Three-Phase Boundary in Cross-Coupled Micro-Mesoporous Networks Enabling 3D-Printed and Ionogel-Based Quasi-Solid-State Micro-Supercapacitors

Feili Lai, Chao Yang, Ruqian Lian, Kaibin Chu, Jingjing Qin, Wei Zong, Dewei Rao, Johan Hofkens, Xihong Lu,* and Tianxi Liu*

The construction of advanced micro-supercapacitors (MSCs) with both wide working-voltage and high energy density is promising but still challenging. In this work, a series of nitrogen-doped, cross-coupled micro-mesoporous carbon–metal networks (N-STC/MₓOᵧ) is developed as robust additives to 3D printing inks for MSCs fabrication. Taking the N-STC/Fe₂O₃ nanocomposite as an example, both experimental results and theoretical simulations reveal that the well-developed hierarchical networks with abundantly decorated ultrafine Fe₂O₃ nanoparticles not only significantly facilitate the ion adsorption at its three-phase boundaries (Fe₂O₃, N-STC, and electrolyte), but also greatly favor ionic diffusion/transport with shortened pathways. Consequently, the as-prepared N-STC/Fe₂O₃ electrode delivers a high gravimetric capacitance (267 F g⁻¹ at 2 mV s⁻¹) and outstanding stability in a liquid-electrolyte-based symmetric device, as well as a record-high energy density of 114 Wh kg⁻¹ for an asymmetric supercapacitor. Particularly, the gravimetric capacitance of the ionogel-based quasi-solid-state MSCs by 3D printing reaches 377 F g⁻¹ and the device can operate under a wide temperature range (−10 to 60 °C).

The performance and application of electrochemical energy storage (EES) devices such as supercapacitors,[1] and alkali-ion batteries,[2] are crucial for the efficient usage of the intermittent renewable and sustainable energies, which increasingly rely on the development of innovative material formulations and scalable manufacturing strategies to enhance the electrolyte adsorption ability on the electrode, surface area accessibility and ion transport. Metal-containing carbons have shown huge potential as electrodes for aqueous supercapacitor assembly, taking into account their combined merits including metallic conductivity, redox activity, and negatively charged surface.[3] However, their working-voltage window and energy density are generally confined in a fairly narrow region (<1.23 V, 5–20 Wh kg⁻¹) since hydrolysis can happen easily under high voltage, with generation of abundant oxygen gases. In order to address this issue, great endeavors are devoted to developing stable electrolytes for high working-voltage operation. Ionic liquid, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), is regarded as an adequate alternative owing to its good fluidity, chemical inertness and improved combustion resistance in contrast to organic electrolytes.[4] The interface connection between the electrode and ionic-liquid-based electrolyte would be significantly restricted, making the fabrication of highly polarized, metal-containing carbons necessary to strengthen the electrode–electrolyte interactions and...
increase the ion density on its surface. In detail, there are several rules that should be obliged to design high-performance metal-containing carbons: i) according to the postulated energy storage mechanism, an optimized cross-coupled micro-mesoporous structure must be present; ii) a reasonable strategy should be put forward to achieve homogeneous anchoring of ultrafine metal nanoparticles in the micro-mesoporous carbon networks, and avoid closed domains (also called as “dead” domains) due to the possible aggregations of metal nanoparticles; iii) the metal-containing carbons must have the ability to adsorb ionic liquid ions strongly and fast. Consequently, it is still a challenge to construct 3D carbon/metal hybrid architectures toward high-performance supercapacitors with adequately tunable pathways for electron/ion transport, massively exposed edges for ions adsorption, and sharply reduced “dead” domains for excessive ions storage.

Apart from the design of electrolyte species and material formulations, the additive manufacturing technologies also play an important role in elevating the energy storage performance, among which the extrusion-based 3D printing method has been demonstrated as a facile and versatile platform to produce various supercapacitor architectures, especially for micro-supercapacitors (MSCs), with high accuracy and programmable patterns. In spite of some preliminary explorations for 3D printing techniques in the fields of lithium-ion micro-batteries, lithium–sulfur batteries, and asymmetric MSCs, further application of this technique in EES microdevice fabrication is severely restricted by the poor fluidity (high loss modulus and low storage modulus) and low solid content (<2 wt%) in conventional graphene oxide (GO) inks. Therefore, it is of great significance to exploit an innovative formulation of GO-based 3D printing ink with both highly shear-thinning behavior for continuous extrusion and modest storage modulus for well-maintained 3D printed shapes.

