Three-dimensional (3D) printing technology has a pronounced impact on building construction and energy storage devices. Here, the concept of integrating 3D-printed electrochemical devices into insulation voids in construction bricks is demonstrated in order to create electrochemical energy storage as an integral part of home building. The low-cost 3D-printed supercapacitor (SC) electrodes are created using graphene/polylactic acid (PLA) filament in any desired shape such as 3D cylindrical- (3Dcy), disk- (3Ddc), and 3D rectangular- (3Drc) shaped electrodes. To obtain excellent capacitive performance, a Ti$_3$C$_2$@polypyrrole (PPy) hybrid is uniformly electroplated on the surface of 3D-printed electrodes. These Ti$_3$C$_2$@PPy-coated 3D-printed electrodes exhibit outstanding electrical conductivity, capacitive performance, cycle life, and power density. The bricks themselves act as an excellent scaffold for electrochemical energy devices as they are electrically insulating, fire-resistant, and contain substantial unused thermal insulation voids. A 3Drc Ti$_3$C$_2$@PPy SC is integrated into a real brick to showcase a smart house energy storage system that allows to reserve power in the bricks and use it as a power backup source in the event of a power outage in the elevator. This concept provides a platform for future truly smart buildings built from added value “smart brick” energy storage systems.

1. Introduction

The technique of three-dimensional (3D) printing has been used for a wide range of applications, \cite{1} such as building construction, \cite{2,3} car parts manufacturing, \cite{4,5} space applications, \cite{6,7} electronics, \cite{8,9} and energy storage devices. \cite{10-12} Among electrochemical and energy storage devices, there has been significant progress made in electrolyzers, \cite{13-17} batteries, \cite{18} and supercapacitors. \cite{19-21} While these energy applications are targeted toward the construction of “green energy” sustainable smart homes, the integration of 3D-printed electrochemical devices into construction building blocks, such as concrete and ceramic bricks, is non-existent. Here, we integrated 3D-printed electrochemical devices into insulation voids in the bricks to create electrochemical energy storage as an intrinsic feature of the home building blocks.

Fused deposition modeling (FDM) has attracted considerable interest as a 3D printing technique due to its low cost and accessibility. For electrochemical capacitor applications, a commonly used graphene/polylactic acid (PLA) filament is the most favorable filament in the FMD 3D printing process. \cite{22-26} The electrochemical properties of 3D-printed electrodes could be improved further by using electrodeposition or atomic layer deposition of metallic 2D materials. \cite{20,23,27} Of the class of 2D materials, Ti$_3$C$_2$ (MXene) has become the most widely used SC electrode material to achieve superior electrochemical performance; this is due to its excellent metallic conductivity.
hydrophilicity, and capacity to undertake redox capacitive reaction at the titania site.\textsuperscript{[28–31]} The preparation of colloidal Ti$_3$C$_2$ solution has made it possible to use it in writing, printing, dipping and drying; thus, fabrication of SC provides a large specific capacitance.\textsuperscript{[32–34]} The capacitance and cycle life of Ti$_3$C$_2$ base SC has been improved by adding 2D carbon-based materials such as graphene, mesoporous C$_{60}$, carbon nanotubes, and so on.\textsuperscript{[35,36]} Moreover, the ability of Ti$_3$C$_2$ to link and to build composites with polymer (e.g., polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene))\textsuperscript{[37,38]} makes it suitable for improving the surface properties of 3D-printed electrodes.

In this context, this work aimed to investigate the use of 3D printing in the fabrication of low-cost SC devices and to demonstrate their practicality by prototyping electrodes of different shape designs (i.e., 3Dcy, 3Ddc, and 3Drc) using graphene PLA filament. Further, 3D-printed electrodes were functionalized with Ti$_3$C$_2$@PPy hybrid using a procedure that included chemical activation of the electrodes followed by immersion of the electrodes in a Ti$_3$C$_2$/pyrrole solution. **Figure 1** presents a schematic view of the fabrication 3Drc Ti$_3$C$_2$@PPy hybrid-facilitated ion diffusion and electron transfer. Intending to develop a smart house energy storage system, as prepared 3Drc Ti$_3$C$_2$@PPy SCs were integrated into...
insulation voids in the bricks, allowing us to store electricity in the house wall and use it later. In addition, power storage in bricks might be used as a backup power source in the event of a power outage in the elevator. We demonstrate this with a scaled-down model.

