



Capillary slit induced graphene laminate films towards enhanced areal capacitive energy storage

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Graphene, self-assembly, nanostructures, oxygen-containing functional groups, areal capacitance, supercapacitor

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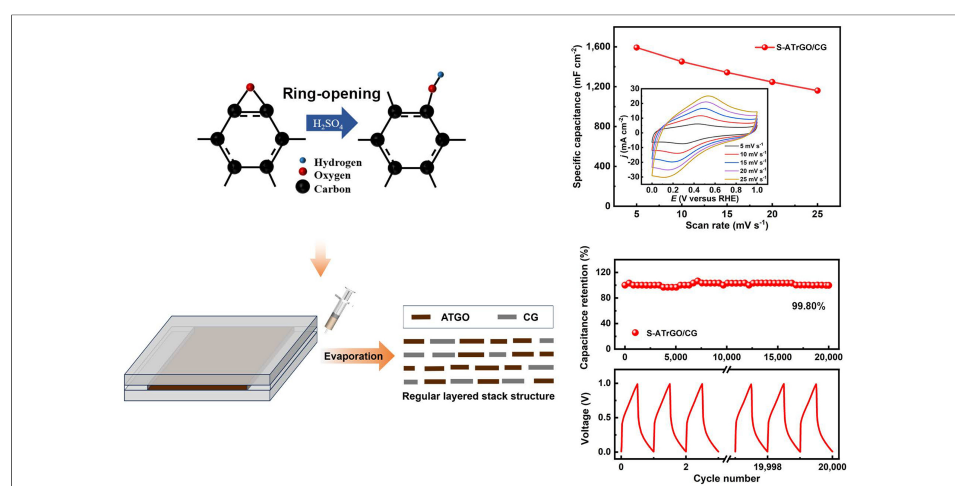
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Abstract

This study presents a novel slit evaporation self-assembly method for fabricating freestanding sulfuric acid-treated reduced graphene oxide/commercial graphene films (S-ATrGO/CG). The unique capillary slit-induced self-assembly process facilitates the alignment and stacking of graphene flakes, resulting in a well-ordered, laminated film. The treatment of graphene oxide (GO) with sulfuric acid facilitates the ring-opening of inert functional groups, converting them into active functional groups. Sulfuric acid-treated graphene oxide (ATGO) can serve as an effective binder for adhering commercial graphene flakes. X-ray photoelectron spectroscopy was used to quantitatively analyze the oxygen-containing functional groups in GO, ATGO, and S-ATrGO/CG. A series of electrochemical tests were conducted to investigate the behavior of the S-ATrGO/CG films, which exhibited well-defined redox peaks, indicating the contribution of unreduced oxygen-containing groups to redox reactions and pseudocapacitance. The S-ATrGO/CG films exhibit superior electrochemical performance, with an ultra-high area-specific capacitance of 1,589.78 mF cm⁻² at a scan of 5 mV s⁻¹ and an impressive initial capacitance retention of 99.80% after 20,000 cycles at a current density of 50 mA cm⁻². This study highlights the potential of S-ATrGO/CG films as high-performance electrodes for supercapacitors, contributing to the advancement of sustainable energy storage systems.

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INTRODUCTION

Nowadays, the escalating demand for future flexible devices, micro-energy storage systems, smart textiles, and other surface-constrained applications has triggered a heightened focus on areal specific capacitance. This metric directly quantifies the performance of energy storage systems in terms of capacitance per unit area, which is crucial for optimizing the efficiency and functionality of these advanced technologies^[1-4]. Graphene emerges as a highly promising electrode material for supercapacitors with ultrahigh areal specific capacitance due to its distinctive two-dimensional structure, large surface area, high conductivity, and excellent physicochemical stability^[5-8]. Moreover, recent reports have demonstrated that properly engineered graphene-based architectures can exploit pseudocapacitive behavior and hierarchical structures to significantly improve both areal capacitance and cycling stability^[9-11]. Nevertheless, the spontaneous clustering and re-stacking of graphene sheets often lead to decreased surface area and a porous structure with low density, limiting its efficacy in high-energy-density devices^[12,13]. To address these challenges, the strategic design of layered-stacked graphene structures is proposed. This approach can effectively counteract sheet re-stacking, establish efficient pathways for ion transport, and enhance spatial utilization, showcasing the immense potential of developing next-generation electrode materials^[14-16]. Scrape-coating, hand-rolling, and controlled evaporation are the typical methods used to prepare aligned graphene sheets with high integrity and good conductivity^[17-21]. Notably, Kim *et al.* discovered that graphene oxide (GO) aqueous dispersions can spontaneously form nematic liquid crystalline phases, and that the macroscopic alignment of these GO liquid crystals can be effectively controlled by mechanical shear^[22]. However, achieving consistent thickness and uniformity in sheet alignment and structure is still challenging.

There are diverse methods that showcase the ongoing efforts to advance the synthesis of layered-stacked graphene, aiming to improve capacitive performance and versatility^[23-25]. For example, Xin *et al.* reported the precise control of the graphene sheet alignment and orientation order via microfluidics design, in which high thermal, electrical, and mechanical properties are realized^[26]. Lee *et al.* fabricated graphene islands using the chemical vapor deposition method and then stacked the graphene islands and reduced GO (rGO) layer by layer to form large-scale layered graphene, which exhibited a long cycling lifetime and high power density^[27]. Moreover, to further expand the extent of the intrinsic capacitance of graphene building units, creating pores, heteroatom doping, and functionalization are rationally designed^[28-32]. These strategies can not only improve the utilization of the materials but also provide additional redox-active sites (pseudocapacitance). Unlike traditional electric double-layer capacitors, which rely solely on the physical adsorption of charge at the electrode surface, pseudocapacitors combine this process with the chemical redox reactions of pseudocapacitive materials. This dual mechanism enables a higher charge storage capacity^[33,34]. However, the active sites involved in redox reactions within pseudocapacitors often exhibit poor chemical stability and durability over extended cycling periods. This limitation leads to a significant drawback in supercapacitors, as they are unable to maintain their performance during prolonged use^[29].

Oxygen-containing groups on graphene enhance pseudocapacitance by acting as redox-active sites, boosting energy storage in supercapacitors^[35-37]. Functional groups such as hydroxyl (C-OH), carboxyl (O-C=O), and epoxy (C-O-C) can significantly influence the electronic and electrochemical properties of graphene. For instance, hydroxyl and carboxyl groups are known to be active oxygen-containing functional groups that facilitate rapid charge transfer and interaction with the electrolyte^[38]. These groups can participate in redox reactions, thereby increasing the number of available redox sites and improving the overall capacitance and energy storage capabilities of the material^[39]. On the other hand, epoxy groups are considered inert and can impede charge transfer, limiting the electrochemical performance. Therefore, converting these inert groups into more active forms - such as hydroxyl and carboxyl groups - through appropriate pre-treatment and thermal reduction processes will be beneficial for enhancing the electrochemical performance^[40]. However, further research is required to optimize the conversion processes for these inert groups, and to

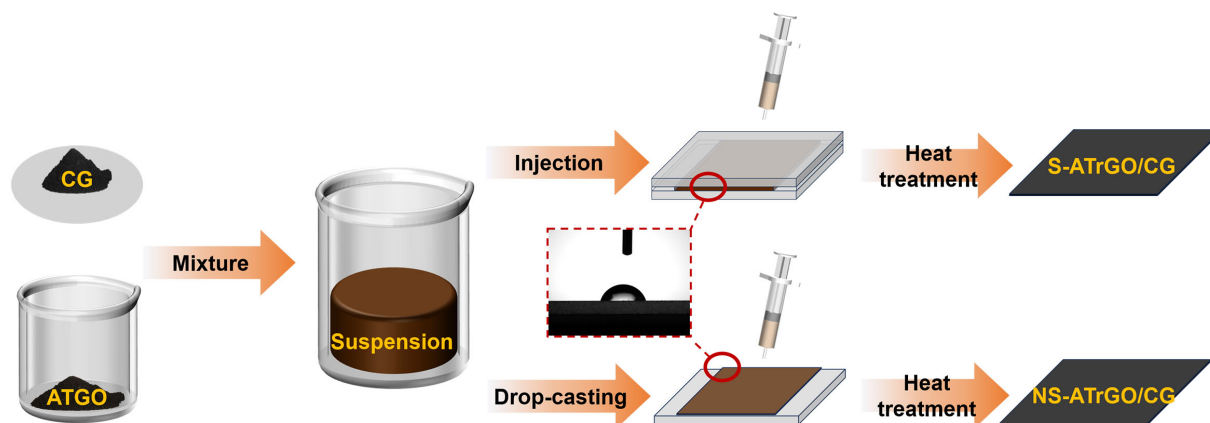


Figure 1. Schematic illustration of graphene electrode preparation by slit evaporation self-assembly method and conventional coating method. Inset shows the contact angle of the slit mold. CG: Commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit.

comprehensively evaluate the performance of modified graphene in various electrochemical applications.

