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Efficient near infrared modulation with high visible transparency using SnO₂-WO₃ nanostructure for advanced smart windows

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Renewable energy technology and effective energy management are the most crucial factors to consider in the progress towards worldwide energy sustainability. Smart window technology has a huge potential in energy management as it assists in reducing energy consumption of indoor lighting and air-conditioning in buildings. Electrochromic (EC) materials, which can electrically modulate the transmittance of solar radiation, are one of the most studied smart window materials. In this work, highly transparent SnO₂ inverse opal (IO) is used as the framework to electrochemically deposit amorphous WO₃ layer to fabricate hybrid SnO₂-WO₃ core-shell IO structure. The hybrid structure is capable of effective near infrared (NIR) modulation while maintaining high visible light transparency in the colored and bleached states. By varying the initial diameter of the polystyrene (PS) opal template and the WO₃ electrodeposition time, optimal results can be obtained with the **smallest PS diameter** of 392 nm and 180 seconds WO₃ electrodeposition. In its colored state, the 392-SnO₂-WO₃-

180 core-shell IO structure shows approximately 70% visible light transparency, 62% NIR blockage at 1200 nm, and approximately 15% drop in NIR blocking stability after 300 cycles. The SnO₂-WO₃ core-shell IO structure in this study is a promising EC material for advanced smart window technology.

1. Introduction

The increase in energy demand coupled with the rapid depletion of the world's fossil fuel resources have necessitated the exploration and implementation of alternative energy technologies, e.g. renewable energy such as wind turbine and photovoltaics. However, such technologies by themselves are insufficient. Effective management of energy consumption is also crucial in order to properly address the issue of energy shortage. As countries become increasingly developed, the construction of many high-rise buildings quickly follows. Consequently, the smart utilization of solar radiation through glass windows becomes a primary concern. Therefore, smart window technology, an effective energy conservation method, is introduced to assist the reduction of energy consumption of indoor lighting and air-conditioning. In this field, electrochromic (EC) materials, which are able to electrically modulate the transmittance of solar radiation, are one of the most widely investigated smart window materials.^[1] Various transition metal oxides and conjugated polymers, such as tungsten oxides (WO₃)^[2], vanadium oxide (V₂O₅)^[3], nickel oxide (NiO)^[4], polyaniline (PANI)^[5] and PEDOT:PSS^[2c, 6], have been studied for this application. Amongst transition metal oxides, WO₃ possesses the best EC effectivity and is thus the focus of many researches to date. The ability of WO₃ to induce color changes was first explored in the early 19th century, while subsequent electrochemical studies began around 1930.^[7] It was reported that WO₃ exhibited reversible changes in optical property (colored/bleached) corresponding to the electrochemical insertion/extraction of small cations such as H⁺ or Li⁺ (Equation 1, M = H, Li,...)^[8]:

Upon the insertion/extraction of cations and electrons, WO_3 can modulate solar radiation from the range of visible to infrared (IR), depending on their crystal structure (amorphous or crystalline) as well as their morphology.^[9] Many studies have reported that amorphous WO_3 has better EC efficiency than its crystalline form due to the higher ion storage capacity at the same applied voltage.^[10] The EC WO_3 material for smart window applications can be fabricated in the form of nanoparticles^[2a-b,m, 6a, 11], thin films^[2c,e,f,h-k, 12], nanorods^[2d,g,l] etc. by various synthetic methods.

It should be noted that most WO_3 EC smart window research focuses only on modulation within the visible range of the solar spectrum.^[2a-d,f-h,k,l] However, since nearly 50% of solar energy comes from IR radiation, dynamic modulation of IR radiation in smart windows at low voltage could hold significant potential in the thermal management of buildings. Several studies have demonstrated the ability of WO_3 EC materials in modulating near IR (NIR) wavelength.^[2e,i,j] However, the tested WO_3 structures showed limited NIR blockage, i.e. low contrast in NIR radiation between the colored and bleached states. A **modified** technique based on three-dimensional inverse opal (IO) structure could be used to improve the overall performance of WO_3 EC material. IO structures have been widely used in optical applications as they show enhanced light absorption with their continuous and periodic structure.^[13] In addition, their large specific surface area also increases the active area and improves charge transfer kinetics during redox reactions. Previously, we reported a novel core-shell TiO_2 - WO_3 IO film deposited onto fluorine doped tin oxide (FTO) glass, for application in NIR-active EC smart windows. The TiO_2 IO framework serves as a template for the electrodeposition of an amorphous WO_3 layer. The TiO_2 - WO_3 core-shell IO film exhibited enhanced NIR contrast of up to 60% at wavelength of 1033 nm at a voltage bias of less than 1 V and maintained more than 90% contrast after 1200 reversible cycles.^[14]

