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Nitrogen and high oxygen-containing metal-free porous carbon nanosheets for supercapacitor and oxygen reduction reaction applications

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Abstract

Herein, the synthesis of heteroatom-containing graphene-like carbon nanosheets (HA-GCNs) by chemical activation of waste biomass, namely peanut shells. As characterized by a variety of analytical and spectroscopy techniques, the as-synthesized HA-GCNs material carbonized at 900 °C was found to possess sheet-like porous nanosheet morphology with high surface areas (>800 m\textsuperscript{2} g\textsuperscript{−1}) and desirable of heteroatom contents such as nitrogen (N; 0.84 atom%), and oxygen (O) as high as 20.25 atom%, which greatly improved the electronic properties of the carbon substrate for prospective applications as metal-free electrodes and electrocatalytic materials. The HA-GCNs were found to exhibit a superior specific capacitance of 148, 145, 125, and 105 F g\textsuperscript{−1} corresponding to the KOH, NaOH, LiOH, and H\textsubscript{2}SO\textsubscript{4} electrolyte solutions, respectively. Although, the HA-GCNs electrode exhibited extraordinary electrochemical performances and cyclic charge-discharge stabilities. Moreover, these novel HA-GCNs exhibited excellent electrocatalytic activities and cyclic stabilities for oxygen reduction reaction (ORR) with a desirable current density of 1.17 mA cm\textsuperscript{−2} in O\textsubscript{2}-saturated 0.1 M KOH solution, surpassing that of noble metal-incorporated activated carbons. The superior electrochemical and electrocatalytic performances observed for the HA-GCNs were attributed to the unique pseudocapacitive behavior of the oxygen surface functional groups as well as their unique textural properties, rendering practical applications as low-cost electrodes for supercapacitors and metal-free electrocatalysts for ORR.

1. Introduction

In view of the increasing energy demands and depletion of fossil fuels, which are accompanied by enormous hardships in environmental pollution, there is an immense demand in R&D of eco-friendly carbon-based nanomaterials for high-performance, cost-effective energy production, and storage as well as for catalytic conversion applications [1–3]. For example, considerable R&D attentions have been drawn for supercapacitors, which have been found in prospective applications in electric vehicles and portable power sources with a reliable life cycle, easy and safe operation, and desirable power density than the traditional energy storage devices [4]. However, unlike other energy storage devices, supercapacitors store electrical energy by reversible surface redox
2. Experimental

2.1. Materials synthesis

The nitrogen-containing HA-GCNs materials were prepared by a facile and eco-friendly chemical activation route using biowaste (peanut shell) as the carbon precursor. Typically, the dried peanut shell carbon precursor was first pulverized and dried at 100°C for 2 d. Then, ca. 3 g of the pulverized carbon precursor was sealed in a 100 ml stainless autoclave together with 5 ml of concentrated sulfuric acid and 50 ml of doubly distilled (DD) water, followed by a heat treatment at 180°C for 48 h. The resultant biochar was collected by filtration, washed...
with DD water, and then dried. Next, a desirable amount of the pretreated biochar sample was impregnated in 10% zinc chloride (ZnCl₂) at 60 °C for 24 h in N₂ atmosphere under continuous stirring conditions. Subsequently, the activated sample was subjected to graphitization treatment in a tube furnace in N₂ atmosphere using a heating rate of 5 °C min⁻¹ till reaching the designated temperature (viz. 700, 800, or 900 °C), then maintained at the final carbonization temperature for 2 h. Finally, the carbonized HA-GCNs powder sample was washed with hot distilled water and 1 M HCl to remove Zn residues and other undesirable impurities, followed by drying at 150 °C overnight before ground to a fine powder. The carbon samples so obtained were found to contain heteroatoms such as nitrogen (N) and sulfur (S), and were denoted as HA-GCNs-x, where x = 700, 800, and 900, representing the carbonization temperature in °C (see text).

2.2. Materials characterization

The surface and structural morphologies of the HA-GCNs samples were studied by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-7100F) and field-emission transmission electron microscopy (FE-TEM, JEOL JEM-3000F). FE-TEM measurements were operated at 300 kV. The structural properties were characterized by x-ray diffraction (XRD) on a Rigaku, MiniFlex II instrument. The x-ray photoelectron spectroscopy (XPS) was performed on a ULVAC-PHI PHI 5000 Versa Probe apparatus. All Raman spectra were recorded at ambient temperature using a WITek CRM200 confocal microscopy Raman system equipped with a 488 nm laser. N₂ adsorption/desorption isotherm measurements were studied using a Micrometrics ASAP 2020 physisorption system. Elemental analyses were performed on an element Vario EL cube (NCSH, Germany).

