Phosphorus doped and defects engineered graphene for improved electrochemical sensing: synergistic effect of dopants and defects

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Abstract

Heteroatom-doped graphene materials emerged as promising metal-free catalysts have recently attracted a growing interest in electrochemical sensing applications. However, their catalytic activity and sensing performances still need to be further improved. Herein, we reported the development of unique phosphorus (P)-doped and plasma-etched graphene (denoted as PG-E) as an efficient metal-free electrocatalyst for dopamine (DA) sensing. It was demonstrated that introducing both P-dopants and plasma-engineered defects in graphene could synergistically improve the activity toward electrocatalytic oxidation of DA by increasing the accessible active sites and promoting the electron transport capability. The resulting PG-E modified electrode showed exceptional DA sensing performances with low detection limit, high selectivity and good stability. These results suggested that the synergistic effect of dopants and defects might be an important factor for developing the advanced graphene-based metal-free catalysts for electrochemical sensing.

Keywords: Heteroatom-doped graphene; Phosphorus doping; Defect-engineering; Dopamine detection; Electrochemical sensor.

1 Introduction

Owing to the pronounced advantages of simplicity, fast response, good sensitivity and low cost, electrochemical sensor as an effective analytical tool has been widely used in environmental protection, food safety, clinical diagnostics and biological/pathological analysis[1, 2]. Since the performance of the electrochemical sensors relies strongly on the activity of the electrode catalysts[3], the development of cost-effective and efficient catalysts is of paramount importance. Albeit the precious metals such as Pt, Pd, Au, Ag and their alloys are the most active catalysts for electrochemical sensing [4], they have the major drawbacks of limited reserves, high cost and insufficient durability. To address these issues, tremendous progress has been made to develop transition metal-based catalysts such as Co, Mn, Ni, Cu and their oxides as alternatives to precious metals due to their low cost and comparable electrocatalytic activity [5]. However, transition metal-based catalysts suffer from low electrical conductivity and problematic dissolution susceptibility to acidic/basic electrolytes. Therefore, these disadvantages of metal-based catalysts impeded their large-scale commercial applications, and the metal-free catalysts hold great promise for electrochemical sensing but are still very challenging.

Heteroatom-doped carbonaceous materials, including carbon nanotubes, carbon nanofibers, porous carbons and graphene have gained noticeable popularity as metal-free electrocatalysts for electrochemical fields [6-8]. Among them, graphene has received the most attention because of its unique 2D structures, earth-abundant raw materials and ease of functionalizations[9]. Graphene naturally shows a high

1 degree of chemical inertness due to its zero band gap, while introduction of
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3 heteroatoms (N, B, S, P, etc.) into graphene frameworks can tailor the electronic
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5 structures to show dramatically enhanced catalytic activity because the introduced
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7 heteroatoms enable the activation of their adjacent carbon atoms to considerably alter
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9 the charge population and spin density [8]. Furthermore, co-doping of two kinds of
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11 heteroatoms (e.g., N and S) can further increase the catalytic activity as compared to
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13 their single-doped counterparts attributed to a synergistic coupling effect of two
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15 heteroatoms [7]. Currently, the graphene-based metal-free materials have been
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17 intensively studied in energy-relevant electrochemical applications, such as fuel cells
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19 [10], supercapacitors [11] and batteries [12], but their applications in electrochemical
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21 sensing have been reported much less in the literature [13].
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31 On the other hand, both experimental and theoretical studies have demonstrated
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33 that the structural defects (edges, vacancies, voids, boundaries, etc.) play a crucial role
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35 in determining the catalyst activity since the electrochemical reactions are most prior
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37 to occur at the defective sites [14-16]. In this regard, the defect-engineering to
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39 introduce more surface defects on graphene can be taken as an effective strategy to
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41 boost its catalytic activity. Several approaches were proposed to create the graphene
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43 defects such as nanostructures regulation [15], chemical modification [17], plasma
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45 etching [18] and dopants removal [19], and obtained defect-rich graphene materials
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47 achieved an considerable enhancement in catalytic performances. Therefore,
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49 considering the aforementioned advantages of heteroatom dopants and structural
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51 defects, it is anticipated that the methods to introduce both target dopants and
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appropriate defects will mostly explore the potentially high catalytic activity of the graphene. However, as far as we are aware no previous study related to this topic for electrochemical sensing has been reported.

