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5 **1 Nitrogen-doped graphene-ionic liquid-glassy carbon microsphere paste electrode**
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7 **2 for ultra-sensitive determination of quercetin**
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11 **Abstract:** The analysis of quercetin (Qu) is of great significance owing to its multiple
12 **biomedical effects.** In this work, a nitrogen-doped graphene-ionic liquid-glassy
13 carbon microsphere paste electrode (N-GE/GCILE) was constructed for the
14 determination of Qu. Cyclic voltammetry (CV) and square wave voltammetry (SWV)
15 were employed to investigate the electrochemical behavior of Qu. In comparison with
16 unmodified glassy carbon microsphere paste electrode, the modified electrode
17 exhibited better electrocatalytic activity towards Qu. The influencing **conditions** on
18 sensitivity such as the amount of modifier, accumulation potential and time, and
19 electrolyte pH value were respectively discussed. Under the optimized conditions, two
20 linear ranges of 0.002- 0.1 μM and 0.1-10 μM were obtained, with a detection limit of
21 1 nM (S/N=3). The method was applied in Qu determination in blueberry juice with
22 the recoveries of 102.5-105.0 %.

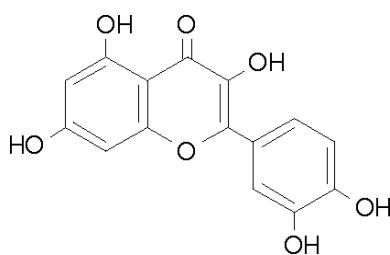
23 **Keywords:** Nitrogen-doped graphene; Ionic liquid; Glassy carbon microsphere;
24 **Modified electrode;** Quercetin.
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63 **1. Introduction**
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3 Flavonoids are naturally distributed in fresh fruits, vegetables and other herbs, and
4 usually used as food additives or the ingredient of health products [1, 2]. They exhibit
5 antioxidant, anti-inflammatory and antineoplastic biomedical effects related to radical
6 scavenging properties of such compounds [3, 4]. Quercetin (Qu, the basic chemical
7 structure is shown in Scheme 1) is one of the most important flavonoids, it can be
8 found in onions, celery, sweet pepper, apples, grapes, honeysuckle, pueraria, and
9 other products. The antioxidant capacity of Qu has been extensively demonstrated in
10 the literature [5-7] and it shows other biological benefits including its role as anti-
11 allergic, anti-viral, anti-tumor activity, lowering blood pressure and blood lipids [8,
12 9]. Therefore, it is important to develop a simple and convenient method for sensitive
13 analysis of Qu.



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15 **Scheme 1. Chemical structure of quercetin (Qu)**

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The traditional techniques for detecting Qu involve high-performance liquid chromatography [10, 11], mass spectrometry [12], capillary electrophoresis spectrophotometry [13, 14], and spectrofluorimetry [15]. These traditional methods have high selectivity and sensitivity but are expensive, time-consuming, and they usually need complicated sample pretreatment [16, 17]. Due to the electrochemical activity of Qu, electrochemical methods show potential application in the analysis of Qu and can overcome the shortcomings of the above-mentioned conventional approaches.

The electrochemical technique exhibits the advantages of rapid response, operational simplicity, high sensitivity, and low cost [18]. Some electrochemical sensors were prepared for the detection of Qu; for example, hexadecyltrimethylammonium bromide functionalized Fe decorated MWCNTs

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122 1 modified carbon paste electrode [19], g-C₃N₄/NiO heterostructured nanocomposite
123 2 modified glassy carbon electrode [20], and Lewatit FO36 nanoresin/multi-walled
124 3 carbon nanotubes modified graphite paste electrodes [21] have been used for the
125 4 electrochemical analysis of Qu.

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129 5 In order to improve the performance of the modified electrodes, various
130 6 materials are synthesized. In recent years, chemical doping has gained attention in the
131 7 field of electrochemistry, it can customize the properties of materials depending on
132 8 your need. Nitrogen (N) can easily modify the local elemental composition of
133 9 graphene (GR), and N-functional groups can effectively improve the affinity and
134 10 binding ability of composite material. This chemically heteroatom-doping in graphene
135 11 optimizes its surface structure, and enhances the properties of GR electrochemical
136 12 performance [22-25]. Therefore, nitrogen-doped graphene (N-GE) composite has
137 13 been extensively applied in the construction of electrochemical sensors ascribed to its
138 14 excellent characteristics including high electrical conductivity, good chemical
139 15 stability, superior selectivity for biomolecules and other benefits [26, 27].

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149 16 Additionally, ionic liquids (ILs) show high conductivity, low volatility, wide
150 17 electrochemical windows and extensive applicability [28, 29], they can provide an
151 18 active interface for the electrochemical processes and further modification [30, 31].
152 19 Glassy carbon microsphere is also an excellent electrode material with good electrical
153 20 conductivity, great biocompatibility, high hardness and corrosion resistance [32, 33].

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158 21 In this paper, a nitrogen-doped graphene-ionic liquid-glassy carbon microsphere
159 22 paste electrode was firstly prepared (N-GE/GCILE) for Qu analysis. The N-GE with
160 23 typically crumpled and folded morphologies exhibited large specific surface area, and
161 24 its special structure could provide plentiful active sites for Qu [34, 35]. With the
162 25 synergistic effect of N-GE and ILs, the modified electrode presented the increased
163 26 active surface area and fast electron transfer ability, and it exhibited excellent
164 27 electrocatalytic activity towards Qu with the negative shift of the oxidation potential.
165 28 The method had high sensitivity and stability. Finally, the presented method was
166 29 successfully applied to analyze Qu content in fruit juice samples with satisfactory
167 30 results.