Herein, we report the design of freestanding graphene laminate films, which are achieved through capillary slit-assisted self-assembly of sulfuric acid-treated graphene oxide (ATGO) sheets with commercial graphene (CG), as shown in Figure 1. In brief, a mixed suspension of ATGO and CG was first prepared, and injected into a capillary slit constructed by two glass plates. Upon heating, the ATGO and CG can self-assemble to form uniform laminated macroscopic structures under the action of π - π stacking effect and electrostatic attraction. The ATGO/CG film was then subjected to heat treatment in an Ar atmosphere, yielding the freestanding laminated graphene film [denoted as sulfuric acid-treated reduced graphene oxide (S-ATrGO)/CG]. For the sake of comparison, freestanding graphene films prepared by drop-casting are also shown (denoted as NS-ATrGO, where NS stands for non-slit). Unless otherwise mentioned, the CG content used in both samples is 75 wt.%. The resultant S-ATrGO/CG film exhibits an ultrahigh areal capacitance of $1,589.78 \text{ mF cm}^{-2}$ at 5 mV s^{-1} , as well as excellent cycling stability (99.80% capacitance retention after 20,000 cycles). Moreover, it shows a high energy density of 0.22 mWh cm^{-2} and a power density of 8.69 mW cm^{-2} . The capillary slit self-assembly process results in S-ATrGO/CG with a high degree of orientation, which enhances electron mobility and heat dissipation. These findings extend the applicability of freestanding graphene across a range of functional applications, including electronics, heat spreaders, energy storage, *etc.*

EXPERIMENTAL

Materials

Graphite powder (325 mesh) and 95% ethanol were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). NaNO_3 , H_2SO_4 , KMnO_4 , H_2O_2 and HCl were supplied by China Medicine Co. Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) was prepared by the equipment of You Pu Ultrapure Technology Co., Ltd. (Sichuan, China) and was used as a solvent in experiments. The CG (90%, industrial grade) was supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). Glass slit molds were fabricated from sailboat slide and were supplied by Haimen Changlong Instrument Co., Ltd. (Haimen, China).

Preparation of ATGO

The GO was synthesized using the Hummers method^[41]. The obtained GO was dispersed in $1 \text{ M H}_2\text{SO}_4$, treated with ultrasonic vibration for 30 min, and subsequently stirred mechanically for 24 h. Afterward, the suspension was washed by repeated centrifugation until a neutral pH was reached, and then freeze-dried for 72 h to yield ATGO^[42].

Preparation of S-ATrGO/CG and NS-ATrGO/CG

The ATGO was configured into a suspension with a concentration of 22 mg mL⁻¹, and CG powder with a mass fraction of 75 wt.% was added to it. Take 2.5 mL of the prepared mixed solution and drop it into a glass mold. The complete slit evaporation self-assembly and coating system was placed in a vacuum drying oven and dried at 60 °C for 48 h. The resulting film, denoted as slit-assisted ATGO/CG (S-ATGO/CG), was then subjected to thermal reduction together with the non-slit-assisted ATGO/CG (NS-ATGO/CG) film. Both films were placed in a tube furnace energized with high-purity argon gas and heated to 350 °C at a heating rate of 2 °C min⁻¹, held for 30 min and then cooled to room temperature in the furnace to obtain S-ATrGO/CG film and NS-ATrGO/CG film. The annealing temperature was set at 350 °C as it represents the optimal balance among electrical conductivity, retention of active functional groups, and electrochemical performance. This temperature can effectively enhance the conductivity of the material while retaining sufficient pseudocapacitive active functional groups. As a result, it significantly improves the electrochemical performance while avoiding the negative effects of high-temperature reduction^[43]. For comparison, a control sample was prepared by replacing ATGO with pristine GO under identical conditions and was denoted as S-OrGO/CG.

Materials characterization

The surface and cross-sectional morphology of the samples were observed using scanning electron microscopy (SEM, Supra 55; Carl Zeiss, Oberkochen, Germany) and laser confocal microscopy (LEXT OLS3000; Olympus, Tokyo, Japan). The crystal orientation consistency was analyzed by wide-angle X-ray scattering (WAXS, Xeuss 2.0; Xenocs, Grenoble, France) to investigate the lamellar arrangement of graphene. To determine the degree of orientation in thin-film crystals, the one-dimensional integrated curve was calculated using

$$I(\varphi) = \exp\left(\frac{-4\varphi^2 \ln 2}{\Delta\varphi^2}\right) \quad (1)$$

$$\langle \cos^2\varphi \rangle = \frac{\int_0^\pi \cos^2\varphi I(\varphi) \sin\varphi d\varphi}{\int_0^\pi I(\varphi) \sin\varphi d\varphi} \quad (2)$$

$$f = \frac{3\langle \cos^2\varphi \rangle - 1}{2} \quad (3)$$

where $\Delta\varphi$ is the full width at half maximum of the intensity peak, $I(\varphi)$ is the light intensity per unit area, $\langle \cos^2\varphi \rangle$ is the mean square value of the cosine statistics of poles, and f is the Hermans orientation factor^[44]. X-ray diffraction (XRD, Empyrean) was used to calculate the crystal spacing illustrate the crystal orientation, and qualitatively analyze it. Defects and the degree of reduction in graphene films were analyzed by Raman spectroscopy (LabRAM HR Evolution; Horiba Scientific, Kyoto, Japan). Changes in functional groups were analyzed using Fourier transform infrared (FTIR) spectroscopy (Nicolet iS20; Thermo Fisher Scientific, Waltham, MA, USA) with the potassium bromide (KBr) disk method. Oxygen-containing functional groups were further characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha; Thermo Scientific, Waltham, MA, USA).

Electrochemical performance measurement

The electrochemical performance was analyzed using an electrochemical workstation (CHI760E; CH Instruments, Austin, TX, USA). The as-prepared electrodes were tested in a three-electrode system using 1 M H₂SO₄ as the electrolyte, Pt electrode as the counter electrode, Ag|AgCl (filled with 3 M KCl and having a potential relative to the standard hydrogen electrode of 0.236 V) as the reference electrode, and a working electrode area of 1 cm² for the graphene film.

To further validate practicality, the electrochemical performance of the S-ATrGO/CG//S-ATrGO/CG CR2032 coin cell symmetric supercapacitor (SSC) was characterized by assembling it with a separator (GF/D6227; Oleggeino, China) soaked in 1 M H₂SO₄ aqueous solution and sandwiched between the cathode and anode electrodes. All tests were conducted at room temperature. The areal capacitance $C_{\text{area,electrode}}$ and volume capacitance $C_{\text{volume,electrode}}$ were calculated using

$$C_{\text{area, electrode}} = \frac{1}{S_{\text{electrode}} \nu \Delta V} \int I(V) dV \quad (4)$$

$$C_{\text{volume, electrode}} = \frac{1}{V_{\text{electrode}} \nu \Delta V} \int I(V) dV \quad (5)$$

The energy density (E_A , Wh cm⁻²) and power density (P_A , W cm⁻²) were calculated using

$$E_A = \frac{1}{7200} C_{\text{area}} \Delta V^2 \quad (6)$$

$$P_A = 3600 \frac{E_A}{\Delta t} \quad (7)$$

where I is the current density, ν is the scan rate, ΔV is the potential window, $S_{\text{electrode}}$ is the area of single electrode, $V_{\text{electrode}}$ is the volume of single electrode, and Δt is the discharging time. The thickness of the electrode films was directly measured from the SEM images of the cross-sections. The reported values are the averages of at least five measurements taken at different spots across the cross-section. The volumetric capacitance was then calculated using this thickness and the electrode area (1 cm²).

The exact ratio between diffusion-controlled and capacitive contributions can be quantified based on

$$i(V) = k'_1 \nu + k''_1 \nu + k_2 \nu^{\frac{1}{2}} \quad (8)$$

where $i(V)$ is the current density, V is the potential, ν is the sweep rate. The total capacitance contribution consists of a diffusion-controlled process and a capacitive-controlled section. Additionally, $k'_1 \nu$ is the double-layer current, $k''_1 \nu$ is the pseudo-capacitance current and $k_2 \nu^{\frac{1}{2}}$ is the diffusive current. The k'_1 , k''_1 and k_2 values can be calculated by plotting the linear fitting.

RESULTS AND DISCUSSION

The surface of ATGO is rich in oxygen-containing functional groups, which can serve as direct binding sites for CG as well as grafting sites for CG. These groups can interact with the defects and edges on the CG. Additionally, ATGO and CG can generate electrostatic attraction and van der Waals forces, thereby promoting their interfacial interaction, without the addition of non-active additives (such as binder or conductive agents)^[45]. Meanwhile, the ATGO still retains sp² conjugated domains with aromatic rings, which can interact with the sp² regions of CG through π - π stacking and van der Waals forces. Therefore, the sp³ regions in ATGO provide chemical bonding/anchoring effects, while the sp² regions maintain π - π and van der Waals interactions with CG. The coexistence of these interactions ensures that the composite film possesses strong interfacial adhesion and efficient electron transport capability. Our recent research results indicate that the use of capillary slits constructed from aluminum foil enables the formation of smooth and stacked graphene films covering the surface of the aluminum foil^[46]. Graphene suspensions exhibit a characteristic tendency to align along the liquid/gas interface, and self-supporting graphene electrodes can be prepared by adjusting the contact angle of the slit mold. The XRD patterns of CG are shown in [Supplementary Figure 1](#). From the pattern, it can be observed that there is only one peak at $2\theta = 26.4^\circ$, indicating that CG is a pure graphene structure.

