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Self-assembling porous network nanostructure 7-aminoindole decorated reduced graphene oxide for high-performance asymmetric supercapacitor



ALLOYS AND COMPOUNDS

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ABSTRACT

The design and preparation of novel green and efficient energy storage electrode materials is a crucial way to solve the problem of intermittent energy storage of renewable energy. In this paper, the composite electrode materials of rGO decorated by organic 7-aminoindole (7-Ai) molecule with the characteristics of fast reversible redox kinetics are synthesized successfully. The modified 7-AirGOs composites can not only produce extra pseudocapacitance, which greatly improve the specific capacitance, but also form a stable mesoporous nanostructure to facilitate the diffusion and transport of ions. By investigating the influence of 7-Ai molecule content on the electrochemical performance of the composite electrodes, the 7-AirGO1 electrode is chosen as the optimum electrode, which exhibits a high specific capacitance of 425.73 F g⁻¹ at 0.5 A g⁻¹ and an excellent rate capability with the current density increased to 20 A g⁻¹. Furthermore, the asymmetric supercapacitor assembled by the 7-AirGO1 and AC as positive and negative electrode respectively delivers an energy density of 14.60 W h kg⁻¹ and a power density up to 10,500 W kg⁻¹, as well as a cycling stability with a capacitance retention of 97.98% at a current density of 4 A g⁻¹ for over 20,000 cycles. These results indicate that rGO-aminoindole composites are of great potential in flexible and wearable micro energy storage devices.

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1. Introduction

In recent years, as high-power, long-life, green and sustainable energy storage device, supercapacitors have attracted much attention, and are promising candidates for the application of energy storage field [1–4]. In order to optimize these excellent characteristics of supercapacitors and further improve the insufficiency of its energy density, and obtain the state-of-the-art supercapacitor devices, the scholars and engineers in this field have studied the energy storage properties of various potential materials such as carbon-based materials, metal oxides/hydroxides, nitrides and organic polymers by using various methods and techniques [5–9]. Among of them, introduction of pseudocapacitive materials into carbon materials is currently one of the best ways to address this low energy density problem for the application of the state-of-theart supercapacitors [10-12].

Among of all carbon-based energy storage materials, graphene is considered to be the most fascinating one for the next generation of flexible and durable energy storage devices due to its excellent electronic conductivity, thermal conductivity, mechanical properties, and super-large specific surface area [13–16]. However, due to the lack of a large number of electroactive groups, the inherent capacitance and energy density of graphene are very low. Therefore, improving the energy storage performance of graphene by modification, doping, recombination and other technologies have become the focus of research [17–20]. Among them, the modification of graphene by organic small molecules can improve the low performance of the electrode, and have attracted people's attention in recent years [21–26]. Song et al. prepared a rGO-based composite electrode using triethanolamine (TEA) as inter-layer spacer

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via a controlled hydrothermal process, and the TEA/rGO electrode exhibited a maximum energy density of 25.7 Wh kg⁻¹ in the organic electrolyte and an outstanding cycling stability with 91.7% capacitance retention after 10,000 cycling tests in 1 M H₂SO₄ electrolyte [27]. These composite electrodes combined the pseudocapacitance of small molecules with the excellent conductivity of graphene, which ultimately improve the electrochemical performance.

The graphene-based organic composite electrodes are of great potential in the field of new green energy storage devices, based on our previous work [28], we optimized the experimental scheme and selected another electrolyte, and focused on the study of the influence of different contents of 7-aminoindole modified rGO on the electrochemical performance of the synthesized composite. In this paper, the hierarchical mesoporous nanostructure 7aminoindole (7-Ai) modified rGO composites were successfully synthesized by one-step hydrothermal method. Reduced graphene oxide with porous nanostructure has abundant mesoporous structure, which provides a broad space for the adhesion of 7-Ai organic molecules. The synthetic 7-AirGO composites not only have abundant electroactive sites, which can obtain a large number of double-layer capacitance and pseudocapacitance, but also have unique structural characteristics, which is in favor of the diffusion of electrolyte ions, promoting the full contact between electrode and electrolyte, and facilitating the rapid transmission of electrons in the conductive network. Therefore, the results of these electrochemical performance tests showed that the optimal 7-AirGO1 electrode exhibited a high capacitance of 425.73 F g^{-1} at 0.5 A g^{-1} , showing a distinct improvement in comparison to rGO electrode and 7-Ai electrode. Furthermore, the assembled 7-AirGO1//AC asymmetric supercapacitor device (ASD) displayed an energy density of 14.60 W h kg⁻¹ (350 W kg⁻¹) and a maximum power density of 10,500 W kg⁻¹ (10.50 W h kg⁻¹) at 15 A g⁻¹, as well as an excellent electrochemical stability with approximately 97.98% of the initial specific capacitance at 4 A g^{-1} after 20,000 cycles. These excellent electrochemical properties prove that this novel material is of great potential in the application of novel supercapacitors.

