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<th><strong>Journal:</strong></th>
<th><em>CrystEngComm</em></th>
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<td><strong>Manuscript ID:</strong></td>
<td>CE-ART-03-2014-000430.R1</td>
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<td><strong>Article Type:</strong></td>
<td>Paper</td>
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<tr>
<td><strong>Date Submitted by the Author:</strong></td>
<td>25-Mar-2014</td>
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Facile Synthesis of One-Dimensional Crystalline/Amorphous Tungsten Oxide Core/Shell Heterostructures with Balanced Electrochromic Properties

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Received (in XXX, XXX) Xth XXXXXXXXXX 201X, Accepted Xth XXXXXXXXXX 201X
First published on the web Xth XXXXXXXXXX 201X
DOI: 10.1039/b000000x

One-dimensional (1D) crystalline/amorphous WO₃ core-shell heterostructures were synthesized by a simple, two-step hydrothermal process. Single-crystalline hexagonal WO₃ (h-WO₃) nanorods with diameters of about 200 nm and lengths of 6-7 µm were obtained in the first step. Amorphous WO₃ (a-WO₃) shells with thicknesses ranging from 8 to 40 nm were grown on the h-WO₃ cores in the second step. The electrochromic properties of the devices based on the a-WO₃/h-WO₃ core-shell heterostructures were measured and compared with those based on the bare a-WO₃ and h-WO₃ nanorods. The optical modulation of coloration/bleaching at λ = 550 nm, is measured to be 44% after coloration at -3.0 V for 180 s and bleaching at +2.0 V for 90 s. The coloration and bleaching times are found to be 41 s and 6 s, respectively, and the coloration efficiency is 82 cm²/C. After cyclic stability tests for 1000 cycles, the transmittance changes comparing with the initial stage at the colored and bleached states are only 2.6 and 3.4 %, respectively. It appears that the h-WO₃/a-WO₃ core/shell heterostructures combine the assets of the constituent phases, and exhibit highly improved and balanced electrochromic properties.

1. Introduction

Since the discovery of the electrochromic effect (EC) in transition metal oxides in the mid-1960s, tungsten oxide (WO₃) has emerged as the most promising electrochromic material for various electrochromic applications, such as energy-saving smart windows, antiglare mirrors, and high contrast displays. Generally, electrochromism can be defined as the electrochemical generation of color in accompaniment with an electron-transfer reaction, and electrochromic materials can be reversibly and persistently switched between two optical states (coloration and bleaching) by applying an external voltage. When a negative electric field is applied, small cations such as H⁺ and Li⁺ in the liquid or solid electrolyte can be intercalated into WO₃ film to reduce WO₃ to MₓWO₃ (M = H⁺, Li⁺) with blue color. Under a positive electric field, the reduced MₓWO₃ can be oxidized and return to original transparent WO₃. The electrochromic performance of WO₃, in terms of optical modulation, coloration/bleaching time, coloration efficiency, and cyclic stability, strongly depends on its nature and structure. In the past decades, most of the studies have been focusing on amorphous WO₃ (a-WO₃) thin films due to their fast coloration/bleaching response and high coloration efficiency. However, a-WO₃ thin films also suffer from poor electrochromic stability due to their poor chemical and structural stabilities. In contrast, crystalline WO₃ (c-WO₃) thin films are much more stable due to their denser structure and slower dissolution rate in electrolytes, yet exhibit the drawbacks of relatively lower charge density, poor coloration efficiency, and slower switching response. Developing an electrochromatic material with balanced electrochromic properties has become a major target pursued by researchers. Antonia et al. proposed an amorphous/crystalline WO₃ double layer and reported that this double layer shows a faster coloration response and a higher transmittance asymptotic value for the bleaching phase than the amorphous or crystalline single layer. The improvements of response time, coloration efficiency, and electrochromic stability were also observed in various nanocrystalline and nanoporous crystalline WO₃ films. One-dimensional (1D) tungsten oxide nanostructures, such as nanorods, nanowires, and nanotubes, are expected to be able to further improve the performance of EC devices by increasing the active surfaces in the electrochromic process due to their large specific surface areas. Recently, 1D WO₃ nanostructures with various crystalline structures have been synthesized using physical and chemical approaches, and the integrated electrochromic properties of the assembled WO₃ nanoparticle films were also reported. Liao et al. synthesized monoclinic W₁₅O₄⁹ nanowires by a thermal evaporation process and prepared an EC device adopting the W₁₅O₄⁹ nanowires as the electrochromic layer. The as-fabricated EC device demonstrated a maximum optical contrast of 34.5% at λ = 700 nm, and could be cycled up to 1000 cycles. Gu et al. prepared hexagonal WO₃ (h-WO₃) nanowires by a simple hydrothermal method without any templates and catalysts. The as-prepared h-WO₃ nanowires when used as the anodic material of a Li-ion battery delivered charge and discharge capacities of 165 and 218 mAhg⁻¹, respectively, implying large promotion of reaction reversibility of Li intercalation/extraction in h-WO₃ nanowires. Wang et al. and Szilágyi et al. also synthesized uniform crystalline WO₃ nanorods using a hydrothermal process, and demonstrated that the as-synthesized crystalline WO₃...
nanorods exhibit high electrochromic stability and comparable color display, contrast, and coloration/bleaching response. Although 1D crystalline WO$_3$ nanostructures demonstrated improvement in the electrochromic stability, further improvements in response time and coloration efficiency of EC devices are still a big challenge. Park et al. developed a sub-5 nm thick tungsten oxide nanorod-based electrochemical system by a colloidal approach and achieved highly improved response time and color efficiency. It is believed that well-defined nm-thick crystalline metal oxide materials, with lots of amorphous surface areas should be good candidates for further improving the performance of EC devices. Accordingly, 1D nanoscale heterostructures comprised of amorphous and crystalline WO$_3$ could be expected to demonstrate better electrochromic performance than reported 1D crystalline WO$_3$ nanostructures. In this work, we synthesized 1D crystalline/amorphous WO$_3$ core-shell heterostructures using a simple, two-step hydrothermal method. EC devices based on the as-grown 1D crystalline/amorphous WO$_3$ core-shell heterostructures were fabricated, and their electrochromic properties were measured and compared with those obtained from devices based on bare crystalline or amorphous WO$_3$ nanorods. We also discussed the possible reasons behind the highly improved and balanced electrochromic properties of our 1D crystalline/amorphous WO$_3$ core-shell heterostructures.

