Supporting Information

Self-Assembled Multifunctional Hybrids: Toward Developing High-Performance Graphene-Based Architectures for Energy Storage Devices

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Preparation of Liquid Crystalline Graphene Oxide (LC GO)

Dry expandable graphite flakes (3772, Asbury Graphite Mills USA) were first thermally treated at 1050 °C for 15 s to achieve fully oxidized graphite and preserve the high initial lateral sizes of the graphite flakes. Thermally treated expanded graphite (EG) was used as the starting material for GO synthesis following previously described methods.\textsuperscript{1, 2} In detail, 5 g EG was mixed with 1 L sulfuric acid and stirred in a flask for 24 h. 50 g KMnO\textsubscript{4} was carefully added to the prepared mixture. The final mixture was transferred into an ice bath, and 1 L Milli-Q water and 250 mL H\textsubscript{2}O\textsubscript{2} were poured slowly into the mixture, resulting in a minute color change of the suspension to light brown. After 30 min additional stirring, the GO particles were washed through centrifugation with a diluted HCl solution (9:1 water: HCl by volume). Liquid crystalline graphene oxide was obtained as an aqueous dispersion by washing with Milli-Q water until the pH of the solution was about 5-6. The resultant ultra-large GO sheets were highly dispersed in deionized water by gentle shaking (i.e., without the aid of a sonication process).
Figure S1. (a) Cross-sectional FE-SEM image, (b) surface FE-SEM image, (c) TEM image and (d) high resolution C1s XPS spectra of as-prepared LC GO.
1 Table S1. Conductivity of the rGCNTPP composites compared to similar flexible composites for energy storage application.

| Composite                        | Conductivity       | Ref.          |
|----------------------------------|--------------------|---------------|
| rGCNTPP 5                        | 32100 ± 7062 S m⁻¹ | Present study |
| rGCNTPP 10                       | 38700 ± 7987 S m⁻¹ | Present study |
| rGCNTPP 15                       | 26900 ± 5631 S m⁻¹ | Present study |
| rGO/PANI                         | 15 Ω sq⁻¹          | 3            |
| rGO/PVP                          | 247.9 S m⁻¹        | 4            |
| PPy nanofibre/Graphene            | 142.08 S cm⁻¹      | 5            |
| SWCNT/PTS bucky paper            | 220 ± 60 S cm⁻¹    | 6            |
| GN-PPy/CNT                       | 15.3 S cm⁻¹        | 7            |
| GNR-CNT/PANI                     | 180 S cm⁻¹         | 8            |
| MWCNT/PANI                       | 331 S cm⁻¹         | 9            |
| Crystalline PANI/rGO film        | 906 S cm⁻¹         | 10           |
| rGO-CNT (6:1) paper              | 360 S cm⁻¹         | 11           |
| rGO fibre                        | 280 S m⁻¹          | 12           |
| SWCNT/PANI                       | 1138 S cm⁻¹        | 13           |
| Graphene/PEDOT hydrogel          | 0.73 S cm⁻¹        | 14           |
| LC GO/SWCNT                      | 15000 S m⁻¹        | 15           |
| rGO paper                        | 32.8 S cm⁻¹        | --           |
| PEDOT:PSS paper                  | 1 S cm⁻¹           | --           |
Structural and Quantitative Analysis of the Layer-by-Layer Ternary Composite

FT-IR analysis

The presence of PEDOT:PSS in the final composite can be confirmed by the FT-IR spectra of rGO, PEDOT:PSS, and rGCNTPP composites. Compared with rGO and PEDOT:PSS, the rGCNTPP 5 composite shows the characteristic peaks of PEDOT:PSS in Figure S2. Peaks at 979, 834, and 687 cm\(^{-1}\) can be assigned to the C‒S bond of the thiophene ring in PEDOT. The bands at 1200, 1095, and 1034 cm\(^{-1}\) are ascribed to stretching modes of the alkylenedioxy group. Vibrations below 600 cm\(^{-1}\), the S=O vibration near 1200 cm\(^{-1}\), and the O‒S‒O signal at 1034 cm\(^{-1}\) are identical to those for the sulfonic acid group of the PSS chain. The following results compared with the pure PEDOT:PSS spectra certainly prove the presence and structural stability of interlayer nano-assembled PEDOT:PSS in the rGCNTPP composites.