2. Results and Discussion

The concept of a smart brick with integrated energy storage is shown in Figure 1. First, we fabricated the electrode to be placed in the brick insulating space. Graphene PLA filament was used to create 3Drc-shaped electrodes, which were then integrated with the brick for a smart house energy storage application. The detailed fabrication process of 3Drc Ti$_3$C$_2$@PPy SC is described in the Experimental Section. However, it is essential to understand the structural and morphological properties of Ti$_3$C$_2$@PPy-coated 3D-printed electrodes before beginning electrochemical studies and their implementation in smart homes.

Ti$_3$C$_2$ and pyrrole were deposited on the surface of a chemically activated 3Drc printed electrode via one-pot electrodeposition in which Ti$_3$C$_2$ has a hydrophilic nature, robust metallic conductivity, and negative charge property. The transmission scanning electron microscopy image of Ti$_3$C$_2$ nanosheet is depicted in Figure S1a (Supporting Information). Ti$_3$C$_2$ would engage with the cation radical of pyrrole during the electropolymerization step without any additional electrolyte. The morphological features of the as-prepared Ti$_3$C$_2$@PPy-coated 3D-printed electrode (3Drc Ti$_3$C$_2$@PPy) with deposition times from 15 to 45 min were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). After chemical activation of the filament, the smooth surface turned very rough (Figure 2a,b). Figures 2c present SEM image of 3Drc electrode surface after 45 min of Ti$_3$C$_2$@PPy electrodeposition. Apparently, there is a significant rise in concentration of Ti$_3$C$_2$@PPy composites on the activated 3Drc electrode surface with the increased deposition time from 15 to 45 min. Figure S1b,c (Supporting Information) displays the SEM images of Ti$_3$C$_2$@PPy on 3Drc electrode after 15 and 30 min of electrodeposition, respectively. However, after 45 min of electrodeposition, the Ti$_3$C$_2$@PPy hybrid had evenly coated on the 3Drc electrode surface (see inset of Figure 2c). These findings suggest that the coated Ti$_3$C$_2$@PPy has a useful property for electrochemical study. Further evidence from SEM-EDS mapping shows the presence of Ti, C, O, and N on the 3Drc electrode surface as seen in Figure 2d (Figures S2a,b and Table S1, Supporting Information), indicating the presence of Ti$_3$C$_2$ and PPy on the surface of the 3Drc electrode.

Figure 3a displays thermogravimetric analysis (TGA) curves of the filament surface before and after Ti$_3$C$_2$@PPy electrodeposition at 45 min. As can be observed, the 3Drc electrode had an onset temperature of 270 °C and a degradation temperature of 351 °C, which rose to 315 °C and 379 °C, respectively, after Ti$_3$C$_2$@PPy was deposited on the electrode surface. This indicates that Ti$_3$C$_2$@PPy was successfully electrodeposited on the surface of the 3Drc electrode. To validate the Ti$_3$C$_2$ crystal phase on the 3Drc electrode surface, an X-ray diffraction (XRD) pattern was obtained for examination as seen in Figure 3b. The diffraction peaks observed at 20.3° and 29.7° were defined as PLA and graphene peaks, respectively. On the other hand, in the Ti$_3$C$_2$@PPy-based 3Drc electrode, the diffraction peak (001) of Ti$_3$C$_2$ exits at a lower angle, which indicates that the...
electrodeposited Ti\textsubscript{3}C\textsubscript{2} crystal structure remains stable.\textsuperscript{[32,42]} To further confirm the surface properties and porous structures, nitrogen adsorption–desorption isotherm analysis was conducted. Figure 3c displays the typical isotherms and the corresponding pore size distribution plots of the pre- and post-electrodeposition of Ti\textsubscript{3}C\textsubscript{2}@PPy on the surface of the 3D-printed electrode. The specific surface area (SSA) of the pristine 3D electrode acquired through the Brunauer–Emmett–Teller (BET) method is calculated to be 5.01 m\textsuperscript{2} g\textsuperscript{−1} while the Ti\textsubscript{3}C\textsubscript{2}@PPy deposited 3Drc electrode has a three-fold high SSA (15.91 m\textsuperscript{2} g\textsuperscript{−1}). This significant rise in SSA is responsible for the existence of Ti\textsubscript{3}C\textsubscript{2}@PPy as evidenced by the above SEM findings. In order to evaluate conductivity, a simple square wave-shaped current circuit was constructed using a pristine 3D-printed cylindrical electrode (3Dcy), chemically activated 3Dcy electrode, and different time electrodeposited Ti\textsubscript{3}C\textsubscript{2}@PPy-based 3Dcy electrodes. Figure 3d illustrates the dependence of the resistivity of the Ti\textsubscript{3}C\textsubscript{2}@PPy on the 3Dcy electrode, which is based on the timing of electrodeposition. The resistance of the Ti\textsubscript{3}C\textsubscript{2}@PPy-based 3Dcy decreased gradually with an increase in the electrodeposition time from 15 to 45 min (Figures S3a–d, Supporting Information). However, a long electrodeposition period (60 min) reduces the electrical conductivity, which is attributed to the increased active material coating on the surface of 3Dcy electrode (see SEM image in Figure S1d, Supporting Information). Comparatively, when the pristine 3Dcy was connected with both ends of the circuit, the red light emitting diode (LED) light was on with very low intensity, whereas the 45 min electrodeposited Ti\textsubscript{3}C\textsubscript{2}@PPy-based 3Dcy electrode had a comparatively high light intensity (Figure S3e,f, Supporting Information). This indicated that the Ti\textsubscript{3}C\textsubscript{2}@PPy-deposited 3D-printed electrode had low electrical resistance (high electrical conductivity), which promotes the directional transfer of electrons.