Herein, we develop a low cost cross-coupled micro-mesoporous carbon (STC) as an universal network for the facile preparation of a series of nitrogen-doped, cross-coupled micro-mesoporous carbon–metal networks (N-STC/M-O), including N-STC/Fe2O3, N-STC/Co3O4, N-STC/NiO, N-STC/CuO, N-STC/MnO2 nanocomposites. Taking N-STC/Fe2O3 as an example, density functional density (DFT) calculations reveal the three-phase boundary (ultrafine Fe2O3 nanoparticles, STC networks, and electrolyte) can lower its adsorption energy value toward BF4− (~3.83 eV) compared with those for N-STC (~3.51 eV) and Fe2O3 bulk (~3.58 eV). Additionally, the well-developed hierarchical micro-mesoporous structure shortens the pathway for the ionic diffusion/transport and enhances the electron transfer within the N-STC/Fe2O3 electrode. Our N-STC/Fe2O3-based electrode delivers a remarkable gravimetric capacitance of 267 F g−1 at 2 mV s−1 and an ultralong-term cycling durability (93.2% capacitance retention after 10 000 cycle). When assembled as an asymmetric supercapacitor in liquid EMIMBF4 electrolyte, the device delivers a high energy density of 114 Wh kg−1. By using N-STC/Fe2O3 as an additive for 3D-printing ink, an ionogel-based quasi-solid-state MSC is successfully fabricated with dramatically boosted gravimetric capacitance of 377 F g−1 and wide working temperature range from −10 to 60 °C.

The synthetic process of N-STC/M2O3 is schematically illustrated in Figure 1a. A polymer/ZnCl2 mixture was first prepared at 160 °C by using sucrose and sulfuric acid as the renewable carbon precursor and catalyst, respectively. After carbonization under the protection of Ar gas at 900 °C, ZnCl2 was completely removed by washing HCl solution. The two broad (002) and (101) peaks from the X-ray diffraction (XRD) pattern of STC (Figure S1a, Supporting Information) confirm the amorphous carbon phase without detectable Zn-contained phase. The thermogravimetric analysis (Figure S1b, Supporting Information) further demonstrates the absence of Zn-contained residues in STC, as evidenced by the less than 1.5 wt% ash content above 700 °C. The successful removal of ZnCl2 creates numerous micropores and mesopores in STC matrix, which is beneficial to the adsorption of gaseous urea during the following N-doping process. The X-ray photoelectron spectroscopy (XPS) survey spectrum (Figure S2a, Supporting Information) verifies the presence of C, N, and O with trace of residual zinc element in N-STC. The high-resolution N 1s spectrum (Figure S2b, Supporting Information) proves there are four types of nitrogen species, pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and oxidized nitrogen (N-O), accounting for 6.22 at%. The transmission electron microscopy (TEM) images (Figure S3, Supporting Information) reveal both prior electrode and N-STC exhibit open and cross-coupled structures with abundant micropores and mesopores, demonstrating the N-doping process does not affect the as-formed morphology. Finally, the N-STC was used as a matrix to anchor various metal-containing nanoparticles (including Fe, Co, Ni, Cu, and Mn NPs), which are defined as nitrogen-doped, cross-coupled micro-mesoporous carbon–metal networks (N-STC/M-O).