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180 **2. Experimental**
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183 **2.1. Reagents and materials**
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186 The quercetin (Qu) was obtained from Shanghai Aladdin Bio-Chem Technology Co.,
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188 Ltd. (www.aladdin-e.com) with a purity of 95%. Glassy carbon microsphere (
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190 particle diameter: 2-12 μM) was purchased from Sigma-Aldrich (<https://www.sigma->
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192 [aldrich.com](http://www.sigma-aldrich.com)), ionic liquid 1-octylpyridinium hexafluorophosphate (OPPF₆) was
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194 obtained from the Lanzhou Institute of Chemical Physics (<http://www.ionicliquid.org>)
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196 and paraffin oil was obtained from Sinopharm Chemical Reagent Co., Ltd. ([http:](http://www.sinoreagent.com)
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198 [//www.sinoreagent.com](http://www.sinoreagent.com)). The nitrogen-doped graphene (surface area: >500 m²/g;
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200 nitrogen content: 3.0 wt% ~ 5.0 wt%) was purchased from Nanjing XFNANO
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202 Materials Tech Co., Ltd. (<http://www.xfnano.com>). 0.2 M acetate buffer solution
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204 (ABS) was used as a supporting electrolyte prepared by mixing appropriate ratio
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206 sodium acetate solution and acetic acid solution. Other chemical reagents involved in
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208 the experiment were of analytical grade without further purification.

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210 **2.2. Apparatus**
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213 CHI660E electrochemical workstation (Shanghai Chenhua Instruments Corporation,
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215 <http://www.chinstr.com>) and PARSTAT 4000 electrochemical workstation (Princeton
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217 Applied Research, <http://www.par-solartron.com.cn>) were used to perform
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219 electrochemical measurements. Nitrogen-doped graphene-ionic liquid-glassy carbon
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221 microsphere paste electrode (N-GE/GCILE, 3 mm in diameter) was used as the
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223 working electrode, saturated calomel electrode (SCE) was the reference electrode, and
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225 Pt wire was the auxiliary electrode. An FE20 pH meter (METTLER TOLEDO
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227 Instrument Shanghai Co., Ltd., <https://www.mt.com>) was utilized to measure the pH
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229 value of the solution. The test solution was stirred with a magnetic stirrer (Model
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231 KMO2, IKA, <http://www.ika.cn>) during the measurement. Ultrapure water was
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233 produced from Heal Force EASY50 water purification system (Shanghai Canrex
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235 Analytic Instrument Co., Ltd., <http://www.canrex.cn>) and used throughout the
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237 experiment.

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1 2.3. Electrode preparation

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4 The nitrogen-doped graphene-ionic liquid-glassy carbon microsphere paste electrode
5 (N-GE/GCILE) was prepared by mixing 0.045 g glassy carbon microsphere, 0.005 g
6 nitrogen-doped graphene (N-GE), 0.025 g ionic liquid 1-octylpyridinium
7 hexafluorophosphate (OPPF₆) and 15 μL paraffin oil in the mortar. The resulting
8 homogeneous paste was tightly stuffed into the Teflon tube (3.0 mm in diameter), and
9 electrical connection was established by a copper wire. Next, the electrode was heated
10 for at least one minute with a hair dryer. A new surface was obtained by carefully
11 polishing it on a piece of weighing paper.

12 For comparison, nitrogen-doped graphene modified glassy carbon microsphere
13 paste electrode (N-GE/GCPE) was prepared by mixing glassy carbon microsphere,
14 nitrogen-doped graphene and paraffin oil. Furthermore, glassy carbon microsphere-
15 ionic liquid paste electrode (GCILE) was made up of glassy carbon microsphere,
16 ionic liquid and paraffin oil. And glassy carbon microsphere paste electrode (GCPE)
17 was fabricated with glassy carbon microsphere and paraffin oil.

18 19 2.4. Analytical procedure

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21 The electrochemical behavior of Qu was studied by square wave voltammetry (SWV)
22 in 0.2 M ABS solution (pH 4.5) under open-circuit condition. The square wave
23 voltammograms (SWVs) were recorded in the range of 0 V- 0.6 V. And the electrode
24 was rinsed by ultrapure water after each measurement.

25 26 2.5. Sample preparation

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28 The real sample was a commercial blueberry juice purchased from a local
29 supermarket. To fit into the linear range, the samples were diluted 100 times by 0.2 M
30 pH 4.5 ABS without any pretreatment before measurement.

31 32 3. Results and discussion

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2 **3.1. Characterization of the modified electrode**
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4 The morphologies and microstructures of bare GCPE, N-GE/GCPE, GCILE, and N-
5 GE/GCILE composites are studied via SEM. As shown in Fig. 1a, the large gap was
6 observed between glassy carbon microspheres on the GCPE. However, GCILE
7 (shown in Fig. 1c) displayed a uniform surface where the ionic liquid was sufficiently
8 filled into the interstice between microspheres due to its high viscosity. As can be seen
9 from Fig. 1b (on N-GE/GCPE), the N-GE was crosslinked with glassy carbon
10 microsphere paste, which exhibited an uneven surface. While in Fig. 1d, the N-
11 GE/GCILE also showed a uniform surface owing to the presence of ionic liquid, and
12 the morphology of N-GE was not visible on the surface, which proved that the
13 modifier was successfully embedded in the matrix.

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15 **3.2. Electrochemical properties of the modified electrode**
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17 Fig. 2 shows cyclic voltammograms (CVs) of GCPE, N-GE/GCPE, GCILE, and N-
18 GE/GCILE recorded in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl in the range of -
19 0.2 to 0.6 V. As can be seen, the N-GE/GCPE (curve b) showed a remarkable
20 decrease in peak potential separation (ΔE_p) and an obvious increase in peak current
21 (I_p) compared with bare GCPE (curve a). When the ionic liquid was added in glassy
22 carbon microsphere paste (GCILE, curve c), peak current obviously increased,
23 meanwhile, the ΔE_p further reduced, which indicated the inherent electrocatalysis
24 property of ionic liquid. Furthermore, the highest peak current response was presented
25 on the N-GE/GCILE (curve d). The results verified that N-GE and ionic liquid
26 composites could improve the electrochemical performance of the modified electrode.

