Owing to their unique nanosize effect and surface effect, pseudocapacitive quantum dots (QDs) hold considerable potential for high-efficiency supercapacitors (SCs). However, their pseudocapacitive behavior is exploited in aqueous electrolytes with narrow potential windows, thereby leading to a low energy density of the SCs. Here, a film electrode based on dual-confined FeOOH QDs (FQDs) with superior pseudocapacitive behavior in a high-voltage ionic liquid (IL) electrolyte is put forward. In such a film electrode, FQDs are steadily dual-confined in a 2D heterogeneous nanospace supported by graphite carbon nitride (g-C\(_3\)N\(_4\)) and Ti-MXene (T\(_3\)C\(_2\)). Probing of potential-driven ion accumulation elucidates that strong adsorption occurs between the IL cation and the electrode surface with abundant active sites, providing sufficient redox reaction of FQDs in the film electrode. Furthermore, porous g-C\(_3\)N\(_4\) and conductive T\(_3\)C\(_2\) act as ion-accessible channels and charge-transfer pathways, respectively, endowing the FQDs-based film electrode with favorable electrochemical kinetics in the IL electrolyte. A high-voltage flexible SC (FSC) based on an ionogel electrolyte is fabricated, exhibiting a high energy density (77.12 mWh cm\(^{-2}\)), a high power density, a remarkable rate capability, and long-term durability. Such an FSC can also be charged by harvesting sustainable energy and can effectively power various wearable and portable electronics.
affects the electrochemical performance in IL electrolytes. This issue seriously hinders the implementation of pseudocapacitive QDs as high-performance electrodes in IL electrolytes.

An effective approach is to confine pseudocapacitive QDs in a suitable nanospace to improve their structural stability as well as their electrochemical properties. In this work, we report a film electrode based on dual-confined FeOOH QDs (denoted FQDs) with superior pseudocapacitive behavior in the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) IL electrolyte, where pseudocapacitive FQDs ($\approx$5 nm) are steadily dual confined in a 2D heterogeneous nanospace supported by graphene carbon nitride (g-C$_3$N$_4$) and Ti-MXene (Ti$_3$C$_2$). Probing of the potential-driven ion accumulation elucidates that strong adsorption occurs between the IL cation (EMIM$^+$) and the electrode surface with abundant active sites, providing sufficient redox reaction of FQDs in the film electrode. Furthermore, porous g-C$_3$N$_4$ and conductive Ti$_3$C$_2$ act as ion-accessible channels and charge-transfer pathways, respectively, allowing highly dynamic motion of IL ions and electrons. As a result, the dual-confined FQDs-based film (denoted FQDs/CNTC film) as a binder-free electrode delivers a large specific capacitance ($\approx$391.78 F cm$^{-2}$) with high durability in the IL electrolyte. Based on this, a high-voltage flexible SC (FSC) based on an ionogel electrolyte is fabricated, which exhibits a high energy density (77.12 mWh cm$^{-2}$), a high power density ($\approx$6000 mW cm$^{-2}$), and a remarkable rate and cycling performance. For a real application, the FSC can be charged by harvesting sustainable energy and effectively power various wearable and portable electronics.

2. Results and Discussion

High-conductivity Ti$_3$C$_2$ nanosheets were successfully prepared by etching the Al layers in Ti$_3$AlC$_2$ using a mixture of LiF and HCl, followed by liquid sonication exfoliation (Figure S1, Supporting Information). As observed in Figure 1a, the Ti$_3$C$_2$ nanosheets are transparent with lateral dimensions of several micrometres. The magnified image reveals the wrinkled silk-like texture of the Ti$_3$C$_2$ nanosheets with an average thickness of 2 nm (Figure 1b, Supporting Information). Moreover, porous g-C$_3$N$_4$ nanosheets were synthesized by a two-step heat treatment involving oxidized etching for pore formation and thermal oxidation for exfoliation (Figure S3, Supporting Information). As shown in Figure 1c, porous g-C$_3$N$_4$ is composed of ultrathin crumpled nanosheets ($\approx$3 nm, obtained from Figure S4, Supporting Information), in which abundant porous structures exist in the layers. These pores are abundant and continuous, while the ultrathin pore wall (Figure 1d) provides numerous facile accessible channels and a short diffusion distance for electrolyte ions. The X-ray diffraction (XRD) results of g-C$_3$N$_4$ and Ti$_3$C$_2$ nanosheets are provided in Figures S5 and S6 of the Supporting Information.

