

A Three Dimensional Graphene Assembly with Hierarchical Pores for Enhanced Electrochemical Detection of Dopamine

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A three dimensional (3D) graphene assembly with hierarchical pores (3DHPG) was prepared by hydrothermal assembly and subsequent carbon-thermal reaction induced etching. The structure and component of the product were characterized by SEM, TEM, Raman, N₂ adsorption-desorption, and XPS. The introduction of mesopores in basal plane of graphene in 3DHPG brings it more edge structure, more oxygen-containing defects, and larger surface area than typical 3D porous graphene foam (3DPG). Electrochemical study revealed the 3DHPG/GCE shows larger current response and improved mass transfer efficiency than 3DPG/GCE. Using dopamine as a model molecule, the 3DHPG/GCE shows much higher current response than that on 3DPG/GCE. The dopamine sensor based on 3DHPG/GCE display a linear range of 0.01- 300 μ M and a detection limit of 3 nM. The linear range is wider than that on 3DPG (0.05-200 μ M), and the detection limit is lower than that on 3DPG (20 nM). The improved sensing performance can be attributed to the hierarchically porous structure with large surface area, efficient mass transfer and enhanced catalysis due to the introduction of mesopores. The 3D hierarchically porous graphene assembly with unique structure and catalysis should be a promising material in electrochemical devices.

Keywords: graphene, hierarchical pore, porous graphene, electrochemical sensor, dopamine

1. INTRODUCTION

Graphene nanosheet is one of the most representative 2D nanomaterial in material science [1-3]. Its unique properties also makes it a promising and popular material in constructing various advanced electrochemical platforms [4,5]. Nevertheless, the aggregation or accumulation tendency, the limited intrinsic catalysis [6] and slow mass transfer across 2D graphene sheet [7] still restrain the application performance of graphene in electrochemical sensing. Therefore, new graphene material is still needed for extending its applications.

To resolve these problems, researchers have explored many approaches and developed varied graphene derived materials. Specifically, 3D porous graphene foam and 2D holey graphene hold great promise in various applications. Graphene foam is a graphene assembly with 3D macroporous skeleton. Its 3D porous structure greatly reduces the aggregation of 2D graphene sheet, and facilitates the mass transfer, which has been widely used in fabricating electrochemical sensors [9-13]. Nevertheless, the catalysis of the graphene material is not improved compared with 2D sheet. Besides, the mass transfer across the macro-pore still encounter large resistance like that for 2D sheet. On the other hand, 2D holey graphene is graphene analogue with nanopores generated on basal plane of original graphene [14]. These nanopores bring two advantages. First, these pores provide a shortcut for molecules to communicate across the member, greatly improving the mass transfer efficiency [15]. Second, plenty of pores introduce more edge structures, the origin of the intrinsic catalysis of graphene [16,17], and thus improves its catalysis [18]. However, the stacking and aggregation still happen on 2D holey sheet.

The advantages and disadvantages of 3D porous graphene and 2D holey graphene sheet inspire us to integrate them to produce a 3D hierarchical porous graphene (3DHPG) to amplify their merits and overcome their corresponding shortages. Indeed, the unique properties of 3DHPG-like material have been tested in electrochemical capacitors [19]. However, few reports have been reported on 3DHPG in electrochemical sensing. Besides, control the pore size is still challenging.

In this study, a 3D hierarchical porous graphene assembly (3DHPG) was prepared by hydrothermal assembly and subsequent carbon-thermal etching. The morphology and structure of the product were characterized in detail. The unique hierarchical porous structure endow it with larger surface area, more nanopores with active edge defect sites and enhanced mass transport than 3DPG. These characteristics make 3DHPG a good modified material to detect electroactive molecules using dopamine as a model, which shows a wider linear range and a lower detection limit than those of 3DPG. The 3DHPG modified electrode was further used to detect dopamine in human serum, which also shows good recovery. Such hierarchical porous graphene with large surface area, efficient mass transfer, good catalysis have great potential in electrochemical devices.

2. EXPERIMENTAL

2.1 Materials and reagents

Graphite powder, concentrated sulfur acid (H_2SO_4), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), sodium dihydrogen phosphate (NaH_2PO_4), disodiumhydrogen phosphate (Na_2HPO_4), dopamine and cobalt oxide nanoparticles (Co_3O_4 NPs) were purchased from Aladdin chemical reagent company (Shanghai, China). All reagents were used without further purification. The water used in this study was purified by Millipore-Q System ($\rho \geq 18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2 Characterization

The morphology of the products were characterized by scanning electron microscopy (S-3400N, Hitachi, Japan) and transmission electron microscopy (JEM-2010, JEOL, Japan). The component of

the products was revealed by X-ray energy diffraction spectroscopy (EDS) attached to SEM, and X-ray photoelectron energy spectroscopy (ESCALAB-MKII, Thermo Scientific, USA) using Al K α as excitation source and C1s (284.6 eV) as reference. The structure of the product was analyzed by Raman spectroscopy (LabRAM HR, Horiba, Japan). The surface area and pore size distribution of the product were analyzed by N₂-adsorption-desorption method using a surface area and porosity analyzer (ASAP 2020, Micromeritics, USA). All glassware were cleaned with aqua regia, washed by ultrapure water and dried before use.

