Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

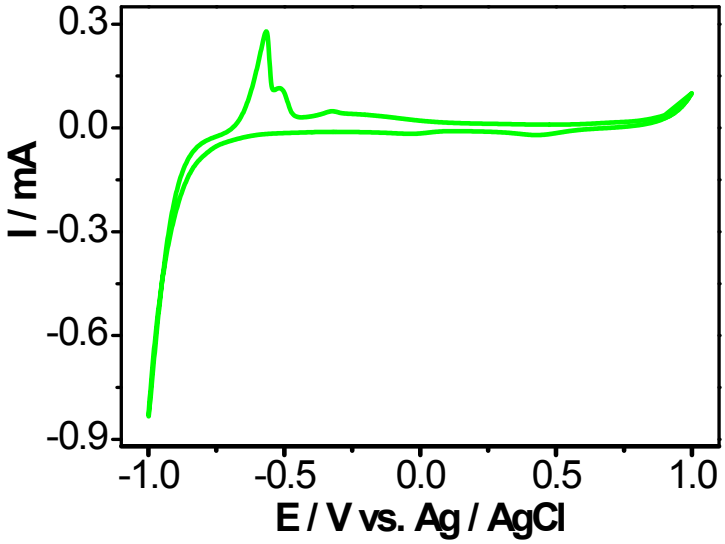

Fig. S1. CV of 2 mM HOPTS in 0.5 M H_2SO_4/Na_2SO_4 solutions (pH = 2.5) on ITO electrode with scan rate of 100 mV/s.

