**Supporting Information** 

pH-Controllable Bioelectrocatalysis Based on "On-Off"

Switching Redox Property of Electroactive Probes for

Spin-Assembled Layer-by-Layer Films Containing

Branched Poly(ethyleneimine)

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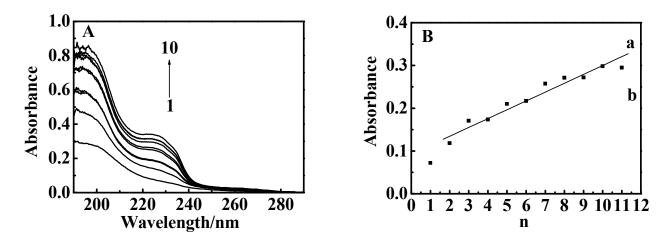
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**Figure S1.** (A) UV-vis absorption spectra of BPEI/ $\{PSS/BPEI\}_n$  films assembled with different number of bilayers (n). (B) Dependence of absorbance at 226 nm on the number of bilayers (n) for BPEI/ $\{PSS/BPEI\}_n$  films.

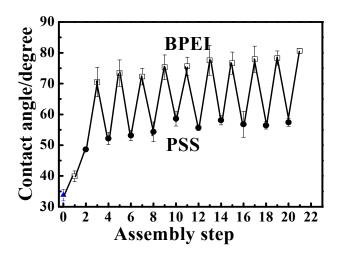
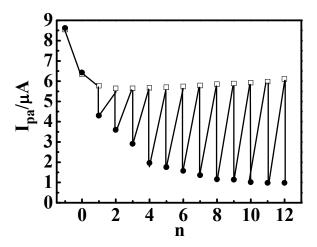
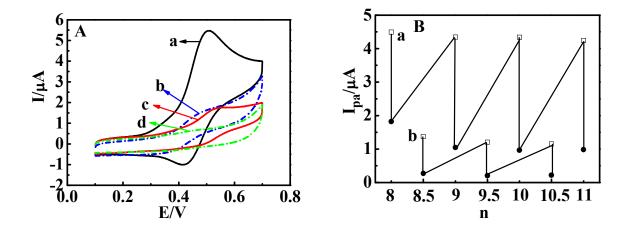


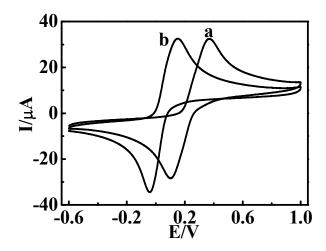
Figure S2. Contact angle measurement of each assembly step for BPEI/ $\{PSS/BPEI\}_n$  films on Au/MPS ( $\blacktriangle$ ) surface: BPEI ( $\square$ ) and PSS ( $\bullet$ ) steps. Every point represents the average of three parallel measurements.



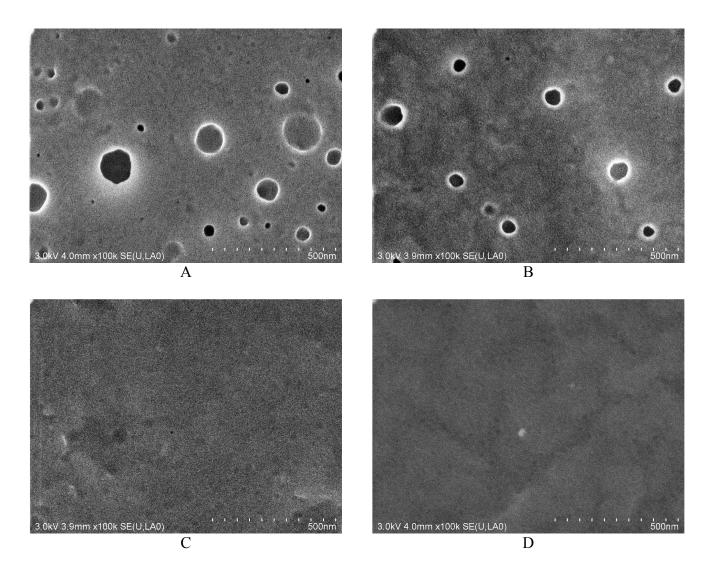
**Figure 3S.** Influence of the number of bilayers (n) of BPEI/ $\{PSS/BPEI\}_n$  films on CV oxidation peak currents ( $I_{pa}$ ) of 0.2 mM Fc(COOH)<sub>2</sub> in buffers at pH 4.0 ( $\square$ ) and 7.0 ( $\bullet$ ) at 0.1 V s<sup>-1</sup>. The first two points are the  $I_{pa}$  values of Fc(COOH)<sub>2</sub> at bare PG electrodes in solutions at pH 4.0 and 7.0, respectively.



**Figure S4**. (A) CVs of 0.2 mM Fc(COOH) at 0.1 V s<sup>-1</sup> for BPEI/{PSS/BPEI}<sub>10</sub> films at pH (a) 4.0 and (b) 7.0 and BPEI/{PSS/BPEI}<sub>10</sub>/PSS films at pH (c) 4.0 and (d) 7.0. (B) The dependence of CV oxidation peak currents ( $I_{pa}$ ) of Fc(COOH)<sub>2</sub> on the bilayer number (n) for (a) BPEI/{PSS/BPEI}<sub>n</sub> and (b) BPEI/{PSS/BPEI}<sub>n</sub>/PSS films at pH 4.0 ( $\square$ ) and 7.0 ( $\bullet$ ).



**Figure S5.** CVs of 0.5 mM hydroquinone at  $0.1 \text{ V s}^{-1}$  at bare PG electrodes in buffers at pH (a) 4.0 and (b) 7.0.



**Figure S6.** SEM top views of PSS/BPEI multilayer films assembled on Au/MPS surface after the films were immersed in buffers at different pH for 10 min: (A) BPEI/{PSS/BPEI}<sub>10</sub> films at pH 4.0, (B) BPEI/{PSS/BPEI}<sub>10</sub> films at pH 7.0, (C) BPEI/{PSS/BPEI}<sub>10</sub>/PSS films at pH 4.0, and (D) BPEI/{PSS/BPEI}<sub>10</sub>/PSS films at pH 7.0.