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More than 50% of solar energy comes from the infrared region (as radiant heat) of the solar spectrum. Electrochromic (EC) materials, which can dynamically modulate the transmittance of Infrared (IR) Radiation, can be effectively applied in smart windows for thermal management in buildings. In this work, a core-shell TiO₂-WO₃ inverse opal (IO) structure was fabricated through the electrodeposition of WO₃ onto TiO₂ IO templates. The TiO₂ IO templates were synthesized by introducing TiO₂ into the voids of a polystyrene (PS) colloidal crystal template, followed by calcination to remove the PS microspheres. It was found that the TiO₂-WO₃ IO core-shell structure can modulate NIR transmittance at wavelengths from 700 to 1600 nm in the NIR range when potential is applied in LiClO₄/PC electrolyte. When -0.3 V is applied, up to 60% of NIR radiation in this range can be blocked. The NIR transmittance can be modulated by tuning the applied potential. This study focuses on comparing the novel TiO₂-WO₃ IO structure with electrodeposited WO₃ thin film to fully elucidate the effect of the inverse opal morphology and the TiO₂-WO₃ hybrid system on the optical properties. Results show that the NIR blockage can be sustained up to 90% after 1,200 reversible cycles for TiO₂-WO₃ IO structure. The greater surface area of the IO structure increases the number of active sites available for the redox reactions by providing a larger contact area with the electrolyte. The more electroactive area with improved charge transfer enhances the overall NIR transmittance contrast as compared to bulk WO₃ thin film. Furthermore, the addition of WO₃ to TiO₂ to form a composite has been shown to enhance cycling performance and device lifespan.

Introduction

In recent years, smart window technology has garnered global attention as they can dynamically modulate solar radiation transmittance at different wavelengths at very low energy consumption. It can maintain indoor comfort while maintaining energy efficiency at the same time, thus assisting the energy management in buildings. Electrochromic (EC) materials are widely used in smart window applications as they can reversibly control the optical properties of windows on application of voltage. Since most of the solar energy (~50%) comes from infrared (IR) radiation, an EC material that can dynamically modulate NIR radiation at low voltage can have great potential in smart window applications for thermal management in buildings.¹ However, most EC smart window research focuses only on modulation within the visible range

of the solar spectrum.²⁻⁵ This limitation could be due to two reasons. Firstly, many polymer-based EC materials such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) cannot exhibit visible and NIR range blockage at the same time. Secondly, there may be little transmittance contrast between the colored and bleached states at IR or NIR wavelengths for some transition metal oxide-based EC materials, thus limiting their IR modulation capacity. Many researchers are also working on controlled coloration of windows and displays using transition metal oxides and conjugated polymers, such as tungsten oxides (WO₃)^{1, 6-9}, vanadium oxide (V₂O₅)^{10, 11}, nickel oxide (NiO)¹²⁻¹⁴, polyaniline (PANI)^{15, 16}, PEDOT:PSS^{7, 17-19} etc. Hybrid EC materials have also attracted much attention due to the vast improvement observed in their EC performance. Meenakshi et al. reported the effect of doping V₂O₅ in WO₃ thin films. Their composite thin films displayed rapid cycling response times and low levels of doping could achieve nearly 50% transmittance contrast between wavelengths ranging from 300-1000 nm.²⁰ In our previous study, WO₃ was also combined with a conductive polymer PEDOT:PSS to form an electrochromic hybrid material capable of coloring, when cathodic potentials are applied.¹⁷ The simultaneous switching of both materials gave rise to enhanced optical contrast and excellent electrochemical reversibility in visible light range.⁷

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*Electronic Supplementary Information (ESI) available: SEM images of self-assembled PS template of different magnifications, Vis-NIR Transmittance Spectrum of FTO and FTO|WO₃ samples refer to air, and transmittance Spectrum of TiO₂ IO samples at applied potentials. See DOI: 10.1039/x0xx00000x

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Figure 1. Schematic illustration of the fabrication process of $\text{TiO}_2\text{-WO}_3$ core-shell inverse opal structure

