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6 **A universal strategy for the facile synthesis of sandwich-**7 **structured Pt-graphene-Pt nanocomposite for Salbutamol sensing** 8 Xiaofei Zhu ^{a,b,†}, Xuemin Duan ^{a,†}, Jingkun Xu ^{a,*}, Limin Lu ^{b,*}, Kaixin Zhang ^c, Huakun Xing ^a, Yansha Gao^a, Taotao Yang^a, Wenmin Wang^b 10 In this work, sandwich-structured Pt-graphene-Pt (P-Gr-P) nanocomposite has been prepared by two-step method 11 including (i) a chemical and (ii) an electrochemical reduction process. P-graphene oxide-P (P-GO-P) nanocomposite was 12 firstly synthesized by an in situ growth method, during which Platinum nanoparticles (PtNPs) grew on both sides of GO. In 13 the second step, P-GO-P was modified onto glass carbon electrode (GCE), GO in P-GO-P nanocomposite was reduced to a 14 more conductive form of graphene (Gr). The obtained sandwich-structured P-Gr-P can effectively separate the individual 15 layers of Gr sheets from each other, prevent the agglomeration of Gr sheets and improve the conductivity of the Gr film. In 16 addition, the electrocatalytic properties of the as prepared P-Gr-P nanocomposite towards the oxidation of salbutamol 17 (SAL) were investigated. Results revealed that the sandwich-structured P-Gr-P nanocomposite with higher 18 electrochemically active surface area showed better electrocatalytic activity toward SAL oxidation than PtNPs-Gr prepared 19 by using one-step electrochemical co-deposition method. On the basis of the excellent electrochemical activity of P-Gr-P 20 nanocomposite, a highly sensitive electrochemical platform was developed for the rapid detection of SAL. The present 21 work provides an interesting strategy to prepare Gr-based nanocomposite for electrochemical sensors.

23 **1. Introduction**

24 Salbutamol $[1-(4-hydroxy-3-hydroxymethylphenyl)-2-(t-25-hutvlamino)ethanol] (SAL) is a β_2 adrenergic receptor agonist$ 25 butylamino)ethanol] (SAL) is a β_2 adrenergic receptor agonist 26 which primarily used in the treatment of bronchial asthma and 26 which primarily used in the treatment of bronchial asthma and 27 other forms of allergic airway disease associated with 27 other forms of allergic airway disease associated with 28 respiratory pathway¹. SAL is also applied as a tocolytic agent 28 respiratory pathway¹. SAL is also applied as a tocolytic agent 29 in humans as well as in veterinary medicine. However, 29 in humans as well as in veterinary medicine. However, 30 residues of SAL in higher doses may display line that effect 30 residues of SAL in higher doses may display lipolytic effect 31 and toxic to humans². Therefore, it is necessary to establish 31 and toxic to humans². Therefore, it is necessary to establish
32 quick and accurate methods to detect SAL residues. 32 quick and accurate methods to detect SAL residues.
33 Electrochemical methods have been proved to be ideal 33 Electrochemical methods have been proved to be ideal
34 methods for the analysis of drugs and related compounds 34 methods for the analysis of drugs and related compounds
35 because of their high accuracy sensitivity low cost and easy 35 because of their high accuracy, sensitivity, low cost and easy 36 operation^{3,4}. A key role played in electrochemical detection 36 operation^{3,4}. A key role played in electrochemical detection 37 should be the modified electrode materials, which determines should be the modified electrode materials, which determines 38 the sensitivity and speed of response to a large extent.
39 However to the best of our knowledge only a few reports in 39 However, to the best of our knowledge, only a few reports in 40 literatures involved the detection of SAL by using modified 40 literatures involved the detection of SAL by using modified
41 GCE and the linear range and detection limit need to be 41 GCE, and the linear range and detection limit need to be
42 improved Therefore development electrochemical method for 42 improved. Therefore, development electrochemical method for 43 detection of SAL with improved performance is significant. detection of SAL with improved performance is significant.

term stored stability of P-Gr-P/GCE. See DOI: 10.1039/x0xx00000x

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44 Gr, a single-atom-thick sheet arranged in honey comb
45 structure, has gained enormous attention due to its large 45 structure, has gained enormous attention due to its large
46 specific surface area, superior mechanical properties and 46 specific surface area, superior mechanical properties and 47 remarkable electronic conductivity⁵⁻⁷. The applications of Gr 47 remarkable electronic conductivity⁵⁻⁷. The applications of Gr 48 have been reported in various fields such as batteries⁸, 49 supercapacitors⁹, chemical sensors and biosensors¹⁰⁻¹². 50 However, Gr easily tends to form irreversible agglomerates or 51 even restock to form graphite due to the π - π interaction 51 even restock to form graphite due to the π -π interaction 52 between individual Gr^{13} . To solve this problem, the 52 between individual \tilde{G}^{-13} . To solve this problem, the 53 preparation of Gr-based composites, including carbon 53 preparation of Gr-based composites, including carbon 54 nanotubes-Gr composites^{14,15}, biomaterials-Gr composites^{16,17}, 55 Gr-polymer composites¹⁸⁻²⁰ and Gr-metals composites²¹⁻²³, is 56 considered to prevent the aggregation of Gr sheets. Especially, 56 considered to prevent the aggregation of Gr sheets. Especially, 57 the design and synthesis of Gr-metal nanohybrids are of great 57 the design and synthesis of Gr-metal nanohybrids are of great
58 interest both for fundamental studies and for potential 58 interest both for fundamental studies and for potential 59 nanodevice applications^{24, 27}. It is well realized that the 59 nanodevice applications^{24,-27}. It is well realized that the 60 dispersion of metal nano-particles on Gr sheets would 60 dispersion of metal nano-particles on Gr sheets would 61 potentially provide a new way to develop novel catalytic, 61 potentially provide a new way to develop novel catalytic, 62 magnetic, and optoelectronic materials²⁸. magnetic, and optoelectronic materials²⁸.

63 As a kind of noble metal, platinum (Pt) has been applied 64 in many catalytic fields due to its unusual physical and 64 in many catalytic fields due to its unusual physical and 65 chemical properties, such as sensors²⁹, fuel cells 65 chemical properties, such as sensors²⁹, fuel cells 66 electrocatalysts³⁰ and counter electrodes in the dye-sensitized 67 solar cells³¹. It has been reported that PtNPs-Gr can display a synergic effect of catalytic characters of both Gr and PtNPs. in 68 synergic effect of catalytic characters of both Gr and PtNPs, in 69 which Gr can give rise to an extraordinary modification to the 69 which Gr can give rise to an extraordinary modification to the 70 PtNPs and PtNPs deposited on Gr accelerated the electron 70 PtNPs and PtNPs deposited on Gr accelerated the electron 71 transfer³². To date, varieties of methods have been developed 71 transfer³². To date, varieties of methods have been developed 72 to synthesis PtNPs-Gr composites, such as chemical method³³. 72 to synthesis PtNPs-Gr composites, such as chemical method³
73 microwave synthesis³⁴ and electrochemical technique⁵ 73 microwave synthesis³⁴ and electrochemical technique³⁵.
74 Among these methods, electrochemical method has attracted a Among these methods, electrochemical method has attracted a

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77 **Scheme 1** The two-step and one-step methods for the synthesis of PtNPs-Gr/GCE.