Following morphological and structural characterisations, we examined the electrochemical performance of Ti\textsubscript{3}C\textsubscript{2}@PPy electrodeposited 3Dcy electrode in a three-electrode system with 1 m H\textsubscript{2}SO\textsubscript{4} solution as electrolyte (Figure S4a,b, Supporting Information). The cyclic voltammetry (CV) plots of the pristine and various time deposited Ti\textsubscript{3}C\textsubscript{2}@PPy on 3Dcy electrodes are shown in Figure S5a (Supporting Information). The CV integral area of the 3Dcy Ti\textsubscript{3}C\textsubscript{2}@PPy electrodes increases as electrodeposition time is raised from 15 to 45 min, suggesting that a longer electrodeposition time is beneficial for increasing capacitance. Thanks to the 2D material (Ti\textsubscript{3}C\textsubscript{2}), the CV curves of the 3Dcy Ti\textsubscript{3}C\textsubscript{2}@PPy electrodes have a greater enclosed area and rectangular shape, suggesting better electron transfer and larger capacitance. But after 60 min of Ti\textsubscript{3}C\textsubscript{2}@PPy electrodeposition, the CV enclosed area of 3Dcy Ti\textsubscript{3}C\textsubscript{2}@PPy electrode starts to decrease (Figure S5a, Supporting Information). This is owing to the loading of Ti\textsubscript{3}C\textsubscript{2}@PPy composite and conductivity of electrode reaches a maximum after 60 min electrodeposition.
On the other hand, the excess active materials on the surface of 3Dcy electrode create the aggregation between the Ti$_3$C$_2$ and PPy, resulting in performance loss. The galvanostatic charge-discharge (GCD) plots of 3Dcy Ti$_3$C$_2$@PPy electrodes with an operating window from −0.2 to 0.6 V at current density of 1 A g$^{-1}$ are shown in Figure S5b (Supporting Information). It is evident that the 3Dcy Ti$_3$C$_2$@PPy electrodeposited for 45 min had a long discharge time, implying a large specific capacitance ($C_{sp}$). Based on discharge time, calculated $C_{sp}$ of the 3Dcy Ti$_3$C$_2$@PPy electrode after an electrodeposition time of 0, 15, 30, and 45 min exhibited 1.73, 41.15, 79.7, and 121.03 F g$^{-1}$, respectively. Furthermore, the GCD curve of the 3Dcy Ti$_3$C$_2$@PPy electrode was similar with the CV profile, suggesting that after 60 min of electrodeposition of Ti$_3$C$_2$@PPy, the electrochemical performance is decreased (Figure S5b, Supporting Information). Based on our findings, we decided that 45 min was the best electrodeposition time. These excellent electrochemical performances are most certainly due to the electrodeposition of the Ti$_3$C$_2$@PPy hybrid, which can enhance conductivity and specific surface area.