2. Experimental

1D crystalline/amorphous WO$_3$ core-shell heterostructures were synthesized using a simple, two-step hydrothermal process. For the crystalline WO$_3$ core nanostructures, an aqueous solution was prepared by dissolving 0.2 g of Na$_2$WO$_4$ and 0.1 g of Na$_2$SO$_4$ in 7 ml of deionized water, and then 1M HCl was slowly dropped into the solution with stirring until the pH value of the solution reached 2.0. The precursor solution, contained in a Teflon-lined stainless steel autoclave, was kept at a constant temperature of 180 °C for 24h without stirring or shaking. Afterwards, the autoclave was cooled to room temperature, and the resultant products were subsequently washed with deionized water and dried naturally in the air. For the thin amorphous WO$_3$ shells, the preparation of the precursor solution was similar to that for single-crystalline WO$_3$ core nanostructures, except that 1.0 g of Na$_2$WO$_4$ and 0.8 g of Na$_2$SO$_4$ were dissolved in 20 ml of deionized water. The precursor solution, mixed with 0.01 g of previously synthesized crystalline WO$_3$ core nanostructures, was introduced in a closed Pyrex bottle with an autoclavable screw cap. The bottle was then bathed in 90 °C water, heated and stirred by a heating magnetic stirrer for 6 h. The resultant products were washed with deionized water and dried naturally in the air. For the purpose of comparison, amorphous WO$_3$ nanorods were also prepared by a similar hydrothermal process. The precursor solution, contained in a Teflon-lined stainless steel autoclave was the same as that for amorphous WO$_3$ shells. The autoclave was heated to 110 °C for 24h. Typical FESEM and TEM bright-field images of the as-grown amorphous WO$_3$ nanorods are shown in figures S1(a) and (b). The highly dispersed selected area electron diffraction (SAED) patterns confirm that the as-grown nanorods are of a completely amorphous state. For the fabrication of EC devices, bare amorphous and crystalline WO$_3$ nanorods, as well as crystalline/amorphous WO$_3$ core-shell heterostructures were dispersed in methanol, respectively, to form a suspension with a WO$_3$ concentration of 0.03 g/l. Then 0.5 ml of suspension was dropped onto a clean ITO glass with a bare area of 1 cm x 1 cm bonded by Scotch tapes, and dried at room temperature to form a transparent film. A mixture of 1 M LiClO$_4$ with 1% UV resin was then dropped onto the WO$_3$ transparent film on the ITO glass, to act as a pure ion conductor (i.e. electrolyte). The half-cell was covered by another ITO glass and UV cured for 12h to harden the polymer electrolyte. Epoxy resin was used to seal the edge of the EC device to provide more mechanical strength, and reduce the absorption of moisture from the atmosphere. The morphologies and crystalline structures of the as-synthesized products were examined and characterized using field-emission scanning electron microscopy (FESEM, JSM-6700), X-ray powder diffractometer (PANalytical X’Pert PRO) using Cu $K_α$ ($\lambda = 0.15405 \text{ nm}$) radiation, and high-resolution transmission electron microscope (HRTEM, JEM-2100) using an acceleration voltage of 200 kV. The electrochemical measurements were carried out by a three-electrode system using 1M LiClO$_4$ with 1% UV resin as the supporting electrolyte, platinum (Pt) wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. In situ coloration/bleaching switching characteristics of the as-fabricated EC devices were recorded by monitoring the variation in transmittance at a wavelength of 550 nm using a SHIMADZU UV-VIS spectrophotometer (UV-1601PC). The coloration and bleaching potentials were kept constant at -3.0 V and +1.5 V, respectively, using a programmable potentiostat. It should be noted that the transmittance measurements were conducted by inserting the EC devices into the standard sample compartment and no reference sample was inserted into the reference side.