Phosphorus (P) is one of the N-group elements and shows similar chemical properties to N due to their same number of valence electrons [20]. It has been reported that P-doped graphene (PG) exhibits a better catalytic activity than N-doped graphene due to the larger atomic radius and higher electron-donating ability of P dopants [20]. Although the PG is extensively investigated for energy-relevant electrochemical applications[21-23], its sensing performances are still rarely evaluated [24]. In addition, plasma-assisted technique is an efficient tool for surface modification of the materials due to the high activity of charged particles in plasma (positive/negative ions, electrons, free radicals and reactive species) [25]. Plasma treatment has been recently confirmed as an effective approach to etch the graphene surface and create high amounts of topological defects without worsening its intrinsic properties [18, 26, 27].

Herein, we developed a unique P-doped and plasma-etched graphene (abbreviated as PG-E) as an efficient metal-free catalyst for electrochemical sensing. P-doping of graphene was realized by the combined hydrothermal/annealing methods, and following plasma treatment was adopted to produce more structural defects on graphene, as illustrated in Scheme 1. The morphology and structure of as-prepared PG-E were comprehensively characterized. As a proof of concept, the PG-E was then applied for metal-free dopamine (DA) sensing. Owing to the synergic effect of

introduced P-dopants and plasma-engineered defects, the PG-E modified electrode was found to show substantially improved activity for electrocatalytic oxidation of DA and good sensing performances for sensitive and selective detection of DA.

2 Experimental

2.1. Synthesis of PG-E

All the reagents were purchased from Lanzhou New Wanke, Ltd. and used as received without further purification. Graphene oxide (GO) was prepared from graphite powders (200 μm , 99.9% purity) using a modified Hummer's method [28]. PG was synthesized by a hydrothermal method followed by annealing treatment [24]. In brief, 50 mL of GO aqueous dispersion (1 $\text{mg}\cdot\text{mL}^{-1}$) was first mixed with 20 μL of phytic acid solution (60 wt%) by ultrasonication for 10 min. Afterwards, the homogeneous solution was transferred into a 100 mL of Teflon-lined autoclave and heated at 180 $^{\circ}\text{C}$. After reaction for 12 h, the autoclave was cooled to room temperature and the resultant precipitates were collected and washed with ethanol and water several times, followed by drying in an oven at 60 $^{\circ}\text{C}$ for 12 h. Finally, the obtained powders were annealed at 850 $^{\circ}\text{C}$ for 2 h under N_2 atmosphere to prepare PG. For comparison, undoped reduced graphene oxide (RGO) was also synthesized without adding phytic acid during the hydrothermal process.

The plasma etching was carried out on a commercial AX-1000 plasma equipment (ADTEC Ltd.) with a radio-frequency (RF, 13.56 MHz) power generator. The as-synthesized samples were treated with Ar plasma for 40 min at a RF power level of 200 W. The plasma-etched PG sample is labeled as PG-E. For comparison,

reduced graphene oxide (RGO) etched by plasma was also synthesized and labeled as RGO-E.

2.2. Characterizations and Electrochemical measurements

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) were conducted on a JEM-2100 (JEOL Ltd.) microscope. X-ray diffraction (XRD) pattern was recorded on a 7000LX powder diffractometer (Shimadzu Ltd.). X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 5702 spectrometer (Perkin-Elmer Ltd.). Raman spectra were recorded using an Alpha 300R Raman spectroscope (WITEC Ltd.). Nitrogen adsorption/desorption isotherms were conducted on an ASAP 2020 instrument (Micromeritics Ltd.).

All the electrochemical measurements (electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), differential pulse voltammetry (DPV) and amperometry) were conducted on a PGSTAT-302N electrochemical workstation (Metrohm Ltd.) using a conventional three-electrode system at room temperature. An Ag/AgCl electrode and a Pt wire were used as reference and counter electrodes, respectively. A modified glassy carbon electrode (GCE, 3 mm in diameter) was used as a working electrode. To prepare the working electrode, each catalyst was firstly mixed with a dimethylformamide (DMF) solution ($1 \text{ mg}\cdot\text{mL}^{-1}$) to form a homogeneous ink. The catalyst ink (10 μL) was then drop-cast onto the surface of GCE and followed by drying at room temperature.