A drawback in using WO₃ based EC materials is the low visible light transparency, especially during the colored state when voltage is applied.^[14] Zhou *et al.* reported Ag/WO₃ nanowires with approximately 59% NIR modulation performance at 1100 nm, but which only has 8.7% transparency at 500 nm.^[2j] In the study of Bathe *et al.*, the WO₃ thin film deposited on ITO glass could improve the transparency at 500 nm up to 57.1%, but only showed about 47.7% NIR contrast at 1100 nm.^[2f] The bilayer WO₃ IO structure synthesized by Li *et al.* showed approximately 57.6% NIR modulation at 1100 nm, but only 27.3% transparency at 500 nm.^[13e] Recently, our previous work on TiO₂-WO₃ IO also exhibited enhanced NIR contrast up to 62.7% at 1100 nm, but allows only 22.7% transparency at 500 nm.^[14] In modern building technology, achieving large IR/NIR modulation with minor reduction in the visible light transparency is highly desired. Here, we propose fabricating an IO transparent conductive oxide, SnO₂ framework for electrodeposition of amorphous WO₃ EC layer, as a means of forming a hybrid SnO₂-WO₃ core-shell IO structure. The structure demonstrates effective NIR modulation with minor impact on the visible light transparency in both the colored and bleached states. The SnO₂-WO₃ core-shell IO structure was fabricated through a facile synthetic process which consists of three steps: (1) Horizontal self-assembly of polystyrene (PS) opal template, (2) dip-coating with SnO₂ precursor and (3) electrodeposition of amorphous WO₃ layer. The formation of different void space dimensions of SnO₂-WO₃ IO and its effect on the EC performance were investigated by using PS suspensions of varying sphere diameters. Furthermore, the effect of WO₃ electrodeposition time was also examined. This study introduces a novel EC material structure for NIR-active smart window applications and provides new insights into the study of smart window materials.

2. Results and Discussions

2.1. Morphology and structure of hybrid SnO₂-WO₃ core-shell inverse opal structure

The detailed fabrication procedure of hybrid SnO₂-WO₃ core-shell IO structure is presented in the experimental section. The uniformity of the hybrid SnO₂-WO₃ core-shell IO structure is highly dependent on the degree of order in the initial PS template (Figure S1). The removal of PS sphere in the calcination step creates void spaces in the IO structure, giving rise to its periodic pore structure. Furthermore, the SnO₂ IO pores are interconnected through openings formed at the interface of two adjacent PS spheres. The high porosity of the SnO₂ IO framework not only provides increased surface area but also enables easy penetration of electrolytes during immersion. During the electrodeposition process, the amorphous WO₃ layer is deposited onto the surface of the SnO₂ IO framework effectively surrounding the framework and forming a core-shell structure. The pore diameter is gradually reduced with longer electrodeposition times. Therefore, the electrodeposition duration should be carefully optimized to prevent overfilling of WO₃ into the void space of the SnO₂ pores. Three initial PS opal diameters (392, 520, 872 nm) and WO₃ electrodeposition duration (150, 180, 200 s) were used in this study. The samples were named in the x-SnO₂-WO₃-y format, where x is the initial opal diameter and y is the WO₃ electrodeposition time.

Figure 1 shows the Field Emission Scanning Electron Microscopy (FESEM) images of as-synthesized SnO₂ and SnO₂-WO₃ core-shell IO structure with various initial pore diameters and WO₃ electrodeposition times. As shown, the SnO₂ IO framework (**Figures 1a-c**) is uniformly produced with different void space dimensions according to the initial PS sphere diameter. The diameter of the SnO₂ pores is smaller than that of the initial PS sphere diameter due to shrinkage in the SnO₂ framework during the calcination process at 500 °C. The SnO₂ IO framework is arranged in a hexagonal array and the openings that connect the adjacent pores can be clearly observed. Following WO₃ electrodeposition, a uniformly deposited WO₃ layer can be observed on the surface of the SnO₂ IO framework (**Figures 1d-l**), forming a hybrid SnO₂-WO₃ core-shell IO structure. The coating thickness of the WO₃ layer

is increased with longer electro-deposition times, almost completely filling the void space in the 392-SnO₂-WO₃-200 sample.

X-ray diffraction (XRD) was employed to characterize the crystallinity of both SnO₂ and SnO₂-WO₃-180 IO samples as shown in **Figure 2a**. From the XRD pattern, both FTO and SnO₂ IO exhibit characteristic diffraction peaks at $2\theta = 26.7^\circ, 33.8^\circ, 38.0^\circ, 51.7^\circ, 55.0^\circ, 61.7^\circ, 66.1^\circ, 78.7^\circ$, which correspond to the planes of (110), (101), (200), (211), (220), (310), (301) and (321) of SnO₂ (ICDD 01-070-4176), respectively. No other peaks were found, therefore SnO₂ should be the sole crystal phase formed during the annealing process. There is a dissimilarity in the peak intensity of the (200) plane of both samples, which may be due to the different preferred crystal orientation in SnO₂ IO structure as compared to the bare FTO glass. From the XRD pattern of the SnO₂-WO₃-180 core-shell IO, there is a lack of distinct WO₃ peaks due to the amorphous nature of the electrodeposited WO₃ layer. In addition, the intensity of the SnO₂ diffraction peaks was also slightly reduced in the SnO₂-WO₃-180 core-shell IO, which could be due to obstruction by the surrounding WO₃ layer.