Due to the similar planar nanosheets of porous g-C$_3$N$_4$ and conductive Ti$_3$C$_2$, FQDs/CNTC was prepared, yielding FQDs confined in g-C$_3$N$_4$ and Ti$_3$C$_2$ sandwich-type nanosheets. The TEM image of FQDs/CNTC in Figure 1e reveals that a large amount of FQDs are uniformly dispersed and sandwiched within the interlayer of the nanosheets, in which the size of the FQDs is $\approx$5 nm (Figure 1f). The high-resolution TEM image in Figure 1g shows lattice fringes with a spacing of 1 nm, corresponding to the (002) plane of Ti$_3$C$_2$ (10), whereas the disordered area is ascribed to g-C$_3$N$_4$. These results strongly indicate that the sandwich-type nanosheets are constructed by g-C$_3$N$_4$ and Ti$_3$C$_2$, thus offering a heterogeneous nanospace for effective dual confinement of FQDs (Figure 1h). More information about the structural characterizations of FQDs in FQDs/CNTC is provided in Figures S7–S9 of the Supporting Information. The natural structure of g-C$_3$N$_4$ contains a large amount of pyrolic N “hole” defects in the lattice and doubly bonded N at the vacancy edges (Figure S10, Supporting Information), while Ti$_3$C$_2$ possesses some surface functional groups (Ti–O and Ti–F) due to its etching process with some chemical agents (Figure S11, Supporting Information) both of which are beneficial for the adsorption and movement of electrolyte ions. As shown in Figure 1i, the corresponding elemental mapping analysis of the constituent elements C, N, Ti, and Fe clearly displays a well-defined compositional profile of FQDs/CNTC, further manifesting the formation of FQDs in the heterogeneous nanospace consisting of g-C$_3$N$_4$ and Ti$_3$C$_2$. This result is also supported by the atomic force microscopy (AFM) image (Figure 1j) of FQDs/CNTC with a height of 5–5.5 nm, which results from g-C$_3$N$_4$ ($\approx$3 nm thickness) and Ti$_3$C$_2$ ($\approx$2 nm thickness). In addition, the X-ray photoelectron spectroscopy (XPS) full spectrum (Figure 1k) reveals that the FQDs/CNTC contains C, N, Ti, Fe, and O atoms. As shown in the high-resolution Fe 2p spectrum (Figure 1l), two main peaks are located at binding energies of 711.3 and 724.8 eV for Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, which are characteristic of the Fe$^{3+}$ of FeOOH in FQDs. Meanwhile, the FQDs exhibit amorphous feature according to the XRD result (Figure S12, Supporting Information). The electrochemical activity of amorphous-state FeOOH has been demonstrated to be better than that of crystalline-state FeOOH with similar particle size and morphology.

For flexible SC application, a freestanding and binder-free FQDs/CNTC film electrode was obtained via facile vacuum-induced filtration. The elimination of an insulating polymeric binder could increase the utilization of electroactive material and enhance the electrical conductivity of the electrode. As shown in Figure S13 of the Supporting Information, the resultant FQDs/CNTC film exhibits a well-aligned layered and a compact structure, in which the robust skeleton is dual supported by g-C$_3$N$_4$ and Ti$_3$C$_2$, thus providing the FQDs/CNTC film with high mechanical stability for use as a flexible electrode (Figure S14, Supporting Information). By contrast, FQDs/g-C$_3$N$_4$ and FQDs/Ti$_3$C$_2$ show poor film forming ability, which are both easily disintegrated after vacuum filtration (Figure S15, Supporting Information). Therefore, the freestanding FQDs/CNTC film electrode can be readily applied in flexible energy-storage devices, catering to the need for portable and wearable electronic technologies.