78 79 lot of interest due to its simple operation, eco-friendly, mild 80 conditions and size controllable. Typically, two types of 80 conditions and size controllable. Typically, two types of 81 strategies have been proposed to electrochemically deposit 81 strategies have been proposed to electrochemically deposit 82 PtNPs on Gr, including two-step and one-step electrochemical 82 PtNPs on Gr, including two-step and one-step electrochemical
83 methods (Scheme 1) In the two-step method GO is dron-cast 83 methods (Scheme 1). In the two-step method, GO is drop-cast 84 or deposited on the electrodes, and then GO or Gr-coated 84 or deposited on the electrodes, and then GO or Gr-coated 85 electrodes are immersed in a metallic precursor solution to 85 electrodes are immersed in a metallic precursor solution to 86 perform electrochemical reduction at negative potential or in 86 perform electrochemical reduction at negative potential or in 87 reverse order. While in the one-step method, simultaneous 87 reverse order. While in the one-step method, simultaneous 88 electrochemical reductions of $H_2P(C)$ and GO are performed. 88 electrochemical reductions of H_2PtCl_6 and GO are performed.
89 However, the above-mentioned methods for PtNPs-Gr 89 However, the above-mentioned methods for PtNPs-Gr 90 synthesis lack control over the distribution of PtNPs. In 90 synthesis lack control over the distribution of PtNPs. In addition, the aggregation of Gr is still unable to avoid because 91 addition, the aggregation of Gr is still unable to avoid because
92 there are large amounts of free GO sheets assembled on the 92 there are large amounts of free GO sheets assembled on the 93 surface of electrode or in the electrolysis solutions during the 93 surface of electrode or in the electrolysis solutions during the 94 electrochemical reduction process 94 electrochemical reduction process.
95 More recently, several resear

95 More recently, several research groups $36,37$ have reported
96 that metal NPs can be strongly anchored onto the GO surface 96 that metal NPs can be strongly anchored onto the GO surface
97 by mixing GO and a metallic precursor aqueous solution 97 by mixing GO and a metallic precursor aqueous solution
98 without applying any additional reductants or surfactants. 98 without applying any additional reductants or surfactants, 99 during which GO acted as both stabilizer and reductant. They 99 during which GO acted as both stabilizer and reductant. They 100 found that the resultant metal NPs can be uniformly dispersed 100 found that the resultant metal NPs can be uniformly dispersed
101 on both surfaces of GO. Inspired by these pioneering works, in 101 on both surfaces of GO. Inspired by these pioneering works, in
102 this article, a novel sandwich-structured P-Gr-P 102 this article, a novel sandwich-structured 103 nanocomposite was synthesized, and was firstly us 103 nanocomposite was synthesized, and was firstly used as the 104 active material for the fabrication of electrochemical SAL 104 active material for the fabrication of electrochemical SAL
105 sensor. The P-Gr-P nanocomposite was prepared by two-step 105 sensor. The P-Gr-P nanocomposite was prepared by two-step 106 method including (i) a chemical and (ii) an electrochemical method including (i) a chemical and (ii) an electrochemical 107 reduction process. In the first step, P-GO-P nanocomposite 108 was synthesized through a simple in situ growth method in 108 was synthesized through a simple in situ growth method, in 109 which GO can successfully reduce H_2 PtCl₆ to PtNPs and 109 which GO can successfully reduce H_2 PtCl₆ to PtNPs and 110 PtNPs grew on both sides of GO. The monolayer GO can be 110 PtNPs grew on both sides of GO. The monolayer GO can be 111 effectively isolated by PtNPs and forming sandwich structure 111 effectively isolated by PtNPs and forming sandwich structure
112 in the solution. In the second step, the as prepared P-GO-P 112 in the solution. In the second step, the as prepared P-GO-P
113 nanocomposite was coated on the GCE and experienced an 113 nanocomposite was coated on the GCE and experienced an 114 electrochemical process. In this process, GO was reduced to 114 electrochemical process. In this process, GO was reduced to 115 Gr and the P-Gr-P nanocomposite was obtained. The 115 Gr and the P-Gr-P nanocomposite was obtained. The 116 sandwich-structure of P-Gr-P can effectively prevent the sandwich-structure of P-Gr-P can effectively prevent the 117 agglomeration of Gr and improve conductivity of the 118 composite. Furthermore, the as-prepared P-Gr-P was used as 118 composite. Furthermore, the as-prepared P-Gr-P was used as 119 sensing material for the sensitive detection of SAL. The 119 sensing material for the sensitive detection of SAL. The 120 sensing performances of the P-Gr-P toward SAL oxidation 120 sensing performances of the P-Gr-P toward SAL oxidation
121 were investigated. Satisfied results demonstrated that the P-Gr-121 were investigated. Satisfied results demonstrated that the P-Gr-
122 P nanocomposite with high electrochemical active surface area 122 P nanocomposite with high electrochemical active surface area
123 showed enhanced electrochemical signal toward the oxidation 123 showed enhanced electrochemical signal toward the oxidation
124 of SAL. This work has expanded the scope of synthesizing Gr-124 of SAL. This work has expanded the scope of synthesizing Gr-
125 based hybrid and explored their sensing applications. based hybrid and explored their sensing applications.

126 **2. Experimental**

2.1. Chemicals and reagents

128
129

SAL was purchased from Aldrich. SAL stock solution (5×10 130⁻³ M) was prepared with absolute ethanol and stored at 277-281 130 ³ M) was prepared with absolute ethanol and stored at 277-281
131 K. GO was obtained from Nanjing Xianfeng nano Co. 131 K. GO was obtained from Nanjing Xianfeng nano Co.
132 H₂PtCl₆•3H₂O, disodium hydrogen phosphate dodecahydrate 132 $H_2PtCl_6^{\bullet}3H_2O$, disodium hydrogen phosphate dodecahydrate
133 (Na₂HPO₄), and sodium dihydrogen phosphate dehydrate 133 ($Na₂HPO₄$), and sodium dihydrogen phosphate dehydrate 134 ($NaH₂PO₄$) were purchased from Sinopharm chemical reagent 134 ($N \text{a}H_2 \text{PO}_4$) were purchased from Sinopharm chemical reagent 135 Co. Ltd. Other reagents were of analytical grade, double 135 Co. Ltd. Other reagents were of analytical grade, double 136 distilled water was used during the experiments. distilled water was used during the experiments.

137
138 138 **2.2. Instrumentation**

139
140 140 SEM images were obtained at Helios NanoLab
141 FESEM/FIB. TEM images were obtained at TecnaiG2 T2 141 FESEM/FIB. TEM images were obtained at TecnaiG2 T2
142 transmission electron microscope. UV/vis spectra analysis was 142 transmission electron microscope. UV/vis spectra analysis was
143 performed using a Perkin-Elmer Lambda 900 ultraviolet-143 performed using a Perkin-Elmer Lambda 900 ultraviolet-
144 visible-near-infrared spectrophotometer (Germanv). Raman 144 visible-near-infrared spectrophotometer (Germany). Raman 145 spectroscopy (invia-reflex) was used to analyze the samples 145 spectroscopy (invia-reflex) was used to analyze the samples 146 using a 633 nm laser. Electrochemical measurements including 146 using a 633 nm laser. Electrochemical measurements including
147 cyclic voltammetry, differential pulse voltammetry and 147 cyclic voltammetry, differential pulse voltammetry and 148 electrochemical impedance spectroscopy techniques were 148 electrochemical impedance spectroscopy techniques were
149 carried out on CHI 660D electrochemical workstation 149 carried out on CHI 660D electrochemical workstation
150 (Shanghai, China). The measurement was carried out in a 150 (Shanghai, China). The measurement was carried out in a 151 three-electrode system, including GCE or composites modified 151 three-electrode system, including GCE or composites modified
152 GCE as working electrode, platinum wire as auxiliary 152 GCE as working electrode, platinum wire as auxiliary
153 electrode and saturated calomel reference electrode (SCE). 153 electrode and saturated calomel reference electrode (SCE).
154 During the experiments, the atmosphere of double distilled 154 During the experiments, the atmosphere of double distilled 155 water was set by passing N_2 for 15 min. water was set by passing N_2 for 15 min.

156 **2.3. Material preparation**

157 **Synthesis of P-GO-P:** GO was dispersed in double 158 distilled water and ultrasonic treatment for 3 h to obtain a 158 distilled water and ultrasonic treatment for 3 h to obtain a
159 concentration of 0.5 mg mL^{-1} . Subsequently, the PtNPs/GO 159 concentration of 0.5 mg mL⁻¹. Subsequently, the PtNPs/GO 160 was prepared by mixing 0.5 mg/mL GO aqueous solution with 160 was prepared by mixing 0.5 mg/mL GO aqueous solution with 161 7.9 mM H_2PtCl_6 at a ratio of 10:1 (v/v) and reacted under **161** 7.9 mM H_2 PtCl₆ at a ratio of 10:1 (v/v) and reacted under **162** vigorous stirring at 80 °C for 24 h³⁷. The obtained product was **162** vigorous stirring at 80 °C for 24 h³⁷. The obtained product was **163** named as P-GO-P. named as P-GO-P.