27 Electrochemical impedance spectroscopy (EIS) was employed to further estimate
28 the electron transfer ability of the modified electrodes. Using the $\text{K}_3[\text{Fe}(\text{CN})_6]$ redox
29 system, the charge transfer resistance (R_{ct}) value can be calculated from the size of
30 the high-frequency semicircle diameter in the Nyquist plots. As seen in Fig. 3, the
31 high electron transfer resistance was observed for GCPE with the R_{ct} value of 2.09

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358 1 $k\Omega$ (curve a). When the N-GE was modified on the electrode, the lower resistance
359 2 value ($R_{ct}=478 \Omega$) was presented at N-GE/GCPE (curve b). As expected, the N-
360 3 GE/GCILE (curve c) showed almost a straight line in the Nyquist plots, suggesting
361 4 that its electron transfer ability was significantly enhanced.
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366 6 **3.3. Surface area study**

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370 8 The effective surface areas of bare GCPE, N-GE/GCPE, GCILE, and N-GE/GCILE
371 9 were discussed in $K_3[Fe(CN)_6]$ redox system using cyclic voltammetry (CV), which
372 10 was displayed in Fig. S1. For a reversible process, the relation on peak current and
373 11 square root of scan rate conforms to the Randles-Sevcik formula [36]:

$$374 12 I_{pa} = (2.69 \times 10^5) n^{3/2} A C_0 D_R^{1/2} \nu^{1/2} \quad (1)$$

375 13 where I_{pa} , A , and ν respectively refers to anodic peak current (A), the effective
376 14 surface area of the prepared electrode (cm^2) and scan rate ($V s^{-1}$); C_0 is the
377 15 concentration of $K_3[Fe(CN)_6]$ which is equal to 5 mM. In $K_3[Fe(CN)_6]$ redox system,
378 16 electron transfer number $n=1$, the diffusion coefficient $D_R=7.6 \times 10^{-6} cm^2 s^{-1}$. The
379 17 surface areas were calculated to be $0.04 cm^2$, $0.055 cm^2$, $0.106 cm^2$ and $0.198 cm^2$ for
380 18 GCPE, N-GE/GCPE, GCILE and N-GE/GCILE, respectively. The results indicated
381 19 that N-GE and ionic liquid could increase the effective surface areas of the modified
382 20 electrode.
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393 21 394 22 **3.4. Electrochemical behaviors of Qu**

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398 24 As shown in Fig. 4, the electrochemical behaviors of $10 \mu M$ Qu at GCPE, N-
399 25 GE/GCPE, GCILE, and N-GE/GCILE were investigated by SWV in 0.2 M ABS (pH
400 26 4.5). On the bare GCPE (curve a), a weak oxidation peak (about $16.68 \mu A$) was
401 27 observed. After N-GE was modified on the electrode, oxidation current ($25.02 \mu A$)
402 28 obviously increased on the N-GE/GCPE (curve b). The phenomenon was attributed to
403 29 the typically crumpled and folded morphologies of N-GE (the TEM image of N-GE is
404 30 shown in Fig. 5). It has large specific surface area like graphene, and the nitrogen

doping leads to the distortion of structure with more structural defects, which could provide abundant high edge plane active sites for electrochemical oxidation [34, 35]. Therefore, the electrochemical response was enhanced at N-GE/GCPE. In addition, GCILE (curve c) presented higher current response to Qu (54.51 μA). This was due to ionic liquid could be filled in the gaps between the microspheres and improved electron-transfer kinetics at the prepared electrode [37]. The peak current of Qu on N-GE/GCILE was almost twice higher than that on GCILE. The results indicated that N-GE/GCILE had better electrocatalytic activity towards Qu, which were ascribed to the following factors: Firstly, the micrometer-sized glassy carbon microsphere with large specific surface area can provide more channels for transferring electrons; secondly, due to the CH- π interaction between a CH group of 1-octylpyridinium hexafluorophosphate and π -electrons of N-GE, the ionic liquid could be effectively combined together with N-GE [38], and the composites synergistically promoted electron transfer in the modified electrode; furthermore, N-GE with large surface area exhibited strong adsorption capacity and high electrocatalytic ability to Qu.

3.5. Effect of scan rates

The effect of scan rate (ν) on the oxidation peak current (I_{pa}) of 10 μM Qu was investigated using CV at the N-GE/GCILE. As shown in Fig. 4, a reversible oxidation peak of Qu was presented, and I_{pa} increased as the increasing scan rate (ν) with a slight positive shift in oxidation peak potential (E_{pa}) in the scan rates range of 25- 400 mV s^{-1} . The insert in Fig. 6 exhibited peak current was proportional to scan rate with a linear regression equation of $I_{pa} (\mu\text{A}) = 0.1262 \nu (\text{mV s}^{-1}) - 0.4629 (r^2=0.9999)$, which confirmed an adsorption-controlled process for the electrochemical oxidation of Qu at the N-GE/GCILE.

