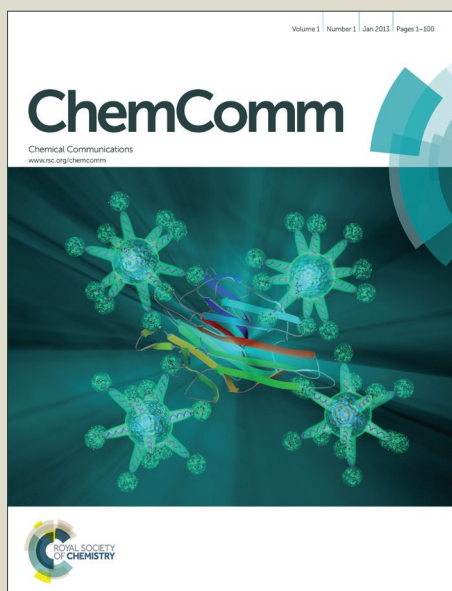


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Flexible electrochromic supercapacitor hybrid electrodes based on tungsten oxide films and silver nanowires

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We successfully fabricate flexible electrochromic supercapacitor (SC) electrode employing novel flexible transparent conducting substrates. The as-synthesized flexible electrochromic SC electrodes exhibit great electrochemical performances (13.6 mF/cm², 138.2 F/g) and high coloration efficiency (80.2 cm²/C), which demonstrate their potential applications in flexible smart windows combining energy storage and electrochromism.

Supercapacitors (SCs), also named electrochemical capacitors, due to their high power density, fast charge/discharge rate and exceptionally long cycle life^{1,2}, SCs have been a promising candidate for the next generation energy storage system and a great number of research efforts have been made in the past decades³⁻⁶. However, with the development of portable intelligent electronic devices, the researches of SCs no longer just focus on improving the electrochemical properties, but also typically introduce some special properties to extend their applications⁷⁻¹⁰. Recently, electrochromic supercapacitors have attracted more and more attentions due to their combined characteristics of electrochromism and energy storage, which have broad applications in prospect of smart windows or intelligent displays^{11,12}. For instance, Xiao *et al.* synthesized paper-like SC devices which exhibit excellent flexibility and superior high volumetric capacitance¹³. Yang *et al.* fabricated multifunctional glass SC devices which combine electrochromism and energy storage simultaneously¹¹. However, few works have previously reported the successful integration of the flexibility and electrochromism into a SC¹². It is still a great challenge to realize the excellent electrochromic supercapacitors on flexible substrate.

In this regard, two main factors impede the development

of flexible electrochromic SCs. The first issue is the difficulty of preparing flexible substrates that possess high transparency and high conductivity. In fact, some research groups have successfully fabricated flexible transparent conducting (FTC) substrates based on carbon nanotubes, graphene, metal or metal nanowires *etc.*¹⁴⁻¹⁶. However, among these as-prepared FTC substrates, either the sheet resistance is relatively too high that cannot meet the requirement of fast charging/discharging, or the synthesis procedures is too complicated or expensive that hinder their scalable preparation. Hence, it is urgently demanded to design a facile, low-cost and effective method for the manufacture of FTC substrates. On the other hand, how to deposit active materials onto the conductive substrates and achieve the desired performance is the second problem. Although a small portion of materials have been confirmed that can simultaneously act as pseudocapacitive and electrochromic materials, such as nickel oxide (NiO), polyaniline (PANI) and Tungsten oxide (WO₃) *etc.*^{11,17-19}, the successful fabrication of these materials on FTC substrates still remains a tough challenge. Especially, to the best of our knowledge, there are yet no reports on the use of metal based FTC substrates for SC applications.

Herein, we develop an effective fabrication of flexible electrochromic SC electrode based on FTC silver nanowires (Ag NWs) substrates and active materials WO₃ film for the first time. As illustrated in FIG.1 (a), a layer of PDMS elastomer was firstly spin-coating on PET to form a pre-cured flexible substrate, and the spin coating process was performed at 1000 rpm for 9 s and then at 3000 rpm for 40 s. Subsequently, 130 μ l of 2 mg/ml Ag NWs ethanol solution (diameter: 50nm, length: >200 μ m, XF Nano, China) was dispersed in deionized water and then vacuum filtered onto a filter membrane. After filtration, the Ag NWs film was easily transferred from the filter membrane to the pre-cured flexible substrate by a uniform pressure to obtain the anticipated FTC substrate. Finally, the uniform WO₃ film with a thickness of 600 nm was directly deposited on the FTC substrate by facile thermal evaporation at a pressure of 5 \times 10⁻⁴ Pa. The main deposition procedure is as follows: Firstly, WO₃ powder (50 nm,