All electrochemical measurements were performed at ambient conditions on an electrochemical workstation (CHI 760D, Shanghai, China) using traditional three-electrode system. The bare glassy carbon electrode or GCE modified with functional material were used as working electrode. Saturated calomel electrode was used reference electrode, and platinum wire as counter electrode.

2.3 Preparation of 3DHPG

First, graphene oxide was prepared by previous modified Hummers' method [20]. Then, 30 mg GO was dispersed in 10 ml water by sonication to form a suspension (3 mg/ml). After that, 12 mg Co₃O₄ was added and the mixture was stirred for 2h, before they are transferred into 20 ml autoclave. After reacted for 12 h at 180°C, the product was separated and washed and then lyophilized for 12 h to obtained the 3D graphene-Co₃O₄ aerogel 3D Co₃O₄-GA [21]. To prepare the 3DHPG, the 3D Co₃O₄-GA was placed into a tube furnace to undergo a carbon-thermal reaction at 900°C under N₂ atmosphere for 2h to drill nanopores on the wall of macropores [22]. After that, the product was cooled to room temperature and immersion into diluted HCl overnight to dissolve the Co₃O₄ particles. The product was washed 3 times with water and lyophilized to get the final product 3DHPG.

For comparison, 3D macroporous graphene aerogel (3DPG) was also prepared in a similar way to that of 3DHPG, except that no Co₃O₄ was added and no HCl treatment was applied.

2.4 Fabrication of modified electrode

3DHPG was dispersed into water to form a suspension (1mg/ml). Then, 90 μ l of the suspension was mixed with 10 μ l Nafion solution (5%). After that, 5 μ l of the mixture was coated onto cleaned and polished GCE and dried in the air to obtain the modified electrode 3DHPG/GCE. Similarly, 3DPG was also used to modify GCE, and the modified electrode was abbreviated as 3DPG/GCE.

3. RESULTS AND DISCUSSION

3.1 Characterization of 3DPG and 3DHPG

Fig. 1 shows the SEM images of 3DHPG and 3DPG. It is clear the 3DHPG displays a 3D porous structure (Fig. 1a), which is similar to that of 3DPG (Fig. 1c). Further magnified image reveals graphene sheets connect with each other to form macropore scaffold, while many nanopores generated on their

macropore wall (Fig. 1b). In contrast, 3DPG shows typical interconnected macropore network and the pore size is larger than that of 3DHPG. However, few nanopores are observed on the their macropore wall (Fig. 1d). Due to their small pore size, most of them cannot be clearly distinguished by SEM, so TEM analysis was conducted in the following.