The electrochemical behaviors of the CNTC (only g-C$_3$N$_4$ and Ti$_3$C$_2$) and FQDs/CNTC film electrodes were evaluated using the three-electrode configuration in the EMIMBF$_4$ IL electrolyte. As shown in Figure 2a, the cyclic voltammetry (CV) curve of the FQDs/CNTC film electrode exhibits broad and obvious redox peaks at $-0.25$ V (cathodic peak) and $-0.05$ V (anodic peak), showing a higher specific capacitance than the CNTC film electrode with limited capacitive storage (detailed description...
in Figure S16, Supporting Information) in the IL electrolyte. Figure 2b shows that the set of redox peaks is visible for the anodic and cathodic sweeps in various CV curves of the FQDs/CNTC film electrode, indicating its dominant pseudocapacitive storage in the IL electrolyte. As calculated using Equation (4), the specific capacitance of the FQDs/CNTC film electrode based on the total volume at 5 mV s$^{-1}$ can reach 391.78 F cm$^{-3}$, considerably larger than that of previously reported film electrodes (mostly <250 F cm$^{-3}$) in IL electrolytes.$^{[41-45]}$ When the scan rate increases to 100 mV s$^{-1}$, the specific capacitance still remains at 201.22 F cm$^{-3}$ (Figure 2c).

With regard to the FQDs/CNTC film electrode, the CNTC with capacitive storage ($\approx$46 F cm$^{-3}$ at 5 mV s$^{-1}$) certainly contributes to the total capacitance, but the total capacitance is mainly contributed by the pseudocapacitive redox reaction of FQDs in the FQDs/CNTC film electrode (Figure 2d). As shown in Figure 1a, b, c, d, e, f, g, h, i, j, k, l, FQDs/CNTC demonstrates a high conductivity and good chemical stability, which is beneficial for the pseudocapacitive storage of FQDs/CNTC in the IL electrolyte.
In Figure 2e,f, the non-diffusion-limited storage in the FQDs/CNTC film electrode is prominent, indicating that the redox reaction originates from the fast pseudocapacitive process instead of the slow diffusion-controlled battery-type energy storage. The nonlinear curves without a plateau (Figure 2g) further indicate that the FQDs/CNTC film electrode mainly stores pseudocapacitive charge in the IL electrolyte, similar to the reported pseudocapacitive electrodes for SCs.\[46,47\] To elucidate the evolution of FQDs in the film electrode during the electrochemical process, the chemical state variation of the Fe element was investigated through XPS analysis at selected charge/discharge states (Figure 2h). The main peak of Fe 2p\(\frac{3}{2}\) at 711.3 eV slightly shifts to a lower binding energy with deepening of discharge owing to the partial conversion of trivalent Fe to divalent Fe.\[48\] In turn, during the charging process, the valence state of the reduced bivalent Fe can change to trivalent Fe, further indicating the reversible redox reaction of FQDs in the electrode with IL ions to generate and store charge. The pseudocapacitive mechanism is associated with the following reaction:

\[
\text{Fe}^{II} + \text{O} + \text{x}[\text{EMIM}]^+ + \text{xe} \leftrightarrow \text{Fe}^{III} + \text{O} + \text{xe}[\text{EMIM}]^+ + \text{x}[\text{EMIM}]^+.
\]

The charge stored in the FQDs/CNTC film electrode, or the capacity (mAh cm\(^{-3}\)), was evaluated using galvanostatic charge–discharge (GCD) curves (on the basis of Equation (5)) at current densities from 0.5 A cm\(^{-3}\) to 4 A cm\(^{-3}\). The specific capacity of the FQDs/CNTC film electrode was calculated to be 227.02 mAh cm\(^{-3}\) at 0.5 A cm\(^{-3}\) and 137.64 mAh cm\(^{-3}\) at 4 A cm\(^{-3}\), or a 60.6% capacity retention in the IL electrolyte.

