Hybrid Transparent PEDOT:PSS Molybdenum Oxide Battery-like Supercapacitors

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Supporting Information

ABSTRACT: We report fabrication of flexible all-solid-state transparent electrochromic patterned microsupercapacitors based on two-dimensional layered nanostructured molybdenum oxide (MoO$_{3-x}$)/poly(3,4-ethylenedioxythiophene)−polystyrenesulfonate (PEDOT:PSS) nanocomposite electrodes. Exceptional electrochemical performance of the transparent microsupercapacitors includes fast kinetics and response times, high specific capacitances (up to 79.2 C/g, 99 F/g, and 2.99 mF/cm$^2$), and Coulombic efficiencies of 99.7% over 2500 cycles. Such exceptional performance is attributed to the synergistic effects of PEDOT:PSS providing high electrical conductivity and high charge storage capacity along with its segregated interfacial nanostructure facilitating the intercalation of the ionic species, H$^+$ (Na$^+$, K$^+$) and SO$_4^{2-}$, into the high surface area tunnel structure of the 2D MoO$_{3-x}$ nanosheets. Supercapacitors using MoO$_{3-x}$ PEDOT:PSS electrodes exhibit optical transmittance above 70% (λ = 380–730 nm). The electrochemical performance of the transparent microsupercapacitor is due to both PEDOT:PSS and cation (H$^+$) intercalation in the tunnel structure of MoO$_{3-x}$.

KEYWORDS: transparent supercapacitor, 2D materials, PEDOT:PSS, molybdenum oxide nanoparticles, nanocomposite electrode, electrochromic

INTRODUCTION

Advanced electrochemical capacitors require high power density, excellent charge storage capability, fast response time, safety, cycle life, and large energy density. Recent requirements for embedded energy storage systems are small, thin, lightweight, and flexible yet high specific capacitance, high energy, and power density. Transparent thin film solid-state flexible supercapacitors are currently under intense investigation for optoelectronics applications. The combination of transparency, electrical conductivity, charge storage capacity, the capability of undergoing redox (and/or intercalation) reactions, and electrochemical stability is extremely difficult to achieve. Optically transparent pristine 1–2 layer thin graphene supercapacitors featured an areal capacitance of 80 μF/cm$^2$ while multilayer graphene oxide demonstrated 394 μF/cm$^2$. Hierarchical Ag–Au nanomaterials have been utilized in transparent supercapacitors exhibiting 136.5–209.9 μF/cm$^2$. Transparent stretchable supercapacitors of wrinkled graphene have shown 57% transparency at 550 nm with areal capacitance of 5.8 μF/cm$^2$ and gravimetric capacitance of 7.6 F g$^{-1}$. Highly stretchable transparent supercapacitors based on Ag–Au core–shell nanowires showed areal capacitance up to areal capacitance of 209.9 μF/cm$^2$. Pseudocapacitor transparent ruthenium oxide aerogel-based supercapacitors with loading levels of 16.3 μg cm$^{-2}$ exhibited gravimetric capacitance of 79.6, 79.2, 75.9, and 72.3 F g$^{-1}$ and areal capacitances of 1.30, 1.29, 1.23, and 1.18 mF cm$^{-2}$ at scan rates of 25, 50, 75, and 100 mV s$^{-1}$. Recently, all-solid-state highly stretchable, transparent, and flexible electrodes of graphene PEDOT:PSS microsupercapacitors showed an excellent performance of 790 μF/cm$^2$ at the discharge current of 50 μA cm$^{-2}$. Transition metal oxides provide opportunities for the next generation of optoelectronics and electrical energy storage systems due to their exceptional electrical properties, optical band gap, and high surface area for intercalation/deintercalation of ionic species. Transparent supercapacitors require high transparency, good electrical conductivity, and large charge storage capacity. Two-dimensional materials such as graphene and transition metal dichalcogenides (e.g., MoS$_2$, MoTe$_2$, WSe$_2$, and MoO$_3$) are excellent potential candidates for advanced optoelectrochemical storage devices. Charge carriers in graphene travel essentially with massless speed of light electron transport ($c^* \approx 10^6$ m s$^{-1}$) in 70