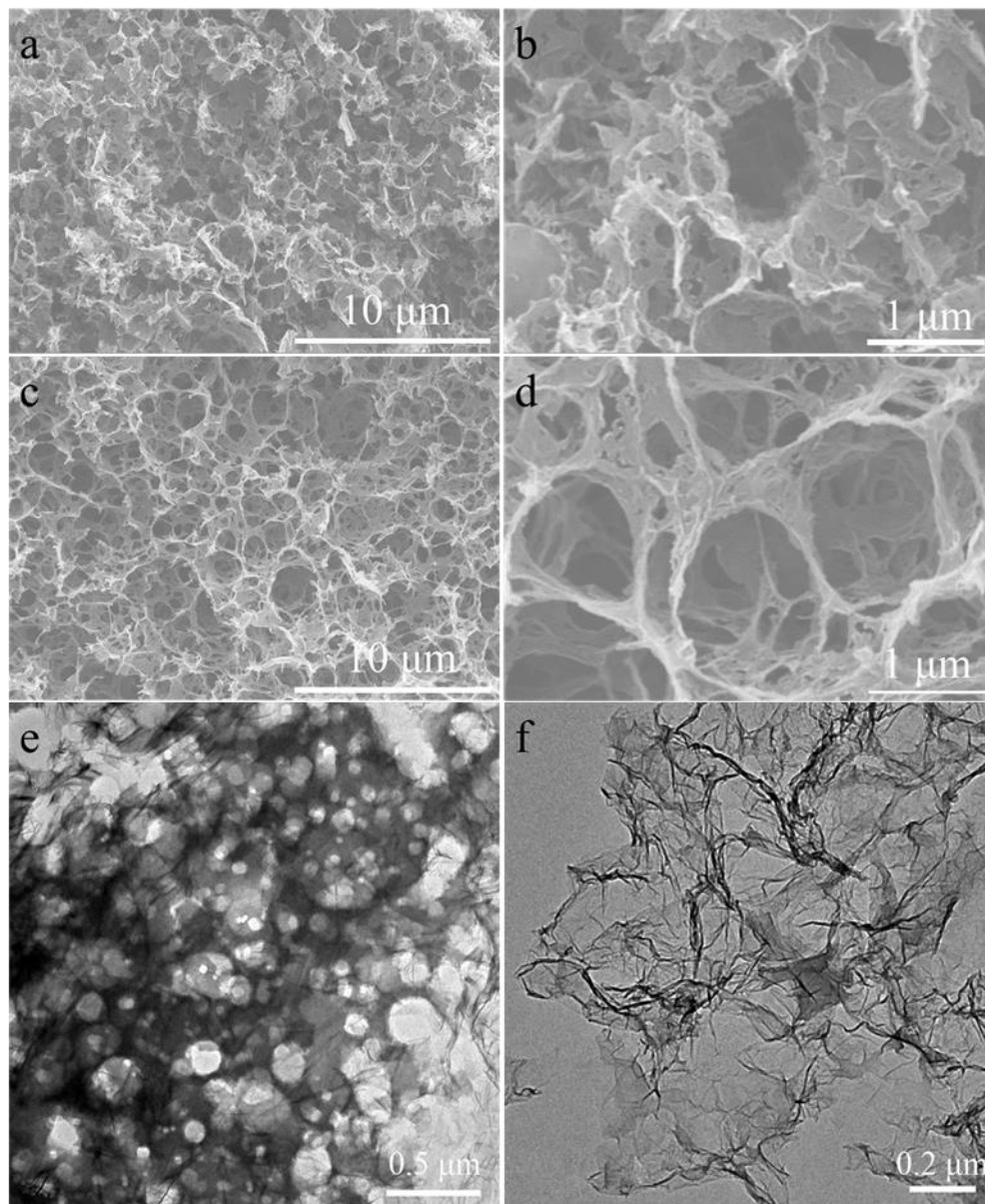


Figure 1. SEM images of 3DHPG (a,b) and 3DPG (c,d), and TEM images of (e) 3DHPG, and (f) 3DPG.

Fig. 1e shows the TEM image of 3DHPG. It is clear many nanopores are generated on the basal plane of graphene sheet in 3DHPG. These pores have a diameter from about 20 nm to 200 nm, and most of them have very regular, rounded outline, indicating they are generated by template NPs etching. TEM image of 3DPG shows the building block of 3DPG is ultrathin wrinkled 2D graphene sheet, on which many nanowrinkles but no nanopores in basal plane were observed (Fig. 1f). According to previous reports [22,23], these nanopores on 3DHPG should be produced through the carbon-thermal reaction,

during which graphene sheet directly contacted with Co_3O_4 NPs was oxidized to CO_2 and thus left nanopores on the sheet. The TEM image of 3DHPG does not show any nanoparticles, indicating that Co_3O_4 NPs was dissolved during the subsequent HCl treatment. All these results confirmed a 3D graphene assembly with hierarchically porous structure (macropore scaffold with nanopores on the macropore wall) was successfully prepared.

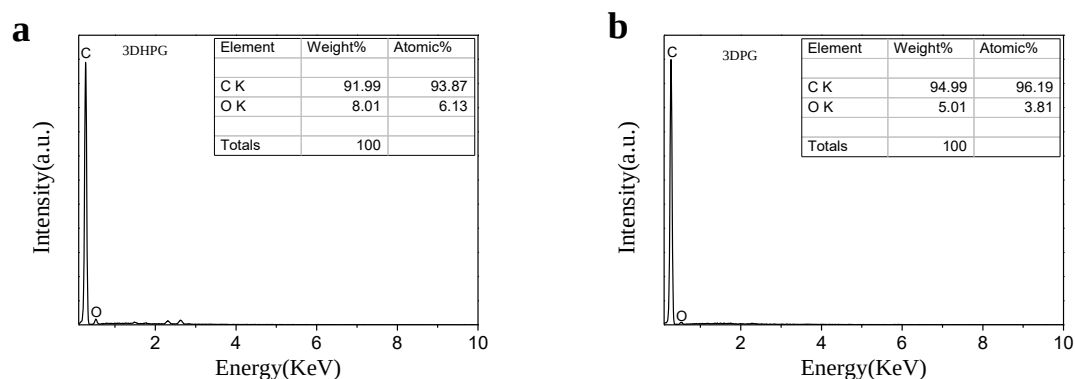


Figure 2. EDX results of (a) 3DHPG and (b) 3DPG.

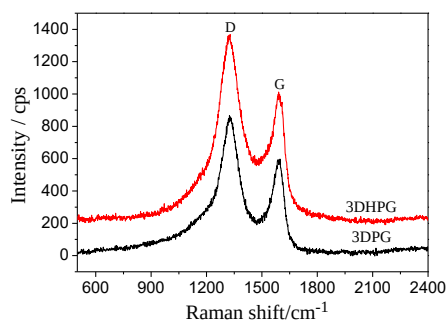


Figure 3. Raman spectrum of 3DHPG and 3DPG.

