Bifunctional flexible electrochromic energy storage devices based on silver nanowire flexible transparent electrodes

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Abstract
Flexible electrochromic energy storage devices (FECESDs) for powering flexible electronics have attracted considerable attention. Silver nanowires (AgNWs) are one kind of the most promising flexible transparent electrodes (FTEs) materials for the emerging flexible devices. Currently, fabricating FECESD based on AgNWs FTEs is still hindered by their intrinsic poor electrochemical stability. To address this issue, a hybrid AgNWs/Co(OH)\textsubscript{2}/PEDOT:PSS electrode is proposed. The PEDOT:PSS could not only improve the resistance against electrochemical corrosion of AgNWs, but also work as functional layer to realize the color-changing and energy storage properties. Moreover, the Co(OH)\textsubscript{2} interlayer further improved the color-changing and energy storage performance. Based on the improvement, we assembled the symmetrical FECESDs. Under the same condition, the areal capacitance (0.8 mF cm\textsuperscript{-2}) and coloration efficiency (269.80 cm\textsuperscript{2} C\textsuperscript{-1}) of AgNWs/Co(OH)\textsubscript{2}/PEDOT:PSS FECESDs were obviously higher than AgNWs/PEDOT:PSS FECESDs. Furthermore, the obtained FECESDs exhibited excellent stability against the mechanical deformation. The areal capacitance remained stable during 1000 times cyclic bending with a 25 mm curvature radius. These results demonstrated the broad application potential of the AgNWs/Co(OH)\textsubscript{2}/PEDOT:PSS FECESD for the emerging portable and multifunctional electronics.

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1. Introduction

Transparent electrodes (TEs) play critical roles in various applications [1–9], including displays, photovoltaic cells, touch panels, and energy-storage devices. Among them, electrochemical energy-storage devices (EESDs) with long cyclic stability and excellent power density have attracted intensive attention and are seen as one of the most potential power supplies for next-generation electronics [10–13]. For example, Li et al. fabricated a highly conductive flexible transparent electrode (FTE) by printing silver nanowires (AgNWs), and a wearable energy-storage device with high capacitance was also fabricated [14–16]. Furthermore, because of the combined color-changing and energy-storage properties, significant attempts have recently been made to fabricate bifunctional electrochromic energy-storage devices (ECESDs) [17–20]. Compared with conventional energy-storage devices, ECESDs can visually present the energy states through color changes [21]. Moreover, with the rapid growth of portable and wearable electronics [22–24], flexible ECESDs with good deformability for powering wearable electronics are in high demand [25, 26].

However, it is still difficult to fabricate ECESDs with both high flexibility and excellent electrochromic energy-storage performance because of the slow development of FTE materials. Indium tin oxide (ITO) is typically used as a TE material for ECESDs [27, 28], but its fragility makes it difficult to satisfy the requirements of flexible devices. In addition, the high processing cost and limited reserves of indium also lead to a high cost [29–32]. Therefore, various substitutes for ITO have been developed, such as conjugated polymers [31, 33], graphene [34, 35], and carbon nanotubes [36]. However, these materials often show poor optoelectrical performance because of inadequate intrinsic electrical conductivity. Among the existing diverse alternatives, AgNW-network-based FTEs with excellent conductivity, high transmittance, low cost, and solution-processability [30, 37–40] seem promising for replacing ITO. Nevertheless, AgNWs have relatively poor electrochemical stability, and they can be easily destroyed in the electrolyte during the anodic electrochemical corrosion; hence, significantly limiting the electrochemical color-changing and energy-storage performance of ECESDs [41].

