

## Supplementary Information

### Direct Electrochemistry and Electrocatalysis of Anthraquinone- monosulphonate/Polyaniline Hybrid Film Synthesized by a Novel Electrochemical Doping-Dedoping-Redoping Method on Pre-activated Spectroscopically Pure Graphite Surface†

Guoquan Zhang, Fenglin Yang\*

Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of  
Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, P.R.  
China

\* To whom correspondence should be addressed. E-mail: [yangfl@dlut.edu.cn](mailto:yangfl@dlut.edu.cn)

To be submitted as an article to *Physical Chemistry Chemical Physics* (Phys. Chem. Chem. Phys.)

## 1 **Electrosynthesis of AQS/PANI hybrid film**

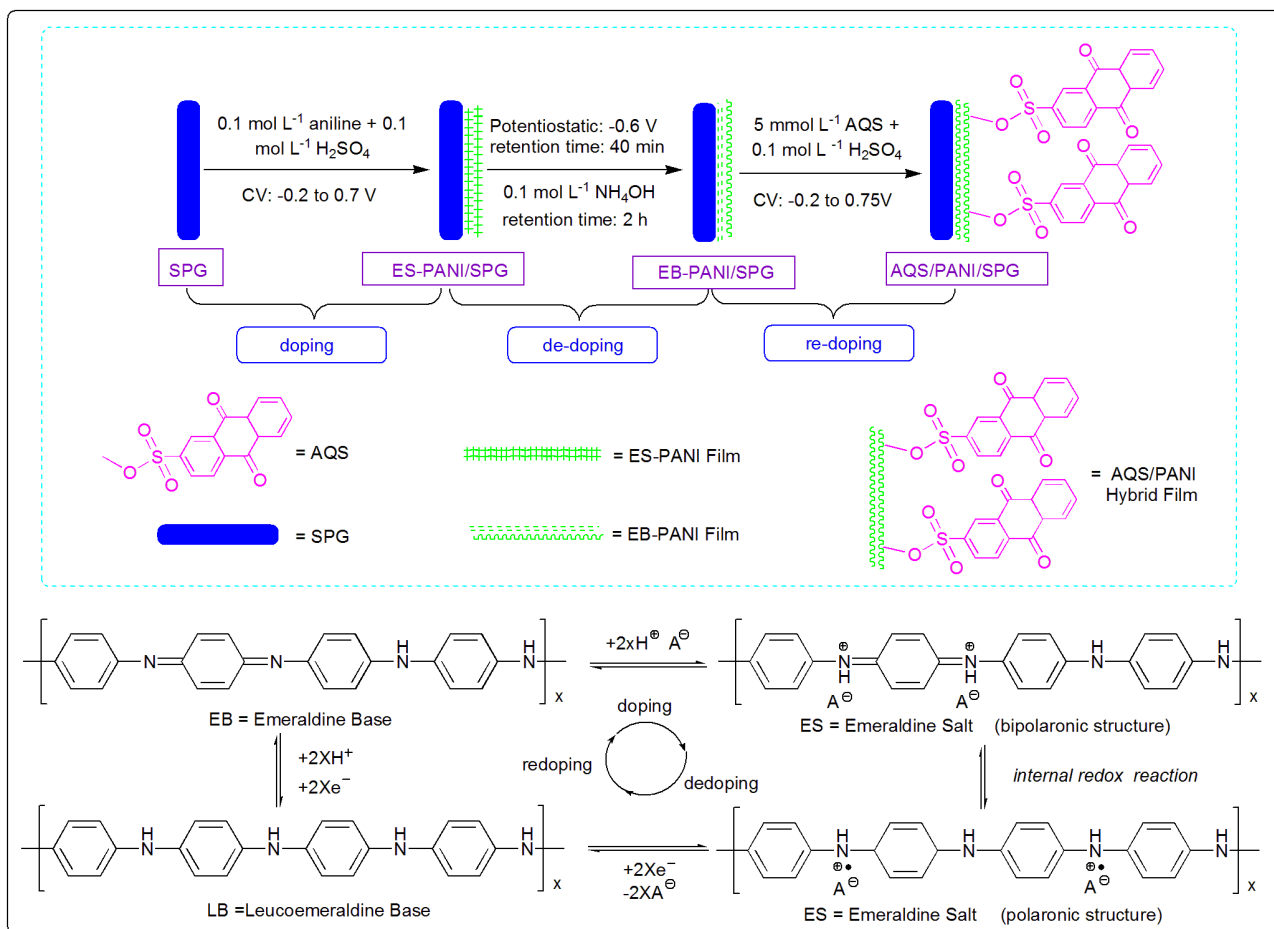
2 The AQS/PANI hybrid film was synthesized by an electrochemical doping–dedoping–redoping  
3 method. Before electropolymerization, the graphite disk electrode impregnated with paraffin was  
4 polished to a mirror-like surface with fine alumina powder and cleaned by mild sonication in pure  
5 water. Then, the working electrode was cycled in potential range from  $-0.5$  V to  $1.8$  V at  $50$   $\text{mV s}^{-1}$  in  
6  $\text{N}_2$ -saturated  $0.1$   $\text{mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution in order to activate the electrode. In the doping process, freshly  
7 distilled aniline was *in situ* electropolymerized on working electrode by CV method in  $0.1$   $\text{mol L}^{-1}$   
8  $\text{H}_2\text{SO}_4$  solution containing  $0.1$   $\text{mol L}^{-1}$  aniline, resulting in the emeraldine salt form of PANI (ES-  
9 PANI). Then, the  $\text{SO}_4^{2-}$  anion was removed from the resulting film to obtain the emeraldine base form  
10 of PANI (EB-PANI) by dedoping method. After dedoping, the obtained EB-PANI was redoped with  
11 AQS to prepare the AQS/PANI hybrid film. A typical example for the preparation of AQS/PANI hybrid  
12 film by the electrochemical doping-dedoping-redoping method is given as follows:

13 The deposition of ES-PANI films on working electrode was performed by CV method rather than  
14 using a constant current method, since it was found that films deposited by cycling display lower  
15 background currents, and thus better insulating properties at the negative end of voltage span. Thin  
16 PANI film was grown on graphite disk electrode in  $0.1$   $\text{mol L}^{-1}$   $\text{H}_2\text{SO}_4$  +  $0.1$   $\text{mol L}^{-1}$  aniline solution  
17 under  $\text{N}_2$  atmosphere to obtain ES-PANI, using the following methodology: (a) first and second  
18 cycles—potentiodynamic polymerization by cycling at  $2$   $\text{mV s}^{-1}$  from  $-0.2$  V to  $+0.9$  V; (b) other cycles  
19 (up to 20)—potential cycling between  $-0.2$  V and  $+0.7$  V at  $10$   $\text{mV s}^{-1}$  at room temperature. Then, the  
20 ES-PANI was dedoped firstly by potentiostatic treatment at  $-0.2$  V in aniline monomer free  $\text{N}_2$ -  
21 saturated  $0.1$   $\text{mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution for 40 min, followed by immersing it in  $0.1$   $\text{mol L}^{-1}$   $\text{NH}_4\text{OH}$  at  
22 room temperature for 2 h and then in ice cold distilled water for 2 h to remove doped or physically  
23 adsorbed  $\text{SO}_4^{2-}$  anion, and thus obtain the EB-PANI.

24 After dedoping by potentiostatic treatment and immersed in  $\text{NH}_4\text{OH}$  aqueous solution and ice water,  
25 the EB-PANI was redoped also by CV method at  $10$   $\text{mV s}^{-1}$  from  $-0.2$  V to  $+0.75$  V in  $\text{N}_2$ -saturated  $0.1$   
26  $\text{mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution containing  $5$   $\text{mmol L}^{-1}$  AQS. This redoping process is assumed to be counter-

1 ion doping during PANI oxidation, and is an irreversible process due to the big bulk of doping AQS  
2 (AQS<sub>doping</sub>). The electrode was cycled repeatedly until stable cyclic voltammograms were obtained and  
3 thus get the AQS/PANI hybrid film. The preparation details can be illustrated in **Scheme S1**. The  
4 resulting electrode was washed with distilled water and ethanol and then dried in a vacuum overnight at  
5 60 °C before use.

6



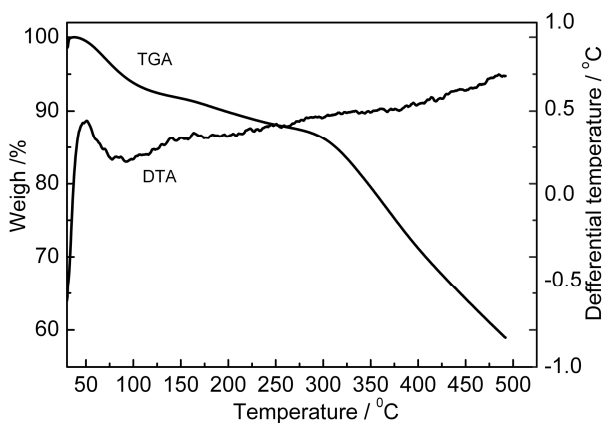
8 **Scheme S1** Electrochemical synthesis of the AQS/PANI hybrid film on graphite electrode surface using an  
9 electrochemical doping-dedoping-redoping method.