3 Results and discussion

3.1. Characterizations of PG-E

The morphologies and microstructures of as-prepared samples were characterized by TEM. It is shown in Fig. 1a that the RGO presents a transparent and wavy morphology, suggesting the well exfoliated or thin layered graphene nanosheets. This can also be reflected from the HRTEM image (Fig. S1a, Supplementary Information† (SI†)), showing that the RGO nanosheets consist of 3-5 graphene layers. After P-doping, as shown in Fig. 1b, the PG exhibits more ripples and wrinkles than RGO, which is attributed to the distorted carbon structure of graphene induced by P-doping [29]. STEM images (Fig. 1c) clearly indicate the presence of C, O, and P elements in PG and P elements are homogeneously distributed throughout the PG, suggesting that the P atoms are successfully incorporated into the graphene frameworks. With further plasma treatment, the PG-E (Fig. 1d) displays a number of nanosized holes on the basin surface of graphene probably resulting from the plasma-etched structure defects, while such nanosized holes are almost absent on original PG under the same TEM magnification (Fig. S1b, SI†). In addition, the corresponding selected area electron diffraction (SAED) pattern (Fig. 1e) of PG-E reveals intense concentric diffraction rings while the SAED pattern of PG (Fig. S1c, SI†) displays obvious hexagonal spots, attesting that the PG-E has more structural defects [30]. The defective structure of PG-E can also be corroborated from the XRD (Fig. S2, SI†) and following Raman/XPS analysis. Moreover, the graphitic crystalline structures of PG-E (Fig. S1d, SI†) remain relatively unchanged as compared to RGO (Fig. S1a, SI†), indicating the plasma etching does not change the intrinsic graphene

structures, consistent with the other reports [18, 26].

Raman spectroscopy was used to gain information about the graphene structural defects. It is seen in Fig. 2a that the Raman spectra of RGO, PG and PG-E display a G-band at $\sim 1590\text{ cm}^{-1}$ and a D-band at $\sim 1350\text{ cm}^{-1}$, corresponding to the graphitic carbons and structural defects, respectively[31, 32]. The I_D/I_G intensity ratio can give a quantitative estimation of defect density in graphene, which increases in the order of RGO (0.98) < PG (1.09) < PG-E (1.38), suggesting that P-doping and plasma-etching can both lead to the increased defects in graphene. It is noteworthy that the ID/IG increment caused by P-doping is only about one third that by plasma-etching, suggesting that the plasma-etching is more powerful than P-doping to produce structural defects on graphene. This can be explained that the heteroatom doping is primarily realized through occupying vacant or edged sites by dopants[33], which can only cause the distortion in carbon lattice, whereas the plasma-etching is able to directly remove a small portion of C atoms (etching effect) resulting in a high level of defects as the form of etched nanoholes (Fig. 1d).

XPS analysis was performed to probe the chemical structures of the samples. It is shown in Fig. 2b that the survey scans of PG and PG-E exhibit the peaks of C 1s, O 1s, and P 2p/P 2s (Fig. 2b), while the P 2p/P 2s peaks are absent in RGO, suggesting once again the successful P-doping of graphene. Based on the XPS quantitative analysis (Table S1, SI[†]), the P concentrations are 2.4 at.% and 2.1 at.% for PG and PG-E, respectively. The slightly decreased P concentration in PG-E is due possibly to the somewhat loss of P dopants during the plasma-etching process. Fig. 2c shows the

high-resolution P 2p spectra of PG and PG-E. The P 2p peak can be deconvoluted into two peaks at binding energies of 131.3 eV and 133.6 eV, which are assigned to P–C and P–O bonds [22], respectively. The relative percentages of P–C and P–O in PG-E change little compared to those in PG (Table S1, SI†), indicating the plasma-etching has little effect on the P bonding configurations. Besides, the deconvoluted C 1s spectra (Fig. S3 & Table S1, SI†) show the increased sp^3/sp^2 ratio (0.386) in PG-E with respect to PG (0.281), further confirming that more defective sites are yielded in PG-E [18]. Moreover, the N₂ adsorption–desorption measurements (Fig. 2d) show the comparable BET surface areas of PG (288 m²·g⁻¹) and PG-E (296 m²·g⁻¹). The pore size distribution curves (Fig. 2d, inset) reveal a slight increase in mesopores populations in PG-E as compared to PG, presumably arising from the formation of plasma-etched nanoholes, as observed in Fig. 1d. A certain amount of mesopores are beneficial for the electrocatalytic activity as they can serve as the channels for the favorable diffusion of reactants and electrolytes [34].

