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Conjugated Microporous Polymer Network Grafted Carbon Nanotube Fibers with Tunable Redox Activity for Efficient Flexible Wearable Energy Storage

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ABSTRACT: Fiber-shaped supercapacitors (FSCs) are promising energy storage devices that meet the growing demands for the miniaturization, flexibility, and compatibility of wearable electronics. However, when compared with batteries, the low energy density remains the main limitation to practical applications. A conjugated microporous polymer (CMP) network synthesized using Buchwald–Hartwig cross-coupling reactions featured tailorable porous structures, reversible redox chemistry, and demonstrated highly efficient capacitive performance. Herein, the CMP network that grafted on carbon nanotube fibers (CNF@CMP) with high areal specific capacitance (671.9 mF cm^{-2} at a current density of 1 mA cm^{-2}) was successfully achieved for a polytriphenylamine (PTPA)-based network. All-solid-state symmetrical-twisted CNF@PTPA FSCs fabricated with PVA/ H_3PO_4 as a gel electrolyte exhibited a high specific areal capacitance of 398 mF cm^{-2} (0.28 mA cm^{-2}), a maximal operating voltage of 1.4 V , and an energy density of $18.33 \text{ } \mu\text{Wh cm}^{-2}$. Moreover, they showed excellent flexibility and mechanical stability retaining 84.5% of the initial capacitance after 10,000 bending cycles. These materials provide a new route to high-performance wearable supercapacitors (HPWS) with wide potential applications in wearable electronics, as shown by the examples provided.

With the growing demands for wearable intelligent electronics in our future lives, wearable power systems with the merits of small size, light weight, high flexibility, high performance, and adaptability to frequent deformation during usage are highly desired.^{1,2} Although enormous research achievements have been focused on planar (2D) flexible supercapacitors,^{3,4} their poor air/moisture permeability and environment compatibility limited their implication in high-standard wearable electronics.⁵ Accordingly, one-dimensional (1D) fiber-shaped supercapacitors (FSCs) offer many distinct features and promising advantages: (i) FSCs exhibit high compatibility with textiles and can be weaved or knitted into air/moisture permeable energy fabrics/textiles;^{6–10} (ii) FSCs exhibit exceptional mechanical flexibility and miniaturization potential; and (iii) FSCs can be easily integrated into multifunctional or self-powered systems by incorporating other fiber-shaped sensors, triboelectric nanogenerators, or photovoltaic devices,^{11–14} providing diverse possibilities.

However, the low energy density of FSCs has limited their practical applications.^{15,16} Given that the energy density of FSCs is dependent on the total capacitance of the FSCs device and the cell voltage ($E = 1/2 C_{\text{cell}} V^2$), increasing these factors is an effective approach to achieve high energy density. To

maximize C_{cell} , considerable efforts have been devoted to the fabrication of fiber electrodes with high specific capacitance. Typically, fiber electrodes consisting of pseudocapacitive active materials, including transition metal oxides, metal hydroxides, and conducting polymers, were developed.^{10,17,18} However, this strategy often sacrificed power density and cycle life since redox reactions in the bulk of pseudocapacitive active materials are diffusion-controlled, leading to sluggish reaction kinetics.¹⁹ Moreover, a conventional coating or deposition technique cannot prevent the fall-off of pseudocapacitive materials from current collectors in flexible FSCs during repeated deformation processes. Such instabilities leave fiber-shaped supercapacitors with unsatisfactory mechanical stability.

Conjugated microporous polymer (CMP) networks, which combines extended π -conjugation and permanent micropores,

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Figure 1. (A) Schematic illustration of the fabrication process for symmetrical fiber-shaped supercapacitors (FSCs). (B) Synthetic route of CNT@CMPs and (C, D) typical CNT@CMP fibers with an average diameter of $\sim 200\ \mu\text{m}$ and a length of $\sim 24\ \text{cm}$.

have attracted tremendous attention owing to their adjustable pore structures, high specific surface areas, reversible redox chemistry, and high chemical stability.^{20–24} Their unique microporous structures and high surface areas endow CMP-based electrodes with electrical double-layer capacitive characteristics. In addition, numerous heteroatom-containing active redox sites can be integrated within the polymer backbone, offering excellent pseudocapacitive performance.^{25,26} Both contributions make CMPs promising materials for supercapacitive electrodes. Moreover, the versatile syntheses of CMPs allow electroactive materials to be readily designed on a molecular level.^{27,28} Unfortunately, CMPs are generally insoluble powders, which cannot be processed into flexible fibers. Therefore, the fabrication of CMP-based FSCs have not yet been achieved.