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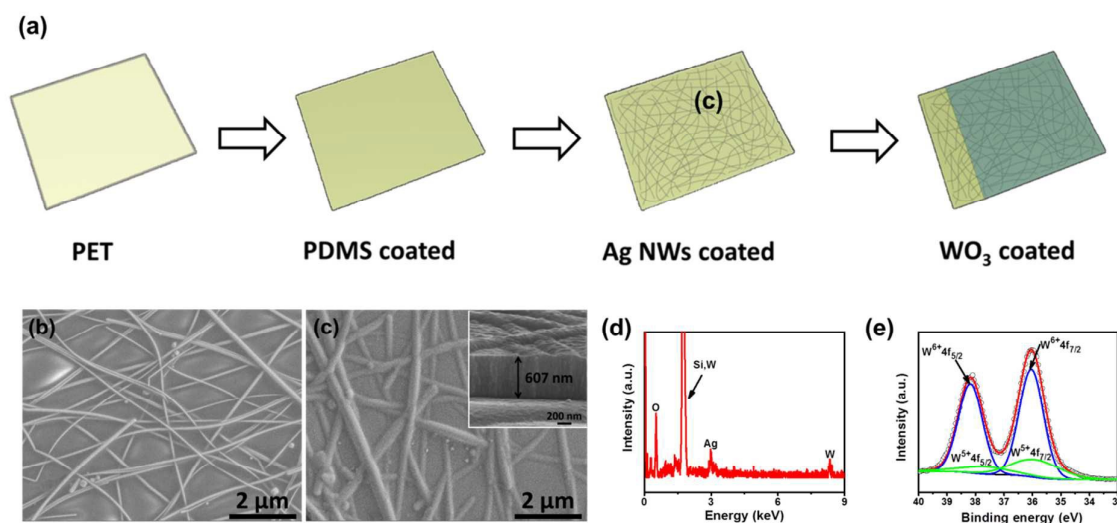


FIG.1 (a) Schematic illustration of the preparation procedure of flexible electrochromic SC electrode. (b) SEM image of the as-prepared flexible transparent conductive substrate. (c) SEM image of the previous substrate coated with WO₃ film, inset is a cross-section SEM image. (d) EDS spectrum of the flexible electrochromic SC electrode. (e) W_{4f} core level XPS spectra of WO₃ film.

99.9%) was load into a tungsten boat and then put it into the chamber; when the background pressure was lower than 5×10^{-4} Pa, the evaporation started by applying a fixed current of 105 amperes and kept at this value for about 30 min; after the evaporation process, uniform WO₃ film was deposited on FTC substrate.

As shown in FIG.1, the morphology of the Ag NWs/WO₃ electrode is clearly observed through the scanning electron microscopy (SEM) images. FIG.1 (b) reveals the sparse and uniform distribution of Ag NWs, which ensures the superior transparency of the substrate. And the high conductivity of the substrate is also assured by the excellent interconnectivity of the ultra-long Ag NWs (>200 μm). In addition, FIG.1 (c) demonstrates the successful deposition of WO₃ film on FTC substrate and the favorable contact between WO₃ and Ag NWs, the thickness of WO₃ film about 600 nm. FIG.1 (d) shows the energy dispersive X-ray spectrometer (EDS) spectrum of the as-prepared flexible electrochromic SC electrode, where the signals of elements W, O and Ag are distinctly revealed. The signal of Si is caused by the PDMS substrate. Furthermore, based on the X-ray photoelectron spectroscopy (XPS) analysis (FIG.1 (e)), it can be inferred that the main oxidation state is W⁶⁺ state (the ratio of W⁶⁺/W⁵⁺ is determined to be 3.88), which indicates the predominant component of the evaporation film is WO₃^{11, 20}.