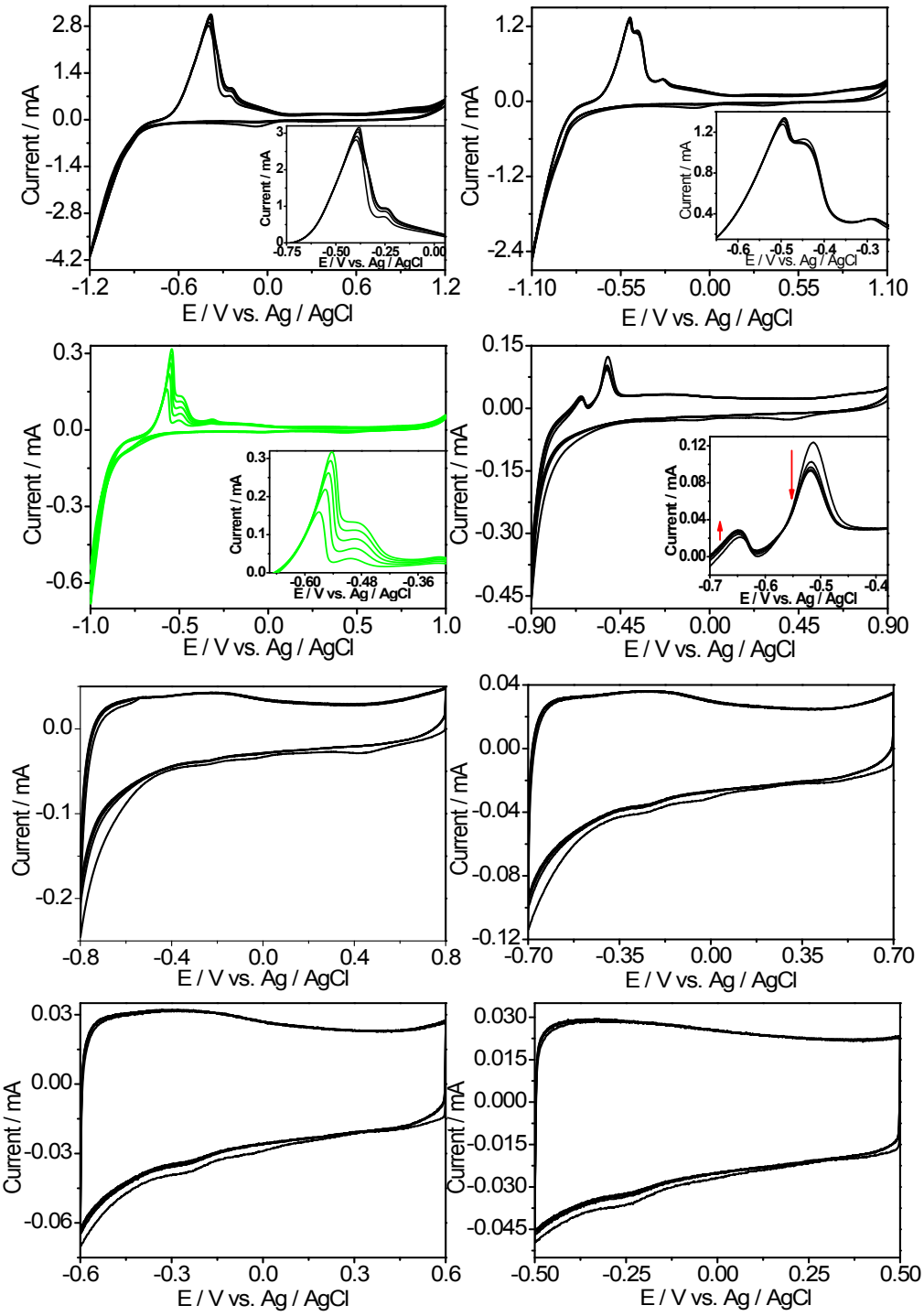

Fig. S2. Electrodeposition CVs at different potential ranges including -1.2 ~ 1.2 V, -1.1 ~ 1.1V, -1.0 ~ 1.0 V, -0.9~0.9 V, -0.8~0.8 V, -0.7~0.7 V, -0.6~0.6 V, -0.5~0.5 V on ITO electrode at scan rate of 100 mV/s in 10 mL 0.5 M H_2SO_4/Na_2SO_4 soutions (pH = 2.5) containing 0.02 mmol HOPTS.