Carbon nanotube fibers (CNFs), exhibiting a 1D structure, light weight, flexibility, and superior mechanical and electrical properties, have emerged as an ideal template and current collector for nanohybrid materials for smart and wearable fiber systems.^{29,30} Many CNF-based materials such as CNF@MnO₂,³¹ CNF@MXene,³² CNF@Co₃O₄,³³ and CNF@PANI³⁴ have been developed for FSCs. However, the development of FSCs with high energy density and long-term bending durability stays a current challenge. Herein, the CMP network grafted on CNFs with high areal specific capacitance was successfully achieved for a polytriphenylamine (PTPA)-based network (CNF@PTPA). All-solid-state symmetrical-twisted CNF@PTPA FSCs fabricated with PVA/H₃PO₄ as a gel electrolyte exhibited excellent flexibility, long-term mechanical stability, and also a high energy density among the conjugated polymer-based FSCs.

RESULTS AND DISCUSSION

The production of CMP-grafted CNFs (CNF@CMPs) is presented in Figure 1. Aniline-, pyridine-, and anthraquinone-based monomers are polymerized with a 1,3,5-tris(3-bromo)-phenylbenzene (TPBA) monomer on the CNF surface through a simple palladium-catalyzed Buchwald–Hartwig cross-coupling reaction, which is an amination reaction for the generation of polar C–N bonds. This approach affords redox-active amine-functionalized CMPs combined with the conductivity and flexibility of CNFs (Figure 1A). The CNFs were first covalently bromo-functionalized (CNF-Br) through the spontaneous reaction of the *p*-bromobenzene diazonium salt with carbon nanotube (CNT).^{35,36} The obtained CNF-Br was then employed as a fiber substrate to adsorb a palladium catalyst (Figures S1–S4), offering a surface-grafting modification *via* the Buchwald–Hartwig coupling reaction (Figure 1B). Tris(4-bromophenyl)amine (TA) was then chosen as a core monomer for polymerization with a linker, *i.e.*, *p*-phenylenediamine (PDA), to obtain CNF@PTPA fibers. The above strategy is shown to be a versatile approach to prepare CNF@CMP fibers. Changing the linker to 2,5-diaminopyridine dihydrochloride (DAP) or 2,6-diaminoanthraquinone (DAQ) provided pyridine- and anthraquinone-based CNFs, *i.e.*, CNF@PAPTA and CNF@PAQTA fibers, respectively. A typical sample of a flexible 1D CNF@CMP fiber obtained by PDA is shown in Figure 1C,D. Notably, these fibers maintained the excellent mechanical properties and flexibility of CNFs (Figure 2A,B and Figure S5).

Scanning electron microscopy (SEM) analyses of CNF@CMPs indicated the formation of CMP network particles on the outer surfaces of CNFs and an inner surface of carbon nanotubes (Figure 2C–F and Figures S6 and S7). Transmission electron microscopy (TEM) images confirmed the

Figure 2. (A) Photograph of CNF@PTPA1 tied to a weight. (B–F) SEM images: (B) CNF@PTPA1 tied in a knot. (C–E) Outer surface and (F) selected inner area of CNF@PTPA1 at different magnifications. (G–H) TEM images of CNF@PTPA1 and (I) the corresponding EDS mapping of the carbon and nitrogen element. (J) FT-IR, (K) Raman, and (L) high-resolution N 1s XPS spectra. Scale bars: (B) 500 μm , (C) 100 μm , (D) 10 μm , (E) 1 μm , (F) 500 nm, (H) 200 nm, (I) 50 nm, and (G) 20 nm.

