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From waste carbonated beverages to high performance electrochromic devices: a green and low-cost synthetic method for self-doped metal oxides†

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Metal oxides with reversible optical modulation capability are in the spotlight for smart windows and other emerging optoelectronic devices. Improving the electrochromic performance at a low cost is the only way to popularize their applications. Herein, we demonstrate a facile and versatile strategy to synthesize high-performance electrochromic metal oxides, in which waste carbonated beverages are used as the raw materials for the first time. It can not only reduce the production cost of electrochromic materials, but also alleviate the environmental pollution caused by such liquid waste. With an ingenious carbonization pre-step, both nanoscale pores and oxygen vacancies are created in an annealed tungsten oxide thin film. Multiscale structure optimization endows the self-doped WO_{3-x} films with excellent electrochromic properties such as large transmittance modulation (81.2%), high coloration efficiency ($98.7 \text{ cm}^2 \text{ C}^{-1}$) and good cycling stability. DFT calculations show that oxygen vacancies reduce the Li^+ ion insertion energy barrier, which is conducive to the interfacial reaction in coloring and bleaching processes. Moreover, this approach is universal to other oxides such as vanadium pentoxide, molybdenum oxide and nickel oxide. The waste-to-value concept paves the way for cost-effective electrochromic materials and sheds light on the multiscale optimization of superior metal oxides.

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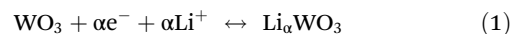
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Introduction

Metal oxides, as important functional materials, are highly sought after for conventional and new optoelectronic applications.^{1–6} In particular, electrochromic oxides represented by tungsten oxide can reversibly change their color and transmittance under external voltage.^{7–9} This fascinating optical modulation capability has broad application prospects in energy and information technology fields, ranging from smart windows to electrochromic batteries and energy-saving displays.^{10–13} However, the high cost of metal oxides limits the popularization of electrochromic devices. There is an urgent need for breakthroughs in low-cost preparation techniques for electrochromic metal oxides.^{14–16} As the electrochromic layer plays a leading role in the device, attention should also be paid to the improvement of its electrochromic properties.

Taking tungsten oxide as an example, the working mechanism of electrochromic metal oxides is summarized as follows:



It can be seen from this electrochemical reaction that the electrochromic process of metal oxides involves the dual insertion/extraction of ions and electrons.^{17–19} Starting from the consensus conclusion that the structure determines properties, the structure optimization of metal oxides can significantly improve the kinetics of the above reversible electrochemical reactions. Typically, the thickness of the metal oxide layer in electrochromic devices ranges from hundred nanometers to a few microns. At this scale, large specific surface areas can be obtained by elaborating nanostructures or artificially creating nanoscale porous films. Such a strategy has been widely adopted for boosting the electrochromic process at the interface between metal oxides and electrolytes.^{20–22} Moreover, changing the crystal structure at the atomic scale is also an effective approach. Doping with oxygen vacancies can not only change the electronic structure, but also improve the ion transport capacity of metal oxides, which are essential to the coloring and bleaching dynamics.^{23–26} Although the above methods can effectively improve the electrochromic properties,

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the high cost of raw materials and high equipment dependence are the main obstacles to mass production. It is still a great challenge to prepare high-performance electrochromic oxides with cheap raw materials and a simple and versatile approach.

On the other hand, food and beverage waste is generated every day and its disposal has become a critical issue worldwide.^{27–29} Massive amounts of carbonated beverages are discarded from restaurant leftovers and expired goods, which easily cause financial loss, water system pollution and nuisances in the surroundings.³⁰ Therefore, it is of great economic and environmental significance to transform waste carbonated beverages into value-added products. Indeed, waste carbonated beverages are rich in glucose, fructose and other sugars, which can be used as reducing agents and excellent carbon sources.³¹ In recent years, the synthesis of advanced functional materials from carbonated beverages has been tried in a few pioneering works. By a self-templating process and *in situ* activation, Dai *et al.* prepared ultrahigh surface area carbons up to 3633 m² g^{−1} with carbonated beverages as abundant carbon sources.³² Lu *et al.* synthesized a molecule-intercalated BiOCl semiconductor–organic framework with enhanced photocatalytic degradation performance, in which carbonated beverages were used as solvents.³³ Developing electrochromic materials from waste carbonated beverages can not only greatly reduce the preparation cost of the electrochromic devices, but also realize the resource utilization of liquid waste. However, to the best of our knowledge, related studies have not been reported so far.

In this study, we report a green and low-cost approach to synthesize electrochromic materials from waste carbonated beverages for the first time. With a facile solution processing method, multiscale structure optimization has been implemented simultaneously inside the electrochromic tungsten oxide thin film. Carbonated beverages serve as the solvent and provide the carbon source for *in situ* derivations of pore-forming agents and reducing agents. After annealing, nanoscale pores and oxygen vacancies are created in the WO_{3−x} film as expected. The self-doped WO_{3−x} films exhibit good electrochromic properties and cycling stability due to the coordination of high specific surface areas and oxygen vacancies. In addition, this approach is universal to a variety of electrochromic oxides such as tungsten oxide, vanadium pentoxide, molybdenum oxide and nickel oxide.