As the TEM images of various N-STC/M-O nanocomposites shown in Figure 1b, the M2O3 NPs with diameter of 5–20 nm are uniformly embedded in the N-STC networks. The lattice fringe spacings of different M2O3 NPs in five N-STC/M2O3 nanocomposites are well matched with those of Fe2O3 (JCPD no. 33–0664), CoO&Co (JCPD no. 42–1467 and 05–0727), NiO&NiO (JCPD no. 14–0481 and 47–1049), CuO&Cu (JCPD no. 49–1830 and 04–0836), and MnO2 (JCPD no. 14–0644)[15] (Figure 1c), which primely fit with their corresponding XRD patterns (Figure 1d). Taking N-STC/Fe2O3 as an example, its high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show abundant ultrafine Fe2O3 NPs have been anchored in the N-STC networks (Figure 1e) and the lattice fringe spacing (0.27 nm) corresponds to the (104) plane of α-Fe2O3 (Figure 1f). Additionally, the elemental analysis from the TEM-energy dispersive X-ray spectroscopy (EDXS) elemental mappings (Figure 1g) indicates that the C and N elements distribute homogeneously while Fe and O atoms appear as individual dots in N-STC/Fe2O3. The quantitative element ratio data for N-STC/Fe2O3 are shown in Figure 1h, indicating the successful formation of the Fe2O3/N-STC composite and the absence of residual Fe2O3. Finally, the Fe2O3 contents in which are displayed in Figure S3a,b, Supporting Information. Obviously, the NPs are prone to form large aggregates in N-STC matrix with the
increase of Fe$_2$O$_3$ content (Figure S6, Supporting Information), leading to diminished Fe$_2$O$_3$-carbon boundaries for following efficient ion adsorption.

N$_2$ (~196 °C) physisorption experiments were operated to investigate their pore structures (Figure 2a–c; Figures S7 and S8, Supporting Information). It can be seen that the pore diameters of all the N-STC/M$_{x}$O$_y$ nanocomposites are focused between 1 and 10 nm, and their specific surface area (SSA) values and total pore volumes (SSA: 1165–1480 m$^2$ g$^{-1}$; total pore volume: 0.8–2.1 cm$^3$ g$^{-1}$) are to some extent smaller than those of N-STC (SSA: 1887 m$^2$ g$^{-1}$; total pore volume: 2.2 cm$^3$ g$^{-1}$), which are summarized in Table S1, Supporting Information. This should be attributed to the slightly blocked cross-coupled micro-mesoporous carbon networks by M$_{x}$O$_y$ NPs. As a proof of concept, with the increase of the Fe$_2$O$_3$ loading capacity from 2% to 30%, both the SSA values and total pore volumes of various N-STC/Fe$_2$O$_3$ samples decrease from 1809 to 912 m$^2$ g$^{-1}$, and from 2.0 to 0.9 cm$^3$ g$^{-1}$ (Figure 2c). It is originated from the ever-increasing nanoparticle size of Fe$_2$O$_3$, which would partially block the porous structure in N-STC network and resulting into its ever-decreasing specific surface area (Inset in Figure 2c). Unexpectedly, a slight loading of Fe$_2$O$_3$ nanoparticles in N-STC/Fe$_2$O$_3$-2% could increase its specific surface area mildly when compared to the N-STC (1778 m$^2$ g$^{-1}$). It is because

![Figure 1. a) Synthetic procedure for the preparation of cross-coupled micro-mesoporous carbon–metal networks (N-STC/M$_{x}$O$_y$). b) TEM images, c) HRTEM images, and d) XRD patterns of various N-STC/M$_{x}$O$_y$. e,f) HAADF-STEM images of N-STC/Fe$_2$O$_3$ at different magnifications. g) EDXS elemental mappings of C, N, Fe, and O elements in N-STC/Fe$_2$O$_3$. The scale-bar is 50 nm.](image-url)
that the flat carbon pores could be divided by thousands of ultrafine Fe₂O₃ nanoparticles to generate thousands of rough pore walls (Figure S9, Supporting Information), which means new surfaces could be produced with corresponding increase in surface area.[14]