3.2. Evaluation of PG-E for DA sensing

Dopamine, an important neurotransmitter, plays a crucial role in functioning the mammalian neurophysiological systems [35-37]. The abnormality of the DA levels can lead to a series of illnesses and symptoms, such as schizophrenia, Parkinson's disease, HIV infection, depression, drug addiction, etc[38]. Thus, the development of efficient electrochemical sensors for highly sensitive and selective detection of DA is of great importance in neurophysiological clinical diagnosis. In the construction of DA electrochemical sensors, the electrocatalytic oxidation of DA (EOD) is a critical

1 reaction in determining the DA sensing performances, and it is a key to develop a
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3 highly active catalyst to promote the EOD activity and improve the DA sensitivity [38,
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6 39]. Electrochemical characterizations were then carried out to evaluate the EOD
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9 activity of the electrodes modified with different catalysts to understand the combined
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12 effect of P-dopants and plasma-engineered defects.
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14 Fig. 3a shows the CVs of bare GCE, RGO/GCE, PG/GCE and PG-E/GCE
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16 electrodes toward EOD in PBS (0.1 M, pH 7.0) containing 0.5 mM DA. As seen, bare
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18 GCE exhibits a negligible EOD activity as evidenced by the weak peak current (I_p)
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20 and broad peak-to-peak separation (ΔE), whereas the RGO/GCE shows a slightly
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22 improved EOD activity due to the strong π - π interactions between the phenyl moiety
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24 of DA molecule and π -conjugation of graphene[40, 41]. In addition, the PG/GCE
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26 presents a noticeably higher I_p and narrower ΔE compared to RGO/GCE, suggesting
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28 the much improved EOD activity as a result of P-doping, correlating well with the
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30 previous reports associated with the N-doping[42] and S-doping[43] for improving
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32 the EOD activity of graphene. Notably, after plasma treatment, the PG-E/GCE
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34 exhibits the best EOD activity with the highest I_p and narrowest ΔE . This clearly
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36 reveals that introduction of P-dopants, coupled with plasma-induced defects, can
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38 significantly improve the EOD activity of graphene. It is worth noting that the
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40 electrodes modified with RGO-E (etched RGO but without P doping) exhibits an
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42 inferior catalytic activity to PG-E/GCE (Fig. S4, SI†), signifying that the synergistic
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44 effect of P dopants and topological defects leads to the considerably enhanced EOD
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46 activity, consistent well with the previous results obtained in other electrochemical
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1 reactions for applications in water splitting [44] and supercapacitors [26].

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3 The amount of active sites is highly associated with the catalytic activity[8].
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6 Given that only accessible sites are active for the electrocatalysis reactions[6], the
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9 electrochemically surface area (ECSA) capable of reflecting the actual amount of
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12 accessible active sites can be determined from the electrochemical behavior of
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14 $[\text{Fe}(\text{CN})_6]^{3-}/^{4-}$ at the modified electrode according to the Randles–Sevcik
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16 equation[45]. Fig. S5 (SI†) shows the representative plot for the determination of
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19 ECSA. Based on the slopes of the linear fitted plots (Fig. 3b), the calculated ECSA
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22 values increase in the order of RGO/GCE (0.11 cm^2) < PG/GCE (0.27 cm^2) <
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25 PG-E/GCE (0.48 cm^2), indicating that the combination of P dopants and
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28 plasma-etched defects offers the large amount of active centers for DA adsorption and
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31 electrocatalytic oxidation, which dramatically boost the EOD activity.