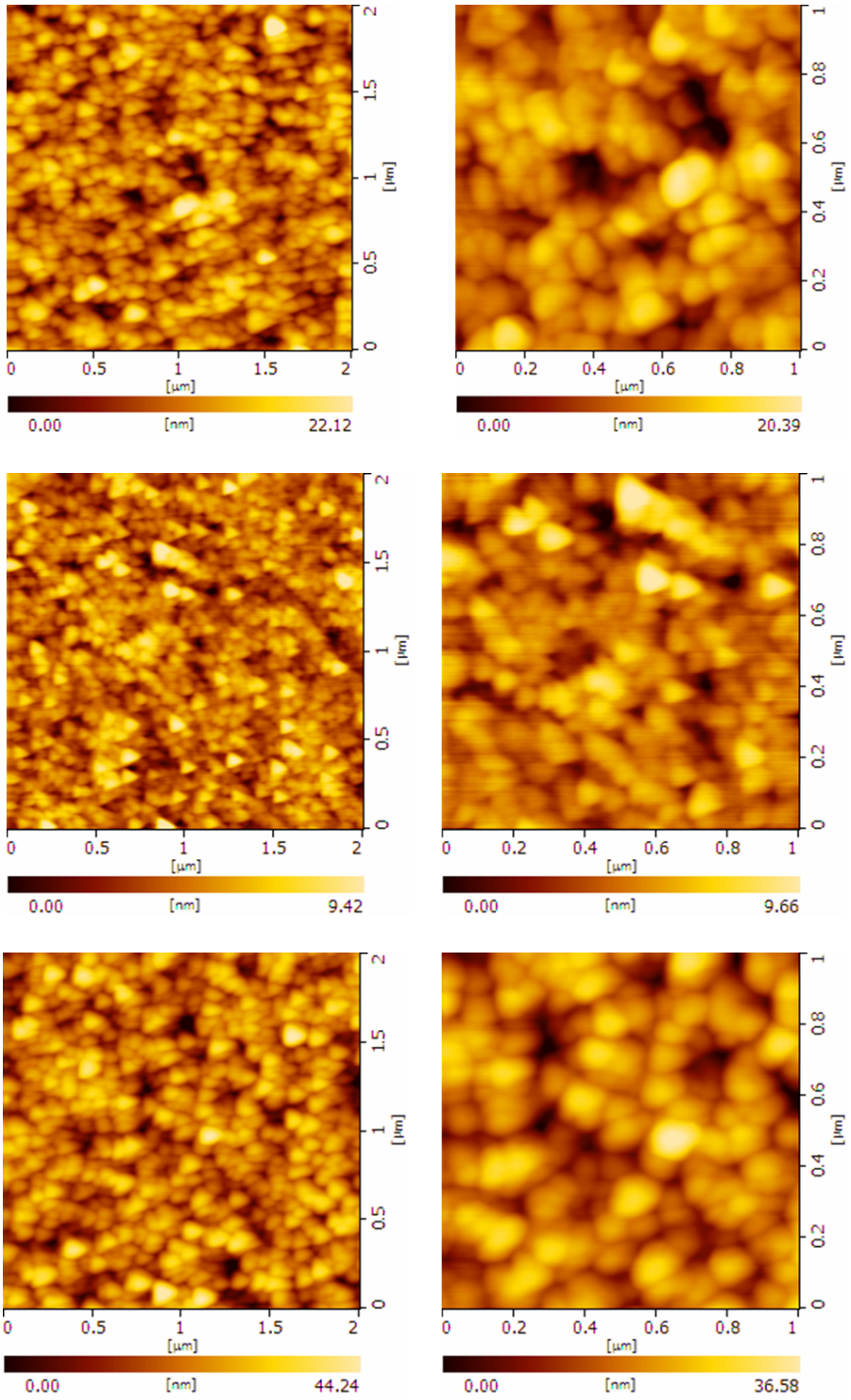

Fig.S3. AFM images of the films $(HOPTS)_{50}$ (top), $(HOPTS)_{10}$ (middle) and $(HOPTS)_{100}$ (bottom) on ITO substrates in scanning range of 2 micrometer (left) and 1 micrometer (right).