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the absence of scattering. 29 Although a graphene single layer is 97% transparent with respect to the incident beam, chemically derived reduced graphene exists in multiple layers and stacks, making the >90% optical transparency required for optoelectronic devices difficult to achieve. The 2D transition metal dichalcogenide MoO3-x family has tunable optical and electrical properties which can be readily tailored, making them of great interest for transparent energy storage devices. 4,22-28

Molybdenum oxide has a wide range of optical and electrical properties which are dependent on its oxidation state (Mo3+), Mo5+, Mo4+, Mo2+, and Mo6+), dopants, doping level, and crystal structure. 22-28 MoO3 has a large work function (6.6 eV) due to its closed shell structure. 27 Shallow oxygen vacancies in MoO3 make it an n-type degenerate semiconductor that can easily donate electrons. 22-28 This makes MoO3 ideal for proton (H+ or Li+) intercalation, resulting in high electrical conductivity suitable for energy storage devices such as pseudocapacitors. Molybdenum oxides have exceptional electrochemical properties due to their tunnel structures created from MoO3 octahedra, where Li+ and H+ ions can be readily intercalated and deintercalated. 25-28 As a result of proton intercalation, the electrical conductivity of MoO3 increases. 4,25-28 Kalantarzadeh et al. proposed the H+ can intercalate in the oxygen of MoO3, resulting in a significant increase in free electron concentration. 25,26 It has been also reported that hydrogen insertion causes extended lattice distortion in α-MoO3, resulting in a significant reduction of the energy gap. 23-28 Simulations predicted any n-type electron doping or charge transfer results in band gap distortion. 23-28 Huang et al. reported proton intercalation significantly deforms O2−—Mo—O2− chains, leading to band gap narrowing and optical band gap reduction. 25-27 The intrinsic conductivity of fully oxidized MoO3 has been reported as 10−3 S/cm and increased to 10−4 S/cm for reduced MoO3. 5 Because of its limited electrical conductivity, molybdenum oxide is used in composite structures with highly conductive additives such as activated carbon or graphene. 22-28 Molybdenum oxides and their nanocomposites have shown excellent performance as supercapacitors where active material loading can be high and there is no transparency requirement. 30-33 Supercapacitors with MoO3—graphene composite electrodes demonstrated a capacitive performance of 148 F/g by using aqueous electrolyte of 1 M Na2SO3. 30-33 Despite reports of MoO3 supercapacitors, 30-33 to the best of our knowledge, there is no report of an organic—Inorganic PEDOT:PSS molybdenum oxide nanocomposite as a transparent microsupercapacitor electrode.

Acid-based electrolytes, such as sulfuric and phosphoric acid, have been incorporated in a network of poly(vinyl alcohol) (PVA) gels to generate all-solid-state supercapacitors where sulfuric acid-doped PEDOT:PSS exhibits 4 times higher electrical conductivity (4380 S cm−1), improved transparency, increased crystallinity, and a change in morphology to a fibrous structure with an enhanced surface area. 37-44

PEDOT:PSS is a transparent conductive polymer with both good electrical and ionic conductivity and a theoretical capacitance of 210 F/g. 37-41 The origin of the PEDOT:PSS complex ionic–electrical coupling has been investigated by describing the cyclic voltammogram using a 2D Poisson–Nernst–Planck analysis. 37-41 The high capacitance has been attributed to the high surface area phase-separated morphology and to a large contribution of the electric double layer (EDL) formation along the interfaces between the electron conducting PEDOT and ion-transporting PSS. 37-44 The charge storage capacity is also enhanced by the free volume of PEDOT. 41 Sulfuric acid-doped PEDOT:PSS exhibits 4 times higher electrical conductivity (4380 S cm−1), improved transparency, increased crystallinity, and a change in morphology to a fibrous structure with an enhanced surface area. 37-44

