

Supporting Information

Electrodeposition of unsubstituted iron phthalocyanine nano-structure film in a functionalized ionic liquid and its electrocatalytic and electroanalysis applications

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Results and Discussion

1. Characterizations of u-FePc electrodeposited film

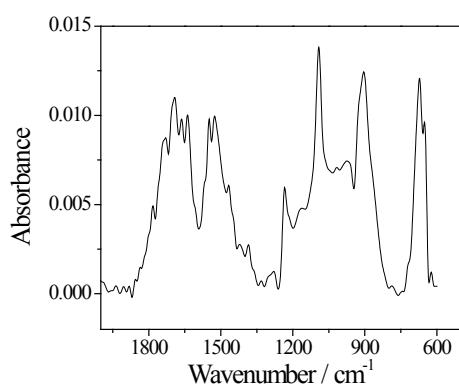


Fig. S1. The reflectance infrared spectrum of the u-FePc film.

Fig. S1 exhibits the reflectance infrared spectrum of electrode surface which was obtained by 40 CV scans continuously recorded at a GCE at the scan rate of 50 mV s^{-1} at 50 °C. As shown in Fig. S1, the peak at 1465 cm^{-1} can be attributed to the presence of the C-N=C asymmetry vibration; peaks at 1384 and 1170 cm^{-1} are observed, which can be assigned to the C-C stretching vibration; and peak at 1091 cm^{-1} can be own to the presence of the C-N bending vibration. All these peaks above are the characteristic absorption peaks of phthalocyanine, which indicates that the phthalocyanine film was successfully immobilized on the electrode surface.

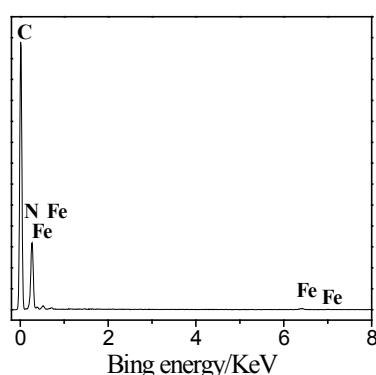


Fig. S2. EDS of the as-prepared u-FePc electrodeposited film.

An extended spectrum (EDS) of the as-prepared u-FePc electrodeposited film can be found in Fig. S2, which presented that the main compositions of u-FePc including C, N and Fe, further indicating the phthalocyanine film was successfully immobilized on the electrode surface.

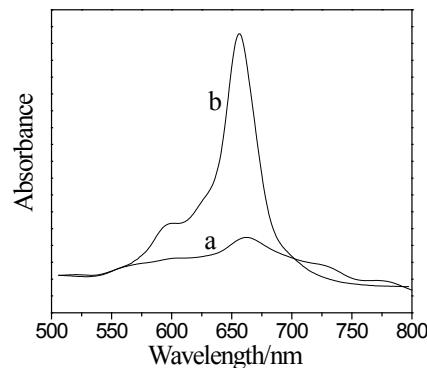


Fig. S3. Absorbance spectra of the as-prepared u-FePc electrodeposited film (a) and the pristine u-FePc powder in [OmimTFA] (b).

In addition, the as-prepared u-FePc film was compared with the pristine u-FePc powder by UV-vis absorption spectra. As shown in Fig. S3, the absorbance at the wavelength of ca. 660 nm was observed at both curves, which was ascribed to the characteristic absorption of u-FePc.¹ Further, compared with the absorbance of

pristine u-FePc powder in [OmimTFA] (curve b), the Q-band peak of the u-FePc film (curve a) shifted from 662 nm to 655 nm, which may due to the interaction between the u-FePc nanoparticles and matrix. And the absorbance of the as-prepared u-FePc film was lower than that of the pristine u-FePc powder, which may due to less amount of u-FePc on the surface of GCE.

2. Chronoamperometry for AA at u-FePc electrodeposited film electrode

Fig. S4 presented the chronoamperometry curves for successive adding 0.01 M AA at u-FePc/GCE in a 0.1 M PBS (pH 7.0) with stirring. As seen from Fig. S4, the modified electrode has high sensitivity, ready response toward to AA and the response time of less than 10 s. The catalytic current had a linear relationship with the concentration of AA in the range of 6×10^{-7} - 3.6×10^{-4} M ($R=0.9993$) with a detection limit (defined as the concentration that could be detected at the signal-to-noise ratio of 3, $S/N = 3$) of 1.7×10^{-7} M (inset in Fig. 5). More extensive and minute researches on electrocatalytic and electroanalytic applications of the u-FePc electrodeposited film will be presented in the near future.