XPS measurements were applied to determine the elemental compositions and chemical states of different N-STC/MₓOᵧ nanocomposites. Except the existence of C, N, and O elements, the appearances of Fe, Co, Ni, Cu, and Mn peaks indicate the corresponding MₓOᵧ species are embedded in N-STC/Fe₂O₃, N-STC/Co₃O₄&Co, N-STC/Ni₂O₃&NiO, N-STC/Cu₄O₃&Cu, and N-STC/MnO₂ (Figure 2d), which confirm the results from the TEM images and XRD patterns. More detailed information for the chemical states of metal elements in N-STC/Co₃O₄&Co, N-STC/Ni₂O₃&NiO, N-STC/Cu₄O₃&Cu, and N-STC/MnO₂ are discussed from their high resolution XPS spectra (Figure S10, Supporting Information) and Auger Cu LMM XPS spectrum (Figure S11, Supporting Information). Taking N-STC/Fe₂O₃ nanocomposite as an example, four types of nitrogen functional groups were discovered in N 1s XPS spectrum (Figure 2e), including pyridinic nitrogen (398.4 eV), pyrrolic nitrogen (399.8 eV), graphitic nitrogen (400.8 eV), and oxidized nitrogen (403.9 eV).[15] In Figure 2f, the Fe 2p 3/2 and Fe 2p 1/2 peaks located at 711.5 and 725.1 eV can be ascribed typically to Fe₂O₃ with a peak separation of 13.6 eV, which is in accordance with previous reports.[16] Besides, two satellite peaks centered at 716.5 and 731.3 eV are attributed to Fe³⁺ in Fe₂O₃. Moreover, a positive shift of 1.4 eV is observed for the Fe 2p 3/2 peak in N-STC/Fe₂O₃ compared to that of the Fe₂O₃ bulk (710.1 eV).[17] It can be ascribed to the electron delocalization from ultrafine Fe₂O₃ NPs to N-STC matrix, resulting in the generation of electron-lacked Fe atoms in N-STC/Fe₂O₃ nanocomposites. Meanwhile, this positive shift also proves the existed chemical bonds between Fe₂O₃ and N-STC phases, such as O–C, Fe–N, and Fe–C bonds,[18] which is well supported by our DFT calculations.