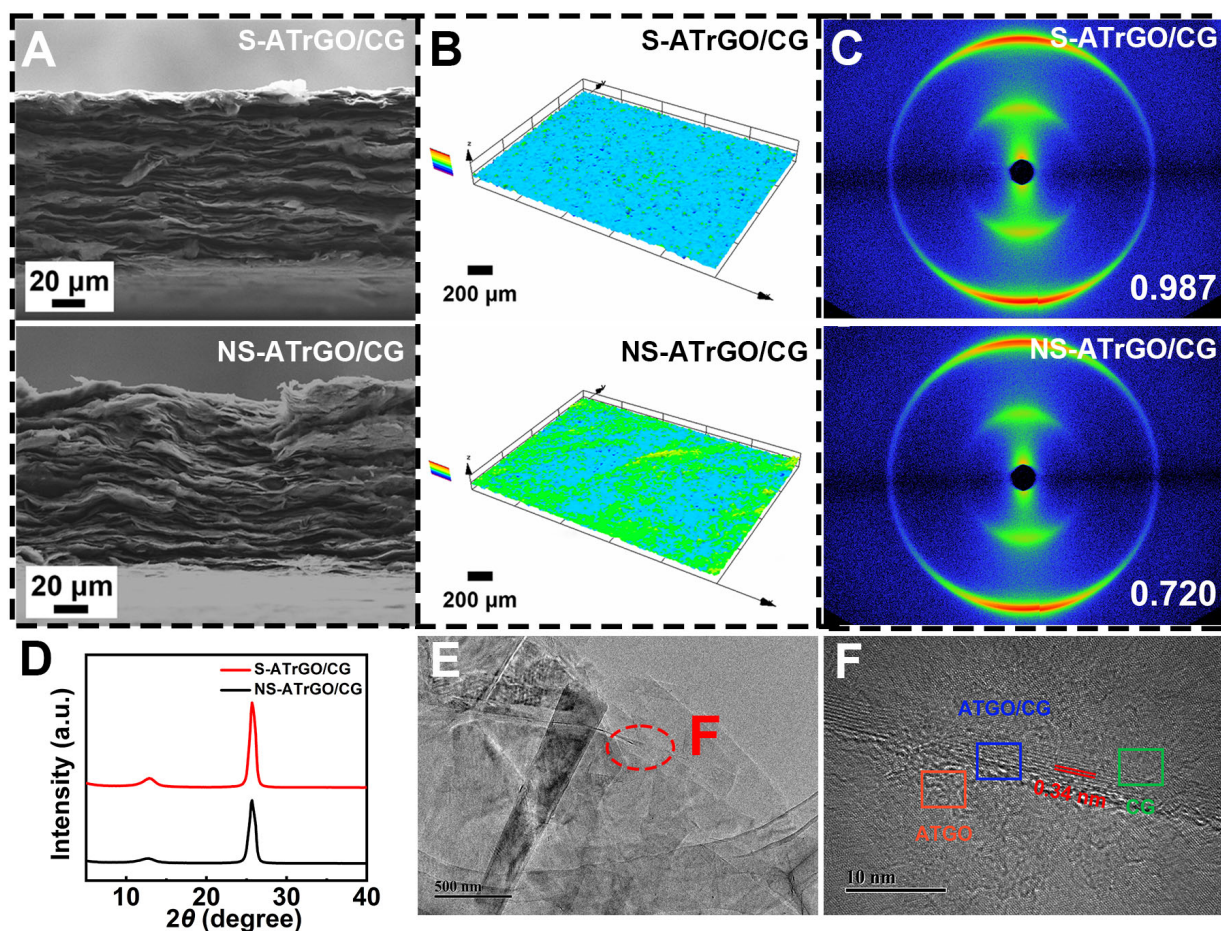


Figure 2. (A) Cross-sectional SEM images of S-ATrGO/CG and NS-ATrGO/CG; (B) Laser scanning confocal microscopy images of S-ATrGO/CG and NS-ATrGO/CG; (C) WAXS two-dimensional scattering maps of S-ATrGO/CG and NS-ATrGO/CG; (D) Corresponding one-dimensional integral curves; (E) TEM micrograph of S-ATrGO/CG; (F) HRTEM micrographs of S-ATrGO/CG. CG: Commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit; SEM: scanning electron microscopy; WAXS: wide-angle X-ray scattering; TEM: transmission electron microscopy; HRTEM: high-resolution TEM.

The cross-sections of the S-ATrGO/CG and NS-ATrGO/CG films are depicted in [Figure 2A](#), in which both films exhibit a dense layered structure with a thickness of approximately 120 μm. When the S-ATrGO/CG film is dried within the slit, the combined influence of capillary force and thermal convection facilitates uniform deposition of graphene sheets. However, as for NS-ATrGO/CG, the suspension was drop-casted directly on the glass mold, exhibiting a slight upward flow during the evaporation process, resulting in a relatively disordered appearance. Confocal microscopy was used to further characterize the topography of the two films. As shown in [Figure 2B](#), the roughness average (R_a) of S-ATrGO/CG is 4.83 μm, with a maximum height variation of 27.50 μm, and no obvious defects or wrinkles are observed. The R_a of NS-ATrGO/CG is 5.58 μm, with the maximum height variation reaching 50.76 μm, and prominent wrinkling is evident in the central region of the image. This result suggests that slit conditions during evaporation are beneficial for achieving a film with a smooth and flat surface.

In order to clarify the effectiveness of enhanced orientation order via a capillary slit, WAXS was conducted on S-ATrGO/CG and NS-ATrGO/CG, and the results are shown in [Figure 2C](#). The image presents a crescent-shaped scattering arc that originated from the crystal plane scattering of rGO and CG flakes. This particular signal is a result of microcrystalline scattering of the tight stacking of rGO and CG flakes. The two

layers of scattering arcs can be identified as hexagonal crystal systems, representing the (100) and (110) crystal planes of the flakes^[47]. In contrast, despite displaying a similar crescent-shaped arc, the scattering pattern of the NS-ATrGO/CG film exhibits a comparatively lower spot intensity than that of the S-ATrGO/CG film. This observation suggests a less optimal crystal orientation and a more chaotic arrangement among the microscopic layered graphene sheets. In order to quantitatively assess the degree of crystal orientation within these films, the scattering pattern obtained from WAXS was integrated to obtain a one-dimensional scattering curve, as shown in [Figure 2D](#). The crystal orientation degree formula calculates that the S-ATrGO/CG film has an orientation degree of 0.987, indicating it is nearly perfectly aligned with the polar axis direction^[40]. On the other hand, NS-ATrGO/CG shows a lower orientation of 0.720, which suggests a certain degree of disorder. This difference in orientation confirms that rGO and CG flakes are assembled into an anisotropic flat structure under the action of the capillary slit, exhibiting increased orientation order of the flakes. This ordered layered structure facilitates rapid transmission of electrolyte ions, leading to a significant improvement in ion transport rate.

To further explain the interaction between ATGO and CG, transmission electron microscopy (TEM) characterization was performed on S-ATGO/CG. As shown in [Figure 2E](#), ATGO and CG form a layered stacking structure, with CG attached to the surface of ATGO. [Figure 2F](#) shows the high-resolution TEM (HRTEM) image of S-ATGO/CG, in which three typical states are observed in different regions. Due to the presence of numerous functional groups and defects in ATGO, which disrupt the lattice structure, the electron diffraction pattern exhibits ring-shaped diffraction spots [[Supplementary Figure 2A](#)]. CG exhibits regular hexagonal symmetric diffraction spots, characteristic of graphite [[Supplementary Figure 2B](#)]. In the region where ATGO and CG combine, the diffraction spots of CG overlap with the diffraction rings of ATGO [[Supplementary Figure 2C](#)]. This suggests that ATGO and CG can interact and bind together through π - π stacking effects and electrostatic attraction. Calculations using Fourier transformation via Digital Micrograph reveal that the interlayer spacing of the layered CG is 0.34 nm, which is consistent with the typical interlayer spacing of graphene. The interlayer spacing of ATGO is 0.64 nm, corresponding to the average interlayer spacing of GO. These results indicate that CG has successfully combined with ATGO with the help of slit microflows and oxygen functional groups.

The effect of sulfuric acid treatment was confirmed by FTIR spectroscopy and XPS. [Supplementary Figure 3](#) shows the FTIR spectra of GO and ATGO. The infrared (IR) peak at $3,446\text{ cm}^{-1}$ corresponds to the stretching frequency of the O-H bond, attributed to water vapor in the environment and crystallized water in KBr. The peak at $1,739\text{ cm}^{-1}$ corresponds to C=O vibration, $1,409\text{ cm}^{-1}$ to C-O-H vibration and $1,066\text{ cm}^{-1}$ to C-O-C vibration. Compared to GO, ATGO shows stronger C-O-H vibration and weaker C-O-C vibration, indicating that some epoxy groups have been converted to hydroxyl groups; more active functional groups are beneficial for enhancing electrochemical performance.