Scanning Transmission Electron Microscopy (STEM) imaging coupled with energy-dispersive X-ray spectroscopy (EDX) mapping was used to reveal the core-shell structure of as-fabricated SnO₂-WO₃ IO (**Figures 2c-d**). It can be clearly observed that the inner SnO₂ framework is surrounded by a layer of amorphous WO₃. Interestingly, the element weight ratio of Sn:W is measured to be approximately 38.7:61.3, 59.9:40.1 and 83.6:16.4 for the 392-SnO₂-WO₃-180, 520-SnO₂-WO₃-180, and 872-SnO₂-WO₃-180 IO samples, respectively (Figure S2). This demonstrates that a smaller IO pore size can promote the deposition of more WO₃ in the same electrodeposition duration, and can be attributed to the higher specific surface area of SnO₂ IO framework with smaller pore sizes. However, a thicker WO₃ layer in a SnO₂ IO framework with smaller pore size could potentially block the pores and openings, thus reducing the porosity and penetration of the aqueous electrolyte into the inner pores.

2.2. Electrochemical and optical performance of SnO₂-WO₃ core-shell inverse opal structure

2.2.1. Electrochemical property of SnO₂-WO₃ core-shell inverse opal structure

The cyclic voltammetry (CV) curves of WO₃ thin film and SnO₂-WO₃ IO core-shell samples are presented in **Figures 3a-b** at a scan rate of 50 mV.s⁻¹ and under argon atmosphere. The CV curves carried out in the potential window of -0.6 V to 1.0 V were representative of the ion insertion/extraction processes in WO₃, which are similar to prior reports on WO₃ electrochromic films.^[13f, 15] The well-defined anodic peak of all CV curves indicates that the ion extraction process occurs approximately from -0.1 to -0.4 V (vs. Ag/AgCl). All porous SnO₂-WO₃ core-shell IO samples exhibit a broader enclosed CV area as compared to WO₃ thin film, which reveals that more trap sites for cation insertion/extraction were available in the core-shell structure. The IO framework which has a much higher specific area promoted the electrodeposition of WO₃, therefore increasing the number of WO₃ trap sites capable of inducing electrochromism.^[14] With increased active WO₃ sites, there is a larger contact area with the 0.1 M LiClO₄/propylene carbonate (PC) electrolyte, thus promoting the redox reactions. Interestingly, the SnO₂-WO₃ IO sample with initial pore size of 520 nm exhibits the largest enclosed CV area for all three deposition duration. However, WO₃ thin film still indicates faster ion insertion/extraction kinetics as compared to the IO structure when considering the peak potential separation (ΔE_p) between the anodic and cathodic peaks of the CV curves (Table S1). The WO₃ thin film samples indicate the smallest ΔE_p of about 0.36, 0.44 and 0.44 V for 150, 180 and 200 s, respectively. For the porous SnO₂-WO₃ IO samples, the 392 nm pore size shows the highest ΔE_p value as compared to 520 and 872 nm, which implies that the 392 nm pore size shows the slowest kinetics of ion insertion/extraction in SnO₂-WO₃ IO structure.

The Electrochemical Impedance Spectroscopy (EIS) of as-fabricated SnO₂-WO₃ IO structure is conducted in 0.1 M LiClO₄/PC electrolyte using the same CV setup (Figure S3).

The Nyquist plot fitting by Randles circuit model (Figure S3d) is shown in **Figures 3d-f**. In general, increasing the electrodeposition duration is detrimental to the EIS value of WO_3 thin films in 0.1 M LiClO_4/PC electrolyte; while in contrast, it promotes the EIS value for the $\text{SnO}_2\text{-WO}_3$ core-shell IO, especially for the initial pore size of 392 nm. The dependence of different EIS parameters on the different electrodeposition times are represented in **Figures 3g-i**. R_1 composes of solution resistance, electrode resistance (FTO- WO_3 and FTO- $\text{SnO}_2\text{-WO}_3$) and contact resistance of the electrolyte; CPE (Constant phase element) refers to the double layer capacitance; and R_2 represents the charge transfer resistance of the active species (Li^+) and the electrode. In general, there is no significant difference in the R_1 value for all WO_3 thin films and novel $\text{SnO}_2\text{-WO}_3$ core-shell IO samples. The R_1 value is approximately 23 – 25 Ω for FTO- WO_3 thin films, 23 – 25 Ω for 392- $\text{SnO}_2\text{-WO}_3$, 22 – 23 Ω for 520- $\text{SnO}_2\text{-WO}_3$, and 20 – 22 Ω for 872- $\text{SnO}_2\text{-WO}_3$ IO. However, the charge transfer resistance (R_2) of WO_3 thin films rises from about 61 to 69 and 78 Ω for 150, 180 and 200 s, respectively. The same trend is observed for 520- $\text{SnO}_2\text{-WO}_3$ (from 56 to 64 Ω) and 872- $\text{SnO}_2\text{-WO}_3$ (from 61 – 73 Ω). Interestingly, the charge transfer resistance of 392- $\text{SnO}_2\text{-WO}_3$ IO shows the reverse, in which there is a dramatic decline from 76 to 52 to 55 Ω for 150, 180 and 200 s, respectively. The decreasing value of R_1 and R_2 were assigned to enhancement in charge transfer and Li^+ ion diffusion for the 392- $\text{SnO}_2\text{-WO}_3$, owing to its high specific surface area as compared to WO_3 thin films and larger pore sizes of $\text{SnO}_2\text{-WO}_3$ IO. In addition, the smaller pore size also reduces the porous material thickness and thereby its resistivity.