Many attempts have been made to fabricate stable electrochemical devices based on AgNW FTE to solve this thorny problem. For example, Lee et al. successfully fabricated an Ag–Au core–shell nanowire network with excellent electrochemical stability to obtain flexible EESDs [42], but the areal capacitance is insufficient (209.9 μF cm⁻²). Also, the energy-storage performance of gold is poor, and the cost is dramatically increased. Energy-storage devices based on AgNW–copper sulfide (CuS) core–shell nanostructures have been successfully fabricated; however, these devices do not possess electrochromic properties [43]. Electrochemically stable poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was successfully coated onto the surface of the AgNW network to fabricate flexible EESDs, exhibiting an areal capacitance of 0.273 nF cm⁻² [44]. Meanwhile, Yu et al. fabricated a flexible electrochromic device using the AgNWs/PEDOT:PSS structure, which significantly changed color from transparent to blue [45]. These results prove the feasibility of fabricating flexible electrochromic energy-storage devices (FCEESDs) based on AgNWs/PEDOT:PSS film. Although significant advances have been made, the actual applications of AgNWs/PEDOT:PSS FCEESDs are still limited because of inadequate energy-storage performance. High energy-storage capacity is crucial for FCEESD to provide a continuous energy supply for electronic devices, but reports regarding the modification of AgNWs/PEDOT:PSS-based FCEESDs are still pretty scarce.

Recently, metal hydroxides with color-changing and energy-storage performances have been widely used for ECESDs. For example, Sheng et al. assembled a flexible supercapacitor utilizing AgNWs/ZnO/Co(OH)₂ electrodes [46]. Tang et al. fabricated an asymmetric supercapacitor using Ni(OH)₂/carbon nanostructure materials [47]. Besides their excellent energy-storage performance, metal hydroxides have electrochromic properties. Ozer et al. reported that the Co(OH)₂ film method exhibited a reversible electrochromic response in 1 M LiClO₄/propylene carbonate (PC) electrolyte for more than 500 cycles [48]. Lee et al. fabricated an electrochromic smart window based on a cobaltous hydroxide and nickel hydroxide hybrid film, which exhibited multiple colors under different voltages (yellow, green, and brown) [49]. Hence, it is feasible to insert a metal hydroxide to improve the electrochromic and energy-storage performance. Ginting et al added Ni(OH)₂ nanoparticles between the AgNWs and PEDOT:PSS layer, which significantly improved the electrochromic and energy-storage performance [50]. This result also proves the feasibility of improving the performance using metal hydroxide, but the nanoscale Ni(OH)₂ particles are always costly and require complex preparation processes.

Herein, we inserted a thin Co(OH)₂ layer between AgNWs and PEDOT:PSS layer using a facile electrodeposition method, avoiding the complex preparation processes of Ni(OH)₂ nanoparticles. As a result, the electrochromic and energy-storage performances were concurrently improved. Based on the modification, a symmetrical FCEESD with good color-changing, energy-storage, and cyclic bending performance was successfully fabricated, demonstrating its great potential for next-generation flexible electronics.
2. Results and discussion

Figure 1 depicts a schematic illustration of the technological process of FECESDs. Long and thin AgNWs were uniformly deposited on flexible polyethyleneterephthalate (PET) polymer, indicating that FTE was obtained. In this study, electrodes with a sheet resistance of 180 Ohm sq$^{-1}$ (transmittance: 95%) were chosen for the following experiments considering the appropriate balance between optical and electrical performance. A Co(OH)$_2$ layer was coated onto the AgNWs layer using a facile electrodeposition method. After coating PEDOT:PSS, the electrochromic energy-storage electrode was fabricated. Then, a symmetrical FECESD was assembled using two electrodes and LiClO$_4$/PC electrolyte. The details of the experiment are described in the supporting information.

The Co(OH)$_2$ layer was prepared by a one-step electrodeposition process. The formation mechanism could be described as follows:

$$8e^- + NO_3^- + 7H_2O \rightarrow NH_4^+ + 10OH^-$$
$$OH^- + Co^{2+} \rightarrow Co(OH)_2.$$ 