2. Experimental section

All of the chemical reagents were analytical grade and used directly without further purification. Deionized water (DI water) was used throughout the sample preparation.

2.1. Preparation of 7-aminoindole (7-Ai)

7-aminoindole (7-Ai) was synthesized according to the previous literature [29]. A catalytic amount of palladium (10%) on activated carbon was added to the 7-nitroindole ethanol solution, and reacted at room temperature overnight with a hydrogen bag. Then, the catalyst was removed by filtration over Celite, and the solvent was evaporated to provide the product as a grey solid (96.5%). The ¹H NMR spectra and XRD pattern of 7-aminoindole sample were shown in Fig. S1 and Fig. S2, respectively.

2.2. Synthesis of 7-aminoindole/rGO composites (7-AirGOs)

Ai-rGOs were synthesized in a simple hydrothermal process. GO (85 mg) prepared according to our previous literature [30] was dispersed in DI water and sonicated for 1 h to form a homogeneous solution (1 mg mL⁻¹) at first. Then, 7-Ai (85 mg) was added to the above suspension and stirred continuously overnight. The obtained suspension was evenly allocated to two 50 mL Teflon-lined stainless steel autoclave and reacted at 140 °C for 15 h. The precipitate after centrifugation with DI water was dried at 70 °C for 12 h. The final

obtained sample was denoted as 7-AirGO1 (according to the mass ratio of 7-Ai to GO is 1:1). A series of 7-AirGOs with different mass ratios were synthesized through the same process, and denoted as 7-AirGO0.5 and 7-AirGO2 respectively.

2.3. Material characterizations

7-Ai was identified by a Bruker DPX-400 MHz NMR spectrometer (Billerica, MA, USA). XRD patterns were characterized on a Bruker D8 Advance X-ray diffractometer with Cu Ka radiation $(\lambda = 1.5417 \text{ Å})$ at a step of 0.02°. Raman measurements were performed on a Renishaw inVia Raman microscope employing a 633 nm laser excitation (25% laser power). The morphologies and microstructures were characterized by field-emission scanning electron microscopy (FESEM, Quanta 250 FEG) and transmission electron microscope (TEM, JEOL JEM-2100). Thermogravimetric analysis (TGA) data were obtained using a SDT Q600 (USA) in N2 from room temperature to 800 °C at a heating rate of 2 °C min⁻¹. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS5 with wavelength range from 400 to 4000 cm⁻¹. N₂ adsorption/desorption isotherms were measured by micromeritics ASAP 2020 analyzer. The samples were out-gassed at 120 °C for 6 h before adsorption. The specific surface area (S_{BFT}) measurements were calculated by a Brunauer-Emmett-Teller (BET). The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB 250 Xi (Al target, Ka radiation, USA).

2.4. Electrochemical measurements

All of the electrochemical performance tests were carried out on a CHI 760E electrochemical workstation (Shanghai CH Instrument Company, China). Cyclic voltammetry (CV), galvanostatic charge/ discharge and electrochemical impedance spectroscopy (EIS) measurements were investigated in 2 M KOH aqueous electrolyte. The working electrode was prepared by blending 7-AirGOs (80 wt %), conductive carbon black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%), the mixture was produced a homogeneous phase by adding a small amount of isopropyl alcohol. Then the slurry was spread on a nickel foam sheet ($0.9 \times 0.9 \text{ cm}^2$) and pressed together followed by drying at 70 °C under vacuum for overnight. The mass of active materials coated on each work electrode was about 1.6 mg.