164 **Preparation of sandwich like P-Gr-P and fabrication** 165 **of P-Gr-P composite modified electrode:** Before 166 modification, GCE was mechanically polished using chamois 167 leather containing 0.05 \mu m Al₂O₃, and then it was **167** leather containing 0.05 μ m Al_2O_3 , and then it was **168** ultrasonically cleaned with double distilled water, absolute 168 ultrasonically cleaned with double distilled water, absolute 169 ethanol and double distilled water, respectively, each for 5 min. 169 ethanol and double distilled water, respectively, each for 5 min.
170 The cleaned GCE was dried with a nitrogen stream prior to the 170 The cleaned GCE was dried with a nitrogen stream prior to the 171 subsequent modification. subsequent modification.

173 **Scheme 2** The preparation process of P-Gr-P/GCE.

174
175

175 To obtain P-Gr-P modified GCE (P-Gr-P/GCE), 5 µL P-
176 GO-P dispersion was dropped on the surface of GCE and dried 176 GO-P dispersion was dropped on the surface of GCE and dried
177 at room temperature. The P-GO-P/GCE was transferred to an 177 at room temperature. The P-GO-P/GCE was transferred to an 178 electrochemical cell containing 0.1 M phosphate buffer 178 electrochemical cell containing 0.1 M phosphate buffer
179 solution (PBS) (pH 7.0). GO in P-GO-P composite film was 179 solution (PBS) (pH 7.0). GO in P-GO-P composite film was 180 electrochemically reduced to Gr by performing successive 180 electrochemically reduced to Gr by performing successive 181 cyclic voltammograms for 400 s in a potential window 181 cyclic voltammograms for 400 s in a potential window
182 between -1.5 to 0 V and the scan rate was set as 50 mV s^{-1}

182 between -1.5 to 0 V, and the scan rate was set as 50 mV s^{-1} .
183 The preparation process was shown in Scheme 2. For 183 The preparation process was shown in Scheme 2. For 184 comparison, Gr modified GCE (Gr/GCE) and GO modified 184 comparison, Gr modified GCE (Gr/GCE) and GO modified 185 GCE (GO/GCE) were also prepared. GCE (GO/GCE) were also prepared.

186 **3. Results and discussion**

187 **3.1. Characterization of P-Gr-P**

188 The morphology and structure of Gr and P-Gr-P were
189 characterized by SEM and TEM. The samples of Gr and P-Gr-189 characterized by SEM and TEM. The samples of Gr and P-Gr-
190 P on indium tin oxide (ITO) glasses were prepared by an 190 P on indium tin oxide (ITO) glasses were prepared by an 191 electrochemical method. Briefly, GO or P-GO-P dispersion 191 electrochemical method. Briefly, GO or P-GO-P dispersion
192 was dropped on the ITO surface and dried, and then GO/ITO 192 was dropped on the ITO surface and dried, and then GO/ITO 193 or P-GO-P/ITO was transferred to an electrochemical cell and 193 or P-GO-P/ITO was transferred to an electrochemical cell and 194 reduced by performing successive cyclic voltammograms for 194 reduced by performing successive cyclic voltammograms for 195 400 s in a potential window between -1.5 to 0 V. As can be 195 400 s in a potential window between -1.5 to 0 V. As can be 196 seen from Fig. 1A, a typical wrinkled structure with the 196 seen from Fig. 1A, a typical wrinkled structure with the 197 corrugation and scrolling is intrinsic to Gr. For P-Gr-P 197 corrugation and scrolling is intrinsic to Gr. For P-Gr-P 198 nanocomposite (Fig. 1B), one can see that a large amount of 198 nanocomposite (Fig. 1B), one can see that a large amount of 199 PtNPs were uniformly distributed on the surface of Gr. In 199 PtNPs were uniformly distributed on the surface of Gr. In 200 addition, the structure of Gr and sandwich-structured P-Gr-P 200 addition, the structure of Gr and sandwich-structured P-Gr-P
201 were further confirmed by TEM techniques. As shown in Fig. 201 were further confirmed by TEM techniques. As shown in Fig. 202 1C, Gr displayed a layered stacking structure. This structure 202 1C, Gr displayed a layered stacking structure. This structure
203 easily tended to agglomeration due to the decrease of oxygen-203 easily tended to agglomeration due to the decrease of oxygen-
204 containing functional groups after experienced an 204 containing functional groups after experienced an 205 electrochemical process. By contrast, it can be observed from 205 electrochemical process. By contrast, it can be observed from 206 Fig. 1D that the P-Gr-P nanocomposite contained three layers 206 Fig. 1D that the P-Gr-P nanocomposite contained three layers 207 of Gr, where Gr layers were regularly spaced by layers of 207 of Gr, where Gr layers were regularly spaced by layers of 208 PtNPs. Since PtNPs were distributed on both sides of Gr layer, 208 PtNPs. Since PtNPs were distributed on both sides of Gr layer,
209 the sandwich structure of P-Gr-P can effectively avoid 209 the sandwich structure of P-Gr-P can effectively avoid 210 aggregation. The sandwich structured nanocomposite could 210 aggregation. The sandwich structured nanocomposite could 211 extremely enhance the active surface area, allow the analyte 211 extremely enhance the active surface area, allow the analyte 212 (here SAL) to fully touch the PtNPs and provide enough 212 (here SAL) to fully touch the PtNPs, and provide enough 213 space for mass transfer of reactants and products. 213 space for mass transfer of reactants and products.
214 Consequently, the resulting modified electrode would exhibit 214 Consequently, the resulting modified electrode would exhibit 215 an excellent electrocatalytic capability towards the oxidation 215 an excellent electrocatalytic capability towards the oxidation 216 of SAL. **216** of SAL.
217 Ra

217 Raman spectroscopy is one of the most effective 218 techniques to characterize the ordered and disordered crystal 218 techniques to characterize the ordered and disordered crystal
219 structures of Gr. Therefore. Raman spectroscopy was used to 219 structures of Gr. Therefore, Raman spectroscopy was used to 220 characterization of Gr based materials. In particular, samples 220 characterization of Gr based materials. In particular, samples 221 of GO and P-GO-P were dropped on ITO surface without 221 of GO and P-GO-P were dropped on ITO surface without 222 conducting electrochemical reduction process. Fig. 2A shows 222 conducting electrochemical reduction process. Fig. 2A shows
223 Raman spectra of GO, Gr, P-GO-P and P-Gr-P composites. 223 Raman spectra of GO, Gr, P-GO-P and P-Gr-P composites.
224 Raman spectra usually shows two peaks (G band and D band), 224 Raman spectra usually shows two peaks (G band and D band), 225 the G band was corresponding to the sp^2 -hybridized carbon 225 the G band was corresponding to the sp^2 -hybridized carbon 226 atoms in the hexagonal framework and the D band was the atoms in the hexagonal framework and the D band was the 227 oxidation of disruption of the sp²-hybridized carbon atoms.
228 The D/G band intensity ratio (I_D/I_C) in the Raman spectrum 228 The D/G band intensity ratio (I_D/I_G) in the Raman spectrum 229 expresses the atomic ratio of sp^2/sp^3 carbons, and is a measure 229 expresses the atomic ratio of sp^2/sp^3 carbons, and is a measure 230 of the extent of disordered graphite. As can be seen in Fig. 2, 231 GO displayed a D band at 1315 cm^{-1} and a G band at 1590 cm 231 GO displayed a D band at 1315 cm^{-1} and a G band at 1590 cm^{-1} 232 ¹. While Gr showed a G band at 1570 cm⁻¹, and the I_D/I_G was 233 up to 1.18 (0.98 for GO). This phenomenon can be explained 234 that the distortion of 6-fold rings caused by oxygen 234 that the distortion of 6-fold rings caused by oxygen 235 functionalities is removed after GO deoxidation³⁸, and the **235** functionalities is removed after GO deoxidation³⁸, and the 236 carbon lattice returns to an essentially graphitic state with 236 carbon lattice returns to an essentially graphitic state with 237 highly defected, resulting in the increase of $\rm Iv/Ic$ ratio³⁹. For P-237 highly defected, resulting in the increase of I_D/I_G ratio³⁹. For P-
238 . GO-P, the I_D/I_G (1.01) increased slightly as compared with GO. 238 GO-P, the I_D/I_G (1.01) increased slightly as compared with GO, 239 indicating the successfully growth of PtNPs on Gr defects⁴⁰. 239 indicating the successfully growth of PtNPs on Gr defects 240 As for P-Gr-P, the I_V/I_C increased to 1.21, higher than P-GO 240 As for P-Gr-P, the I_D/I_G increased to 1.21, higher than P-GO-P
241 or Gr. The increased I_D/I_G can be attributed to the reduction 241 or Gr. The increased I_D/I_G can be attributed to the reduction 242 process altered the structure of GO in P-GO-P, and the 242 process altered the structure of GO in P-GO-P, and the 243 presence of PtNPs deter the recovery of the sp^2 carbon domain 243 presence of PtNPs deter the recovery of the sp² carbon domain 244 and decrease the G band intensity of $\text{Gr}^{40,41}$. 244 and decrease the G band intensity of $\text{Gr}^{40,41}$
245 The reduction process was demon

