A High Energy Density Self-supported and Bendable Organic Electrode for Redox Supercapacitors with a Wide Voltage Window

Rashid Iqbal\textsuperscript{a,c,†}, Aziz Ahmad\textsuperscript{b,c,†}, Li-Juan Mao\textsuperscript{a,c}, Zahid Ali Ghazi\textsuperscript{a,c}, Abolhassan Imani\textsuperscript{a,c}, Chun-Xiang Lu\textsuperscript{a,c}, Li-Jing Xie\textsuperscript{b,c}, Saad Melhi\textsuperscript{d}, Fang-Yuan Su\textsuperscript{b,c}, Cheng-Meng Chen\textsuperscript{b,c,†}, Lin-Jie Zhi\textsuperscript{c,†}, and Zhi-Xiang Wei\textsuperscript{b,c,†}

\textsuperscript{a} Chinese Academy of Sciences (CAS) Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China
\textsuperscript{b} CAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
\textsuperscript{c} University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{d} Department of Chemistry, College of Science, University of Bisha, Bisha 61922, Saudi Arabia

\textsuperscript{†} These authors contributed equally to this work.
\textsuperscript{*} Corresponding authors, E-mail: ccm@sxicc.ac.cn (C.M.C.)
E-mail: zhijl@nanoctr.cn (L.J.Z.)
E-mail: weizx@nanoctr.cn (Z.X.W.)

Abstract

Redox-active organic electrode materials are highly desirable in realizing next-generation all-in-one bendable electronic systems. Herein, a novel flexible supercapacitors (SCs) electrode is fabricated from poly(anthraquinonyl sulfide) (PAQS) and single-walled carbon nanotubes (SWCNTs) suspension by a simple vacuum filtration and named as PAQS-SWCNTs. The PAQS-SWCNTs electrode offered an initial capacitance of 223 F·g\textsuperscript{−1} and outstanding capacitance retention up to 78.4% after 3 × 10\textsuperscript{5} charge-discharge cycles at 0.5 A·g\textsuperscript{−1} current density. In a high potential range (0−3 V) and aprotic electrolyte, the PAQS-SWCNTs electrodes in coin cell exhibited an outstanding energy density of 69 Wh·kg\textsuperscript{−1} at a power density of 90.6 W·kg\textsuperscript{−1}, whereas in the fabricated flexible SCs it retained 63.2 Wh·kg\textsuperscript{−1}. The PAQS-SWCNTs electrodes also showed extraordinary performance at a higher current density (20 A·g\textsuperscript{−1}) and maintained a specific capacitance of 55 and 47 F·g\textsuperscript{−1} for coin and flexible SCs, respectively. Moreover, the flexible SC is further verified to be able to illuminate up multiple LEDs. These future studies showed that the SCs assembled with flexible PAQS-SWCNTs electrodes have potential application in energy-storage devices and make them highly appealing for future redox supercapacitors.

Keywords

Redox-active; High energy density; PAQS; SWCNTs; Flexible SCs

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INTRODUCTION

With the rapid growth of smart textiles or wearable electronics in healthcare, rehabilitation, physiological signals in sports and high-risk environments, energy storage devices with high energy density as well as good flexibility have gained significant attention.\textsuperscript{[1]} Among the reported flexible devices, flexible supercapacitors (SCs) based on carbon electrodes are regarded as a promising candidate for the wearable power supply due to their fast charge and discharge rates, high power density, excellent flexibility, and exceptional safety.\textsuperscript{[2,3]} However, their applications are still limited due to relatively low specific energy density.\textsuperscript{[4−6]} To enhance deliverable energy of flexible SCs, various studies have focused on introducing additional charge-storage capacity via surface redox processes,\textsuperscript{[7−9]} and yielding higher specific capacitance than those comprised with only electrochemical double layer (EDL). Generally, SCs can be mainly divided into two categories, e.g., the EDL capacitors, which store the pure electrostatic charge in electric double layer constructed at the electrode/electrolyte interfaces, and the pseudocapacitors that store the charge through fast reversible redox reactions occurring in the electroactive species.\textsuperscript{[4,8]} The EDL capacitors mainly use carbonaceous materials such as porous carbons, carbon fibers, graphene and carbon nanotubes\textsuperscript{[10−14]} owing to their huge surface area, high electronic conductivity and remarkable chemical stabilities. The latter uses transition metal oxides\textsuperscript{[15,16]} conducting polymers\textsuperscript{[17,18]} and other redox-active organic compounds.\textsuperscript{[17,19]}