The component of the 3DHGP and 3DPG were characterized by EDS. Fig. 2 shows both of these 3D graphene materials are composed of C and O, without Co element, further confirming the Co_3O_4 was washed away by acid leaching. Comparing the element content, it is found 3DHPG has higher O content compared with that of 3DPG, indicating more oxygen-containing defect structure was introduced during drilling pores by carbon-thermal reaction [24,25].

Fig. 3 presents the Raman spectroscopy of the 3DPG and 3DHPG. The spectrum were dominated by the D band at 1350 cm^{-1} and G band at 1595 cm^{-1} . The calculation indicates the I_D/I_G value of 3DHPG (1.58) is higher than that of 3DPG ($I_D/I_G=1.51$), further confirming that more defect structure was introduced after carbon-thermal reaction [26], which is consistent with the results from EDS.

To learn more about the pore structure of the 3DHPG and 3DPG, N_2 -adsorption and desorption experiment was conducted to measure the pore size and surface area of these materials. Both 3DHPG and 3DPG display a combination of typical I and type IV isotherm [27]. Compared with 3DPG, 3DHPG display a much more obvious hysteresis loop (Fig. 3a), indicating more mesopores are generated on

3DHPG. Micropores on 3DPG or 3DHPG are generated due to the heat treatment, during which some defective sites on basal plane were degraded. For 3DPG, the pore size mainly lies in two values: 55 nm and 85 nm, implying that 3DPG is a macroporous material (Fig. 3b). In contrast, the pore size of 3DHPG mainly locates at 25 nm and 50 nm, indicating lots of mesoporous are generated (Fig. 3b). The generation of pores (50-100 nm) on 3DPG is mainly caused by the hydrothermal assembly. For 3DHPG, its typical pore size is consistent with the particle diameter of Co_3O_4 (25 nm), implying the etching of carbon is located around the Co_3O_4 NPs. That means both hydrothermal assembly and Co_3O_4 etching contribute to the generation of pores on 3DHPG. The more mesoporous structure of 3DHPG leads to higher specific surface area, which is about $930 \text{ m}^2/\text{g}$ compared with that of $680 \text{ m}^2/\text{g}$ for 3DPG determined by MB adsorption method [28].

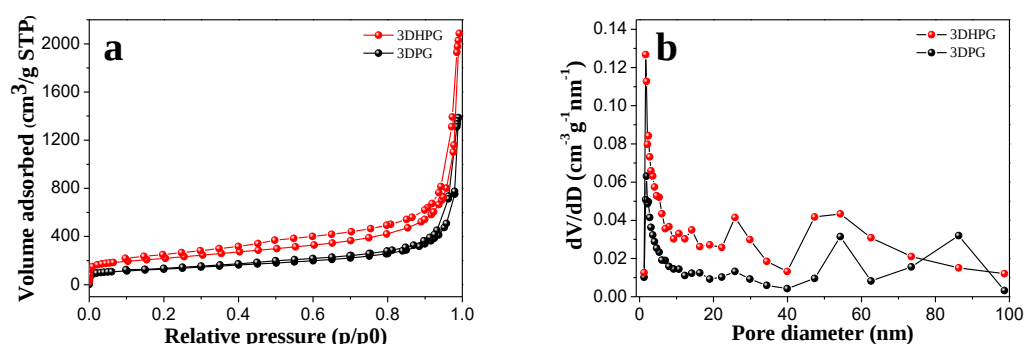


Figure 4. (a) N_2 adsorption-desorption isotherm curve and (b) pore size distribution of 3DHPG and 3DPG.

The component of these materials were further characterized by XPS. The overview of the XPS spectrum indicate both of 3DHP and 3DHPG are composed of C and O, while the peak intensity for O is stronger for 3DHPG than that for 3DPG, indicating more oxygen group was introduced for 3DHPG. These results are consistent with those from EDS. High resolution XPS spectrum indicates the C1s can be fitted into four peaks with binding energy at 284.5 eV (C-C/C=C), 285.8 eV(C-O), 286.8 eV(C=O), and 289.1 eV(O-C=O)[29]. The calculation indicated 3DHPG has higher content of C-O and O-C=O group, while 3DPG has higher content of C=O group.

Based on these characterization, it is clear that 3DHPG with hierarchical macro-meso pores, large surface area, abundant edge active structure and more oxygen group has been successfully prepared.

