

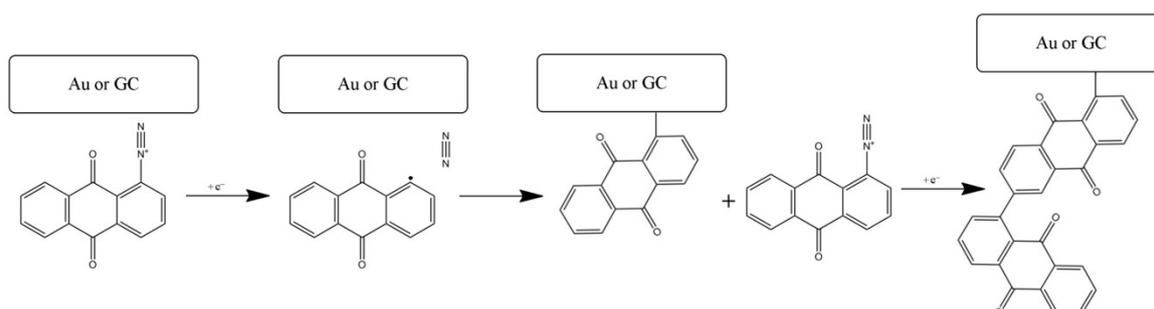
## Electronic supplementary information

### Electrochemical properties of gold and glassy carbon electrodes electrografted with anthraquinone diazonium compound using the rotating disc electrode method

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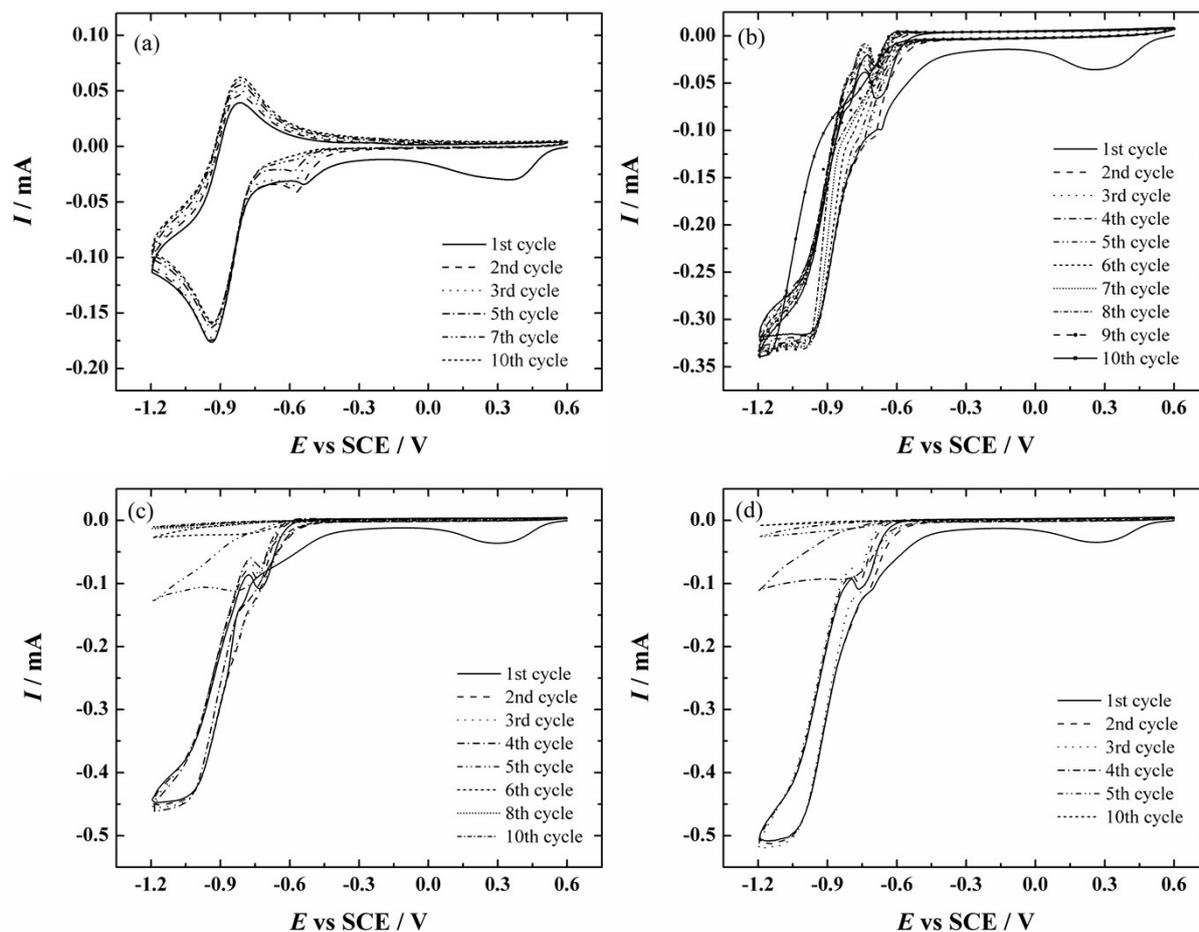
**Scheme S1.** The illustration of electrografting process of anthraquinone-1-diazonium compound on Au or GC surface by electro-chemical reduction of AQ diazonium salts.<sup>1,2</sup>