Characterization

Both the surface and cross-sectional morphologies of the obtained samples were characterized by Field Emission Scanning Electron Microscope (Zeiss GeminiSEM). An X-ray diffractometer (Panalytical X'Pert Pro) with $\text{Cu K}\alpha$ radiation was used to identify the crystalline structure of $\text{TiO}_2\text{-WO}_3$ and WO_3 samples. The atomic compositions were examined by an Energy Dispersive X-ray spectrometer (EDX) equipped in a separate FESEM (JEOL JSM-7400F) as well as with the Scanning Transmission Electron Microscope (JEOL 2100F STEM equipped with INCA EDS detector). The samples were also examined using a Brunauer-Emmett-Teller (BET) surface area and porosity analyser (ASAP 2020 Micro-meritics). Cyclic voltammetry (CV) was measured using a CHI 750E potentiostat in 1 M lithium perchlorate (LiClO_4)/propylene carbonate (PC) solution at scan rates of 25 and 50 mV/s within a potential range from -1.5 to $+1.0$ V. 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 the thin films were recorded in the wavelength range of 300 nm to 1600 nm at potentials of -0.3 , 0, and 0.6 V, respectively. For each thin film, dynamic optical transmittance was also recorded at wavelength of interest under repeating square wave potentials oscillating between $+0.6$ and -0.3 V at a time step of 50 s. It was recorded for more than 1000 reversible cycles to characterize its long-term stability.

Results and discussion

Fabrication and Morphology of $\text{TiO}_2\text{-WO}_3$ Core-Shell IO Structure

In this work, the $\text{TiO}_2\text{-WO}_3$ core-shell inverse opal structure was fabricated through the process illustrated in Fig. 1. Firstly, a PS opal template was formed through vertical self-assembly at 70°C for 72 hours as shown in the SEM image (Fig. S1). This clearly shows an excellent ordering of closed-packed spheres assembled onto an FTO substrate. Upon coating the TiO_2 precursor onto the PS template through dip-coating, the sample was calcinated to obtain a TiO_2 IO structure as observed in Fig. 2(a-c). The TiO_2 IO structure is arranged in a macroporous hexagonal array with three openings in the framework of each pore. As shown in Fig. 2(a-c), the pore size of TiO_2 IO is approximately 450 nm with thin TiO_2 framework in the range of a few nanometers. The diameter of the pores is smaller than the original template size of 520 nm (Fig. S1b) due to shrinkage in the TiO_2 framework following the calcination process. WO_3 was then electrodeposited onto the TiO_2 IO structure from 0.03 M PTA aqueous solution at -0.6V (vs. Ag/AgCl) for 100 s. The PTA solution can easily penetrate the TiO_2 IO owing to its high porosity. As a result, a uniformly deposited WO_3 layer could be observed on top of the TiO_2 surface (Fig. 2(d-f)) forming a $\text{TiO}_2\text{-WO}_3$ core-shell hybrid

structure. Fig. 2 (c and f) shows the cross-sectional view of the IO structures from which approximately 6 layers of IO can be observed, indicating a thickness of approximately 2-3 μm . In the core-shell sample, the pore size is further reduced to ~ 400 nm (Fig. 2e). From this, the thickness of the deposited WO_3 layers was approximately 50 nm. An SEM image depicting the ordered IO structure of the hybrid system on a larger scale has also been included (Fig. S2).

Figure 2. SEM images of TiO_2 IO (90° view) at magnification of around (a) 75K and (b) 150K, and (c) 45° cross-sectional view. SEM images of TiO_2 - WO_3 core-shell IO (90° view) at magnification of around (d) 75K and (e) 150K, and (f) 45° cross-sectional view.