core–shell structure of CNF@PTPAs (Figure 2G). Elemental mapping analyses showed that carbon and nitrogen are uniformly distributed in CNF@PTPAs (Figure 2H,I). For comparison, CNF@PTPA0 fibers were also prepared without *p*-bromobenzene diazonium salt functionalization of the CNFs, displaying an incomplete coating (Figures S8 and S9). Notably, the morphology of CNF@PTPAs and the thickness of the shell are readily controlled by the concentrations of the monomers applied (Figures S10–S12 and Table S1). At high concentrations (0.938–1.25 mM, CNF@PTPA1 and CNF@PTPA2), the CNFs were coated with a PTPA shell that exhibited an aggregated nanoparticle morphology (Figure 2C–E and Figure S10), while at low concentrations (0.625 mM, CNF@PTPA3), the PTPA shell displayed a dense film morphology (Figures S11 and S12). The residues obtained by thermogravimetric analysis (TGA) were conducted in air following the sequence CNF@PTPA3 > CNF@PTPA2 > CNF@PTPA1 with mass loading values of 0.43 (38.51 wt %), 0.57 (49.14 wt %), and 0.84 mg cm^{-1} (58.64 wt %), supporting the observed continuous thin polymer coating found for CNF@PTPA3 (Figure S13). The comparison of the loading amount of active materials in the fiber electrode with the other conjugated polymer-based fiber electrode is shown in Table S2. Using different types of amine linkers and treating the products post-synthetically at different temperatures further confirmed

the versatility of the proposed strategy (Figures S14 and S15) to produce variable coating morphologies. The porous characteristics of the CNF@CMPs were investigated by N_2 adsorption/desorption isotherm analyses (Figures S16–S20). CNF@PTPA1 exhibits an apparent Brunauer–Emmett–Teller surface area of 123.6 $\text{m}^2 \text{g}^{-1}$ of which $\sim 50\%$ is attributed to the micropores with pore diameters from 0.7 to 1.2 nm (Figure S16 and Table S3). The microporosity is also confirmed by high-resolution TEM measurements (Figure S21). In comparison, the other two CNF@PTPA fibers with less loading amounts of PTPA exhibited relatively lower surface areas and less amounts of micropores (Figures S17 and S18 and Table S3). Previous studies showed that 0.7–1.2 nm micropores are close to the desolvated ion size.^{37,38} This suitable microporosity could produce additional specific capacitance for CNF@CMP fibers.

The Fourier transform infrared (FT-IR) spectra of CNF@PTPAs exhibited two characteristic stretching vibrations located at 1585 ($\nu_{\text{C}=\text{C}}$ for quinoid rings) and 1485 cm^{-1} ($\nu_{\text{C}=\text{C}}$ for benzenoid rings)³⁹ (Figure 2J), suggesting their polyaniline-like structures. This structure proposal is further supported by the two main intensive bands at 1487 ($\nu_{\text{C}=\text{N}}$ for quinoid rings) and 1587 cm^{-1} ($\nu_{\text{C}-\text{C}}$ for benzene rings),⁴⁰ as observed in Raman spectra (Figure 2K). The N 1s X-ray photoelectron spectroscopy (XPS) analyses of CNF@PTPAs

Figure 3. CV curves of (A) CNF@PTPAs and (B) CNF@PTPA3. (C) Nyquist plot fitted with the $R(C(RW))(C(RW))$ equivalent circuit with the inset showing the high-frequency region. (D) GCD curves of CNF@PTPA3. (E) Specific areal capacitance and Coulombic efficiencies and (F) cycling life and Coulombic efficiencies of CNF@PTPAs. (G) Relationship and fitted lines between $\log(\text{peak current})$ and $\log(\text{scan rates})$. (H) Separation of capacitive and diffusion-limited currents. (I) Contribution ratios of capacitance- and diffusion-limited processes of CNF@PTPA3.

showed two peaks located at ~ 399.3 ($-\text{NH}-$) and ~ 397.8 eV ($-\text{N}=\text{N}-$) (Figure S21),⁴¹ which transform to three peaks with an additional peak located at 401.0 eV (quaternary $\text{N}-\text{Q}$)⁴² upon post-synthesis heat treatment (Figure S22). Note that CNF@PTPA3 exhibited the highest ratio of area (A_{1487}/A_{1587}) observed for $-\text{N}=\text{N}-$ and $-\text{NH}-$ peaks, as detected by both Raman and N 1s XPS spectra (Figures S23 and S24), revealing the highest amount of quinoid units.⁴³ It is well known that aromatic compounds can readily interact with the basal plane of graphitic surfaces *via* π -stacking.⁴⁴ For polyaniline/carbon nanotube composites, the interactions preferentially take place on the quinoid rings.⁴⁵ Therefore, the strongest π -stacking interaction would be achieved on CNF@PTPA3 with the highest amount of quinoid units. Replacing the PDA monomer with DAP and DAQ monomers, the resulting CNF@PAPTA and CNF@PAQTA fibers showed similar structures to the PAPTA and PAQTA, as confirmed by FT-IR and XPS spectral analyses (the presences of typical pyridyl and carboxyl groups) (Figures S25 and S26). Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectra of PTPA, PAPTA, and PAQTA showed three main peaks at ~ 145 , ~ 127 , ~ 117 ppm assigned to $\text{C}=\text{N}$, $\text{C}-\text{N}$, and $\text{C}=\text{C}$ bonds, respectively, originating from the aryl carbons and pyridyl carbon of the starting material (Figure