2.3. Preparation of HA-GCN-modified electrodes

To prepare the electrode for supercapacitor application, a desirable amount (85 wt%) of each HA-GCNs activated carbon, graphite (15 wt%), and polyvinylidene difluoride (PVDF) membrane (5 wt%) were mixed with 0.4 ml of N-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry. Subsequently, ca. 1 µl of the optimum slurry was brush coated on stainless steel (area 1 × 1 cm²), then, the electrode was dried overnight at 60 °C. The mass loading of the coated material was determined by the weight difference of the substrate before and after loading the active material. The electrode was soaked in 1.0 M H₂SO₄ and 6.0 M of KOH, NaOH, LiOH electrolyte solution for a few hours before carrying out the electrochemical measurements. Finally, the electrochemical performance of the electrodes was investigated in a three-electrode cell system using 1.0 M H₂SO₄ aqueous solution as the electrolyte. For the preparation of the electrode for the ORR, the as-prepared HA-GCN sample was dispersed in ethanol, then, subjected to a sonication treatment for 2 h. Prior to modification, the surface of the glassy carbon electrode (GCE) was first carefully polished with an alumina slurry till mirror finish, followed by washing with distilled water, then, the ultrasonicated in ethanol containing water for a few minutes. Subsequently, ca. 10 µl of the dispersed HA-GCNs sample was drop cast on the pre-cleaned GCE and dried in an air oven at 30 °C. Then, the HA-GCNs/GCE was applied for electrochemical measurements by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The CV measurements were performed from 0 to 1.2 V versus RHE in O₂- and N₂-saturated 0.1 M KOH electrolyte, with a scan rate of 10 mV s⁻¹. Rotating disk electrode (RDE) measurements were performed from 0.2 to −1 V versus RHE in O₂-saturated 0.1 M KOH and electrolyte at a scan rate of 10 mV s⁻¹ under a disk rotation rate of 100–2500 rpm. All electrochemical measurements were conducted on a CHI 6271E apparatus using a three-electrode cell system using modified HA-GCNs as the working electrode, Ag/AgCl as the reference electrode, and Pt wire as the counter electrode. The electrochemical performance of the metal-free HA-GCNs/GCE was also compared with that obtained from a commercial Pt-C electrode (10 wt% Pt; Sigma-Aldrich). In the main text the potentials measured against the Ag/AgCl electrode was converted to reversible hydrogen electrode, $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0591 \text{pH}$.

3. Results and discussion

The morphology and structural properties of nitrogen-containing sheet-like carbon nanosheets prepared by chemical activation of peanut shells with ZnCl₂ graphitized at different temperatures, denoted as HA-GCNs-x (where x = 700, 800, and 900 °C, denotes the carbonization temperature), were examined by both field-emission scanning electron microscopy (FE-SEM) and field-emission transmission electron microscopy (FE-TEM). As an example, the SEM images of the HA-GCNs-900 sample are shown in Figure 1. It can be seen that the activated carbon material exhibited sheet-like nanosheet morphology, as also verified by FE-TEM results shown in Figures 2 and S2. The FE-TEM images of the HA-GCNs-900 showed a highly interconnected porous nanosheet structure, which is consistent with the atom-molecular structures of sheet-like materials [20, 21]. The crystalline structures of the as-synthesized HA-GCNs-x (x = 700, 800, and 900 °C) samples carbonized at different temperatures were characterized by x-ray diffraction (XRD), as shown in Figure 3(A). All samples
showed similar XRD profiles with two broad diffraction peaks at 2θ angles of ca. 24.5 and 44.3° due to the presence of amorphous (002) and graphitic (100) carbons, respectively [22]. In addition, a sharp diffraction peak at 2θ = 26.54° along with other weak peaks were also observed, revealing the presence of (002) reflection of graphite [23].

Table 1 depicts the elemental contents obtained from elemental analysis (EA). It is evident that, in addition to carbon (C, ca. 53 atom%) and hydrogen (H, ca. 2.9 atom%), the HA-GCNs so fabricated were also found to contain desirable heteroatoms. For example, the HA-GCNs-900 sample was found to contain nitrogen (N, 0.84%), sulfur (S, 0.26%), and a substantial amount of oxygen (O, 20.25%). It will be shown later that the high oxygen content observed in these as-synthesized HA-GCNs in the absence of post-synthesis doping renders a supply of stable pseudo-capacitance through faradaic charge-transfer reactions [24]. Similar trends in elemental contents may also be inferred from results obtained based on measurements by x-ray photoelectron spectroscopy (XPS).