2.2.2. Visible transparency and NIR modulation performance of $\text{SnO}_2\text{-WO}_3$ core-shell inverse opal structure

As mentioned previously^[14], the FTO glass allows less than 30% NIR transmittance from 1600 to 2500 nm. As such, the following range was omitted from our study as there is little capacity for NIR modulation. Therefore, in this study, the focus of NIR modulation is in the range of 700 - 1600 nm, while the visible transparency is characterized between 300 - 700

nm. **Figures 4a-c** shows the UV-vis spectra of WO₃ thin films and SnO₂-WO₃ core-shell IO samples recorded at constant potentials of +0.8 V and -0.5 V from 300 to 1600 nm in 0.1 M LiClO₄/PC electrolyte. In the colored state (-0.5 V), the UV-vis spectra of all SnO₂-WO₃ core-shell IO show low transmittance in the NIR region, with a dramatic improvement in visible light transparency as compared to the previous work.^[14] In the bleached state, all SnO₂-WO₃ core-shell IO samples demonstrate high transmittance in both NIR and visible region. Interestingly, the NIR transmittance in the bleached state of the WO₃ thin film is lower than that of the SnO₂-WO₃ core-shell IO. This means that the IO structure enables a much higher NIR modulation capability ($\Delta T\%$) while maintaining a similar visible range transparency as WO₃ thin films.

The detailed electrochromic performance of novel SnO₂-WO₃ core-shell IO structure is presented in **Figures 4d-i**. The visible wavelengths at 400, 500, 600 nm (**Figure 4d-f**), and NIR wavelengths at 800, 1200, 1600 nm (**Figure 4g-i**) were selected for comparison. In **Figure 4d**, the samples with 150 s WO₃ electrodeposition **are** presented. The WO₃ thin film indicates a visible transparency of about 83.7 – 92.7% during the bleached state and about 71.7 – 83.1% during the colored state. All three SnO₂-WO₃ IO samples show a comparable transparency: about 71.6 – 85.8% (bleached) and 63.3 – 70.3% (colored) for 392-SnO₂-WO₃ IO, about 72.7 – 86.9% (bleached) and 61.3 – 71.2% (colored) for 520-SnO₂-WO₃ IO, and about 70.2 – 82.4% (bleached) and 68.1 – 73.7% (colored) for 872-SnO₂-WO₃ IO, respectively. With thicker WO₃ layers (180 and 200 s) (**Figure 4e-f**), the visible transparency in the samples is reduced. In the 392 and 520 nm pore sizes, the visible transparency in the colored state is reduced slightly, whereas it remains relatively unchanged in the bleached state. However, the transparency reduces quite remarkably for the 872 nm pore size, which is about 8% lower than that of 392 and 520 nm in both colored and bleached states. In comparison with our previous report^[14], the visible transparency of SnO₂-WO₃ IO is at least twice higher than that of TiO₂-WO₃ IO when bleached, and 3 times higher when colored. This significant

improvement in visible light transparency is due to the excellent optical transparency of the SnO_2 framework as compared to TiO_2 .