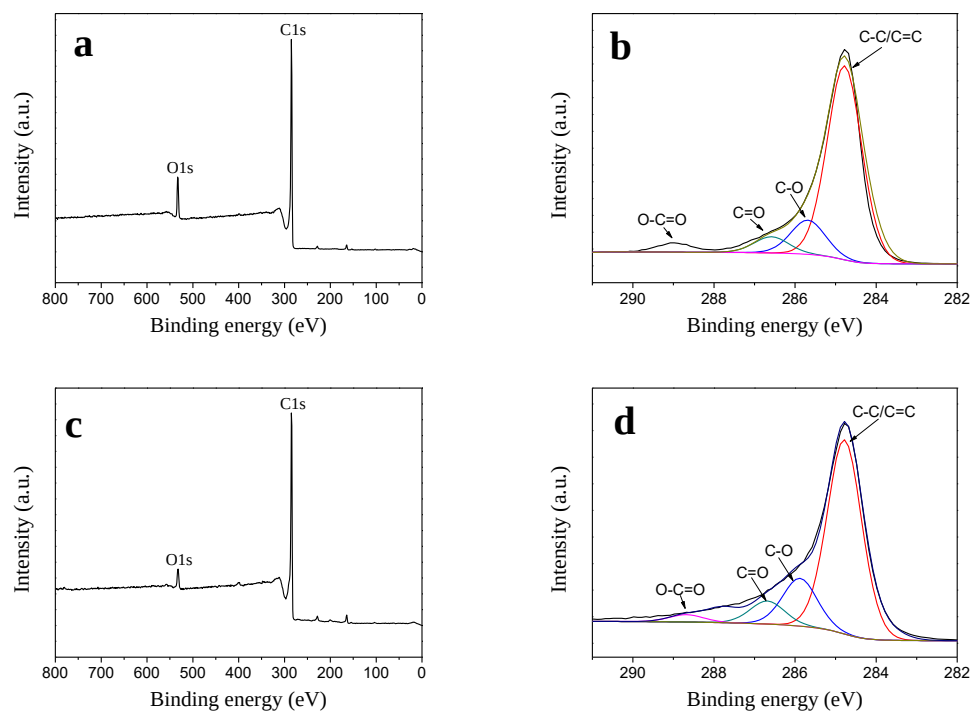


Figure 5. XPS spectrum of 3DHPG (a) and 3DPG (c), and corresponding high definition spectrum of C1s for 3DHPG (b) and 3DPG (d).

3.2 Electrochemical characterization of 3DHPG

The unique structures of 3DHPG implies that it may have potential application in electrochemical devices. Here, 3DHPG was used to modify GCE, and its electrochemical behavior was first studied using CV methods.

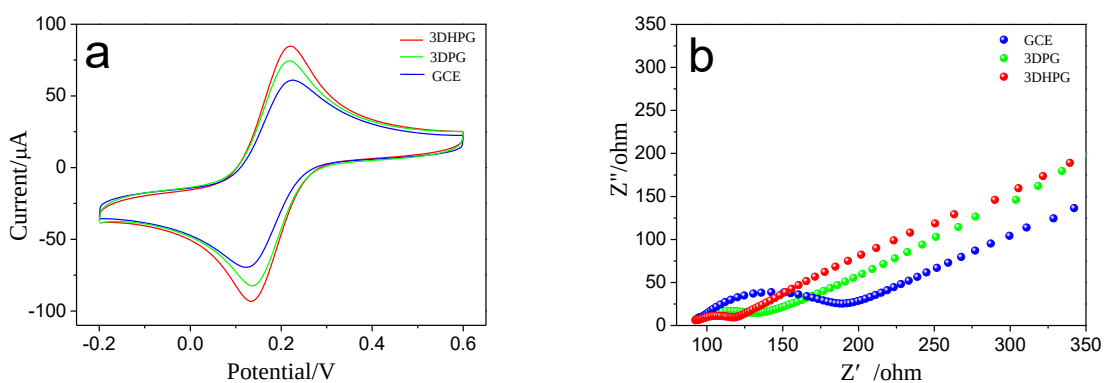


Figure 6. (a) CVs of different modified electrodes in 5 mM $K_3Fe(CN)_6$. (b) EIS curve of bare GCE, 3DPG and 3DHPG modified GCE.

Fig. 6a show the CVs response of bare GCE, GCE modified with 3DPG (3DPG/GCE) or 3DHPG (3DHPG/GCE). The current response on 3DPG/GCE increases while the redox peak separation for $K_3Fe(CN)_6$ decreases compared with those on bare GCE, indicating a larger surface area and better conductivity were obtained on 3DPG/GCE. The current response further increases after it was coated with 3DHPG, implying 3DHPG has larger surface area than that of 3DPG.

