

SHORT COMMUNICATION

Highly dispersed single-wall carbon nanotube thin film on WO₃ film for ultrafast multi-functional electrochemical devices

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Summary

A highly dispersed single-wall carbon nanotube (HD-SWCNT) thin film is introduced on a WO₃ film (HD-SWCNT/WO₃) by ultrasonic spray coating method to accelerate electron and Li-ion transport for realizing ultrafast multi-functional electrochromic (EC) energy-storage electrodes. Uniform grafting of polyvinylpyrrolidone onto the SWCNTs induces their amicable debundling without any surface defects. The highly debundled and continuous morphology of the HD-SWCNT thin film enables accelerated electron transport along the sp² carbons, which leads to excellent electrical properties (electrical conductivity of ~1361 S/cm and sheet resistance of ~7.3 Ω/□). Functional groups such as amides and carbonyls on the HD-SWCNTs enhance Li-ion wettability, which accelerates Li-ion diffusion kinetics. In addition, the uniform structure of the HD-SWCNT thin film with its porosity effectively shortens the Li-ion diffusion pathways and increases the contact area between the functional groups and the electrolyte, improving the electrochemical activity of the electrode. Such behaviors to promote electron and Li-ion transport at the interface between the electrolyte and the WO₃ film enhance the EC energy-storage performances compared to those of aggregated SWCNT film on WO₃ and a bare WO₃ electrode. The corresponding performances of HD-SWCNT/WO₃ include the transmittance modulation (58.7% at 633 nm), switching speeds (3.1 s for coloration and 4.5 s for bleaching), coloration efficiency (51.9 cm²/C), and specific capacitance (87.9 F/g at 2 A/g). In particular, owing to the synergistic effect of the accelerated electrical conductivity and the Li-ion diffusivity of the HD-SWCNT thin film for ultrafast electrochemical kinetics, HD-SWCNT/WO₃ exhibits a remarkable high-rate capability (82.9%, specific capacitance retention at 20 A/g compared to 2 A/g), which demonstrates ultrafast charge/discharge characteristics. In this regard, the introduction of an HD-SWCNT thin film as a functional layer to improve the ultrafast charge transport at the interface between a WO₃ and an electrolyte could be a promising strategy for ultrafast multi-functional electrochemical devices.

KEYWORDS

dispersibility, functional groups, multi-functional electrochemical electrode, single-wall carbon nanotube, ultrafast charge transport

1 | INTRODUCTION

With the acceleration of the concentration of greenhouse gases in the atmosphere, governments worldwide are focusing on net-zero greenhouse gas emissions to prevent further increases in the global mean temperature.^{1,2} To overcome this global challenge, technological advances in energy storage and conversion devices, such as Li-ion batteries, electrochemical capacitors, solar cells, and electrochromic (EC) devices, have been achieved by many research groups.^{3–5} Among them, EC devices are generating interest because their controllable optical properties (transmittance, absorbance, and reflectance) can save significant energy consumption as much as ~40% of the energy wasted by heating and air-conditioning in buildings.⁶ In general, EC devices consist of laminated structures including a transparent conducting film/cathodic film/electrolyte/anodic film/transparent film configuration, and optical variations are generated by the insertion/extraction of ions and electrons in the electroactive films (cathodic and anodic films). Because these optical variations are caused by the reversible charge transport in the electroactive films, EC devices simultaneously retain pseudocapacitive energy-storage ability.⁷ Recently, owing to the multi-functionality of optical variations and energy-storage, the applicability of EC devices has been expanded in the form of EC energy-storage devices, such as EC supercapacitors and EC batteries. In this area, studies have led to performance optimization, such as transmittance modulation, switching speeds, coloration efficiency (CE), and specific capacitance, of multi-functional EC energy-storage devices by promoting ion and electron transport in the electroactive films.^{8,9} In addition, ultrafast electrochemical kinetics, which attains high capacity at ultrafast current density, should be considered to realize ultrafast charge/discharge of the devices. However, to our best knowledge, the achievement of ultrafast electrochemical kinetics in EC energy-storage electrodes under high-rate conditions has been insufficiently studied.

Electroactive materials, which generate optical variations, are categorized into inorganic (transition metal oxides) and organic (conjugated polymers and viologens). Transition metal oxides, particularly WO₃, have emerged as potential electroactive materials owing to their excellent capability for ion and electron transport, leading to excellent EC and pseudocapacitive performance. A vast majority of studies have demonstrated high-performance WO₃ films for enhanced transmittance modulation, specific capacitance, switching speeds, and CE.^{10,11} However, the critical disadvantages of WO₃ are its low electrical conductivity and poor rate performance, which

limit the feasibility of its applications in ultrafast devices. To overcome these drawbacks, a few studies have developed composite structures of WO₃ with conducting materials such as conducting polymers and graphene.^{12,13} Until now, most research has mainly focused on introducing conductive materials into WO₃ as composite structures for efficient ion and electron transport in the electrodes. However, the rate capability is still insufficient to realize devices with feasible ultrafast charge/discharge characteristics. Therefore, interfacial engineering, which introduces a functional thin film to accelerate electron and ion transport between an electroactive film and an electrolyte, can be a new direction for realizing high-rate capability without reduction in the optical properties of EC energy-storage devices.

In this study, a highly dispersed single-wall carbon nanotube (HD-SWCNT) thin film was introduced as a functional layer on a WO₃ film by ultrasonic spray coating for preparing ultrafast EC energy-storage electrodes. Effective debundling of the SWCNTs was successfully realized by uniform grafting of polyvinylpyrrolidone (PVP) onto their surfaces. In contrast, the SWCNTs without PVP exhibited dynamic aggregation (A-SWCNT), producing bundled tubes, owing to their intrinsic nature. In addition, high uniformity and coverage of the HD-SWCNT thin film on the WO₃ film were accomplished through the overall advantages of the ultrasonic spray coating process. Fine droplets of 1 μm or less enriched via ultrasonic atomization were homogeneously provided to the target substrate, which induced high uniformity and coverage of the coated thin film. In addition, in-situ HD-SWCNT thin film formation was realized by continuous thermal energy supply for the evaporation of the entire water solvent and affecting the robust chemical interactions between PVP and the WO₃ film. Consequently, the successful realization of highly dispersed SWCNT thin film on WO₃ films, HD-SWCNT/WO₃ exhibited enhanced ultrafast EC energy-storage performances compared to those of A-SWCNT and bare WO₃.

2 | EXPERIMENTAL DETAILS

2.1 | Characterization of HD-SWCNT

An HD-SWCNT dispersion was prepared by dissolving SWCNTs (TUBALL, OCSiAl) and PVP as a dispersing agent in deionized water (DI water). To achieve uniform PVP grafting onto the SWCNTs, an ultrasonic homogenizer was used in the dispersion. The uniform PVP grafting and dispersibility of the HD-SWCNTs were confirmed

by transmission electron microscopy (TEM, Jeol) and energy-dispersive X-ray spectroscopy (EDS). To fabricate an HD-SWCNT sheet, the HD-SWCNT dispersion was vacuum filtered through a membrane paper, followed by drying in an oven at 50°C. The electrical properties of the HD-SWCNT sheet were measured using a Hall effect measurement system (HMS-3000). The optical properties of the HD-SWCNT dispersion (25 mg/L) were compared with those of an A-SWCNT dispersion by investigating the ultraviolet-visible (UV-vis) spectroscopy (PerkinElmer). The chemical binding of the HD-SWCNT was confirmed by X-ray photoelectron spectroscopy (XPS, Escalab). To characterize the thermal behavior of the HD-SWCNT dispersion, thermogravimetric analysis (TGA-50) was conducted in the range of 24 to 800°C.