Figures 2(a) and (b) depict the electrode morphology before and after cobalt hydroxide was electrodeposited. Figure S1 shows the transmission electron microscopy (TEM) and high resolution-TEM (HR–TEM) images of the Ag/Co(OH)$_2$ structure. The Co(OH)$_2$ layer was surrounded by AgNWs. Lattice fringes were depicted in the HR–TEM image (figure S1), which corresponded to the (101) crystal plane of Co(OH)$_2$, indicating the crystal structure of Co(OH)$_2$. Figures 2(c) and (d) show the morphology after covering the PEDOT:PSS layer onto the AgNW FTE with and without the Co(OH)$_2$ layer. Figure 2(e) shows the X-ray photoelectron pectroscopy (XPS) spectra of the Co element. The two peaks at 781 eV and 767.9 eV correspond to the 2p3/2 and 2p1/2 of Co(OH)$_2$, respectively. The difference between the peaks was 15.9 eV, further proving the formation of Co(OH)$_2$ [46].

For electrochromic applications, the transmittance ($T$) is of great importance. Hence, we measured the transmittance (400–800 nm) of four types of electrodes (figure 2(f)). The pristine AgNW FTE exhibited the highest transmittance of 94.3% at 550 nm. After the Co(OH)$_2$ layer was electrodeposited, the transmittance slightly decreased to 90.2%. After adding PEDOT:PSS, the transmittance dropped to 78.3%, slightly lower than the transmittance (81%) of the AgNWs/PEDOT:PSS structure. These results confirm that the inserted Co(OH)$_2$ had a minor effect on the transmittance.

We further measured the sheet resistance ($\rho$) and obtained the figure of merit (FoM) value after electrodepositing
Figure 2. SEM images of (a) AgNWs, (b) AgNWs/Co(OH)$_2$, (c) AgNWs/PEDOT:PSS, and (d) AgNWs/Co(OH)$_2$/PEDOT:PSS. (e) XPS spectra of Co element after depositing onto the AgNW network; (f) Transmittance spectra of the four different electrodes: AgNWs, AgNWs/Co(OH)$_2$, AgNWs/PEDOT:PSS, and AgNWs/Co(OH)$_2$/PEDOT:PSS.

Co(OH)$_2$ and spin coating PEDOT:PSS. The FoM value was calculated using the following formula:

$$\text{FoM} = \frac{188.5\sqrt{T}}{R(1 - \sqrt{T})}.$$

Initially, the sheet resistance was 180 Ohm sq$^{-1}$, and the transmittance was 94.3%. Hence, the FoM value was 35.16. After a thin Co(OH)$_2$ layer was electrodeposited, the sheet resistance decreased to 172 Ohm sq$^{-1}$ because the Co(OH)$_2$ layer can weld stacked AgNWs together. As previously reported, the welding between AgNWs is beneficial for the conductivity of the electrode [50, 51]. However, the transmittance decreased to 90.2%, and the FoM was 20.71. After coating PEDOT:PSS, the sheet resistance and transmittance decreased (220 Ohm sq$^{-1}$ at a transmittance of 78.3%) because of the poorer conductivity of PEDOT:PSS, and the FoM value was 6.59.