245 The reduction process was demonstrated by UV-vis 246 absorption spectra and the results are shown in Fig. 2B. It can 246 absorption spectra and the results are shown in Fig. 2B. It can 247 be found that the UV-vis spectra of GO (a) and P-GO-P (c) 247 be found that the UV-vis spectra of GO (a) and P-GO-P (c) 248 exhibited two characteristic peaks, one was at 229 nm 248 exhibited two characteristic peaks, one was at 229 nm 249 corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds, and 249 corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bonds, and 250 the other at 300 nm was attributed to $n \rightarrow \pi^*$ transitions of C=O **250** the other at 300 nm was attributed to $n \rightarrow \pi^*$ transitions of C=O **251** bonds⁴². After the electrochemical reduction process, the peak 251 bonds⁴². After the electrochemical reduction process, the peak 252 at 229 nm was red shifted to 246 nm (Fig. 2B, b and d), which 252 at 229 nm was red shifted to 246 nm (Fig. 2B, b and d), which
253 was an indication of the restoration of the electronic 253 was an indication of the restoration of the electronic 254 conjugation within the Gr sheets⁴³. The results of UV-vis 254 conjugation within the Gr sheets⁴³. The results of UV-vis 255 spectra indicated that the electrochemical reduction of GO 255 spectra indicated that the electrochemical reduction of GO
256 indeed took place. 256 indeed took place.
257 Electrochemic

257 Electrochemical impedance spectroscopy (EIS) is widely 258 used to study the interface properties of the modified electrode 258 used to study the interface properties of the modified electrode.
259 The impedance spectrum includes two parts, a semicircle 259 The impedance spectrum includes two parts, a semicircle 260 diameter at higher frequencies corresponds to the electron-260 diameter at higher frequencies corresponds to the electron-
261 transfer resistance (R_{α}) and a linear part at lower frequencies 261 transfer resistance (R_{el}) and a linear part at lower frequencies 262 corresponds to the diffusion process. Fig. 2C shows the results 262 corresponds to the diffusion process. Fig. 2C shows the results 263 of EIS of bare GCE (a), GO/GCE (b), Gr/GCE (c) and P-Gr-263 of EIS of bare GCE (a), GO/GCE (b), Gr/GCE (c) and P-Gr-
264 P/GCE (d) in the presents of 5 mM $[Fe(CN)₆]$ ^{3-/4} containing **264** P/GCE (d) in the presents of 5 mM $[Fe(CN)_6]^{3-4}$ containing 265

267 **Fig. 1** SEM images of Gr (A), P-Gr-P (B) and TEM images of Gr layer (C), sandwich structure of P-Gr-P (D).

$$
\frac{200}{269}
$$

270 0.1 M KCl at scan rate of 50 mV s⁻¹. It was observed that bare 271 GCE displays a \mathbb{R}_{α} of 500 Ω . While the \mathbb{R}_{α} of GO/GCE was **271** GCE displays a R_{et} of 500 Ω. While the R_{et} of GO/GCE was **272** 4900 Ω, possibly due to the poor conductivity of GO. 272 4900 Ω , possibly due to the poor conductivity of GO.
273 However, dramatically decreased \mathbb{R}_{α} , value can be found when 273 However, dramatically decreased R_{et} value can be found when 274 Gr was modified on GCE, which was attributed to the 274 Gr was modified on GCE, which was attributed to the 275 excellent electronic property of Gr, forming a fast electron 275 excellent electronic property of Gr, forming a fast electron
276 conduction pathway between the electrode and the 276 conduction pathway between the electrode and the 277 electrochemical probe. As for P-Gr-P/GCE, the semicircle in 277 electrochemical probe. As for P-Gr-P/GCE, the semicircle in 278 the plot became much smaller than that of electrode without 278 the plot became much smaller than that of electrode without 279 PtNPs. The excellent conductivity was probably due to the fact 279 PtNPs. The excellent conductivity was probably due to the fact 280 that PtNPs accelerated the electron transfer and the sandwich 280 that PtNPs accelerated the electron transfer and the sandwich
281 structure of P-Gr-P can effectively prevent Gr from 281 structure of P-Gr-P can effectively prevent Gr from 282 agglomerating. agglomerating.

283

284 **3.2. Electrochemical behaviour of SAL on P-Gr-P/GCE**

285 To evaluate the electrochemical performence of P-Gr-P, 286 P-Gr-P/GCE was characterized by cyclic voltammetry in the 286 P-Gr-P/GCE was characterized by cyclic voltammetry in the 287 presence of SAL in the potential range from 0.3 V to 0.9 V. 287 presence of SAL in the potential range from 0.3 V to 0.9 V.
288 Fig. 3 presents typical cyclic voltammograms of bare GCE Fig. 3 presents typical cyclic voltammograms of bare GCE 289

290

291 **Fig. 2** (A) Raman spectra of GO (a), Gr (b), P-GO-P (c) and P-292 Gr-P (d). (B) UV-vis absorption spectra of GO (a), Gr (b), P-GO-
293 P (c) and P-Gr-P (d). (C) The impedance spectrum of bare GCE P (c) and P-Gr-P (d). (C) The impedance spectrum of bare GCE (a), GO/GCE (b), Gr/GCE (c) and P-Gr-P/GCE in 5 mM Fe(CN) $_6^{3}$ 294 /4- 295 $^{1/4}$ (1:1) solution containing 0.1 M KCl. Scan rate: 50 mV s⁻¹.

Current / µA

297 **Fig. 3** Cyclic voltammograms of 20 µM SAL in 0.1 M PBS (pH 298 7.0) at bare GCE (a), GO/GCE (b), Gr/GCE (c) PtNPs-Gr/GCE (d)
299 and P-Gr-P/GCE (e). Scan rate: 50 mV s⁻¹. 299 and P-Gr-P/GCE (e). Scan rate: 50 mV s^{-1} .