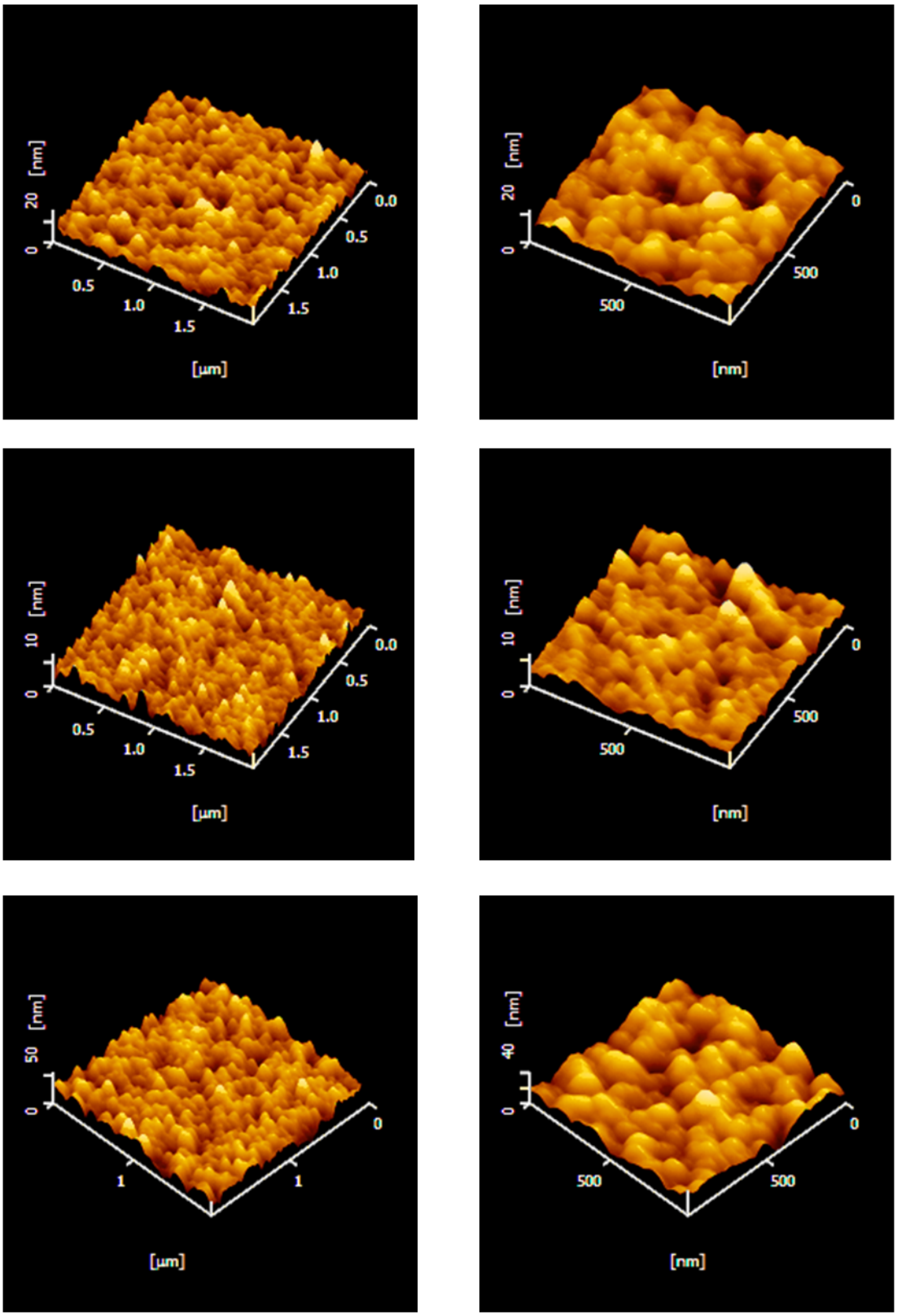

Fig. S4 AFM top images of the films $(HOPTS)_{50}$ (top), $(HOPTS)_{10}$ (middle) and $(HOPTS)_{100}$ (bottom) on ITO substrates in scanning range of 2 micrometer (left) and 1 micrometer (right).

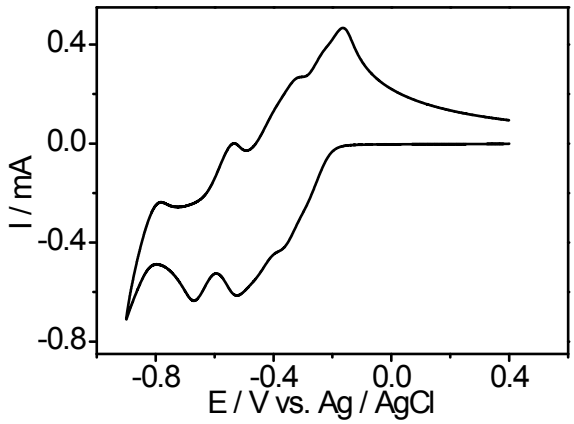

Fig. S5. Cyclic voltammogram (CV) of 1 mM P_5W_{30} in 0.5 M H_2SO_4/Na_2SO_4 solution (pH = 2.5) on ITO electrode with scan rate of 100 mV/s.