Experimental

Materials

Ammonium metatungstate hydrate (AMT, (NH₄)₆H₂W₁₂O₄₀·xH₂O, 99.5%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ammonium metavanadate (NH₄VO₃, 99%) was purchased from Meryer Chemical Technology Co., Ltd. Nickel chloride hexahydrate (NiCl₂·6H₂O) was purchased from Tianjin Dengfeng Chemical Reagent Co., Ltd. Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) was purchased from Sinopharm Chemical

Reagent Co., Ltd. The 1.0 M LiClO₄ electrolyte in a mixed solvent of ethylene carbonate (EC):dimethyl carbonate (DMC):ethyl methyl carbonate (EMC) with 1:1:1 vol% were purchased from Dodochem Technology Co., Ltd. Waste carbonated beverages (Coca-Cola Co., Ltd) including Coca-Cola, Sprite and Fanta were recycled from daily life, and the ingredient lists are shown in the ESI† All the reagents and carbonated beverages were directly used without further purification.

Fabrication of metal oxide thin films and electrochromic devices

A simple solution processing method was adopted to prepare electrochromic thin films as schematically shown in Fig. 1a. As a case study, 3 g AMT powder was added to 27 g carbonated beverage (Coca-Cola) and then stirred for 30 min until completely dissolved to obtain a dark brown tungsten oxide precursor. The precursor was aged for 24 h before use. The conductive fluorine-doped tin oxide (FTO) glasses were ultrasonically cleaned with acetone, ethanol and deionized water for 15 min, respectively. Air plasma treatment was applied for hydrophilic improvement of the FTO glass subsequently. Then, the precursor was spin-coated on the cleaned FTO glass at 1800 rpm for 8 s and dried at 300 °C for 5 min. The spin-coating step was repeated six times to reach the appropriate thickness. Next, the spin-coated sample was transferred to a 350 °C hot plate for a 30 min carbonization process. Finally, the carbonized black thin film was annealed at 450 °C for 2 h in a muffle furnace to obtain the self-doped WO_{3−x} thin film. For the pure WO₃ thin films, we used deionized water instead of Coca-Cola, and the other steps are the same as the preparation procedure of WO_{3−x}, see the ESI† for more details.

The same solution processing method was used to synthesize other electrochromic metal oxides such as vanadium pentoxide, molybdenum oxide, and nickel oxide. The precursors were prepared by dissolving water-soluble compounds such as NH₄VO₃, (NH₄)₆Mo₇O₂₄·4H₂O, or NiCl₂·6H₂O in different carbonated beverages respectively. The electrochromic device was assembled based on the self-doped WO_{3−x} thin film as the electrochromic electrode, the self-doped V₂O_{5−y} thin film as the counter electrode, and 1.0 M LiClO₄ in a mixed solvent as the electrolyte.

Characterization

The TG–DTG analysis of the AMT precursor was conducted on a Netzsch STA 449 F5. The crystalline structure of the films was obtained *via* Raman spectroscopy (LabRAM HR Evolution) at an excitation wavelength of 532 nm. The surface and cross-sectional morphologies of the films were examined by scanning electron microscopy (SEM, Zeiss Gemini 500). The element and valence states of the WO_{3−x} films were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+). The electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMXplus 10/12. The transmittance spectra of all the samples and devices were recorded using a spectrophotometer (Mapada V-1600PC). The chronoamperometry curve was obtained using a digital source meter