2.2 | Fabrication of bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃ electrodes

Bare WO₃ electrodes were fabricated on a commercial fluorine-doped tin oxide (FTO)/glass substrate (7.7 Ω/□, Pilkington) by spin-coating a precursor solution to deposit a WO₃ film. The precursor solution was prepared by dissolving 10 wt% tungsten chloride (WCl₆, Sigma Aldrich) in 2-propanol (C₃H₈O, Sigma Aldrich) in a glove box filled with argon. After stirring for 3 hours, the resultant precursor solution was spin-coated twice on an FTO/glass substrate at a speed of 2000 rpm for 30 seconds. Thereafter, the spin-coated electrode was annealed in a box furnace at 300°C for 1 hours, which resulted in a homogeneous WO₃ film on the FTO/glass. An HD-SWCNT/WO₃ electrode was fabricated by depositing an HD-SWCNT thin film on a bare WO₃ electrode using the ultrasonic spray coating method. For this, an HD-SWCNT solution was prepared by diluting the HD-SWCNT dispersion described in the previous section to a concentration of 4 mg/mL. For uniform ultrasonic spray coating, the vibration frequency of the ultrasonic atomizer nozzle and the feeding rate of the coating solution was established as 130 kHz and 1 mL/h. Before the ultrasonic spray coating process, the air pressure and the hot plate temperature were maintained at 1 bar and 100°C, respectively. Finally, the HD-SWCNT solution was uniformly ultrasonically spray-coated on a bare WO₃ electrode for 60 seconds. To compare the dispersion effect of the SWCNTs on the WO₃ film, an A-SWCNT/WO₃ electrode was prepared by ultrasonic spray coating of a diluted A-SWCNT dispersion on a bare WO₃ film similar to HD-SWCNT/WO₃.

2.3 | Characterization of bare WO₃, A-SWCNT/WO₃, and FD-SWCNT/WO₃ electrodes

The top and cross-view morphologies of all electrodes were imaged by high-resolution scanning electron microscopy (HR-SEM, Hitachi) with EDS. The chemical binding of all electrodes was investigated by XPS (Escalab). Multi-functional electrochemical properties, which are related to the EC energy-storage performances, were measured using a three-electrode system consisting of bare WO₃, A-SWCNT/WO₃, or HD-SWCNT/WO₃ as the working electrode, a Pt wire as the counter electrode, an Ag wire as the reference electrode, and a 1 M lithium perchlorate (LiClO₄, Sigma Aldrich) in propylene carbonate (C₄H₆O₃, Sigma Aldrich) as the electrolyte. Cyclic voltammetry (CV) was conducted at a scan rate of 20 mV/s in a potential range from −0.7 to 1.0 V using a potentiostat/galvanostat (Metrohm Autolab). Li-ion diffusion coefficients of all electrodes were investigated by CV measurements at consecutive scan rates of 20, 40, 60, 80, and 100 mV/s. Electrochemical impedance spectroscopy (EIS) was conducted using a sinusoidal signal with an amplitude of 10 mV in the frequency range of 0.1 to 100 kHz using potentiostat/galvanostat. The ultrafast EC performances were investigated by measuring in-situ transmittance variations under applied voltages using an association of a UV-vis spectroscopy and a potentiostat. To induce coloration and bleaching of the electrodes, chronoamperometry (CA) was performed by applying voltages of −0.7 and 1.0 V for 60 seconds, respectively. The ultrafast energy-storage performances were evaluated by galvanostatic charge-discharge (GCD) measurements in the range from −0.7 to 1.0 V at different current densities of 2, 4, 6, 8, 10, and 20 A/g.

3 | RESULTS AND DISCUSSION

The intrinsic nature such as hydrophobicity and large specific surface area of SWCNT, which leads to their dynamic aggregation in the form of bundled tubes, has limited their peaceful application in electrochemical electrodes.^{14,15} In this study, we successfully resolved these problems at once by introducing a highly uniform grafting of PVP onto the SWCNTs, which induces their effective debundling without any surface defects. The TEM image of the HD-SWCNT dispersion shown in Figure 1A confirms the highly dispersed morphology of the SWCNTs with amicable debundling. The average tube diameter (~10.6 nm) and length (>3 μm) of the HD-SWCNT are similar to those of the pristine SWCNT

powder. As shown in the enlarged TEM image of HD-SWCNT in Figure 1B, linear PVPs are uniformly grafted on the SWCNT surfaces, which produces electrostatic/steric repulsive forces to prevent the SWCNT aggregation. In addition, the PVP modification can effectively lower the surface tension of the HD-SWCNT, which results in their effective dispersion in water.¹⁶ The fast Fourier transform (FFT) image of the selected area in Figure 1B shown in Figure 1C exhibits a hexagonal crystalline structure with ring patterns for graphene planes, which clearly shows the crystalline nature of the HD-SWCNTs.¹⁷ C, N, and O elemental mapping images of the HD-SWCNT are shown in order in Figure 1D. Major C mapping (red dots) is observed along with the carbon nanotubes. Notably, N (blue-green dots) and O (green dots) mappings are uniformly detected along with the carbon nanotubes, which are derived from the amide and carbonyl groups in PVP, respectively.¹⁸ The C, N, and O element contents are 95.38, 3.06, and 1.56 at%, respectively (Figure 1F). Therefore, the elemental mapping images and composition results of the HD-SWCNT demonstrate the uniform grafting of PVP on the SWCNT surfaces, which leads to their debundling and dispersion.

Figure 2 shows the optimal properties for accelerating electron and Li-ion transport in the HD-SWCNT. The

top-view HR-SEM image of the HD-SWCNT sheet displays a highly dispersed morphology with debundled and continuous SWCNTs with a diameter of ~ 16 to 28 nm (Figure 2A). The uniformly grafted PVPs on the HD-SWCNT enable effective debundling of the SWCNTs without any damage, such as bundle cut-off and surface defects, when compared to acid-treated SWCNTs.¹⁹ Such damage to SWCNTs reduces the electron transport pathways and increases electrical resistance, which leads to low electrical conductivity. The highly debundled and continuous morphology of the HD-SWCNTs via the uniform PVP grafting result in excellent electrical properties of the HD-SWCNT sheet (electrical conductivity of ~ 1361 S/cm and sheet resistance [R_{sh}] of $\sim 7.3 \Omega/\square$). Figure 2B demonstrates the excellent aqueous dispersion stability of the HD-SWCNT dispersion, as determined by UV-vis absorbance spectroscopy. To confirm the PVP grafting effect on the SWCNT dispersion, an SWCNT dispersion without PVP was also investigated. As shown in the photographs in Figure 2B, the SWCNT dispersion without PVP contains aggregated SWCNT (A-SWCNT) produced by the poor aqueous dispersibility of the SWCNTs. In contrast, the HD-SWCNT shows excellent aqueous dispersibility. The aqueous HD-SWCNT dispersion presents a specific absorbance peak at ~ 273.4 nm,