**Table S1.** The modification procedures of Au electrode surface with anthraquinone groups. Modification solution: 2 mM Fast Red AL salt in acetonitrile containing 0.1 M TBABF<sub>4</sub> as a supporting electrolyte.

<b>Designation</b>	<b>Modification conditions</b>
Au/AQ-0.4	10 cycles between 0.5 and -0.4 V at 100 mV s <sup>-1</sup> , $\omega = 0$ rpm
Au/AQ-200	10 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 200$ rpm
Au/AQ-500	10 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 500$ rpm
Au/AQ-1	1 cycle between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-2	2 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-3	3 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-6	6 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-8	8 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-10	10 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 1000$ rpm
Au/AQ-10*	10 cycles between 0.5 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega = 0$ rpm
Au/AQ-a	5 potential steps (10 s at -1.2 V + 10 s at -0.5 V), $\omega = 1000$ rpm
Au /AQ-b	5 potential steps (15 s at -1.2 V + 10 s at -0.5 V), $\omega = 1000$ rpm
Au /AQ-b*	5 potential steps (15 s at -1.2 V + 10 s at -0.5 V), $\omega = 0$ rpm
Au /AQ-c	5 potential steps (20 s at -1.2 V + 10 s at -0.5 V), $\omega = 1000$ rpm

**Table S2.** The modification procedures of GC electrode surface with anthraquinone groups. Modification solution: 2 mM Fast Red AL salt in acetonitrile containing 0.1 M TBABF<sub>4</sub> as a supporting electrolyte.

<b>Designation</b>	<b>Modification conditions</b>
GC/AQ-1.1	10 cycles between 0.6 and -1.1 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-1.3	10 cycles between 0.6 and -1.3 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-200	10 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 200 rpm
GC/AQ-500	10 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 500 rpm
GC/AQ-1	1 cycle between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-2	2 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-3	3 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-6	6 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-10	10 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 1000 rpm
GC/AQ-10*	10 cycles between 0.6 and -1.2 V at 100 mV s <sup>-1</sup> , $\omega$ = 0 rpm
GC/AQ-a	5 potential steps (10 s at -1.2 V + 10 s at -0.5 V), $\omega$ = 1000 rpm
GC/AQ-b	5 potential steps (15 s at -1.2 V + 10 s at -0.5 V), $\omega$ = 1000 rpm
GC/AQ-b*	5 potential steps (15 s at -1.2 V + 10 s at -0.5 V), $\omega$ = 0 rpm
GC/AQ-c	5 potential steps (20 s at -1.2 V + 10 s at -0.5 V), $\omega$ = 1000 rpm