In order to elucidate the structure-performance relationships, N-STC/MₓOᵧ, N-STC, and STC were assembled into different symmetric supercapacitors by using liquid EMIMBF₄ as the solvent-free electrolyte. Their electrochemical properties were characterized in detail by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectroscopy (EIS), and cycling tests. As shown in Figure 3a,b and Figure S12, Supporting Information, the capacitance of N-STC is 167 F g⁻¹/1.02 F cm⁻² at a scan rate of 2 mV s⁻¹ (based on the active materials) which is 33.6% higher than that of STC (125 F g⁻¹/0.76 F cm⁻²). Taking account to the smaller SSA and total pore volume of N-STC, the capacitance enhancement can be attributed to the polarized N dopants which activate the N-STC network and thereby facilitate the adsorption of ionic liquid (EMIM⁺ and BF₄⁻). The CV curves of N-STC/Fe₂O₃ electrodes show nearly rectangular shapes from 0 to 4.0 V, indicating their characteristic of double-layer capacitive behavior. With a low Fe₂O₃ content in N-STC/Fe₂O₃-2%, its specific capacitance reaches 184 F g⁻¹/1.12 F cm⁻² (Figure 3a,b and Figure S13, Supporting Information). With the continuous increase of the Fe₂O₃ content, the specific capacitance shows a drastic rise to 267 F g⁻¹/1.63 F cm⁻² for N-STC/Fe₂O₃, which then falls to 217 F g⁻¹/1.32 F cm⁻² for N-STC/Fe₂O₃-30%. It is because the overloaded Fe₂O₃ NPs (≈30%) would dramatically
hinder the cross-coupled micro-mesoporous carbon networks, thus decreasing its specific capacitance. All these CV curves of Fe2O3-containing samples at low scan rate of 2 mV s−1 exhibit several inconspicuous peaks below 2.5 V, which are attributed to the conformation change of EMIMBF4 ions inside the micropores of N-STC.[19] However, the inconspicuous peaks disappear with the increase of scan rates (Figure 3c), indicating the structural transition of EMIMBF4 ions happens slowly and needs enough relaxation time. The GCD curves of N-STC/Fe2O3 (Figure 3d) show typical triangular shapes with a linear voltage–time relation, demonstrating its purely capacitive behavior once more. The capacitance retention for N-STC/Fe2O3 after 10 000 cycles (Figure S16, Supporting Information), even being comparable to some of the Li-ion batteries (Figure 3h).[2c,20] Furthermore, ex situ XPS measurements were conducted to unveil the energy storage mechanism in N-STC/Fe2O3 electrode by using EMIMBF4 electrolyte. Figure 4a shows the second GCD curve of the N-STC/Fe2O3-based symmetric supercapacitor, where the status of the positive electrode at five representative moments (A, B, C, D, and E) are extracted to track its surface variations at different charging/discharging states. According to the ex situ XPS C 1s spectra (Figure 4b), at the very beginning, the two pronounced peaks at 284.7 and 285.1 eV corresponding to C−O and C−N groups see negligible variation during the charge/discharge process, demonstrating the excellent stability of N-STC matrix. Moreover, a new peak at 288.8 eV was detected at the full charging state and gradually faded away during discharging course.[21] This should
be caused by the reversible chemical interaction between C matrix and BF$_4^-$ ions via semi-ionic bonding. Normally, two kinds of supercapacitors can be divided based on different energy storage mechanisms, pseudocapacitor and electrical double-layer capacitor, both of which are not consistent with the behaviors for N-STC/Fe$_2$O$_3$ electrode: 1) the rectangular CV curves of N-STC/Fe$_2$O$_3$ (Figure 3a,c) imply there is no pseudocapacitive reaction during charging/discharging process; 2) the appearance of C–F bonds (Figure 4b) run counter to the traditional electrical double-layer capacitor with physical interactions between electrode and electrolyte ion. Therefore, the N-STC/Fe$_2$O$_3$-based supercapacitor processes a new energy storage mechanism with a mixed state of pseudocapacitor and electric double layer capacitor. According to the XPS C 1s spectra (Figure 4c), at full charging state, the ratio of the C–F increased from 9.4% to 23.7% after anchoring Fe$_2$O$_3$ NPs onto the N-STC matrix, which infers the existence of more strongly adsorbed BF$_4^-$ ions in N-STC/Fe$_2$O$_3$ nanocomposites. That is to say, the anchored Fe$_2$O$_3$ NPs could activate the neighboring carbon areas to form a better three-phase boundary of N-STC, Fe$_2$O$_3$ NPs, and electrolyte ions, which could be regarded as a “crowded” region with abundantly gathered ions after fully charged. In order to detailly address how does the boundary of C atom alter the adsorption/desorption process of BF$_4^-$/EMIM$^+$ ions on the interface of N-STC/Fe$_2$O$_3$, DFT calculations were then conducted. For the adsorption of EMIM$^+$ ions (Figure 4d and Figure S21, Supporting Information), its adsorption energy value on N-STC (−1.51 eV) is more negative than that non-doped STC (−1.28 eV), demonstrating the heteroatom-doping strategy could enhance its ion storage property under the premise of same microstructures. As for the BF$_4^-$ adsorption on N-STC/Fe$_2$O$_3$ (Figure 4d), its adsorption energy value is as negative as −3.83 eV, much lower than the values for N-STC (−3.51 eV), STC (−3.19 eV), and Fe$_2$O$_3$ bulk (−3.58 eV). These results