Recently, all-conjugated electrochromic supercapacitors based on polyaniline capacitive coating and electrochromic conjugated polymers demonstrated dual functionality promising potential for smart windows. 2 Metal oxides such as tungsten oxide (WO3), niobium oxide (Nb2O5), and titanium dioxide (TiO2) have shown electrochromic behavior where anodic electrochromism is reported for nickel oxides and special vanadium pentoxide. 42-44 Self-powered electrochromic microsupercapacitors with an average visible optical modulation (ΔTλ) of 15.3% and a response time of 10 s have been recently reported. 42-44 PEDOT:PSS silver grid films were coated with electrochromic WO3 to generate flexible hybrid structure with large optical modulation (81.9% at 633 nm), fast switching, and high coloration efficiency (124.5 cm2 C−1). 45

In this study, we report a solid-state hybrid organic–inorganic PEDOT:PSS—MoO3 transparent supercapacitor device prepared in a facile, yet scalable method. We designed all-solid-state flexible thin transparent pseudocapacitor electrodes based on 2D nanosheet stacks of an orthorhombic (α)-MoO3 PEDOT:PSS hybrid structure with a poly(vinyl alcohol)—sulfuric acid (PVA–SA) gel electrolyte. These microsupercapacitors were prepared in two configurations: an interdigitated pattern and a window and frame design using a CO2 (λ = 10.6 μm) laser patterning method. The microsupercapacitors exhibited excellent electrochemical performance with high specific capacitances up to 79.2 C/g, 99 F/g, 2.99 mF/cm2 as well as Coulombic efficiencies of 99.7% over 2500 cycles. The device performance is attributed to the high surface area fibrous morphology of the sulfuric acid-doped PEDOT:PSS, enabling high charge storage capacity (H+ or SO42− which makes the charges readily available for intercalation into the tunnel structure of the o-MoO3−x−.

### EXPERIMENTAL SECTION

#### Materials

Molybdenum(II) acetae dimer (Alfa Aesar), poly(vinyl alcohol), acetone, and NMP (Sigma-Aldrich) were used as received. PEDOT:PSS-coated PET films were generously donated by Kimoto Tech.

Molybdenum Oxide Synthesis. Molybdenum(II) acetae dimer (MoAD) was used as an organometallic precursor. In a typical preparation method, 0.25−1 mol of MoAD was dissolved in 3−5 cm3 of NMP and then added dropwise to the anhydrous NMP solution at 190°C while stirring under nitrogen. The dispersion was stirred at 190°C for 15 min, 30 min, 45 min, and 1 h. The resultant dispersion was centrifuged and washed with acetone three times until clear. Subsequently, the resulting nanoparticles were annealed at 400°C to yield light blue nanoparticles.

Fabrication of the Flexible All-Solid-State Supercapacitors: Electrode Preparation. The molybdenum oxide nanoparticles were
RESULTS AND DISCUSSION