As shown in Figure 3(B), the survey spectra obtained from the HA-GCNs-900 sample confirmed the presence of surface C, N, and O species. The O 1 s core-level spectrum (Figure S3) clearly shows the presence of oxygen–based species such as carbonyl/quinone (C=O), carbonate structures on the surface; and hydroxyl and

Figure 1. FE-SEM images of the HA-GCNs-900 sample collected from (A,B) middle portion and (C,D) supernatant of the sonicated solution.

Figure 2. (A–D) FE-TEM images of the HA-GCNs-900 sample at different magnifications.
ethers (C–OH, C–O–C) type groups \[24, 25\]. The core level C 1 s (Figure 3(C)) revealed the presence of C=C–C, C=O, and C–O bonds with binding energies (BEs) of 284.5, 285.8, and 286.7 eV, respectively. Moreover, the core level N 1 s spectrum (Figure 3(D)) exhibited three overlapping peaks that may be attributed to pyridinic (N1, at 397.4 eV), pyrrolic (N2 at 398.8 eV), and graphitic (N3 at 400.8 eV) groups, indicating the successful incorporation of nitrogen groups on to the carbon network.

The Raman spectra of as-synthesized HA-GCNs samples are displayed in Figure S1 [Supporting Information is available online at stacks.iop.org/NANOX/1/010036/mmmedia; (hereafter denoted as SI)]. All spectra obtained from HA-GCNs carbonized at different temperatures showed similar profiles with two prominent Raman peaks centered at 1347 and 1601 cm\(^{-1}\), which may be ascribed due to the D and G bands of the activated carbons, respectively. In general, the G band corresponds to the in-plane bond-stretching motion of graphitized sp\(^2\) carbon pairs (i.e., the E\(_{2g}\) phonons). While the D band represents the presence of defects in the substrates. As such, the peak intensity ratio of the D and G bands, \(I_D/I_G\), is commonly been used to estimate the degree of disordered carbon structure and the average size of the sp\(^2\) domains in the graphitic materials \[26–28\]. As shown

| Sample             | \(S_{\text{BET}}\) | \(S_{\text{Micro}}\) | \(V_{\text{Tot}}\) | \(V_{\text{Micro}}\) | \(V_{\text{Meso}}\) | \(d_{\text{BJH}}\) | \(I_D/I_G\) | C   | H   | N   | S   | O   |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------------|-----|-----|-----|-----|-----|
| HA-GCNs-700        | 813             | 296             | 0.39            | 0.13            | 0.26            | 1.9             | 0.92        | 50.76| 2.91| 1.21| 0.27| 20.60|
| HA-GCNs-800        | 855             | 346             | 0.42            | 0.15            | 0.27            | 2.0             | 0.93        | 53.55| 2.94| 1.14| 0.29| 21.34|
| HA-GCNs-900        | 859             | 349             | 0.43            | 0.15            | 0.28            | 2.1             | 0.98        | 53.82| 2.86| 0.84| 0.26| 20.25|

\(a\) Brunauer–Emmet–Teller surface area \((S_{\text{BET}}; \text{in m}^2 \text{ g}^{-1})\) and total pore volume \((V_{\text{Tot}}; \text{in cm}^3 \text{ g}^{-1})\) calculated at \(P/P_0 = 0.99\).

\(b\) Microporous surface area \((S_{\text{Micro}})\) and pore volume \((V_{\text{Micro}})\) obtained from t-plot analysis and mesopore volume \(V_{\text{Meso}} = V_{\text{Tot}} - V_{\text{Micro}}\).

\(c\) Pore diameter (in nm) derived by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch of the isotherm.

\(d\) Peak intensity ratio of the D and G bands obtained from Raman spectrum.

\(e\) Obtained from elemental analysis.

**Figure 3.** (A) XRD patterns for HA-GCNs-700, HA-GCN-800, HA-GCNs-900 samples. (B–D) XPS spectra of the HA-GCNs-900: (B) full survey spectrum, and (C) C 1s and (D) N 1s core-level spectra. Inset in (B) is the corresponding deconvoluted O 1s core-level spectrum.
in table 1, the $I_D/I_G$ ratios observed for the HA-GCNs-700, HA-GCNs-800, and HA-GCNs-900 carbons were 0.92, 0.93, and 0.98, respectively, reflecting a progressive increase in defect sites with increasing carbonization temperature.