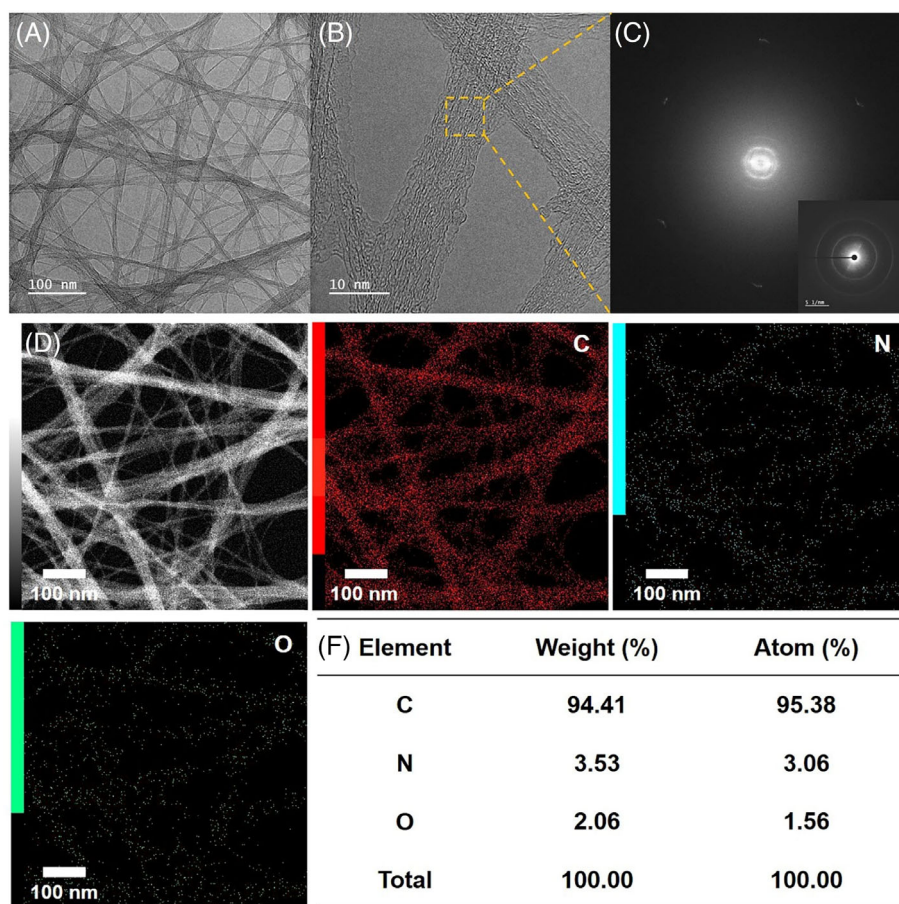


FIGURE 1 (A) TEM image of HD-SWCNT, (B) enlarged TEM image of HD-SWCNT, (C) FFT image of the selected area of HD-SWCNT, (D) EDS C, N, and O elemental mapping images of HD-SWCNT, and (F) quantitative results from EDS C, N, and O elements in HD-SWCNT