The electron transfer resistance on the modified electrode was also investigated by electrochemical impedance spectroscopy (EIS). Fig. 6b show all the EIS pattern of these electrodes display a semicircle outline. The diameter of the semicircle decrease in the order: $GCE > 3DPG > 3DHPG$, indicating 3DHPG has the best electron conductivity. Previous reports indicate that the introduction of edge structure can enhance catalysis, while these edge structure often containing many oxygen-containing group, which may degrade the conductivity of the material [25]. Thus the number of pores on graphene sheet should be in a reasonable range. The EIS results here indicate the introduction of nanopores on 3DHPG in our case did not show obvious side effect on its conductivity. Moreover, it is observed the initial part of the linear section of the EIS pattern increases in the order of $GCE < 3DPG/GCE < 3DHPG/GCE$, indicating the 3DHPG has the best mass transfer efficiency. The improved mass transport efficiency is mainly due to the abundant nanopores on the graphene sheet generated by Co_3O_4 etching, which greatly shorten the diffusion distance from one side to the other of graphene sheet (wall of graphene macropore) [23].

3.2 Electrochemical response to dopamine

Previous reports demonstrate creating nanopores on the basal plane of graphene can introduce more edge structure, and these edge structure with abundant defective sites may be one of the main source for graphene's intrinsic catalysis [30]. The 3DHPG with lots of mesopores on graphene sheet is expected to have higher catalysis than that of 3DPG. To test this hypothesis, the electrochemical sensing performance of 3DHPG was evaluated using dopamine as a probe molecule. Dopamine is an essential neurotransmitter in our nervous system. The abnormal level of dopamine are related to schizophrenia, Parkinson's disease, HIV infection, and other afflictions [31-37]. Therefore accurate detection of dopamine is of great importance.

The 3DPG and the 3DHPG were used to modify GCE, respectively and their response for dopamine was tested. Fig. 7 show the CVs of dopamine on the 3DPG/GCE and 3DHPG/GCE. It is clear to see, both modified electrodes show good response for dopamine (Fig. 7a,b). A pair of well-defined redox peaks of dopamine with obvious current response were observed on these electrodes. As more dopamine was injected, the redox current steadily increases. The current response on 3DHPG/GCE (Fig. 7a) is much stronger than that on 3DPG/GCE (Fig. 7b), while both are stronger than that on bare GCE (Fig. 7c). The enhanced sensitivity is more obvious by plotting the current response versus DA concentration. Fig. 7d shows the current response (background current response has been subtracted) for 1, 2, 4 mM dopamine on 3DHPG/GCE is at least 2-fold of that on 3DPG/GCE. As the surface area of 3DHPG is only 50% higher than that of 3DPG, so the enhanced current response should be due to the

combination of enlarged surface area and the improved catalysis of 3DHPG induced by the introduction of mesopores.

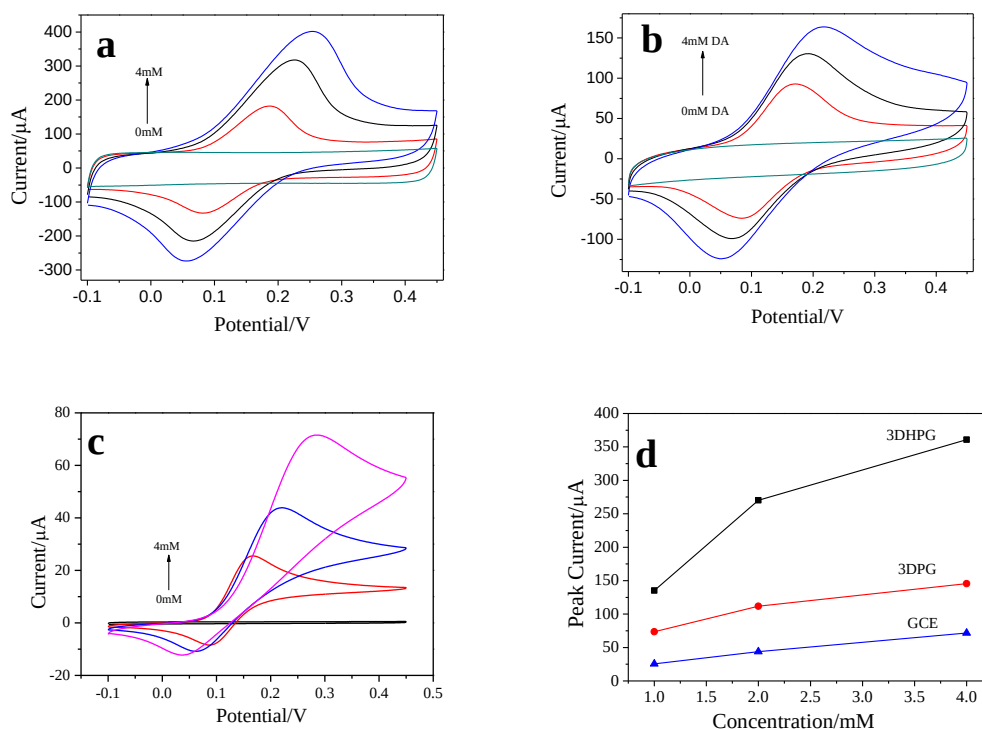


Figure 7. CVs of 0-4 mM dopamine on (a) 3DHPG/GCE, (b) 3DPG/GCE, (c) GCE, and (d) their corresponding current-concentration plots. The background current response has been subtracted.