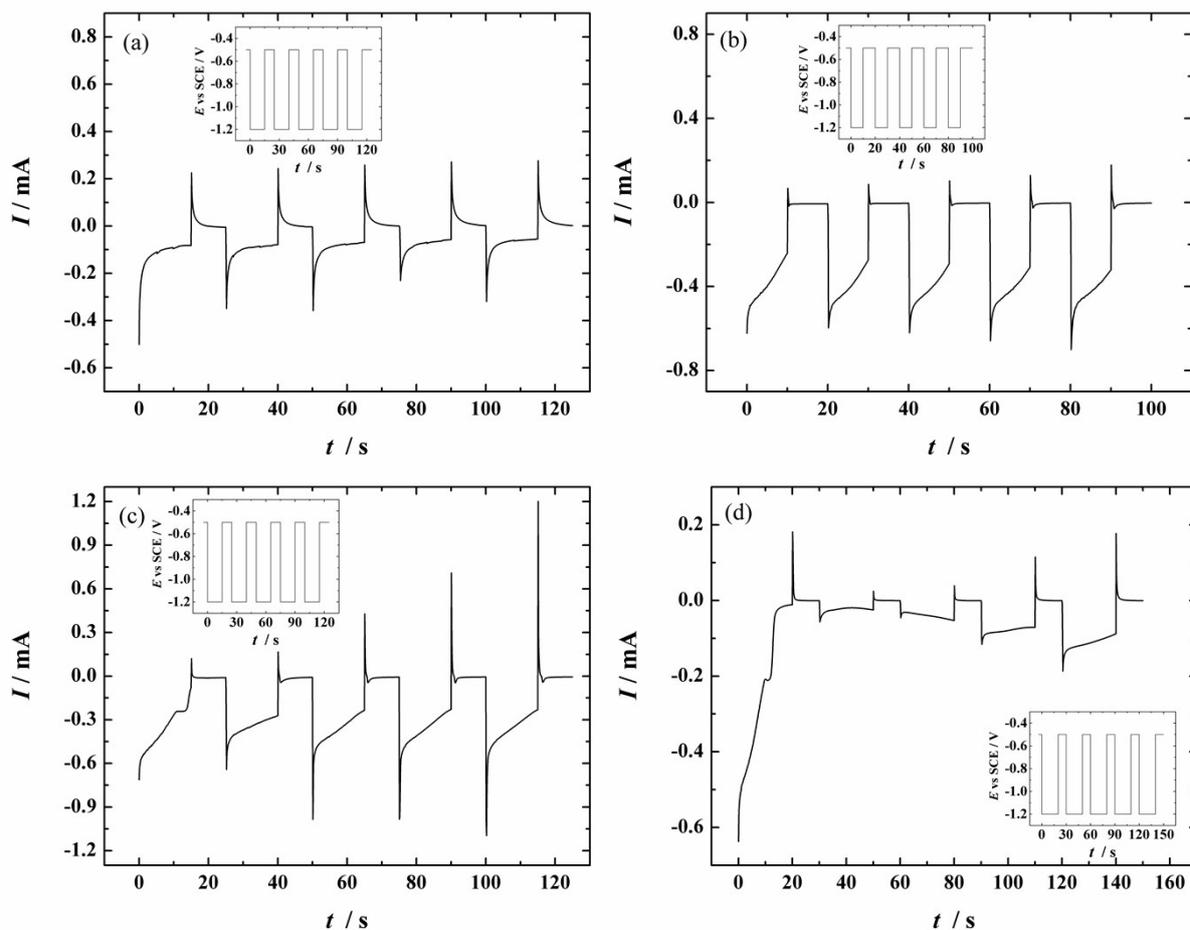


**Fig. S1** Redox grafting of anthraquinone on glassy carbon electrode using 2 mM Fast Red AL salt in Ar-saturated ACN containing 0.1 M TBABF<sub>4</sub> as a base electrolyte by: (a) cyclic voltammetry ( $v = 100 \text{ mV s}^{-1}$ ), (b-d) combination of CV and the RDE method ( $v = 100 \text{ mV s}^{-1}$ ,  $\omega =$  (b) 200 rpm ; (c) 500 rpm; (d) 1000 rpm). In all Figs, up to 10 potential cycles are shown.