3. Results and Discussion

Fig. 1(a) shows a typical FESEM image of the as-synthesized products prepared in the first step. TLarge-scale and uniform rod-like nanostructures (nanorods) with diameters of 150-200 nm and lengths of 6-7 $\mu$m were obtained. As we closely examined the morphologies of the as-synthesized nanorods (shown in the inset of Fig. 1(a)), it can be seen that these nanorods have flat tip ends and are enclosed by numerous nanostrips. The representative XRD diffraction patterns of the nanorods are shown in Fig. 1(b). All of the diffraction peaks can be readily indexed to the hexagonal WO$_3$ ($h$-WO$_3$) phase with lattice constants of $a = 7.32 \text{ Å}$ and $c = 7.67 \text{ Å}$, which agrees well with the reported value ($a = 7.324 \text{ Å}$, $c = 7.668 \text{ Å}$) from the JCPDS card (No. 85-2460). No other tungsten oxide phases and tungsten oxide hydrates (WO$_3$·xH$_2$O) were detected, indicating that pure $h$-WO$_3$ nanorods were obtained in the first step. Fig. 1(c) shows a representative TEM bright-field image and the SAED patterns of a single $h$-WO$_3$ nanorod. It is clear that the as-synthesized $h$-WO$_3$ nanorod has a fairly uniform diameter along almost its entire length. The SAED patterns can also be perfectly indexed to $h$-WO$_3$, and the growth direction of the nanorod is determined to be along the [0001] direction (c-axis). Regular diffraction spots support that the as-synthesized $h$-WO$_3$ nanorods are single crystalline. It is known that WO$_3$ can crystallize into several crystalline structures.
Among them, hexagonal WO$_3$ is of particular interest for electrochromic applications, because its tunnel structure makes it act as an ideal intercalation host for obtaining hexagonal tungsten borazines M$_x$WO$_3$. Normally h-WO$_3$ is a metastable phase, and will transform into monoclinic WO$_3$ phase at higher temperatures. The formation of the hexagonal WO$_3$ nanorods in this work can be attributed to the presence of Na$^+$ ions, which stabilize the hexagonal structure by locating in the hexagonal channels to block the thermodynamically favored hexagonal-to-monoclinic transformation. It is also believed that the capping action of Na$^+$ ions is responsible for the preferential growth of h-WO$_3$ nanorods along the c-axis.

After the synthesis of crystalline h-WO$_3$ nanorod cores, amorphous WO$_x$ shells were subsequently grown onto the cores by another hydrothermal process in the second step. Fig. 2(a) shows a typical FESEM image of the resultant h-WO$_3$/a-WO$_x$ core/shell nanostructures. It can be seen that the morphologies of the nanostructures remained a rod-like shape, indicating that conformal a-WO$_x$ shells have been grown on the surfaces of the h-WO$_3$ nanorods. Figs. 2(b) and 2(c) show the representative TEM and HRTEM images of a single h-WO$_3$/a-WO$_x$ core/shell nanorod, respectively. Clearly, a thin layer of a-WO$_x$ shell with a thickness of about 8 nm, has been uniformly grown on the single-crystalline h-WO$_3$ cored nanorod to form the crystalline/amorphous WO$_3$ core/shell heterostructure. The lattice spacing of 0.39 nm of adjacent lattice planes in the h-WO$_3$ cored nanorod,
corresponds to the d-spacing of (0001) planes. This confirms again that the \( h \)-\( \text{WO}_3 \) nanorods grow along the c-axis. It should be noted that the thickness of the \( a \)-\( \text{WO}_3 \) shell can be controlled by the synthesis time in the second step. As the synthesis time was increased to 12 and 24 h, the average thickness of the \( a \)-\( \text{WO}_3 \) shell increased to ~15 and 40 nm, respectively.