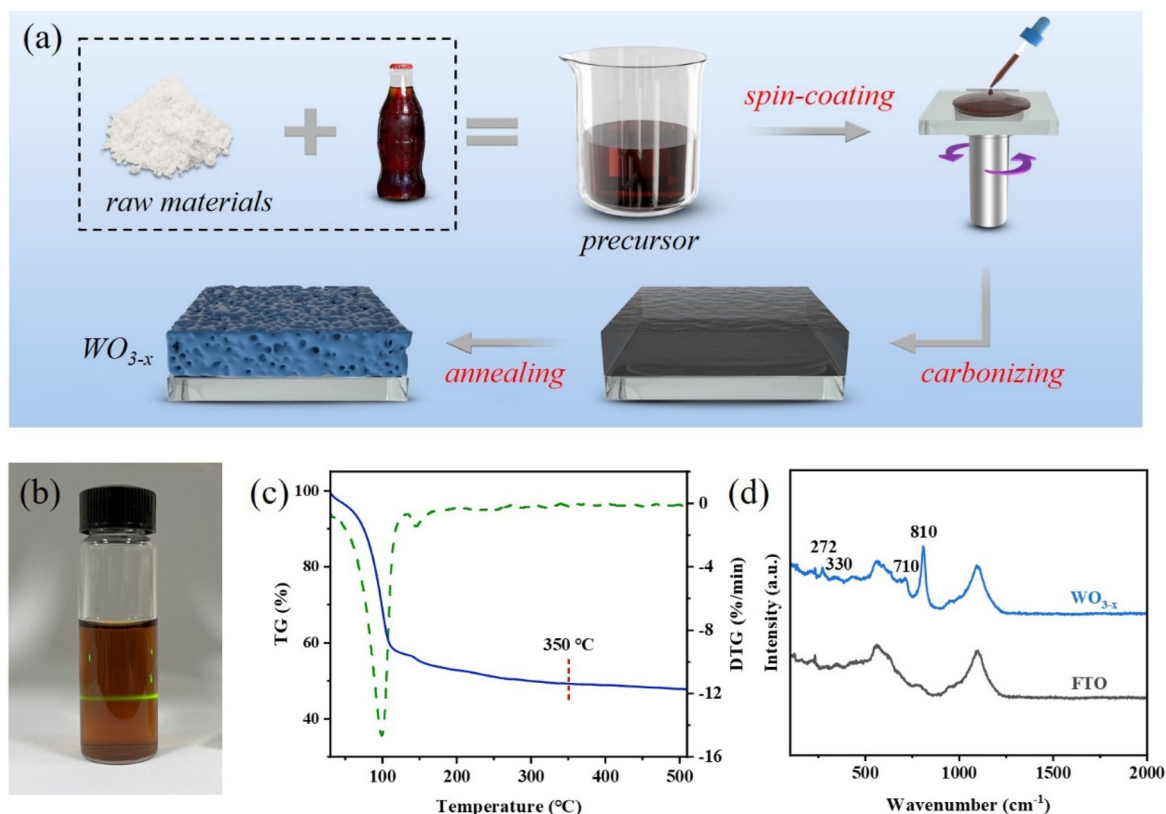


Fig. 1 (a) Schematic of the preparation process of self-doped metal oxide thin films with key steps including dissolving, spin-coating, carbonizing and annealing. (b) The digital photograph of the colloidal precursor; the Tyndall effect is visible when irradiated with a green laser beam. (c) TG–DTG curves of the precursor with AMT dissolved in Coca-Cola. (d) Raman spectra of the FTO substrate and the annealed thin film.

(Keithley 2410). The cyclic voltammetry (CV) curves and the impedance of tungsten oxide thin films were measured using an electrochemical workstation (Zennium Pro, Zahner, Germany).

Results and discussion

Synthesis and structural analysis of self-doped metal oxides

The flow process diagram in Fig. 1a clearly demonstrates the key steps to fabricate the self-doped electrochromic metal oxide thin films. The water-soluble compound containing the target metal element and carbonated beverages were chosen as the raw materials to prepare the precursor. For example, ammonium metatungstate hydrate (AMT) powder was used to synthesize the self-doped WO_{3-x} thin film. As is well known, carbonated beverages are composed of mostly water, sugars and other food additives. Water-soluble compounds, therefore, have good solubility in carbonated beverages to obtain the precursor with the desired concentration. After aging at room temperature, the colloidal properties of the precursor can be indicated by the Tyndall effect as shown in Fig. 1b. After a longer period of time (more than 30 days) the precursor remains in a stable state (see Fig. S1, ESI†). The colloidal precursor was then spin-coated on FTO glass, forming a thin film

sample. Crucially, carbohydrates introduced by the carbonated beverage will carbonize under the pyrolysis temperature conditions.^{34,35} The spin-coated samples turn black intuitively because of the *in situ* formed carbon. In the annealing step, tungsten oxides were obtained through the complete decomposition of the precursor. A large number of oxygen vacancies are generated due to the accompanying carbothermal reduction reaction. At the same time, nanoscale pores are formed and uniformly distributed in the thin film after burning off the *in situ* formed carbon. As a result, the self-doped WO_{3-x} film with a porous structure is obtained.

Fig. 1c shows the TG–DTG curve of the precursor with 50 wt% AMT dissolved in Coca-Cola from room temperature to 520 °C. The TG data show a dramatic weight loss before 150 °C and a DTG peak is found at 100 °C, which can be assigned to the evaporation of water. In the temperature range of 150–350 °C, the thermal decomposition of carbohydrates and other residues leads to further weight loss. In the last stage, only a tiny weight loss can be seen during the carbothermal reduction reaction at high temperatures. Fig. S2 (ESI†) shows a photograph of the carbonized sample at 350 °C and the corresponding Raman spectra. Two obvious Raman peaks were found at 1376 and 1588 cm^{-1} , which belong to the typical D and G bands of carbon materials.^{36,37} This is sufficient to prove that the carbon source in carbonated beverages (such as

glucose and other sugars) has been successfully converted to carbon. Fig. 1d shows the Raman spectra of the FTO glass and the 450 °C annealed thin film. After high-temperature annealing, the carbon in the film is completely decomposed and the film is converted from its original black color to a transparent state. Besides the Raman peaks of FTO glass, the annealed film shows four peaks at 272, 330, 710, and 810 cm^{-1} , indicating the presence of tungsten oxide.³⁸ The peaks at 710 and 810 cm^{-1} are ascribed to the W–O–W stretching mode, whereas the bands observed at 272 and 330 cm^{-1} are ascribed to the W–O–W bending vibration in the monoclinic WO_3 . Later on, we extended this solution processing method to fabricate other electrochromic metal oxides. Different thin films including vanadium oxide (V_2O_5), molybdenum oxide (MoO_3), and nickel oxide (NiO) have been prepared as expected. Details about the Raman spectra of these metal oxides can be found in Fig. S3–S5 (ESI).[†] Furthermore, X-ray diffraction (XRD) analysis confirmed that both WO_{3-x} and WO_3 are in the crystalline state (Fig. S6, ESI[†]).