The NIR contrast between the bleached and colored states of as-studied SnO_2 - WO_3 core-shell IO is shown in **Figure 4g-i**. In general, the porous SnO_2 - WO_3 IO demonstrates much higher NIR modulation capability as compared to WO_3 thin films. The 392- SnO_2 - WO_3 IO shows the highest NIR contrast amongst the other pore sizes despite its smaller enclosed CV area mentioned previously. This implies that the NIR modulation performance of SnO_2 - WO_3 IO structure is not only enhanced by the electrochromic kinetics, but is also promoted by its photonic crystal structure, i.e. smaller size of SnO_2 pore. For sample, for 150 s WO_3 electrodeposition, the NIR contrast at the wavelength of 1200 nm is approximately 57.2, 55.3 and 53.4% for the SnO_2 - WO_3 IO with initial pore sizes of 392, 520, 872 nm, respectively. As such, the SnO_2 - WO_3 core-shell IO has a much better NIR blocking capability as compared to only 40.3% contrast for WO_3 thin film. When the electrodeposition duration was increased to 180 s, the samples show a higher NIR contrast than that of 150 s. The NIR contrast is increased to 43.1% for WO_3 thin film and 62.5, 62.7, and 60.7% for the SnO_2 - WO_3 IO with initial pore sizes of 392, 520, 872 nm, respectively. However, when the WO_3 electrodeposition time was further increased to 200 s, only the NIR contrast at 1200 nm of WO_3 thin film showed significant improvement to the value of 51.3%; while there were negligible changes for SnO_2 - WO_3 IO samples. The NIR contrast were approximately 62.6, 63.8 and 63.1% for initial pore sizes of 392, 520, 872 nm, respectively. This shows the limitation of WO_3 thickness that can be electrodeposited to obtain the optimal NIR modulation effectivity. Overall, the core-shell IO structure of SnO_2 - WO_3 demonstrates two main advantages in the enhancement of NIR modulation: 1) Promoting the electrochromic kinetics of WO_3 , i.e. increasing the amount of Li^+ ions that intercalated into the core-shell IO structure, which is revealed by the CV curves; 2) Enhancing the photonic crystal effect on the NIR range absorption. Upon the Li^+ insertion, the pore size of SnO_2 - WO_3 IO structure

becomes smaller and can also tune the solar radiation transmittance. Amongst three examined PS suspension solutions, the smallest PS opal size (392 nm) exhibits the most effective assistance in the NIR modulation of SnO₂-WO₃ core-shell IO structure as discussed above.

In comparison with other reports, as-fabricated SnO₂-WO₃ core-shell IO also demonstrates enhanced visible transparency and NIR modulation performance. **Table 1** presents the comparison of the visible transparency and NIR contrast between bleached and colored states at specific wavelengths for different EC materials. The SnO₂-WO₃-180 samples were selected for comparison. It can be observed that as-prepared SnO₂-WO₃-180 core-shell IO demonstrates the optimum performance in terms of visible transparency during colored state and its NIR contrast. For example, Zhou *et al.* reported the Ag/WO₃ nanowires with about 59% NIR modulation at 1100 nm, and only about 8.7% transparency at 500 nm.^[2j] The bilayer WO₃ IO structure synthesized by Li *et al.* showed about 57.6% NIR modulation at 1100 nm, but only 27.3% transparency at 500 nm.^[13e] In comparison with as-fabricated 392-SnO₂-WO₃-180 IO sample, it demonstrated the value of 63.2% for NIR modulation at 1100 nm, and about 67.1% transparency at 500 nm, respectively. These are the highest reported values to date. Therefore, the SnO₂-WO₃ core-shell IO structure developed in this study can provide two promising advantages in the smart windows technology: 1) Large thermal radiation modulation and 2) Low detriment on visible transparency. These advantages will be beneficial for the optimization of in-door lighting and air-conditioning.

2.2.3. NIR electrochromic stability of SnO₂-WO₃ core-shell inverse opal structure

The electro-optical response time on switching between the bleached and colored states of SnO₂-WO₃-180 IO is showed in **Figures 5a-b**. The switching time becomes slightly faster with increasing initial pore sizes, taking approximately 29.5, 25.9 and 25.8 s for the 392-SnO₂-WO₃-180, 520-SnO₂-WO₃-180, and 872-SnO₂-WO₃-180 IO, respectively. This is in agreement with the ΔE_p value in above electrochemistry characterization. **Figures 5d-f** show the electrochromic stability of the SnO₂-WO₃-180 IO samples for 300 reversible cycles

at 1033 nm. It was found that the NIR transmittance during bleached state remains stable for over 300 cycles. However, the NIR blocking capability is reduced. The 392-SnO₂-WO₃-180 IO sample shows the best electrochromic stability, with only 14.7% reduction in NIR blockage after 300 cycles, as compared to 17.7% and 17.9% for 520-SnO₂-WO₃-180 and 872-SnO₂-WO₃-180 IO samples, respectively. These values are lower than the EC stability of TiO₂-WO₃ core-shell IO structure, which only showed 10% drop of NIR blocking after 1000 cycles.^[14]