As mentioned earlier, the performance of an EC device is usually evaluated by the metrics of optical modulation, coloration/bleaching response time, coloration efficiency, as well as cyclic stability. Fig. 3 shows the in situ coloration/bleaching switching responses of the EC devices based on the \( a \)-\( \text{WO}_3 \) and crystalline \( h \)-\( \text{WO}_3 \) nanorods, and \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures, by applying a coloration voltage of \(-3.0 \text{ V} \) for 180 s and a bleaching voltage of \(+1.5 \text{ V} \) for 90 s. It can be seen that the transmittance at \( \lambda = 550 \text{ nm} \) for \( a \)-\( \text{WO}_3 \) and crystalline \( h \)-\( \text{WO}_3 \) nanorods, and \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures dropped from 77, 80, and 78 % to 26, 45, and 32 %, respectively, after applying a coloration voltage of \(-3.0 \text{ V} \). The transmittance then returned to 71, 71, and 76 %, respectively, after applying a bleaching voltage of \(+1.5 \text{ V} \). The \( a \)-\( \text{WO}_3 \) nanorods could reach the deepest coloration level, while the \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures exhibited the highest transmittance asymptotic value for the bleaching phase. Moreover, the EC devices based on \( a \)-\( \text{WO}_3 \) nanorods and \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures exhibited similar optical modulations of 45 and 44 %, respectively, which are much higher than that of 25% for the device based on the crystalline \( h \)-\( \text{WO}_3 \) nanorods. Here, the coloration and bleaching times were defined as the time required for 70% changes in optical modulation. For coloration, the response time for \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures (41 s) is slightly longer than that for \( a \)-\( \text{WO}_3 \) nanorods (39 s), but much shorter than crystalline \( h \)-\( \text{WO}_3 \) nanorods (65 s). For bleaching, all of the devices demonstrated a fast response time of only 6 s. The coloring response times were much longer than bleaching response times, because the conductivity of bleached-state \( \text{WO}_3 \) is slower than that of colored-state \( \text{LiWO}_3 \). The optical modulation and coloration and bleaching response times of \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures are similar to those of \( a \)-\( \text{WO}_3 \) nanorods, but are much superior to those of crystalline \( h \)-\( \text{WO}_3 \) nanorods.

It is well-known that the coloration/bleaching switching of \( \text{WO}_3 \) in \( \text{Li}^+ \) electrolytes, is due to the intercalation/deintercalation of electrons and charge-balancing \( \text{Li}^+ \) ions. In order to explore the \( \text{Li}^+ \) ion storage capacities of \( a \)-\( \text{WO}_3 \) nanorods, crystalline \( h \)-\( \text{WO}_3 \) nanorods, and \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures, chronoamperometry measurements were carried out, and the current density responses with time were recorded when a cycling pulse potential was applied between \(-3.0 \text{ V} \) and \(+1.5 \text{ V} \), as shown in Fig. 4(a). The integration of current density with time extracted from coloration parts, representing cathodic charge density or ion storage capacity, is indicative of the amount of \( \text{Li}^+ \) ions incorporated into the electrochromic layer during coloration. The cathodic charge density for maximum contrast for \( h \)-\( \text{WO}_3/a \)-\( \text{WO}_3 \) core/shell heterostructures was calculated to be about 8.0 mC cm\(^{-2}\), which is slightly higher than that for crystalline \( h \)-\( \text{WO}_3 \) nanorods (7.7 mC cm\(^{-2}\)), but is much lower than that for \( a \)-\( \text{WO}_3 \) nanorods (9.5 mC cm\(^{-2}\)). For practical EC applications, lower charge insertion and extraction usually implies that a long-term.
Another important parameter to characterize the performance of an electrochromic material, is its coloration efficiency (CE), which can be expressed as:

\[ CE = \frac{\Delta OD}{Q} = \log\left(\frac{T_h}{T_a}\right)/Q \]  

where \(\Delta OD\) is the change in optical density (OD), Q is the charge density (mC cm\(^{-2}\)), and \(T_h\) and \(T_a\) are the transmittance in bleached and colored states, respectively. High CE means that the EC values for our core/shell heterostructures, and crystalline \(h\)-WO\(_3\) nanorods were determined to be 102, 82, and 43 cm\(^{-2}\)/C, respectively. It indicates that the \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures can preserve a relatively high CE, which is about 80% of the \(\alpha\)-WO\(_3\) nanorods, and almost twice of that of the crystalline \(h\)-WO\(_3\) nanorods. It should be noted that the CE values for our \(\alpha\)-WO\(_3\) nanorods and \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures are easily comparable with the state-of-the-art of about 84 cm\(^{-2}\)/C, for nanostructured WO\(_3\) films transformed from sol-gel derived amorphous WO\(_3\) films reported by Deepa et al.\(^5\)