XPS was adopted to quantitatively analyze the oxygen-containing functional groups of the samples. The survey spectra of GO and ATGO revealed that their C/O ratios were comparable [[Supplementary Figure 4A and B](#)], indicating that treatment with sulfuric acid does not drastically alter the C/O stoichiometry. Moreover, [Figure 3A](#) is the C 1s spectrum of GO, which can be deconvoluted into five peaks centered at 284.80 eV (C-C/C=C), 286.86 eV (C-OH), 287.30 eV (C-O-C), 288.77 eV (C=O), and 290.39 eV (O-C=O), respectively. Analogously, five peaks centered at 284.80 eV (C-C/C=C), 286.65 eV (C-OH), 287.10 eV (C-O-C), 288.55 eV (C=O), and 290.17 eV (O-C=O) can be deconvoluted for the spectrum of ATGO, as shown in [Figure 3B](#). The O 1s spectra of GO and ATGO are shown in [Figure 3C and D](#), respectively. The fitted peak is consistent with the peak of the C 1s spectrum. The chemical atomic composition is summarized in [Table 1](#). It can be observed that the proportion of epoxy groups decreased from 25.04% to 22.02%. The phenomenon where the epoxy groups decrease, accompanied by the increased hydroxyl groups, can be

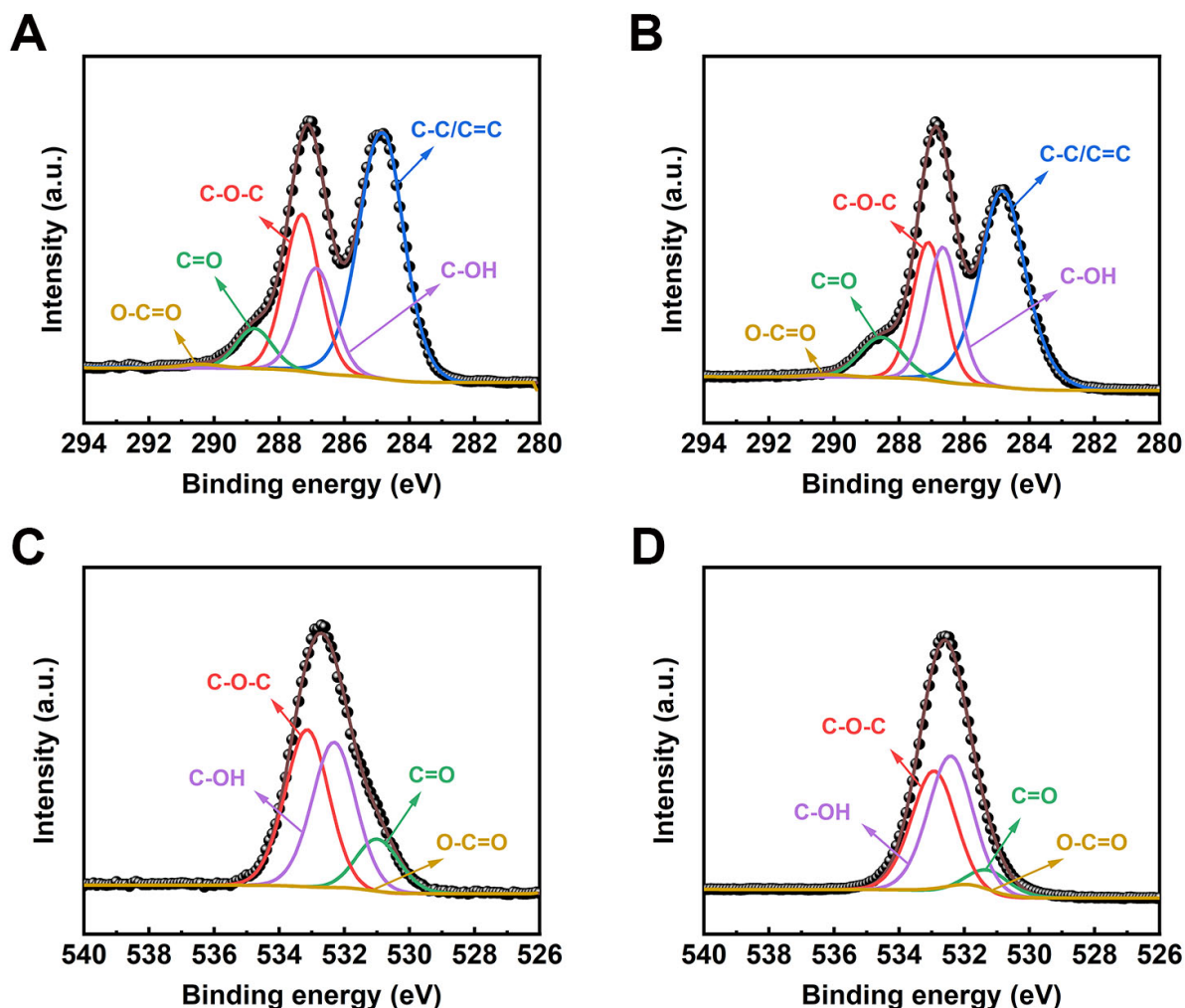


Figure 3. (A) XPS C 1s spectra of GO; (B) XPS C 1s spectra of ATGO; (C) XPS O 1s spectra of GO; (D) XPS O 1s spectra of ATGO. XPS: X-ray photoelectron spectroscopy; ATGO: acid-treated graphene oxide; GO: graphene oxide.

attributed to the hydrogen ions present in dilute sulfuric acid. These ions protonate the epoxy groups in GO, lowering the bonding strength between C and O. Thereby, the O atom in epoxy groups is more prone to accepting a hydrogen ion, which disrupts the epoxy structure and generates open-form functional groups such as hydroxyl^[38]. This mechanism drives the ring-opening reaction of the epoxy groups. The ring-opening reaction directly yields hydroxyl groups, leading to an increase in their proportion from 16.74% to 21.54%. Under mild acidic conditions, the primary chemical transformations involve the protonation and ring-opening of epoxy groups, leading to the formation of hydroxyl groups. While carbonyl and carboxyl groups can form through other oxidation processes, the specific mechanisms at play in this context do not directly support their formation, leaving their proportion relatively unchanged.

The S-ATGO/CG and S-ATrGO/CG samples were also analyzed by XPS. After thermal reduction, the intensity of the O 1s peak decreased, and the C/O ratio increased from 2.07 to 5.35 [Supplementary Figure 4C and D]. This noteworthy change can be ascribed to the elimination of oxygen-containing functional groups through pyrolysis^[48,49]. The XPS C 1s spectrum of S-ATGO/CG can be deconvoluted into five peaks centered at 284.80 eV (C-C/C=C), 286.65 eV (C-OH), 287.10 eV (C-O-C), 288.45 eV (C=O), and 289.37 eV (O-C=O) [Figure 4A]. The XPS C 1s spectrum of S-ATrGO/CG can be deconvoluted into five peaks centered

Table 1. Chemical atomic composition obtained through XPS scan on GO, ATGO and S-ATrGO/CG

	C/O	sp ² C	C-O-C	C-OH	O-C=O	C=O
GO	2.03	51.11%	25.04%	16.74%	0.68%	6.43%
ATGO	2.24	47.31%	22.02%	21.54%	0.46%	8.67%
S-ATrGO/CG	5.35	71.17%	4.63%	13.97%	4.12%	6.38%

XPS: X-ray photoelectron spectroscopy; GO: graphene oxide; ATGO: acid-treated graphene oxide; CG: commercial graphene; S-ATrGO: sulfuric acid-treated reduced graphene oxide.

at 284.80 eV (C-C/C=C), 286.35 eV (C-OH), 287.12 eV (C-O-C), 288.86 eV (C=O), and 291.45 eV (O-C=O) as shown in [Figure 4B](#). The O 1s spectrum of S-ATGO/CG and S-ATrGO/CG can be deconvoluted into the same four peaks centered at 531.22 eV (C=O), 531.89 eV (O-C=O), 532.71 eV (C-OH), and 533.25 eV (C-O-C) as shown in [Figure 4C](#) and [D](#). The atomic percentage of functional groups is consistent with the C 1s spectrum. This detailed analysis reveals that even after thermal treatment at 350 °C, S-ATrGO/CG retains a notable amount of oxygen-containing functional groups, which can provide extra pseudocapacitance. Within the aromatic domain of ATGO, the hydroxyl groups situated in the interior are removed during the pyrolysis process, whereas those located at the edges remain stable due to the decomposition temperature of hydroxyl groups being approximately 650 °C. The dissociated hydroxyl groups migrate toward the edges of the CG sheets, where they find favorable sites for bonding^[50]. During the heat treatment process, the epoxy group will form a small amount of carboxyl group, but the carboxyl group is difficult to remove at 350 °C, so there will be a slight increase. Carbonyl groups have a higher thermal decomposition temperature (over 1,000 °C), so their content remains almost unchanged. Further evidence of the partial thermal reduction provided by XRD and Raman is shown in [Supplementary Figure 5A](#) and [B](#). An emerged broad diffraction peak near $2\theta = 11.0^\circ$ with low intensity indicates the presence of rGO [inset of [Supplementary Figure 5A](#)]. Moreover, after heat treatment, the ratio of the intensities of the D band and G band (I_D/I_G) in Raman spectra exhibited a decrease from 0.95 to 0.74 for S-ATrGO/CG. Since the D band is associated with structural defects and disorder in the carbon lattice, while the G band reflects the vibration of sp² hybridized carbon atoms, the reduction in I_D/I_G indicates a decrease in defect density. This suggests that thermal annealing removed oxygen-containing groups and amorphous carbon, thereby restoring the conjugated sp² domains and improving the structural order of graphene.