Compared with CVs, the DPV method can provide high sensitivity for molecule detection. Here, the DPV responses of dopamine at different concentration on the modified electrodes were investigated (Fig. 8). As can be seen, the injection of dopamine cause an obvious oxidation current response. As more dopamine was injected, the current steadily increases.

Again, the current response for the same concentration of dopamine is higher on 3DHPG/GCE (Fig. 8a) than that on 3DPG/GCE (Fig. 8c). The corresponding calibration plots indicate the oxidation current displays a good linear dependence on the concentration of dopamine in the range of 0.01- 300 μ M for 3DHPG/GCE ($R^2=0.9982$) (Fig. 8b), and 0.05-200 μ M for 3DPG ($R^2=0.9812$) (Fig. 8d). The detection limit for dopamine on 3DHPG/GCE is calculated as 3 nM, and that obtained on 3DPG is 20 nM. The results indicate 3DHPG/GCE display a wider linear range and a lower detection limit compared with 3DPG/GCE, further confirming the advantages of the hierarchical pores in enhanced catalysis and improved electrochemical sensing [18]. Compared with other functional material modified electrodes (Tab. 1) [31-37], our sensor based on the 3DHPG modified electrode still shows significant advantages in the aspects of detection limit and linear range. These results imply the 3DHPG with hierarchical porous structure may have unique potential in electrochemical sensing devices.

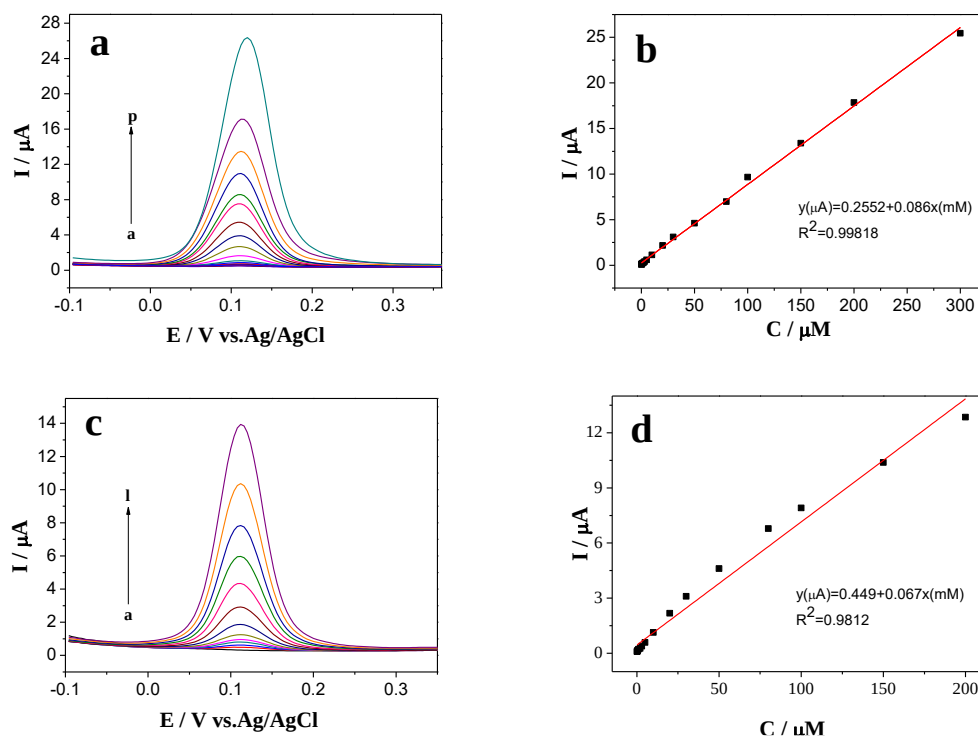


Figure 8. DPV responses on (a) 3DHPG/GCE or (c) 3DPG/GCE for successive injection of DA in 0.1 M PBS (pH=7.0), and corresponding current-concentration calibration plot for (b) 3DHPG/GCE or (d) 3DPG/GCE.