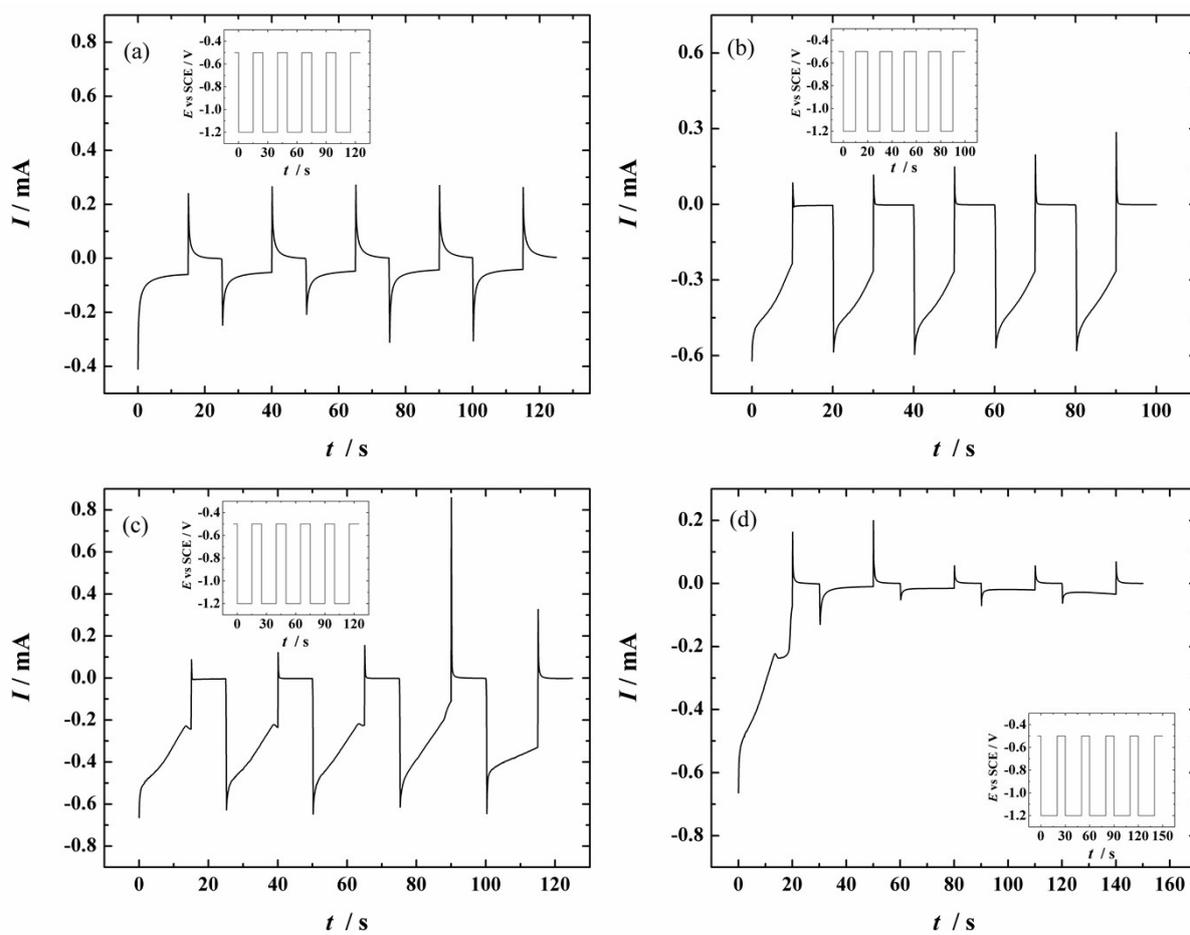
### Electrografting of Au and GC electrodes with AQ groups using potential step method with and without the RDE method

For the electrochemical reduction of aryldiazonium salts on metal and carbon electrodes, the potential step method has been quite extensively used.<sup>3-10</sup> However, to our knowledge there is no literature about electrografting of Au and GC electrodes using the combined potential step and RDE methods. Firstly, the potential of  $-1.2 \text{ V}$ , which is significantly more negative than the reduction wave of AQ to AQ<sup>-</sup> (see Fig.