3.6. Optimization of analytical conditions

3.6.1. Effect of pH value

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477 2 The effects of pH value on the oxidation peak current (I_{pa}) and peak potential (E_{pa})
478 3 of 10 μM Qu were discussed. Fig. S2 exhibits SWVs of 10 μM Qu in 0.2 M ABS with
479 4 the pH range of 2.5-6.0. As shown in the figure, the E_{pa} shifted towards negative
480 5 position as the pH value of supporting electrolyte increased, and the linear
481 6 relationship of E_{pa} and pH value was described as follows: $E_{pa} (\text{V}) = -0.07 \text{ pH} + 0.61$
482 7 ($r=0.9922$). The slope value of 70 mV pH^{-1} deviated from the theoretical value.
483 8 According to the Nernst equation, it may be attributed to the properties of the
484 9 constructed electrode and the influence of the temperature. This finding was
485 10 consistent with the results in previous reports [39, 40], 70 mV pH^{-1} was considered to
486 11 be close to the theoretical value, suggesting that the number of transferred electrons
487 12 and protons involved in the electrochemical process of Qu was equal [41].
488 13 Furthermore, as the pH value increased from 2.5 to 4.5, the current response of Qu
489 14 increased. However, the further increase of the pH value led to the gradual decrease of
490 15 peak current. The results may be stated by the following reasons: at higher pH values,
491 16 the deprotonation of Qu influences the accumulation of Qu at the electrode surface
492 17 and electrochemical reaction. On the contrary, the hydroxyl groups of Qu are active at
493 18 lower pH values [42]. Therefore, 0.2 M pH 4.5 ABS was chosen as supporting
494 19 electrolyte in the next experiment.
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496 21 **3.6.2. Effect of the amount of the modifier**

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498 23 The effect of the amount of the N-GE on the voltammetric response towards 10 μM
499 24 Qu was investigated. In Fig. S3, the current response increased with the increasing
500 25 amount of N-GE from 0 to 2.5%, and reached the maximum as the amount of
501 26 modifier was 2.5%. Then a gradual decrease on the response signal was observed
502 27 when the proportion of N-GE exceeded 2.5%. The rising trend in current response
503 28 could be ascribed to the large electroactive surface area and the improved absorption
504 29 capacity when a certain amount of N-GE was modified on the electrode. However,
505 30 excessive N-GE in the paste would increase the film thickness, block the electron

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535 1 transfer and then influenced the oxidation process of Qu. Therefore, 2.5 wt% N-GE
536 2 was chosen for preparation of the modified electrode in the subsequent experiments.
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540 4 **3.6.3. Effect of accumulation potential and accumulation time**

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544 6 The influence of the accumulation potential and open-circuit condition on the
545 7 voltammetric response was discussed under the same **experimental conditions** (not
546 8 shown). The response signal showed no significant difference between an
547 9 accumulation potential and an open-circuit condition, so the open-circuit condition
550 10 was selected in the follow-up experiment. The obtained results had confirmed that the
551 11 oxidation of Qu at N-GE/GCILE was a typical adsorption-controlled process, thence
552 12 accumulation time was a key factor on current response of Qu. As shown in Fig. **S4**,
553 13 with the accumulation time varied from 10 to 180 s, the current response increased
554 14 gradually because more Qu was adsorbed on the electrode surface. After 180 s, the
555 15 peak current changed a little because the adsorption of Qu reached saturation.
556 16 Ultimately, the accumulation process of Qu was performed at 180 s under open-
557 17 circuit condition considering sensitivity and work efficiency of analysis.
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567 19 **3.7. Determination of Qu**

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571 21 The SWV was used to determine Qu at the N-GE/GCILE. Fig. **7** exhibits SWVs of
572 22 different concentrations of Qu. From Fig. **7A**, peak currents gradually increased with
573 23 the increasing concentrations. Two linear ranges were obtained in Fig. **7B** and Fig.
574 24 **7C**, they were 0.002-0.1 μM and 0.1-10 μM , respectively; and the linear regression
575 25 equations were: $I_{pa} (\mu\text{A}) = 49.5354 c (\mu\text{M}) + 0.1528$ ($r^2=0.9984$) and $I_{pa} (\mu\text{A}) =$
576 26 $6.3114 c (\mu\text{M}) + 4.4662$ ($r^2=0.9985$), respectively. The limit of detection (LOD) was
577 27 calculated as 1 nM ($S/N=3$). Furthermore, the better analysis parameters were
578 28 achieved at N-GE/GCILE in comparison to other reported analytical methods [**20**, **21**,
579 29 **43-45**]. Table 1 summarizes the key parameters of various modified electrodes for Qu
580 30 detection.
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594 2 **3.8. Reproducibility and stability**
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598 4 The reproducibility and stability of the N-GE/GCILE were investigated in the
599 5 presence of 10 μM Qu. The relative standard deviation (RSD) was calculated to be
600 6 1.35% by six repetitive measurements using the same electrode. Similarly, for six
601 7 modified electrodes prepared in the same procedure, the RSD was 2.37%. The results
602 8 exhibited good reproducibility of the modified electrode. Moreover, the current
603 9 response of Qu retained 98.3% of the initial value after one month under room
604 10 temperature, confirming the outstanding stability of the sensor.
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611 12 **3.9. Selectivity**
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614 14 Some potential interfering substances were measured on the detection of Qu (not
615 15 shown). The results showed that common inorganic interferences, such as 500-fold
616 16 excess of K^+ , Na^+ , Mg^{2+} , Pb^{2+} , NO_3^- , Cl^- , 400-fold concentration of Co^{2+} and 200-fold
617 17 concentration of Ca^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} had no interference on the detection of Qu.
618 18 Furthermore, the response of Qu was hardly interfered by some organic substances,
619 19 including 500-fold glucose, 400-fold cystine, tyrosine, 200-fold glycine, arginine,
620 20 100-fold ascorbic acid, 50-fold dopamine, uric acid, and the same concentration of
621 21 luteolin and rutin (the current value changed less than $\pm 5\%$). The analysis method
622 22 could be used for selective determination of Qu with outstanding anti-interference
623 23 ability.
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633 25 **4. Real sample analysis**
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636 27 The analysis of blueberry juice was undertaken using the proposed method in order
637 28 to evaluate the practicality of the modified electrode. The standard addition method
638 29 was used, and the results were summarized in Table 2. The recoveries ranged from
639 30 102.5% to 105.0%, and the RSD was found to be less than 1.85%, suggesting that the
640 31 method had significant potential for practical application.
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652 **1 5. Conclusions**
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655 3 In this work, we have developed a nitrogen-doped graphene-ionic liquid-glassy
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657 4 carbon microsphere paste electrode by a simple fabrication procedure. The modified
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659 5 electrode exhibited excellent electrocatalytic performance towards Qu compared to
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661 6 other electrodes. The method provided wide linear ranges (0.002-0.1 μM and 0.1-10
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663 7 μM), low detection limit (1 nM), good reproducibility, stability, and high selectivity.
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665 8 The fabricated electrode was successfully applied for Qu detection in blueberry juice
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667 9 with satisfactory recoveries. The results confirmed the feasibility of the modified
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669 10 electrode for the determination of Qu in food samples.
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1007 **Figure captions**

1008 **Fig.1.** SEM images of (a) GCPE, (b) N-GE/GCPE, (c) GCILE and (d) N-GE/GCILE.