To investigate the role of g-C\(_3\)N\(_4\) and Ti\(_3\)C\(_2\) in the FQDs/CNTC electrode, a film electrode of FQDs grown on common high-temperature activated carbon nanofibers (FQDs/ACNFs)
was obtained, and its electrochemical behavior was compared with that of the FQDs/CNTC electrode in the EMIMBF₄ IL electrolyte. Figure 3a displays the CV curves of the FQDs/CNTC and FQDs/ACNF film electrodes at a scan rate of 20 mV s⁻¹. Obvious redox peaks are observed in the anodic and cathodic sweeps, suggesting that the dominant pseudocapacitive storage of the FQDs/CNTC and FQDs/ACNF film electrodes in the IL electrolyte results from the reversible redox reactions of the FQDs in the electrodes with IL ions (EMIM⁺). In addition, the FQDs/CNTC film electrode shows higher peak currents and a larger CV area, thus revealing sufficient redox reaction and superior pseudocapacitive behavior of the FQDs/CNTC film electrode in the IL electrolyte.

Potential-driven ion accumulation can be probed using the differential capacitance, which has been regarded as an effective indicator of the IL ion density near the electrode, and interpreted based on Kornyshev theory.⁴⁹ Therefore, the differential capacitance of FQDs/CNTC and FQDs/ACNF film electrodes in the EMIMBF₄ IL electrolyte were investigated using Cₐ−E curves.⁴⁹,⁵⁰ Electrostatic interactions cause counterions to accumulate on the surface of the charged electrode, forming a compact stern layer and a loose diffuse layer.⁵¹ In the Cₐ−E curve, the differential capacitance depends on the accumulated ion density in the stern layer.⁴⁹,⁵⁰,⁵² Figure 3b shows the Cₐ−E curves of FQDs/CNTC and FQDs/ACNF film electrodes in the EMIMBF₄ IL electrolyte, both displaying two obvious peaks in the curves. According to Kornyshev theory, for camel-shaped curves, the potential of zero charge (PZC) is the potential corresponding to the minimum capacitance between the two peaks.⁵³,⁵⁴ When the electrode potential negatively moves away from the PZC, the cations move towards the stern layer to shield the negative charge on the electrode surface (more details are provided in Figure S17, Supporting Information). For the EMIMBF₄ IL electrolyte (Figure S18, Supporting Information), movement of the larger-sized EMIM⁺ cations in the diffuse layer and accumulation in the stern layer are more difficult compared with the smaller BF₄⁻ anions.⁵⁵,⁵⁶ As a result, the differential capacitance of the FQDs/ACNF electrode is lower under negative polarization than positive polarization, indicating its inefficient EMIM⁺ accumulation in the stern layer. However, EMIM⁺ is the working ion triggering the pseudocapacitive reaction with FQDs in the electrode, so the unsatisfactory pseudocapacitive storage of the FQDs/ACNF electrode is due to the lack of EMIM⁺ for sufficient redox reaction with FQDs in the FQDs/ACNF electrode (the left model in Figure 3c). By contrast, the Cₐ−E curve of the FQDs/CNTC electrode is nearly asymmetric, in which the differential capacitance is significantly increased when the electrode is negatively charged, indicating a high-accumulated EMIM⁺ ion density in the stern layer. This phenomenon is mainly due to the abundant active sites consisting of numerous lone pair electrons, such as N defects of g-C₃N₄ and surface functionality of Ti₂C₃ in the FQDs/CNTC electrode, which easily overlap with the electron cloud of the positively charged imidazole ring. The overlap of electron clouds could effectively form strong adsorption between EMIM⁺ cations and the electrode surface, leading to large numbers of EMIM⁺ cations being adsorbed and arranged in the stern layer over a short distance (the right model in Figure 3c). The higher the EMIM⁺ cation accumulation, the more these cations fully participate in the redox reaction with FQDs, leading to the FQDs/CNTC film electrode exhibiting excellent pseudocapacitive behavior.