1a) was chosen for recording the chronoamperometry (CA) response. The  $I-t$  curves of stationary Au electrode during surface modification are presented in Fig. S2a and the inset shows the potential profile applied during the electrografting experiment. In the beginning the current registered at  $-1.2$  V quickly drops within a second, then gradually decreases and finally linearly descends forming a plateau similarly to the modification of Au electrodes by potential step with different diazonium salts used in the literature.<sup>3, 7, 10, 11</sup> Thereafter, the RDE method was combined with the potential step method. In Figs. S2b-d, the current vs. time transient of Au electrodes was recorded five times at  $\omega = 1000$  rpm for holding time of 10, 15 and 20 s, respectively. As can be seen from Fig. S2b the reduction current decreases after sharp drop almost linearly until the potential is changed to  $-0.5$  V. In general, the overall reduction current increases during the 5 rectangular potential waves, which may refer to the increase in the number of electroactive AQ groups in the aryl film. This kind of electrochemical behaviour resembles that of the Au/AQ-10 electrode, when the reduction current increased with subsequent modification cycles between  $-1.0$  and  $-1.2$  V (see Fig. 1d). In case of applying potential step for 15 s (see Fig. S2c), a change in reduction current can be seen after ca. 10 s. This behaviour does not recur in the following potential waves but in case of GC (see Fig. S3c) the current vs. time response was similar up to the 3rd wave. When 20 s step (see Fig. S2d) is used the reduction current declines close to zero during the first potential step applied, which may indicate that the channels in aryl film are clogged with physisorbed species and the aryl film becomes insulating.<sup>1, 12</sup> During the subsequent CA responses at  $-1.2$  V for 20 s the current increases again, which may indicate that the electrode surface or electroactive species in the film become accessible reduction sites once again. In case of GC (see Fig. S3d) the current stayed relatively low during the following rectangular potential waves indicating that the aryl film formed on GC may be more densely packed than on Au and the reduction sites remain blocked.<sup>9, 10</sup>



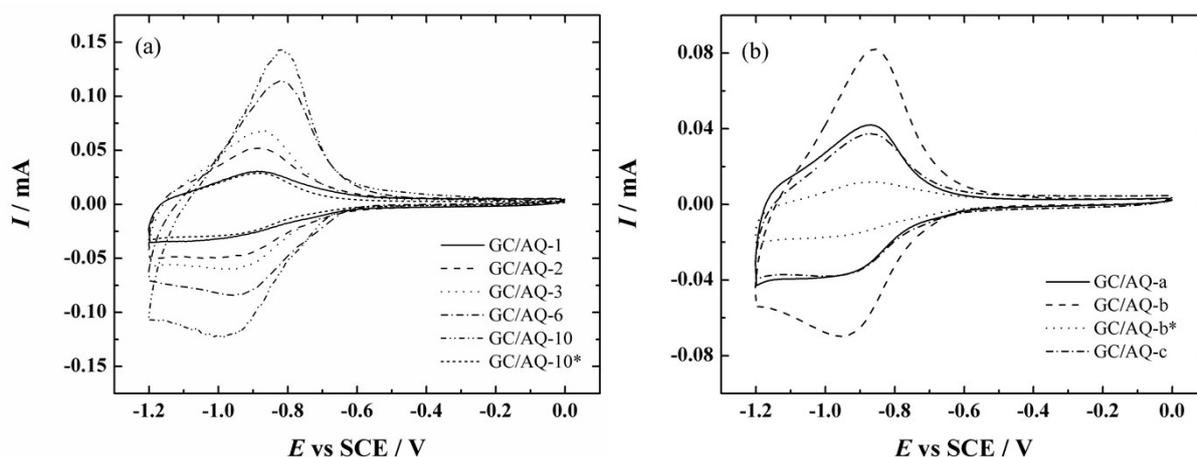
**Fig. S2** Electrografting of anthraquinone groups on gold electrode by: (a) potential step method and (c-d) combined potential step and the RDE method using 2 mM Fast Red AL salt in Ar-saturated ACN containing 0.1 M TBABF<sub>4</sub> as a base electrolyte. Five rectangular potential waves were applied: (a) 15 s at -1.2 V and then at -0.5 V for 10 s; (b) 10 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm); (c) 15 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm); (d) 20 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm). The insets present the potential waveform used during surface modification.