The electrochromic performance of the WO_{3-x} thin film

As shown in Fig. 2a, a polycrystalline morphology consisting of fine grains can be observed from the SEM image of the annealed WO_{3-x} thin film. The inset of Fig. 2a is the statistical

analysis of grain size. Tungsten oxide grains are mainly 40–80 nm in size (~71% of the total crystal grain population) with a mean size of 61 nm. Besides, the annealed thin film has a large number of nanoscale pores located at the grain boundaries, which contrasts with the flat surface of pure tungsten oxide (see Fig. S7, ESI[†]). These uniformly distributed pores will undoubtedly increase the specific surface area of the film and facilitate the rapid diffusion of ions in electrochromic reactions. The morphology of the annealed film has also been characterized by AFM (see Fig. S8, ESI[†]). The rough surface was further confirmed and the RMS roughness of the WO_{3-x} thin film was calculated to be 3.54 nm, which is higher than that of the WO_3 thin film (1.01 nm) (see Fig. S9, ESI[†]), and it also demonstrates the higher specific surface area of carbonated beverage formulation films. According to the cross-sectional SEM image (Fig. S10, ESI[†]) of the annealed sample, the thickness of the WO_{3-x} thin film is around 300 nm. Then, we tested the electrochromic performance of this WO_{3-x} thin film with 1.0 M LiClO_4 electrolyte. The transmittance of the WO_{3-x} thin film was recorded in both bleached and colored states, see Fig. 2b. The bleached WO_{3-x} thin film has a large transmittance of up to 90% in the wavelength range of 400–1000 nm. It is worth noting that in addition to the thickness, the nanostructure of coatings and

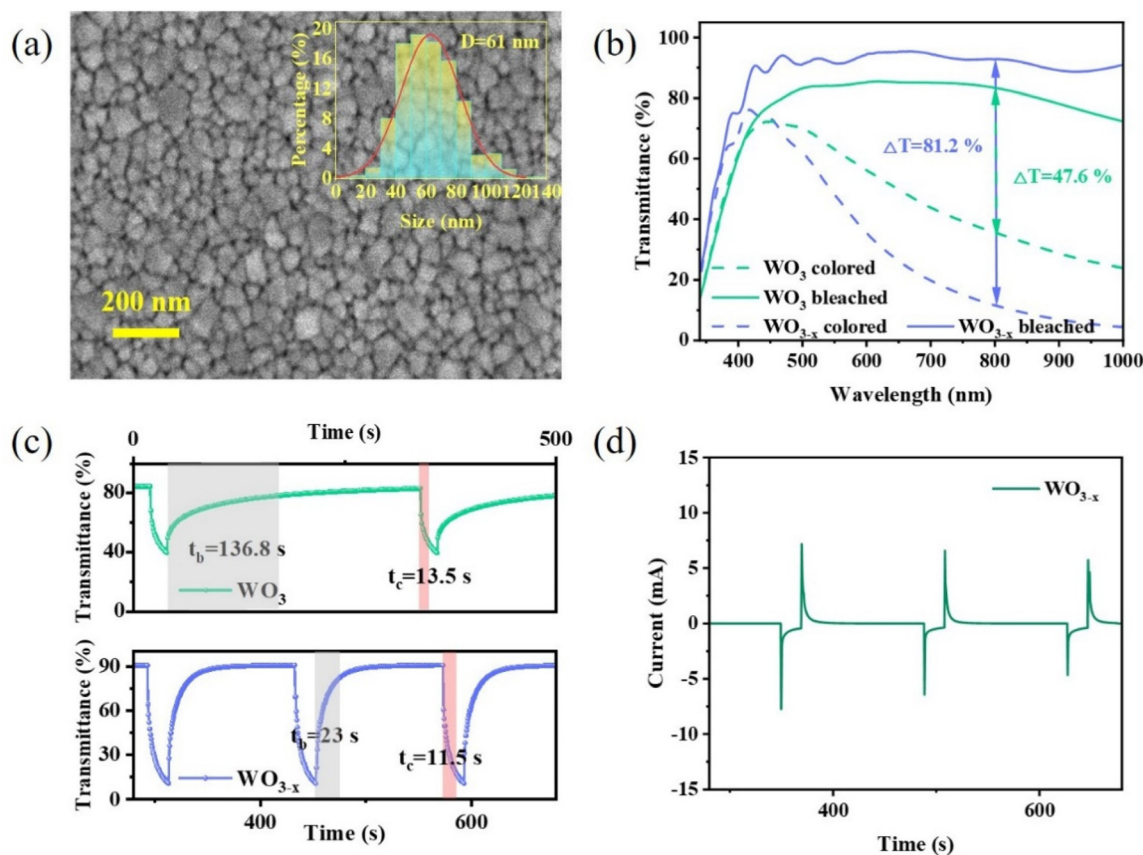


Fig. 2 (a) SEM image of the annealed self-doped WO_{3-x} film; the inset is the statistical distribution diagram of grain size. (b) Transmittance spectra of the WO_3 and self-doped WO_{3-x} thin films in colored and bleached states. (c) The switching behavior of the WO_3 and WO_{3-x} thin films at 800 nm. (d) The chronoamperometry curve of the WO_{3-x} thin film during the switching test.

thin films is also closely related to their transmittance. Since the tungsten oxide grain size is much smaller than the wavelength of visible light, it has little interference with the linear propagation of light, which is conducive to the high transmittance of thin films. But in the colored state, the transmittance is drastically reduced, especially in the near-infrared band. At a wavelength of 800 nm, the transmittance modulation between the two curves is around 81.2%, indicating the great near-infrared light shielding ability. Several other metal oxides fabricated by the same solution processing method also demonstrate electrochromic activity. The transmittance spectra of vanadium pentoxide, molybdenum oxide, and nickel oxide thin films in different states are shown in Fig. S11–S13 (ESI†), respectively. These results fully prove the universality of this green method for preparing electrochromic oxides.