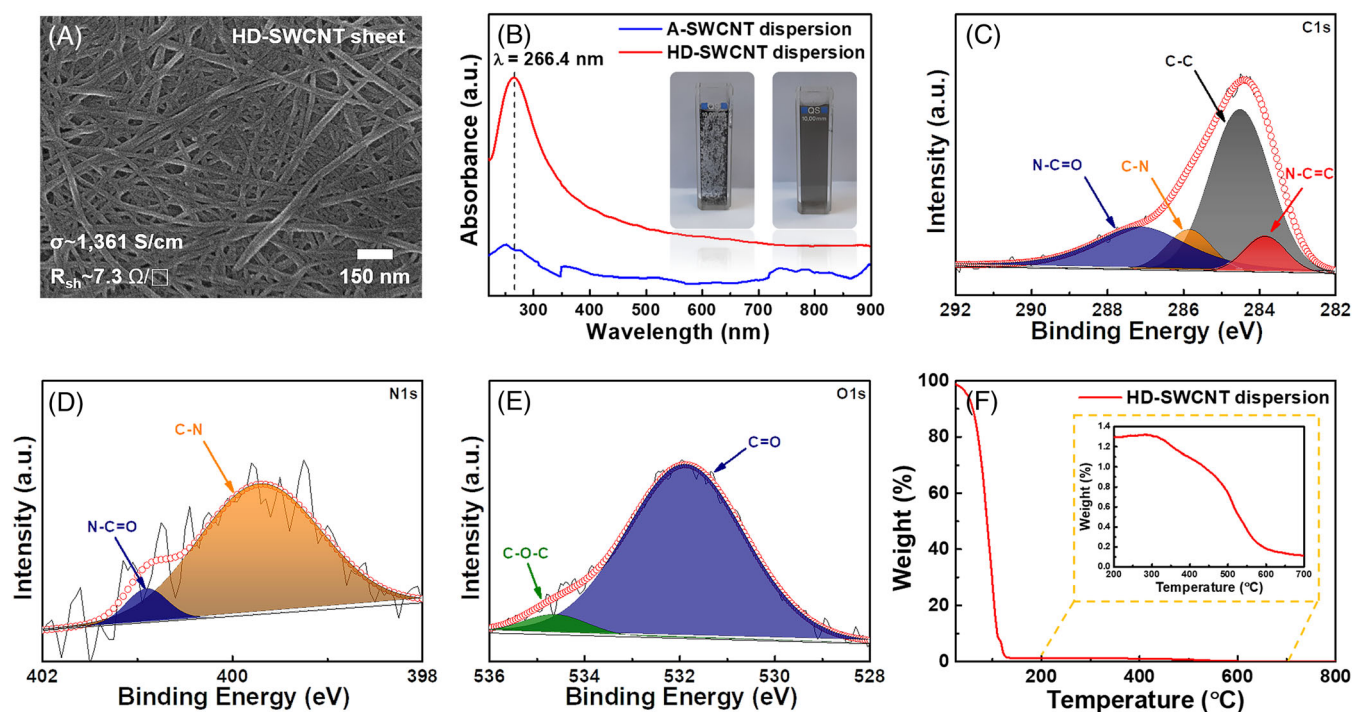


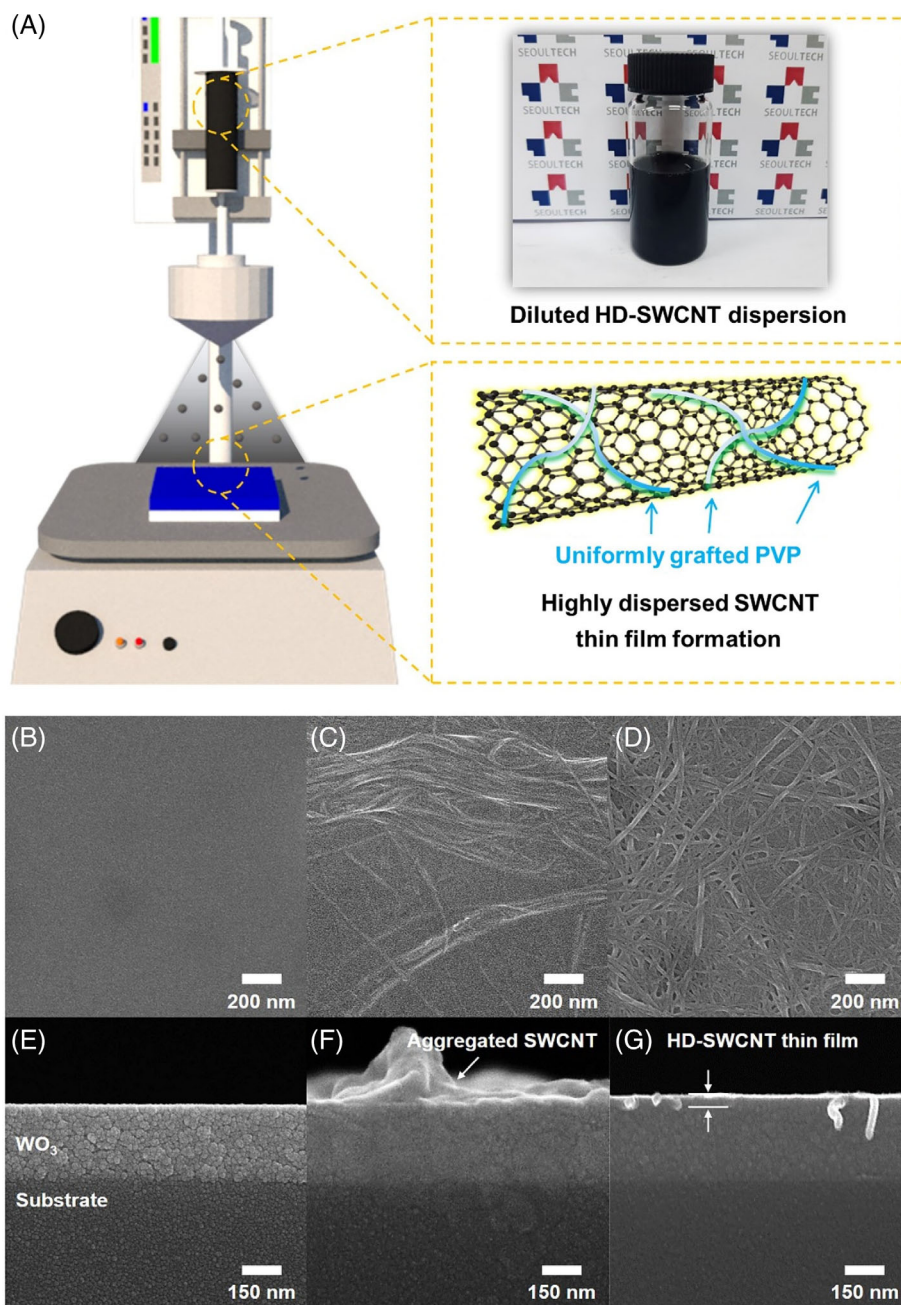
FIGURE 2 Optimal properties of HD-SWCNT for electron and Li-ion transport: (A) HR-SEM image of HD-SWCNT sheet and its electrical properties, (B) UV-vis absorbance spectra of HD-SWCNT and A-SWCNT dispersions (25 mg/mL, respectively), XPS of (C) C1s, (D) N1s, and (E) O1s spectra of HD-SWCNT sheet, and (D) TGA of HD-SWCNT dispersion in range of 24 to 800°C with enlargement of 200 to 700°C region

which originates from the individual absorption of the debundled SWCNTs.²⁰ In contrast, A-SWCNT exhibits little absorbance without specific peaks in the entire wavelength range, which is a result of the bulky SWCNT aggregates. Therefore, the introduction of an electrically conductive HD-SWCNT thin film with a highly dispersed morphology as a top layer can be an effective approach to accelerate electron transport for realizing ultrafast EC energy-storage electrodes. To investigate the chemical bindings of the HD-SWCNT sheet, XPS analysis was conducted, and the results are shown in Figure 2C–E. All XPS results are analyzed after aligning C1s to 284.5 eV as a reference peak. The C1s XPS spectrum exhibits specific chemical bonds of N–C=C, C–C, C–N, and N–C=O at ~283.8, ~284.5, ~285.8, and ~287.1 eV, respectively (Figure 2C).^{21–23} The C–C binding is a result of the covalent sp² bonds in single-layer graphene, which provides a fast electron pathway.²¹ In particular, the presence of N–C=C binding, which is derived from the covalent bonds between the amide nitrogens in PVP and carbons in the SWCNTs, verifies the robust PVP grafting onto the SWCNTs.²⁴ The N–C=O and C–N bonds are derived from the amide groups in PVP uniformly grafted onto the SWCNT surface. Additionally, as shown in the N1s XPS (Figure 2D), the amide groups of C–N and N–C=O in PVP are observed at ~399.7 and ~400.9 eV, respectively.²⁵

The O1s XPS is composed of C=O at ~531.9 eV and C–O–C at ~534.6 eV, and the main peak of C=O confirms the carbonyl groups in PVP.²⁶ Generally, amide and carbonyl groups, which retain significant polarity owing to their partial negative charge, improve the Li-ion wettability of electrolytes.^{10,27,28} Therefore, the uniformly distributed amide and carbonyl groups in the HD-SWCNT thin film probably promote the Li-ion transport from the electrolyte to the WO₃ film. TGA was conducted in the range of 24 to 800°C to confirm the presence of the functional groups of PVP in the HD-SWCNT dispersion (Figure 2F). The TGA curve exhibits a sharp decrease from 24 to 140°C, which indicates the evaporation of water molecules in the aqueous dispersion. In the enlarged TGA curve, in the range of 200 to 700°C, a gradual weight decrease is caused by the detachment and thermal decomposition of the functional groups in PVP (inset graph). Owing to the synergistic effects of the high electrical conductivity and abundant functional groups in the HD-SWCNT, the introduction of an HD-SWCNT thin film as the top layer in electrochemical electrodes can be a novel strategy to accelerate electron and Li-ion transport to realize ultrafast EC energy-storage electrodes.

Figure 3A shows a schematic representation of the HD-SWCNT thin film formation process using the ultrasonic spray coating method. Ultrasonic spray coating is

FIGURE 3 (A) Schematic representation of HD-SWCNT thin film formation process via ultrasonic spray coating method, (B–D) top-view HR-SEM images of bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 , and (E–G) cross-view HR-SEM images of bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3



considered an effective method for producing a uniform thin film by ultrasonic atomization of fine droplets of 1 μm or less from a spray nozzle.^{29,30} An ultrasonic spray coating system consists of an automatic syringe pump, an ultrasonic spray nozzle, an ultrasonic atomizer, an air compressor, and a hot plate. Parameters such as the feeding rate of the coating solution, the distance between the spray nozzle and the substrate, air pressure, and degree of dispersion of the coating solution can influence the uniformity and thickness of the film. Among these parameters, the degree of dispersion is regarded as the most decisive factor for film uniformity. With a low degree of dispersion, ultrasonically atomized droplets can

undergo discontinuous atomization and a non-uniform size distribution greater than microns. As demonstrated in the TEM and HR-SEM images (Figures 1A and 2A), the diluted HD-SWCNT dispersion shows excellent dispersibility without any aggregation and sedimentation (inset photograph in Figure 3A), which is suitable for ultrasonic spray coating. Consequently, a uniform HD-SWCNT thin film is successfully introduced onto a bare WO_3 electrode via ultrasonic spray coating of the diluted HD-SWCNT dispersion. For in-situ thin film formation, a bare WO_3 electrode was placed on a hot plate (100°C) to provide continuous thermal energy for the evaporation of the entire water solvent and robust chemical interactions