S27). One additional peak at ~ 181 ppm was attributed to the $\text{C}=\text{O}$ group of PAQTA. Combined with FT-IR and XPS analyses, the NMR results further verified the successful formation of the conjugated polymer network consisting of amine linkages.

The CNF@CMP fibers to be applied as electrodes for electrochemical energy storage were first tested in a three-electrode cell in a 0.5 M H_2SO_4 aqueous electrolyte. Note that the pure CNF electrode showed negligible redox activity compared with CNF@CMPs. The cyclic voltammetry (CV) curves of CNF@CMPs revealed the pseudocapacitive characteristics, which derived from Faradaic reactions of the grafted CMPs (Figure 3A,B and Figures S28 and S29). For CNF@PTPA3, two pairs of redox peaks with oxidation peaks located around 0.37 and 0.58 V were observed at a scan rate of 20 mV s^{-1} . Increasing the scan rate yielded a similar shape of the CV curves but a slight shift of the position of the two oxidation peaks from 0.31 to 0.38 V and 0.52 to 0.59 V. These results indicated the rapid transport of ions and electrons, fast charge/discharge property, and good rate capability of CNF@PTPA3. Notably, the redox activity of CNF@CMPs is affected by the thickness of the CMP shell (Figure 3A). From the impedance curves (Figure 3C), the calculated charge-transfer resistances based on the equivalent circuit are 4.6, 6.6, 7.2, and 8.5 Ω for

Figure 4. (A) CV and (B) GCD curves of CNF@PTPA3 FSCs at different operation potential windows. (C) $C_{\text{cell,A}}$, $E_{\text{cell,A}}$, and $P_{\text{cell,A}}$ calculated based on GCD curves. (D) CV and (E) GCD curves of CNF@PTPA3 FSCs and (F) areal, volumetric, and gravimetric capacitance of calculated based on GCD curves. (G) Comparison of the electrochemical performances of CNF@PTPA FSCs with other FSCs in areal specific capacitance and (H) areal Ragone plots of the CNF@PTPA-based FSCs compared with other previously reported conjugated polymer-based symmetric FSCs using an aqueous gel electrolyte.

CNF, CNF@PTPA3, CNF@PTPA2, and CNF@PTPA1 (Table S1), respectively. Nevertheless, all fiber electrodes showed a vertical line at low frequencies, indicating efficient ion diffusion and almost ideal capacitive performance. The nearly symmetric shapes of the galvanostatic charge/discharge (GCD) curves with the small internal resistance (IR) drop shown in Figure 3D further verified the promising capacitive behavior, reversibility, and conductivity of the CNF@PTPA3 fiber electrode. The maximal specific areal capacitance calculated from GCD curves for CNF@PTPA3 was 670 mF cm^{-2} at a current density of 1 mA cm^{-2} , ~ 100 times that for the pure CNF (Figure S30). The value was slightly lower than that for CNF@PTPA1 (751 mF cm^{-2} at a current density of 1 mA cm^{-2}) owing to the lower grafting amount of PTPA3. However, the CNF@PTPA3 displayed a much better rate capability (retaining about 86% from 20 to 1 mA cm^{-2}) and high Coulomb efficiencies (90–98%) (Figure 3E). More importantly, owing to the stronger interaction between CNFs and the PTPA film, the CNF@PTPA3 fiber electrode also showed a much better durability upon an 8000 charge/

discharge cycling (70 vs 50%) compared to CNF@PTPA1 and CNF@PTPA2. In contrast, the CNF@PTPA0 prepared without grafting modification showed the lowest cycling ability (Figure 3F). SEM observations indicated negligible changes occurred in morphologies for CNF@PTPA1, CNF@PTPA2, and CNF@PTPA3 upon an 8000 charging/discharging cycling, while a certain amount of polymer particles fell off from CNF@PTPA0 (Figure S31) as an additional indicator of good durability of CNF@PTPA1, CNF@PTPA2, and CNF@PTPA3.