According to studies of a single 3Dcy Ti$_3$C$_2$@PPy electrode, the Ti$_3$C$_2$@PPy hybrid layer deposited after 45 min of electrodeposition offered the best overall results; hence, the same electrodeposition time was used for the preparation of other two 3D electrode designs: 3Ddc Ti$_3$C$_2$@PPy (Figure S4c, Supporting Information) and 3Drc Ti$_3$C$_2$@PPy (Figure S4e,f, Supporting Information). To prove high electrochemical performance in two electrode system, we first investigate the capacitive performance of the 3Ddc Ti$_3$C$_2$@PPy electrode. Thus, we fabricated a freestanding symmetric solid-state SC with two 3Ddc Ti$_3$C$_2$@PPy electrodes and F108/H$_2$SO$_4$ hydrogel electrolyte

![Figure 4. Electrochemical performance of symmetric 3D disk (3Ddc) Ti$_3$C$_2$@PPy supercapacitor (SC): a) cyclic voltammetry (CV) plot at different scan rates, b) galvanostatic charge-discharge (GCD) plots at different current densities, c) $C_{sp}$ as a function of current density, d) Nyquist plot, e) cycling stability, f) Ragone plot of energy density versus power density.](image)
sandwiched between them as shown in the inset of Figure 4a and Figure S4d (Supporting Information).

Figure 4a shows the CV plots of 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC at scan rates from 5 to 100 mV s\(^{-1}\). The CV curves have not been modified dramatically, suggesting high-rate capability and outstanding capacitive behavior of the 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy electrode. Further, when scan rates increase, the area of the CV curves increases, showing excellent capacitive characteristics. Figure 4b displays the symmetric linear shape of GCD curves, indicating that the 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC exhibits perfect ideal capacitive behavior with an operating voltage of 0.8 V. Figure 4c shows that the 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC has a higher \(C_{\text{sp}}\) of 118.14 F g\(^{-1}\) at a current density of 1.5 A g\(^{-1}\) with a good rate capacity of 92.9% \(C_{\text{sp}}\) retention (109.8 F g\(^{-1}\)) when the current density is raised two-fold. The Nyquist plot in Figure 4d presents that the 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC has a comparatively small equivalent series resistance (ESR) of 4.8 \(\Omega\), which leads to rapid electron transfer in the electrodes. Furthermore, a test of long-term cycling of 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC by GCD shows a current density of 5.0 A g\(^{-1}\). Figure 4e shows that after 1000 and 6000 GCD cycles, the \(C_{\text{sp}}\) retained 97.88% and 81.4% of its initial \(C_{\text{sp}}\) respectively, which is superior to the reported MXene and 3D-printed electrodes. Figure 4f illustrates the Ragone plot of 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC of which the values of power density (P) and energy density (E) are calculated from the GCD curves at different current densities. The E of 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC can achieve up to 2.64 W h kg\(^{-1}\) (1.60 mW h cm\(^{-2}\)) at \(P\) of 150 W kg\(^{-1}\) (93.7 mW cm\(^{-2}\)) while maintaining 2.44 W h kg\(^{-1}\) at 336 W kg\(^{-1}\). It has been noted that the E findings show higher performance when compared to other 3D-printed SC devices such as CoNi\(_{2}\)S\(_{4}\)/NiCo-LDHs/Ni/PL,\(^{[41]}\) PLA/nanoC,\(^{[42]}\) MoS\(_{2}\)/3D-PE,\(^{[40]}\) and MoS\(_{2}\)/3DnCF/Ti\(_{3}\)C\(_{2}\).\(^{[44]}\) A comparison performance of 3Ddc Ti\(_{3}\)C\(_{2}\)@PPy SC with previously reported 3D printed SCs is depicted in Table S2 (Supporting Information).