Electrochemical impedance spectroscopy (EIS) is a powerful technique that provides much information regarding the electrochemical kinetic characteristics of the FQDs/CNTC and FQDs/ACNF film electrodes in the EMIMBF₄ IL electrolyte. The point intersecting the real axis in the high frequency region represents the equivalent series resistance (Rₛ), which reveals the total inner resistance of the electrode.⁵⁷ As shown in the inset of Figure 4a, the Rₛ of the FQDs/CNTC film electrode is lower than that of the FQDs/ACNF film electrode owing to the ultrahigh electrical conductivity of Ti₂C₃ in the FQDs/CNTC film electrode. Moreover, the diameter of the semicircle in the high frequency region is related to the charge-transfer resistance (Rₜ), and the straight-line part in the low-frequency region represents the Warburg impedance

![Figure 3](https://www.advancedscience.com)
which is described as the diffusive impedance of the IL ions within the film electrode. Clearly, the FQDs/CNTC film electrode shows a smaller semicircle and a more vertical straight line (Figure 4a), indicating the favorable kinetic behavior of ionic diffusion and charge transport for the FQDs/CNTC film electrode in the IL electrolyte. To deeply analyze the IL ion dynamics, the diffusion coefficient of IL ions in the film electrode can be estimated using impedance data at a low frequency. In this frequency range, the magnitude of the impedance varies linearly with $\omega^{-1/2}$, in accordance with Equation (1)

$$Z = \frac{L}{C_I (D \cdot \omega)^{1/2}}$$

where $D$, $C_I$, and $L$ are the diffusion coefficient, low-frequency redox capacitance, and film thickness, respectively. The value of $C_I$ can be obtained from the plot of $-Z_{im}$ versus $1/\omega$, which is linear with a slope of $1/C_I$, in accordance with Equation (2)

$$-Z_{im} = \frac{1}{C_I \omega}$$

As shown in Figure S19 of the Supporting Information, the $C_I$ values of the FQDs/ACNF and FQDs/CNTC film electrodes are calculated to be 19 and 25 mF, respectively. By substituting the latter value into Equation (1), the diffusion coefficient of the IL ions in the FQDs/CNTC film electrode is calculated to be $2.003 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ (Figure 4b), which is much higher than that in the FQDs/ACNF film electrode ($3.455 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$), further confirming the enhanced IL ion dynamics of the FQDs/CNTC film electrode.

Wettability is one of the most crucial properties of a film electrode. The microstructure of the film electrode influences its wettability to a large extent. For a liquid droplet on a flat solid, the wetting behavior is determined by Young's equation