1009 **Fig.2.** Cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl at GCPE
1010 (a), N-GE/GCPE(b), GCILE(c) and N-GE/GCILE(d), respectively, with a scan
1011 rate of 50 mV s^{-1} .

1012 **Fig.3.** Nyquist plots of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl at GCPE (a), N-
1013 GE/GCPE(b) and N-GE/GCILE(c).

1014 **Fig.4.** SWVs of 10 μM quercetin in 0.2 M ABS (pH 4.5) at the (a) GCPE, (b) N-
1015 GE/GCPE, (c) GCILE and (d) N-GE/GCILE.

1016 **Fig.5.** TEM image of N-GE.

1017 **Fig.6.** Cyclic voltammograms of 10 μM quercetin in 0.2 M ABS (pH 4.5) at the N-
1018 GE/GCILE at scan rate of 25, 50, 100, 150, 200, 250, 300, 350, 400 mV s^{-1}
1019 (from inner to outer); The insert is the relationship between the peak currents
1020 and scan rates.

1021 **Fig.7.** (A) SWVs for different concentrations of quercetin (from bottom to top: 0,
1022 0.001, 0.002, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, 10 μM quercetin; the amplified
1023 SWVs for quercetin in lower concentrations are shown in the insert); (B) The
1024 relationship between the peak currents and the quercetin concentration in the
1025 range of 0.002-0.1 μM ; (C) The relationship between the peak currents and
1026 the quercetin concentration in the range of 0.1-10 μM (the error bars were
1027 derived from the standard deviation of two parallel measurements).

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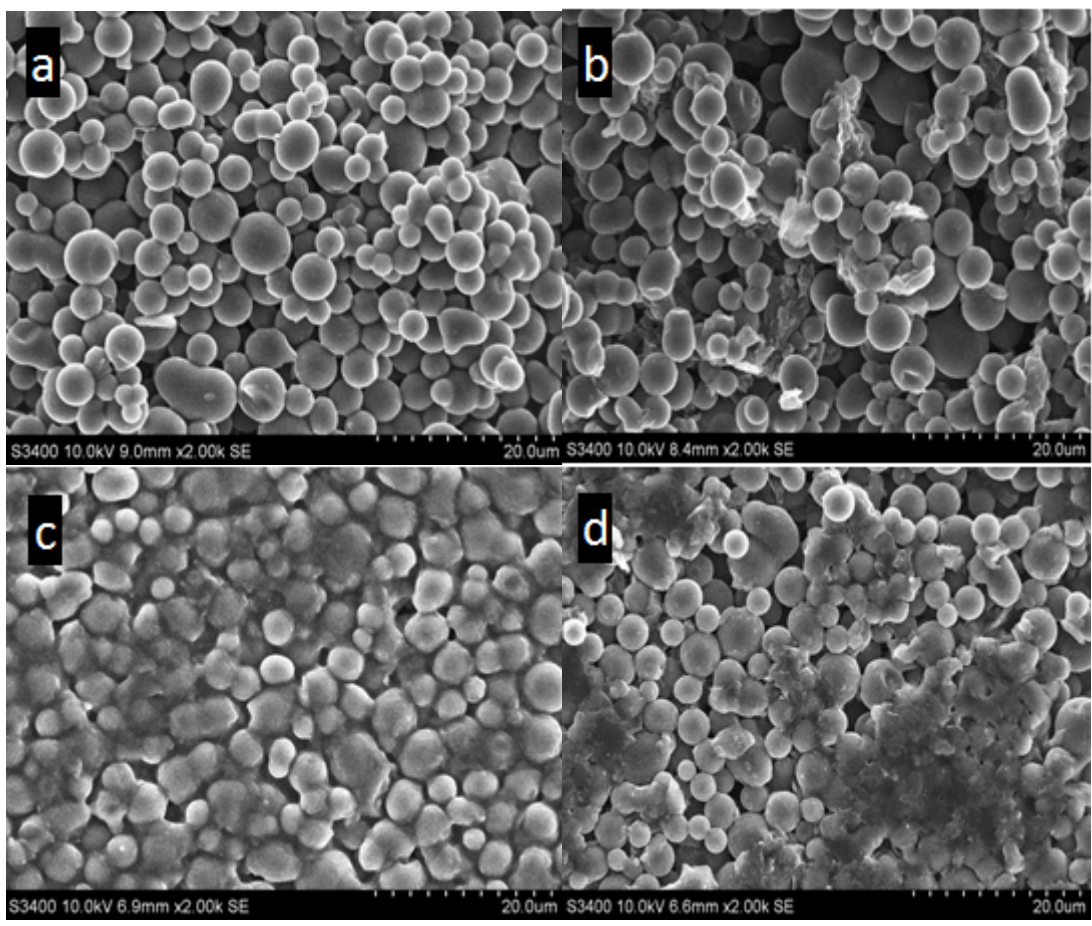