Based on the experimental results, it can be confirmed that \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures inherit all the advantageous electrochromic properties from \(\alpha\)-WO\(_3\), such as a large optical modulation, short coloration and bleaching response times, and high coloration efficiency. However, \(\alpha\)-WO\(_3\) films synthesized from wet-chemical methods usually suffer from poor long-term durability due to their poor chemical and structural stabilities. To evaluate the capability of our \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures for use in practical EC device, a series of cyclic stability tests were conducted. Fig. 5 shows the transmittance variations as a function of coloration-bleaching cycle for EC devices based on \(\alpha\)-WO\(_3\) and \(h\)-WO\(_3\) nanorods, and \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures. It can be seen that for all three types of EC devices, the transmittance at the bleached state showed abrupt drops after 10 cycles, and then decreased gradually, while the transmittance at colored state increased gradually. After 1000 cycles, the transmittance deviations for the \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures at bleached and colored states, compared with values measured after 10 cycles, were found to be 2.6 and 3.4%, respectively. This resulted in a 6.0% degradation of the optical modulation. Meanwhile, the transmittance deviations at bleached and colored states, and degradation of optical modulation were found to be 6.8, 6.3, and 13.1%, respectively, for \(\alpha\)-WO\(_3\) nanorods, and 3.5, 1.4, and 4.9%, respectively, for \(h\)-WO\(_3\) nanorods. It is evident that \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures also show comparable electrochromic stability with crystalline \(h\)-WO\(_3\) nanorods, which agrees with the previous prediction based on cathodic charge density for maximum contrast.

Table 1 summaries the optical modulations, cathodic charge densities, coloration and bleaching times, coloration efficiencies, and degradation of optical modulation after 1000 cycles for EC devices based on \(\alpha\)-WO\(_3\) and \(h\)-WO\(_3\) nanorods and \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures. Without a doubt, \(h\)-WO\(_3/\alpha\)-WO\(_3\) core/shell heterostructures combine assets of the constituent phases, which are large optical modulation, fast coloration/bleaching responses, and high coloration efficiency from \(\alpha\)-WO\(_3\) and good cyclic stability from crystalline \(h\)-WO\(_3\).