$$\gamma_d = \gamma_{sl} - \gamma_{lg} \cdot \cos \theta$$

where $\gamma_d$, $\gamma_{sl}$, and $\gamma_{lg}$ are the surface free energy of the liquid, the surface free energy of the solid, and the interfacial free energy between the solid and liquid, respectively. Figure 4c shows the wetting process of EMIMBF$_4$ IL droplets in contact with the FQDs/ACNF and FQDs/CNTC film electrodes. The FQDs/CNTC film electrode is almost completely wetted by the IL electrolyte, exhibiting significantly better wettability than the FQDs/ACNF film electrode. The small $\theta$ ($20.3^\circ$) and large $\gamma_{sl}$ (50.2 mJ m$^{-2}$) of the FQDs/CNTC film electrode in the IL electrolyte (Figure 3d) both confirm its excellent wettability. The $\gamma_d$ of the EMIMBF$_4$ IL electrolyte is measured to be $\approx 52.4$ mJ m$^{-2}$, and the $\gamma_{sl}$ of the FQDs/CNTC film electrode in the IL electrolyte is calculated to be $1.05$ mJ m$^{-2}$, which is $\approx 2.6$ times lower than that of the FQDs/ACNF film electrode ($2.71$ mJ m$^{-2}$). The low $\gamma_{sl}$ value indicates strong adhesion between the FQDs/CNTC film electrode and the IL electrolyte, which is mainly due to the abundant pore channels (Figure S20, Supporting Information) and active sites of the FQDs/CNTC film electrode. As shown in Table S1 of the Supporting Information, the calculated liquid electrode uptake (EU) and porosity (P) of the FQDs/CNTC film are higher than those of the FQDs/ACNF film, further indicating the superior wettability of the FQDs/CNTC film in the EMIMBF$_4$ IL electrolyte. Furthermore, the
The superior electrochemical energy storage of the FQDs/CNTC film electrode in the IL electrolyte is schematically illustrated in Figure 5, which can be attributed to the following aspects. (1) Abundant active sites consisting of numerous lone pair electrons, such as nitrogen defects of g-C3N4 and surface functionality of Ti3C2, are favorable for the adsorption of IL ions. Meanwhile, the rich porous structure of g-C3N4 provides accessible channels for IL ions (blue arrows). Both these factors ensure that IL ions are involved in the sufficient redox reaction with FQDs, leading to the FQDs/CNTC film electrode exhibiting a high specific capacitance. (2) FQDs are dual confined in g-C3N4 and Ti3C2 heterogeneous nanosheets, forming a robust sandwich-type architecture. This can provide a suitable nanospace for the dual protection of FQDs (black arrows), which effectively inhibits the aggregation and dissolution of FQDs during the cycling process, rendering the high cycle stability of the FQDs/CNTC film electrode. (3) Highly conductive Ti3C2 acts as a “highway” to facilitate efficient charge transport (red arrows), which benefits the rate capability of the FQDs/CNTC film electrode in the IL electrolyte. Similar to the IL electrolyte, an ionogel as a solid-state electrolyte exhibits nonvolatility, nonflammability, high thermal stability, and a wide electrochemical potential window (Figure S23, Supporting Information).[16,62] Hence, a flexible SC (FSC) has been fabricated with an ionogel electrolyte using poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) copolymer as a polymer matrix and hydrophobic EMIMBF4 IL as a solvent. Differentiated by the stable potential ranges in the EMIMBF4 IL electrolyte (Figure S25, Supporting Information), the FQDs/CNTC film and CNTs/RGO film (Figure S24, Supporting Information) are used as negative and positive electrodes, respectively, in the device. As seen from the CV curves in Figure 6a, an FSC with a wide potential window of 3.0 V and a large specific capacitance of 71.26 F cm⁻³ (calculated by Equation (6)) is achieved at 10 mV s⁻¹. Figure 6b shows the GCD curves of the FSC in the range of 0.5–4 A cm⁻². As calculated using Equations (7) and (8), the maximum energy density based on the total volume of the FSC (≈0.0105 cm³), configuration illustrated in Figure S26, Supporting Information) is 77.12 mWh cm⁻³ at a power density of 750 mW cm⁻³. Additionally, the maximum power density of the FSC is ≈6000 mW cm⁻³ at an energy density of 48.49 mWh cm⁻³, which is much better than those of previously reported state-of-the-art FSCs (Figure 6c).[63–69] In addition, the cycling stabilities of the fabricated FSC in the straight and bent states reveal a high retention above 80% after 10 000 cycles (Figure 6d). Importantly, the FSC is highly flexible, mechanically stable, and randomly bendable without destroying the structural integrity or electrochemical performance of the device (Figures S27 and S28, Supporting Information). During the deformation, the device can still light up a lamp (1 W, 2.0 V) with a bright red color (inset in Figure 6d).

To further demonstrate practical potential applications, we integrated the FSC as an energy-storage device to power some common electronic products in real life. As is notably observed in Figure 6e, two FSCs are connected in a series or parallel arrangement, which can easily power portable and wearable electronics, such as handheld game players and smart bracelets. More importantly, the FSCs as efficient energy-storage devices can power electronic products in complex motion states. This result indicates the great electrochemical reliability of the FSCs with high flexibility. Apparently, the FSCs are practically promising as a supplemental power source replacing microbatteries. Furthermore, an attempt to store renewable solar energy in FSCs was made, in which sustainable energy could be harvested for portable and wearable electronics. A commercial miniature solar-cell panel (5.5 V, 20 mA) was assembled using the fabricated FSCs as a sustainable energy system. Four FSCs in a series and parallel arrangement serve as an energy-storage module (Figure 6f), collecting solar energy generated by the solar-cell panel. After charging, the FSCs with high energy density could effectively power electronic products. The corresponding videos are shown in Movie S1 of the Supporting Information. The self-discharging performance is a crucial parameter for the practical application of FSCs. As shown in Figure S29 of the Supporting Information, the fabricated FSCs present a rapid self-discharge process in the first few minutes that gradually slows down over several hours. Finally, the open-circuit voltage of the devices is maintained at ≈2.5 V beyond 10 h, indicating a low self-discharge rate of the fabricated FSCs after harvesting sustainable energy. Therefore,
this study introduces a new avenue for flexible energy-storage devices, which is of great significance for the development of sustainable wearable and portable electronics.