To investigate the effect of sulfuric acid ring-opening pretreatment on electrochemical performance, electrochemical tests were conducted on S-OrGO/CG and compared with S-ATrGO/CG. Cyclic voltammetry (CV) curves at scan rates ranging from 5 mV s⁻¹ to 25 mV s⁻¹ are shown in [Supplementary Figure 6A](#) and [B](#). A distinct feature is the well-defined redox peaks observed within a similar potential range, indicating that the unreduced oxygen-containing groups on ATGO and original GO contribute to redox reactions and pseudocapacitance^[51]. Oxygen-containing functional groups, such as hydroxyls and carboxyls, exist on the surface of heat-treated films, undergoing redox reactions during the charge transfer process, thereby generating faradaic capacitance. The presence of these pseudocapacitors further enhances the specific capacitance of the films.

Based on the CV tests, the pseudocapacitance and electric double layer capacitance (EDLC) contributions of ATGO and original GO were further investigated. Specifically, the EDLC originates from the electrostatic adsorption of ions at the electrode/electrolyte interface, which is a non-faradaic process and does not involve charge transfer or chemical reactions. In contrast, pseudocapacitance arises from fast and reversible faradaic reactions occurring at or near the electrode surface, leading to additional charge storage beyond the electric double layer. It should be noted that in practical electrode systems, pseudocapacitive and diffusion-controlled behaviors are often intertwined. The capacitive contribution also includes a portion of

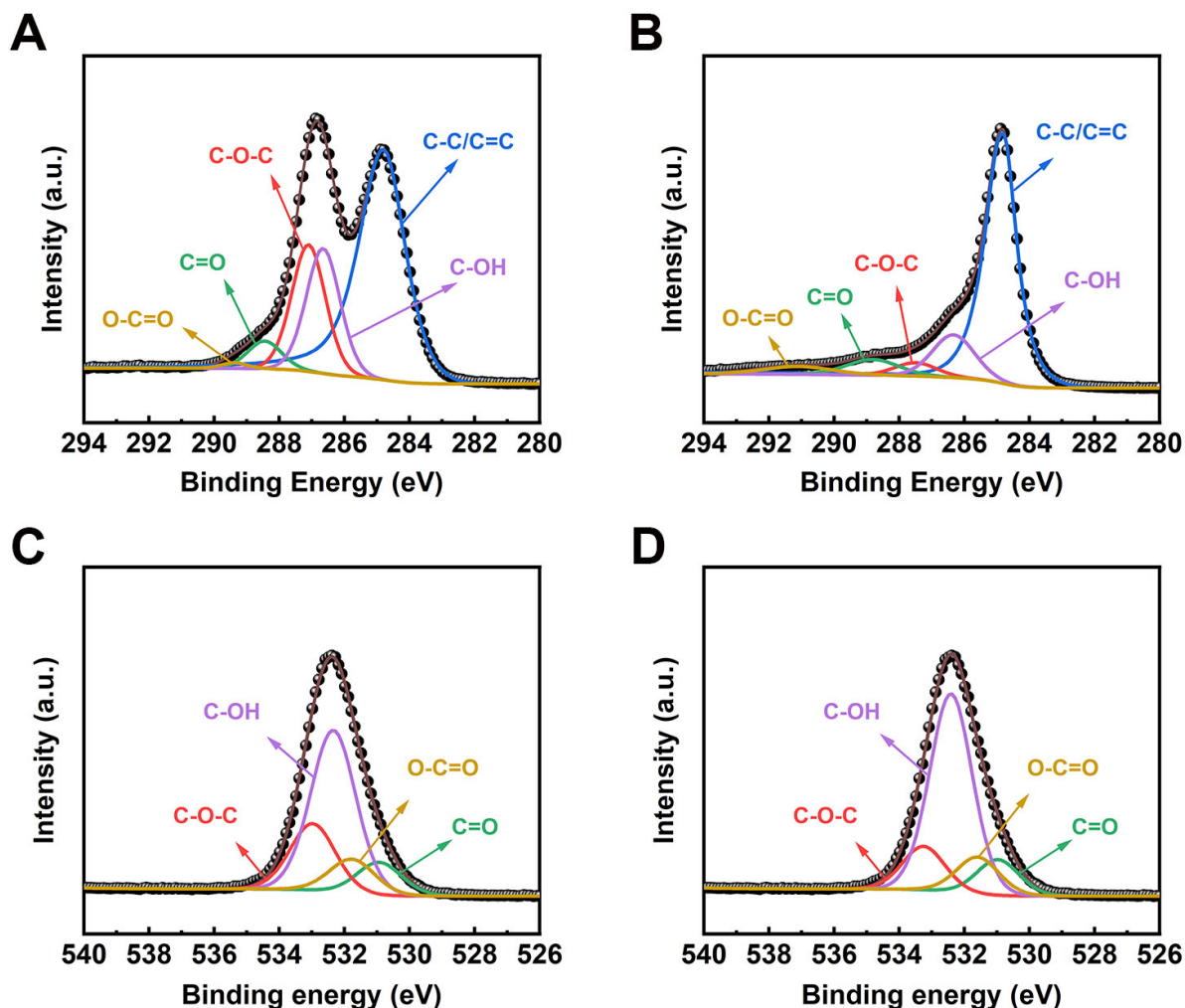


Figure 4. (A) XPS C 1s spectra of S-ATGO/CG; (B) XPS C 1s spectra of S-ATrGO/CG; (C) XPS O 1s spectra of S-ATGO/CG; (D) XPS O 1s spectra of S-ATrGO/CG. XPS: X-ray photoelectron spectroscopy; CG: commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit.

diffusion-controlled charge storage, since both processes contribute to the overall faradaic reaction. Therefore, the term “pseudocapacitance” in this work broadly refers to the total faradaic contribution, including both surface redox and diffusion-related processes. The capacitance contributions were calculated using capacitance differentiation analysis based on the CV curves, as shown in [Figure 5A](#) and [B](#). At a scan rate of 5 mV s^{-1} , the shaded areas represent the capacitance-controlled contribution (including pseudocapacitance and EDLC). Regarding the overlap in the capacitive contribution, this phenomenon can be attributed to the partial coupling of capacitive and diffusion-controlled processes during charge storage. [Figure 5C](#) shows the proportional relationship among the pseudocapacitive, EDLC and diffusion-controlled contribution^[52]. Accordingly, the diffusion-controlled capacitance contributions are 49% and 28%, respectively. At lower scan rates, the surface-active functional groups can fully interact with electrolyte ions. Compared to the original GO, ATGO exhibits a higher ratio of pseudocapacitance contribution, indicating that more active functional groups are involved in diffusion control, thus contributing more to the pseudocapacitance.

The capacitance values of S-OrGO/CG, calculated from the CV curves at different scan rates, are shown in [Supplementary Figure 6C](#). Limited by the ion diffusion rate, the capacitance decreases as the scan rate