 \prime $\overline{\mathsf{V}}$ vs. SCE

Potential

300
301

301 (curve a), GO/GCE (curve b), Gr/GCE (curve c), PtNPs-
302 Gr/GCE (curve d) and P-Gr-P/GCE (curve e) in pH 7.0 PBS 302 Gr/GCE (curve d) and P-Gr-P/GCE (curve e) in pH 7.0 PBS
303 containing 20 µM SAL. As can be seen, no obvious redox 303 containing 20 μ M SAL. As can be seen, no obvious redox 304 peak can be observed at bare GCE, which might be due to the 304 peak can be observed at bare GCE, which might be due to the 305 sluggish electron transfer of GCE (curve a). While GO/GCE 305 sluggish electron transfer of GCE (curve a). While GO/GCE 306 exhibited a slightly obvious oxidation peak current response, 306 exhibited a slightly obvious oxidation peak current response, 307 possibly due to the fact that GO hold strong adsorption 307 possibly due to the fact that GO hold strong adsorption 308 capacity, but exhibited poor conductivity (curve b). However, 308 capacity, but exhibited poor conductivity (curve b). However, 309 as shown in Fig. 3 (curve c), the oxidation peak current as well 309 as shown in Fig. 3 (curve c), the oxidation peak current as well 310 as background current increased significantly at Gr/GCE, 310 as background current increased significantly at Gr/GCE, 311 ascribing to the excellent conductivity and large surface area 311 ascribing to the excellent conductivity and large surface area
312 of Gr. Larger oxidation peak current can be observed on 312 of Gr. Larger oxidation peak current can be observed on 313 PtNPs-Gr/GCE, which was prepared by one-step 313 PtNPs-Gr/GCE, which was prepared 314 electrodeposition method, indicating PtNPs on 314 electrodeposition method, indicating PtNPs distributed on Gr 315 surface improved the electrochemical oxidation of SAL (curve 316 d). As for P-Gr-P/GCE, the oxidation peak current increased 316 d). As for P-Gr-P/GCE, the oxidation peak current increased 317 again, which was three times higher than that at Gr/GCE 317 again, which was three times higher than that at Gr/GCE
318 (curve e). Moreover, it also can be seen that the oxidation peak 318 (curve e). Moreover, it also can be seen that the oxidation peak
319 current of SAL at the sandwich-structured P-Gr-P electrode 319 current of SAL at the sandwich-structured P-Gr-P electrode 320 was much higher than that at the PtNPs-Gr/GCE, adding to 320 was much higher than that at the PtNPs-Gr/GCE, adding to 321 evidence that the special sandwich structure of P-Gr-P showed 321 evidence that the special sandwich structure of P-Gr-P showed
322 better performance as compared to ordinary PtNPs-Gr 322 better performance as compared to ordinary PtNPs-Gr 323 composites. Therefore, the excellent electrochemical catalytic 323 composites. Therefore, the excellent electrochemical catalytic 324 properties of P-Gr-P can be summarized in the following three 324 properties of P-Gr-P can be summarized in the following three 325 aspects: firstly, Gr has good electrical conductivity and large 325 aspects: firstly, Gr has good electrical conductivity and large 326 specific surface area, which can provide an excellent 326 specific surface area, which can provide an excellent 327 microenvironment for the catalytic oxidation of SAL. 327 microenvironment for the catalytic oxidation of SAL.
328 Secondly, the well-distributed PtNPs on the surface of Gr with 328 Secondly, the well-distributed PtNPs on the surface of Gr with 329 a high density would provide more active sites for the catalytic 329 a high density would provide more active sites for the catalytic 330 oxidation reaction and greatly increase the electrocatalytic 330 oxidation reaction and greatly increase the electrocatalytic 331 activity. Thirdly, for the sandwich-structure of P-Gr-P, SAL 331 activity. Thirdly, for the sandwich-structure of P-Gr-P, SAL 332 molecules can rapidly diffuse from the solution into the nano-332 molecules can rapidly diffuse from the solution into the nano-
333 P-Gr-P modified membranes. P-Gr-P modified membranes.

334
335 335 **3.3. Optimization of the experimental conditions**

336 Accumulation can improve the amount of SAL absorbed 337 on the electrode surface, and then improve sensitivity 337 on the electrode surface, and then improve sensitivity 338 determination. Then, the influence of accumulation time was 338 determination. Then, the influence of accumulation time was 339 investigated. As can be seen from Fig. 4A, the influence of 339 investigated. As can be seen from Fig. 4A, the influence of 340 accumulation time ranging from 10 to 90 s on the oxidation of 340 accumulation time ranging from 10 to 90 s on the oxidation of 341 SAL at P-Gr-P/GCE was investigated. It was observed that the 341 SAL at P-Gr-P/GCE was investigated. It was observed that the 342 oxidation current response increased sharply with increasing 342 oxidation current response increased sharply with increasing 343 the reduction time from 10 s to 60 s, and then reached a 343 the reduction time from 10 s to 60 s, and then reached a 344 constant limiting value. which demonstrated that the 344 constant limiting value, which demonstrated that the 345 adsorption of SAL was fast and easily reached saturation on P-345 adsorption of SAL was fast and easily reached saturation on P-
346 Gr-P/GCE. Based on the sensitivity and short analysis time. 60 346 Gr-P/GCE. Based on the sensitivity and short analysis time, 60
347 s accumulation time was chosen in subsequent experiments. s accumulation time was chosen in subsequent experiments. 348

350

 351 **Fig. 4** (A) Variation of the peak current with accumulation time in 0.1 M PBS (pH 7.0). SAL concentration: 20 μ M. Scan rate: 50 mV s⁻¹. (B) S52 Cyclic voltammograms of P-Gr-P/GCE in PBS with different pH containing 20 µM SAL. (C) Effect of pH value on the anodic peak potentials
353 and anodic peak currents of SAL. (D) Cyclic voltammograms of 20 µM SAL with dif 353 and anodic peak currents of SAL. (D) Cyclic voltammograms of 20 μ M SAL with different scan rates (v) on P-Gr-P/GCE in 0.1 M PBS (pH 7.0)
354 (from the inner to the outer are 10, 25, 50, 75, 100, 125, 150, 175, 200, 354 (from the inner to the outer are 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375 and 400 mV s⁻¹, respectively.). 355 Accumulation time: 60 s. (E) Linear relationship of anodic peak current I versus the natural logarithm of v. (F) The relationship between E_p
356 and natural logarithm of v. and natural logarithm of v.

357

358 Fig. 4B shows the effect of pH of the supporting 359 electrolyte on electro-oxidation of 20 μ M SAL at P-Gr-P/GCE 359 electrolyte on electro-oxidation of 20 μ M SAL at P-Gr-P/GCE 360 in 0.1 M PBS with a scan rate of 50 mV s⁻¹. As can be seen, 360 in 0.1 M PBS with a scan rate of 50 mV s⁻¹. As can be seen, 361 with the increase of pH value, the oxidation potential (E_{na}) of 361 with the increase of pH value, the oxidation potential (E_{pa}) of 362 SAL shifted toward less positive values, suggesting the 362 SAL shifted toward less positive values, suggesting the 363 involvement of proton in the oxidation reaction⁴⁴. The plot of **363** involvement of proton in the oxidation reaction⁴⁴. The plot of **364** the peak potential vs. pH showed one straight line between pH 364 the peak potential v_s . pH showed one straight line between pH 365 4 and 8 and it can be expressed by the following equation (Fig. 365 4 and 8 and it can be expressed by the following equation (Fig. 366 4C):

367 $E_{pa} = 1.054 - 0.068 \text{ pH } (R^2 = 0.990)$
368 The slope of the above equation was -68 mV pH

368 The slope of the above equation was -68 mV pH^{-1} , which was **369** close to -59 mV pH^{-1} , indicating the equal numbers of proton 369 close to -59 mV pH^{-1} , indicating the equal numbers of proton 370 and electron involved in electrode reaction. In addition, it was 370 and electron involved in electrode reaction. In addition, it was 371 also found that the peak current increased with the pH from also found that the peak current increased with the pH from 372 4.0 to 7.0, and then decreased from 7.0 to 8.0. Therefore, pH
373 7.0 was employed for further studies. 373 7.0 was employed for further studies.
374 The kinetics of the electrode real

374 The kinetics of the electrode reaction was investigated by
375 studying the effects of scan rate on the oxidation of SAL at the 375 studying the effects of scan rate on the oxidation of SAL at the 376 P-Gr-P/GCE. As shown in Fig. 4D, with the increase of the 376 P-Gr-P/GCE. As shown in Fig. 4D, with the increase of the 377 scan rate, the anodic peak currents also increased. The anodic 377 scan rate, the anodic peak currents also increased. The anodic 378 peak currents increased linearly with the natural logarithm of 378 peak currents increased linearly with the natural logarithm of 379 scan rates (ln v) from 10 mV⁻¹ to 400 mV⁻¹ (Fig. 4F) 379 scan rates (ln v) from 10 mV^{-1} to 400 mV^{-1} (Fig. 4E), 380 corresponding to the following equation: I (μ A) = -12.974 + 381 5.793 ln v (R^2 = 0.990), suggesting that electrode process of **381** 5.793 ln v $(R^2 = 0.990)$, suggesting that electrode process of **382** SAL was diffusion-controlled⁴⁵. Similarly, a linear relationship SAL was diffusion-controlled⁴⁵. Similarly, a linear relationship 383

386 **Scheme 3** Chemical structure of SAL and its oxidation 387 mechanism at P-Gr-P/GCE.