The electrochemical property of the as-synthesized flexible electrochromic SC electrode was evaluated by employing a three-electrode configuration. A piece of the Ag NWs/WO₃ electrode was dipped into 1 M H₂SO₄ solution with an effective area of 1 cm² to act as the work electrode, a Ag/AgCl electrode as the reference electrode and a Pt electrode as the counter electrode. FIG.2 (a) shows the cyclic voltammetry (CV) curves of the flexible and electrochromic SC electrode at different scan rates. Typical galvanostatic charge/discharge curves of the flexible electrochromic SC

electrode collected at various current densities are shown in FIG.2 (b). The relatively symmetrical profiles between the charge curves and the corresponding discharge parts also demonstrate their outstanding capacitance behaviors. Moreover, based on the CV curves, the areal capacitances (C_a) and the specific capacitances (C_m) of the Ag NWs/WO₃ electrode can be calculated by the following equations⁹:

$$C_s = \frac{Q}{A\Delta U} = \frac{\int I dU}{2A\nu\Delta U}$$

$$C_m = \frac{Q}{m\Delta U} = \frac{\int I dU}{2m\nu\Delta U}$$

where Q is the average charge, ΔU is the potential window, ν is the scan rate, A is the effective area of the Ag NWs/WO₃ electrode, and m is the mass of the WO₃ film (the mass load of the WO₃ is 0.0984 mg/cm²). As shown in FIG.2 (c), at a scan rate of 10 mV/s, the areal capacitance of the flexible and electrochromic SC electrode is 13.6 mF/cm², and the corresponding specific capacitance is 138.2 F/g. In addition, to better examine the Ag NWs/WO₃ electrode, electrochemical impedance spectroscopy (EIS) measurement was also performed. The Nyquist plots of the Ag NWs/WO₃ electrode are shown in FIG.2 (d), revealing that the equivalent series resistance (ESR) of the electrode is as small as 29.7 Ω. More importantly, FIG.2 (e) shows that the CV curves measured in different conditions experience no obvious changes, demonstrating the excellent flexibility of the Ag NWs/WO₃ electrode. FIG.2 (f) exhibits that the capacitance still remains 72.6 % of the initial capacitance at a scan rate of 100 mV/s after 5000 charge/discharge cycles, demonstrating the outstanding stability of the flexible electrochromic SC

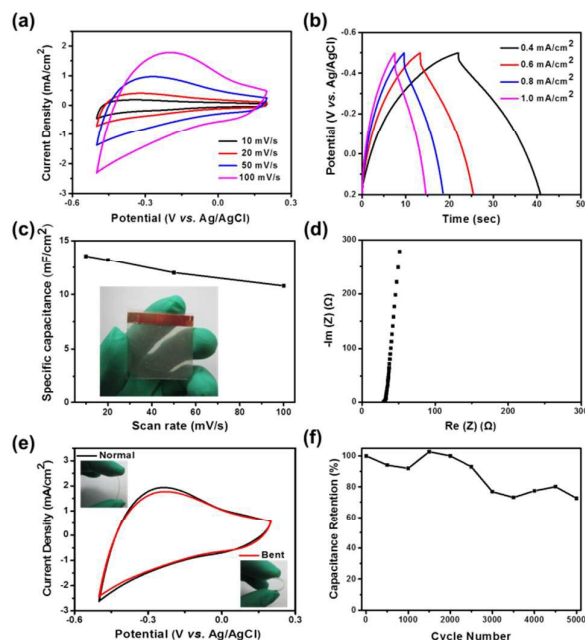
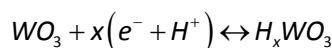


FIG.2 Electrochemical performance of the flexible electrochromic SC electrode: (a) CV curves collected at different scan rates. (b) Galvanostatic charge/discharge curves collected at various current densities. (c) Areal capacitance as a function of scan rate. Inset is the digital images of the flexible electrochromic SC electrode. (d) Nyquist plots. (e) CV curves collected under normal and bent conditions at the same scan rate of 100 mV/s, and insets are the corresponding digital images. (f) Cycle life performance measured at scan rate of 100 mV/s.

electrode.

Except for the admirable electrochemical performance, the electrochromic property of the as-obtained Ag NWs/WO₃ electrode was also conducted. Previous studies demonstrate that the electrochromic behaviors of WO₃ electrode are caused by H⁺ insertion/extraction with WO₃, which is synchronized with the pseudocapacitive reactions^{11, 21, 22}:



When a negative bias potential is applied on the Ag NWs/WO₃ electrode, the insertion of H⁺ ions into the electrode cause the dark blue color change. When a positive bias potential is applied on the Ag NWs/WO₃ electrode, the color of the electrode changes from dark blue to transparent due to the extraction of H⁺ from the electrodes. Thus, with the H⁺ insertion and extraction process, the color of the electrode can reversibly convert between the dark blue and transparent state. In order to describe the electrochromic property of the Ag NWs/WO₃ electrode more clearly, the optical transmittance spectra of the electrode were measured under different voltage conditions shown in FIG.3 (a). The Ag NWs/WO₃ electrode presents an optical transmittance of 55.9 % in its original state at a wavelength of 633 nm. When a voltage of -0.5 V (vs. Ag/AgCl electrode) was applied on the Ag NWs/WO₃ electrode, its color changed to dark blue with an optical transmittance of 11.8 % at the same wavelength.