Figure S2. Structural characterization and effects of chemical reduction of the as-prepared rGCNTPP composites on the polymer integrity: FT-IR spectra of (1) rGO, (2) PEDOT:PSS and (3) rGCNTPP 5 composite.
UV-Vis analysis

The UV-Vis spectra of the as-prepared rGCNTPP composites compared with rGO, PEDOT:PSS, and GCNTPP (Figure S3) reveal the stability of the PEDOT:PSS after chemical reduction. The characteristic absorption peaks for MWCNTs and PEDOT:PSS at 200 and 225 nm, respectively, are noticeable before and after chemical reduction of the composites.\(^3\) No superfluous absorption peaks are obtained, and the peak at 227 nm for GO is shifted to 265 nm as deoxygenation takes place, suggesting that the electronic conjugation is restored.\(^{18}\)

Figure S3. UV-Vis spectra of (1) PEDOT:PSS, (2) GCNTPP 5, (3) rGO, and (4) rGCNTPP 5 show the effects of the chemical reduction of the as-prepared composites and the stability of the PEDOT:PSS.
EDS analysis

The as-prepared ternary rGCNTPP composites contain different amounts of PEDOT:PSS on
the MWCNTs that are decorated on the chemically reduced GO sheet surfaces. The contents
of PEDOT:PSS were determined by EDS spectroscopy of the film (Figure S4) and are listed
in Table S2. By comparing the existing sulfur atom ratio in commercial PEDOT:PSS and in
the as-prepared composites, we have calculated the total PEDOT:PSS content in the
rGCNTPP composites. As we have predicted, it can be briefly stated that an increased
amount of MWCNTs influences the polymer content in a negative way. The highest amount
of PEDOT:PSS, incorporation of 20%, is observed in the rGCNTPP 5 composite, and the
amount decreases to 16 and 9% for rGCNTPP 10 and rGCNTPP 15, respectively. The atomic
percentage of C noticeably increases with an increasing amount of carbon-rich MWCNTs in
the composite. As the PEDOT:PSS is attached to the MWCNT decorated GO sheets, a very
thin polymer layer can influence the appearance of interlayer CNTs. Small amounts of
MWCNTs (5 wt%) leave comparatively more functional space on the GO sheet surface and
allow the interaction of more PEDOT:PSS on it, making the MWCNT network less visible
[Figure 3(a-b)]. Whereas, a higher ratio of MWCNTs (15 wt%) decreases the interacting
PEDOT:PSS content and makes the MWCNT network more visible [Figure 3(c)]. High
resolution TEM images reveal the homogeneous distribution of MWCNTs in the
PEDOT:PSS on the GO layers [Figure 3(a-c(v))].
Figure S4. Elemental mapping images of carbon (C) and sulfur (S) in the rGCNTPP composites. The uniformly distributed sulfur in the elemental mapping images of the rGCNTPP composites clearly indicates the homogeneous distribution of PEDOT:PSS in the layered structure.

Table S2. Atomic percentage compositions of the as-prepared rGCNTPP composites from EDS analysis.

| Material        | C (at. %) | O (at. %) | S (at. %) | PEDOT:PSS content (%) |
|-----------------|-----------|-----------|-----------|------------------------|
| PEDOT:PSS       | 69.75     | 22.71     | 7.54      | 100                    |
| rGO             | 76.49     | 23.51     | 0         | 0                      |
| rGCNTPP 5       | 79.12     | 19.69     | 1.51      | 20.02                  |
| rGCNTPP 10      | 81.09     | 17.72     | 1.19      | 15.78                  |
| rGCNTPP 15      | 82.03     | 17.29     | 0.68      | 9.02                   |