Fabrication and Characterizations of o-MoO3 Nanoparticles. We developed a solvent-based synthesis method to prepare two-dimensional o-MoO3 nanosheets and/or nanoscrolls examined using high-resolution transmission electron microscopy (HR-TEM) (Figure 1a–d). The chemical and crystalline structure and the morphology of the molybdenum oxide nanosheets were characterized by using wide-angle X-ray scattering (WAXS), X-ray photoelectron microscopy (XPS), atomic force microscopy (AFM), and high-resolution microscopy (HR-TEM). The crystalline structures of the MoO3 nanosheets and nanoscrolls were determined to be orthorhombic by using WAXS (Figure 2).46–48 During this reaction, Mo4+ atoms of molybdenum(II) acetate dimer (MoAD) were oxidized from Mo4+ to Mo6+ and Mo5+. The resultant o-MoO3 nanosheets had a small atomic percent of Mo5+ in addition to Mo6+, leading to a higher conductivity and enhanced electrochemical performance (WAXS, AFM, and XPS, Figures 2–5). The molybdenum acetate dimer precursor was oxidized to o-MoO3−x in N-methyl-2-pyrrolidone (NMP) at 190 °C followed by thermal annealing at 400 °C (Figure 3a). At higher temperatures once the carbon species bonded to the oxygen atoms were decomposed, the oxygen atoms were oxidized from Mo4+ to Mo5+ and Mo6+. An inert atmosphere was used to limit the availability of free oxygen atoms and molecules to generate reduced MoO3. This resulted in a light blue color for o-MoO3 after annealing. The o-MoO3 consists of stacks of two-dimensional nanosheets forming nanoparticles. A typical o-MoO3 nanoparticle with lateral dimensions of 190 nm X 100 nm consisting of o-MoO3 nanolayers and stacks is shown in Figures 1b,c and 3a–c. The single or few nanosheets of o-MoO3 appear to be nearly transparent with respect to the incident beam and have a tendency to fold at the edges of single or few layer nanosheets. The particle size distribution determined by dynamic light scattering features lateral dimensions ranging from 60 nm to 1.6 μm, with an average particle size of 339 ± 166 nm (Table S1). The single or few nanolayers of o-MoO3 are extremely thin and nearly transparent with respect to the incident electron beam (HR-TEM, Figures 1c and 3a–c). This indicates that the 2D layered structure materials can be exfoliated to atomically thin single layer (or few layers) of low color MoO3 which makes them ideal for transparent supercapacitors. The thin layered structure of MoO3 has excellent optical properties and low absorption in the visible wavelength range. The optical transparency of composite layers of MoO3 thin layer and silver layer deposit is reported as 70% normal transmittance in the wavelength range of 350 nm < λ < 550 nm.49 The two-dimensional layered structure of MoO3 that can be readily exfoliated into single and few atomic thin layers provides an excellent opportunity for their application in transparent energy storage devices. The 2D layered nanosheet structure materials of the o-MoO3 results in a high surface area per nanoparticle and is ideal for EDL charge storage and ion intercalation. The X-ray diffraction pattern was matched with JCPDS 01-089-5108, indicating an orthorhombic MoO3 structure.46–48 The orthorhombic MoO3 structure consists of edge and corner-sharing MoO6 with a unit cell of a = 3.962 Å, b = 266 C

Figure 2. Wide-angle X-ray diffraction pattern of the molybdenum oxide nanoparticles indexed to orthorhombic MoO3 (JCPDS 01-089-5108).

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Figure 1. (a) A reaction scheme for molybdenum acetate dimer in NMP forming MoO3 on heating at 195 °C followed by annealing at 400 °C. (b) TEM micrograph of a typical MoO3 nanoparticle. (c) At higher TEM magnification a stack of MoO3 nanosheets appears to be semitransparent under the electron beam. (d) TEM micrograph of MoO3 nanoscrolls.
13.855 Å, and $c = 3.701$ Å. The Scherrer equation ($\tau = K \lambda / \beta \cos \theta$) was used to calculate the mean crystallite size ($t$) by using the full width half-maximum (peak broadening, $b$), taking into account the instrument broadening constant ($K = 0.94$), wavelength $\lambda = 1.5418$ Å, and the peak position ($\theta$) Rietveld refinement using the least-squares minimization approach for fitting the shape of the measured peak profile to the calculated one based on the wave vector diffraction principle ($q = 4\pi \sin(\theta) / \lambda$) in reciprocal space ($q = \text{wave vector}$) for crystal unit cell calculations. This refinement resulted in cell unit parameters of $a = 3.965$ Å, $b = 13.79$ Å, and $c = 3.72$ Å and space group of $pnm$ (shown in the Supporting Information).