In order to investigate the dynamic electrochromic properties of annealed tungsten oxide films, we recorded the switching behavior as shown in Fig. 2c. By applying positive (3.2 V) and negative voltages (−3.5 V) periodically, the coloring time (t_c) and bleaching time (t_b) are calculated to be 23 s and 11.5 s, respectively. Coloration efficiency (CE), defined as the

change in optical density (ΔOD) per unit charge (ΔQ) inserted into the film per unit area, is another important property. It can be calculated as follows:³⁹

$$CE = \frac{\Delta OD}{\Delta Q} = \log \frac{T_b}{T_c} / \Delta Q \quad (2)$$

where T_b and T_c refer to the transmittance of the self-doped WO_{3-x} film in bleached and colored states. ΔQ can be obtained by testing the device area and the chronoamperometry ($I-t$) curve corresponding to the switching behavior (Fig. 2d). The CE value of the annealed WO_{3-x} thin film is calculated to be $98.7 \text{ cm}^2 \text{ C}^{-1}$.

The electrochromic process of tungsten oxide is essentially an electrochemical reaction involving both ions and electrons. To further evaluate the kinetic behavior of this electrochromic process, we used cyclic voltammetry (CV) to analyze lithium ion diffusion in the self-doped WO_{3-x} thin film. As shown in Fig. 3a, CV curves were measured between −0.4 V and 1.0 V at different scanning rates from 20 mV s^{-1} to 200 mV s^{-1} . All the CV curves show similar shapes but the enclosed area increases gradually. According to the peak current density (j_p) at

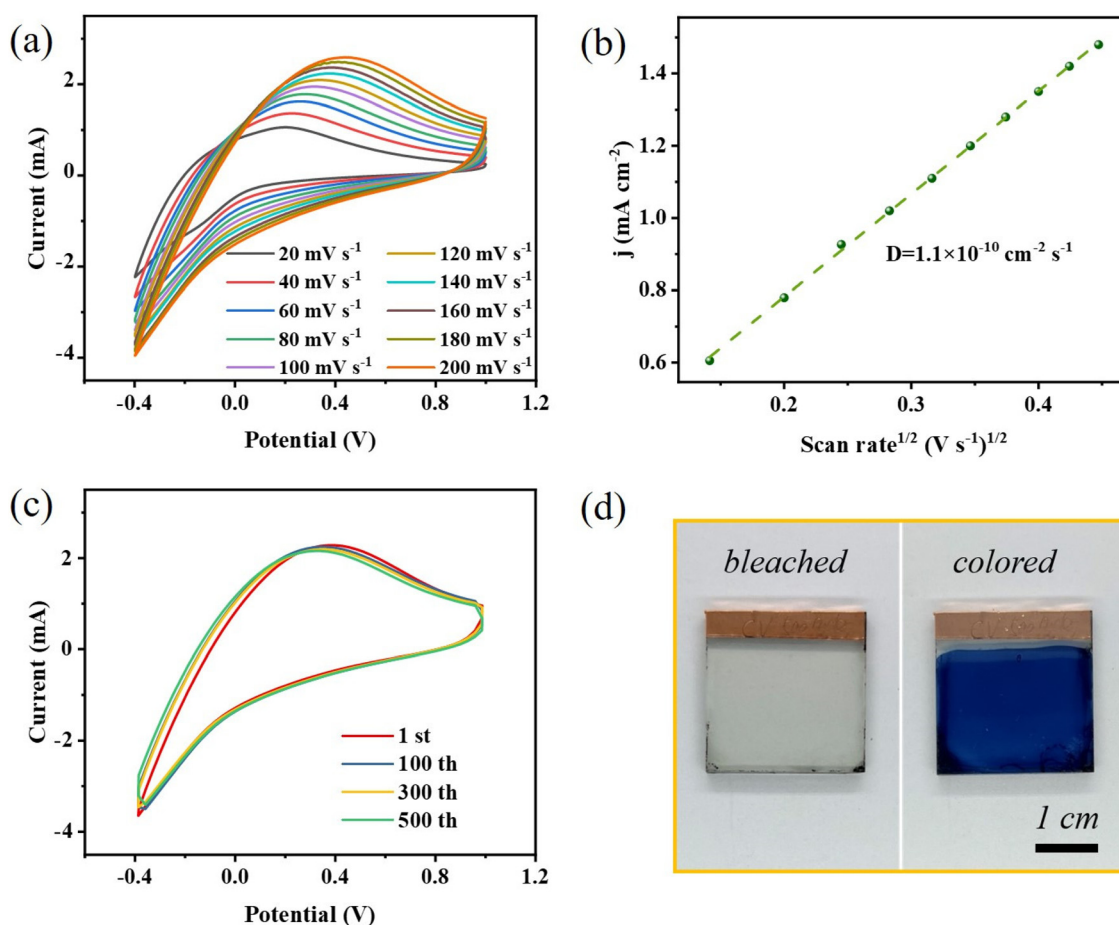


Fig. 3 (a) CV curves of the annealed WO_{3-x} film measured in 1.0 M $LiClO_4$ electrolyte at different scan rates from 20 to 200 mV s^{-1} . (b) The peak current density is a function of the square root of scan rates. (c) CV cycling stability of the self-doped WO_{3-x} film. (d) Photographs of the annealed WO_{3-x} film in the bleached and colored states after the 500 cycle test.