Figure 4. a) A second galvanostatic charge-discharge profile of N-STC/Fe$_2$O$_3$ at 0.1 A g$^{-1}$. b) Ex situ C 1s XPS spectra of N-STC/Fe$_2$O$_3$. c) C 1s spectra of N-STC/Fe$_2$O$_3$ and N-STC at 4 V. d) Calculated adsorption energy of electrolyte anion (BF$_4^-$) and cation (EMIM$^+$) on STC, N-STC, and N-STC/Fe$_2$O$_3$ electrodes, respectively. Inset shows the atomic diagram for the adsorption of BF$_4^-$ ions on the polarized phase boundary. e,f) Electron density difference of the N-STC/Fe$_2$O$_3$ (e) and independent N-STC and Fe$_2$O$_3$ (f) samples. g) Proposed electrochemical behaviors in N-STC/Fe$_2$O$_3$ electrode.
confirm the analysis from the XPS spectra (Figure 4b,c) that the intimate heterojunction between Fe$_2$O$_3$ NPs and N-STC could stimulate the strongest adsorption toward BF$_4^-$ ions, especially at the three-phase boundary (Inset in Figure 4d). Furthermore, the charge density distribution mapping (Figure 4e,f) depicts how do the chemical bonds affect the electronic states in Fe$_2$O$_3$ and N-STC components. Specifically, after anchoring Fe$_2$O$_3$ onto N-STC, the electrons of the adjacent Fe atoms tend to flow toward N-STC with higher electronegativity (N and C), bringing about more positive charges concentrated on Fe atoms and relatively higher electron density on N-STC atoms. This simulation result is in high accordance with the positive shift of the Fe 2p$_{3/2}$ peak of N-STC/Fe$_2$O$_3$ (Figure 2f) as partial electron has been delocalized from Fe$_2$O$_3$ to N-STC networks. Owing to the vibrant electron transfer between ultrafine Fe$_2$O$_3$ NPs and N-STC networks, abundant active boundaries are formed in the close vicinity of ultrafine Fe$_2$O$_3$ NPs (Figure 1e,f). Additionally, the cross-coupled micro-mesoporous carbon–metal networks can not only favor the ion diffusion with shortened transport length, but also enhance the electron transfer within the electrode (Figure 4g), leading to the significantly boosted energy storage performance.

Inspired from previous works,[22] the successful development of quasi-solid-state capacitors could endow them not only boosted energy storage properties but also extraordinary device performance to meet the ever-increasing practical demand. As an innovative additive manufacturing technology, extrusion-based 3D printing method could fabricate MSCs with specified architectures and quasi-solid-state property. Figure 5a briefly shows the ink preparation and 3D printing process for the MSC.

![Figure 5](https://www.advancedsciencenews.com/)

**Figure 5.** a) Schematic illustration for 3D printing of the ionogel-based quasi-solid-state MSC device. b) Apparent viscosity as a function of shear rate for the N-STC/Fe$_2$O$_3$/AC/CNT/GO and GO inks. c) Storage modulus and loss modulus as a function of shear stress for the N-STC/Fe$_2$O$_3$/AC/CNT/GO and GO inks. d) Dynamic modulus ($G'$ and $G''$) as a function of frequency for the STC/Fe$_2$O$_3$/AC/CNT/GO and GO inks. e) CV curves tested at 2 mV s$^{-1}$ of two MSCs connected in series and in parallel. f) GCD profiles of MSCs connected in series, measured at 9.6 mA cm$^{-2}$. g) CV curves tested at 50 mV s$^{-1}$ of MSC device.
device (see details in Figures S22–S24, Supporting Information). As the rheological behaviors of inks are essential to the properties of printed structure, the compositions and concentrations of the prepared inks are carefully controlled with additives of activated carbon (AC), carbon nanotube (CNT) and GO. Compared to pure GO ink, the N-STC/Fe₂O₃/AC/CNT/GO ink exhibits a much higher apparent viscosity with strong shear-thinning behavior (Figure 5b). The decreased apparent viscosity of the N-STC/Fe₂O₃/AC/CNT/GO ink under the high shear rate demonstrate it could flow through a fine nozzle under extruding, while the infinite viscosity around the low shear-rate indicates the ink behaves a Bingham plastic with yield stress. Meanwhile, both the storage modulus (G′) and loss modulus (G″) of the N-STC/Fe₂O₃/AC/CNT/GO ink increase dramatically, and reach a plateau G′ of ≈1.1 × 10⁵ Pa and a yield stress (τ₀) of ≈120 Pa (Figure 5c). These improved properties ensured that the N-STC/Fe₂O₃/AC/CNT/GO ink could be extruded smoothly under shear stress.²³ The G′ of N-STC/Fe₂O₃/AC/CNT/GO ink is larger than the G″ in the range of 0.01–100 rad s⁻¹ (Figure 5d), demonstrating its viscoelastic behavior with typical gel at rest.²⁴ As suggested by the frequency-independent modulus, a 3D network of force has formed within the ink to enable long-term dispersion stability in static state.²⁴ The rheological behavior of N-STC/Fe₂O₃/AC/CNT/GO ink demonstrates its favorable printability for desirable structures without deformation.