Figure 3 shows the electrochemical characterization of the electrode in 1 M LiClO$_4$/PC electrolyte. The electrodes without PEDOT:PSS are very easily destroyed because of their poor resistance to electrochemical corrosion, which is consistent with a previous report [52]. Figure 3(a) shows the cyclic voltage (CV) measurements of the AgNW and AgNWs/Co(OH)$_2$ electrodes. No reduction peak was observed in the curves, indicating damage to the AgNW network. By contrast, after the PEDOT:PSS layer was coated, CV curves with rectangular shapes were observed (figure 3(b)), suggesting excellent energy-storage behavior. Figure S2 shows the scanning electron microscope (SEM) image of AgNWs with and without the PEDOT:PSS layer after electrochemical corrosion. The pristine AgNWs were easily broken and disconnected, but the morphology remained stable, which corresponded to the CV results. In addition, a bigger area is shown in the CV curve of the AgNWs/Co(OH)$_2$/PEDOT:PSS electrode under the same scanning rate (10 mV s$^{-1}$), confirming the improved energy-storage performance. Galvanostatic charge/discharge (GCD) measurements were also performed on the electrode with and without the Co(OH)$_2$ layer at a current density of 10 µA cm$^{-2}$ (figure 3(c)). Longer discharging time was also observed after Co(OH)$_2$ was added, indicating a higher areal capacitance, which is consistent with the CV curves. It was also discovered that adding Co(OH)$_2$ resulted in a lower voltage (IR) drop, which can be attributed to the improved electrical conductivity (AgNWs were welded). As reported in the reference, the IR drop is highly relevant to the ohmic resistance of the electrodes [53]. When the thickness of the Co(OH)$_2$ layer was further increased (8-s electrodeposition), the areal capacitance (1.66 mF cm$^{-2}$) improved (figure S3) because of the higher loading of active materials. However, the IR drop also increased. The intrinsic electrical conductivity of Co(OH)$_2$ as a metal hydroxide was poorer than that of metal nanowires. An overly thick Co(OH)$_2$ layer would have a negative effect on the conductivity. Figures 3(d) and S4(a) show the CV curves at different
scanning rates of AgNWs/Co(OH)$_2$/PEDOT:PSS and AgNWs/PEDOT:PSS electrodes, respectively. No obvious deformation was observed with the increasing scanning rate. Even though the scanning rate increased to 100 mV s$^{-1}$, the shape remained rectangular. Triangular GCD curves of AgNWs/PEDOT:PSS and AgNWs/Co(OH)$_2$/PEDOT:PSS electrodes at different current densities can be observed in figures 3(e) and S4(b). In addition, we calculated the areal capacitance to quantitatively compare the energy-storage performance between these two electrodes. It was observed that higher areal capacitance values were obtained after the Co(OH)$_2$ layer was inserted. For example, when the discharge current density is 10 $\mu$A cm$^{-2}$, the areal capacitance of the AgNWs/PEDOT:PSS electrode is only 0.46 mF cm$^{-2}$. By contrast, the areal capacitance increased to 1.41 mF cm$^{-2}$ after the Co(OH)$_2$ layer was induced as shown in figure 3(f). Moreover, it is worth pointing out that both electrodes show good ratio discharge properties.

Based on the hybrid electrode, a symmetrical FECESD was assembled using 1 M LiClO$_4$ gel electrolyte in PC/poly(methylmethacrylate) (PMMA) solution. Figure 4(a) shows the CV measurements of the two types of FECESDs at a scanning rate of 10 mV s$^{-1}$. Similar to the results of half cell, the CV results of both devices present a rectangular shape, indicating excellent energy-storage properties. Moreover, a larger area was observed after Co(OH)$_2$ was added. The GCD curves in figure 4(b) also show that AgNWs/Co(OH)$_2$/PEDOT:PSS FECESD has a longer discharge time, indicating that more energy is stored. Electrochemical Impedance Spectroscopy (EIS) tests were performed over a frequency range of 0.1–100 kHz to determine the ion diffusion behavior. As depicted in figure 4(c), the Nyquist plots show that the slope at the low-frequency part of AgNWs/Co(OH)$_2$/PEDOT:PSS FECESD is higher than that of AgNWs/PEDOT:PSS FECESD, which demonstrates a lower diffusion resistance for ions during cyclic discharge and charge process. In the high-frequency region, a smaller diameter of the semicircle was observed, indicating a lower charge transfer resistance. We fitted the EIS curve based on the equivalent circuit (figure S5), and the fitted result is depicted in figure S6. The detailed parameters are listed in table S1. In the equivalent circuit, $R_s$ represents the equivalent series resistance, $R_{ct}$ represents charge transfer resistance, $C_{DL}$ represents the double-layer capacitance, and $W_o$ represents the Warburg resistance. A smaller resistance was obtained after inserting Co(OH)$_2$. The added Co(OH)$_2$ layer can effectively reduce the surface roughness of AgNW FTE, which enlarges the surface area, leading to efficient charge transfer pathways and fast ion diffusion, as reported in the previous literature [50]. Figure 4(d) shows the CV curves of the AgNWs/Co(OH)$_2$/PEDOT:PSS FECESD at different scanning rates (5–500 mV s$^{-1}$), and their shape remains rectangular with increasing scanning rates. Symmetrical GCD curves of the AgNWs/Co(OH)$_2$/PEDOT:PSS FECESD at various current densities were observed, suggesting its excellent reversibility. The CV and GCD curves of the AgNWs/PEDOT:PSS FECESD are shown in figures S7(a) and (b), respectively. Based on the GCD curves, we calculated the areal capacitance at 20–100 $\mu$A cm$^{-2}$.
As shown in figure 4(f), at a discharge current density of 20 \( \mu \text{A cm}^{-2} \), the FECESD based on AgNWs/PEDOT:PSS and AgNWs/Co(OH)\(_2\)/PEDOT:PSS electrodes deliver capacitances of 0.39 mF cm\(^{-2}\) and 0.80 mF cm\(^{-2}\), respectively, suggesting a better energy-storage performance after the Co(OH)\(_2\) layer was induced. Similar results were also observed at other discharge current densities. Figure 4(g) shows the energy and power density-dependent Ragone plot of the two symmetric FECESDs, which was calculated based on the GCD curves. The FECESD based on AgNWs/Co(OH)\(_2\)/PEDOT:PSS electrode has an energy density of 0.254 mWh cm\(^{-2}\) at a power density of 0.008 mW cm\(^{-2}\), which is higher than that of the FECESD based on AgNWs/PEDOT:PSS electrode (energy density of 0.124 mWh cm\(^{-2}\) at a power density of 0.008 mW cm\(^{-2}\)).