Further, we designed a 3D rectangular-shaped SC (3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC) device using a 3D printing technique (i.e., 3D pen) and integrated it into a brick to store energy in the house wall. Our idea is to create a smart house energy storage system that allows us to store electricity in the wall and use it later.\(^{[45]}\) For example, you could store the electricity generated by solar panels during the day and use it at night.\(^{[46]}\) We can also transfer unused stored electricity through the on-grid system. As a proof of concept for an energy storage brick, a 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC was fabricated using F108 hydrogel that serves as electrolyte and separator (inset of Figure 5a and Figure S4f, Supporting Information) and installed into the brick. Before evaluating the electrochemical performance of 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick, it is important to study the mechanical properties of 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC. To demonstrate the mechanical robustness of the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC for practical application, the GCD curves of the SC were recorded in their original and pressure states. The applied pressure is more than 500 times the weight of 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC (inset Figure S6a, Supporting Information). As presented in Figure S6a (Supporting Information), there is only a slight deviation in the GCD curves, showing its remarkable stability under mechanical pressure. Another mechanical property is impact strength, which was investigated by dropping 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC from various meter heights and observing electrochemical performance (inset Figure S6b, Supporting Information). The 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC exhibits outstanding mechanical impact strength with only a 6% loss in \(C_{\text{sp}}\) after a long-distance drop (Figure S6b, Supporting Information). These results indicate that the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC has good mechanical properties and is a potential candidate for brick integration. Figure 5 depicts the electrochemical performance of the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick. It can be seen that the CV curves have a rectangular shape even at very high scan rates, demonstrating that an efficient double-layer capacitance has been developed in the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC electrodes (Figure 5a). GCD curves at different current density rates ranging from 0.5 to 2 A g\(^{-1}\) are shown in Figure S5c (Supporting Information). The triangular shape of the GCD curve is typical of capacitive and reversible capacitive behavior. At a scan rate of 0.5 A g\(^{-1}\), a high \(C_{\text{sp}}\) of 46.2 F g\(^{-1}\) was recorded.

Despite having excellent electrochemical and mechanical properties of 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick may be suitable for real-world practical applications. To reach the desired \(C_{\text{sp}}\) or energy and power density, the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick might be connected either in parallel or in series depending on the application. Figure 5b shows the CV curves of three smart brick SC devices connected in series and in parallel configurations. By connecting three brick SCs in series, the voltage window for an individual brick SC can be expanded from 0.8 to 2.4 V for a tandem device. While single-brick SC output current density was enhanced three-fold (e.g., \(C_{\text{sp}}\) value almost triplets that of an individual brick SC) by simply combining three brick SCs in parallel. As shown by the GCD plot in Figure 5c, the operating voltage window can be increased from 0.8 V for an individual brick SC to 2.4 V by connecting three brick SCs in series, demonstrating better capacitive properties with low internal resistance. As a demonstration, such fabricated tandem brick SCs can power traffic signs (red, green, and yellow LEDs) with a minimal working voltage of 1.5 V for up to 180 s (Figure 5e, Figure S5d, and Movie S1, Supporting Information). Additionally, photovoltaic panels linked through cables might charge the brick SCs to provide an in-house power backup for emergency lighting (e.g., flashlights and ceiling lamps) and other uses.\(^{[46]}\)

We demonstrate on this model the application of such 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick as a reserve power source in elevator elevators such as during ride power failure. To provide specific power and energy for operating the elevator motor (≈3.5 V), multiple energy storage bricks were connected in a series configuration. To maximize voltage window, the five 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated bricks connected in series achieved 4.0 V. Figure 5d depicts a self-discharge curve of five series-connected 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated bricks after they were fully charged (up to 4.0 V) at a current density of 3.0 A g\(^{-1}\). In the first 150 s, the 3Drc Ti\(_{3}\)C\(_{2}\)@PPy SC-integrated brick self-discharge curve drops up to 3.70 V and then retains 3.55 V for the next 600 s. These self-discharge properties proved the ability to use this tandem brick SC as a power source to operate the elevator. Furthermore, as shown in Figure 5e, Figure S5f and Movie S2 (Supporting Information) the device of multiple brick SCs connected in series can drive an elevator. If the elevator main power supply fails, then it can use the energy stored in the brick SC to come to stop at the closest floor level. To the best knowledge of the authors, this
is the first operative brick SC demo device using Ti$_3$C$_2$@PPy-based 3D-printed electrodes.

3. Conclusion

To illustrate the possibility of a 3D handheld printer with graphene/PLA filament in the manufacture of 3D electrodes, we proposed three designs: cylindrical- (3Dcy), disk- (3Ddc), and 3D rectangular- (3Drc). 3D-printed electrodes were activated by chemical method and then electroplated with Ti$_3$C$_2$@polypyrrole (PPy) hybrid to achieve excellent capacitive performance. All of the 3D SC devices had outstanding capacitive performance, low resistance, and high energy and power density. Specifically, 3Ddc Ti$_3$C$_2$@PPy SC exhibited an excellent cycle life; the $C_{sp}$ retained around 81.4% of its initial value after charge/discharge at 5 A g$^{-1}$ for 6000 cycles. Further, we integrated a 3Drc Ti$_3$C$_2$@PPy SC into a real brick to showcase a smart house energy storage system. A proof of concept for this system was demonstrated by operating the building elevator model and turning on the model traffic signal. The authors anticipate that the 3D pen will make 3D-printed electrode production easier and more widespread and open up new possibilities for the surface modification of 3D-printed electrodes for application in high-performance energy storage devices.