XPS analysis

The elemental composition and the PEDOT:PSS content in the rGCNTPP composites were also evaluated by XPS analysis (Figure S5 and Table S3). The core level C 1s XPS spectra [Figure S5(a)] reveal several carbon groups in PEDOT:PSS such as C=C at 284.1 eV, C-C at 285.3 eV, C-S at 286.5 eV, and C-O-C/C=O at 288.3 eV. The peaks were slightly shifted for the composites in Figure S5(b-d) and reveal four peak components with binding energies at about 284.4, 285.5, 286.6, and 287.5 eV, which can be assigned to the C=C, C-C, C-S, and C-O/C=O/O-C=O species, respectively. This is due to the electron contribution of PEDOT:PSS to the reduced graphene oxide surface through the strong π-π interaction.

Comparing with the LC GO (Figure S1) the oxygen ratio was decreased to one third of the carbon ratio as an effect of chemical reduction, although certain amounts of oxygenated groups are still present. Moreover, with increasing CNT content in the composites, the significant decrease in the C-S bond ratio from 1.53% (rGCNTPP 5) to 0.69% (rGCNTPP 15) indicates a similar change in the amount of interlayer PEDOT:PSS to that revealed by EDS analysis. The S 2p signal intensity of the rGCNTPP composites compared to rGO and PEDOT:PSS [Figure S5(e)] strongly indicates that the amount of sulfur-containing PEDOT:PSS decreases significantly with increased MWCNT content. The high resolution S 2p spectra of rGCNTPP 5 [Figure S5(f)] can be deconvoluted into peak at 165 eV for the sulfur atom of PEDOT and peak at 169.1 eV for the sulfur atom of PSS which represents the ratio of PEDOT:PSS (26:74) in the rGCNTPP composites. This analysis evidenced that the centrifugation and low temperature reduction doesn’t change the ratio of PEDOT to PSS and remain same like the commercial PEDOT:PSS (27:73) obtained by similar technique.
Figure S5. XPS core level C 1s spectra of (a) PEDOT:PSS, (b) rGCNTPP 5, (c) rGCNTPP 10, and (d) rGCNTPP 15 composites; and (e) survey spectra of (1) rGO, (2) PEDOT:PSS, (3) rGCNTPP 5, (4) rGCNTPP 10, and (5) rGCNTPP 15, revealing the residual oxygen content in the composites along with the presence of sulfur in PEDOT:PSS. The S 2p signal intensity decreases with increasing amounts of MWCNTs in the composites and indicates a decrease in the effects of PEDOT:PSS; (f) high resolution S 2p XPS of rGCNTPP 5 represents the ratio of PEDOT and PSS in the final composite.
Table S3. Elemental compositions of the as-prepared rGCNTPP composites obtained from XPS analysis.

| Material     | C (at. %) | O (at. %) | S (at. %) | PEDOT:PSS content (%) |
|--------------|-----------|-----------|-----------|------------------------|
| PEDOT:PSS    | 69.61     | 22.76     | 7.63      | 100                    |
| rGO          | 77.42     | 22.58     | 0         | 0                      |
| rGCNTPP 5    | 79.63     | 18.84     | 1.53      | 20.03                  |
| rGCNTPP 10   | 81.35     | 17.43     | 1.22      | 15.99                  |
| rGCNTPP 15   | 82.47     | 16.84     | 0.69      | 9.04                   |

Table S4. Composition of the rGCNTPP composites.

| Sample      | PEDOT:PSS (%)\(^{a}\) | MWCNTs (%)\(^{b}\) | rGO (%)\(^{c}\) |
|-------------|------------------------|--------------------|-----------------|
| rGCNTPP 5   | 20.03 (26:74)          | 4                  | 75.97           |
| rGCNTPP 10  | 15.99 (26:74)          | 8.4                | 75.61           |
| rGCNTPP 15  | 9.04 (26:74)           | 13.61              | 77.35           |

\(^{a}\) calculated from the XPS analysis. \(^{b, c}\) calculated by consideration of the ternary components in final composition.
XRD analysis