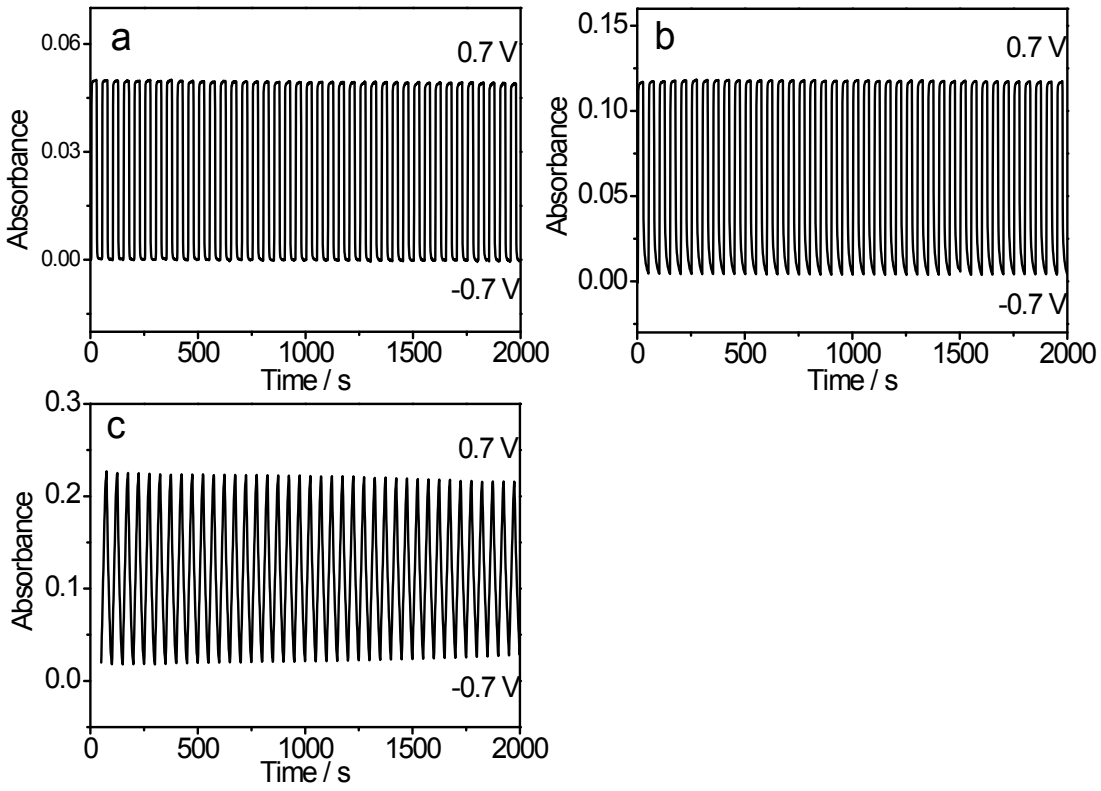

Fig. S6. UV-visible dynamic curves of absorbance at 650 nm of three composite films during subsequent double-potential steps from -0.7 V to +0.7 V in 0.5 M Na_2SO_4/H_2SO_4 (pH = 2.5) solutions: (a) ITO/[$(HOPTS)_{50}$/$(PDDA/P_5W_{30})_{10}$]; (b) ITO/[$(HOPTS)_{50}$/$(PDDA/P_5W_{30})_{27}$]; (c) ITO/[$(HOPTS)_{50}$/$(PDDA/P_5W_{30})_{57}$].