between the PVP and the WO_3 film. Figure 3B–D show the top-view HR-SEM images of the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 electrodes. The bare WO_3 shows a dense uniform surface morphology without any distinctive particles (Figure 3B). A-SWCNT/ WO_3 exhibits noticeable aggregation of SWCNT bundles on the WO_3 film, resulting from the non-uniform ultrasonic atomization of the bundled SWCNTs during the ultrasonic spray coating process (Figure 3C). The aggregated SWCNTs on the WO_3 film can lead to inefficient electron transport owing to the reduced electron pathways and increased electrical resistance of the SWCNT bundles.³¹ Furthermore, the aggregated SWCNTs can act as a blocking layer for Li-ion diffusion between the electrolyte and the WO_3 film. In the case of HD-SWCNT/ WO_3 , highly debundled and continuous SWCNTs without any damages are observed, which is a result of uniform ultrasonic spray coating of the diluted HD-SWCNT dispersion (Figure 3D). The elemental mapping and the quantitative EDS results demonstrated the highly dispersed SWCNT morphology of HD-SWCNT/ WO_3 (Figure S1). HD-SWCNT/ WO_3 presented homogeneous distributions of C and N, which reflect the dispersed SWCNTs and the uniform PVP grafting, respectively (Figure S1A). In contrast, A-SWCNT/ WO_3 exhibited a concentrated distribution of C along the bundled SWCNTs (Figure S1B). Thanks to its highly dispersed morphology, the HD-SWCNT thin film can effectively enhance the electrical conductivity and Li-ion transport to a WO_3 film. The high electrical conductivity stems from the effective debundling of the SWCNTs via the PVP grafting. The enhanced Li-ion transport originates from the uniform structure with porosity of the SWCNT thin film, which shortens the Li-ion diffusion pathways and increases the contact area between the hydrophilic functional groups in PVP and the electrolyte. Figure 3E–G shows cross-view HR-SEM images of the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 electrodes. The film thickness of the bare WO_3 is in the range of $\sim$ approximately 292.7 to 296.6 nm (Figure 3E). A-SWCNT/ WO_3 and HD-SWCNT/ WO_3 include almost similar WO_3 film thickness in the range of $\sim$ approximately 294.2 to 299.4 nm, which removes the possibility of the effect of the variability in the WO_3 film thickness on the electrochemical performances of the electrodes. Aggregated SWCNTs with a significant thickness in the range of approximately $\sim$ 105.7 to 299.8 nm are identified in A-SWCNT/ WO_3 (Figure 3F). In contrast, in HD-SWCNT/ WO_3 , an HD-SWCNT thin film with a thickness of approximately $\sim$ 28.2 to 44.3 nm is uniformly formed on the WO_3 film (Figure 3G). The HD-SWCNT thin film on the top layer almost retains the transparency of the WO_3 film compared to the bare WO_3 film (Figure S2), which

can provide high transmittance in the bleached state during the EC reaction. Therefore, the highly dispersed morphology of HD-SWCNT thin film can accelerate electron and Li-ion transport for ultrafast EC energy-storage electrodes.

To identify the chemical bonds in the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 films, XPS analysis was carried out, and the results are shown in Figures 4A–D. The $\text{W}4f$ XPS spectra of the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 identically present two dominant peaks at $\sim$ 35.18 eV for $\text{W}4f_{7/2}$ and $\sim$ 37.31 eV for $\text{W}4f_{5/2}$, which correspond to the binding energy of W^{6+} in the WO_3 phase (Figure 4A).³² Thus, the presence of two main W^{6+} peaks indicates the successful formation of the WO_3 phase in all electrodes. The $\text{O}1s$ XPS spectrum of HD-SWCNT/ WO_3 shows specific chemical binding as a result of the functional groups in PVP (Figure 4B). Compared to the bare WO_3 and A-SWCNT/ WO_3 spectra, which show two characteristic peaks of $\text{W}-\text{O}$ ($\sim$ 530.15 eV) and $-\text{OH}$ ($\sim$ 531.31 eV), an additional peak of $\text{C}=\text{O}$ ($\sim$ 532.45 eV) is observed in the HD-SWCNT/ WO_3 spectrum, which is derived from the carbonyl groups in PVP.^{33,34} In addition, the $\text{C}1s$ XPS spectrum of HD-SWCNT/ WO_3 verifies the presence of specific functional groups (Figure 4C). The bare WO_3 film spectrum shows a weak peak intensity, which is related to the $\text{C}-\text{C}$ bond ($\sim$ 284.5 eV) in the organic compounds of the precursor. The A-SWCNT/ WO_3 film spectrum presents two main peaks of sp^2 ($\sim$ 284.5 eV) and sp^3 ($\sim$ 286.5 eV) carbons. The sp^3 carbon is a result of the four-coordinated states of the bundled SWCNTs.³⁵ In contrast, the HD-SWCNT/ WO_3 spectrum displays three characteristic peaks related to $\text{N}-\text{C}=\text{C}$, sp^2 carbon, and $\text{C}=\text{O}$ at $\sim$ 283.2, $\sim$ 284.5, and $\sim$ 287.2 eV, respectively, which demonstrate the presence of its functional groups.²⁴ The $\text{N}-\text{C}=\text{C}$ bond is derived from the covalent interaction between the amide nitrogens in PVP and carbon atoms in the SWCNTs, which suggest a robust PVP grafting onto the SWCNT surfaces. The major sp^2 carbon peak originating from the crystalline graphene layer is consistent with the high electrical conductivity of the HD-SWCNT. The electroactive carbonyl group ($\text{C}=\text{O}$), owing to its partial negative charge, can enhance the Li-ion wettability of the electrolyte, thereby improving the Li-ion diffusion kinetics.³⁶ The $\text{N}1s$ XPS spectrum of HD-SWCNT/ WO_3 confirms the presence of amide groups (Figure 4D). As expected, the bare WO_3 and A-SWCNT/ WO_3 films do not show any characteristic peak owing to the absence of an N source. HD-SWCNT/ WO_3 exhibits two peaks of $\text{C}-\text{N}$ and $\text{N}-\text{C}=\text{O}$ at $\sim$ 399.3 and $\sim$ 400.5 eV, respectively.²⁵ These peaks originate from the amide groups in the PVP grafts, which retain significant polarity to enhance Li-ion wettability. Because of the

FIGURE 4 XPS of (A) W4f, (B) O1s, (C) C1s, and (D) N1s spectra of bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃, respectively