It has been reported that the electrochromic coloration of tungsten oxide upon \(\text{H}^+\) or \(\text{Li}^+\) ion insertion is influenced by crystallinity, microstructure, and oxygen deficiency of the film.\(^{20,21}\) For the amorphous case, the coloration mechanism resulting from injection of positive ions and electrons is usually attributed to small polaron absorption proposed by Schirmer et al.\(^{22}\) The inserted electrons are localized in the W\(^5+\) sites and polarize their surroundings to induce lattice vibrations.\(^{23,24}\) The inserted ions (M\(^+\)) either lie in the centers of perovskite units, or are chemically bonded with the interstitial oxygen atoms. Consequently, they are spatially separated from the electrons and this spatial separation creates a polaron.\(^{25}\) The incident photons are absorbed by these small polarons that can hop from one site to another between two adjacent sites of tungsten W\(^5+\) and W\(^6+\), where transfer of electrons between sites denoted as \(i\) and \(j\) can be schematically written as W\(_i\)\(^{5+}\) + W\(_j\)\(^{6+}\) + photon \(\rightarrow\) W\(_i\)\(^{6+}\) + W\(_j\)\(^{5+}\).\(^3\) For the crystalline case, there is no spatial separation between inserted ions and electrons, and the coloration mechanism is attributed to a Drude-mode-like free electron absorption with a behavior very similar to a heavily doped semiconductor with ionized impurities.\(^3,23\) As cations and electrons are inserted into crystalline tungsten oxide films, the electrons enter extended states in the WO\(_3\) band structure and experience scattering by impurities and/or phonons, rather than enter localized states as in amorphous
tungsten oxide. This makes the material slightly metallic with a small increase in absorption across the spectrum, and a slight increase in reflection in the infrared. Therefore, crystalline tungsten oxide films tend to have a smaller degree of color change compared to their amorphous counterparts. This can explain why $a$-WO$_3$ nanorods exhibit a much higher optical modulation than $h$-WO$_3$ nanorods. Similar results have been reported by other researchers. For the case of $h$-WO$_3$/a-WO$_3$ core/shell heterostructures, the coloration mechanism might be attributed to the combined effect resulting from both small polaron absorption and Drude-like free electron scattering. Fig. 6 schematically illustrates possible working principle of EC device based on $h$-WO$_3$/a-WO$_3$ core/shell heterostructures. The thickness of $a$-WO$_3$ shells are only about 8 nm, this cannot prevent Li$^+$ ions from penetrating into the underlying crystalline $h$-WO$_3$ cores. It is then reasonable to expect that the insertion of Li$^+$ ions and electrons into $h$-WO$_3$/a-WO$_3$ core/shell heterostructures, will form small polarons in the $a$-WO$_3$ shells, and free electrons in crystalline $h$-WO$_3$ cores. It is also known that the kinetics of ion intercalation can be provided by a diffusion constant, which depends on ionic species, relative film density, intercalation level, temperature, and so on. In general, Li$^+$ ion diffusion in amorphous tungsten oxide is much faster than that in crystalline tungsten oxide, and the diffusion coefficient of Li$^+$ ion will drop rapidly as intercalation level increases. Moreover, it has been reported that the volumetric charge density for a fully tinted WO$_3$ is $68 \text{ mC/cm}^2\mu\text{m}^2$, and the extinction coefficient $k$ of tinted WO$_3$ at $\lambda = 550$ nm increases from 0 to 0.19 when injected charge density increases from 0 (clear state) to $68 \text{ mC/cm}^2\mu\text{m}$ (fully tinted state). During coloration, the Li$^+$ intercalation level in $a$-WO$_3$ shells will increase rapidly once a coloration voltage is applied, and shortly develop into the fully tinted state, while the intercalation level in the crystalline $h$-WO$_3$ cores will gradually increase. After a short time, the volumetric charge density will reach $68 \text{ mC/cm}^2\mu\text{m}$ in $a$-WO$_3$ shell and then decrease abruptly with distance from $a$-WO$_3$/h-WO$_3$ interface, as shown in Fig. 6(b). As a result, incident photons will be absorbed mainly by small polarons in $a$-WO$_3$ shells and partially by free electrons in crystalline $h$-WO$_3$ cores, leading to a substantial decrease in transmittance. For bleaching, it is known that the kinetics is governed by a field-driven space-charge limited diffusion current of counter-ions in M$_x$WO$_3$ next to the electrolyte. Since most of the intercalated Li$^+$ ions are accumulated in $a$-WO$_3$ shells, Li$^+$ deintercalation will occur promptly in $h$-WO$_3$/a-WO$_3$ core/shell heterostructures once a bleaching voltage is applied, as shown in Fig. 6(d). This leaves a trace amount of Li$^+$ ions in $a$-WO$_3$ shells and near $a$-WO$_3$/h-WO$_3$ interfaces. Apparently, the $a$-WO$_3$ shells should play a dominant role during coloration and bleaching processes. As our $h$-WO$_3$/a-WO$_3$ core/shell heterostructures have large specific surface areas, contribution from the $a$-WO$_3$ shells will be amplified so that the integrated EC device shows similar optical modulation, coloration/bleaching responses, and coloration efficiency to devices based on $a$-WO$_3$ nanorods. Regarding the durability, it is generally accepted that amorphous tungsten oxides synthesized from wet-chemical methods, suffer from mechanical deterioration and therefore have relatively poor long-term durability. On the other hand, crystalline tungsten oxides with much denser structures have highly improved durability during cycling. Recently, Lin et al. reported that disordered porous semi-crystalline WO$_3$ films composed of WO$_3$ crystals surrounded by amorphous WO$_3$ layers, demonstrate fast switching kinetics and excellent durability. They suggested that the structural modification (i.e. densification and/or crystallization) occurring in WO$_3$ during extended durability test should be responsible for the improvement in durability. Since the $h$-WO$_3$/a-WO$_3$ core/shell heterostructures can be considered to be analogous to their disordered porous semi-crystalline WO$_3$ films, we believe that a similar structural modification is occurring in $a$-WO$_3$ shells during cyclic stability tests, which is responsible for the good cyclic stability for $h$-WO$_3$/a-WO$_3$ core/shell heterostructures. Similar enhancements in electrochromic properties have been achieved in electrochromic thin films consisted of monoclinic WO$_3$ nanorods, after post-treated with ozone exposure and thermal annealing. The improvements in optical modulation, coloration efficiency, switching speed, and charge/discharge reversibility are attributed to an ozone induced surface amorphization, meaning that thin amorphous layers form on surfaces of the monoclinic WO$_3$ nanorods after ozone exposure. The resultant tungsten oxide nanostructures are analogous to our $h$-WO$_3$/a-WO$_3$ core/shell heterostructures.