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34 Aside from the increased accessible active sites, the superior EOD activity of
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37 PG-E is believed to originate from the improved electron transfer capability caused by
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40 the combined effect of P-doping with enriched defects. EIS measurement was
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43 conducted to examine the electron-transfer properties. Fig. 3(c) shows the EIS spectra
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45 of RGO/GCE, PG/GCE and PG-E/GCE electrodes. The impedance data can be fitted
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47 well by an equivalent circuit model (Fig. 3(c), inset), and the charge transfer
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49 resistance (R_{ct}) can be estimated from the semicircle diameter in the high-frequency
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51 region. Noticeably, the PG-E/GCE presents the much lower R_{ct} ($58.6 \text{ }\Omega$) than
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53 PG/GCE ($82.7 \text{ }\Omega$) and RGO/GCE ($136.2 \text{ }\Omega$), demonstrating that P-doping and
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56 structural defects can both effectively lower the charge transfer resistance of the
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1 electrochemical reactions. This can be explained that P dopants can increase the
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3 charge mobility of carbon because of its electron-donor properties[46], while the
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5 defects are able to enhance the density of state (DOS) resulting in a high carrier
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7 concentration[47]. Both factors facilitate the fast electron transport across the
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9 catalyst-GCE interface for accelerating the electrochemical reaction kinetics.
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11 Therefore, it can be concluded that introducing both topological defects and P-dopants
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13 in graphene can synergistically lead to the significantly elevated EDO activity of
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15 graphene by increasing the accessible active sites and promoting the electron transport
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17 capability. Moreover, the CVs of PG-E/GCE with the presence of DA at different
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19 scan rates reveal that the peak current is linearly proportional to the scan rate (Fig. 3d),
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21 indicating that the EDO on the PG-E/GCE electrode is an adsorption-controlled
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23 electrochemical process. The perfect linear response to scan rate is another indication
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25 of fast electron transfer efficiency for the EDO reaction process[38, 48].
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29 The outstanding EGO activity makes the PG-E modified electrode a promising
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31 sensor for DA detection. DPV technique was employed to quantitatively assess the
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33 DA sensing performances of PG-E/GCE. Fig. 4a shows the DPV curves of
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35 PG-E/GCE in PBS (0.1 M, pH 7.0) containing different concentrations of DA
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37 (0.1-160 μ M). A group of well-defined oxidation peaks of DA are observed at 0.18 V.
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39 The calibration plot (Fig. 4b) shows that the DPV peak current is linear with the DA
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41 concentration with a wide linear range of 0.1-120 μ M. From the slope of the
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43 calibration plot, the limit of detection (LOD) is determined to be 0.006 μ M at a
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45 signal-to-noise ratio of 3. Such sensing performances are better than those of most
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1 carbon-based metal-free catalysts and even superior or comparable to those of most
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3 recently reported metal-based catalysts (Table S2, SI[†]), suggesting that the present
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5 PG-E is a promising metal-free electrocatalyst for DA sensing. It is demonstrated that
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7 the significantly enhanced EGO activity of PG-E resulting from the synergetic effect
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9 of P-dopants and plasma-engineered defects contributes to the excellent DA sensing
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11 performances of PG-E/GCE.
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17 The foreign species of uric acid (UA) and ascorbic acid (AA) are normally
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19 co-existed with DA in the human serum, and it is difficult to identify DA in the
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21 mixture because their oxidation potentials greatly overlap[40]. The interference study
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23 was then conducted by DPV testing in PBS (0.1 M, pH 7.0) containing a ternary
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25 mixture of 0.2 mM AA, 0.04 mM DA and 0.05 mM UA. As shown in Fig. 4c, one can
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27 observe three well-resolved peaks with marked peak separations of 185 mV (AA-DA)
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29 and 128 mV (DA-UA), indicating the PG-E/GCE is able to simultaneously distinguish
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31 DA, UA and AA. In addition, as seen in Fig. 4d, the amperometric response of
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33 PG-E/GCE to DA remains almost unchanged after the sequential addition of glucose
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35 (Glu), UA, AA, lactose (Lac) and fructose (Fru). The long-term stability of
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37 PG-E/GCE was investigated by measuring the CV of DA after 10 days storage. It is
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39 seen in Fig. 4e that the CV curve shows a negligible difference compared with the
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41 initial one. Furthermore, as shown in Fig. 4f, the PG-E/GCE retains 95.6 % its initial
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43 amperometric current after running time of 3000s. These results prove that the
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45 PG-E/GCE possesses the extraordinary selectivity and stability for DA detection.
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58 To verify the applicability of the present sensor, the PG-E/GCE was then
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employed to detect the concentrations of DA in human serum samples using a standard adding method[39]. All the samples were diluted with PBS (0.1 M, pH 7.0) and each determination is the average of three measurements. The detecting results are listed in Table S3. It is found that the recoveries for the determination of DA are within the acceptable range of 98.5-103.2%, demonstrating that the present PG-E/GCE sensor can be practically utilized for the accurate detection of DA in the real samples.