different scanning rates (Fig. 3b), the diffusion coefficient of Li^+ ions is calculated by the Randles–Sevcik equation:

$$j_p = 2.72 \times 10^5 n^{3/2} D^{1/2} c v^{1/2} \quad (3)$$

where n is the number of electrons assumed to be 1 for Li^+ , D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), c is the Li^+ ion concentration of the LiClO_4 electrolyte (mol cm^{-3}), and v is the scan rate (V s^{-1}). The Li^+ diffusion coefficient in the annealed self-doped WO_{3-x} thin film is $1.1 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$; this value is close to the reported values of tungsten oxide thin films, see Table S1 (ESI†). In addition, cycling stability is also an important parameter to evaluate the electrochromic performance. We measured the cycling performance of the annealed WO_{3-x} thin film by CV curves for more than 500 cycles. The CV curves in Fig. 3c show only a slight change, indicating excellent stability during the electrochromic process. Moreover, photographs in Fig. 3d show the annealed WO_{3-x} thin film sample in bleached and colored states after the 500 cycle test. The self-doped WO_{3-x} film still exhibits high transparency in the bleached state and a dark blue color in the colored state. The excellent cycling stability is attributed to the crystalline state and nanostructure of the WO_{3-x} thin film. As mentioned

above, nanoscale pores uniformly distributed in the film can provide more channels for lithium ion insertion and extraction, thereby effectively alleviating the structural failure caused by the interfacial electrochemical reactions.⁴⁰

The effect of oxygen vacancies

The functional properties of metal oxides are also closely related to their crystal defects. An oxygen vacancy as a common point defect can significantly change the photoelectric and electrochemical properties of metal oxides.^{41,42}

To elucidate the relationship between the oxygen vacancies of WO_{3-x} films and their electrochromic performance, further tests and mechanistic analysis were performed. The chemical valences of all elements in the annealed WO_{3-x} films were investigated by XPS (Fig. S14, ESI†). As shown in Fig. 4a, the O 1s XPS spectrum can be deconvoluted into three peaks at 530.5, 531.1, and 532.5 eV, corresponding to the W–O bond of tungsten oxides, an oxygen vacancy, and adsorbed oxygen (–OH).⁴³ The percentage of the oxygen vacancy calculated from the fitting data is 14.74% for the annealed WO_{3-x} film. The electron paramagnetic resonance (EPR) spectrum is also a powerful experimental method to study defects in metal oxides, since the intensity of the EPR signal is related to the

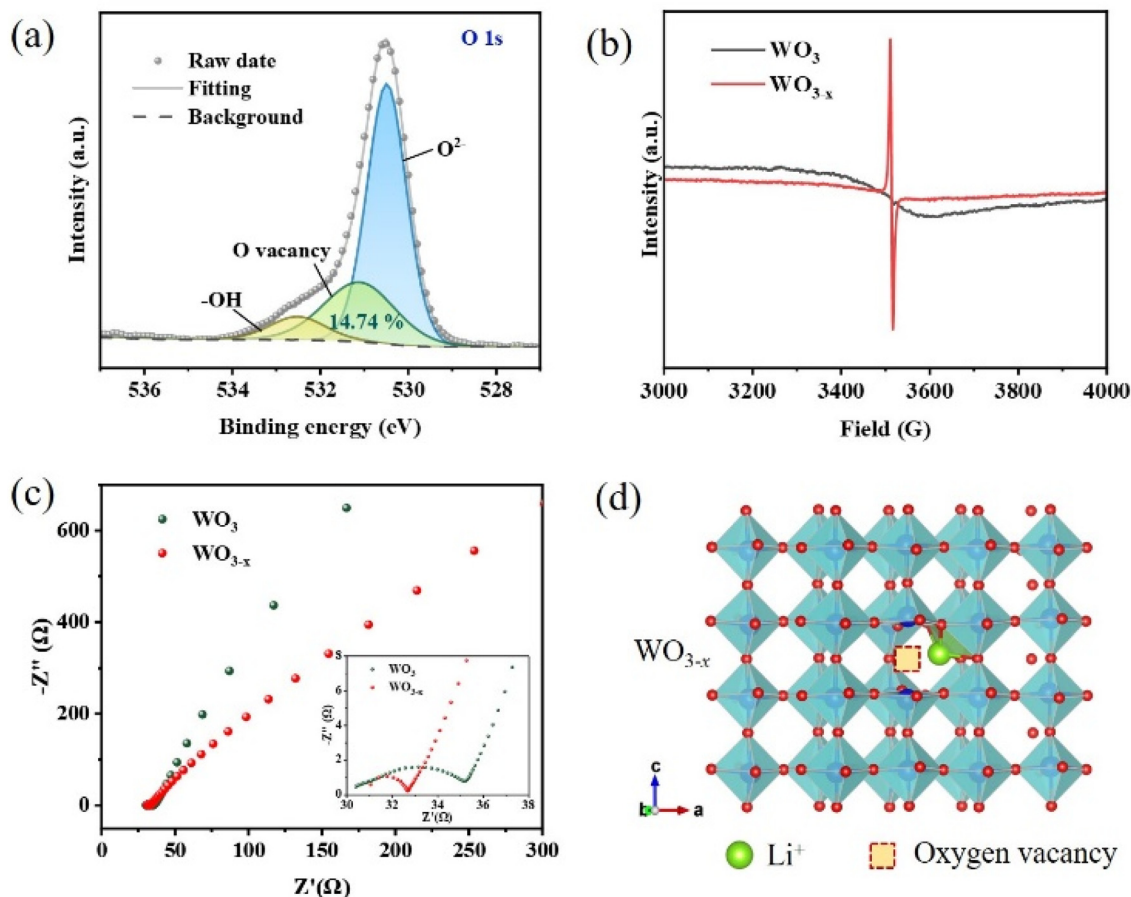


Fig. 4 (a) O 1s XPS spectrum of the annealed WO_{3-x} films. (b) The EPR spectra of self-doped WO_{3-x} and WO_3 films. (c) Nyquist plots of impedance data for self-doped WO_{3-x} and WO_3 films. (d) Structure models of Li^+ inserted into the lattice of self-doped WO_{3-x} .

density of the oxygen vacancy.⁴⁴ Fig. 4b shows the EPR spectra of different samples, in which the pure WO_3 sample has a negligible signal. In contrast, the self-doped WO_{3-x} film exhibits a significant symmetrical EPR signal caused by unpaired electrons, revealing the existence of an oxygen vacancy. Both the XPS and EPR results confirm that an oxygen vacancy has been generated by the carbothermal reduction reaction during the annealing step.

