**Figure S1.** TEM image of a (PV/NP)$_3$ multilayer edge obtained by 3 min dipping time in the NP solution.

**Figure S2.** Voltammetric responses recorded at different potential scan rates for (PV/NP)$_6$ multilayer in 0.1 M PBS, and the dependence of $i_{p,c}$ on $v$ (inset).
Figure S3. Voltammetric responses recorded at different potential scan rates for (PV/NP)$_6$ multilayer in 1 mM [Fe(CN)$_6$]$^{4-}$ in 0.1 M PBS and the dependence of $i_{p,c}$ on $v^{1/2}$ (inset).

Figure S4. Voltammetric responses recorded at different potential scan rates for (PV/NP)$_6$ multilayer in 1 mM [Ru(NH$_3$)$_6$]$^{3+}$ in 0.1 M PBS, and the dependence of $i_{p,c}$ on $v^{1/2}$ (inset).
**Figure S5.** Voltammetric responses of 1 mM [Fe(CN)$_6$]$^{3+}$ in 0.1 M PBS on a (PV/PSS)$_6$ multilayer. 0.050 Vs$^{-1}$ potential scan rate.

**Figure S6.** Voltammetric responses of 1 mM [Ru(NH$_3$)$_6$]$^{3+}$ in 0.1 M PBS on a (PV/PSS)$_{10}$ multilayer. 0.050 Vs$^{-1}$ potential scan rate.