We calculated the contribution of diffusion and capacitive behaviors during the electrochemical reactions based on the following formula:

\[
I(V)/v^{1/2} = k_1v^{1/2} + k_2
\]

where \( v \) represents the scan rate, \( V \) represents the voltage, and \( k_1 \) and \( k_2 \) are adjustable parameters. Figure S8 depicts the capacitive contribution (red shadow) at different scan rates. The capacitive and diffuse controlled behaviors are concurrence. The capacitive behavior gradually increased as the scan rate increased. Figure S9 and table S2 show the detailed contributions.

We measured the cyclic stability of the FECESD using AgNWs/Co(OH)\(_2\)/PEDOT:PSS electrode as shown in figure S10. The capacitance remained at 73\% original value after
1000 times cyclic charge–discharge process at a current density of 0.1 mA cm\(^{-2}\), indicating excellent stability. Stability against mechanical deformation is critical for the effective use of flexible devices. Hence, we measured the change in the areal capacitance during the cyclic bending with a radius of curvature of 25 mm. As shown in figure 4(h), even after 1000 times cyclic bending, the GCD curve at 80 \(\mu\)A cm\(^{-2}\) retained its triangular shape, and no significant decrease in performance was observed. Figure 4(i) visually shows that the areal capacitance (calculated based on figure 4(h)) exhibited a tiny change during the cyclic bending test, which proves the good flexibility of the FECESD in this work, exhibiting the potential for further applications in flexible electronics. The electrode morphology after 1000 cyclic bending with a curvature radius of 25 mm, as shown in figure S11, revealed only some small cracks.

Moreover, we measured the change in resistance during the cyclic bending process with different curvature radii (25 mm and 10 mm), as shown in figure S12. It was found that the conductivity remained stable during the bending tests. With the decreasing curvature of the radius, the change in resistance gradually increased, but the resistance remained stable after 1000 cycles under a curvature radius of 10 mm. We also characterized the morphology after 1000 times bending with a curvature radius of 25 mm as depicted in the inset image. The morphology of AgNWs shows a negligible change, which is also consistent with the change in resistance.