388

389 between E_{pa} and ln v was also observed in the range of 10 – 390 – 400 mV s⁻¹ (Fig. 4F), and the linear regression equation can be 390 400 mV s⁻¹ (Fig. 4F), and the linear regression equation can be 391 expressed as $E_{\text{eq}} = 0.502 + 0.024$ ln v ($R^2 = 0.991$). According **391** expressed as $E_{pa} = 0.502 + 0.024$ ln v ($R^2 = 0.991$). According

392 to the following equation⁴⁶:
393 $E_{na} = E^0 + (RT/\alpha nF)$ [0.780] **393** $E_{pa} = E^0 + (RT/\alpha nF) [0.780 + ln(D_R^{1/2}/k^0) + ln(\alpha nFv/RT)^{1/2}] =$

394 K + (RT/2 α nF) ln v
395 where E^{0'} is 395 where $E^{0'}$ is the formal potential, k^{0} is the standard 396 heterogeneous rate constant, α is transfer coefficient of the 396 heterogeneous rate constant, α is transfer coefficient of the 397 oxidation of SAL. D_p is diffusion coefficient of SAL, other 397 oxidation of SAL, D_R is diffusion coefficient of SAL, other 398 symbols have their usual significance. The value of αn can be 398 symbols have their usual significance. The value of α n can be 399 calculated to be 0.53 from the slope. Generally, α is assumed calculated to be 0.53 from the slope. Generally, α is assumed 400

401
402 402 **Fig. 5** (A) Plot of Q-t curves of bare GCE (a), PtNPs-Gr/GCE 403 prepared by one-step electrodeposition method (b) and P-Gr-
404 P/GCE (c) in 0.1 mM K₂[Fe(CN)_c] containing 1.0 M KCl. Insert: 404 P/GCE (c) in 0.1 mM $K_3[Fe(CN)_6]$ containing 1.0 M KCl. Insert: 405 Plot of $Q-t^{1/2}$ curves on bare GCE (a'), PtNPs-Gr/GCE (b') and 406 P-Gr-P/GCE (c').

407

409 **Fig. 6** Differential pulse voltammograms of 0.03, 0.07, 0.2, 0.4, 410 0.6, 0.8, 1, 3, 5, 7, 10, 20, 40, 80, 100, 130, 160, and 180 µM 411 SAL on P-Gr-P/GCE in 0.1 M PBS (pH 7.0) at the scan rate of 50
412 mV $s⁻¹$. Insert: plot of the oxidation peak current against the 412 mV s⁻¹. Insert: plot of the oxidation peak current against the 413 concentration of SAL.

414
415

408

415 as 0.5 in the totally irreversible electrode process. Therefore, 416 one electron is involved in the oxidation of SAL. In summary, 416 one electron is involved in the oxidation of SAL. In summary, 417 SAL takes place a one-electron, one-proton irreversible 417 SAL takes place a one-electron, one-proton irreversible 418 reaction (shown in Scheme 3). reaction (shown in Scheme 3).

419
420 420 **3.4. Chronocoulometry**

421 The electrochemically effective surface areas (A) of bare 422 GCE (Fig. 5, curve a), PtNPs-Gr/GCE (prepared by one-step 422 GCE (Fig. 5, curve a), PtNPs-Gr/GCE (prepared by one-step 423 electrodenosition) (Fig. 5, curve b) and P-Gr-P/GCE (Fig. 5 423 electrodeposition) (Fig. 5, curve b) and P-Gr-P/GCE (Fig. 5, 424 curve c) have been investigated. According to the previous 424 curve c) have been investigated. According to the previous 425 literature⁴⁷, A can be determined by chronocoulometry using 425 literature⁴⁷, A can be determined by chronocoulometry using 426 0.1 mM $K_3[Fe(CN)_6]$ containing 1 M KCl as model complex, 426 0.1 mM $K_3[Fe(CN)_6]$ containing 1 M KCl as model complex, 427 based on Anson equation:
428 $O(t) = 2nFA$

428 $Q(t) = 2nFAcD^{1/2}t^{1/2}/\pi^{1/2} + Q_{dl} + Q_{ads}$

429 where Q_{ads} is the Faradic charge, Q_{d1} is the double-layer charge, 430 D_0 is the diffusion coefficient (the diffusion coefficient of 430 D₀ is the diffusion coefficient (the diffusion coefficient of 431 K₃[Fe(CN)₆] in 1 M KCl is 7.6 \times 10⁻⁶ cm² s⁻¹), c is the 431 K₃[Fe(CN)₆] in 1 M KCl is 7.6 \times 10⁻⁶ cm² s⁻¹), c is the 432 concentration of the substrate, and A is the surface area of the 433 working electrode. Other symbols have their usual meanings. 433 working electrode. Other symbols have their usual meanings.
434 The linear regression equation of $Q-t^{1/2}$ curves on GCE (Inset **434** The linear regression equation of $Q-t^{1/2}$ curves on GCE (Inset 435 of Fig. 5, curve a'), PtNPs-Gr/GCE (Inset of Fig. 5, curve b') 436 and P-Gr-P/GCE (Inset of Fig. 5, curve c') were Q $(10^{-6}C)$ = -436 and P-Gr-P/GCE (Inset of Fig. 5, curve c') were Q $(10^{-6} \text{C}) = -437 \cdot 3.670 + 20.394 \cdot t^{1/2}$ ($R^2 = 0.999$), Q $(10^{-6} \text{C}) = -13.762 + 73.182$ **437** 3.670 + 20.394 t^{1/2} ($\mathbb{R}^2 = 0.999$), Q (10^{-6} C) = -13.762 + 73.182 438 $t^{1/2}$ ($R^2 = 0.999$) and Q (10^{-6} C) = 37.596 + 205.990 $t^{1/2}$ ($R^2 =$ 439 0.999), respectively. Based on the slopes of the linear 440 relationship between Q and $t^{1/2}$, A was calculated to be 0.068 441 cm² for bare GCE, 0.244 cm² for PtNPs-Gr/GCE. While the A 442 of P-Gr-P/GCE was 0.682 cm^2 , 10 times larger than that of 443 bare GCE and 3 times larger than that of $PHPs-Gr/GCE$. 443 bare GCE and 3 times larger than that of PtNPs-Gr/GCE.
444 These results indicated that P-Gr-P sandwich structure showed 444 These results indicated that P-Gr-P sandwich structure showed
445 a large surface area, which could increase the electrochemical 445 a large surface area, which could increase the electrochemical 446 active site, enhance the electrochemical response and decrease 446 active site, enhance the electrochemical response and decrease 447 the detection limit. the detection limit.

448
449

449 **3.5. Determination of SAL on P-Gr-P/GCE** 450 Under the optimal experimental conditions established 451 above, the calibration curves of SAL in PBS were measured 451 above, the calibration curves of SAL in PBS were measured 452 by differential pulse voltammetry (DPV). Fig. 6 shows the 452 by differential pulse voltammetry (DPV). Fig. 6 shows the 453 typical differential pulse voltammograms obtained from 453 typical differential pulse voltammograms obtained from
454 different SAL concentrations at P-Gr-P/GCE. As can be seen, 454 different SAL concentrations at P-Gr-P/GCE. As can be seen,
455 the peak current was proportional to the concentration of SAL 455 the peak current was proportional to the concentration of SAL 456 over 0.03 to 180 μ M range with the regression equation of I 456 over 0.03 to 180 μ M range with the regression equation of I
457 (μ M) = 0.862 + 0.133 c (R^2 = 0.991) (Inset of Fig. 6). The 457 (μM) = $0.862 + 0.133$ c ($R^2 = 0.991$) (Inset of Fig. 6). The 458 detection limit was down to 9 nM ($S/N = 3$). Simultaneously. 458 detection limit was down to 9 nM $(S/N = 3)$. Simultaneously, 459 the comparison of P-Gr-P/GCE with other modified electrodes 459 the comparison of P-Gr-P/GCE with other modified electrodes 460 for SAL determination was also listed in Table 1. It can be 460 for SAL determination was also listed in Table 1. It can be 461 seen that P-Gr-P/GCE was more sensitive with a wider linear 461 seen that P-Gr-P/GCE was more sensitive with a wider linear 462 range and lower detection limit. These results indicate that P-462 range and lower detection limit. These results indicate that P-
463 Gr-P/GCE is an appropriate platform for the determination of 463 Gr-P/GCE is an appropriate platform for the determination of SAL.

