 0.5 mM Fc(COOH)<sub>2</sub> at 0.1 V s<sup>-1</sup> at bare PG electrodes in buffers at pH (a) 4.0 and (b) 9.0. (B) CVs of 0.5 mM Fc(COOH) at 0.1 V s<sup>-1</sup> at bare PG electrodes in buffers at pH (a) 4.0 and (b) 9.0.



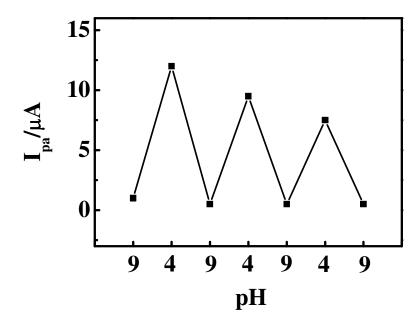
**Figure S10.** Dependence of CV oxidation peak current ( $I_{pa}$ ) of 0.5 mM Fc(COOH)<sub>2</sub> at 0.1 V s<sup>-1</sup> on solution pH switched between pH 4.0 and 9.0 for the same {Con A/Dex}<sub>4</sub> films.



**Figure S11.** Dependence of CV oxidation peak/wave current ( $I_{pa}$ ) at 0.005 V s<sup>-1</sup> on concentration of glucose for {Con A/Dex}<sub>4</sub> films in pH 4.0 buffers containing 0.5 mM Fc(COOH)<sub>2</sub>, 1.0 mg mL<sup>-1</sup> GOD and glucose.



**Figure S12.** CVs at  $0.005 \text{ V s}^{-1}$  at bare PG electrodes in pH (a) 4.0 and (b) 9.0 buffers containing 0.5 mM Fc(COOH)<sub>2</sub>, 1.0 mg mL<sup>-1</sup> GOD and 4.0 mM glucose.



**Figure 13.** Dependence of CV catalytic oxidation peak/wave current ( $I_{pa}$ ) at 0.005 V s<sup>-1</sup> on solution pH switched between pH 4.0 and 9.0 for the same {Con A/Dex}<sub>4</sub> films. The solution contained 0.5 mM Fc(COOH)<sub>2</sub>, 4.0 mM glucose, and 1.0 mg mL<sup>-1</sup> GOD.