Besides the monomer concentrations, the different amine linkers and post-synthesis heat treatments also provided a degree of control over the electrochemical properties of the CNF@CMPs (Figures S28 and 29). The redox reaction mechanism for CNF@PTPA is presented in Figure S32.^{46,47} Besides the aniline monomer, pyridine- and anthraquinone-based amine linkers exhibit extra redox groups for which two-proton/two-electron processes and an exclusive two-electron process are involved,^{48,49} respectively (Figure S33). This determined the controllable electrochemical properties of

Figure 5. (A) GCD curves of CNF@PTPA3 FSCs in five different states at a current density of 0.68 mA cm^{-2} . (B) Relationship between capacitance retention and bending times at State 3. (C) Photo images, (D) CV, and (E) GCD curves for three FSCs connected in series and parallel. (F–I) Photo images: (F) a cross-stitched logo, (G) a powered logo, (H) a knitted watchband, and (I) a powered digital watch.

CNF@CMPs. Upon heat treatment, CNF@PTPA fibers could maintain a reasonable pseudocapacitance (519 mF cm^{-2}) but showed significantly improved cycling stability (50 vs 85%) (Figures S34 and S35). The capacitance contribution was analyzed to explain the high performance of CNF@PTPA3. In principle, two processes contribute to the whole capacity for the polyaniline-like material: (i) diffusion-limited capacity, primarily generated from the insertion of the electrolyte ions through the Faradaic reactions of $-\text{NH}-$ centers requiring H^+ doping/dedoping in bulk phase; (ii) capacitance-controlled capacity, mainly originating from both the surface electrical double layer and pseudocapacitive Faradaic current associated with redox reaction processes of surface $-\text{NH}-$ centers. The electrode kinetics were therefore investigated to explain whether a diffusion-limited or capacitance-controlled mechanism, or both, contributed to the total capacities of our CNF@CMP electrodes.⁵⁰ As shown in Figure 3G, the calculated values of parameter b based on Dunn's method⁵¹ in anode and cathode reactions are close to 1.0 (see the Supporting Information). The calculated results implied that the surface capacitive process dominated the whole charge storage process.

Figure 3H shows the capacitive contribution for the whole capacitance obtained at 20 mV s^{-1} , which was calculated to be 87.6%. The capacitive contribution was approximately 83%, even at a low scan rate of 5 mV s^{-1} , and a 97% contribution was achieved at 100 mV s^{-1} (Figure 3I). Therefore, the fiber electrodes showed high rate performance in the aqueous electrolyte. A similar capacitive contribution behavior can also be observed for the CNF@PTPA1 electrode (Figure S36).

As CNF@PTPA3 showed the best comprehensive properties, flexible symmetric FSCs were assembled by twisting two fibers, used as both active materials and current collectors, using PVA/ H_3PO_4 as a solid electrolyte. The CV curves of the FSCs measured in different potential windows at a scan rate of 30 mV s^{-1} are shown in Figure 4A. Notably, the fabricated FSCs showed an extended operational potential window of 1.4 V. The CV and GCD curves (Figure 4B) obtained in different potential windows displayed a nearly symmetrical shape, indicating a highly reversible Faradaic reaction and capacitive properties of the FSCs. The $C_{\text{cell,A}}$, $E_{\text{cell,A}}$, and $P_{\text{cell,A}}$ of CNF@PTPA3 calculated from the GCD curves are shown in Figure 4B,C. The maximum $C_{\text{cell,A}}$ of 83.4 mF cm^{-2} was obtained at a