10

### 11 Thermogravimetric analysis/Simultaneous differential thermal analysis (TGA/SDTA)

12 Thermal degradation studies were performed under nitrogen atmosphere at a linear heating rate of 10  
13 °C /min from room temperature to 500 °C. TGA/SDTA measurement of the AQS/PANI hybrid film  
14 shown in **Fig. S1** indicates that the mass loss undergoes three steps: (1) starts at 50 °C and continues up

1 to 100 °C; (2) a slow weight loss in the temperature range from 100 to 300 °C; and (3) a significant  
2 mass loss up to 500 °C. For the first-step weight loss, the AQS/PANI hybrid film shows 2–5% weight  
3 loss, which is attributed to the loss of surface water.<sup>1–3</sup> SDTA measurement suggests that this step is  
4 endothermic process. We interpreted the second-step weight loss as dopant loss (AQS<sub>doping</sub> dedoping).  
5 The third-step weight loss starting at 300 °C and up to 500 °C is due to the decomposition of  
6 AQS/PANI hybrid film, which corresponds to the decomposition temperature, 296 – 300 °C, of  
7 AQS<sub>doping</sub>. This result is consistent well with the fact that ES forms of PANI films begin to decompose  
8 at a temperature much lower than the decompose temperature of EB (around 500 °C).<sup>1</sup> In addition, it is  
9 an exothermic process according to the SDTA curve.

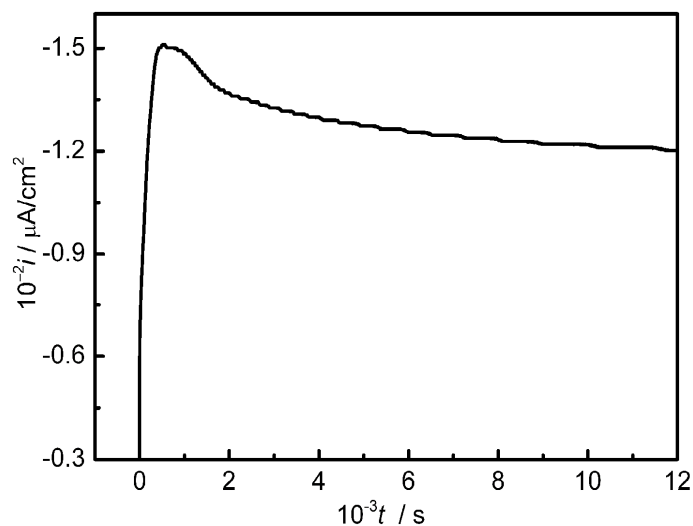


10  
11 **Fig. S1** TGA and SDTA curves of the AQS/PANI hybrid film

### 12 13 **The stability of AQS/PANI hybrid film**

14 The performance of the AQS/PANI hybrid film modified electrode towards ORR in pH 3.07 O<sub>2</sub>-  
15 saturated solution was further investigated by single potential-step chronoamperometry method at a  
16 cathodic potential of -0.5 V for over 3–4 hours at room temperature. During test, O<sub>2</sub> gas was  
17 continuously bubbled around the working electrode. As seen from **Fig. S2**, the AQS/PANI hybrid film  
18 modified electrode is quite stable as it produces an approximately constant value of oxygen reduction  
19 current during the entire period of investigation. This result should be firstly attributed to the excellent  
20 environmental stability of PANI layer. On the other hand, AQS on account of its high degree of

1 planarity contributes also to the stability of hybrid film, because the stability and the electronic  
2 conductivity of conducting polymer films doped with various anthraquinone sulfonate correlate well  
3 with the number of sulfonate groups attached, and the best result attained at one sulfonate group per  
4 dopant molecule.<sup>4</sup>



5

6 **Fig. S2** Single potential-step chronoamperometric response of the AQS/PANI hybrid film modified  
7 electrode in pH 3.07 O<sub>2</sub>-saturated solution at -0.5 V under continues O<sub>2</sub> bubbling conditions.

8

## 9 **References**

- 10 (1) W. G. Li and M. X. Wan, *J. App. Polym. Sci.*, 1999, **71**, 615–621.
- 11 (2) K. Huang and M. X. Wan, *Chem. Mater.*, 2002, **14**, 3486–3492.
- 12 (3) J. Gong, X. J. Cui, Z. W. Xie, S. G. Wang, L. Y. Qu, *Synth. Met.*, 2002, **129**, 187–192.
- 13 (4) M. Hepel, *Electrochim. Acta*, 1996, **41**, 63–76.