It was reported that the amorphous WO₃ thin films suffered from ion-trapping-induced degradation of optical modulation and reversibility on extended Li⁺-ion exchange, causing the electrochromic performance to drop.^[16] In the current study, the results in **Figures 5d-f** indicate that the kinetics of ion extraction process (bleached state) is stable for over 300 cycles and only the ion insertion process (colored state) is affected. This implies that there is a reduction in the Li⁺ ions amount that can be intercalated into SnO₂-WO₃ IO structure after each cycle. In order to better understand the phenomenon, the SnO₂-WO₃ IO samples were characterized by XRD again after the stability test. **Figure 6** presents the XRD pattern of SnO₂-WO₃-180 core-shell IO samples after the stability test for 300 cycles. For 392-SnO₂-WO₃-180 and 520-SnO₂-WO₃-180 sample, there is no difference in the crystal structure for the sample before and after the stability test, except for the relative diffraction peak intensity. The higher diffraction peak of SnO₂-WO₃ IO sample after the stability test implies the loss of the surrounding WO₃ layer after 300 cycles. The loss in the active layer could explain the drop of EC performance of as-fabricated SnO₂-WO₃ IO structure. Interestingly, along with the higher diffraction peak intensity, the 872-SnO₂-WO₃-180 IO sample after cycling test shows characteristic diffraction peaks at 21.17°, 23.05°, 26.33°, 31.52°, 44.52°, which corresponds to the (001), (110), (101), (111) and (211) planes of crystalline WO₃ (ICCD 00-005-0388). This demonstrates the crystallization of amorphous WO₃ layer under electrochemical condition during 300 cycles. As mentioned previously, many studies reported that amorphous

WO₃ indicates better EC effectivity than its crystalline form due to the higher ion storage capacity at the same applied voltage.^[10] This could also contribute as a factor to the reduction in the electrochromic performance of SnO₂-WO₃ core-shell IO structure. As a large number of switching cycles is essential for a practical smart window system, as-synthesized SnO₂-WO₃ nanostructures have to demonstrate a stable and effective EC performance. One of the most effective methods to improve the EC cycle stability of WO₃ is via doping or compositing with metal cations or metal oxides, e.g. Nb^[18a] and Mo^[18b], and most commonly with Ti^[14].

3. Conclusion

In this study, a novel EC material with a combination of high visible transparency of SnO₂ and efficient NIR contrast of WO₃ EC materials have been fabricated for advanced smart window applications. The hybrid SnO₂-WO₃ core-shell IO structure is obtained by electrodeposition of amorphous WO₃ EC layer onto the SnO₂ IO framework. The effect of pore size is also investigated by varying the initial PS template size and electrodeposition time. The 392-SnO₂-WO₃-180 core-shell IO structure demonstrates the highest reported values to date in term of visible transparency (about 70% at colored state) and NIR contrast (62% at 1200 nm). In addition, it also indicates the most stable electrochromic performance, with about 14.7% NIR blocking, drops after 300 cycles.

4. Experimental Section

Synthesis of SnO₂-WO₃ core-shell inverse opal: Figure S1 illustrates the fabrication procedure of hybrid SnO₂-WO₃ core-shell IO structure. Mono-dispersed polystyrene (PS) spheres (Thermo Fisher Scientific) of varying sizes (392, 520, 872 nm) were diluted in DI water and sonicated for 30 mins. The clean FTO glasses (1.5 x 2.5 cm²) were immersed in the PS dispersion solution horizontally at 60 °C for 3 days to achieve a self-assembled PS opal template on the FTO glass substrate.

The SnO₂ IO was obtained by a dip-coating method using aqueous SnO₂ precursor. The precursor solution was prepared by mixing 25 mL of ethylene glycol (EG) (Sigma-Aldrich) and 5 mmol of SnCl₄·5H₂O (Sigma-Aldrich) in a glass beaker with continuous stirring, then heated up to 120 °C for 1h. After cooling of the mixture, 25 mL of ethanol (Sigma-Aldrich) was added into the mixed solution to reduce the viscosity. The PS opal template was dipped into the resulting solution for 3 mins, followed by calcination at 500 °C for 2 h (ramping rate 1 °C/min) to obtain the SnO₂ IO.

Finally, the hybrid SnO₂-WO₃ core-shell IO was prepared by electrodeposition. The WO₃ precursor solution was prepared by mixing 1.03 g of Na₂WO₄·2H₂O (Sigma-Aldrich) and 0.65 mL of H₂O₂ (Sigma-Aldrich) in 250 mL of DI water. After that, 2 mL of HClO₄ (Sigma-Aldrich) was gradually added into such mixed solution until the pH reaches the value of 1.2.^[17] The electrodeposition process was conducted at a constant potential of −0.7 V for 150, 180 and 200 seconds for comparison. A WO₃ thin film was electrodeposited onto the FTO glass as the reference using the same parameters. The obtained samples were rinsed with DI water and dried with nitrogen gas.

Characterization: The morphology of the obtained samples was characterized by Field Emission Scanning Electron Microscope (JEOL 7600F). The crystal structure of SnO₂-WO₃ IO was characterized by an X-ray diffractometer (Shimadzu XRD-6000, with the λ Cu-K α = 0.15418 nm). The atomic compositions and core-shell structure were identified by a Scanning Transmission Electron Microscope (JEOL 2100F STEM equipped with INCA EDS detector).