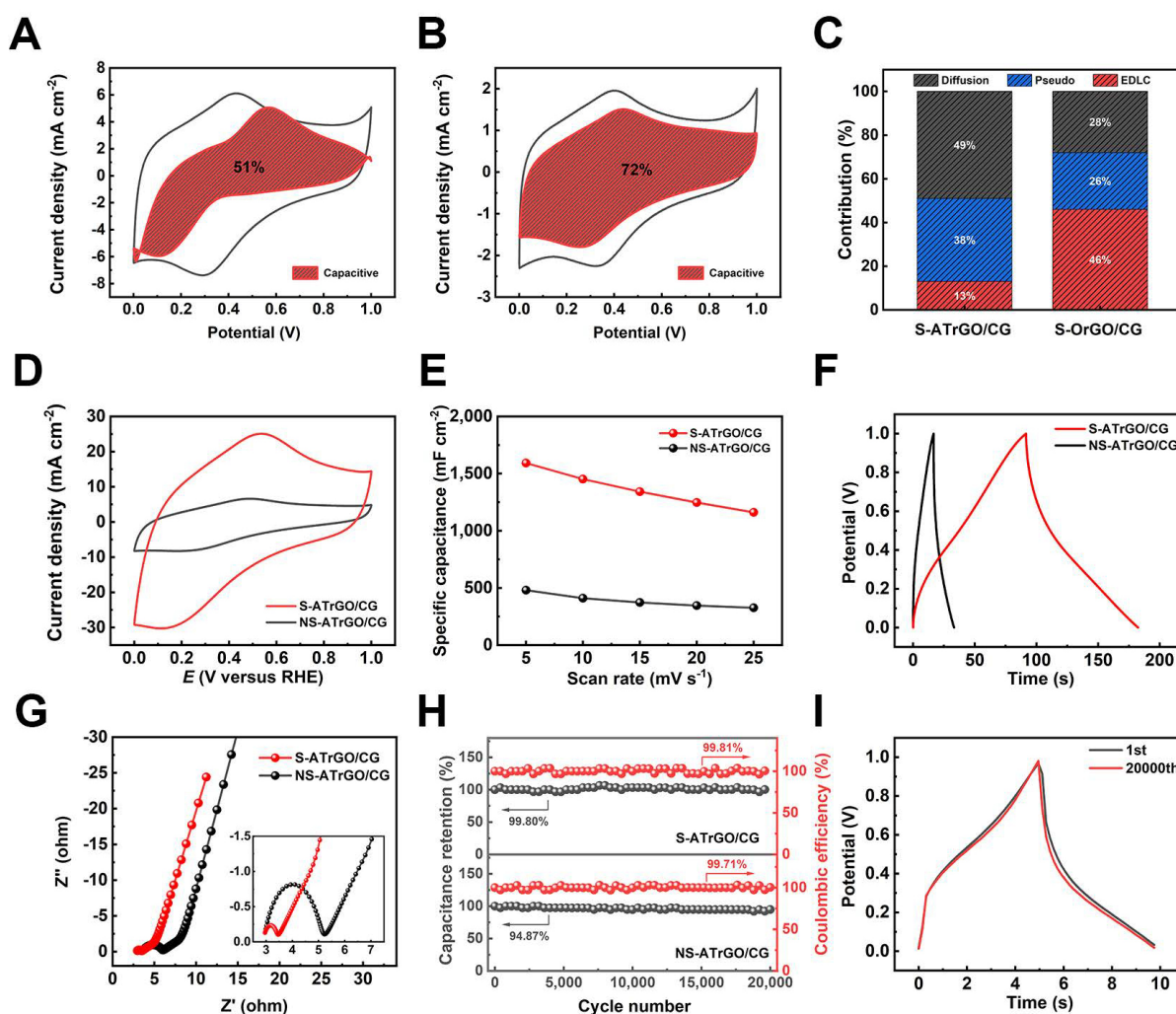


Figure 5. Differentiation of capacitive and diffusion-controlled contribution from CV curves at 5 mV s⁻¹ for (A) S-ATrGO/CG; (B) S-OrGO/CG; (C) Capacitance contribution calculation from CV curves of 5 mV s⁻¹; (D) CV curves of S-ATrGO/CG and NS-ATrGO/CG at a scan rate of 25 mV s⁻¹; (E) Specific capacitance from CV plots with variation of scan rates; (F) Comparison of GCD curves at a current density of 5 mA cm⁻²; (G) The Nyquist plots measured in a frequency range between 0.01 and 10⁵ Hz. (inset: the enlarged high-frequency region); (H) The specific capacitance retention and coulombic efficiency with 20,000 cycling numbers; (I) The GCD curves from the first cycle and the last cycle. EDLC: Electric double layer capacitance; CV: cyclic voltammetry; CG: commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit; GCD: galvanostatic charge-discharge; RHE: reversible hydrogen electrode.

increases. In the Nyquist plot, the charge transfer resistance of S-OrGO/CG is 42.84 Ω [Supplementary Figure 6D], which is higher than that of S-ATrGO/CG as described below. This is because the untreated GO contains a high content of epoxy groups, which cannot undergo ring-opening to form hydroxyl groups. These epoxy groups cannot be removed during thermal annealing at 350 °C, resulting in incomplete restoration of the sp² network and inferior electrochemical performance. The galvanostatic charge-discharge (GCD) curve of S-OrGO/CG presents an approximately symmetrical triangular shape [Supplementary Figure 6E], indicating that only a small number of active functional groups participate in the redox reactions. These results confirm that the sulfuric acid ring-opening treatment of ATGO can convert more inert functional groups (epoxy groups) into active functional groups (hydroxyl groups). The cycling stability of S-OrGO/CG was evaluated at a current density of 50 mA cm⁻² over 20,000 cycles [Supplementary Figure 6F]. Although the Coulombic efficiency remained at 100% of the initial value, the capacitance retention decreased to 89.76%, which is inferior to that of S-ATrGO/CG.

To further emphasize the role of the regular layered structure, prepared by the slit evaporation self-assembly method, in enhancing the capacitance, the electrochemical performance of NS-ATrGO/CG was also evaluated under the same conditions for comparison. The CV curves of both film electrodes were obtained at a scan rate of 25 mV s^{-1} [Figure 5D]. It can be observed that the current density range of S-ATrGO/CG is much larger than that of NS-ATrGO/CG, accompanied by an increased peak current. This indicates that the regular layered arrangement of the S-ATrGO/CG creates optimal conditions for the transport of electrolyte ions, thereby accelerating the ion transport rate and enabling a fast current response^[53]. The CV curves of the NS-ATrGO/CG film electrode were recorded at scan rates ranging from 5 mV s^{-1} to 25 mV s^{-1} , within the potential window of 0–1 V [Supplementary Figure 6G]. The areal capacitance values were calculated by analyzing the charge derived from the current response in the CV curve at a scan rate of 5 mV s^{-1} . As shown in Figure 5E, S-ATrGO/CG exhibits an areal capacitance of $1,589.78 \text{ mF cm}^{-2}$, significantly higher than that of NS-ATrGO/CG, which measures $480.78 \text{ mF cm}^{-2}$. For volumetric capacitance, the same trend is observed. The volumetric capacitance of S-ATrGO/CG reaches 132.48 F cm^{-3} , which is significantly higher than that of NS-ATrGO/CG at 40.07 F cm^{-3} . As the scan rate increases, the areal capacitance values of both samples decrease to varying degrees. To further evaluate the electrochemical performance of the electrode, CV tests were conducted on S-ATrGO/CG at higher scan rates (5 mV s^{-1} to 500 mV s^{-1}). The results revealed that when the scan rate exceeded 200 mV s^{-1} , both the anodic and cathodic peaks nearly disappeared [Supplementary Figure 7A]. As shown by the areal capacitance values derived from the CV curves at different scan rates, the areal capacitance decreased from $1,589.78 \text{ mF cm}^{-2}$ to $214.64 \text{ mF cm}^{-2}$ as the scan rate increased from 5 mV s^{-1} to 500 mV s^{-1} , retaining about 13.5% of its initial value [Supplementary Figure 7B]. This decline is mainly attributed to the insufficient diffusion of electrolyte ions at high scan rates, which hinders the occurrence of surface redox reactions and consequently leads to a reduced capacitance. The capacitance contribution of S-ATrGO/CG at different scan rates is shown in Supplementary Figure 8. As the scan rate increases, the pseudocapacitance provided by ion diffusion gradually decreases.

Figure 5F illustrates the GCD curves of the two samples at a current density of 5 mA cm^{-2} . The single charge-discharge cycle time for S-ATrGO/CG is 183 s, significantly better than the 33 s observed for NS-ATrGO/CG. GCD tests were also performed on S-ATrGO/CG at higher current densities (5 mA cm^{-2} to 100 mA cm^{-2}). The results showed that, as the current density increased, the GCD curves became more triangular [Supplementary Figure 9]. This behavior can be attributed to the limited diffusion and migration rates of ions within the electrode pores at high current densities, which prevent them from fully keeping pace with the rapid changes in the electric field. Since the charge storage of pseudocapacitance relies on fast surface Faradaic reactions, the sluggish reaction kinetics at high current densities lead to significant polarization of the electrode. Electrochemical impedance spectroscopy (EIS) measurements on the two samples provide a further understanding of the rate capability and the corresponding Nyquist plots are displayed in Figure 5G. The rapid ion transport of S-ATrGO/CG is evidenced by the distinct steep slope observed at low frequency, which can be attributed to the layered structure. This structure provides efficient ion transport channels, enabling rapid adsorption and desorption of ions within the graphene layers. The inset illustrates an enlarged Nyquist plot in the high-frequency region, where semicircular impedance arcs reveal the low electrochemical impedance exhibited by both samples. In the high-frequency region, the intercept of the curve on the real axis represents the electrolyte resistance (R_s), and the diameter of the semicircle corresponds to the charge transfer resistance (R_{ct}) of the sample in the electrolyte^[54,55]. Specifically, S-ATrGO/CG demonstrates an electrochemical impedance of 0.48Ω , while this value for NS-ATrGO/CG is 2.19Ω . The S-ATrGO/CG film constructed from anisotropic graphene flakes establishes rapid ion transport channels, thereby achieving excellent electrical conductivity.

Furthermore, long-term cycling stability is evaluated by subjecting the two samples to 20,000 cycles at a current density of 50 mA cm^{-2} [Figure 5H]. S-ATrGO/CG shows excellent cycling stability (99.80%)

Table 2. Comparison of graphene supercapacitor electrodes with recently reported studies

Materials	Method	Areal specific capacitance (mF cm ⁻²)	Capacitance retention (cycles)	Ref.
S-ATrGO/CG film	Capillary slit-induced self-assembly	1,589.78	99.80% (20,000)	This work
rGO/GO	Heating pattern on GO film	94.8	57.1% (20,000)	[2]
Functionalized graphene hydrogel	Electrolytic deposition	400	100% (10,000)	[4]
Graphene paper	Coating method	44	95.21% (10,000)	[14]
GO/rGO film	Blade-casting thermal reduction	24.8	55.8% (4,500)	[41]
Activated graphene compact film	Repeated filtration	89.5	NA	[56]
3D graphene/graphite paper	Chemical vapor deposition	15.5	112% (10,000)	[57]
GO hydrogel	Blade-casting	71	98.3% (5,000)	[58]

GO: Graphene oxide; rGO: reduced GO; CG: commercial graphene; S-ATrGO: sulfuric acid-treated reduced graphene oxide.

compared to that of NS-rGO/-CG (94.87%). [Figure 5I](#) shows the charge-discharge curves of the first and 20,000th cycles from the cycling stability test of S-ATrGO/CG. The curves exhibit no significant changes, and the single charge-discharge cycle time remains consistent, indicating excellent cycling stability of S-ATrGO/CG^[56]. The obtained areal capacitance value and cycling stability performance of S-ATrGO/CG are higher than the state-of-the-art supercapacitors based on graphene-derived materials [[Table 2](#)]^[2,4,14,41,57–59]. To further assess the long-term stability of the electrode under high current operation, a cycling test was performed at 100 mA cm⁻² for 20,000 charge-discharge cycles. As shown in [Supplementary Figure 10A](#), the electrode exhibited remarkable stability, maintaining 96.91% of its initial capacitance after 20,000 charge-discharge cycles with a high coulombic efficiency of 97.66%. This excellent stability demonstrates the robust structural integrity and electrochemical reversibility of the electrode material even at high current densities. To further evaluate the stability of the S-ATrGO/CG electrode after long-term cycling, post-cycling electrochemical and structural characterizations were carried out. As shown in [Supplementary Figure 10B and C](#), the CV and GCD curves after 20,000 cycles retain almost identical shapes to the initial curves. This phenomenon confirms the excellent reversibility and capacitive behavior of the electrode. The Nyquist plots [[Supplementary Figure 10D](#)] reveal only a slight increase in the internal resistance (0.58 Ω), implying stable ion transport and charge transfer during cycling. The SEM image [[Supplementary Figure 10E](#)] shows that the layered architecture of the electrode remains well preserved, without visible cracks or delamination. The FTIR spectra [[Supplementary Figure 10F](#)] indicate that the characteristic functional groups of S-ATrGO/CG remain almost unchanged after cycling. These results collectively demonstrate that the S-ATrGO/CG electrode exhibits outstanding structural robustness and electrochemical stability, consistent with its excellent capacitance retention and coulombic efficiency.