4 Conclusions

In summary, the PG-E with both P-dopants and plasma-engineered defects was successfully synthesized by the combined hydrothermal/annealing and followed plasma treatment, as confirmed by the microscopic and spectroscopic techniques. Electrochemical measurements indicated that the PG-E modified electrode exhibited a dramatically improved EOD activity, which could be ascribed to the synergistic effect of P-dopants and plasma-etched defects that led to the increased active sites and enhanced electron transport. The PG-E based DA sensor showed excellent sensing performances with a low detection limit of 0.006 μM and a wide linear range of 0.1-120 μM , which are superior or comparable to those of most recently reported metal-free and metal-based catalysts. The PG-E sensor also displayed high selectivity, good stability, and accurate analysis in real samples, making PG-E a promising metal-free electrocatalyst for DA sensing. We believe that there is still a room to further enhance the EOD activity and sensing performances of PG-E by optimizing the processing of P-doping and plasma treatment, which are currently being

investigated. The present work may provide a new strategy to design and prepare highly active graphene-based metal-free for electrochemical sensing applications.

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Scheme 1. Illustration of the synthesis of PG-E.

Fig. 1. TEM images of (a) RGO and (b) PG. (c) STEM image of PG and corresponding elemental mapping images of C, O, and P. (d) Magnified TEM image of PG-E and corresponding SAED pattern (e).

Fig. 2. (a) Raman spectra of RGO, PG and PG-E. (b) XPS survey scans of RGO, PG and PG-E. (c) High-resolution P 2p spectra of PG and PG-E. (D) Nitrogen adsorption/desorption isotherm curves of PG and PG-E and their corresponding pore size distributions (inset).

Fig. 3. (a) CVs of bare GCE, RGO/GCE, PG/GCE and PG-E/GCE in PBS (0.1 M, pH 7.0) containing 0.5 mM DA at the scan rate of 50 mV/s. (b) Plots of peak potentials (I_p) vs. square root of the scan rate ($v^{1/2}$) (Fig. S5, SI†) to extract the ECSA values of RGO/GCE, PG/GCE and PG-E/GCE. (c) EIS spectra of RGO/GCE, PG/GCE and PG-E/GCE in 0.1 M KCl solution containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The inset is the equivalent circuit where C_{dl} is double layer capacitances, R_s is the solution resistance, R_{ct} is the charge transfer resistance and Z_w is the Warburg impedance. (d) CVs of PG-E/GCE in PBS (0.1 M, pH 7.0) containing 0.5 mM at different scan rates of 20-160 mV/s (inset: plot of peak current (I_p) versus scan rate).

Fig. 4. (a) DPV responses of PG-E/GCE in PBS (0.1 M, pH 7.0) containing different concentrations of DA (0.1-160 μ M). (b) Calibration curve of DPV peak current (I_p) versus DA concentration (C). (c) DPV response of PG-E/GCE in PBS (0.1 M, pH 7.0) containing 0.2 mM AA, 0.04 mM DA and 0.05 mM UA. (d) Amperometric responses of PG-E/GCE with successive addition of 0.01 mM DA and each 0.1 mM of glucose (Glu), UA, AA, lactose (Lac) and fructose (Fru) in PBS (0.1 M, pH 7.0) at the applied potential of 0.18 V. (e) CV responses of PG-E/GCE initially and after 10 days storage. (f) Amperometric response of PG-E/GCE with addition of 0.02 mM DA after 3000s running time.