In considering the layered structure of rGO, the ternary composites present distinct structural changes as an effect of the interlayer nano-assembled components, as shown in Figure S6(a). The XRD pattern of the as-prepared rGO shows a characteristic peak at 23.80°, corresponding to a $d$-spacing of 3.73 Å for typical rGO sheets. The introduction of 5, 10, and 15% MWCNTs into the composites along with the PEDOT:PSS downshifts the characteristic peak of rGO to 16.57, 14.6, and 13.8°, respectively, which is analogous to $d$-spacing of 5.35, 6.06, and 6.41 Å, representing the distances between neighboring composite layers. Small amounts of MWCNTs allow greater interaction with PEDOT:PSS, which increases the self-assembled graphene oxide sheet thickness and affects the interlayer $d$-spacing. The characteristic peak of rGO content in the rGCNTPP composites is broad, due to the impact of the PEDOT:PSS content in the composites and its characteristic peaks at 16° and 25° [Figure S6(b)].

![Figure S6. Structural characterization of as-reduced layer-by-layer 3D architecture. (a) XRD spectra of as-prepared flexible composites: (1) rGO, (2) rGCNTPP 5, (3) rGCNTPP 10, (4) rGCNTPP 15; and (b) XRD spectrum of commercial PEDOT:PSS film obtained by solution casting.](image-url)
Specific surface area analysis by the BET method

The interlayer nano-assembly of MWCNTs-PEDOT:PSS prevents the restacking of graphene sheets in the rGCNTPP composites. Furthermore, the simultaneous decoration of MWCNTs and PEDOT:PSS polymer chains takes place prior to the self-assembly of the graphene oxide sheets in the layer-by-layer growth of the structure (Figure 1), where it plays a very crucial role in separating the layers and providing higher specific surface area as a flexible 3D architecture (Figure S7 and Table S5). We have provided evidence that with the insertion of more MWCNT content, the amount of PEDOT:PSS decreases, which may leave more interlayer space vacant in the layered architecture and provide higher specific surface area.

Figure S7. (a) Nitrogen adsorption-desorption isotherms and (b) multipoint BET graph of rGCNTPP 10 composites. The specific surface area of the composite was calculated from the BET equation by using the slope of the straight line.
Table S5. Comparison of specific surface areas of rGCNTPP composites and rGO prepared in this study, obtained by N₂ adsorption (BET method).

| Composite    | Surface area (m² g⁻¹) |
|--------------|------------------------|
| rGO          | 93                     |
| rGCNTPP 5    | 216                    |
| rGCNTPP 10   | 278                    |
| rGCNTPP 15   | 291                    |

Thermogravimetric analysis

The naturally interacting interlayers of MWCNTs-PEDOT:PSS have an impact on the thermal stability of the composites, as shown in Figure S8. The mass loss between 100-200 °C is due to the pyrolysis of the residual oxygen-containing groups and volatilization of water involved in the π-π interaction.²¹ The as-prepared composites show better thermal stability than rGO, with major degradation starting at temperatures over 250 °C due to the PEDOT:PSS content. Increasing the amount of MWCNTs affects the content of PEDOT:PSS and hence, the thermal stability of the as-prepared composites. According to the EDS and XPS analysis, the rGCNTPP 5, 10, and 15 composites contain 20, 16, and 9% PEDOT:PSS, respectively. This can be correlated and compared with the weight loss of rGO, PEDOT:PSS, and the composites at 700 °C. The thermal stability of rGO and the rGCNTPP 5, 10, 15 composites results in 79, 70, 74, and 76% weight loss correspondingly, which may be due to the strong interaction of the 20, 16, and 9% PEDOT:PSS on the MWCNTs that are decorated on the rGO sheets and the 56% degradation of the adsorbed PEDOT:PSS at 700 °C.
Figure S8. TGA analysis of the rGCNTPP composites compared with rGO and PEDOT:PSS in argon.