3. Conclusions

We have successfully developed a new strategy to obtain a unique FQDs/CNTC film electrode, which was realized by the dual confinement of pseudocapacitive FQDs in porous g-C₃N₄ and conductive Ti₃C₂ nanosheets. Porous g-C₃N₄ and conductive Ti₃C₂ nanosheets not only act as ion-accessible channels and charge-transfer pathways, respectively, but also jointly offer a heterogeneous nanospace for the dual protection of FQDs. Probing of the potential-driven ion accumulation elucidated that strong adsorption can occur between the IL cation (EMIM⁺) and the electrode surface with abundant active sites, providing sufficient pseudocapacitive behavior of the FQDs/CNTC film electrode in the IL electrolyte. As a consequence, a 3 V high-voltage FSC could be fabricated using an ionogel as a solid-state electrolyte, which presented a high energy density (77.12 mWh cm⁻³), a high power density (6000 mW cm⁻³), and a remarkable rate and cycling performance. The FSCs could effectively power various wearable and portable electronics, making them suitable for a wide range of applications in stylish energy-storage devices. Considering the facile fabrication and outstanding performance, this work provides new insight into fabricating superior pseudocapacitive QDs electrode materials for flexible energy-storage devices towards portable and wearable electronics.

4. Experimental Section

Synthesis of Porous g-C₃N₄: Briefly, 5 g melamine was put into a crucible and heated at 520 °C for 4 h in air to obtain an agglomerate (bulk g-C₃N₄). Then, 1 g bulk g-C₃N₄ powder was placed in an open
crucial, followed by heat treatment at 550 °C for 3 h in air with a heating rate of 10 °C min⁻¹. Afterward, the obtained powder was dispersed in isopropanol, sonicated for 0.5 h and then separated by centrifugation at ~5000 rpm to remove the residual incompletely exfoliated part, finally obtaining yellowish-white porous g-C₃N₄ under vacuum drying.

**Synthesis of Ti₃C₂**: Typically, 1 g Ti₃AlC₂ was slowly added to a mixed aqueous solution of LiF (1.82 g) and 20 mL HCl (10 M). An ice water bath was used to avoid overheating due to the exothermic reaction. Subsequently, the solution was kept at 38 °C for 48 h to etch the Al in Ti₃AlC₂. Afterward, the resultant Ti₃C₂ was collected via centrifugation, washed, and dispersed in deionized water to form a homogeneous solution by liquid-phase ultrasonication.

**Preparation of FQDs/CNTC Film**: First, 40 mg porous g-C₃N₄ was added to 50 mL ethanol with sonication for 5 min. Then, 1 mmol FeCl₃·6H₂O and 3 mmol NH₄HCO₃ were dissolved separately in the above solution with stirring for 10 h. Next, 30 mL Ti₃C₂ dispersion (2 mg mL⁻¹) was added with continuous stirring for another 12 h to obtain FQDs/CNTC, which was then dispersed into 100 mL deionized water to form a homogeneous solution (1 mg mL⁻¹) under ultrasonic treatment. Finally, 30 mL FQDs/CNTC solution was vacuum filtered through a cellulose ester filter membrane (pore size of 0.22 µm) and then peeled from the membrane to obtain the FQDs/CNTC film. For comparison, high-temperature ACNFs film was immersed in 50 mL ethanol containing 1 mmol FeCl₃·6H₂O and 3 mmol NH₄HCO₃, followed by continuous stirring for 10 h, to obtain FQDs/ACNF film. In addition, CNTC film was prepared using a similar method without the addition of FeCl₃·6H₂O and NH₄HCO₃. FQDs/g-C₃N₄ and FQDs/Ti₃C₂ were also prepared through a procedure similar to that mentioned above. (More experimental details are presented in Figure S22, Supporting Information.)