Under the operation in 3D-printed quasi-solid-state MSC devices (Figure 5a), the electrochemical property of N-STC/Fe₂O₃ was significantly promoted, exhibiting a superior specific capacitance of 1.79 F cm⁻² (377 F g⁻¹) than the symmetric supercapacitor in liquid EMIMBF₄ electrolyte (1.63 F cm⁻²/267 F g⁻¹) by using conventionally fabricated N-STC/Fe₂O₃ electrode (Figure S25, Supporting Information). The energy storage performance of our 3D-printed quasi-solid-state MSC device is superior or comparable with previously reported 3D-printed supercapacitors (Table S4, Supporting Information). The superior electrochemical performance of 3D-printed quasi-solid-state MSC device is because of the accelerated mass transfer in 3D-printed N-STC/Fe₂O₃ electrode with porous electrode structure and good electrode–electrolyte contact interface.²³ The robust flexibility of the quasi-solid-state MSC device is demonstrated by its well-maintained shape integrity after the bending angles recover from large angles (90° and 180°) to original state of 0° (Figure S26, Supporting Information). Moreover, quasi-solid-state MSCs could be easily connected in series or in parallel to meet various capacitance and working-voltage requirements for practical applications. As demonstrated in the CV and GCD measurements (Figure 5e,f), the capacitance output and working-voltage output could be easily doubled by two quasi-solid-state MSCs connected in parallel and in series, respectively. Two devices connected in parallel and series could easily light 2 red light-emitting diodes as shown in Figure S27, Supporting Information. Taking advantage of the temperature resistance of EMIMBF₄-based ionogel, the quasi-solid-state MSC also exhibits excellent temperature resistance. When the MSC devices were operated at −10, 0, 25, 50, 60 °C, the areal capacitances were 0.45, 0.53, 0.80, 0.97, and 1.04 F cm⁻² (Figure 5g and Figure S28, Supporting Information). This is because higher temperature leads to higher ionic conductivity and lower viscosity of EMIMBF₄. These results demonstrate quasi-solid-state MSC is a promising candidate for robust and wide-temperature energy storage.

In summary, a 3D-printed quasi-solid-state MSC with outstanding super-capacitive performance and a wide-temperature range is demonstrated by employing nitrogen-doped, cross-coupled micro-mesoporous carbon–metal networks as the electrode (especially for N-STC/Fe₂O₃). The advanced N-STC/Fe₂O₃ favors fast ion/electron transport and ensures sufficient space for ion storage because it integrates the advantageous properties including the hierarchically cross-coupled networks, large specific surface area, and good conductivity. Meanwhile, its ultrafine Fe₂O₃ NPs could activate the neighboring areas in N-STC networks to efficiently enhance the adsorption energy value with mass generation of semi-ionic C−F bonds, as evidenced by the ex situ XPS measurements and DFT calculations. As a consequence, the as-prepared N-STC/Fe₂O₃ electrode delivers a high gravimetric capacitance of 267 F g⁻¹ at 2 mV s⁻¹ and an ultralong-term cycling durability (93.2% capacitance retention after 10 000 cycle), as well as a record high energy density of 114 Wh kg⁻¹ in a liquid-electrolyte-based ASC device. Furthermore, when printed into an ionogel-based quasi-solid-state MSC, it reaches to a high gravimetric capacitance of 377 F g⁻¹ and could operate under a wide temperature range (−10 to 60 °C). This work provides enlightening insights to create abundant three-phase boundaries by well modifying the electrode surface and unveil the rational development of next-generation supercapacitors for intermittent renewable energy utilization.

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

Acknowledgements
The authors greatly acknowledge the technique support by the Max Planck Institute of Colloids and Interfaces (electron microscopy tests from Dr. Tobias Heil) and Technische Universität Berlin (partial XPS measurements from Dr. Johannes Schmidt). This work was also financially supported by the National Natural Science Foundation of China (51433001, 21674019), the Shanghai Scientific and Technological Innovation Project (18JC140660), the Program of Shanghai Academic Research Leader (17XD1400100).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
3D printing, carbon, Fe₂O₃, ionic liquids, micro-supercapacitors