In a three-electrode system, platinum plate and Ag/AgCl electrode were acted as counter electrode and reference electrode respectively. Before the electrochemical performance test, the working electrode was pre-soaked in electrolyte for about 6 h to obtain a sufficient contact for working electrode and electrolyte. Specific capacitance ($C, F g^{-1}$) of the working electrode was calculated from the galvanostatic discharge process based on the following formula:

$$C = \frac{I\Delta t}{m\Delta U} \tag{1}$$

Where C (F g⁻¹) is the specific capacitance, I (A) is the discharge current, Δt (s) is the discharge time, ΔU (V) is the voltage change during the discharge process, m (g) is the mass of active material.

The asymmetric supercapacitor device (ASD) was assembled by using a relative size membrane between the 7-AirGOs electrodes and AC electrode, and the insulation board was used as the shell for packaging in 2 M KOH aqueous electrolyte. The specific capacitance $(C, F g^{-1})$, energy density $(E, W h kg^{-1})$ and power densit y $(P, kW kg^{-1})$ of the ASD were tested and calculated according to the following equations:

$$C = \frac{I\Delta t}{M\Delta U} \tag{2}$$

$$\frac{m_{+}}{m_{-}} = \frac{Sc_{-} * \Delta V_{-}}{Sc_{+} * \Delta V_{+}}$$
(3)

$$E = \frac{C^* \Delta U^2}{2^* 3.6} \tag{4}$$

$$P = \frac{3600E}{\Delta t} \tag{5}$$

Where I(A), $\Delta U(V)$, $\Delta t(s)$ and M(g) were the response current, the range of potential, the discharge time and the total mass of both electrodes, respectively. The m_+ (g) is the mass of positive electrode, m_- (g) is the mass of negative electrode, Sc_+ (F g⁻¹) and Sc_- (F g⁻¹) is the specific capacitance of positive electrode and negative electrode respectively calculated from a three-electrode system tests.

3. Results and discussion

The crystal structure, phase composition, degree of

graphitization and defect of the prepared samples were characterized by XRD and Raman. As presented in Fig. 1a, a sharp peak at $2\theta = 10.2^{\circ}$ is the characteristic peak of the (002) crystalline plane of GO. After hydrothermal reduction, the sharp characteristic peak located at $2\theta = 10.2^{\circ}$ disappears and a broad diffraction peak occurred at around $2\theta = 25.8^{\circ}$ for rGO. 7-AirGO0.5. 7-AirGO1 and 7-AirGO2 samples, corresponding to the typical drum peak of graphene, which indicates that GO is reduced after hydrothermal reaction [14,26]. It is worth noting that, after careful observation, the diffraction peak of 7-AirGOs materials at around $2\theta = 25.8^{\circ}$ shifts slightly to a small angle than that of pure rGO material, which means that the interplanar spacing of rGO becomes larger in 7-AirGOs materials. What is more, the weak peak located at near $2\theta = 43.1^{\circ}$ indicates that a very thin rGO sheets are existed in 7-AirGOs composites [14]. These results indicate that the introduction of 7-Ai molecule extends the interplanar spacing of rGO and results in a thinner graphene lamellar structure. The Raman spectra of GO, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 were exhibited in Fig. 1b. The typical characteristic peaks located at 1334.12 cm⁻¹ and 1592.82 cm⁻¹ are corresponded to the D band and G band respectively, which are represented the presence of structure defects and disorder in graphitic structure derived from the A_{1g} mode of 3D graphitic-like lattice vibrations, and the E_{2g} in-plane vibration of sp²-bonded carbon atoms, respectively [31–33]. The intensity



Fig. 1. (a) XRD patterns and (b) Raman spectra of GO, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2; (c) FTIR spectra of rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2; (d) TGA and DTG curves of 7-AirGO1 with a heating rate of 2 °C min⁻¹ under N₂ atmosphere.

ratio of D band to G band (I_D/I_G) reflects the disorder degree of the internal microstructures of carbon-based materials [34]. The calculated I_D/I_G values of GO, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 are 0.86, 1.25, 1.14, 1.17 and 1.21, respectively. The higher I_D/I_G value in rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 suggest that more defects and more serious disorder are produced on rGO and 7-AirGOs materials after chemical hydrothermal reduction process. Furthermore, a slight increase of the I_D/I_G value from 7-AirGO0.5 to 7-AirGO2 indicates more defects with the increase of reactant 7-Ai content, which can be inferred that more 7-Ai molecules are grafted onto the surface graphene sheets [27].