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4. Conclusions

One-dimensional $h$-WO$_3$/α-WO$_3$ core/shell heterostructures have been successfully synthesized using a facile two-step hydrothermal method, and the thickness of the α-WO$_3$ shell can be controlled by the synthesis time in the second step. The $h$-WO$_3$/α-WO$_3$ core/shell heterostructures combine the assets of the constituent phases, and exhibit highly improved and balanced electrochromic properties. The large optical modulation, fast coloration/bleaching responses, and high coloration efficiency are attributed to the rapid Li$^+$/ion intercalation/deintercalation through the α-WO$_3$ shells, and high specific surface areas of the nanoscale core/shell heterostructures. While good cyclic stability may be attributed to the structural modification (i.e. densification and/or crystallization) occurring in the α-WO$_3$ shells during cyclic stability tests.

Acknowledgement

This work was sponsored mainly by the National Science Council of the Republic of China under Grant No. NSC100-2221-E005-046 and supported in part by the Ministry of Education under the ATU plan. The authors also thank Edward Young for reviewing the manuscript.

Notes and references

2. S. K. Deb, Appl. Optics 1969, 8, S1, 192.
Supplementary Information

Figure S1 Typical (a) FESEM and (b) TEM bright-field images of the as-grown amorphous WO$_x$ nanorods.
The $h$-WO$_3$/a-WO$_x$ core/shell heterostructures combine the assets of the constituent phases, and exhibit highly improved and balanced electrochromic properties.
Responses to Reviewers’ comments
(CE-ART-03-2014-000430)

First of all, we would like to thank the reviewers for their helpful comments. Based upon the reviewers’ comments, we have made several revisions in response to each reviewer. The followings are our responses to the reviewers’ comments:

**Referee 1**

**Comments:** The article presents a two-step hydrothermal route to synthesize h-WO3/a-WO3 core/shell 1D heterostructure for electrochromic device application. H-WO3 nanorod with a thin a-WO3 shell shows high optical modulation and coloration efficiency which is very close to amorphous tungsten oxide and its cyclic stability is almost as good as crystalline WO3. These good optical results come from the amorphous tungsten oxide shell with large surface area, while the high stability is ascribed to the structure modification of a-WO3 on top of h-WO3. It is an interesting paper. But there are a few comments I have before considering the publication in CrystEngComm.

1. The preparation of amorphous tungsten oxide (nanorod) is not described in the manuscript. It would be better to have some characterization comparison among three different materials.
2. Have authors checked the effect of the amorphous tungsten oxide thickness on electrochromic performance?
3. In Fig. 6, a possible working principle of EC device is proposed. In the Figure, the charge density is marked as 68 mC/cm2, but it is 68 mC/(cm2.um) volumetric charge density by citing other references in the main text. Why there is a discrepancy? Any additional experimental support for that number?
4. Authors should check the manuscript for typos, such as caions in ln 110 of p.5.

**Responses:**

(1) We have added the description for the preparation of amorphous WO3 nanorods in the experimental procedure. Typical FESEM and TEM images of the as-synthesized a-WO3 nanorods are also added in the supplement materials (figures S1(a) and (b)). To make it clear, we add the following descrit in the main text:

“For the purpose of comparison, amorphous WO₃ nanorods were also prepared by a similar hydrothermal process. The precursor solution, contained in a Teflon-lined stainless steel autoclave was the same as that for amorphous WO₃ shells. The autoclave was heated to 110 °C for 24h. Typical FESEM and TEM
bright-field images of the as-grown amorphous WO₃ nanorods are shown in figures S1(a) and (b). The highly dispersed selected area electron diffraction (SAED) patterns confirm that the as-grown nanorods are of a completely amorphous state.” [Please see Page 2, lines 48-57]