Fig. 1

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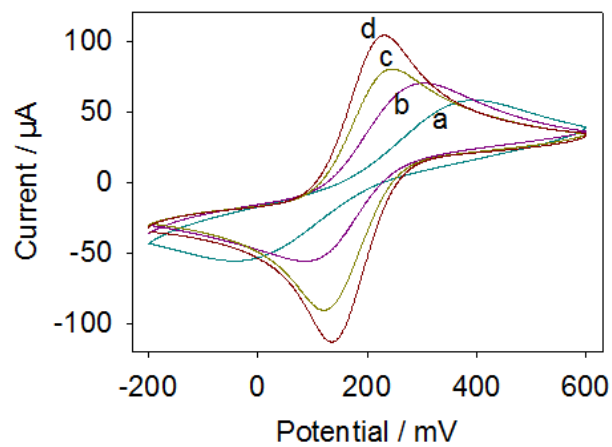


Fig. 2

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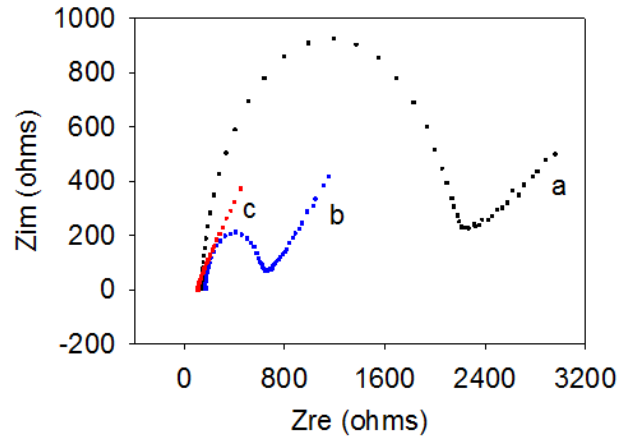
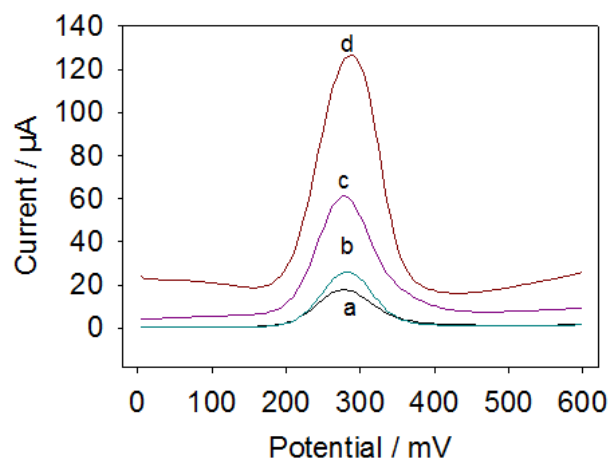


Fig. 3

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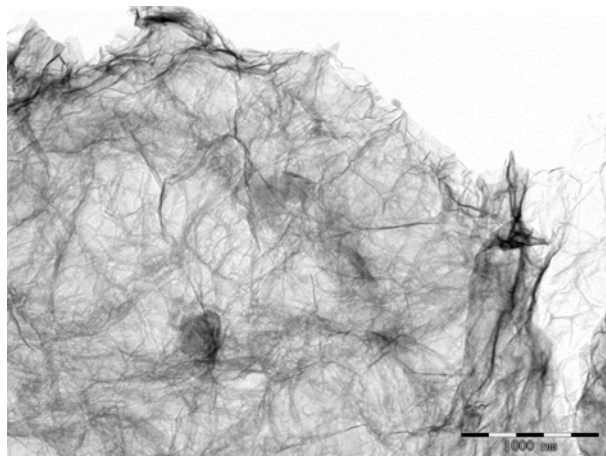
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Fig. 4

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Fig. 5

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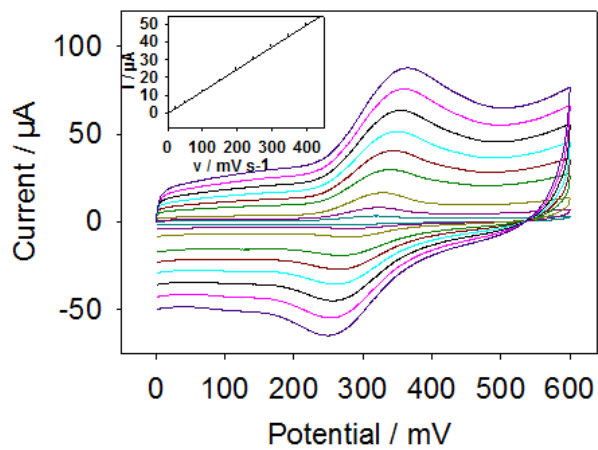