The electrochemical behavior of S-ATrGO/CG film was thoroughly investigated via a series of electrochemical tests. The ATGO here is acting as the conductive additive, flexible backbone, active material, and binder, enhancing the structural integrity of the films and contributing to their overall performance. In order to optimize the loading amount, ATGOs with varying contents of CG were prepared, including 0 wt.%, 30 wt.%, 70 wt.%, 75 wt.%, and 80 wt.%; they were named as S-ATrGO/CG₀, S-ATrGO/CG₃₀, S-ATrGO/CG₇₀, S-ATrGO/CG₇₅, and S-ATrGO/CG₈₀, respectively. Their CV curves at a scan rate of 25 mV s⁻¹ are summarized in [Figure 6A](#). Experimental results show that with the addition of CG, the electrochemical active area gradually increases, reaching its maximum value at a content of 75 wt.%. The CV curves of all the samples within the potential range of 0–1 V are shown in [Supplementary Figure 11](#), in which the electrochemical active area also increases linearly with the increased scan rate. The shape of these CV curves remained largely unchanged even with a fivefold increase in the scan rate from 5 mV s⁻¹ to 25 mV s⁻¹, demonstrating the superior reversibility of the samples^[60].

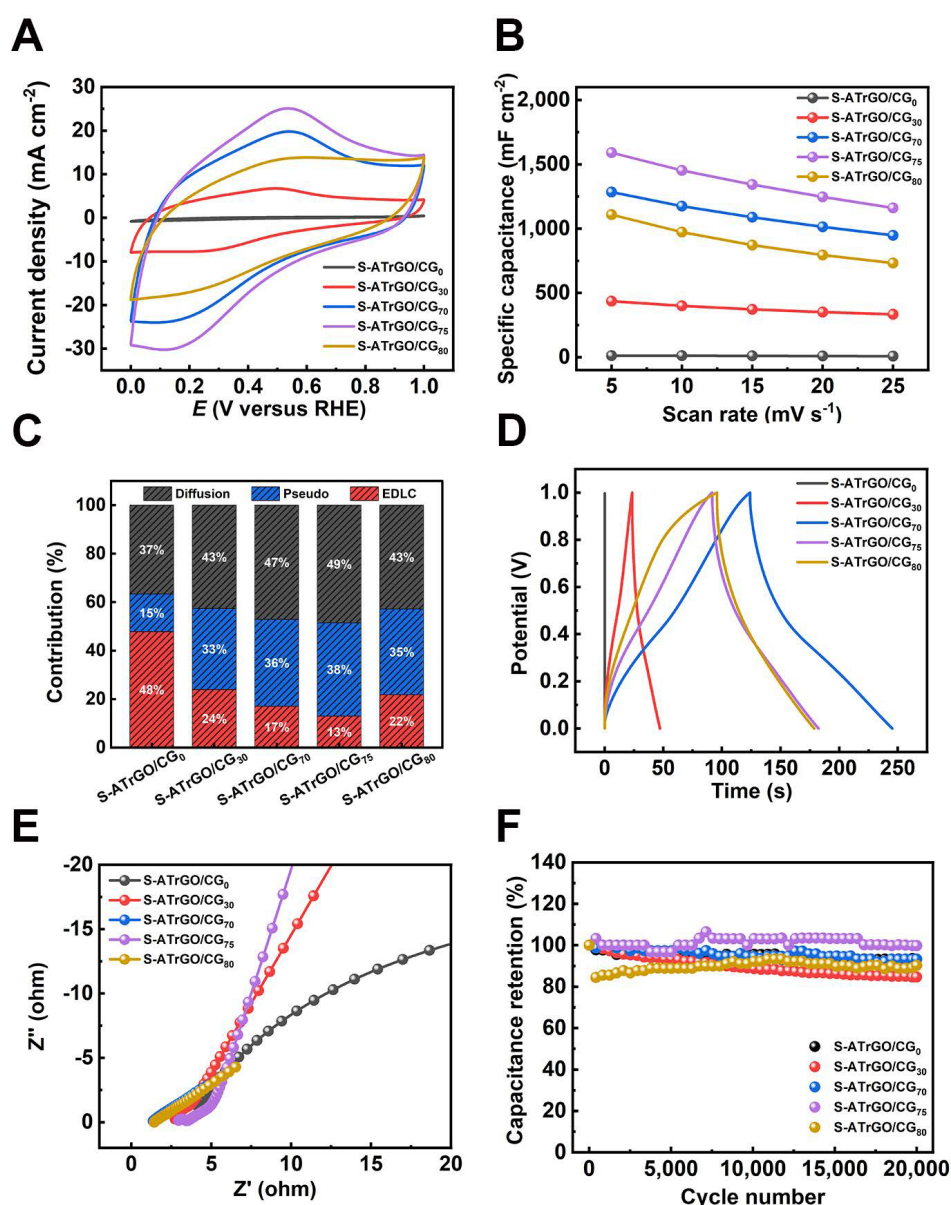


Figure 6. (A) CV curves of S-ATrGO/CG₀, S-ATrGO/CG₃₀, S-ATrGO/CG₇₀, S-ATrGO/CG₇₅ and S-ATrGO/CG₈₀ at scan rate of 25 mV s⁻¹; (B) Specific capacitance from CV plots with variation of scan rates; (C) Contributions of capacitive and diffusion-controlled charge storage at various scanning rates; (D) Comparison of GCD curves at a current density of 5 mA cm⁻²; (E) The Nyquist plots measured in a frequency range between 0.01 and 10⁵ Hz; (F) The specific capacitance retention with 20,000 cycling numbers. CG: commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit; GCD: galvanostatic charge-discharge; CV: cyclic voltammetry; GCD: galvanostatic charge-discharge; RHE: reversible hydrogen electrode.

The variation of specific capacitance values with the scan rate is illustrated in Figure 6B. It clearly demonstrates that an increase in the scan rate leads to a reduction in specific capacitance. This occurs because, as the scan rate increases, the contribution of faradaic capacitance decreases, while the EDLC-type specific capacitance becomes dominant. Moreover, the areal capacitance of the films varies greatly under different CG loading amounts. For example, at the scan rate of 5 mV s⁻¹, when 30 wt.% of CG was added, the areal capacitance value increased significantly from 12.54 mF cm⁻² for S-ATrGO/CG₀ to 436.24 mF cm⁻² for S-ATrGO/CG₃₀. The areal capacitance reached its maximum value of 1,589.78 mF cm⁻² at 75 wt.%. When the CG loading was further increased to 80 wt.%, the electrochemical performance decreased. This decline can be attributed to the agglomeration of an excessive amount of CG in the film.

As shown in [Supplementary Figure 12](#), the capacitance differentiation analysis of CV curves for samples with different CG loading amounts was performed at the same scan rate (5 mV s^{-1}). The results indicate that all the samples with added CG exhibit a mixed capacitance contribution from both pseudocapacitance and EDLC. The ratio of pseudocapacitance contribution is shown in [Figure 6C](#). It can be observed that as the CG loading amount increases, more graphene nanosheet edges are available for hydroxyl group attachment, thereby providing more pseudocapacitance. When the CG loading reaches 80 wt.%, the number of CG nanosheets exceeds the bonding limit of ATGO, and the remaining unbonded CG nanosheets disrupt the structure of the electrode sheet, leading to a decrease in performance.