The complete list of values, lattice spacing, crystallite size, and unit cells from both Scherrer calculations and Rietveld refinement are listed in Table S2. The Scherrer calculation values are the crystallite size, which is different from particle size. This approximation is well within the validity range of the Scherrer equation (<100 nm). X-ray diffraction patterns indicate that the orthorhombic MoO$_3$ structure consists of edge and corner-sharing MoO$_6$ octahedra with crystallite sizes ranging from 31.3 to 76.2 nm in different lattice (hkI) planes, 040 and 021, respectively, based on the Scherrer equation (Figure 2 and Table S2). The crystallite’s shape could be approximated as spherical, as indicated by the absence of asymmetric peak broadening. To further investigate the morphology of the two-dimensional MoO$_3$ nanoparticles, high-resolution TEM and AFM were utilized (Figures 3 and 4). High-resolution micrographs of MoO$_3$ nanosheets show the growth of o-MoO$_3$ in the 110 direction with a lattice spacing of 3.8 Å (Figure 3a–c). The high-resolution micrograph confirms thin layers of o-MoO$_3$ with a wavy and wrinkled structure; the nanosheets are prone to rolling up and forming tubular structures. The fast Fourier transform of the MoO$_3$ micrographs confirms the lattice spacing as 3.8 Å in the 110 direction. The AFM images of the o-Mo$_3$ show the thin layers of the highly exfoliated particles with height ranging measured between 1.3 and 26 nm (Figure 4a,b). The exfoliated o-Mo$_3$ nanolayers were prepared by dispersing the particles in the mixture of acetone and alcohol followed by sonication and drop-casting from a dilute dispersion on Au-coated sapphire. The exfoliation protocol was followed closely to the protocol used for generating the MoO$_3$ aerosol for electrode preparation. The o-MoO$_3$ nanosheets were flexible and conformed to the gold substrate morphology. A stack of MoO$_3$ nanosheets (408 $\times$ 532 nm$^2$) with a height of $\sim$9 nm with the top nanosheet rolled up can be observed in Figure 4a. Figure 4b demonstrate a MoO$_3$ nanosheet (238.5 $\times$ 71.9 nm$^2$) with a height of 3.13 nm. The Raman spectra exhibit peaks at 996, 818, 666, 244, 290, and 337 cm$^{-1}$ due to o-MoO$_3$ (shown in the Supporting Information). High-resolution XPS peak deconvolution shows a peak at 232.5 eV corresponding to Mo$^{6+}$ (Mo 3d$\bar{5}/2$) with a contribution from a peak at 231.2 eV corresponding to Mo$^{4+}$ 3d$\bar{5}/2$ (Figure 5). The separation of the Mo 3d$\bar{5}/2$, 3d$\bar{3}/2$, and Mo 3d$\bar{3}/2$ doublet was $\sim$1.3 eV, confirming the presence of Mo$^{6+}$ in MoO$_3$. The smaller peak at a lower binding energy of 231.2 eV is due to a lower oxidation state slightly reduced MoO$_3$. The ratio of Mo 3d$\bar{5}/2$ to Mo 3d$\bar{3}/2$ peaks was $\sim$3:2, in good agreement with the binding energies and area ratios.

Figure 3. (a) Layered structure of the MoO$_3$ nanoparticles. (b) High-resolution images of the synthesized MoO$_3$ nanoparticles showing the lattice fringes in the stacked nanosheet structure. (c) The FFT of the image shows the 110 plane (at point A, 3.8 Å). Atomic structure of the molybdenum and oxygen in the planar structure are presented.

Figure 4. Topography of MoO$_3$ measured by AFM for a layered particle deposited on Au-coated sapphire. (a) Larger stack of MoO$_3$ particle (408 $\times$ 532 nm$^2$). (b) Nanosheet of MoO$_3$ (238.5 $\times$ 71.9 nm$^2$).
reported for o-MoO$_3$. The higher conductivity and pale blue color of the synthesized o-MoO$_3$ are in agreement with slightly reduced MoO$_3$ approximated as MoO$_3$-$0.05$ (based on the area ratio of Mo$^{5+}$/Mo$^{6+}$). The presence of lower oxidation states (Mo$^{5+}$, Mo$^{4+}$) has been associated with increased electrical conductivity and electrochemical activity.

**Device Fabrication.** PEDOT:PSS is a conductive polymer with a mixed mode of electrical and ionic conductivity (Figure 6) that has been used both as an active material and as a transparent current collector. PEDOT:PSS has a phase-segregated morphology. PEDOT:PSS forms a crystalline solid, and the degree of crystallinity increases with sulfuric acid doping. Studies have shown that the increase in sulfuric acid doping results in high electrical conductivity reaching $\sigma_{dc\text{-max}}$ of 4380 S/cm at 100% sulfuric acid doping, while maintaining a high level of transparency comparable to that of indium tin oxide (ITO). Therefore, based on reports on doping PEDOT:PSS with PVA sulfuric acid electrolyte, a high electrical conductivity can be achieved, along with a fibrillar highly phase-separated morphology which generates high surface area and improved transparency. This will facilitate charge storage ($H^+$, SO$_4^{2-}$) via intercalation into the tunnel structure of o-MoO$_3$. To further process and form the electrodes, the o-MoO$_3$ stacked nanosheets were dispersed in acetone and sonicated for 15 min before using a high-pressure spray-coater to create PEDOT:PSS-coated PET films (Figure 7). This method promotes dispersion of the layers and maximizes the surface area. The dispersions were applied using an air brush which even promotes finer aerosols, resulting in a more uniformly dispersed nanoparticles on the supercapacitors is evident in Figure 8 where average transmittances of >70% can be seen in the visible region. The o-MoO$_3$ particle size and particle dispersion can affect the light transmission and scattering especially if large aggregates form. The oscillations observed in the spectra are due to interference fringes from the thin film of PEDOT:PSS coated on the PET surface.