FTIR spectra of rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 samples were shown in Fig. 1c. In the FTIR spectrum of rGO, a series of characteristic weak peaks located at around 1015.8, 1560.1, 1712.3, and 3400.0 cm^{-1} can be attributed to C–O vibrations from the alkoxy groups, C=C vibrations, C=O of carboxyl, and O-H stretching vibration on the surface or edges of the rGO sheets, respectively [35]. Upon functionalization, the more obvious absorption peaks at 1196.6, 1568.3, and 1714.4 cm⁻¹ are recognized as the aromatic ring vibration of C–N–C originated from the surface grafting of graphene with amines, N-H bending vibration of primary amine, C=O stretching vibration in amide bond [17]. And the bulge peak located at ~3347.8 cm⁻¹ should be inferred as the -NH stretching vibration (originated from the organic 7-Ai molecule and the formed amide bond), -NH₂ stretching vibration (in 7-Ai), and the stretching vibration of -OH functional groups in a small amount rGO that are not reduced in hydrothermal reduction reaction. Compared with the FTIR spectrum of rGO, the appearance of the peak (1196.6 cm^{-1}) and the unconspicuous peak (~1015.8 cm^{-1}) in the FTIR spectrum of 7-AirGOs, as well as the analysis of the above results, confirm the presence of the 7-Ai molecules in the rGO structure in 7-AirGOs composites [17,27].

The thermal stability of the 7-AirGO1 sample was evaluated by thermogravimetric analysis (TGA), and carried out under nitrogen atmosphere with a heating rate of 2 °C min⁻¹. As illustrated in Fig. 1d, the weight loss before 150 °C is mainly due to the evaporation of water in the composite material. While another weight loss from 150 °C to about 420 °C is mainly attributed to the sublimation of organic 7-Ai material that intercalated in-between rGO layers and the decomposition of a small amount of unstable oxygen functionalities groups. The slight weight loss in the third stage around 635 °C should be attributed to the sublimation of 7-Ai that grafted on the outer surface of rGO (i.e. 7-Ai molecules linked by amide bond) and the decomposition of relatively stable functional groups. In addition, combined with TGA curve analysis of rGO (Fig. S3c), it is can be concluded that the content of organic 7-Ai molecule in 7-AirGO1 composite is about 10.2 wt%. Similarly, we inferred that the content of organic 7-Ai molecule in 7-AirGO0.5 and AirGO2 composites is about 9.0 wt% and 11.6 wt%, respectively (Fig. S3 (a-b)). Simultaneously, comparing the TGA curves of 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 composites, the weight loss of 7-AirGO2 composite in the second stage (150 °C to about 420 °C) is largest, which indicates that the organic 7-Ai molecules that mainly exist in the form of intercalation in-between rGO layers.

The microstructure and morphology of the prepared samples were characterized by SEM and TEM. As presented in Fig. 2a, the prepared GO samples show multi-layer and yarn-like nanosheet structure. However, due to the large number of functional groups and the strong van der Waals force in GO materials, the agglomeration of obtained GO nanosheets is obviously. And after hydrothermal reduction, the degree of aggregation of graphene is obviously reduced, and it presents a fluffy, porous, densely interconnected nanosheet structure (Fig. 2b). After functionalization of rGO, we can found that all 7-AirGOs composites exhibit more fragmented and dispersed lamellar structure (Fig. 2c-e). And with

the increase of organic 7-Ai content, the rGO lamellar arrangement is more orderly and denser. The high-magnification SEM image in Fig. 2f further shows that 7-AirGO1 material has a very thin and dispersed lamellar structure, and the porous structure with thin pore wall that is very conducive to the transfer of electrolyte ions. The microstructure of 7-AirGO1 composite was further characterized by TEM, as shown in Fig. 2g-h. The 7-AirGO1 material shows the typical structural characteristics of graphene nanosheet, with folded and highly transparent multilayered lamellar morphology (Fig. 2g). The TEM image of 7-AirGO1 material with a higher magnification shows that there are a lot of attachments evenly distributed on the rGO nanosheets (Fig. 2h). Although single organic 7-Ai molecule is not enough to be observed by SEM characterization, while combined with the characteristics of the synthetic material and the synthesis process, it is believed that these attachments are formed by a small amount of organic 7-Ai molecules gathered together due to the intermolecular force. The welldefined rings shown in the selected-area electron diffraction (SAED) are consistent with the XRD characterization results, indicating a relatively good crystallinity for the nano-porous structure of 7-AirGO1 composite.