The textural properties of various HA-GCNs samples were investigated by N$_2$ adsorption/desorption isotherm measurements performed at 77 K. As shown in Figure 4, the isotherms observed for HA-GCNs exhibited typical Type IV isotherm, revealing the co-existence of micro- and meso-porosities, in agreement with the pore size distribution results (insets, Figure 4). The textural parameters viz. BET surface areas ($S_{BET}$), total pore volume ($V_{Tot}$), and Barrett–Joyner–Halenda pore size ($d_{BJH}$) are depicted in table 1 together with microporous surface area ($S_{Micro}$) and pore volume ($V_{Micro}$) derived from the $t$-plot analyses. As anticipated, the ZnCl$_2$ activated graphitized HA-GCNs carbons showed high $S_{BET}$ (ca. 800–860 m$^2$ g$^{-1}$), $V_{Tot}$ (ca. 0.39–0.43 cm$^3$ g$^{-1}$), and average $d_{BJH}$ of ca. 2 nm. A progressive increase in $S_{BET}$ and $V_{Tot}$, mainly due to increases in mesoporous surface area and pore volume, with increasing carbonization temperature may be inferred. As will be shown later that the presences of these micro- and meso-porosities, which facilitate rapid transport of electrolyte ions during the oxygen reduction reaction (ORR) process, are responsible for the superior electrochemical and electrocatalytic performances of the HA-GCNs materials [2, 29, 30]. It is noteworthy that mesoporous carbon nanosheets have been widely employed as electrode and catalyst support materials for supercapacitors and fuel cells [3, 17, 31–33].

To assess the electrochemical properties of the HA-GCNs materials, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) analyses were performed by using a three-electrode system. The GCD and CV curves observed for the HA-GCNs-700, HA-GCNs-800, and HA-GCNs-900 modified electrodes are shown in Figures 5(A) and S4. It is clear that the HA-GCNs-900 modified electrode showed enhanced capacitance compared to its HA-GCNs-700 and HA-GCNs-800 counterparts, revealing a specific capacitance of 105, 93, and 101 F g$^{-1}$, respectively. Moreover, the HA-GCNs-900 modified electrode also showed a much lower voltage drop (i.e., IR drop) compared to the HA-GCNs-700 and HA-GCNs-800 modified electrodes, revealing a better rate performance. Moreover, the CV profiles observed for the HA-GCNs-900 modified electrodes displayed typical quasi-rectangular shape (figure 5(B)), revealing the desirable redox behaviors surpassing its HA-GCNs-700 and HA-GCNs-800 counterparts (Figures S5(A,B); SI) modified electrodes. Interestingly, the quasi-rectangular behavior remained practically intact even at varied scan rates (2–100 mV s$^{-1}$), indicating the good electrochemical reversibility with the scan rate. As shown in Figure 5(C), a progressive decrease in the observed specific capacitance with scan rate may be inferred. The high specific capacitance observed for the HA-GCNs-
900 modified electrode may be ascribed due to the pseudocapacitive behavior of the surface oxygen functional groups [17], which are favorable for improving the wettability with maximized electroactive surface area [34]. The GCD profiles measured at different current densities (0.5–15 A g⁻¹) for the HA-GCNs-700 and HA-GCNs-800 (Figures S5(C,D); SI), and HA-GCNs-900 (Figure 5(D)) modified electrodes allow for monitoring the variations of specific capacitance with current density, as displayed in Figure 5(E). Again, the HA-GCNs-900 modified electrode showed the best performance over the range of current density examined, indicating an excellent rate capability. Further cyclic stability studies over the HA-GCNs-900 modified electrode at two different the current densities (see Figure 5(F)) demonstrated that the HA-GCNs modified electrodes have remarkable cyclic stability over consecutive charge-discharge runs up to 10,000 cycles. The specific capacitance decreased by only ca. 1% during the first 5,000 cycles at a current density of 3 A g⁻¹, even at a higher current density (7 A g⁻¹). Overall, the specific capacitance descended by 2% of its initial value after a total of 10,000 charge-discharge cycles. Such excellent electrochemical stability observed for the HA-GCNs modified electrode is, again, attributed to the high electrocatalytic activity of the porous HA-GCNs, which tend to promote intercalation and deintercalation processes of the active surface species during the GCD cycles [35–37].