Composition of the TiO_2 - WO_3 Core-Shell IO samples

X-ray diffraction (XRD) was employed to characterize the crystallinity of both TiO_2 and TiO_2 - WO_3 IO samples as shown in Fig. 3a. From the XRD pattern, both FTO and TiO_2 exhibit characteristic peaks: $2\theta = 26.68^\circ, 33.80^\circ, 37.98^\circ, 51.74^\circ, 54.96^\circ, 61.70^\circ, 66.06^\circ, 78.68^\circ$ which correspond to the planes of (110), (101), (200), (211), (220), (310), (301) and (321) of the FTO glass substrate (ICDD 01-070-4176); $2\theta = 25.42^\circ, 37.88^\circ, 48.2^\circ, 54.9^\circ, 62.8^\circ, 71.34^\circ$, which correspond to the planes of (101), (004), (200), (211), (213) and (220) of the anatase phase of the TiO_2 layer (ICDD 00-001-0562).^{32, 33} The WO_3 layer electrodeposited onto the TiO_2 IO without further annealing produced an amorphous structure, which can be observed from the lack of distinct WO_3 peaks in the XRD pattern of the hybrid core-shell structure. The intensity of the characteristic TiO_2 peaks located at 25.42° and 37.88° in the TiO_2 - WO_3 IO sample was reduced compared to that of the TiO_2 IO sample. The XRD of the amorphous WO_3 thin film was also included for comparison. No distinct WO_3 peaks could be observed but the intensity of the FTO peaks were slightly reduced due to the

WO_3 layer deposited over it. This could indicate that the TiO_2 layer was obstructed by the electrodeposited WO_3 layer surrounding it. EDX analysis was performed to determine the chemical composition of the obtained samples. Fig. 3b shows the atomic percentage (at%) of W and Ti measured by EDX. The EDX data shows an atomic ratio of 2.05 between W and Ti and confirms the presence of WO_3 as the major component in the core-shell sample.

Figure 3. (a) XRD patterns of WO_3 thin film (amorphous), TiO_2 IO and TiO_2 - WO_3 (amorphous) IO structure. (b) Atomic percentage of elements, namely W and Ti in TiO_2 - WO_3 IO samples measured by STEM-EDX.

STEM image, as shown in Fig. 4 confirms the formation of the core-shell structure. The inner TiO_2 framework is surrounded by a layer of amorphous WO_3 . In the composition characterization, the formation of TiO_2 - WO_3 core-shell IO structure can be confirmed, and the atomic percentage of each component in this hybrid system was determined.

Figure 4. STEM images with EDX mapping indicate the successful formation of the core-shell structure in TiO_2 - WO_3 inverse opal.

Electrochemical and Optical Performances

In this work, the WO_3 film was deposited onto the FTO at -0.6V (vs. Ag/AgCl) for 100 s as the reference sample.

Electrochemical Performances. To understand the electrochemical behaviour of the obtained samples, CV was conducted using a standard three-electrode system. The CV curves of TiO_2 IO, WO_3 thin film, and TiO_2 - WO_3 IO core-shell samples are presented in Fig. 5 at scan rates of 50 and 100 mV/s respectively. The area of the CV curves indicates the amount of charges inserted or extracted from the samples due to the increased surface area. The area enclosed in the TiO_2 IO CV curve for both scan rates is almost negligible, while the hybrid IO CV curves exhibited a much larger enclosed area

compared with that of the WO₃ thin film sample. This reflects that the insertion/extraction of small ions (Li⁺) into the host lattice is facilitated in the TiO₂-WO₃ core-shell system, which may be caused by: 1) enhanced electronic or ionic properties according to a previous study²⁵ and 2) promoted WO₃ electrodeposition process due to the high specific area of TiO₂ IO template. As a result, the EC performance of the core-shell sample could be improved compared with that of WO₃ thin film samples, especially in terms of their optical contrast during electrochromic activity.

Figure 5. CV curves of TiO₂ IO, neat WO₃ and TiO₂-WO₃ IO samples coated on FTO glasses with WO₃ deposition time of 100 s at scan rate of (a) 50 and (b) 100 mV/s in 1 M LiClO₄/PC

Optical Reflectance of Hybrid IO Sample. Due to its periodicity, the 3D inverse opal structure usually exhibits a distinct reflectance peak at a region which can be attributed to the photonic stop band, where light propagation is prevented along certain crystal directions of the structure.³⁴ Given a face-centered cubic (FCC) arrangement with close-packed (111) planes, the stop band position, λ , can be calculated using a modified Bragg's law equation as shown below (Eq. 2).³⁵ D is the diameter of the inverse opal pore, and n_s and n_v are the refractive indices of the material framework and the voids in the TiO₂-WO₃ IO structure respectively; f refers to the volume fraction of the IO framework and θ is the angle of incident light.