The nitrogen adsorption/desorption isotherms of GO, rGO, and 7-AirGOs samples were shown in Fig. 3a. According to the IUPAC classification, the isotherms displays a typical type-IV isotherm with a hysteresis loop at P P_0^{-1} of around 0.4–0.6, indicating the presence of a large number of mesoporous structures and a certain amount of macroporous structures. In this hierarchical porosity composed of mesopores connected with macropores nanostructure, the macropores can be served as solution buffering reservoir to minimize the diffusion distance to the mesopores, facilitating mass transport, and also reducing the volume change during the charge/discharge cycling, thereby ensuring a high cycling performance [36–38]. However, for GO materials, the poor porosity can be obtained from the isotherm, which is mainly due to the serious agglomeration and stacking of GO nanosheets. Fig. 3b shows the pore size distribution curves of the prepared samples. It is found that, compared with the pure rGO, the 7-AirGOs composites modified by organic 7-Ai molecules mainly reduce the macropores and the larger mesopores in rGO, however, the porosity of 7-AirGOs composites are greatly improved. In addition, the pore size of the composite is mainly concentrated around 3-7 nm, which can be observed from the insert in Fig. 3b. The BET surface area (S_{BET}) and textural properties of the GO, rGO, and 7-AirGOs samples were further confirmed by the experimental data which were summarized in Table S1. Compared with rGO materials, the decrease of specific surface area and pore volume of 7-AirGOs composites is mainly due to the existence of organic 7-Ai molecule, whether intercalated in-between rGO layers or grafted on outer rGO surfaces. And the intermolecular interaction between 7-Ai and rGO, and the formation of amide bond reduce the layer spacing as well as the pore size of rGO, which usually exists in organic-based carbon (such as rGO/graphene, CNTs) composites [31,39,40].

The electrochemical performance of the prepared electrodes was first measured in 2 M KOH electrolyte by means of a traditional three electrode system. The GCD curves of 7-Ai, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 electrodes at current density of 0.5 A g⁻¹ were described in Fig. 4a. The 7-AirGO1 electrode shows a superior specific capacitance of 425.73 F g⁻¹, which is much higher than that of 7-Ai (65.94 F g⁻¹), rGO (80.29 F g⁻¹), 7-AirGO0.5 (363.28 F g⁻¹) or 7-AirGO2 (322.60 F g⁻¹) electrodes. Furthermore, the GCD curves of 7-AirGOs electrodes present a nonlinear triangle, which indicate that the high-capacitance exhibited by the composite electrodes is composed of double-layer capacitance and pseudocapacitance. In addition, the highest specific capacitance of electrode 7-AirGO1 in



Fig. 2. Low-magnification SEM images of (a) GO, (b) rGO, (c) 7-AirGO0.5, (d) 7-AirGO1, (e) 7-AirGO2 samples, (f) high-magnification SEM image of 2-AprGO1 sample, (g-h) TEM and (i) SAED images of 7-AirGO1 sample.



Fig. 3. (a) N₂ adsorption-desorption isotherms, and (b) pore size distribution curves of the prepared GO, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 samples.

all 7-AirGOs electrodes indicates that rGO modified by an appropriate amount of 7-Ai molecule can effectively exert the advantage of synergistic enhancement effect of rGO and the functional 7-Ai molecules. The comparison of the electrochemical performance of each electrode and the composition of the capacitance produced by the composite electrode can be further proved by CV curves (Fig. S5). Fig. 4b displays the GCD curves of 7-AirGO1 electrode at different current densities from 0.5 to 20 A g^{-1} . The approximately symmetrical triangle and the almost negligible voltage (IR) drop in discharge curves demonstrate that the 7-AirGO1 electrode has the



Fig. 4. (a) GCD curves of 7-Ai, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 electrodes; (b) GCD curves of 7-AirGO1 electrode at different current densities; (c) rate capability and (d) Nyquist plots of 7-Ai, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 electrodes.