Redox-active organic molecules and polymers are an attractive choice to meet the energy demand of various areas, from portable electronics to electric grids because of their high capacities and energy densities.\textsuperscript{[7,20−28]} Actually, the utilization of \(n\)-aromatic redox-active organics is a good choice compared with the redox-active metal oxides, which may sig-
nify a promising and new insight for the sustainable energy storage devices at a relatively low-cost.[7,29] Moreover, the electrochemically active organic electrode materials are scalable, environmentally benign, and very safe during operations.[29] If their electronic conductivity and stability could be improved, they would further provide a sustainable option and could also be integrated as high energy density electrode materials for the organic SCs with long cycle-life. Redox-active organic molecules and polymers are the primary pseudocapacitive candidates and have the ability to be designed with the multi-electron reactions to achieve high specific capacitance, which will address the low specific capacity of carbon-based electrodes.[5,14,30,31] Generally, the redox-active organic materials can be divided into different categorizations, such as conducting microporous polymers,[5,30] organosulfur compounds, organic free radical compounds and organic carbonyl compounds.[21,22]

Quinone, a typical family of the carbonyl compounds, is of great concern due to their superior electrochemical performances, high discharge potential, and reaction reversibility.[32–34] However, there are still some intrinsic problems in the efficient utilization of quinone electrodes, such as the dissolution of these compound in organic electrolytes and the poor electrical conductivity, which significantly limit their rate capacity and cycling stability. To this end, efficiently prohibiting the dissolution of quinone electrodes in organic electrolytes while improving their electrical conductivity is highly desirable for developing quinone electrodes that can perform well in all aspects. Very recently, quinones have shown promising cyclic and rate performances, when combined with carbon materials.[35,36] The carbon materials with a porous structure and high electrical conductivity can not only restrict quinones from dissolving in liquid electrolytes but also provide conductive support to hamper the degradation of quinones upon cycling.

In this manuscript, for the aim of assembling SCs with high flexibility, high energy density, good rate capability as well as excellent cyclic lifespan, we have designed and constructed a self-supported PAQS-SWCNTs flexible electrode from PAQS and SWCNTs compositing through a simple vacuum filtration method and used it as high energy density electrode in redox SCs. To the best of our knowledge, applications of PAQS based electrode for SCs with organic electrolytes and high voltage window have not been reported so far. In the obtained PAQS-SWCNTs composite electrode, the function of the SWCNTs is to act both as the long-range conductive network and an intercrossed mechanical scaffold, while PAQS particles are well distributed in the composed framework. An initial specific capacitance of 223 F·g⁻¹ and 78.4% of capacity retention after 3 × 10⁶ cycles was achieved for the PAQS-SWCNTs electrode. The PAQS-SWCNTs electrode delivered high energy density of 69 Wh·kg⁻¹ at a power density of 90.6 W·kg⁻¹ within a wide voltage range of 3 V, while in the fabricated flexible SCs, it offered 63.2 Wh·kg⁻¹ energy density at a power density of 90.6 W·kg⁻¹ and lightening several light-emitting diodes (LEDs). The Young’s modulus and stress-strain curves of the pure SWCNTs and PAQS-SWCNTs flexible films were tested and we found improvement in the mechanical properties of the PAQS-SWCNTs flexible film, which confirmed the efficient mechanical contribution of SWCNTs in the constructed electrode as mentioned in previously published report.[37] Hence, the excellent electrochemical performance and mechanical properties of PAQS-SWCNTs electrode in SCs are attributed to the synergistic effect of the stable polymer structure and SWCNTs scaffold.