Fig. 6

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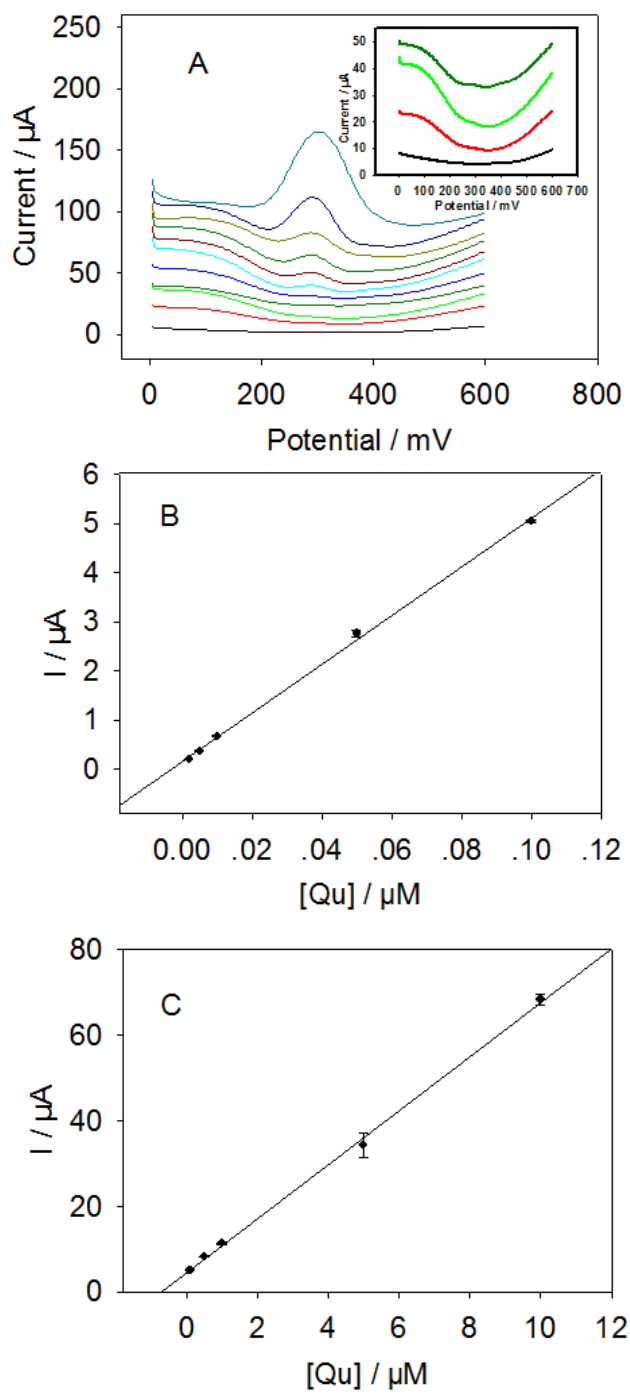


Fig. 7

Table 1 Comparison of analysis parameters of Qu detection for various modified electrodes

Modified electrode	Method	Linear range (μM)	Limit of detection (μM)	Reference
g-C ₃ N ₄ /NiO/GCE	DPV	0.010 – 250	0.002	20
LFONR-MWCNT/GPE	LSV	1.8–25/25-570	0.213	21
GOD/AuNP/GCE	DPV	0.01–6	0.002	43
3D-coumarin- SWCNTs/GCE	DPSV	0.25–3	0.020	44
Pt-PDA@SiO ₂ /GCE	SWV	0.05 -0.383	0.016	45
N-GE/GCILE	SWV	0.002-0.1/0.1-10	0.001	This work

g-C₃N₄: Graphitic carbon nitride; NiO: nickel oxide; GCE: glassy carbon electrode; DPV: differential pulse voltammetry; LFONR: Lewatit FO36 nanoresin; MWCNT: multi-walled carbon nanotube; GPE: graphite paste electrode; LSV: linear sweep voltammetry; GOD: graphene quantum dot; AuNP: gold nanoparticle; 3D: a three-dimensional architecture; SWCNTs: single walled carbon nanotubes; DPSV: differential pulse stripping voltammetry; Pt-PDA@SiO₂: platinum-polydopamine coated silica particles; SWV: square wave voltammetry; N-GE: nitrogen-doped graphene; GCILE: ionic liquid-glassy carbon microspheres paste electrode

Table 2 Determination of quercetin in blueberry juice samples using N-GE/GCILE (n=3^a)

	Sample 1	Sample 2	Sample 3
Detected / μ M	2.68	2.48	2.53
Added / μ M	2.00	2.00	2.00
Found / μ M	4.74	4.58	4.58
Recovery / %	103.0	105.0	102.5
R.S.D. / %	1.64	1.85	1.59

^a Three different measurements were made for each sample.

Electronic Supplementary Material

Nitrogen-doped graphene-ionic liquid-glassy carbon microspheres paste
electrode for ultra-sensitive determination of quercetin