characteristics of the relatively ideal capacitor behavior. The specific capacitance vs current densities of all prepared electrodes were illustrated in Fig. 4c. It can be seen that with the increase of current density, the specific capacitance of 7-AirGO1 electrode is higher than that of other 7-AirGOs electrodes. And even when the current density is increased to 20 A g^{-1} , the 7-AirGO1 electrode still has a specific capacitance of 241.96 F g^{-1} , implying an excellent rate capability. On the contrary, as the current density increase, the capacitance of 7-Ai electrode decreases sharply, indicating a poor rate capability, which is also the characteristic of pure organic material electrode.

Electrochemical impedance spectroscopy (EIS) test was used to investigate the resistive properties and the ionic diffusion kinetics features of the electrodes in electrolyte. The comparison of the Nyquist plots of 7-Ai, rGO and 7-AirGOs electrodes in the frequency range from 10⁵ to 0.01 Hz were all presented in Fig. 4d. It can be seen that these complex-plane impedance plots are composed of a semicircle arc at the medium-high frequency region followed by an approximate straight line at the low frequency region. The intersection of the semicircle arc with the real axis at high frequency refers to the equivalent serial resistance (R_{ESR}), which reflects the sum of ionic resistance of electrolyte, intrinsic resistance of electrodes, and contact resistance at the electrolyte/electrode interface [41–44]. The diameter of semicircle represents charge-transfer resistance (Rct), by careful observation from the insert in Fig. 4d. we can clearly obtained the order of Rct for 7-Ai, rGO, 7-AirGO0.5, 7-AirGO1 and 7-AirGO2 electrodes: Rct (rGO) < Rct (7-AirGO2) < Rct (7-AirGO1) [<] Rct (7-AirGO0.5) ^{<<} Rct (7-Ai), which shows that the introduction of organic 7-Ai molecule slightly compromises the charge transfer kinetic properties of rGO materials. The slope of the straight line in the low frequency region represents the diffusion resistance of electrolyte ions (Warburg resistance), and a vertical line would be observed for an ideal capacitor. Therefore, the more vertical line of the 7-AirGOs electrodes indicates a more ideal capacitance behavior, especially for the case of 7-AirGO1 electrode [27,43,45]. What is more, the slopy line of Nyquist plots of these electrodes fabricated by composite materials also reveals that the capacitance contributed by the 7-AirGOs electrodes not only includes the electric double layer capacitance, but also the pseudocapacitance.

To further evaluate the practical applicability of electrochemical energy storage performances of the 7-AirGO1 composite electrode, an asymmetric supercapacitor device (ASD) was assembled based on 7-AirGO1 electrode as the positive electrode and AC as the negative electrode in 2 M KOH aqueous electrolyte. The mass ratio of 7-AirGO1 electrode to AC electrode depended on the theory of charge balance (equation (3)). The CV curves of 7-AirGO1//AC asymmetric supercapacitor device (ASD) at different potential



Fig. 5. The electrochemical performances of 7-AirGO1//AC asymmetric supercapacitor device (ASD): (a) CV curves at different potential windows from 0-0.8 V to 0-1.5 V; (b) CV curves at different scan rates; (c) GCD curves at various current densities; (d) Ragone plot, (e) cyclic stability and coulombic efficiency; (f) Nyquist plots before and after 20,000 cycles.

windows were shown in Fig. 5a. It can be seen that the voltage can be extended to 1.4 V, so as to achieve better electrochemical properties, while the polarization phenomenon in the reaction process can be avoided as much as possible. Fig. 5b presented the CV curves of 7-AirGO1//AC ASD at various scan rates from 10 to 200 mV s⁻¹. We can observe that the CV curves exhibit a guasirectangular shape with less obvious wide redox peaks, even though the scanning rate is as high as 200 mV s^{-1} , indicating that the ASD has excellent capability. The GCD curves of the 7-AirGO1// AC ASD recorded at different current densities display approximate symmetrical distribution (Fig. 5c), implying an excellent electrochemical reversibility and capacitive behavior. The Ragone plots obtained from the GCD curves are used to further evaluate the energy-power properties of the ASD, as shown in Fig. 5d. It demonstrates that the maximum mass energy density is 14.60 W h kg⁻¹ achieved at a power density of 350 W kg^{-1} , and even when the power density is as high as 10,500 W kg⁻¹, the device still retains a high energy density of 10.50 W h kg⁻¹, showing excellent energy density and power density, which are both relatively higher than the previously reported organic molecular based supercapacitors [31,46-48].