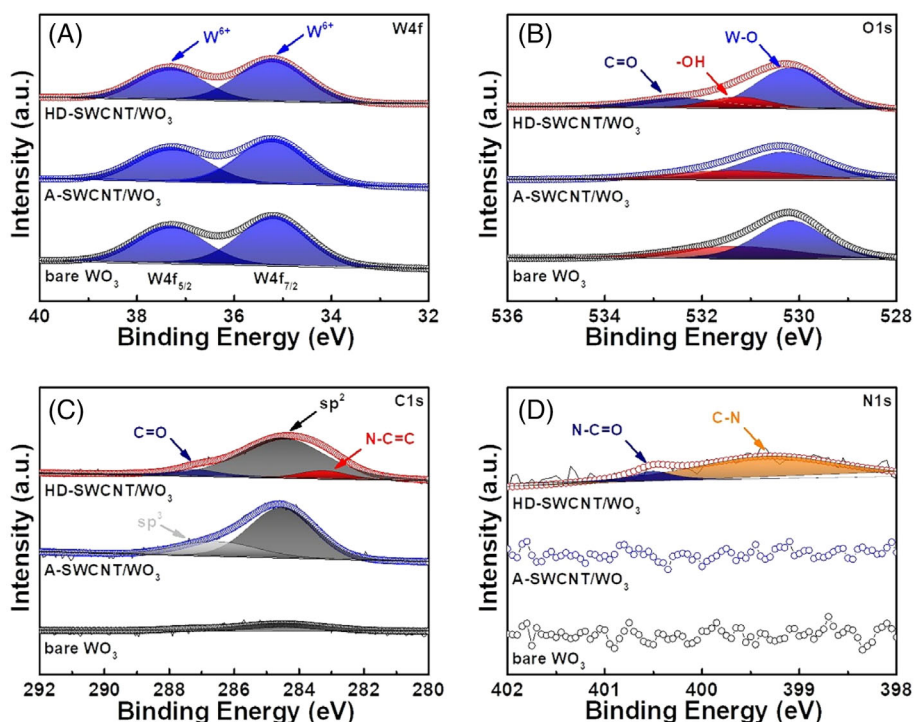
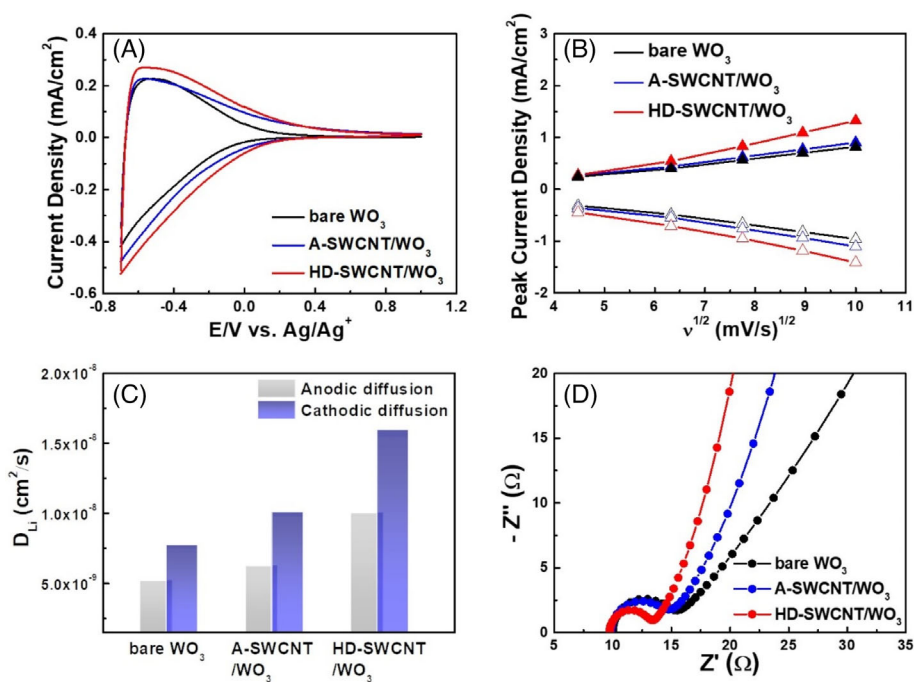


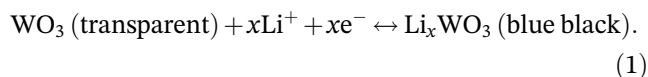
FIGURE 5 (A) CV curves in a potential range from -0.7 to 1.0 V, (B) Plots of peak current density vs square root of stepwise scan rates (filled and empty triangles for anodic and cathodic reactions, respectively), (C) D_{Li} of anodic and cathodic diffusion, and (D) EIS curves of bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃



presence of amide and carbonyl functional groups, which promote the Li-ion diffusion kinetics, HD-SWCNT/WO₃ is expected to present ultrafast EC energy-storage performances.

Figure 5 shows enhanced electrochemical kinetics and activity of HD-SWCNT/WO₃ owing to the effects of the HD-SWCNT thin film facilitating both Li-ion and electron transport in the electrode. Figure 5A shows the CV curves in the range from -0.7 to 1.0 V at a scan rate of 20 mV/s

to trace the electrochemical behavior of the bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃ electrodes. All electrodes identically exhibit a broad reduction-oxidation (redox) peak with respect to the applied negative-positive potential, which corresponds to the general electrochemical behavior of amorphous WO₃.^{10,32} The redox reaction, which accompanies reversible insertion/extraction of Li ions and electrons, generates the EC behavior of the WO₃ matrix expressed as Equation (1)⁵:



Notably, HD-SWCNT/ WO_3 has an increased CV curve area with higher current densities for both anodic and cathodic peaks than the bare WO_3 and A-SWCNT/ WO_3 electrodes, which indicates enhanced electrochemical activity with the increased quantity of inserted and extracted Li-ions. The enhanced electrochemical activity of HD-SWCNT/ WO_3 can be attributed to the uniform structure with porosity of the HD-SWCNT thin film shortening the Li-ion diffusion pathways and increasing contact area between the polar functional groups in the PVP grafts and the electrolyte. The polar amide and carbonyl groups in the HD-SWCNT thin film, which enhance the Li-ion wettability, lead to facile accessibility of Li ions between the WO_3 matrix and the electrolyte compared to the bare WO_3 and A-SWCNT/ WO_3 electrodes. The AFM results demonstrate the increased contact area with the enhanced surface roughness of highly dispersed and porous SWCNT interfacial thin film compared to bare WO_3 (Figure S3). In good agreement with the SEM images, HD-SWCNT/ WO_3 exhibits highly dispersed SWCNTs on WO_3 film while bare WO_3 exhibits flat surface morphology of WO_3 film. Notably, HD-SWCNT/ WO_3 shows a higher root mean square roughness (R_{ms}) of 4.76 nm compared to bare WO_3 (0.39 nm), which links to the increased contact area between the WO_3 film and electrolyte due to the dispersed and porous SWCNT interfacial thin film. Thus, the electrochemically active HD-SWCNT/ WO_3 electrode is probable to present a higher Li-ion capacity than the bare WO_3 and A-SWCNT/ WO_3 electrodes, which directly affects the transmittance modulation and specific capacitance for EC energy-storage. To evaluate the Li-ion diffusion kinetics, we calculated the Li-ion diffusion coefficients of bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 electrodes (Figure 5B,C, and Figure S4, respectively). Figures S3A–C show the CV curves at stepwise scan rates of 20, 40, 60, 80, and 100 mV/s for the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 , respectively. A-SWCNT/ WO_3 presents slightly increased peak current densities for anodic and cathodic diffusion compared to the bare WO_3 , which can be attributed to the presence of highly conductive SWCNT bundles on the WO_3 film. Interestingly, HD-SWCNT/ WO_3 shows a drastic increase in the current densities for both the anodic and cathodic peaks at all the stepwise scan rates, which suggest rapid insertion/extraction of Li ions and electrons during the redox reaction under a rapid potential sweep. Figure 5B shows the peak current densities for the anodic and cathodic reactions against the square root of the stepwise

scan rate (filled and empty triangles for the anodic and cathodic reactions, respectively) based on the results shown in Figure S4. Notably, HD-SWCNT/ WO_3 exhibits higher line slopes for both the anodic and cathodic reactions than the bare WO_3 and A-SWCNT/ WO_3 , a trend that is directly related to the Li-ion diffusion coefficient (D_{Li}). The Randles–Sevcik equation was used to calculate D_{Li} using Equation (2)³⁷:

$$J_p = 2.72 \times 10^5 \times D_{\text{Li}}^{1/2} \times C_0 \times v^{1/2}, \quad (2)$$

where J_p (mA/cm²) is the peak current density, D_{Li} (cm²/s) is the Li-ion diffusion coefficient, C_0 (mol/cm³) is the active ion concentration in the electrolyte, and v (V/s) is the scan rate during the CV. Consequently, as shown in Figure 5C, HD-SWCNT/ WO_3 exhibits higher anodic and cathodic diffusion rates (10.00×10^{-9} and 15.95×10^{-9} cm²/s) than the bare WO_3 (5.16×10^{-9} and 7.69×10^{-9} cm²/s) and A-SWCNT/ WO_3 (6.22×10^{-9} and 10.00×10^{-9} cm²/s). These can lead to ultrafast EC energy-storage performances of the former. Figure 5D shows the EIS curves of the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 , which confirms the interfacial charge transfer resistance. Notably, HD-SWCNT/ WO_3 curve displays a smaller semicircle in the high-frequency region than bare WO_3 and A-SWCNT/ WO_3 , which is associated with the lower ionic diffusion resistance at the interface between the electrolyte and HD-SWCNT/ WO_3 . This lower ionic diffusion resistance mainly originates from the highly dispersed morphology of the PVP grafted SWCNTs. The uniformly distributed amide and carbonyl functional groups along the dispersed SWCNTs facilitate Li-ion transport in the WO_3 film.^{11,38–40} In addition, the linear slope of the Nyquist plot in the low-frequency region suggests ionic diffusion kinetics, which is known as the Warburg impedance.^{13,41} The steepest linear slope in the Warburg impedance of HD-SWCNT/ WO_3 proves its superior Li-ion diffusion kinetics compared to the bare WO_3 and A-SWCNT/ WO_3 . These interfacial charge transfer resistance results from EIS are highly consistent with the electrochemical activity and kinetic results of all electrodes shown in Figure 5A,C. Thus, the introduction of an HD-SWCNT thin film, which improves the electrical conductivity and Li-ion transport, as a top layer on the WO_3 matrix can be an effective strategy to accelerate charge transport for ultrafast EC energy-storage performances.

Figure 6 shows the multi-functionality of the bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 films to serve as EC energy-storage electrodes. As shown in Figure 6A, the EC performances are evaluated by measuring the in-situ visible transmittance changes under double-stepped potentials of -0.7 V (coloration) and

FIGURE 6 (A) In-situ transmittance variation curves at 633 nm under repetitive potentials of -0.7 V (coloration) and 1.0 V (bleaching) for 60 seconds, respectively, (B) optical density variations at 633 nm vs charge density, (C) GCD curves under a potential range from -0.7 V (charge) and 1.0 V (discharge) at 2 A/g, and (D) plots of specific capacitance at current densities of bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3

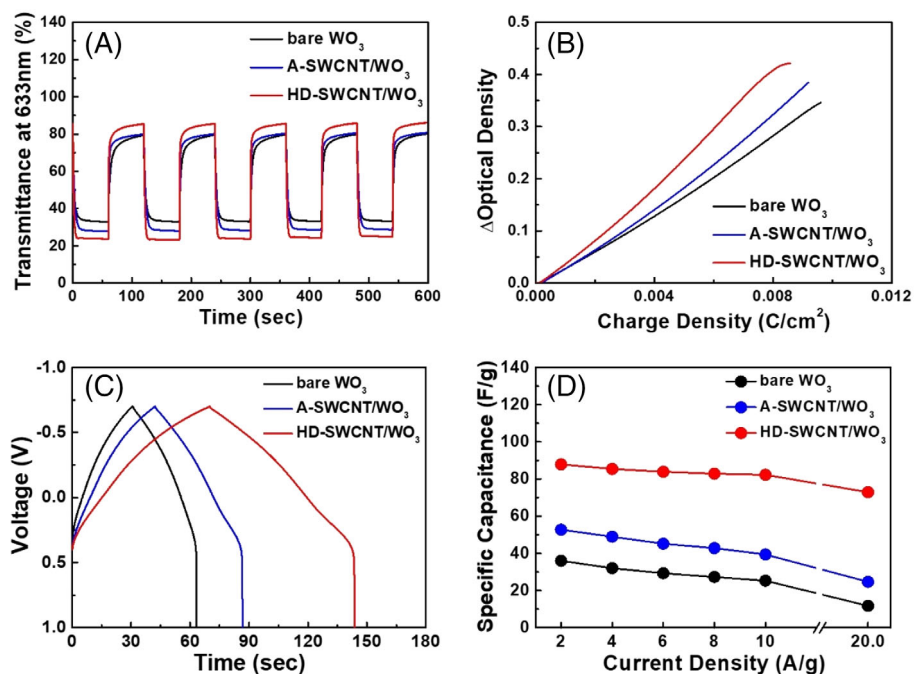


TABLE 1 Summary of EC performances of bare WO_3 , A-SWCNT/ WO_3 , and HD-SWCNT/ WO_3 electrodes

	Transmittance modulation (% , 633 nm)	Coloration speed (s)	Bleaching speed (s)	CE (cm^2/C)
Bare WO_3	47.0	8.2	15.3	35.3
A-SWCNT/ WO_3	51.0	7.4	6.4	40.0
HD-SWCNT/ WO_3	58.7	3.1	4.5	51.9

1.0 V (bleaching) for 60 seconds, respectively, and the results are summarized in Table 1. The HD-SWCNT/ WO_3 presented widened transmittance modulation (transmittance modulation = $T_b - T_c$, where T_b and T_c is the transmittance in the bleached and colored states, respectively) of 58.7% than the bare WO_3 (47.0%) and A-SWCNT/ WO_3 (51.0%). As the transmittance modulation is determined by the level of insertion/extraction quantities of Li ions and electrons, which is in proportion to the area of the CV curve, the enhanced transmittance modulation of HD-SWCNT/ WO_3 suggests the increased number of Li ion and electron insertion/extractions compared to the bare WO_3 and A-SWCNT/ WO_3 during the EC reaction. This is mainly attributed to the enhanced electrochemical activity of HD-SWCNT/ WO_3 due to the uniform structure with porosity of the HD-SWCNT thin film with amide and carbonyl groups promoting Li-ion wettability. Furthermore, the uniform porous structure of the HD-SWCNT thin film enables uniform distribution of the functional groups along the SWCNTs, which effectively shortens the Li-ion diffusion pathways and increases the contact area between the functional groups and the electrolyte. In the case of A-SWCNT/ WO_3 , the

distribution of bundled SWCNTs, confirmed in SEM and EDS result (Figure 3C and Figure S1B), alleviate the efficient electron transport along the sp^2 carbons during the EC reaction, which reduces the electrical conductivity of SWCNTs. As a result, the A-SWCNT/ WO_3 results in the unsatisfactory enhancement of transmittance modulation (51.0%) compared to that of HD-SWCNT/ WO_3 . It should be noted that faster switching speeds (the times to reach 90% transmittance modulation for coloration and bleaching, respectively) are achieved with HD-SWCNT/ WO_3 (3.1 seconds for coloration and 4.5 seconds for bleaching) than those with the bare WO_3 (8.2 seconds for coloration and 15.3 seconds for bleaching) and A-SWCNT/ WO_3 (7.4 seconds for coloration and 6.4 seconds for bleaching). In general, the switching speeds of EC electrodes are limited by the ionic diffusion, electrical conductivity, and thickness of their materials.^{42–44} As confirmed by the cross-view HR-SEM images (Figures 3E–G), all electrodes contain almost the same level of WO_3 film thicknesses, which demonstrates that the enhanced switching speeds of HD-SWCNT/ WO_3 are influenced by the properties at the interface between the HD-SWCNT thin film and the electrolyte. The debundled and continuous morphology