**Device Characterization.** The transmittance of visible light ($\lambda = 380$–730 nm) through the PEDOT:PSS films and through the PEDOT:PSS/o-MoO$_3$/sulfuric acid gel devices was measured (Figure 8). The transparency of the PEDOT:PSS PET films (Figure 7a,b). Then, the composite electrodes were patterned by using a CO$_2$ laser ($\lambda = 10.6$ $\mu$m) into interdigitated patterns or window and frame configurations. The devices were designed using 2D molybdenum oxide nanoparticles and PEDOT:PSS, which both contribute to the capacitance, while PEDOT:PSS also acts as a current collector. This processing method has the advantage of facile scale up to roll-to-roll processing.

**Figure 5.** High-resolution XPS spectra of Mo of the MoO$_3$ showing Mo$^{6+}$ and some contribution of Mo$^{5+}$.

**Figure 6.** Schematic of the chemical structure of PEDOT:PSS.

**Figure 7.** A dispersion of o-MoO$_3$ nanosheets was air-brushed onto the PEDOT:PSS PET films followed by laser patterning to form the electrodes. (a) A dispersion was spray-coated using a high-pressure nozzle. (b, c) The coated films were dried and laser patterned by using a CO$_2$ laser. (d) Fabricated devices exhibited electrochromic and blue color in negative electrode when voltage was applied.

**Figure 8.** Transmittance of visible light ($\lambda = 450$–750 nm) for an MoO$_3$/PEDOT:PSS/PET device compared with a PEDOT:PSS/PET film. The interference fringes are due to the thin film of PEDOT:PSS coated on the PET surface.

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phenomena: (1) the intercalation of protons into the tunnel structure of o-MoO₃ upon application of a voltage and (2) the electrochromic response of PEDOT:PSS. The positive electrode remains nearly transparent likely because the negative ions (HSO₄⁻, SO₄²⁻) are too large for intercalation within the MoO₃ crystal structure. Electrochromic energy storage devices can be used in smart windows with dual functionality of energy storage capability.

**Electrochemical Measurements.** The main parameters of microsupercapacitor performance are (1) high specific capacitance, (2) fast charge/discharge rates, (3) efficiency and cyclability, (4) safety, (5) flexibility, and (6) facile production, i.e., low cost. Cyclic voltammetry of a typical transparent supercapacitor device (two identical electrodes, 0.9−1 mm nonconductive separator in PVA−SA gel electrolyte) in the sweeping voltage range from 0 to 0.8 V and scan rates of 1, 3, 5, and 8 mV/s is presented in Figure 9a. The current increased immediately as the voltage was increased followed by a redox peak showing nearly ideal supercapacitor behavior with excellent rate capacity. The discharge was rapid and exhibited a reverse peak, indicating reversible redox activity. It has been reported that molybdenum oxide-based supercapacitors show an irreversible peak Li⁺ ion intercalation in the first cycle. The first cycle in the molybdenum oxide:PEDOT:PSS supercapacitors exhibited an irreversible peak which was not taken into account for the measurements and calculations. The devices demonstrated electrochromic behavior. Once the voltage was applied, the negative electrode color changed to a darker blue, while the positive electrode remained transparent. This response is indicative of mixed redox and ion diffusion activities. Both PEDOT:PSS and o-MoO₃ are electrochemically active; therefore, the presence of redox peaks indicates the electrochemical response of both PEDOT:PSS and H⁺ intercalation into the tunnel structure of o-MoO₃. Diffusion-controlled H⁺ insertion occurs at low scan rates where the time scale of the processes allows ion diffusion in the inner structure of the o-MoO₃ (Figure 9b).