Cyclic voltammetry (CV) was measured using a CHI 750E potentiostat in 0.1 M lithium perchlorate (LiClO₄)/propylene carbonate (PC) electrolyte (Sigma-Aldrich) at scan rates of 50 mV.s^{−1} within a potential range from −0.6 to +1.0 V under Ar saturated condition. The Electrochemical Impedance Spectroscopy (EIS) was conducted using the same CV setup, with the frequency range of 1 MHz-100 Hz, applied AC potential of 5 mV. The spectro-electrochemical properties of obtained samples were measured using a Solartron potentiostat

(Model 1470E) and a UV-Vis-NIR spectrophotometer (Shimadzu UV 3600). The UV-Vis spectra of all samples were recorded in the wavelength range of 300 nm to 1600 nm at potentials of -0.5 and $+0.8$ V. The dynamic optical transmittance was also recorded for the $\text{SnO}_2\text{-WO}_3\text{-180}$ IO samples in the wavelength range of interest under repeating square wave potentials oscillating between $+0.8$ and -0.5 V at a time step of 100 s and 120 s respectively. It was recorded for more than 300 reversible cycles to characterize its long-term stability.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure 1. FESEM images of SnO_2 IO (a-c) and $\text{SnO}_2\text{-WO}_3$ core-shell IO structure with initial pore-size of 392 (d, g, j), 520 (e, h, k), 872 (f, i, l) nm and electro-deposition duration of 150 (d-f), 180 (g-i), 200 (j-l) seconds. All images were acquired under the same magnification.

Figure 2. XRD patterns of FTO, SnO_2 IO and $\text{SnO}_2\text{-WO}_3$ core-shell IO structure with the electro-deposition duration of 180s (a). STEM images coupled with EDX mapping of 392- $\text{SnO}_2\text{-WO}_3$ -180 (b), 520- $\text{SnO}_2\text{-WO}_3$ -180 (c), and 872- $\text{SnO}_2\text{-WO}_3$ -180 (d) core-shell IO structure.

Figure 3. Cyclic voltammetry (a-c) and Nyquist plot (d-f) of WO_3 thin film and $\text{SnO}_2\text{-WO}_3$ core-shell IO structure. Each CV curve Nyquist plot is plotted from the average of three independent CV and EIS scans. The Nyquist plots are obtained from the fitting of EIS curve using Randel model. Dependence of EIS value of WO_3 thin film and $\text{SnO}_2\text{-WO}_3$ IO core-shell structure on the electro-deposition duration (g-i).

Figure 4. UV-vis-NIR spectra of WO_3 thin film and $\text{SnO}_2\text{-WO}_3$ core-shell IO structure at bleached and colored state in 0.1 M LiClO_4/PC electrolyte (a-c). Visible transparency (d-f) and NIR contrast (g-i) between colored and bleached state of WO_3 thin film and $\text{SnO}_2\text{-WO}_3$ IO core-shell structure. Each UV-vis-NIR spectrum is obtained from the average of three independent scans. **Note:** The dotted connecting lines in Fig. 4d-i are only visual aids and are not extrapolations of the data.

Figure 5. Electro-optical response time between bleached and colored state (a-b) of SnO₂-WO₃-180 core-shell IO structure. Kinetics stability (d-f) of SnO₂-WO₃-180 core-shell IO structure at bleached and colored state for over 300 cycles.

Figure 6. XRD patterns of SnO₂-WO₃-180 core-shell IO structure with initial pore size of 392 (a), 520 (b), and 872 nm (c) before (as-fabricated) and after kinetics stability test (cycled) for 300 cycles.

Table 1. Comparison of visible transparency and NIR modulation of different electrochromic materials at specific wavelength.

Sample	Visible transparency (%) ^{a)} (colored state)			NIR modulation (%) ^{b)} ($T_{\text{bleached}} - T_{\text{colored}}$)		
Wavelength (nm)	400	500	600	1100	1200	1600
392-SnO ₂ -WO ₃ -180	70.3	67.1	54.1	63.2	62.5	47.4
520-SnO ₂ -WO ₃ -180	70.6	66.5	52.4	62.7	62.7	46.1
872-SnO ₂ -WO ₃ -180	65.7	61.0	46.4	61.6	60.7	46.9
ITO/WO ₃ [2f]	64.0	57.1	43.5	47.7	48.0	43.5
Ag NW/WO ₃ [2j]	6.2	8.7	10.5	59.0	46.0	62.8
^{c)} 2L WO ₃ IO [13e]	18.2	27.3	24.8	57.6	-	-
^{d)} L2 WO ₃ IO [13f]	23.2	45.2	56.6	35.2	38.6	-
TiO ₂ -WO ₃ IO [14]	23.1	22.7	15.3	62.5	65.0	45.2

^{a),b)} Value estimated from reported data; ^{c)}Bilayer; ^{d)}Bilayer

Hybrid SnO_2 - WO_3 core-shell IO structure is obtained by electro-deposition of amorphous WO_3 EC layer on highly transparent SnO_2 IO framework. As-fabricated SnO_2 - WO_3 core-shell IO structure with initial pore size of 392 nm demonstrates the optimal visible transparency (about 70% at colored state) and NIR contrast (62% at 1200 nm).