potential window of 0.8 V and decreased to 67.7 mF cm^{-2} when the window extended to 1.4 V (current density of 2 mA cm^{-2}). Both $E_{\text{cell,A}}$ and $P_{\text{cell,A}}$ showed an upward trend with the increase of potential window range. The maximal value is $18.33 \mu\text{Wh cm}^{-2}$ (4.07 mWh cm^{-3}) at 0.99 mW cm^{-2} (220 mW cm^{-3}) (current density of 2 mA cm^{-2}) at a potential window of 1.4 V. Therefore, an intermediate operation window (1.0 V) was chosen for the detailed electrochemical characterization of FSCs. The CV curves of as-prepared FSCs at different scan rates ranging from 10 to 60 mV s^{-1} and GCD curves at different current densities ranging from 0.5 to 5 mA cm^{-2} are presented in Figure 4D,E. The CNF@PTPA3 FSCs showed a high specific areal capacitance value of 398 mF cm^{-2} (or 88.4 F cm^{-3} or 346 F g^{-1}) at 0.28 mA cm^{-2} . To the best of our knowledge, this value is competitive with those of recently reported conjugated polymer-based FSCs fabricated with PVA-based solid electrolytes (Figure 4G).^{16,52–57} The CNF@PTPA3 FSCs displayed an energy density of $13.61 \mu\text{Wh cm}^{-2}$ (3.02 mWh cm^{-3}) with a maximal power density of 1.25 mW cm^{-2} (277 mW cm^{-3}), as shown in the Ragone plots (Figure 4H). The electrochemical performance comparison between the CNF@PTPA3 FSCs and reported conjugated polymer-based FSCs is listed in Table S4. The volumetric energy density is 3 times higher than those of the commercially available supercapacitors ($<1 \text{ mWh cm}^{-3}$) and comparable to those of $4 \text{ V}/500 \mu\text{Ah}$ thin-film lithium batteries ($0.3\text{--}10 \text{ mWh cm}^{-3}$).⁵⁸ And the areal energy density is well comparable to those of recently reported conjugated polymer-based FSCs.^{53,56,59,64}

The mechanical stability and flexibility of FSCs are crucial when used in wearable and portable electronics. The CNF@PTPA3 FSCs showed negligible variations of capacitances when knotted in five different states, as confirmed by the GCD curves (Figure 5A). Moreover, the CNF@PTPA3 FSC devices could retain 85% of initial capacitance upon 10,000 bending cycles ($\sim 135^\circ$ bending), demonstrating the high flexibility and mechanical and electrochemical stability (Figure 5B). The CNF@PTPA3 FSCs could be easily connected in series or in parallel to boost the operating voltage and capacitance output of a single device. Figure 5C demonstrates the images of the single, in-series, and parallel FSCs. Figure 5D and Figure 5E show the CV and GCD curves of these three cases, respectively. Both CV curves of in-series and parallel connections exhibited symmetric shapes. An in-series connection enabled the extension of the output voltage to 3.0 V (3 times the 1.0 V for a single device). Meanwhile, the parallel connection gave an apparently larger areal CV curve and displayed much improved capacitance (130.8 F) compared with a single device (43.1 F) at a current of 0.56 mA , demonstrating potential for device integration. To further demonstrate the potential applications of our FSCs in wearable and portable electronics, four FSCs (2.5 cm in length) connected in series (as the red circle indicates in Figure 5F) were cross-stitched into a section of textile fabric to power five white light-emitting diodes (LEDs) for 4 min (3.3 V each; Figure 5G and Video S1 in the Supporting Information). Four fully charged integrated FSCs connected in series (as the red arrows indicated in Figure 5H) were also knitted into a watchband to power a digital watch (Figure 5I). These results indicated that the flexibility, electrochemical stability, output energy, and power of connected FSCs could meet the requirements for practical wearable and portable electronics.

CONCLUSIONS

In summary, a series of CMP networks were successfully grafted on CNFs via a Buchwald–Hartwig coupling reaction using tris(4-bromophenyl)amine as a core and different amines as linkers. The resulting CNF@CMPs were applied to fabricate high-performance wearable supercapacitors (HPWS). Specifically, the conjugated microporous PTPA network grafted on CNFs using a low monomer concentration (0.625 mM , CNF@PTPA3) shows promise for wearable energy storage owing to the flexibility and high conductivity of the CNFs, porosity and strong redox property of PTPA3, and the enhanced synergistic interaction between the CNF core and PTPA shell. The CNF@PTPA3 fiber electrodes exhibited a high three-electrode areal specific capacitance of 670 mF cm^{-2} at current density of 1 mA cm^{-2} with 70% of initial capacitance retained after 8000 cycles at a current of 2 mA cm^{-2} . Moreover, a durable symmetrical FSC based on two CNF@PTPA3 fibers exhibited a maximum specific capacitance of 398 mF cm^{-2} at a current density of 0.28 mA cm^{-2} and delivered an energy density of $18.33 \mu\text{Wh cm}^{-2}$ with excellent flexibility and mechanical stability retaining 84.5% of the initial capacitance after 10,000 bending cycles. Such CNF@CMP fibers with tunable redox activity and CNF@PTPA3-based FSCs devices provide insight into the rational design for highly efficient flexible HPWSs.