**EXPERIMENTAL**

**Synthesis of PAQS**

The synthesis of PAQS was conducted by a method reported before.[21] For the polymerization of PAQS, dry sodium sulfide (Na₂S) was required, and therefore, benzene (C₆H₆) solvent was used as an entrainer at 150 °C to remove water. In the first step, sodium nanohydrated (Na₂S·9H₂O, 4.80 g/0.02 mol) and 50 mL of N-methyl pyrrolidone (C₆H₇NO, NMP) were added into a reaction flask. In the second step, when the water from the nanohydrated sodium sulfide was removed completely through benzene entrainer, 1,5-dichloranthraquinone (C₁₄H₈ClO₂, 5.54 g/0.02 mol) was added into the solution and the reaction started with the anhydrous Na₂S at 200 °C for overnight. In the third step, the reaction was completed and a light-weight brown color powder (PAQS) was obtained. In the fourth step, the PAQS powder was thoroughly washed with hot deionized water and acetone (C₂H₅O) to remove the impurities and unreacted monomers and oligomers. The final product was then vacuum dried at 120 °C for overnight. Thereafter, it was further calcined at 300 °C for 3 h to make sure the complete degradation of small unreacted molecules and oligomers. After this step, the calcined PAQS polymer was washed again by hot waters and acetone to remove the unwanted degraded impurities and oven dried at 120 °C. Thus, after these processes, a high molecular weight PAQS was obtained that was used for the SCs electrochemical measurements.

**Fabrication of Flexible Films**

A stable suspension of SWCNTs in water was prepared using sodium deoxycholate as a stabilizer by a 1:2 ratio. In the next step, PAQS powder and SWCNTs suspension were mixed together in a proper weight ratio and probe sonicated for 2 h. After 2 h, a homogenous suspension of PAQS and SWCNTs was achieved, which was filtered under vacuum environment using polytetrafluoroethylene (PTFE) filter paper. The obtained film on the PTFE membrane was repeatedly washed with distilled water and ethanol to remove the surfactant and other impurities completely. After drying, the fabricated film was peeled off from the PTFE filter and used as self-supported PAQS-SWCNTs electrode in flexible SCs application.[38]

**Electrochemical Measurement**

Electrochemical measurements were performed in a traditional two-electrode symmetric SCs system (a coin-type cell of 2032 size) using 1 mol·L⁻¹ lithium bis(trifluoromethanesulfonyl)imide ([Li[N(CF₃SO₂)₂]₂, LITFSI] as the electrolyte, respectively. 1 mol·L⁻¹ LITFSI electrolyte used consisted of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1/1, W/W). The working electrode (PAQS-SWCNTs) was made of 60 wt% of the PAQS electrode and 40 wt% of the purified SWCNTs. The active mass of PAQS was used to calculate the specific capacitance. The fabricated film achieved a high molecular weight PAQS polymer that was used for the SCs electrochemical measurements.
RESULTS AND DISCUSSION

The preparation and redox mechanism of the PAQS are shown in Schemes 1(a) and 1(b), whereas the fabrication procedure of the composited electrode is elaborated in Scheme 2. The PAQS was synthesized through a simple polymerization route called the Phillips reaction method (Scheme 1a).[19] 1,5-Dichloroanthraquinone (DCAQ) was used as a precursor material for the preparation of PAQS. The Fourier-transform infrared spectroscopy (FTIR), $^{13}$C-CP/MAS NMR, powder XRD and TGA of PAQS were reported in our recently published work.[19] The scanning electron microscopy (SEM) technique was employed to elucidate the surface morphology of PAQS, SWCNTs and the fabricated flexible PAQS-SWCNTs electrodes as described by Figs. 1(a)–1(c). Fig. 1(a) shows that pure PAQS held flat, soft and bulky type morphology with micrometer sizes, while the SWCNTs exhibited length in micrometer ranges with a unidimensional porous structure. When the bare PAQS was composited with SWCNTs via a probe sonication and vacuum filtration processes into a free-standing flexible electrode (PAQS-SWCNTs), it was found that the PAQS particles were well distributed in SWCNTs framework (Fig. 1c). In other words, the SWCNTs strongly firmed the PAQS particles and functioned as a binder, while the fabricated film was flexible and could be bent and deformed easily without cracks or other damage (Fig. 1d).