In previous studies, doping with oxygen vacancies was regarded as an effective way to boost the ion transfer kinetics of the electrode materials in electrochemical energy storage devices.^{45–47} As shown in Fig. 4c, electrochemical impedance spectroscopy (EIS) measurements were carried out to analyze the electrochromic kinetics. In the low-frequency region, the self-doped WO_{3-x} film displays a straight line with a smaller slope than that of the pure WO_3 sample, indicating a higher ion diffusion rate. While in the high-frequency region, both samples have semicircle EIS spectra as shown in the inset. Compared to the pure WO_3 film, the self-doped WO_{3-x} film displays a smaller semicircle radius, which indicates its better

charge transfer ability. Since lower charge transfer resistance means faster electron transfer, this feature is an extremely important factor in improving electrochromic performance. As proof, the electrochromic performance of the pure WO_3 thin film has been measured (Fig. 2b and c). The poor optical modulation and slow response speed of pure WO_3 confirmed the important role of oxygen vacancies. To further explore the effect of oxygen vacancies on ion insertion, we analyzed the energy barrier during the Li^+ insertion process (ΔE_{insert}) by density functional theory (DFT) calculations as follows:^{48,49}

$$\Delta E_{\text{insert}} = E_{\text{W-Li}} - E_{\text{W}} - E_{\text{Li}} \quad (4)$$

where $E_{\text{W-Li}}$ represents the total energy of Li^+ inserted tungsten oxide and E_{W} and E_{Li} stand for the total energy of tungsten oxide and Li^+ , respectively. Fig. 4d shows the structure model of Li^+ insertion in self-doped WO_{3-x} ; the energy barrier was calculated to be -1.98 eV, lower than the value (-1.57 eV) of pure WO_3 (Fig. S15, ESI†). The DFT results suggest that the Li^+ ion is energetically favorable to insert into the lattice in the presence of an oxygen vacancy, which agrees well with the