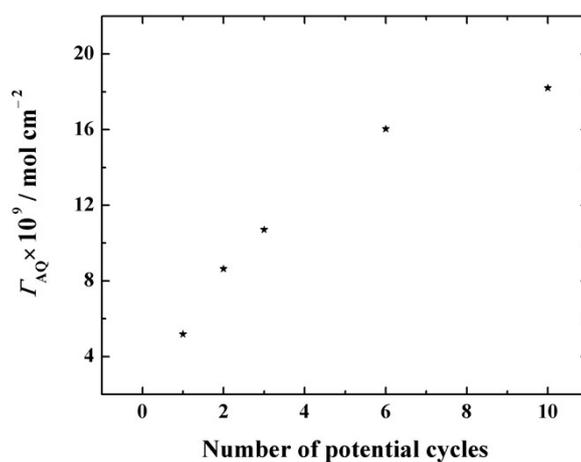
**Fig. S3** Electrografting of anthraquinone groups on glassy carbon electrode by: (a) potential step method and (c-d) combined potential step and the RDE method using 2 mM Fast Red AL salt in Ar-saturated ACN containing 0.1 M TBABF<sub>4</sub> as a base electrolyte. Five rectangular potential waves were applied: (a) 15 s at -1.2 V and then at -0.5 V for 10 s; (b) 10 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm); (c) 15 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm); (d) 20 s at -1.2 V and then at -0.5 V for 10 s ( $\omega = 1000$  rpm). The insets present the potential waveform used during surface modification.

**Table S3.** Surface concentrations of anthraquinone ( $\Gamma_{AQ}$ ) on GC and Au electrodes. Modification solution: 2 mM Fast Red AL salt in acetonitrile containing 0.1 M TBABF<sub>4</sub> as a supporting electrolyte.