EXPERIMENTAL METHODS

Preparation of *p*-Bromobenzene-Modified CNF (CNF-Br).

The purchased CNF (100 cm, 11.6 mg) was first placed into aqueous solution (10 mL) containing a 1 wt % dodecylbenzene sulfonic acid (DSA) surfactant for 1 h followed by the addition of a predissolved 4-bromobenzenediazonium tetrafluoroborate (3.87 mmol) in a minimum amount of water. After stirring for 1 h, MQ water and acetone were used to wash the CNF several times to remove the surfactant and excessive diazonium salt and obtain the final CNF-Br.

Preparation of CMP-Grafted CNFs (CNF@CMPs). CNF@CMPs were synthesized by the Buchwald–Hartwig cross-coupling reaction method but with a modified charge sequence.⁶⁵ Typically, $\text{Pd}(\text{dba})_2$ (0.006 mmol) was placed into a Schlenk tube containing CNF-Br (50 cm) under a nitrogen atmosphere. Anhydrous toluene (10 mL) was added into the Schlenk tube to dissolve $\text{Pd}(\text{dba})_2$ under stirring at room temperature (RT). During this period, the adsorption phenomenon of $\text{Pd}(\text{dba})_2$ on fibers can be observed with the pink color turning pale with the increased adsorption time. After 2 h, TBA (0.225 mmol), amine linker (0.15 mmol , PDA, 2,5-DAP, or 2,6-DAQ), Xphos (0.009 mmol), NaOtBu (0.4 mmol), and another 2 mL of anhydrous toluene were added and the reaction mixture was heated under stirring at 110°C . After 48 h, the reaction was cooled to RT and fibers were collected. Followed by washing with CHCl_3 , CH_3OH , and hot MQ water (12 h each) and drying for 24 h in a vacuum oven, final corresponding fibers labeled as CNF@PTPA1, CNF@PAPTA, CNF@PAQTA, respectively, can be gained. Meanwhile, the fibers that adopted the PDA amine linker with different monomer concentrations (*i.e.*, 0.938 and 0.625 mM) using the same method were named as CNF@PTPA2 and CNF@PTPA3, respectively. For comparison, the adoption of the same procedure for CNF without *p*-bromobenzene functionalization (*i.e.*, coating directly) afforded CNF@PTPA0. Moreover, post-synthesis heat treatments of CNF@PTPA2 fiber under a N_2 atmosphere at different temperatures ranging from 100 to 400°C with a heating rate of $10^\circ\text{C}/\text{min}$ afforded CNF@PTPA2-100, CNF@PTPA2-200, CNF@PTPA2-300, and CNF@PTPA2-400.

Fabrication of the Flexible All-Solid-State Fiber-Shaped Symmetrical Supercapacitors (FSCs). A H_3PO_4 /PVA gel polyelectrolyte was prepared according to a previously reported method.⁵⁹ In a typical process, 1.0 g of H_3PO_4 was dissolved in 10 mL

of MQ water and 1.0 g of PVA ($M_w = 105,000 \text{ g mol}^{-1}$, Sinopharm Group Co.) powder was added. The whole mixture was heated steadily to $\sim 85^\circ\text{C}$ under vigorous magnetic stirring until the solution became clear. A single-fiber electrode was drop-coated with the H_3PO_4 /PVA gel and then dried under RT until the gel solidified. The flexible all-solid-state FSCs were fabricated by intertwining two precoated dry fibers with the same length and drop-coating with the H_3PO_4 /PVA gel electrolyte again and finally drying under RT before performance tests.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02089>.

Materials; material characterization; electrochemical characterization of individual fibers; characterization of the flexible all-solid-state fiber-shaped symmetrical supercapacitors (FSCs); electrode kinetics; theoretical capacitance calculations; the mechanism of the CNT-supported BH reaction; and proposed redox reaction, i.e., the charge/discharge mechanism of PTPA, pyridine, and anthraquinone (PDF)

Video of four FSCs being cross-stitched into a section of textile fabric to power five white LEDs (MP4)

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Notes

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