Mechanical performance

A conducting polymer (CPs) is basically a charged backbone where the band structure of the π-electron system of the polymer allows the formation of charge-transfer complexes with oxygen, which cause the polymer chains to become unstable and mechanically weak, whereas the graphene oxide layers are more stable and provide excellent flexibility in the stacked film form. Simple solution mixing of CP and GO directs the insertion of CPs into the graphene oxide layers without any chemical interaction. In this kind of structure, flexible GO layers are separated by unstable and mechanically rigid CP layers, resulting in interruption to the natural mechanical nature of GO film. For this reason, the combination of CPs with graphene oxide can certainly decrease the mechanical performance of the composite. Moreover, increasing the CP content effectively increases the thickness of the CP layers and continues this degradation of mechanical properties.
In our previous study, we used a controlled amount (25, 50 and 75%) of PEDOT:PSS and mixed it mechanically with graphene oxide to prepare binder-free composite electrode. Without any chemical interaction between the graphene oxide and the PEDOT:PSS, the polymer chains act as independent $\pi$-conjugated structures and are naturally unstable as a pure charged backbone in the composite. For this reason, the rGO-PP composites become less flexible compared to rGO film and more rigid with increasing PEDOT:PSS content, which causes poorer mechanical performance than for chemically reduced graphene oxide film. The aggregate-free nature and self-assembly properties of our present composites have enabled us to obtain an ultra-strong layered 3D architecture. As reported by Rouff et al., excellent mechanical properties can be achieved by the ordering and alignment of fibrils/macromolecules. Compared to multidirectional oriented composites prepared by traditional casting or filtration, the liquid crystalline route and homogeneous nano-assembly of MWCNTs – conductive polymer (CP) in our rGCNTPP composites provide us with a self-mediated ordered periodic assembly, resulting in better mechanical strength compared to rGO and similar reported graphene-based composites. The mechanical performance is proportional to the amount of MWCNTs. The nano-engineered flexible rGCNTPP composites showed satisfactory mechanical performance compared to rGO and the reported flexible composite electrodes (Figure S9, Table S6).
**Figure S9.** Stress-strain curves of rGCNTPP 5, rGCNTPP 10, and rGCNTPP 15 composites.

**Table S6.** Mechanical properties of the free-standing rGCNTPP composite films (thickness: 8-11 µm).

| Composite          | Young’s modulus (GPa) | Tensile Strength (MPa) | Break elongation (%) | Toughness (MJ m⁻³) | Ref.            |
|--------------------|-----------------------|------------------------|----------------------|---------------------|-----------------|
| rGCNTPP 5          | 23.6                  | 217                    | 6.8                  | 5.4                 | Present report  |
| rGCNTPP 10         | 26.1                  | 252                    | 7.5                  | 7.3                 | Present report  |
| rGCNTPP 15         | 29.2                  | 287                    | 7.9                  | 9.1                 | Present report  |
| rGO                | 12.1                  | 119                    | --                   | --                  | --              |
| PEDOT:PSS          | 3.8                   | 27                     | --                   | --                  | 27              |
| rGO/PANI           |                      |                        |                      |                     |                 |
| rGO/PVP            | 9.5 ± 0.8             | 121.5 ± 10.8           |                      |                     | 4               |
| PPy                | 2.1                   | 35                     |                      |                     | 5               |
| nanofibre/Graphene |                      |                        |                      |                     |                 |
| GO/SWCNT           | 51.3                  | 505                    | 9.8                  |                     | 15              |
| SWCNT/PTS          | 2.0 ± 0.3             | 15 ± 6                 | 0.05 ± 0.03          |                     | 6               |
| GO/PPA             | 33.3 ± 2.7            | 91.9 ± 22.4            |                      |                     | 28              |
|                  | Values         | References |
|------------------|----------------|------------|
| **LBL MWCNTs**   |                |            |
| nanocomposite    | 4.5 ± 0.8      | 29         |
|                  | 150 ± 35       |            |
| **LBL PVA/MTM/GA** |                |            |
| nanocomposite    | 106 ± 11       | 30         |
|                  | 400 ± 40       |            |
| **Graphene paper** |                |            |
| Prepared by vacuum | 41.8          | 26         |
| filtration       | 293.3          |            |