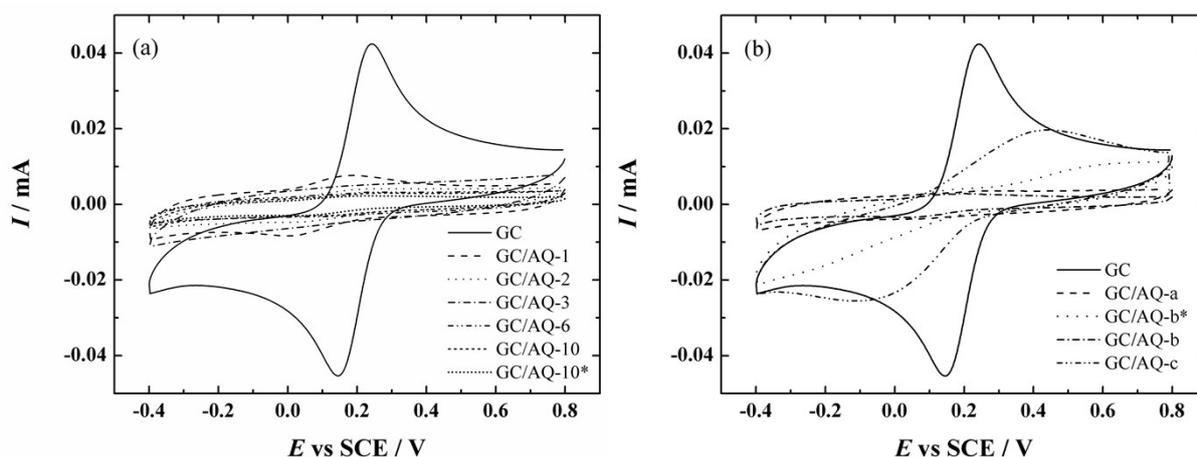
<b>Designation</b>	<b><math>\Gamma_{AQ}</math> (mol cm<sup>-2</sup>)</b>	<b>Designation</b>	<b><math>\Gamma_{AQ}</math> (mol cm<sup>-2</sup>)</b>
Au/AQ-0.4	$2.6 \times 10^{-9}$	GC/AQ-1.1	$1.1 \times 10^{-8}$
Au/AQ-200	$1.8 \times 10^{-8}$	GC/AQ-1.3	$1.0 \times 10^{-8}$
Au/AQ-500	$1.6 \times 10^{-8}$	GC/AQ-200	$1.3 \times 10^{-8}$
Au/AQ-1	$4.6 \times 10^{-9}$	GC/AQ-500	$1.2 \times 10^{-8}$
Au/AQ-2	$6.8 \times 10^{-9}$	GC/AQ-1	$5.2 \times 10^{-9}$
Au/AQ-3	$1.2 \times 10^{-8}$	GC/AQ-2	$8.6 \times 10^{-9}$
Au/AQ-6	$1.7 \times 10^{-8}$	GC/AQ-3	$1.1 \times 10^{-8}$
Au/AQ-8	$1.8 \times 10^{-8}$	GC/AQ-6	$1.6 \times 10^{-8}$
Au/AQ-10	$2.1 \times 10^{-8}$	GC/AQ-10	$1.8 \times 10^{-8}$
Au/AQ-10*	$8.0 \times 10^{-9}$	GC/AQ-10*	$4.9 \times 10^{-9}$
Au/AQ-a	$9.1 \times 10^{-9}$	GC/AQ-a	$6.8 \times 10^{-9}$
Au/AQ-b	$1.7 \times 10^{-8}$	GC/AQ-b	$1.2 \times 10^{-8}$
Au/AQ-b*	$3.1 \times 10^{-9}$	GC/AQ-b*	$2.4 \times 10^{-9}$
Au/AQ-c	$8.9 \times 10^{-9}$	GC/AQ-c	$6.0 \times 10^{-9}$



**Fig. S4** Cyclic voltammograms of GC/AQ electrodes with various AQ surface concentration registered in Ar-saturated ACN containing 0.1 M TBABF<sub>4</sub> ( $\nu = 100 \text{ mV s}^{-1}$ ). The electrografting of GC electrode with AQ groups was carried out using: (a) cyclic voltammetry and the RDE method, (b) potential step and the RDE method.



**Fig. S5** The dependence between the AQ surface concentration ( $\Gamma_{AQ}$ ) and the number of potential cycles used during the electrografting of the GC electrode. The modifying solution was Ar-saturated ACN containing 2 mM Fast Red AL salt and 0.1 M TBABF<sub>4</sub>. The modification conditions: the GC electrode was cycled between 0.6 and -1.2 V by applying 1, 2, 3, 6 and 10 potential cycles,  $\nu = 100 \text{ mV s}^{-1}$  and  $\omega = 1000 \text{ rpm}$  were used.



**Fig. S6** Cyclic voltammograms of bare and different AQ-modified GC electrodes registered in Ar-saturated 0.1 M  $K_2SO_4$  containing 1 mM  $K_3Fe(CN)_6$  ( $v = 100 \text{ mV s}^{-1}$ ). The electrografting of GC electrode with AQ groups was carried out using: (a) cyclic voltammetry and the RDE method, (b) potential step and the RDE method.

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