Table 1. Comparison of dopamine sensors

Electrodes	Technique	Linear range (μ M)	Detection limit (μ M)	Ref.
Nafion/CCINPs/CS/GCE	DPV	2-60	0.83	31
Cu ₂ O/Graphene/GCE	CV	0.1-10	0.01	32
EDTA-RG/Nafion/GCE	DPV	0.2-25	0.01	33
Graphene/GCE	DPV	4-100	2.64	34
AuNPs/ERGO/GCE	DPV	0.1-10	0.04	35
Pt Graphene/GCE	DPV	0.03 -8.13	0.01	36
3D Graphene/GCE	--	Up to 25	0.025	37
3DHPG/GCE	DPV	0.01-300	0.003	This work

3.3 Selectivity, reproducibility and stability

Besides sensitivity, the selectivity of an electrochemical sensor is also important to evaluate its performance. In human serum, dopamine often coexists with ascorbic acid (AA) and uric acid (UA). All these molecules are electrochemical active molecules, and their oxidation potential are too close that bare GCE cannot distinguish them. To selective detect dopamine in the presence of AA and UA, functional nanomaterials are often used to modify GCE. Graphene modified GCE has been used to

achieve selective detection of DA. Here, the DPV response of 3DHPG/GCE and 3DPG/GCE for dopamine in the presence of AA and UA were investigated. Fig. 9 shows the injection of DA produces a strong oxidation peak at about 0.1 V with large current response. After AA was injected, a new oxidation peak at about -0.05 V appears, indicating the electrochemical oxidation of AA on both modified electrodes. Then, UA was added, and a small oxidation current at about 0.22 V was observed. After the background current correction, it is found the current response for DA almost unchanged on both 3DHPG/GCE (Fig. 9a) and 3DPG/GCE (Fig. 9b), indicating both modified electrodes have good selectivity for dopamine sensing. Besides, the current response for DA or AA on 3DHPG is about 2-fold of that on 3DPG/GCE, while the value is 1.6- or 1.2-fold for AA or UA. This indicates that the 3DHPG is more sensitive to DA or AA than to UA. The enhanced response to DA may be ascribed to the enhanced interaction between graphene and dopamine through π - π interaction and electrostatic interaction ($pI(\text{dopamine})=9.7$). This selective enhancement effect further proves the advantage of 3DHPG in electrochemical sensing.

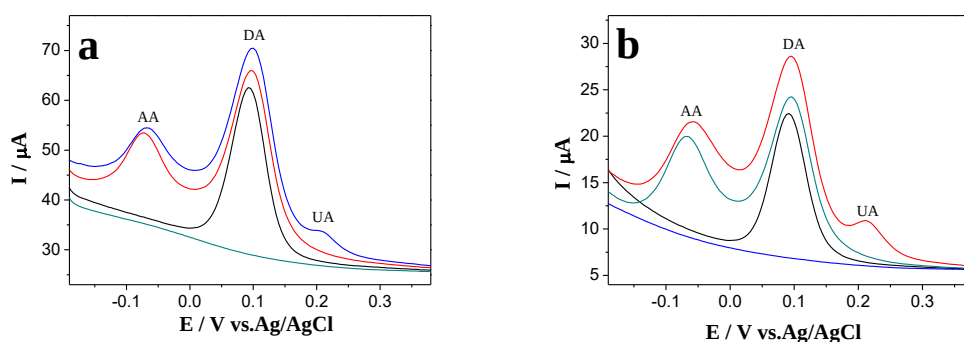


Figure 9. The DPV responses of (a) 3DHPG/GCE or (c) 3DPG GCE for 0.2 mM DA, 2 mM AA and 2 mM UA.

Stability and reproducibility are also important parameters for electrochemical sensors. After the modified electrode was stored in ambient conditions for one month, the current response for the same concentration of DA is 95% of original value, indicating a good stability. For five independent prepared electrodes, the RSD value of the current response on these modified electrodes for DA is calculated as 4.5%, indicating a good reproducibility.

3.4 Real Sample analysis

To test its potential practical application, the developed 3DHPG/GCE was used to detect DA in human serum using standard addition method. Certain amount of DA was injected into the human serum and then 1 ml of the sample was diluted with 9 ml PBS. After that, the current response for DA was recorded using DPV at 0.1 V, and then the concentration of DA was calculated. Table 2 show the results. It is revealed the sensor display a recovery range of 98-104.3% with low RSD. That indicate the sensor may have great potential in practical analysis.

Table 2. Determination of DA in serum (n=3).

Sample	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
1	10.0	9.8	3.2	98.0
2	20.0	20.4	2.7	102.0
3	30.0	31.3	4.1	104.3

4. CONCLUSION

A 3D graphene assembly with hierarchical pores was prepared by combining hydrothermal assembly and carbon-thermal etching. The former generates macroporous scaffold, and the later drilling nanopores on its pore wall, forming a hierarchical porous structure 3DHPG. The 3DHPG shows increased surface area, more edge structure and increased mass transfer than those of 3DPG. The unique structure of 3DHPG leads to enhanced electrochemical sensing performance for model molecule DA. The 3DHPG modified electrode display much higher sensitivity, wider linear rang, lower detection limit than those of 3DPG modified electrode, which also shows great potential for real sample analysis. By further tailing its pore size and distribution, and integrating it with other functional materials, such 3D hierarchically porous graphene should be a promising material in constructing advanced electrochemical devices.

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DECLARE OF INTEREST CONFLICT

No interest conflict to be declared.

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