These discoveries elaborated the fine intermingling of SWCNTs, which is of high importance for the efficient utilization of PAQS capacitance during the electrochemical tests. Moreover, the presence and smooth distribution of C, O and S elements in the PAQS are confirmed by the energy-dispersive spectroscopy (EDS) mapping as shown in Fig. S1 (in ESI). To investigate the supercapacitive performance of the PAQS-SWCNTs electrodes, we have assembled a two-electrode coin type SC using 1 mol·L$^{-1}$ LITFSI in DOL and DME (1/1, W/W) as the organic electrolyte. Electrochemical performance of the working electrode was explored through cyclic voltammetry (CV), galvano-
static charge-discharge limiting (GCPL), electrochemical impedance spectroscopy (EIS), and cyclic stability test. To verify the charge-storage capability of the PAQS-SWCNTs through pseudocapacitive or EDL phenomenon, CV characterization was performed at various scan-rates with a broad applied potential from 0 V to 3 V (Fig. 2a). The CV curves of PAQS-SWCNTs displayed a distinct redox behavior due to the presence of stable carbonyl groups on the PAQS-skeleton. Therefore, capacitance of the PAQS-SWCNTs electrode derived mainly from the Faradaic reactions at the electrode, which is distinctive from that of the EDL capacitance of carbon-based electrode materials. A pair of redox waves is resolved at 0.83 and 1.65 V, respectively. A redox pair of the polymer moiety is attributed to the steady one-electron reduction of quinone to semi-quinone and then to dianion quinol associated by the migration of Li-ions to the carbonyl groups of the PAQS (Scheme 1b). Furthermore, CV curves of the working electrodes at various scan sweeps retained the original shape, which reveals their electrochemical stability. The characteristic charge-voltammetry curves of the SCs based on PAQS-SWCNTs electrodes were

![Graphs and figures showing CV curves, charge-discharge curves, specific capacitance, Ragone plot, cyclic stability, and EIS spectra.](https://doi.org/10.1007/s10118-020-2378-x)
recorded at various current densities for coin cell as given in Fig. 2(b). The charge-discharge (CD) curves indicate redox behaviour with voltage-time response and depict linear relationship. Even at higher current density of 4 A·g⁻¹ redox behaviour in CD curve is unchanged in shape, suggesting the fast-ion Li⁺ and electron transportation occurred on the surfaces of PAQS-SWCNTs electrodes and electrolyte. The CD curves of PAQS-SWCNTs electrodes are not straight and showing lobes on their shoulders, which make clear that redox reactions took place during the capacitance storage. These results are consistent with the CV curves. The galvanostatic discharge method is the most accepted measurement method for determining the capacities of SCs.[42] Hence, the specific capacitance of PAQS-SWCNTs based coin SCs is evaluated from the discharge curve using Eq. S1 (in ESI) and was found to be 223 F·g⁻¹ at 0.5 A·g⁻¹ (Fig. 2c). The high capacitance and the fast ion transfers can be assigned to the stable carbonyl moiety on the skeleton of PAQS without side reactions. The main contribution of SWCNTs in the fabricated electrodes is to anchor the PAQS particles and provide high enough conductivity due to its porous skeleton that enhances the SCs performance.[43] Furthermore, the charge-discharge current of the PAQS-SWCNTs electrodes ensured no noticeable insulation resistance at a higher current density of 4 A·g⁻¹, signifying minor electrode resistance. Over the observed current densities (0.5 A·g⁻¹ to 20 A·g⁻¹), the calculated specific capacitance of PAQS-SWCNTs electrodes decreases gradually with the increase in current density (Fig. 2c). However, the electrode still holds a specific capacitance of 55 F·g⁻¹ at 20 A·g⁻¹ current density, demonstrating that the fabricated electrode could be operated at a very high current density to allow the rapid charge and power supply. In order to confirm the capacitive contribution of pure SWCNTs, electrochemical performances (CV and CD tests) were also tested as described by Figs. S2(a)–S2(c) (in ESI). Consequently, the pure SWCNTs electrodes offered 11.3 F·g⁻¹, showing that the PAQS film was fabricated with the polytetrafluorethylene (PTFE) binder at a weight ratio of 8:2. However, the film did not show any conductivity on the Keithley 4200-SCS electrometer at room temperature. It is well conversant to say that the PAQS film was fabricated with the polytetrafluorethylene (PTFE) binder at a weight ratio of 8:2. However, the film did not show any conductivity on the Keithley 4200-SCS electrometer at room temperature. It is well conversant to say that the PAQS film was fabricated with the polytetrafluorethylene (PTFE) binder at a weight ratio of 8:2. However, the film did not show any conductivity on the Keithley 4200-SCS electrometer at room temperature. It is well conversant to say that the PAQS film was fabricated with the polytetrafluorethylene (PTFE) binder at a weight ratio of 8:2. However, the film did not show any conductivity on the Keithley 4200-SCS electrometer at room temperature.