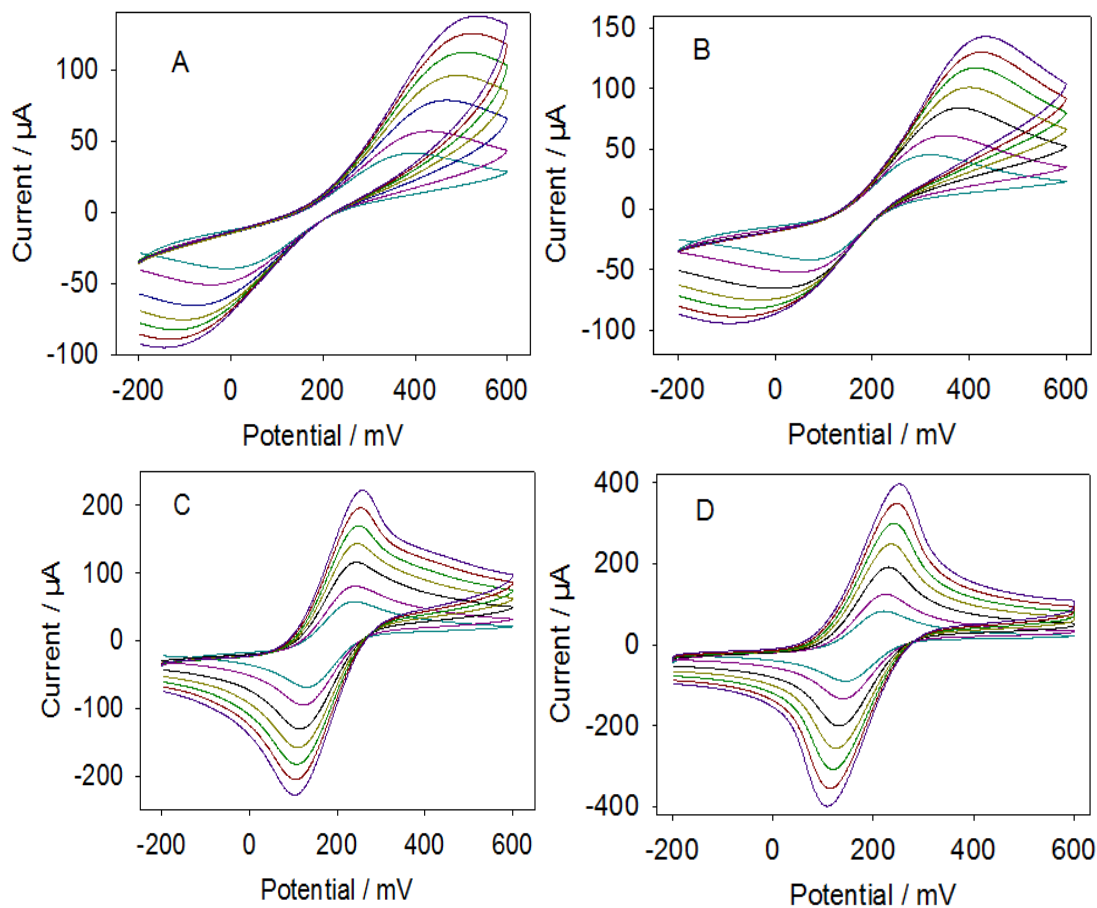
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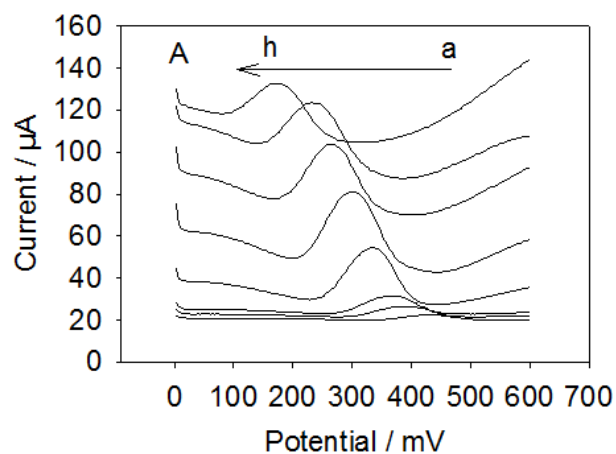
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4 **Fig. S1** Cyclic voltammograms of GCPE(A), N-GE/GCPE(B), GCILE(C),
 5 N-GE/GCILE(D) in 5mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1M KCl at scan rate of
 6 25,50,100,150,200, 250, 300 mVs^{-1} (from inner to outer).

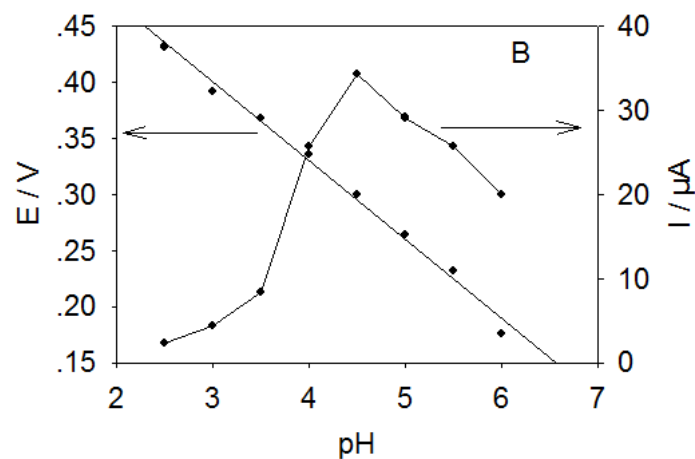
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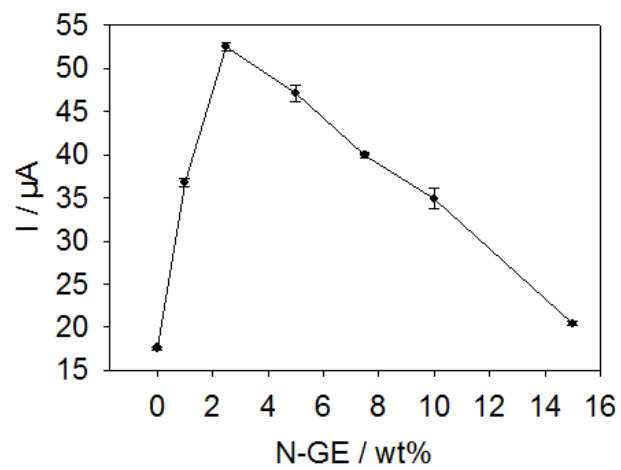
3

4 **Fig. S2 (A)** SWVs of 10 μM quercetin in 0.2 M ABS with different pH value (From a

5 to h: pH 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6); (B) Effects of pH value on the peak current (I_{pa})

6 and peak potential (E_{pa}).

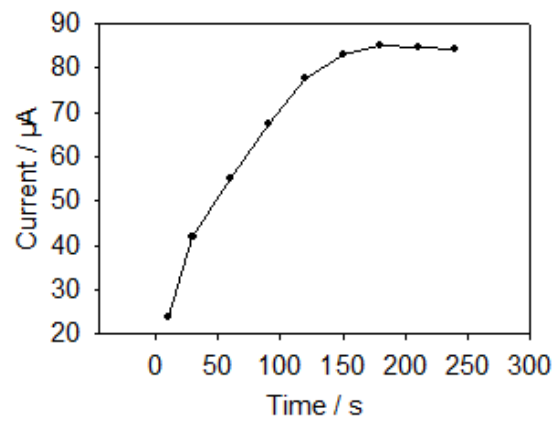
7



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2 **Fig. S3** Effect of the amount of N-GE in carbon paste on the oxidation peak current of
3 10 μM quercetin in 0.2 M ABS (pH 4.5).

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1

2 **Fig. S4** Effect of accumulation time on the oxidation peak current of 10 μM quercetin

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in 0.2 M ABS (pH 4.5).

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