Figure 5. Electrochemical performance and applications of energy storage bricks: a) cyclic voltammetry (CV) plot of three-dimensional rectangular (3Drc) Ti$_3$C$_2$@PPy supercapacitor (SC) integrated brick at different scan rates. b,c) CV and galvanostatic charge-discharge (GCD) plots of three 3Drc Ti$_3$C$_2$@PPy SC-integrated bricks connected in series and parallel configurations. d) Self-discharge rate of five series-connected 3Drc Ti$_3$C$_2$@PPy SC integrated bricks. e) 3Drc Ti$_3$C$_2$@PPy SC-integrated brick can be used as a power backup source in the event of a power outage in the traffic light or elevator.
4. Experimental Section

**Materials**: Sodium hydroxide (NaOH), block copolymer (F108), pyrrole, sulphuric acid (H₂SO₄), and lithium chloride (LiCl) were purchased from Sigma-Aldrich. Conductive graphene/PLA filament and 3D pen were purchased from Black Magic 3D, USA and Polaroid, China, respectively. Toys (traffic light and elevator) were purchased at a local shop in Prague, Czech Republic. Mini cement bricks (Size: 3.3 × 1.7 × 1.7 cm³) were purchased from Amazon in the Czech Republic.

**Preparation of Ti₃C₂@PPy-Coated 3D-Printed Electrodes**: The 3D-printed designs were prepared using a 3D pen at a temperature of 220 °C and a commercially available filament called “Black Magic” (graphene-based PLA). The 3D-printed electrodes were made using three different shape designs: cylindrical (3Dcy, diameter = 1.0 mm and length = 2.5 cm), 3D disk (3Ddc, thickness = 1.0 mm) and 3D rectangular (3Drc, 3.0 × 1.4 × 1.4 cm²). After that, the printed electrodes were chemically activated by immersing in 1 M NaOH for 30 min. The electrodeposition of the Ti₃C₂@PPy hybrid was carried out in a deposition bath containing 2.0 mg mL⁻¹ Ti₃C₂, 0.2 mg pyrrole and 1.0 mg mL⁻¹ lithium chloride by the cycling potential of 0 to 0.8 V. The reference and counter electrodes used were Ag/AgCl and platinum electrodes, respectively, with deposition duration extended from 15 to 45 min. After deposition, the Ti₃C₂@PPy hybrid on 3D-printed electrodes were gently washed to remove the unabsorbed species and then dried at 40 °C.

**Materials Characterizations**: Morphology study of Ti₃C₂@PPy-deposited 3D-printed electrodes was carried out using SEM (JEOL JSM-8401, Japan) and energy-dispersive spectroscopy (EDS) (SDD detector INCA XRF 250, Oxford Instruments). Structural characterisation of samples was performed by XRD (Bruker, D8, Germany), TGA (TG-750, Stanton Redcroft, England), and BET surface area analysis (NOVAtouch, Quantachrome Instrument).

**Device Configurations and Electrochemical Measurements**: The Autolab PGSTAT204 workstation (Metrohm, Netherlands) was used to conduct all the electrochemical experiments in this work. In three-electrode configurations, 3Dcy Ti₃C₂@PPy, platinum, and Ag/AgCl electrodes were used as working, counter, and reference electrodes in 1 M H₂SO₄ electrolyte, respectively. In the two-electrode configuration, the Ti₃C₂@PPy hybrid was electroplated on the surface of the 3Ddc and 3Drc electrodes served as cathode and anode; a piece of the porous membrane was immersed in hydrogel (35 w/w% F108 dissolved in 1 M H₂SO₄ electrolyte), which acts as a separator. CV and CCV were carried out at different scan rates and current densities, respectively. Electrochemical impedance spectroscopy (EIS) was performed in AC amplitude of 10 mV and frequency range from 10⁻² to 10⁶ Hz. The gravimetric specific capacitance (Csp, Fg⁻¹) of 3D printed electrodes was obtained from GCD plots using the equation Csp = i × Δt/ΔV × m, where ΔV, m, Δt, and I represent the operating window (V), the active mass of the electrode (g), discharge time (s), and current (A), respectively.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.
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