$$\lambda = 2 \sqrt{\frac{2}{3}} D \sqrt{n_s^2 f + n_v^2 (1 - f) - \sin^2 \theta} \quad (\text{Eq. 2})$$

Due to the FCC arrangement, the volume fraction, f , is taken to be 0.26. The volume ratio of WO₃ and TiO₂ in the TiO₂-WO₃ IO framework is calculated from the STEM-EDX data and approximated as 3.58 (Calculation available in the Supplementary Information). The filling factor is then adjusted to consider the refractive indices of both materials. ~~Considering that the volume ratio of TiO₂ and WO₃ in the TiO₂-WO₃ IO framework is approximately 4.29, the filling factor is adjusted to consider the refractive indices of both materials.~~ The refractive index of WO₃ remains generally constant at 2.1 for $\lambda > 600\text{nm}$ while that of anatase TiO₂ is a constant value of 2.5.³⁶⁻³⁸ The medium in the inverse opal voids is air and thus ($n_v = 1$). From the SEM image (Fig. 1e), the diameter of the inverse opal void is measured to be 400 nm.

As the specular reflectance spectrum was recorded at an incident angle of 70°, the calculated stop band was also measured at the same angle. Based on Eq. 2, the stop band wavelength is calculated to be at 687 nm, which varies slightly from the measured peak 722 nm shown in Fig. 6. Since the

calculated peak is highly dependent on D , this suggests that the mean inverse opal pore diameter is higher when a larger sample area is considered. This discrepancy could be due to several reasons: (1) The temperature gradient during calcination is not uniform throughout the furnace, resulting in different extents of shrinkage or (2) due to the PS $\leq 3\%$ coefficient of variation of the commercial PS spheres suspension. ~~Based on Eq. 2, the stop band wavelength is calculated to be at 683 nm, which is in line with the experimental result of 722 nm shown in Fig. 4.~~ The peak located at around 1322 nm is attributed to the reference FTO glass. Nevertheless, the obtained core-shell sample was well-fabricated with a long range periodic structure (Fig. S2). Ongoing works focus on the manipulation of the optical properties to maintain visible wavelength transparency during the modulation of NIR radiation through changing the diameter of the PS spheres. Some strategies include a functionally gradient and gradient composite structure.

Figure 6. Specular Reflectance at 70° of TiO₂-WO₃ hybrid core-shell IO sample

Optical Transmittance. The electrochromic properties in NIR region of the obtained samples were characterized in a three-electrode electrochemical cell while immersed in 1 M LiClO₄/PC electrolyte solution. The transmittance of the reference FTO glass substrate was recorded from 300 to 2500 nm and the spectrum is shown in Fig. S3. The FTO glass allows less than 30% NIR radiation transmitted from 1600 to 2500 nm, thus the transmittance contrast during application of voltage could not be observed in this wavelength range and was subsequently removed from further transmittance measurements. Based on the CV curves shown in Fig. 5, the TiO₂ IO sample exhibits limited charge insertion or extraction, leading to negligible EC performance (Fig. S4). Transmittance of WO₃ thin film and TiO₂-WO₃ core shell IO samples were recorded at constant potentials of +0.6 V and -0.3 V from 300 to 1600 nm. As shown in Fig. 7(a & b), the TiO₂-WO₃ core shell sample presented a much higher contrast in NIR region compared with that of WO₃ thin film deposited with the same parameters. At the wavelength of 1033 nm, WO₃ thin film showed a contrast of approximately 43%, while the core-shell sample could reach up to 65%. Though the TiO₂-WO₃ core shell sample showed excellent transmittance contrast at different potentials, it was also necessary to investigate its long-term stability. As such, dynamic transmittance of WO₃ thin film and TiO₂-WO₃ IO samples were recorded under oscillating

potentials cycling between +0.6 V and -0.3 V at time interval of 50 s for cycles as shown in Fig. 7c. The coloration time for both WO₃ thin film and TiO₂-WO₃ IO sample that can be observed in Fig. 7c, are 15 and 6 seconds respectively. The corresponding coloration efficiency (CE) can also be obtained as 55.48 C/cm² and 111.88 C/cm² for WO₃ thin film and TiO₂-WO₃ IO samples, respectively. (shown in Fig. 7d) The hybrid IO structure shows significantly improved CE with more active electrochromic active units. The WO₃ thin film has completely lost its original contrast after 600 cycles. While, the TiO₂-WO₃ IO sample could sustain more than 90% of the original contrast after 1200 cycles. This shows that the novel core-shell structure provides significant improvements in long-term stability.