### Table 1: Comparison of the fabricated electrode performance with previously reported pseudocapacitive electrode materials in SCs application.

| Material                  | Capacitance (Gravimetric (F·g⁻¹)) | Energy density (Gravimetric (Wh·kg⁻¹)) | Power density (Gravimetric (W·kg⁻¹)) | Potential window | Cycle stability | Electrolyte | Ref. |
|---------------------------|------------------------------------|----------------------------------------|-------------------------------------|------------------|----------------|-------------|------|
| PANI-coated MoO₃-CDC      | 9.7                                | 0.8                                    | 90% @ 1 × 10⁴                       | H₂SO₄            | [44]           |             |      |
| Meso-NiO/Ni-3/CNCs battery | N/A                                | 19.1                                   | 13.6                                |                  |                |             |      |
| Ni₃S₄/rGO                 | 46                                 | 17.2                                   | 80% @ 5000                          | KOH              | [45]           |             |      |
| rGO/MnO₂                  | 202                                | 47.9                                   | 96% @ 8 × 10⁴                       | [C2MIm]BF₆       | [46]           |             |      |
| Ni₃S₄/3D rGO              | 1886                               | 58.9                                   | 92% @ 3 × 10⁴                       | PVA/KOH          | [48]           |             |      |
| rGO-wrapped Fe-doped MnO₂ | 59.4                               | 3.0 × 10⁴                              | 91.6% @ 8000                        | DMF-LiClO₄       | [49]           |             |      |
| HPC/PANI-HPC              | 1080                               | 60.3                                   | 91.6% @ 5000                        | H₂SO₄ NaxSO₄     | [50]           |             |      |
| Nanoporous carbon         | 75.4                               | 1.8 × 10⁴                              | 85% @ 4500                          | H₂SO₄ VOSO₄Sn₂O₆| [51]           |             |      |
| PAQS-SWCNTs               | 223                                | 69                                     | 78.4% @ 3 × 10⁴                     | LITFSI           | This work      |             |      |
EIS was conducted to know the resistance of the flexible PAQS-SWCNTs electrode. **Fig. 2(f)** shows the Nyquist plot, obtained for the flexible electrode after 5, 1000, and 3000 cycles with a frequency range from 0.01 Hz to 100 kHz. The Nyquist plot consists of three parts and each part shows various processes during the electrochemical tests. The diameter of the semicircle corresponds to the charge transfer resistance and interfacial capacitance. Except for the charge-transfer resistance through the surface film/particle interface, some other factors, for example, interparticle electronic resistance, may also impact the width of the semicircle. At very low frequencies, it is a sloping line, which reflects solid-state diffusion, acting likewise to a finite space type Warburg impedance. As diameter of the semicircle reflects the charge transfer resistance $R_{ct}$, a smaller semicircle implies a faster charge transport through the electrode surface. The Nyquist plots of the PAQS-SWCNTs electrode show a smaller semicircle and no obvious increase in resistance when tested after 5, 1000, and 3000 cycles.
cycles, respectively (Fig. 2f). Based on these observations, it has been confirmed that the PAQS-SWCNTs electrodes provide homogeneous pathways for the Li-ion diffusion with no extra resistance during the electrochemical process. This phenomenon could be attributed to the high conduction channels provided by the SWCNTs, which supports the basis for the high performance and long lifetime of the PAQS-SWCNTs electrodes.