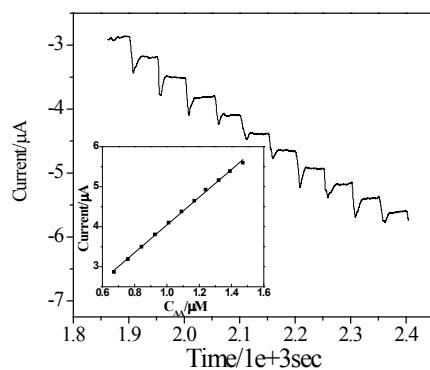


Fig. S4. Current-time curves for successive 0.01 M increments of AA at u-FePc/GCE in a stirring 0.1 M PBS (pH 7.0), applied potential: +0.207 V.

3. Stability and reproducibility of luminol ECL at u-FePc electrodeposited film electrode

The stability was further studied by continuous potential scanning for 10 circles. Fig. S5 showed that the first cycle was a bit lower and the signal was increased due to the absorption of luminol in the vicinity of the working electrode,² and further, no obvious change was observed. The as-prepared electrode still kept over 96% activity towards 3.0 μM luminol after being stored in air for 20 days (data from continuous potential scanning for 6th circle) and the RSD of ECL intensity for measurement of 3.0 μM luminol at five independently as-prepared electrodes was 5.6%, which proved good reproducibility of the as-prepared u-FePc electrodeposition film.

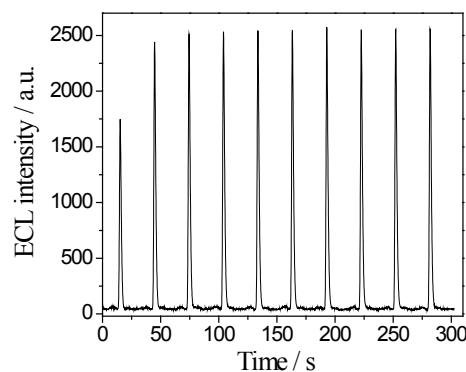


Fig. S5. ECL emission from the u-FePc/GCE in 0.1 M pH 7.4 PBS containing 5.0 μM luminol under continuous cyclic scans for 10 cycles. Scan rate: 100 mV s⁻¹.

4. Effect of pH on luminol ECL at u-FePc/GCE

Previous investigations have revealed that the ECL behavior of luminol is strongly affected by many factors such as the electrode material, surface state of the electrode and pH.^{3,4} So in our work, the dependence of pH value on the luminol ECL intensity at u-FePc/GCE was also studied. As displayed in Fig. S6, although with the increase

of pH value range from 7.0 to 11.0, the ECL intensity was enhanced apparently, the ECL intensity of luminol in pH 7.4 PBS at u-FePc/GCE was higher than that at the CNT/Nafion modified gold electrode in pH 10.0 basic buffer solution.³² Thus, in order to explore the bioanalytical applications of the luminol ECL at u-FePc/GCE, we chose pH 7.4 in the subsequent experiments in our work.

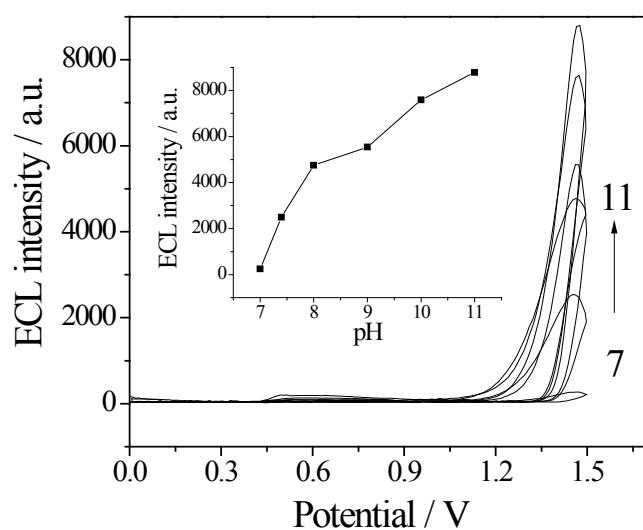


Fig. 6S The ECL behavior of u-FePc/GCE in 0.1 M PBS of different pH value in the presence of 3.0 μ M luminol. Inset: the effect of pH on the ECL behaviors of u-FePc/GCE.

Reference

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