Electrochromic materials, core-shell inverse opal, pore size variation, visible transparency, near infra-red modulation

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Efficient near infra-red modulation with high visible transparency using SnO_2 - WO_3 nanostructure for advanced smart windows

Supporting Information

Efficient near infra-red modulation with high visible transparency using $\text{SnO}_2\text{-WO}_3$ nanostructure for advanced smart windows

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Figure S1. The synthesis procedure of hybrid $\text{SnO}_2\text{-WO}_3$ core-shell IO structure

The hybrid $\text{SnO}_2\text{-WO}_3$ core-shell IO structure was fabricated onto commercial FTO glass via 2-step synthesis procedure, including the dip-coating in SnO_2 precursor solution and electro-deposition of WO_3 precursor solution. The as-received FTO glass was cut into piece with a desired size ($1.5 \times 2.5 \text{ cm}^2$), and followed by a cleaning procedure using methanol, acetone and ethanol. The FTO glass piece was kept in the mixed solution of ethanol and DI water before sample fabrication. The PS spheres were dispersed in DI water solvent with the concentration of 0.01 wt.%. For each fabrication, three pieces of pre-cleaning FTO glass were immersed in 100 mL of PS dispersion solution.

Figure S2. The element weight ratio of 392-SnO₂-WO₃-180 (a), 520-SnO₂-WO₃-180 (b), and 872-SnO₂-WO₃-180 (c) core-shell IO structures obtained from STEM-EDX analysis.

By STEM-EDX analysis, the element weight percentage (wt.%) of Sn and W is measured to be about 38.7 and 61.3% for 392-SnO₂-WO₃-180 sample, 59.9 and 40.1% for 520-SnO₂-WO₃-180 sample, 83.6 and 16.4% for 872-SnO₂-WO₃-180 sample, respectively. The atomic percentage (at.%) of Sn and W is also estimated to be about 49.4 and 50.6% for 392-SnO₂-WO₃-180 sample, 69.9 and 30.1% for 520-SnO₂-WO₃-180 sample, 88.7 and 11.3% for 872-SnO₂-WO₃-180 sample, correspondingly.

Figure S3. EIS of different WO₃ thin films and SnO₂-WO₃ core-shell IO structures (a-c). Illustration of Randles circuit model used for EIS fitting.

The EIS measurement was conducted using a three electrode system, including as-fabricated FTO-SnO₂-WO₃ IO sample served as working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The EIS was measured using a CHI 750E potentiostat in 0.1 M LiClO₄/PC electrolyte with the frequency range of 1 MHz – 100 Hz, applied AC potential of 5 mV. The obtained EIS curve was fitted by Randel circuit model using the EC-lab software.

Figure S4. UV-vis-NIR spectra of as-fabricated WO₃ thin film and SnO₂-WO₃ core-shell IO structure immersed in 0.1 M LiClO₄/PC electrolyte.

Figure S4 presents the UV-vis-NIR spectra of as-fabricated WO₃ thin film and SnO₂-WO₃ IO immersed in 0.1 M LiClO₄/PC electrolyte. Obviously, the inverse opal structure significantly changed the optical property of WO₃ thin films. With a certain electrodeposition time, the WO₃ thin films indicate stronger NIR absorption (starting at the wavelength of about 900 nm) as compared to the SnO₂-WO₃ IO structure. The inverse opal core-shell structure does not strongly effect on the visible transparency of WO₃ EC material, as all samples demonstrate the high visible transparency of about 80 – 90%.

Figure S5. The apparent color of $\text{SnO}_2\text{-WO}_3\text{-200}$ core-shell IO structure in as-fabricated form (a-c), at colored state (d-f) and bleached state (g-i).

Figure S5 shows the apparent color of $\text{SnO}_2\text{-WO}_3\text{-200}$ core-shell IO sample in as-fabricated form (a-c), at colored (d-f) and bleached state (g-i). Obviously, the as-fabricated $\text{SnO}_2\text{-WO}_3$ IO sample with the initial pore size of 392 nm indicates the highest visible transparency, as compared to the pore size of 520 and 872 nm. Upon the voltage apply, the $\text{SnO}_2\text{-WO}_3$ IO structures turn blue, but with different levels of colored state. Based on the initial pore size, the visible transparency of $\text{SnO}_2\text{-WO}_3$ IO sample at colored state can be arranged as $392 > 520 > 872$ nm. At bleached state, all $\text{SnO}_2\text{-WO}_3$ IO structures almost return back to the original transparency as in as-fabricated form.

Table 1. Peak potential separation (ΔE_p) of the CV profile for WO₃ thin film and SnO₂-WO₃ core-shell IO structure.

Sample	ΔE_p (V)			
	FTO	392 nm	520 nm	872 nm
150 s	0.36	0.59	0.52	0.53
180 s	0.44	0.58	0.52	0.53
200 s	0.44	0.59	0.50	0.44

Supporting Information

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