In flexible SC, mechanical properties of the flexible electrodes play a key role. Therefore, the stress-strain and nanoindentation tests were conducted for the pure SWCNTs and PAQS-SWCNTs as reported in previous study. To further test the flexibility and performance of the PAQS-SWCNTs films, flexible SCs were assembled by using Al-coated film as packing material and the Al strips as current collectors. A PAQS-SWCNTs film with 3 cm² in width and height as an electrode, celgard separator, and 1 mol L⁻¹ LiTFSI electrolyte were used to assemble a flexible supercapacitor. Fig. 3(a) presents schematic illustration of the assembled SCs. The constructed symmetric SC was remarkably flexible, and illuminated several LEDs when bent at various angles without deteriorating the structural purity of the assembled device as shown by Fig. 3(b). Furthermore, the flexible SC did not offer any changes in the CV and galvanostatic charge-discharge curves when tested at flat, acute and obtuse angle positions as shown by Figs. 3(c) and 3(d) and Fig. S3 (in ESI). Interestingly the CV and charge-discharge curves of the coin and bendable SCs are similar, identifying the electrode stability. Using Eq. S(1) (in ESI), the capacitance of the electrode based on the galvanostatic charge-discharge curves for flexible SC reached 210 F g⁻¹ at 0.5 A g⁻¹ and 47 F g⁻¹ at 20 A g⁻¹ current density (Fig. 3e). The energy density and power density were calculated using Eqs. S(2) and S(3) (in ESI). The flexible SC achieved 63.2 Wh kg⁻¹ energy density at a power density of 90.6 W kg⁻¹ (Fig. 3f). The energy and power densities are the two important parameters to evaluate the performance of SCs and therefore, the aforementioned results for coin and flexible SCs signify their high enough energy storage abilities.

CONCLUSIONS

In conclusion, we prepared a free-standing and binder-free PAQS-SWCNTs electrode, which could be used as an electrode for the rechargeable redox SCs. The PAQS was prepared through the Philips method and successfully acted as a high energy density redox pseudocapacitive material for SCs. In addition, the SWCNTs also provided a random network and interconnected web. The PAQS-SWCNTs electrode in coin and flexible SCs were assembled by using Al-coated film as packing material and the Al strips as current collectors. A PAQS-SWCNTs film with 3 cm² in width and height as an electrode, celgard separator, and 1 mol L⁻¹ LiTFSI electrolyte were used to assemble a flexible supercapacitor. The PAQS-SWCNTs electrode, which is superior to most of the reported electrode materials with a working voltage from 0 V to 3 V, respectively, reached up to 69 Wh kg⁻¹ at a power density of 90.6 W kg⁻¹ with a working voltage from 0 V to 3 V, respectively, which is superior to most of the reported electrode materials used in redox supercapacitors. The PAQS-SWCNTs electrode retained 18 Wh kg⁻¹ energy density even at a power density of 3.8 kW kg⁻¹. Likewise, the PAQS-SWCNTs electrode also exhibited remarkable cyclic stability, which retained 78.4% of the initial specific capacitance after 3 × 10⁷ cycles with a current density of 0.5 A g⁻¹. The cyclic stability and outstanding energy density of fabricated SCs make them superior among the redox supercapacitors and reach the level nearly to lithium-ion batteries. These findings suggest that the carbonyl groups of the PAQS polymer indeed show a successful redox behavior in SCs application. Additionally, the fabrication process of the PAQS-SWCNTs is simple and promising. Hence, we expect that the strategy employed in this paper will provide an exciting avenue for the researchers to integrate the carbonyl-based redox polymers with stable conductive-network and introduce them as novel electrodes for redox SCs with long-cycle life and high energy density.

Electronic Supplementary Information

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