**Characterization**: Field emission scanning electron microscopy (FEI Sirion 200) and TEM (JEM-2100F) were carried out to characterize the morphology of the samples. AFM images were recorded on a MultiMode 8 (Bruker) in ScanAsyst mode. XRD patterns were characterized on a powder XRD system with Cu Kα radiation, and XPS measurements were performed on a Kratos AXIS Ultra DLD spectrometer with an Al Kα X-ray source. Nitrogen absorption and desorption measurements were performed with an Autosorb IQ instrument at 77 K. The specific surface area was calculated using the Brunauer–Emmett–Teller method, and the pore size distribution was determined from the adsorption branch of the isotherm according to density functional theory. The surface tension of the EMIMBF₄ IL was measured using a contact angle measuring instrument (DCA300, Germany), in which the surface free energy of the films was determined using the conventional two-liquid-phase method.

**Electrochemical Measurements**: All electrochemical tests were performed using a VMP3 multifunctional electrochemical analysis instrument (Bio-Logic, France) via CV, GCD, and EIS methods. The CV and GCD tests were performed at various scan rates and current densities. The EIS measurements were performed in the frequency range of 0.01 Hz to 100 kHz. Additionally, Cₚ-E curves were obtained from EIS measurements according to the previously reported method based on Kornyshev’s models. For flexible SC application, FQDs/CNTC film and CNTs/RGO film (additional details are presented in Figure S19, Supporting Information) were used as negative and positive electrodes, respectively. Then, an ionogel electrolyte was slowly sandwiched between the two film electrodes, which were pressed together for 30 min. The ionogel electrolyte was prepared as follows. First, 0.6 g P(VDF-HFP) was dissolved in an acetone solution. Then, 2.0 g EMIMBF₄ IL was added to the resulting solution under stirring until the solution became clear. The resulting viscous solution was cast onto a glass petri dish to evaporate the acetone for 1 h to obtain the ionogel electrolyte.

**Calculations for the Electrochemical Tests**: The specific capacitance of a single electrode (Cₛₚ) was calculated from the anodic scan of the CV curve on the basis of Equation (4)

$$C_{sp}(F \cdot cm^{-2}) = \int \frac{j \cdot dv}{\nu \cdot U}$$  \hspace{1cm} (4)

Here, i is the current change over time t, v is the volume of a single electrode, and U is the voltage window of the CV scan.

According to Gogotsi’s previous reports, when the GCD curve is nonlinear, the specific capacity of a single electrode, instead of the capacitance, is evaluated using Equation (5)

$$C(\text{mAH cm}^{-2}) = \frac{\int \Delta t}{\Delta \text{It}} \cdot \frac{1}{3.6}$$ \hspace{1cm} (5)

where \( \Delta t \) (s) is the discharging time and I (A cm⁻²) is the constant current density.

For the two-electrode system, the specific capacitance of the fabricated FSC was evaluated on the basis of the CV curve using Equation (6)

$$C_{FSC}(F \cdot cm^{-2}) = \int j \cdot dt \cdot \frac{1}{\nu_{total} \cdot U_{FSC}}$$ \hspace{1cm} (6)

where \( \nu_{total} \) is the total volume of film electrodes and \( U_{FSC} \) is the voltage window of the fabricated FSC.

The energy density of the FSC was calculated on the basis of the discharge branch of the GCD curve using Equation (7), and the power density was further evaluated using Equation (8)

$$E(\text{mWh cm}^{-2}) = \frac{1}{2} \cdot \frac{1}{18} \cdot \frac{U_{0}^{2}}{U_{max}^{2}}$$ \hspace{1cm} (7)

$$P(\text{mW cm}^{-2}) = 3600 \cdot E/\Delta t$$ \hspace{1cm} (8)

where E (mWh cm⁻²) is the energy density, P (mW cm⁻²) is the power density, \( I_{c} \) (A cm⁻²) is the constant discharge current density, \( \Delta t \) (s) is the discharging time, and \( U_{0} \) to \( U_{max} \) is the voltage window of the FSC.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors greatly acknowledge the funding for this project through the National Nature Science Foundations of China (Grant Nos. 21573265 and 51873083), the Opening Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University) (No. sklpme2018.4-27), the Six Talent Peaks Project in Jiangsu Province (No. 2015-XCL-028), the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX18_0759, SJCX19_0584), and the Key University Science Research Project of Jiangsu Province (18KJA130001).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

dual confinement, flexible supercapacitors, ionic liquids, pseudocapacitive behavior, quantum dots