As important requirement for practical application of supercapacitors, the long-term cycling stability of the ASD was evaluated by performing galvanostatic charge-discharge at a current density of 4 A g⁻¹. As shown in Fig. 5e, the ASD still displays excellent cycle stability with 97.98% capacitance retention after 20,000 cycles. What's more, the ASD always maintains a relatively stable and very high Coulomb efficiency over the 20.000 cycles. The EIS was carried out to further examine the electrochemical performance of the ASD before and after 20,000 cycles (Fig. 5f). A slight increase in the diameter of the semicircle arc in the medium-high frequency regions and the nearly vertical line in the low frequency regions indicates the slight increase of Rct and Warburg resistance after 20,000 cycles, which means that the ASD still maintains good charge transfer kinetics and electrolyte ion diffusion kinetics due to the stable structure of the electrode material. The result further proves the reason why the ASD has excellent ultra-long cycle stability.

These excellent electrochemical properties with high energy and power density, super-long cycling stability and good Coulomb efficiency for the synthesized composite electrodes were also verified by 7-AirGO0.5//AC ASD and 7-AirGO2//AC ASD (Fig. S6). The performance enhancement of 7-AirGOs composite electrodes is mainly attributed to the following aspects: (1) in the chargedischarge process, the introduction of the 7-Ai organic material containing amino functional groups can formed electron donor/ acceptor with graphene, which can not only produce pseudocapacitance generated by charge difference, but also promote the electron transfer process between surface bound amino group and rGO, thus improving the electrochemical performance of composite electrode materials. In addition, the pyrrolic N, as an electrochemically active functional group that participates in hydrogen bonding and easily disrupted, can also increase the capacitance, thus improving the electrochemical properties of the composite [49,50]; (2) the hydrophilicity of amino group is helpful to reduce the contact resistance of electrode/electrolyte and enhances the diffusion rate of electrolyte ions; (3) The interconnected and stable porous network structure of 7-Ai molecules decorated rGO, as well as the synergetic enhancement of 7-Ai and rGO, are conducive not only to the rapid transport of ions/electrons, but also to the stability of the nanostructure, thus improving the ultra-long cycling stability of the composite electrode. As a result, the electrochemical energy storage performance of the synthesized composite is significantly enhanced, which is superior to the similar composite electrode reported previously (Table S2).

4. Conclusions

In summary, we demonstrated a promising composite electrode based on the organic 7-Ai molecule decorated rGO nanosheets successfully synthesized by a facile hydrothermal method. The electrochemical performance test results of the composite electrodes with different doping amount of 7-Ai show that the composite electrode is of excellent electrochemical energy storage performance rooted from the synergetic enhancement of the two electrode materials. The 7-AirGO1 electrode exhibits optimal electrochemical properties with a specific capacitance of 425.73 F g⁻¹ at a current density of 0.5 A g⁻¹ and an outstanding rate capability. Furthermore, an asymmetric supercapacitor device (ASD) of 7-AirGO1//AC assembled based on 7-AirGO1 electrode and AC electrode displays a high energy density of 14.60 W h kg⁻¹ (350 W kg^{-1}) and a high power density of 10,500 W kg⁻¹ (10.50 W h kg^{-1}), as well as a super-long cycling stability with a capacitance retention of 97.98% after 20,000 cycles at a large current density of 4 A g⁻¹. These results show that the porous network composite obtained by modifying graphene with redox functional organic molecules can help to harvest the excellent electrochemical energy storage performance of these novel electrode materials, which is expected to be applied to the new generation of green and efficient energy storage devices.

Declaration of competing interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Weiyang Zhang: Investigation, Writing - original draft. Chunyan Sun: Investigation, Writing - original draft, Validation. Yonggui Xu: Data curation, Writing - review & editing. Hongwei Kang: Conceptualization, Methodology, Writing - review & editing. Baocheng Yang: Project administration. Huili Liu: Formal analysis. Zhikun Li: Writing - review & editing.

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Appendix A. Supplementary data

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