466 **Table 1** Comparison of the proposed sensor for determination of SAL with others

467 1 single-walled-multi-walled and nafion composites

468 2 nano gold particles modified indium tin oxide

469 3 pre-treated carbon paste electrode

470 4 multi-carbon nanotubes

471 a cyclic voltammetry

472 b linear sweep voltammetry

473 c differential pulse voltammetry

474 d osteryoung square wave voltammetry

475 e square wave voltammetry

476 $*$ The linear range and detection limit in the literature is 50-2000 ng/ml and 75 ng/ml, respectively, equal to 0.21-8.36 μM, 0.31 μM, 477 respectively.

respectively.

478

Page 7 of 9 **Page 7 of 9 New Journal of Chemistry**

Journal Name ARTICLE

479 **Table 2** Recovery measurements of the SAL in the urine samples using P-Gr-P modified GCE

Samples	Added (μM)	Found (μM)	RSD(%)	Recovery $(\%)$
	0	θ	$\overline{}$	$\overline{}$
2	0.02	0.019	2.3	95.0
3	0.10	0.105	1.6	105.0
4	0.18	0.177	2.1	98.3
5	2.6	2.51	1.9	96.5
6	8.4	8.33	2.5	99.2

^{480 &}lt;sup>*</sup>RSD (%) calculated from six separate experiments.

481
482 482 **3.6. Stability and reproducibility**

483 The stability of P-Gr-P/GCE was verified by recording 484 successive cyclic voltammograms in a potential range of 0.3 -484 successive cyclic voltammograms in a potential range of 0.3 -
485 0.9 V. No obvious change could be observed in cyclic 485 0.9 V. No obvious change could be observed in cyclic 486 voltammograms after 10 cycles (current signal change less 486 voltammograms after 10 cycles (current signal change less 487 than 2 %) and the electrodes also remained stable in the 487 than 2 %) and the electrodes also remained stable in the 488 presence of SAL up to 20 successive cycles (current change 488 presence of SAL up to 20 successive cycles (current change 489 less than 4 %) (Fig. S1), which indicated P-Gr-P/GCE 489 less than 4 %) (Fig. S1), which indicated P-Gr-P/GCE 490 exhibited very stability. Furthermore, no significant change of 490 exhibited very stability. Furthermore, no significant change of 491 the oxidation currents can be observed (current change less 491 the oxidation currents can be observed (current change less 492 than 3.06 %) after the electrodes have been stored at room 492 than 3.06 %) after the electrodes have been stored at room 493 temperature for more than 30 days (Fig. S 2) indicating the 493 temperature for more than 30 days (Fig. S2), indicating the 494 sensor has acceptable reproducibility and repeatability. sensor has acceptable reproducibility and repeatability.

495
496 496 **3.7. Real sample analysis**

497 Furthermore, the proposed sensor was applied to the 498 determination of SAL in urine samples. Urine samples were 498 determination of SAL in urine samples. Urine samples were
499 obtained from health volunteers, which were diluted 50-fold 499 obtained from health volunteers, which were diluted 50-fold
500 with 0.1 M PBS (pH 7.0) and centrifused at 5000 rpm for 5 500 with 0.1 M PBS (pH 7.0) and centrifuged at 5000 rpm for 5
501 min to remove the suspended particles. The analytical 501 min to remove the suspended particles. The analytical 502 applicability of the sensor was evaluated by determining the 502 applicability of the sensor was evaluated by determining the 503 recoveries of six target samples with different concentrations 503 recoveries of six target samples with different concentrations 504 by the standard addition method. As can be seen in Table 2, 504 by the standard addition method. As can be seen in Table 2, 505 the results were satisfactory with a recovery in the range from 505 the results were satisfactory with a recovery in the range from 506 95.0% to 105.0% indicating that the proposed method can be 506 95.0% to 105.0%, indicating that the proposed method can be 507 successfully applied in the detection of SAL concentration in 507 successfully applied in the detection of SAL concentration in 508 urine sample. urine sample.

509 **Conclusions**

510 In summary, a simple two-step approach has been
511 developed for the preparation of the Pt-graphene-Pt composite 511 developed for the preparation of the Pt-graphene-Pt composite
512 with a novel sandwich-like structure. Pt nanoparticles not only 512 with a novel sandwich-like structure. Pt nanoparticles not only 513 acted as a spacer between graphene sheets to prevent acted as a spacer between graphene sheets to prevent 514 aggregation, but also accelerated the electron transfer. Pt-515 graphene-Pt modified GCE showed a good performance for 516 sensitive determination of salbutamol due to its excellent 516 sensitive determination of salbutamol due to its excellent 517 electronic conductivity and large specific surface area. Under 517 electronic conductivity and large specific surface area. Under 518 optimized conditions, the Pt-graphene-Pt modified glass 518 optimized conditions, the Pt-graphene-Pt modified glass 519 carbon electrode exhibited a good performance in terms of low 519 carbon electrode exhibited a good performance in terms of low
520 limit of detection (9 nM) and wide linear range (0.03 - 180 520 limit of detection (9 nM) and wide linear range (0.03 - 180
521 uM) it also exhibited good stability repeatability and 521 μ M), it also exhibited good stability, repeatability and 522 reproducibility. These results indicate that the novel sandwich-522 reproducibility. These results indicate that the novel sandwich-
523 like structure of Pt-graphene-Pt is scientifically interesting and 523 like structure of Pt-graphene-Pt is scientifically interesting and 524 has great potential for use in sensors, nanoelectronics, and 524 has great potential for use in sensors, nanoelectronics, and 525 other electrochemical applications. other electrochemical applications. 526

527

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539 **Notes and references**

- 540 1 C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song, 541 C. M. Li, Angew. Chem. Int. Ed., 2010, 49, 3014. 541 C. M. Li, *Angew. Chem. Int. Ed.*, 2010, 49, 3014.
- 542 2 X. Jia, J. Campos-Delgado, M. Terrones, V. Meunier, M. 543 S. Dresselhaus, *Nanoscale*, 2011, 3, 86. 543 S. Dresselhaus, *Nanoscale*, 2011, 3, 86.
- 544
545 545 3 S. A. Ozkan, B. Uslu, P. Zuman, *Anal. Chim. Acta*, 2002,
- 546 457, 265.
547 4 B. Uslu, 9
- 547 4 B. Uslu, S. A. Ozkan, *Electrochim. Acta*, 2004, 49, 4321. 548 5 A. K. Geim, K. S. Novoselov, *Nat. Mater.*, 2007, 6 183.
- 549 6 C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science*, 2008, 550 321, 385.
551 7 R. F. Serv
- 551 7 R. F. Service, *Science*, 2009, 324, 875.
- 552 8 E. Yoo, J. Kim, E. Hosono, H. S. Zhou, T. Kudo and I. 553 Honma, Nano Lett., 2008, 8, 2277. 553 Honma, *Nano Lett.*, 2008, 8, 2277.
- 554 9 S. Chen, J.W. Zhu, X.D. Wu, Q.F. Han and X. Wang, 555 ACS Nano, 2010, 4 2822. 555 *ACS Nano*, 2010, 4 2822.
- 556 10 L. M. Lu, H. B. Li, F. L. Qu, X. B. Zhang, G. L. Shen, R. 557 Q. Yu, *Biosens. Bioelectron.*, 2011, 26, 3500. 557 Q. Yu, *Biosens. Bioelectron.*, 2011, 26, 3500.
- 558 11 L. Zhang, Y. P. Wen, Y. Y. Yao, Z. F. Wang, X. M. Duan, 559 J. K. Xu, Chinese Chem. Lett., 2014, 25, 517. 559 J. K. Xu, *Chinese Chem. Lett.*, 2014, 25, 517.
- 560 12 F. L. Qu, T. Li, M. H. Yang, *Biosens. Bioelectron.*, 2011, 561 26, 3927.
562 13 Y. Si, E.
	- 562 13 Y. Si, E. T. Samulski, *Chem. Mater.*, 2008, 20, 6792.
- 563 14 V. C. Tung, L. M. Chen, M. J. Allen, J. K. Wassei, K. 564 Nelson, R. B. Kaner and Y. Yang, *Nano Lett.*, 2009, 9, 565
566
- 566 15 Z. J. Fan, J. Yan, L. J. Zhi, Q. Zhang, T. Wei, J. Feng, M. 567 L. Zhang, W. Z. Qian and F. Wei, Adv. Mater., 2010, 22. 567 L. Zhang, W. Z. Qian and F. Wei, *Adv. Mater.*, 2010, 22, 568 3723.
569 16 C.H.
- 569 16 C. H. Lu, H. H. Yang, C. L. Zhu, X. Chen and G. N. Chen, 570 Angew. Chem. Int. Ed., 2009. 121, 4879. 570 *Angew. Chem. Int. Ed.*, 2009, 121, 4879.
- 571 17 H. X. Chang, L. H. Tang, Y. Wang, J. H. Jiang and J. H. 572 Li. Anal. Chem.. 2010. 82. 2341. 572 Li, *Anal. Chem.*, 2010, 82, 2341.
- 573 18 T. Ramanathan, S. Stankovich, D. A. Dikin, H. Liu, H. 574 Shen, S. T. Nguyen, L. C. Brinson, J. Polym. Sci. Part B: 574 Shen, S. T. Nguyen, L. C. Brinson, *J. Polym. Sci. Part B:* 575 *Polym. Phys*, 2007, 45, 2097.
	- 576 19 X. S. Zhou, T. B. Wu, B. J. Hu, G. Y. Yang, B. X. Han,