TABLE 2 Summary of energy-storage performances of bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃ electrodes

	2 A/g	4 A/g	6 A/g	8 A/g	10 A/g	20 A/g	High-rate capability (%)
Bare WO ₃	36.0	32.0	29.3	27.3	25.3	11.7	32.5
A-SWCNT/ WO ₃	52.7	48.9	45.2	42.8	39.4	24.7	46.9
HD-SWCNT/ WO ₃	87.9	85.4	83.9	82.9	82.2	72.9	82.9

without any surface defects of the HD-SWCNT thin film promotes accelerated electron conductance along the sp² carbons. Moreover, the polar functional groups in the uniformly grafted PVP onto the SWCNTs induce a lower Li-ion diffusion resistance at the interface than the bare WO₃, which accelerates Li-ion transport in the WO₃ film. Owing to the simultaneous improvement in the electrical conductivity and Li-ion diffusion kinetics in the HD-SWCNT thin film, HD-SWCNT/WO₃ exhibits superior switching speeds, which is highly consistent with the investigated D_{Li} shown in Figure 5C. On the other hand, A-SWCNT/WO₃ exhibits enhanced switching speeds than that of bare WO₃, which demonstrates the excellent electron conductivity of SWCNTs. However, the bundled and discontinuous morphology of aggregated SWCNT film reduces their electrical conductivity in the electrode, resulting in inferior switching speeds than that of HD-SWCNT/WO₃. The CE, which reflects both transmittance modulation and switching kinetics, was investigated, and the results are shown in Figure 6B. The CE can be calculated by an optical density variation (ΔOD) with the applied charge density (Q/A) as follows Equations (3) and (4):⁶

$$CE = \Delta OD / (Q/A), \quad (3)$$

$$\Delta OD = \log (T_b/T_c). \quad (4)$$

HD-SWCNT/WO₃ presents a higher CE (51.9 cm²/C) than the bare WO₃ (35.3 cm²/C) and A-SWCNT/WO₃ (40.0 cm²/C), which is attributed to the synergetic effects of the improved transmittance modulation and switching speeds (Table 1). The energy-storage performances of bare WO₃, A-SWCNT/WO₃, and HD-SWCNT/WO₃ are evaluated as shown in Figure 6C,D. Figure 6C shows the GCD curves at a current density of 2 A/g under the potential range from −0.7 V (charge) to 1.0 V (discharge), which demonstrates a pseudocapacitive ability of the fabricated WO₃ films. All electrodes exhibit symmetric curves during the charge-discharge process, suggesting appropriate electrochemical reversibility. Interestingly, HD-SWCNT/WO₃ exhibits pronounced long cycle stability for consecutive 10 000 charge-discharge cycles compared to that of bare WO₃ (Figure S5). As shown in

Figure S5A, HD-SWCNT/WO₃ shows specific capacitance retention (87.12% at 2 A/g) after 10 000 cycles, while bare WO₃ shows drastic specific capacitance retention reduction (53.10% at 2 A/g). With the effect of interfacial HD-SWCNT thin film to promote electron and Li-ion transport kinetics, which are attributed to the highly debundled SWCNTs and uniformly distributed polar functional groups, respectively, HD-SWCNT/WO₃ can result in enhanced redox reversibility during the repetitive charge-discharge reactions. Significantly, HD-SWCNT/WO₃ has the longest charge-discharge times, that is, it has a higher energy-storage capacity than the bare WO₃ and A-SWCNT/WO₃. This result is highly consistent with the widened transmittance modulation induced by the increased electrochemical activity due to the uniform porosity of the HD-SWCNT thin film. Accordingly, HD-SWCNT/WO₃ has a higher specific capacitance than the bare WO₃ and A-SWCNT/WO₃ in the applied current density range from 2 to 20 A/g (Figure 6D and Table 2). Additionally, the increased specific capacitance of A-SWCNT/WO₃ when compared with that of bare WO₃ confirms the effective electron transport effect of SWCNTs at the interface between the WO₃ film and electrolyte, which can be confirmed in the EIS result (Figure 5D). Notably, HD-SWCNT/WO₃ exhibits a remarkable high-rate capability (specific capacitance retention of 20 A/g compared to 2 A/g), which is directly related to its ultrafast characteristics of 82.9%; in contrast, the bare WO₃ and A-SWCNT/WO₃ exhibit inferior rate capabilities of 32.5% and 46.9%, respectively. Because the HD-SWCNT thin film simultaneously accelerates the transport of electrons and Li ions to the WO₃ film during the electrochemical reaction, a feasible charge-discharge process can occur even at a high current density of 20 A/g in HD-SWCNT/WO₃. Furthermore, HD-SWCNT/WO₃ electrode shows notable energy-storage performances in both high-rate charge-discharge capability and long cycle stability compared to previously reported WO₃-based electrochemical capacitors (Table S1).^{45–54} Overall, the resultant multi-functional electrochemical kinetic properties such as D_{Li} (10.00 × 10^{−9} for anodic and 15.95 × 10^{−9} for cathodic diffusion), switching speeds (3.1 seconds for coloration and 4.5 seconds for bleaching), and high-rate capability (82.9%) validate the

ultrafast EC energy-storage performances of the HD-SWCNT/ WO_3 electrode.

4 | CONCLUSION

Ultrafast and high-performance EC energy-storage electrodes were developed by introducing an HD-SWCNT thin film on a WO_3 film by ultrasonic spray coating. Owing to the effect of uniform grafting of PVP onto the SWCNTs, the HD-SWCNT thin film retains a highly dispersed morphology with effective functional groups. The debundled and continuous morphology without any damage to the SWCNTs induces accelerated electrical conductivity. The functional groups of the amide and carbonyl groups in PVP enhance the Li-ion wettability, which improves the Li-ion diffusion kinetics. Furthermore, the uniform structure with porosity of the HD-SWCNT thin film increases the Li-ion accessibility by shortening the ionic diffusion pathways and increasing the contact area between functional groups and the electrolyte. Consequently, the HD-SWCNT/ WO_3 electrode exhibits enhanced EC energy-storage performances: transmittance modulation (58.7% at 633 nm), switching speeds (3.1 seconds for coloration and 4.5 seconds for bleaching), CE (51.9 cm^2/C), and specific capacitance (87.9 F/g at 2 A/g). Remarkably, HD-SWCNT/ WO_3 presents ultrafast charge-discharge performance with a high-rate capability (72.9 F/g at 20 A/g and specific capacitance retention of 82.9% at 20 A/g). Thus, the introduction of an HD-SWCNT thin film on WO_3 films, which accelerates both electron and Li-ion transport, can offer a novel strategy for realizing ultrafast EC energy-storage electrodes.

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DATA AVAILABILITY STATEMENT

Data available in article supplementary material.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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