* Toughness of the composites was calculated by using the formula: $U = \frac{E \varepsilon^2}{2}$, where $E$ is the Young’s modulus and $\varepsilon$ is the strain.
Cyclic voltammograms of rGO, PEDOT:PSS, and the rGCNTPP composites at 5 mV s\(^{-1}\) are presented in Figure S10(a). At the same scan rate, there is significant current separation in the as-prepared composites compared to rGO and PEDOT:PSS, demonstrating the substantial influence of the MWCNTs-PEDOT:PSS conductive network on the chemically-reduced graphene oxide layered composites. The almost rectangular cyclic voltammograms of rGO have been slightly distorted and significantly enlarged for the different rGCNTPP composites, which can be attributed to the \(\pi-\pi\) interaction of MWCNTs and PEDOT:PSS on the graphene sheets. Using Equation (1), we have calculated the specific capacitances \((C_s)\) from the CVs at 5 mV s\(^{-1}\) and plotted them against the PEDOT:PSS content to further highlight the synergetic effect of MWCNTs and PEDOT:PSS in various ratios between the final composite layers [Figure S10(b)]. Increasing the amount of MWCNTs decreases the content of interlayer nano-assembled PEDOT:PSS and has an impact on the overall electrochemical performance of the composite.

Small amount of MWCNTs (5\%) allow more PEDOT:PSS interaction (20\%) on the rGO-CNT network which results high conductivity (32100 S m\(^{-1}\)) but this certain amount of polymer interaction make the ion conductive channels narrower (evidenced by the XRD) thus partially hinder the electrolyte ion transportation throughout the electrode surface, \(\frac{31}{g}\) decrease the charge transport as well as charge storage capacity and a specific capacitance of 593 F g\(^{-1}\) can be observed. The ion transport is enhanced in rGCNTPP 10 with 10\% MWCNTs and 16\% PEDOT:PSS. This particular ratio of MWCNTs to PEDOT:PSS represent the most suitable combination for facilitating the depletion of graphene sheets agglomeration, spacing between the successive graphene layers which assist abundant space to fabricate PEDOT:PSS coated superfast conductive network (38700 S m\(^{-1}\)) by continuous ion passing and an increase of effective surface area for provision of huge charge storage facility. All these properties
reinforce the synergistic effects of the components, so that they provide the layer-by-layer architecture with continuous conductive channels of MWCNTs-PEDOT:PSS on rGO support that lead to a highly conductive advanced specific surface area for higher specific capacitance of 657 F g⁻¹ compared to rGCNTPP 5.

**Figure S10.** Electrochemical performance of rGCNTPP composites in a three electrode system: (a) comparison of cyclic voltammograms of rGO, PEDOT:PSS, and rGCNTPP composites at 5mV s⁻¹; (b) effects of PEDOT:PSS content on the specific capacitance of the as-prepared composites at 5mV s⁻¹; (c) variation of the specific capacitance at different scan rates; and (d) cyclic voltammograms of rGCNTPP 10 composite at different scan rates.

On the other hand, the rGCNTPP 15 composite with the highest amount of MWCNTs (15%) experience intermittent self-agglomeration and provides the least functional space for PEDOT:PSS, and leading to only 9% PEDOT:PSS interaction on rGO surface. This agglomerated MWCNTs and discontinuous π–π interaction of PEDOT:PSS form an improper interlayer conductive network with rGO (26900 S m⁻¹). Though MWCNTs inhibit the
restacking of graphene sheets and results a bit higher specific surface area of rGCNTPP 15
compare to others but due to the insufficiency of conductive PEDOT:PSS continuous layer
with rGO-MWCNTs network, the performance of the composite as an charge storage and
charge transportation network drops down. Hence rGCNTPP 15 features less capacitive and
less conductive rGO/MWCNTs/PEDOT:PSS scaffolding compared to former, displaying
specific capacitance of 561 F g⁻¹.