New Journal of Chemistry Accepted ManuscriptNew Journal of Chemistry Accepted Manuscript

- *Chem. Commun.*, 2010, 46, 3663. 20 R. Verdejo, M. Martin-Gallego, L. J. Romasanta, M. Hernάndez, M. M. Bernal, M. A. Lopez-Manchado, *J. Mater. Chem.*, 2008, 18, 2221.
- 581 21 X. Z. Zhou, X. Huang, X. Y. Qi, S. X. Wu, C. Xue, F. Y. 582 C. Boey, Q. Y. Yan, P. Chen and H. Zhang, *J. Phys.* C. Boey, Q. Y. Yan, P. Chen and H. Zhang, *J. Phys. Chem. C*, 2009, 113, 10842.
- 22 J. B. Liu, S. H. Fu, B. Yuan, Y. L. Li and Z. X. Deng, *J. Am. Chem. Soc.*, 2010, 132, 7279.
- 586 23 J. F. Shen, Y. Z. Hu, M. Shi, N. Li, H. W. Ma and M. X.
587 Ye, J. Phys. Chem. C, 2010, 114, 1498. Ye, *J. Phys. Chem. C*, 2010, 114, 1498.
- 588 24 A. Liu, T. Xu, J. Tang, H. Wu, T. Zhao, W. Tang, 589 Electrochim. Acta, 2014,119, 43. *Electrochim. Acta*, 2014,119, 43.
- 25 Y. Chu, Z. Wang, Q. Pan, *ACS Appl. Mater. Inter.*, 2014, 591 6, 8378.
592 26 M. Li, 2
- 26 M. Li, X. Bo, Z. Mu, Y. F. Zhang, L. Guo, *Sensor Actuat B-Chem.*, 2014, 192, 261.
- 27 L. Wang, J. H. Ma, *Acta. Phys-Chim. Sin.*, 2014, 30, 1267.
- 28 Y. H. Lu, M. Zhou, C. Zhang, Y. P. Feng, *J. Phys. Chem. C*, 2009, 113, 20156.
- 597 29 M. H. Yang, Y. H. Yang, Y. L. Liu, G. L. Shen, R. Q. Yu, 598 *Biosens. Bioelectron.*, 2006, 21, 1125. *Biosens. Bioelectron.*, 2006, 21, 1125.
- 30 E. Antolini, T. Lopes, E. R. Gonzalez, *J. Alloy. Compd.*, 600 2008, 461, 253.
601 31 A. Hauch, A. G
- 31 A. Hauch, A. Georg, *Electrochim. Acta*, 2001, 46, 3457.
- 602 32 E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura, I. 603 Honma. Nano Lett., 2009. 9. 2255. Honma, *Nano Lett.*, 2009, 9, 2255.
- 33 Y. M. Li, L. H. Tang, J. H. Li, *Electrochem. Commun.*, 605 2009, 11, 846.
606 34 S. Sharma, A.
- 606 34 S. Sharma, A. Ganguly, P. Papakonstantinou, X. Miao, M. 607 Li. J. L. Hutchison. M. Delichatsios. S. Ukleia. *J. Phys.* Li, J. L. Hutchison, M. Delichatsios, S. Ukleja, *J. Phys. Chem. C*, 2010, 114, 19459.
- 35 C. Chen, M. Long, H. Wu, W. Cai, *Sci. China. Chem.*, 610 2013, 56, 354.
611 36 M. O. Yang
- 36 M. Q. Yang, X. Y. Pan, N. Zhang, Y. J. Xu, *Crystengcomm*, 2013, 15, 6819.
- 613 37 L. N. Zhang, H. H. Deng, F. L. Lin, X. W. Xu, S. H. 614 Weng, A. L. Liu, X. H. Lin, X. H. Xia, W. Chen, Anal. Weng, A. L. Liu, X. H. Lin, X. H. Xia, W. Chen, *Anal. Chem.*, 2014, 86, 2711.
- 616 38 J. I. Paredes, S. Villar-Rodil, P. Sol *f*-Fern ández, A. 617 Mart nez-Alonso, J. M. D. Tascon, *Langmuir*, 2009, 25 Mart *fiez-Alonso, J. M. D. Tascon, Langmuir*, 2009, 25
5957. 618
619
- 39 S. Woo, Y.R. Kim, T. D. Chung, Y. Piao, H. Kim, *Electrochim. Acta*, 2012, 59, 509.
- 40 C. Chen, M. Long, H. Wu, W. Cai, *Sci. China. Chem.*, 622 2013, 56, 354.
623 41 J. Xu, Y. Li, J
- 41 J. Xu, Y. Li, J. Cao, R. Meng, W. Wang, Z. Chen, *Catal. Sci. Technol.*, 2015, 5, 1821.
- 625 42 J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso, J. M. D. 626 Tasc ón, *Langmuir*, 2008, 24, 10560. Tascón, *Langmuir*, 2008, 24, 10560.
- 627 43 D. Li, M. B. Muller, S. Gilje, R. B. Kaner, G. G. Wallace, 628 *Nat. Nanotechnol.*, 2008, 3, 101. *Nat. Nanotechnol.*, 2008, 3, 101.
- 44 Y. Gao, L. Wu, K. Zhang, J. Xu, L. Lu, X. Zhu, Y. Wu, *Chinese Chem. Lett.*, 2015, 26, 613.
- 631 45 A. J. Bard, L. R. Faulkner, Wiley, New York, 1980.
632 46 E. Laviron. J. Electroanal. Chem., 1974. 52, 355.
- 46 E. Laviron, *J. Electroanal. Chem.*, 1974, 52, 355.
- 47 F. Anson, *Anal. Chem.*, 1964, 36, 932.
- 48 K. C. Lin, C. P. Hong, S. M. Chen, *Sensor. Actuat. B-Chem.*, 2013, 177, 428.
- 49 R. N. Goyal, M. Oyama, S. P. Singh, *J. Electroanal. Chem.*, 2007, 611, 140.
- 638 50 D. Boyd, J. R. B. Rodriguez, A. J. M. Ordieres, P. T. 639 Blanco, M. R. Smyth, Analyst, 1994, 119, 1979. Blanco, M. R. Smyth, *Analyst*, 1994, 119, 1979.
- 640 51 Y. L. Wei, Q. Zhang, C. Shao, C. Li, L. P. Zhang, X. L. 641 Li *L* Anal Chem 2010 65 398 Li, *J. Anal. Chem.*, 2010, 65, 398.

Graphical Abstract

Sandwich-structured Pt-graphene-Pt was prepared by two step method including in situ growth and electrochemical reduction process.