

## **Supplementary Information**

**Fig. S1** A and B are the effects of the potential window -0.5 to 1.0 V and the potential window -0.8 to 1.0 V in electrode pretreatment.



**Fig. S2** A and B are the effects of the GCE<sub>-10-6</sub> (GCE in potential window 0.5~2.0 V sweep rate 0.05 V·s<sup>-1</sup> CV scanning 10 turns after 6 turns in the potential window -0.5~1.0 V sweep rate 0.05 V·s<sup>-1</sup> CV scanning) and GCE<sub>-10-7</sub> (GCE after 10 turns of potentiometric window 0.5~2.0 V sweep rate 0.05 V·s<sup>-1</sup> CV scan and 7 turns of the potentiometric window -0.5~1.0 V sweep rate 0.05 V·s<sup>-1</sup> CV scan ) in electrode pretreatment.



Fig. S3 Elemental mapping of (A) GCE and (B) AGCE.

Table S1 C and O mass distribution of GCE	and AGCE.
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Electrodes	C(wt%)	O(wt%)
GCE	100	0
AGCE	96.90	3.10



Fig. S4 FTIR spectra of unmodified GCE and AGCE.



**Fig. S5** Nyquist plots and fitted results of (A) GCE, (B) GCE<sub>-ox</sub>, and (C)AGCE in 0.1 M NaCl with  $5.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-/4-}$  as an electrochemical probe; (D) The equivalent circuits for simulation of different systems: (1) for GCE, AGCE and (2) for GCE<sub>-ox</sub>.

Electrodes	GCE	GCE-ox	AGCE
$R_{ m S}/\Omega$	107.0	92.7	108.2
$C_{d1}$ or $Q_{dl}/S \cdot s^n$	9.72×10 -7	3.63×10 <sup>-6</sup>	2.45×10 -5
<i>n</i> (0 <n<1)< td=""><td>/</td><td>0.86</td><td>/</td></n<1)<>	/	0.86	/
$R_{ m ct}/\Omega$	61.3	1.43×10 <sup>3</sup>	149.5
$Z_{ m w}/{ m S}\cdot{ m s}^{0.5}$	1.59×10 -3	1.65×10 <sup>-3</sup>	1.67×10 -3
chi-squared	1.55×10 -3	7.13×10 -4	1.31×10 -3

Table S2 Fitting parameters of electrochemical impedance spectroscopy for different electrodes.

 $R_{\rm s}$  is the resistance of electrolyte solution;  $C_{\rm dl}$ , double layer capacitance;  $Q_{\rm dl}$ , constant phase element relating to the electric double layer; *n* is a number ranging from 0 to 1 with n = 1 for the ideal capacitor;  $R_{\rm ct}$ , charge transfer resistance;  $Z_{\rm w}$ , Warburg impedance; chi-squared, A measure of goodness of fit.

Electrodes	GCE	AGCE
solution	5.0×10 <sup>-5</sup> mol·L <sup>-1</sup> EP	5.0×10 <sup>-5</sup> mol·L <sup>-1</sup> EP
$E_{\rm pa}({ m mV})$	205	129
<i>i</i> <sub>pa</sub> (μA)	1.27	35.57

Table S3 Summary of CV results obtained in Fig. 5.



**Fig. S6** CV curves of (A) AGCE for the detection of  $5 \times 10^{-5}$  mol·L<sup>-1</sup> EP at different accumulation times (from 0 to 480 s), (B) the effect of different accumulation times on the peak EP anode current.



**Fig. S7** (A) LSV curves after baseline subtraction of EP (a), EP equimolar AA (b), EP 10-fold AA (c), and EP 20-fold AA (d) detected by AGCE; (B) AGCE detection of EP(a), EP equimolar UA(b), and EP 10-fold UA(c); (C) AGCE detection of EP(a) and EP equimolar PE(b); (D) AGCE detection of EP(a), EP 100-fold Glu(b), and EP 100-fold Gly(c). All the experiments were performed in pH 7.4 phosphate buffer with  $5.0 \times 10^{-5}$  mol·L<sup>-1</sup> EP.

AA		EP		UA		PE	- -
$E_{\rm pa}({\rm mV})$	i <sub>pa</sub> (μA)	$E_{\rm pa}({ m mV})$	$i_{\rm pa}(\mu A)$	$E_{\rm pa}({\rm mV})$	$i_{\rm pa}(\mu A)$	$E_{\rm pa}({\rm mV})$	$i_{\rm pa}(\mu A)$
-25	0.80	145	40.24	269	3.95	615	1.84

Table S4 Summary of LSV results obtained in Fig. 6B.

Table S5 Comparison of AGCE with those reported in the literature for the determination of EP using

different techniques.

Sensor	Method	Linear range (umol·L <sup>-1</sup> )	Detection limit (umol·L <sup>-1</sup> )	Reference	
5011001		Zinear range (pinter 2-)			
PGCE	SWV	10.3–102.7	2.86	[11]	
AuNPs/PEDOT/G			1.4	[12]	
CE	CV	10-040	1.4	[12]	
CuO/CQDs/ GCE	SWV	10-100	15.99	[13]	
MoS <sub>2</sub> /MW-	CV	0.0.127.0	2	[14]	
CNTs/GCE	Cv	9.9–137.9	3	[14]	
MGO/GCE	CV	100-600	0.13	[15]	
Lac/GC@B <sub>4</sub> C/NF	i-t	0.1–2600	0.04	[17]	
	LOV	0.1–8.0, 10–100, 100–	0.022		
AGCE	LSV	700	0.032	I his work	

Table S6 Detection of EP in the identical EP solution in pH 7.4 phosphate buffer using the same

AGCE electrode.

n	added	found	Average	Relative	RSD
	(µmol·L <sup>-1</sup> )	$(\mu mol \cdot L^{-1})$	$(\mu mol \cdot L^{-1})$	error (%)	(%)
1		50.21			
2	50.00	49.02	49.69	0.62	1.23
3		49.84			

Table S7 Detection of EP in the identical EP solution in pH 7.4 phosphate buffer using different

electrode	added	found	Average	Relative	RSD
	$(\mu mol \cdot L^{-1})$	$(\mu mol \cdot L^{-1})$	$(\mu mol \cdot L^{-1})$	error (%)	(%)
1		51.60		0.18	
2	50.00	50.42	50.09		3.40
3		48.24			

AGCE electrodes prepared in identical conditions.



**Fig. S8** AGCE measured the (a) LSV curve of  $5 \times 10^{-5}$  mol·L<sup>-1</sup> EP at first detection and the (b) LSV curve after 8 days of storage at room temperature.