To clarify the electrochemical consistency of the self-assembled rGCNTPP 3D
architectures, we have carried out a scan rate study [Figure S10(c)], which can be directly
correlated with the power capability of the electrode. At higher scan rates, electrolyte ions do
not get sufficient time to occupy all the available sites for charge storage, and there is an
expected reduction in specific capacitance with increasing scan rate. Higher scan rates also
affect the capacitance due to the effect of low resistivity between the electrolyte and the free-
standing electrodes. This is evidenced by the greater distortion in the shape of the cyclic
voltammograms [Figure S10(d)] and the drop in capacitance at higher scan rates [Figure
S10(c)].
Performance of the Asymmetric Supercapacitor

Figure S11. Galvanostatic charge-discharge profiles of the ASC at different current densities.

Figure S12. IR drops of ASC device at different current densities; insets represent the relevant magnified parts of the charge discharge profiles.
Table S7. Values of specific capacitance of single electrode in the ASC, total capacitance of ASC device, energy density ($E$), and power density ($P$) obtained by galvanostatic charge-discharge testing.

| Current density | Specific capacitance of single electrode in the ASC [C_s (F g^{-1})] | Total capacitance of the ASC device [C_T (F g^{-1})] | Energy density [E (Wh kg^{-1})] | Power density [P (W kg^{-1})] |
|----------------|-------------------------------------------------|---------------------------------|-----------------|------------------|
| 1 A g^{-1}     | 328                                             | 82                              | 11.4            | 145              |
| 2 A g^{-1}     | 305                                             | 76.25                           | 10.37           | 292              |
| 5 A g^{-1}     | 278                                             | 69.5                            | 9.27            | 902              |
| 10 A g^{-1}    | 266                                             | 66.5                            | 8.7             | 2235             |

The following equations from reports in the previous literature have been used to analyze the electrochemical performance:

\[
C_s = \frac{1}{m \nu (V_a - V_c)} \int_0^{0.9} I(V) dV
\]  

(1)

Where \( C_s \) is the specific capacitance in a three electrode system, \( m \) is the mass of active material (rGCNTPP) (g), \( \nu \) the scan rate (mV s\(^{-1}\)), \( I \) the current, and \( V \) the voltage, while \((V_a - V_c)\) represents the potential window and the integrated area under the cyclic voltammograms.

\[
C_s = \frac{1}{m \pm \nu (V_a - V_c)} \int_0^{1} I(V) dV
\]  

(2)

Here, \( C_s \) is the specific capacitance of a single electrode in the ASC cell; \( m \pm \) is the total mass of the cathode and anode electrodes in grams.

\[
C_T = \frac{I \times \Delta t}{\Delta V \times m \pm}
\]  

(3)

\[
C_s = 4 \times C_T
\]  

(4)

Where \( I \) is the discharge current in Amperes, \( \Delta t \), the discharge time in seconds, \( \Delta V \), the voltage change in the discharge process excluding the \( IR \) drop, \( m \pm \), the total mass of both electrodes in grams, and \( C_T \) is the total capacitance of the ASC cell. The multiplier of 4 adjusts the capacitance of the cell to the mass of a single electrode.

Volumetric capacitance (F cm\(^{-3}\)) of the free-standing ternary composite electrode was calculated based on the volume \( v \) (cm\(^3\)) of the electrode according to the following formula:

\[
\text{Volumetric capacitance} = \frac{C_s \times m}{v}
\]  

(5)

Where \( C_s \) is the specific capacitance and \( m \) is the mass of electrode.

The energy density \( (E) \) and power density \( (P) \) of the assembled ASC device calculated from the following formula:
\[ E = \frac{1}{2} C_T (\Delta V)^2 / 3.6 \] (6)

\[ P = \frac{E \times 3600}{t} \] (7)

Where \( C_T \), \( \Delta V \), and \( t \) are the total capacitance of the ASC device, the potential window (\( V \)) of the supercapacitor, and the discharge time (\( s \)) respectively.

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