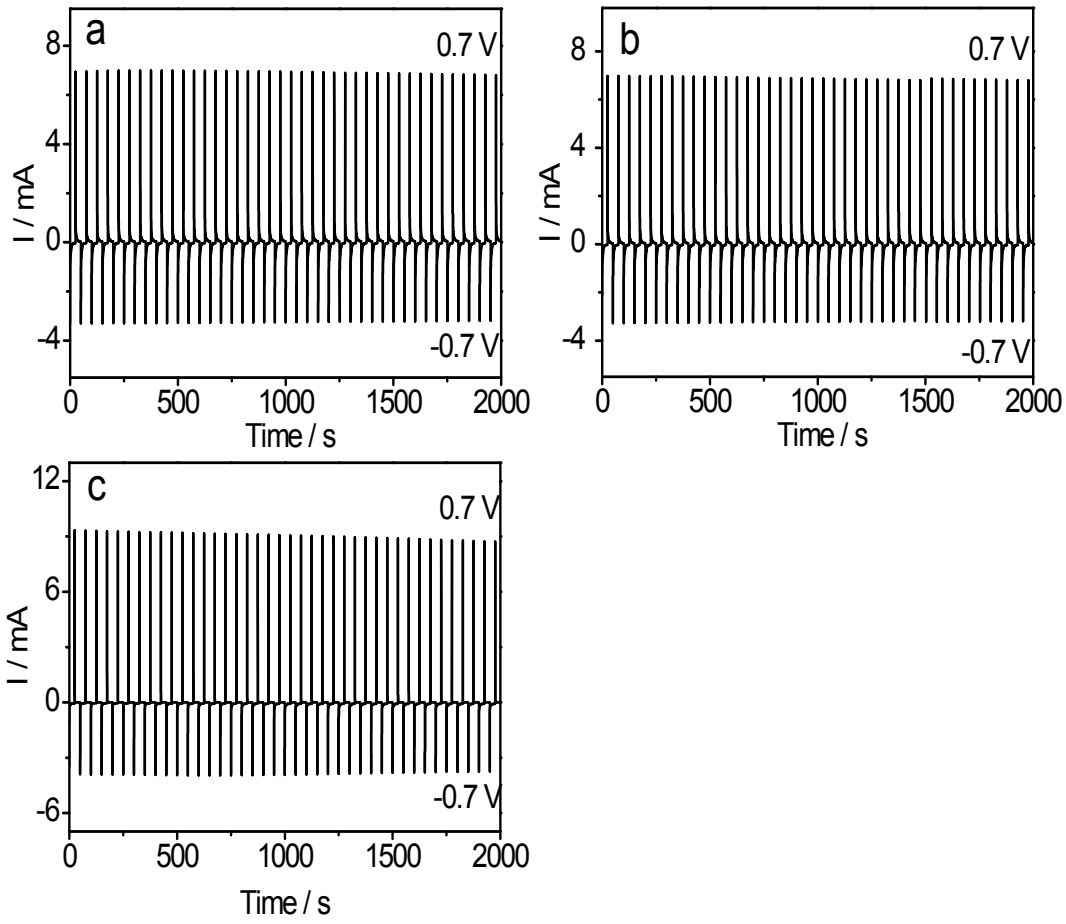

Fig. S7. Chronoamperometry curves of three composite films during subsequent double-potential steps from -0.7 V to +0.7 V in 0.5 M Na_2SO_4/H_2SO_4 (pH = 2.5) solutions: (a) ITO/$[(HOPTS)_{50}/(PDDA/P_5W_{30})_{10}]$; (b) ITO/$[(HOPTS)_{50}/(PDDA/P_5W_{30})_{27}]$; (c) ITO/$[(HOPTS)_{50}/(PDDA/P_5W_{30})_{57}]$.

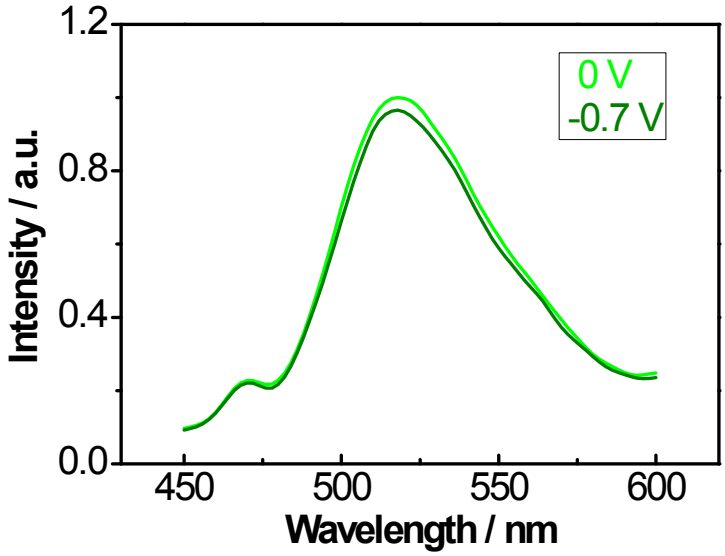

Fig. S8. Luminescent spectra of $(HOPTS)_{50}$ film in open circuit condition and with a potential of -0.7 V for 30 min in 0.5 M H_2SO_4/Na_2SO_4 solutions (pH = 2.5)

Table S1. Roughness of different HOPTS film in scanning range of 2 micrometer and 1 micrometer.

	Film 1	**Film 2**	**Film3**
$\mathbf{R_1}$	1.466 nm	3.481nm	6.981 nm
$\mathbf{R_2}$	1.520 nm	3.244 nm	5.856 nm

Note: R_1: scanning range of 2 micrometer; R_2: scanning range of 1 micrometer; Film 1: $(HOPTS)_{10}$; Film 2: $(HOPTS)_{50}$; Film 3: $(HOPTS)_{100}$.