Figure 7. UV-Vis-NIR transmittance spectrum of (a) neat WO₃ and (b) TiO₂-WO₃ IO samples at applied potentials of +0.6 and -0.3 V. (c) Dynamic optical transmittance curves and (d) the corresponding coloration efficiency of neat WO₃ and TiO₂-WO₃ IO films obtained under square wave potential oscillating between +0.6 V and -0.3 V at a time interval of 50 s. Transmittance between bleached (black) and blocked (red) states of (e) WO₃ and (f) TiO₂-WO₃ IO films as a function of switching cycles. The transmittance of each film was measured at wavelength of 1033 nm.

The enhancement in the electrochromic performance of TiO₂-WO₃ core-shell IO sample in NIR region compared to the WO₃ thin film may be attributed to two main factors: 1) uniform and periodic core-shell IO structure; and 2) improved electronic and ionic properties in the hybrid system. The novel core-shell IO structure has a larger surface area compared with WO₃ thin film, which provides an increased number of active sites available for the redox reactions by providing a larger contact area with the electrolyte. BET surface area analysis

was used to confirm the specific surface area of the porous samples (Fig. S5). The specific surface area of TiO₂-WO₃ core-shell IO was measured to be about 7.4 m²/g, which is about 24 times higher than that of WO₃ thin film which is approximately 0.3 m²/g (as approximated using its film thickness). The greater porosity of the IO structure also enables better infiltration of the electrolyte, which shortens diffusion pathways of the charges, and thus promotes more effective redox reactions and enhances the overall NIR transmittance contrast as compared to bulk WO₃ thin film.^{39, 40} Based on numerous studies, the addition of WO₃ to TiO₂ to form a composite structure has commonly been found to improve electrochromic performance significantly in terms of cycling performance and device lifespan.^{41, 42} The poor cycling performance of WO₃ thin films has generally been ascribed to the trapping of Li⁺ ions in a-WO₃ during the redox reactions. However, the hybrid TiO₂-WO₃ IO samples maintained more than 90% of its original contrast in NIR region. It indicates that 1) the hybrid system exhibits large contract area with electrolyte for easy ion insertion/extraction; 2) the ion insertion/extraction process also occurs in the TiO₂ IO, which may act as a buffer layer for WO₃ in the hybrid.^{25, 42} Upon introduction of TiO₂, it is generally thought that its presence impedes the rearrangement of the [WO₆] octahedra for crystallization, thus improving cycling performance.⁴³ In addition, the low voltage applied (-0.3V) helps to improve long-term reversibility by preventing over intercalation during the redox reactions. In terms of thermal energy management, high blockage at low power consumption is a highly desired feature in smart window applications.

Conclusions

The TiO₂-WO₃ core-shell IO samples have been successfully fabricated through PS self-assembly, TiO₂ dip coating, calcination, and electrodeposition of WO₃. The obtained samples were well periodically structured, showing reflectance peak in line with the theoretical estimation. On the other hand, the TiO₂-WO₃ core-shell structure improves the electronic and ionic properties of the hybrid samples to improve the charge transportation and ion insertion during the redox reactions, giving enhanced contrast up to 60% in NIR region at only -0.3 V. In addition, the long-term reversibility of the hybrid IO samples has been significantly improved, which can sustain more than 90% of its original contrast after 1200 cycles. The structure of the hybrid system may be the main factor of this improvement. The low bias applied to the system, that may prevent the over-intercalation, could also contribute to it. In conclusion, based on the obtained results, the novel TiO₂-WO₃ core-shell IO structure has great potential in smart window applications, especially for the thermal management.

Conflicts of interest

There are no conflicts to declare.

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