The capacitive response changed to EDLC type when the scan rate was increased to 20 mV/s, where the fast scan rate does not provide enough time for redox reactions and intercalation and deintercalation of protons (H⁺) into the tunnel structure of o-MoO₃ (Figure 9b). The majority of the capacitive contribution can be attributed to EDLC formation in the two-phase structure of PEDOT. The charge storage mechanism was evaluated by fitting the change of the current, \( I(\nu) \), as a function of scan rate \( \nu \) at a specific voltage \( V \) to a power law: \( I(\nu) = a\nu^b \) (Figure 9c). The \( b \) value variations are indicative of Faradaic and non-Faradaic currents. When the \( b \) value is close to 1, this indicates capacitive control, while a \( b \) value close to 0.5 indicates diffusion-controlled currents. Figure 9c shows \( b \) values close to 1 at low voltage (0.1 V) followed by a sudden decrease to 0.64 at 0.2 V, indicative of diffusion-controlled reactions at low voltage (≤0.2 V). The \( b \) value then increased to ~0.8 above 0.4 V, indicating that the charge storage mechanism is now dominated by the electric double layer formation at higher voltage. The change in \( b \) value in this system is an indication of mixed intercalation, redox, and EDLC currents. The Faradaic reactions occur at low
The gravimetric capacitance ($C_g$ F/g), the specific capacitance ($C_s$ F/g), and the footprint areal capacitance ($C_f$ in mF/cm²) were calculated from the CV curves at each scan rate (eqs S1 and S2) (Figure 9a,b). The gravimetric capacitance (and specific capacitance) values are 99.8 F/g (79.8 C/g), 95.0 F/g (76 C/g), 90.4 F/g (72.3 C/g), and 86.8 F/g (69.4 C/g) at scan rates of 1, 3, 5, and 8 mV/s, respectively. The footprint areal capacitance values are 3.0, 2.9, 2.7, and 2.6 mF/cm² at scan rates of 1, 3, 5, and 8 mV/s, respectively. The gravimetric and areal capacitance values are high, and the device maintained its capacitance within the examined scan rate range (Figure 10). Dai et al. reported a supercapacitors with transparency higher than 70% at 550 nm F/g, 2.99 mF/cm²), and Coulombic efficiency high, and the device maintained its capacitance within the examined scan rate range (Figure 10).

The Nyquist plot (Figure 11a) shows a semicircle followed by a diffusion-related impedance and then a change of $Z''$ to almost parallel to $-Z''$ at low frequencies indicating nearly ideal supercapacitive behavior. The resistance at high frequency due to contact resistance was negligible (A in Figure 11a). The PEDOT:PSS acts as both a current collector and an active material; therefore, there is essentially no contact resistance. The electrode resistance was negligible compared to the bulk electrolyte, mass transfer, and charge transfer resistances. The semicircle resistance (B) represents a combination of the bulk electrolyte, mass transfer, and charge transfer resistances of 838.2 Ω, in reasonable agreement with that calculated from the IR drop as 766.6 ± 14.4 Ω. This high value is likely due to the high resistance of the gel electrolyte. The low-frequency Warburg impedance at 45 °C can be attributed to diffusion processes. A linear fit of $Z''$ vs $ω^{−1/2}$ (frequency < 25 Hz) resulted in a Warburg coefficient ($σ$) of $357 ± 58$ ohm. This value is higher than comparable low-viscosity electrolyte devices, likely due to slow diffusion of the ions through the high-viscosity PVA gel.