Figure 5(a) shows the electrochemical window of the AgNWs/Co(OH)\(_2\)/PEDOT:PSS FECESD. The shape of the CV curves remained rectangular, even with the electrochemical window expanding to 0–1.6 V. Figure 5(b) shows the absorption spectra from 400 to 800 nm of FECESD at 0 and 1.6 V, respectively. A higher absorption peak was observed when 1.6 V was applied, indicating that the color was darker. We, in situ, measured the change in transmittance with the change in voltage at 683 nm as shown...
in figure 5(c). When different voltages were applied, the device exhibited different optical modulation ranges. For the AgNWs/Co(OH)₂/PEDOT:PSS FECESD, when 0 V was applied, the transmittance was about 57.5%. After 0.8 V was inputted, the transmittance decreased to 48%. When the voltage was further increased to 1.6 V, the transmittance was 35%. This result confirmed that the energy-storage level was reflected in the transmittance. It was also observed that a higher optical modulation range was obtained after the Co(OH)₂ layer was added. This might be caused by the contribution of Co(OH)₂, which is also an electrochromic material, as reported in the previous literature [49]. Figures 5(d) and (e) show the optical image of the FECESD in bleached and colored states at the bending state. The color change was visible to the naked eye, suggesting excellent electrochromic properties. We also measured the colorimetric properties of the FECESD at different states using an international commission on illumination (CIE) system. As shown in figures 5(f) and (g), with the increase in voltage, the color gradually moved from light green to blue, which is also consistent with the optical images. The details of the parameters are listed in table 1. In the CIE system, the lightness, green–red, and blue–yellow components were described by L*, a*, and b*, respectively. In the bleached state, the values were 53.12, −5.87, and −5.82, respectively. In contrast, after a voltage of 1.6 V was applied, the values changed to 39.23, −7.55, and −22.21, respectively. The decrease in the L* value also indicated a decrease in transmittance.

Moreover, the change of a* from −2.82 to −22.21 also proved that the color had turned blue. Figure 5(h) shows the transmittance of the FECESD in a wavelength range of 400–700 nm. When different voltages were applied, the transmittance changed. We calculated the coloration efficiency (CE) according to the [18]. The CE value (269.80 cm² C⁻¹) of AgNWs/Co(OH)₂/PEDOT:PSS FECESD was significantly higher than that of the pristine AgNWs/PEDOT:PSS FECESD, which can be ascribed to the improvement of the optical modulation range. We also measured the cyclic color-changing performance under a periodic voltage from 0 V to 1.6 V. The FECESD remained stable after 100 cyclic coloring and bleaching processes, suggesting good stability. Finally, we compared the performance of the FECESD in this work with that of the previous reports [42, 44, 50, 53, 54, 55–60] as shown in table S3. Compared with the pure PEDOT:PSS material reported in the references, the areal capacitance and CE improved after adding the Co(OH)₂ layer. Compared with other modifications, such as inducing graphene or Ni(OH)₂, the performance in this work is not the best, but we provide a new idea for developing bifunctional FECESDs.

### Table 1. CIE parameters of the FECESD under different voltages.

| Voltage | 0 V | 0.8 V | 1.6 V |
|---------|-----|-------|-------|
| L*      | 53.12 | −5.87 | −2.82 |
| a*      | 46.48 | −6.35 | −13.31|
| b*      | 39.23 | −7.55 | −22.21|

### 3. Conclusions

In summary, highly flexible electrochromic and energy-storage devices were successfully fabricated using the AgNWs/Co(OH)₂/PEDOT:PSS hybrid electrodes. The PEDOT:PSS layer concurrently served as an electrochromic energy-storage and protective layer. After the PEDOT:PSS layer was coated, the electrochemical stability of the AgNW FTE improved. Furthermore, Co(OH)₂, a commonly used energy-storage material, was electrodeposited onto the surface of the AgNW network to enhance the energy storage and electrochromic performance of the AgNWs/PEDOT:PSS electrode. Owing to these improvements, a dual-functional flexible electrochromic and energy-storage device was fabricated, which showed a CE value of 269.80 cm² C⁻¹ and an areal capacitance of 0.80 mF cm⁻². Moreover, after 1000 bending cycles, the performance of the FECESD showed a negligible change, demonstrating its potential for flexible electronics.

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