The GCD curves of the films with different CG contents at a current density of 5 mA cm^{-2} are illustrated in [Figure 6D](#). The shape of the discharge curve exhibits distinct characteristics of pseudocapacitance, which is consistent with the results obtained from the CV. The incorporation of CG significantly enhances the charge-discharge cycle time. [Figure 6E](#) shows the EIS curves, with the response over a frequency range from 0.01 Hz to 10^5 Hz. The curve consists of a high-frequency intercept on the real Z axis, a semicircle, and a sloping line in the low-frequency region. This is caused by the pseudocapacitive redox reactions and the double-layer capacitance at the electrode surface^[50]. The R_{ct} values for S-ATrGO/CG₀, S-ATrGO/CG₃₀, S-ATrGO/CG₇₀, S-ATrGO/CG₇₅, and S-ATrGO/CG₈₀ are 29.10, 0.52, 0.30, 0.48, and 0.11Ω , respectively. The S-ATrGO/CG₇₅ electrode shows a slope close to vertical in the low-frequency region, indicating a low ionic diffusion resistance and good ionic diffusion properties. The film with CG loading exhibits a significant reduction in charge transfer resistance compared to the undoped film. [Figure 6F](#) illustrates the capacitance retention of the film electrodes after 20,000 charge-discharge cycles. The capacitance retention rates are as follows: S-ATrGO/CG₀ at 93.33%, S-ATrGO/CG₃₀ at 84.68%, S-ATrGO/CG₇₀ at 93.33%, S-ATrGO/CG₇₅ at 99.80% and S-ATrGO/CG₈₀ at 90.28%.

To further investigate the properties of the S-ATrGO/CG electrode material, SSCs with S-ATrGO/CG//S-ATrGO/CG in a CR2032 coin cell were constructed. Both the positive and negative electrodes maintained consistent area and volume. The CV curves of the SSC at scan rates from 1 mV s^{-1} to 25 mV s^{-1} are shown in [Figure 7A](#). It can be observed that after assembly into SSC, the redox peaks are significantly reduced compared to the CV curves of the three-electrode testing system. Even at a scan rate of 1 mV s^{-1} , the redox peaks are not obvious. The areal capacitance performance is also significantly reduced, with a value of $532.75 \text{ mF cm}^{-2}$ [[Figure 7B](#)]. The contributions of the double-layer capacitance and the diffusion capacitance were analyzed through capacitance differentiation analysis. At a scan rate of 1 mV s^{-1} , the contribution from diffusion capacitance is 59%, with the EDLC contributing the main capacitance [[Figure 7C and D](#)]. This phenomenon is caused by the membrane restricting the ion transport rate of the electrolyte, and the limited electrolyte ions being unable to reach the active oxygen functional groups within the electrode, resulting in insufficient time for redox reactions to occur. The combined effects of double-layer formation and charge transfer at the electrode surface enable a rapid capacitance response. The GCD curves at different current densities present a symmetrical triangular shape, demonstrating excellent stability during charge and discharge cycles [[Figure 7E](#)]. In addition, the SSC was also tested through long-term GCD tests to evaluate durability, with results shown in [Figure 7F](#). As the number of cycles increases, the SSC capacity gradually decreases. Remarkably, after 7,500 charge-discharge cycles, the capacitance retains 92.59% of its initial value and the coulombic efficiency is 100% of the initial value, indicating excellent cycling stability. The energy and power densities of the SSC device were calculated from the GCD curves, and the corresponding Ragone plot is shown in [Supplementary Figure 13](#). The device achieves an energy density of $31 \mu\text{Wh cm}^{-2}$ at a power density of $560 \mu\text{W cm}^{-2}$, while a maximum power density of $2,840 \mu\text{W cm}^{-2}$ corresponds to an energy density of $20 \mu\text{Wh cm}^{-2}$. These results indicate that the device maintains a favorable balance between energy and power performance, exceeding other recent reported pure graphene-based supercapacitors.

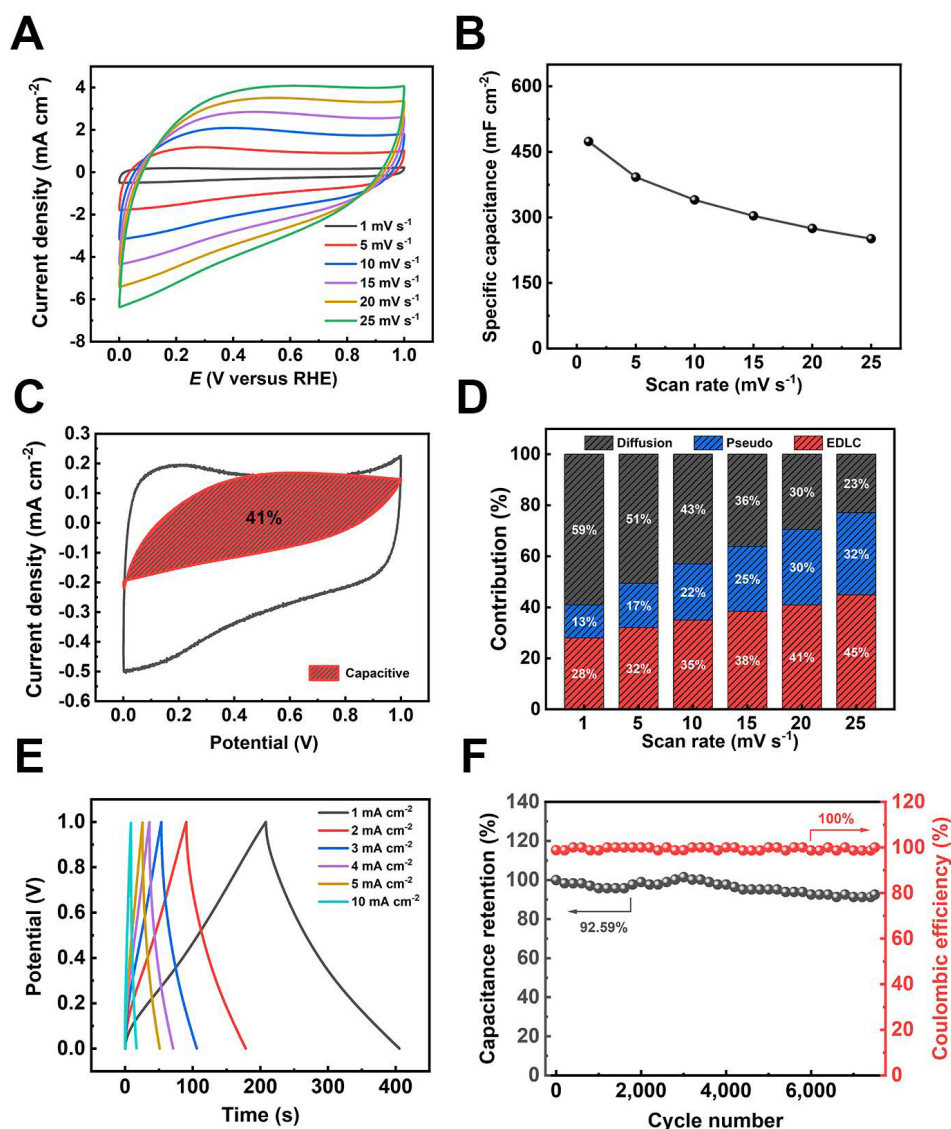


Figure 7. Electrochemical characterization of S-ATrGO/CG//S-ATrGO/CG. (A) CV curves of scan rates ranging from 1 to 25 mV s⁻¹; (B) Specific capacitance from CV plots with variation of scan rates; (C) Differentiation of capacitive and diffusion-controlled contribution from CV curves at 1 mV s⁻¹ for SSC; (D) Contributions of capacitive and diffusion-controlled charge storage at various scanning rates; (E) GCD curves at different current density; (F) The specific capacitance retention and coulombic efficiency of SSC with 7,500 cycling numbers. EDLC: Electric double layer capacitance; CV: cyclic voltammetry; CG: commercial graphene; ATGO: acid-treated graphene oxide; S-ATrGO: sulfuric acid-treated reduced graphene oxide; NS: non-slit; GCD: galvanostatic charge-discharge; SSC: cell symmetric supercapacitor; RHE: reversible hydrogen electrode.

CONCLUSIONS

In summary, by means of a novel slit evaporation self-assembly strategy, this study has successfully fabricated a freestanding S-ATrGO/CG film, which exhibits superior electrochemical properties. The capillary slit-induced self-assembly process facilitates the alignment and stacking of graphene flakes, resulting in a smooth and well-ordered laminated film. The mixed suspension of ATGO and CG was prepared and injected into a capillary slit constructed by two glass plates. Upon heating, the ATGO and graphene self-assembled to form a uniform laminated macroscopic structure under the π - π stacking effect and electrostatic attraction. The resultant films were then subjected to heat treatment in an Ar atmosphere, yielding the freestanding rGO and CG laminate film (S-ATrGO/CG). Heat treatment further improves the properties by removing inert functional groups while retaining active ones, thereby enhancing the specific

capacitance and structural stability of the electrodes. The S-ATrGO/CG electrodes exhibit an ultra-high area-specific capacitance of $1,589.78 \text{ mF cm}^{-2}$ and an excellent volume capacitance of 132.48 F cm^{-3} at 5 mV s^{-1} . Moreover, at a current density of 50 mA cm^{-2} , the initial capacitance retention rate reaches 99.80% after 20,000 cycles. This highlights the potential of S-ATrGO/CG electrodes in high-performance supercapacitors. These findings underscore the importance of S-ATrGO/CG film in the development of advanced energy storage devices, which are essential for the transition to sustainable energy systems.

DECLARATIONS

Authors contributions

Wrote and reviewed the manuscript, made substantial contributions to the conception, performed data acquisition and design of the study, and conducted data analysis and interpretation: Cui, H.; Zhang, J.; Fan, J. Provided administrative, technical, and material support: Zhang, J.

Availability of data and materials

Morphology and structure for the material characterizations and the electrochemical performance of materials for exploration and comparison are presented in the [Supplementary Materials](#). Further data are available from the corresponding author upon reasonable request.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

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