In contrast, the electrochemical performance of HA-GCNs modified electrodes was also studied in alkali cations. GCD performance of HA-GCNs-900 °C modified electrode measured with different electrolyte solutions and the corresponding results shown in figures 6 and S6. In Figure 6(A), GCD profiles of the HA-
GCNs-900 modified electrode in 6.0 M KOH, NaOH, and LiOH electrolyte solution at 0.5 A g⁻¹ current densities and the obtained specific capacitance values are 148, 145 and 125 F g⁻¹, respectively. Subsequently, GCD profiles measured at different current densities from 0.5–15 A g⁻¹ and analogous results represented in Figure S5. The result reveals that the alkali cations remarkably providing higher specific capacitance values than the anions (SO₄) solutions because of different radii [38–40]. Hence, the attained results were compared with previously reported literature and data were shown in Table S1.

Finally, electrochemical impedance spectroscopy (EIS) was also employed to monitor the transport properties of ion and electron at interfaces of the electrode and electrolyte. The EIS measurements were carried out in a frequency range of 0.1 to 10 MHz with a perturbation potential amplitude of 10 mV. As shown in Figure S5(E) (SI), the Nyquist plots observed for HA-GCNs samples all displayed a single semicircle in the high to medium frequency region accompanied by a vertical line in the low-frequency region, which is likely arising from the capacitive behavior of the HA-GCNs modified electrodes. Among them, HA-GCNs-900 modified electrode showed a straight line with a steep slope due to the better capacitive behavior. Moreover, the Warburg-type line of the HA-GCNs-900 modified electrode was much shorter than the other HA-GCN-700 and HA-GCNs-800 modified electrodes, indicating shorter electrolyte diffusion paths due to its graphene-like carbon nanosheet structure. The intersection of the semicircle in the high-frequency region, which represents the equivalent series resistance (ESR), is a combined resistance from the electrolyte solution resistance, the active electrode material, and interfacial resistance between the electrode and the current collector. Moreover, the diameter of the observed semicircle defines the charge-transfer resistance at the interfaces of the electrode and the electrolyte solution. As such, it is obvious that the HA-GCNs-900 modified electrode exhibited the lowest charge-transfer resistance compared with its HA-GCNs-700 and HA-GCNs-800 counterparts, revealing the synergic effects of large surface area, abundant porosity, and good electrical conductivity of the electrode, which warrant fast and efficient transfer of electrons and ions on its surfaces.

N-doped Porous carbons have been extensively used as metal-free ORR electrocatalysts over the past decade [12–15]. Here, the catalytic activities of the metal-free HA-GCNs toward ORR were assessed by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements and the results were compared with a commercial Pt-based carbon electrode, Pt/C (Pt loading 10 wt%). The effect of carbonization temperature (x) on the electrocatalytic properties of the as-prepared HA-GCNs-x materials was investigated. The CV profiles obtained for the HA-GCNs-700, HA-GCNs-800, and HA-GCNs-900 are shown in Figure 7(A), which were recorded at a scan rate of 10 mV s⁻¹ in N₂- and O₂-saturated 0.1 M KOH electrolyte solutions. All modified GCEs exhibited enhanced reduction peak in O₂-saturated electrolyte compared to that in N₂-saturated counterpart. For example, the HA-GCNs-900 modified electrode exhibited a single cathodic reduction peak at 0.72 V with a current density of 1.17 mA cm⁻² in O₂-saturated 0.1 M KOH electrolyte solution, while a reduction peaks at 0.70, and 0.69 V was found for the HA-GCNs-700 and HA-GCNs-800 modified electrode with corresponding peak currents of 0.98, and 1.10 mA cm⁻², respectively. Thus, it is indicative that the HA-GCNs modified electrodes are indeed suitable for ORR.