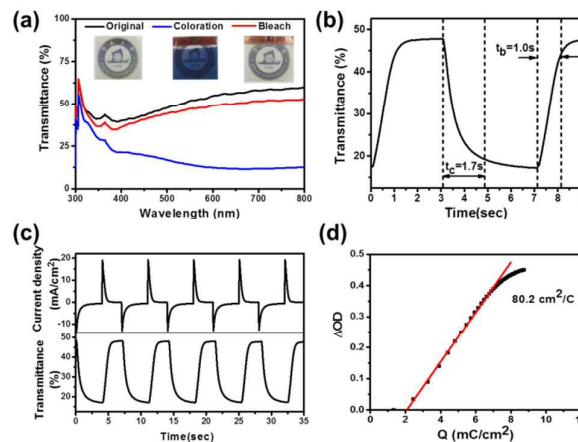


FIG.3 (a) Transmittance spectra of the Ag NWs/WO₃ electrode measured under different voltage conditions, and insets are the corresponding digital images of the electrode. (b) Typical magnified *in situ* transmittance spectrum of the Ag NWs/WO₃ electrode between the colored and bleached states collected under an alternating potential of -0.5 V and +0.2 V vs. Ag/AgCl electrode. (c) Chronoamperometry curve and the corresponding *in situ* transmittance curve at 633 nm for the Ag NWs/WO₃ electrode. (d) Optical density versus charge density of the Ag NWs/WO₃ electrode, from which calculating a coloration efficiency of 80.2 cm²/C.

Moreover, as a crucial parameter for the electrochromic materials, the coloration switching time is defined as the time that required for an electrode to reach 90 % of the full transmittance modulation between the steady colored and bleached states. As shown in FIG.3 (c), chronoamperometry was performed on the Ag NWs/WO₃ electrode under an alternating potential of -0.5 V and +0.2 V vs. Ag/AgCl electrode, and the corresponding *in situ* transmittance curve was collected. From the magnified transmittance spectrum (FIG.3 (b)), the coloration time t_c is determined to be 1.7 s and the corresponding bleaching time t_b is 1.0 s, which are much faster than those of previous reports. For instance, nickel oxide nanoflakes glass (2.7, 1.8 s)¹⁷ and silver-decorated WO₃ film (3.9, 3.2 s)²³. The fast switching speed of the Ag NWs/WO₃ electrode is attributed to the high conductivity of FTC substrate and the compact contact between the FTC substrate and the WO₃ film. Similarly, for electrochromic materials, the coloration efficiency (CE) is as important as the coloration switching time, which is defined as the change in optical density (ΔOD) per unit of inserted or extracted charge at a certain wavelength. That is the CE can be obtained from the following equations:

$$CE(\lambda) = \frac{\Delta OD(\lambda)}{Q}$$

$$\Delta OD(\lambda) = \log \frac{T_b}{T_c}$$

where T_b and T_c are the corresponding transmittance in the bleached and colored states, respectively. The plots of ΔOD as a function of charge density at 633 nm is shown in FIG.3 (d), and the CE of the as-synthesized Ag NWs/WO₃ electrode is

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calculated from the slope of the quasi-linear curve, which is as high as 80.2 cm²/C. This promising value indicates that the Ag NWs/WO₃ electrode possesses superior optical modulation with a slight charge affect, and which is much higher than those of previously reports, such as WO₃ film glass (54.8 cm²/C)¹¹ and nickel oxide nanoflakes glass (63.2 cm²/C)¹⁷.

In summary, a facile and well controllable fabrication strategy is designed in this work for the preparation of Ag NWs/WO₃ electrode for the first time. The as-prepared electrode exhibits excellent flexibility, and the gravimetric capacitance reach up to 138.2 F/g. Furthermore, this electrode shows high coloration efficiency (80.2 cm²/C) and fast response speed (coloring in 1.7 s and bleaching in 1.0 s). More importantly, this work is probably the first report that silver NW based FTC substrates are applied in electrochromic supercapacitors and the novel FTC substrates have demonstrated their enormous potentials for multifunctional energy storage device in the near future.

Acknowledgement

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