The Bode plot shows two step changes: one at high frequency (~632.9 Hz) followed by a second at lower frequency (0.06 Hz) (shown in the Supporting Information). This resulted in a 2.8 s response time (at a phase angle of −45°), indicating a complex electrochemical activity with a contribution from both capacitive moieties—PEDOT:PSS and o-MoO₃—affecting the electrochemical activities of the supercapacitor. The fast response time of the device can be attributed to the fast kinetics of proton intercalation/deintercalation in the tunnel structure of o-MoO₃. Hydrogen doping decreases the MoO₃ bandgap, expands and contracts its lattice structure upon intercalation and deintercalation, and changes its color. PEDOT:PSS has also been reported as an electrochromic material. Doping PEDOT:PSS with sulfuric acid results in a nanofibrillar segregated PEDOT structure with high surface area which can store charge (H⁺ and SO₄²⁻) and provide ions for intercalation and deintercalation.

The o-MoO₃-based supercapacitors showed both a hybrid battery-supercapacitor behavior demonstrating high energy and power densities for transparent microsupercapacitors as shown in the Ragone plot of Figure 12a obtained by direct integration of the instantaneous power under the CV curve.
The designed morphology of the PEDOT:PSS with the o-MoO$_3$ tunnel structure enables intercalation of protons (H$^+$) from the sulfuric acid electrolyte which results in supercapacitors having high energy densities. The Coulombic efficiency measured over 2500 cycles (at 2.5 A/g) was 99.7% (Figure 12b), and the device exhibited excellent areal capacitance retention. Similar life cycles have been reported for complex redox-EDLC systems.$^{57,58}$ Meanwhile, our device exhibits aerial capacitance up to 2.99 mF/cm$^2$; flexible transparent supercapacitors of embedded PEDOT:PSS/AgNFs network exhibited areal capacitance of 0.91 mF/cm$^2$.\footnote{59}

Systems without transparency requirements are a different class of supercapacitors. Spicule-like Ni$_3$S$_2$ shells grown on molybdenum nanoparticle doped nickel foams are recently reported with 1.06 C cm$^{-2}$ (361 C/g) at 1 mA/cm$^2$ and good rate capability.\footnote{61} More recently, high-performance supercapacitors consisting of NiMoO$_4$ nanowire arrays and carbon nanotubes film have been reported to demonstrate 91.6% capacitance retention.\footnote{60-62} More recently, a range of supercapacitors with complex electrodes have been studied and reported.\footnote{63-69}

The transparent MoO$_3$/PEDOT:PSS/PET devices are completely flexible. The electrochemical performance of the devices was measured while under bending conditions at bending angles of 60° and 90°. The device was mounted on a two-piece flat substrate of equal lengths movable in specific angles. These angles can also be measured by knowing triangle dimensions. The device was connected to the potentiostat where cyclic voltammetry was performed at 5 mV/s while bending at 60° and 90° angles. The excellent electrochemical performance nearly remained unchanged while bending (Figure 13).

\section*{CONCLUSIONS}

In summary, high performance transparent (T > 70% at 550 nm) supercapacitor/electrochromic devices have been fabricated by using PEDOT:PSS and 2D o-MoO$_3$ nanosheets as both pseudocapacitive and EDLC active materials. The exceptional performance is attributed to the high charge (H$^+$, SO$_4^{2-}$) storage capacity enabled by high surface area PEDOT:PSS doped with sulfuric acid facilitating proton intercalation/deintercalation into and out of o-MoO$_3$. PEDOT:PSS, an ionic and electronic conductor, acts both as an active layer storing ionic species and as a current collector. Upon application of a voltage, protons (H$^+$) intercalate into o-MoO$_3$, resulting in a color change for this negative electrode. The positive electrode is designed to remain as a transparent window for the supercapacitor. This provides an opportunity to create charge storage devices with electrochromic functionality.

Figure 12. (a) A Ragone plot of areal energy density vs power density comparing transparent PEDOT:PSS/MoO$_3$/SA devices with Li ion batteries, electrolytic supercapacitors, and microsupercapacitors. (b) The Coulombic efficiency (○) and capacitance of the devices (■) vs number of cycles.

Figure 13. (a) Supercapacitor films were placed on a substrate and moved to 60° and 90° where measurements were performed while bending. (b) Cyclic voltammetry measurements of the MoO$_3$/PEDOT/PSS film supercapacitors at bending angles of 60°, 90°, and 90° at a scan rate of 5 mV/s.
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