Moreover, LSV measurements over different HA-GCNs-modified GCE were performed by using a rotating disk electrode (RDE) in O₂-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. As shown in Figure 7(B), the onset potential observed for the HA-GCNs-700, HA-GCNs-800, and HA-GCNs-900 was 0.88, 0.910, and 0.913 V, respectively. Although the HA-GCNs-900 modified electrode showed the lowest overpotential, it is still slightly higher than that observed for the Pt-C electrode (0.913 V versus 1.02 V). The limiting current density values determined at 0.3 V versus RHE for the HA-GCNs-700, HA-GCNs-800,
HA-GCNs-900 electrodes and Pt/C are $-2.35$, $-5.02$, $-4.566$, and $-3.41$ mA cm$^{-2}$, respectively. HA-GCNs-900 electrode exhibits the highest limiting current density, showing that its ORR performance is superior to the rest. The Tafel slope values of HA-GCN-700, HA-GCN-800, HA-GCN-900, and Pt/C are 145, 69, 72 and 78 mV dec$^{-1}$, respectively. It is the evidence that the HA-GCNs-900 exhibits the smallest Tafel slope value of 69 mV dec$^{-1}$, revealing improved reaction kinetics during ORR (Figure 7(C)). Additional LSV measurements performed at different rotating speed (400–2500 rpm; Figures 7(D) and S7; SI) further verified that the higher electrocatalytic activity of observed for the metal-free HA-GCNs-modified electrode may be ascribed due to the higher surface area, pore-volume, and natural presence of heteroatoms on the carbon nanosheet substrates (see Table 1).

The Koutecky–Levich (K-L) plot derived at different potentials such as 0.55, 0.41, 0.31, and 0.21 V is shown in Figure 7(E), indicating the first-order reaction kinetic towards the HA-GCNs electrodes. The average electron transfer per oxygen molecules was calculated by using the K-L equation [41]. The calculated electron transfer number ($n$) values are 3.57, 3.64, 3.67, and 3.76, which are nearly equal to the four-electron transfer pathway [42]. Since then values at different potentials are close to four and as the ORR reaction proceeds by a four-electron pathway in the tested potential range, the generation of H$_2$O$_2$ onto the surface of HA-GCNs-modified electrode should be negligible. Note that the unmodified carbon structures exhibit two-electron transfer.
pathways leading to H$_2$O$_2$ generation at low potentials [42, 43], while the hierarchically porous nitrogen-doped electrodes produce negligible (<5%) H$_2$O$_2$ at all potentials, with the H$_2$O$_2$ yields dropping to less than 1.5% at 0.8 V versus RHE due to the enhanced electron transport (n = ~4), improved electrolyte access, and superior diffusion/or mass transport through the pores [44]. Because the nitrogen-doped HA-GCNs-modified electrode prepared at 900 °C is porous and as it contains more micro and mesoporous, we expect negligible generation (<5%) of H$_2$O$_2$ in the tested potential range wherein ORR occurred. To determine the durability of the HA-GCNs-900 and the Pt/C electrodes, chronoamperometric (CA) i-t curves were recorded at 0.88 V in O$_2$-saturated 0.1 M KOH electrolyte solution at a rotation rate of 1600 rpm, as shown in Figure 7(F). It is indicative that while the HA-GCNs-900 showed a slightly lower current density than that of Pt-C (41%), it can sustain 70% of its initial current density even after a period of 8000 s.

Thus, the metal-free HA-GCNs materials reported herein, which may be facilely mass-produced from a biowaste resource (peanut shells), represent a novel series of cost-effective and active electrode materials for prospective new applications in high-performance green energy devices. The specific capacitances and stabilities observed for the HA-GCNs-modified electrode are comparable or superior to the majority of ACs and sheet-like materials derived from biomass resources [2, 45–47], hence, represent promising platform materials for energy storage and conversion device applications. These unique properties, together with their cost-effective and environmentally friendly nature, rendering biomass-derived HA-GCNs for perspective and practical applications in high-performance supercapacitors and metal-free electrocatalysts for ORR.

4. Conclusions

In summary, a novel series of heteroatom-containing graphene-like carbon nanosheets (HA-GCNs) were successfully fabricated from an abundant biowaste, namely peanut shells, through a facile and eco-friendly method. Among various samples examined, the metal-free HA-GCNs-900 materials obtained with a carbonization temperature of 900 °C displayed the optimal electrochemical performances, viz. high catalytic activity, desirable long-term stability, large specific capacitance, low overpotential during ORR, comparable to the conventional Pt-C catalyst and most graphene-based nanomaterials. The superior specific capacitance and excellent ORR activity observed for these metal-free HA-GCNs electrocatalysts have been attributed to the naturally abundant heteroatom (such as N, S, and O), high surface area and porous volume, and good electrical conductivity, making them promising electrode and catalyst materials for next-generation, highly efficient electrocatalysts, particularly for fuel cells and metal-air batteries.

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Conflict of interest

The authors declare no competing financial interest.

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