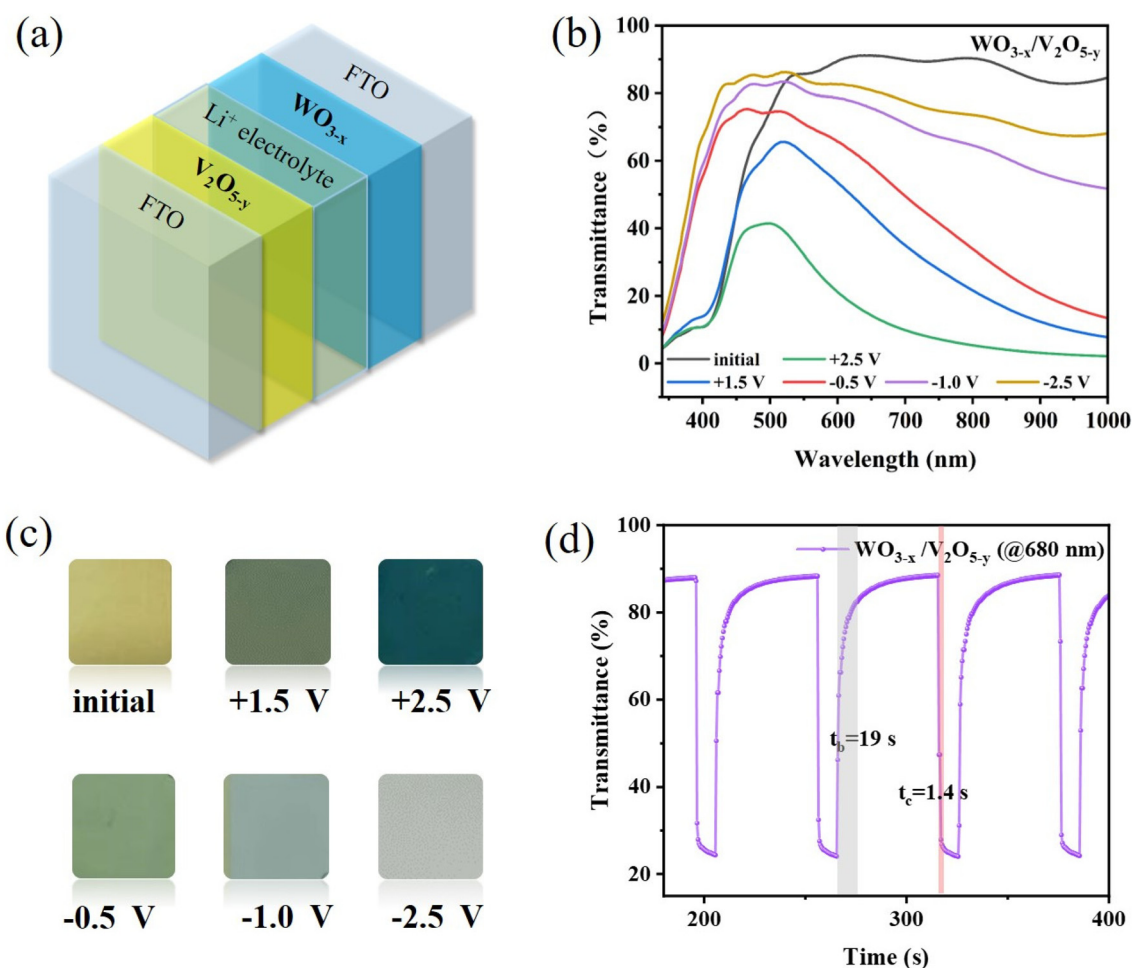


Fig. 5 (a) Schematic diagram of an electrochromic device based on WO_{3-x} and V_2O_{5-y} thin films. (b) Transmittance spectra of the $\text{WO}_{3-x}/\text{V}_2\text{O}_{5-y}$ electrochromic device at different voltages. (c) Photographs of the $\text{WO}_{3-x}/\text{V}_2\text{O}_{5-y}$ electrochromic device at different voltages. (d) The switching behavior of the $\text{WO}_{3-x}/\text{V}_2\text{O}_{5-y}$ electrochromic device at 680 nm.

experimental data. Subsequently, we characterised the oxygen vacancies and electrochromic properties of self-doped tungsten oxide prepared from different carbonated beverages, thus demonstrating that the oxygen vacancy content has a significant effect on the properties of the films (Fig. S16 and S17, ESI†). Subsequently, we further characterized the effect of the carbonated beverage content on the morphology, structure, and electrochromic properties of the prepared films, as shown in Fig. S18 and S19 (ESI†). In general, reducing the amounts of carbonated beverages will lead to uneven or even discontinuous film morphology. At the same time, the reduction of the carbon source is not conducive to a carbothermal reduction reaction, and the oxygen vacancy content in the annealed film decreases accordingly. Both the above factors decreased the electrochromic performance of tungsten oxide films, proving that the amounts of carbonated beverages play a crucial role in the structure and electrochromic performance of the metal oxide films.

Multicolor electrochromic device

Next, we assembled a complementary electrochromic device based on two different self-doped metal oxides. The annealed V_2O_{5-y} thin film is selected as the counter electrode since it presents an opposite trend to that of WO_{3-x} during the electrochromic process. The transmittance of the self-doped V_2O_{5-y} thin film at different biases is shown in Fig. S11 (ESI†). When a negative voltage is applied, the transmittance in the near-infrared band decreases, while the transmittance between 340 and 500 nm increases significantly. When a positive voltage is applied, the transmittance spectrum of the V_2O_{5-y} film returns to its initial state. The device structure is shown in Fig. 5a, where the annealed WO_{3-x} and V_2O_{5-y} films are assembled face to face, and 1.0 M $LiClO_4$ in a mixed solvent was used as the electrolyte. Fig. 5b shows the transmittance spectra of the complementary electrochromic device at different biases. In the initial state, since the WO_{3-x} film is highly transparent, the device shows the yellow color of vanadium pentoxide. Lithium ions are inserted into the WO_{3-x} thin film when a positive voltage is applied. As a result, the device gradually changes from light green to dark blue. When a negative voltage is applied, lithium ions are extracted from the WO_{3-x} film until it is completely bleached. Meanwhile, lithium ions in the electrolyte are inserted into the V_2O_{5-y} film for coloring. As shown in Fig. 5c, the complementary electrochromic device can achieve a rich color transformation in a small voltage range (−2.5 V–2.5 V). The multicolor state switching makes the device promising to be applied as an energy-saving display. The switching time of the WO_{3-x}/V_2O_{5-y} electrochromic device in visible and near-infrared bands has also been measured, see Fig. 5d and Fig. S20 (ESI†). At a wavelength of 680 nm, the device exhibits response times of coloring and bleaching of 1.4 s and 19 s, respectively. Similar response times of coloring (1.2 s) and bleaching (22 s) were obtained at 800 nm, which proves that the device has good modulation capability in both visible and near-infrared bands. In

addition, the fast response time, especially for the coloring time, indicates that the complementary electrochromic device has an improved electrochemical kinetic process resulting from the charge balance between the working electrode and the counter electrode.

Conclusion

In summary, we demonstrated a novel and environmentally friendly method for fabricating self-doped metal oxides with high electrochromic performance. Water-soluble compounds and waste carbonated beverages were used as raw materials so that manufacturing costs could be greatly reduced. Sugars contained in the carbonated beverages served as the carbon source and played a crucial role in generating nanoscale pores and oxygen vacancies inside the metal oxide thin film. It was found that the self-doped WO_{3-x} thin film with a large specific surface area exhibited good optical modulation (81.2% at 800 nm), fast switching speeds, superior coloration efficiency ($98.7 \text{ cm}^2 \text{ C}^{-1}$) and long-term cycling stability. Both the charge transfer resistance and ion insertion energy barrier of the self-doped WO_{3-x} film are lower than those of the pure WO_3 film, which were beneficial for improving electrochromic performance. Moreover, a complementary electrochromic device with V_2O_{5-y} as the counter electrode realized multi-color state switching and rapid response speed. By the resource utilization of waste beverages, this work not only realizes the low-cost manufacturing of electrochromic materials, but also provides a general strategy towards the optimization of metal oxides.

Conflicts of interest

There are no conflicts to declare.

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