(2) Undoubtedly, the a-WO₃ thickness plays an important role on the electrochromic performance of EC device based on h-WO₃/a-WO₃ core/shell nanorods. Roughly, the behavior of our core-shell nanorods can be considered to be the sum of the contribution of the crystalline and the amorphous parts. In this work, we expected that the core/shell nanorods with about 8 nm-thick a-WO₃ shells should exhibit a more balanced electrochromic performance than those with ~15 and 40 nm-thick a-WO₃ shells based on the cyclic stability tests since the core/shell nanorods with 15 nm-thick a-WO₃ shells showed a larger degradation of the optical modulation after 100 cycles. We believe that there should be an optimal thickness combination of the crystalline core and the amorphous shell that has an optimal electrochromic performance. Further investigation is undergoing right now. We try to control the size of crystalline cores to a smaller regime (for example, < 50 nm) with amorphous shells of 5-10 nm in thickness, and study the effect of thicknesses of amorphous and crystalline parts on the electrochromic performance of EC device.

(3) We have changed the title and unit to volumetric charge density (68 mC/cm² µm) in Fig. 6. Rubin et al. [ref. 31] characterized WO₃ films that are colored by injection of lithium (Li), not only in the extreme bleached and colored states, but also a range of intermediate charge states. Coloration states corresponding to injected volumetric charge densities of 11, 23, 36, 50, and 68 mC/(cm².µm) were created by inserting Li into the WO₃ films in a liquid cell to produce LiₓW₁₋ₓO₃. These values were obtained from the areal charge densities determined directly by electrical charge measurements and the thickness of each individual film. In their work, the use of the volumetric charge density as the parameter to normalize for thickness is deliberate so that the extinction coefficient of WO₃ films at a given injected charge density should not depend on thickness or mass density. The volumetric charge density for a fully tinted WO₃ is 68 mC/cm² µm. This data was also referred by Lim et al. for modeling of optical and energy performance of tungsten-oxide-based electrochromic windows including their intermediate state [S. H. N. Lim, J. Isidorsson, L. Sun, B. L. Kwak, A. Anders, Sol. Energy Mater. Sol. Cells 2013, 108, 129.]. Neither additional experimental results can be found in the literatures to support that number, nor can we conduct necessary experiment to prove that number.

(4) We have carefully checked the manuscript and some typographical errors have been corrected.
Referee 2

Comments: This manuscript shows persuasive experimental data and analysis to demonstrate a novel alpha-WOx/h-WO3 heterostructures with improved electrochromism performance. The proposed nanostructures employ the advantages of both crystalline h-WO3 and amorphous alpha-WOx to achieve larger optical modulation, faster coloration/bleaching responses, higher coloration efficiency, and better cyclic stability. However, several places were left for improvement and modification:

1) Grammar or typos: e.g., P2, Line 110 'interested' should be 'interesting'; P4, Line 31, 'shower' should be 'slower'.
2) In experiment description, how did you grow alpha-WOx was missing.
3) P2, were the 3 devices, i.e., device with hetero-structures, device with pure h-WO3, and device with alpha-WOx fabricated with same specs, e.g., same weight, same size, or same solution density? This is important since all your data is comparison of these 3 devices.
4) P2, Line 64, you said the morphologies and crystalline structure analysis was conducted on 'resultant products', that's make no sense since the devices were sandwiched with glass and sealed.
5) P3, Line 12-14, for 'capping action of Na ion' sentence, either reference or further statement is needed.
6) P3, Line 19-22, Fig. 2(a) shows uniform alpha-WOx shell was grown on h-WO3, however, Fig. 2(a) can barely tell this information, but Fig. (b) does show clear detailed morphology.
7) P4, Line 10-14, you discussed the transmission data. What's the reference for this measurement, air, or single/double FTO glass?
8) Fig. 4(b) for OD measurement data, it is a average across the surface or several points, or just single point data?
9) Please further polish your English and make your statement more concise.

Responses:

(1) We have carefully checked the manuscript and some grammatical and typographical errors have been corrected.
(2) We have added the experimental procedure for the growth of a-WOx nanorods.

The following description has been added in the main text:

“For the purpose of comparison, amorphous WOx nanorods were also prepared by a similar hydrothermal process. The precursor solution, contained in a Teflon-lined stainless steel autoclave was the same as that for amorphous WOx..."
shells. The autoclave was heated to 110 °C for 24h. Typical FESEM and TEM bright-field images of the as-grown amorphous WO₃ nanorods are shown in figures S1(a) and (b). The highly dispersed selected area electron diffraction (SAED) patterns confirm that the as-grown nanorods are of a completely amorphous state.” [Please see Page 2, lines 48-57]

(3) All the three EC devices with a-WOₓ, h-WO₃, and h-WO₃/a-WOₓ core/shell nanorods are fabricated with the same specifications. They have same size, same weight, and same solution concentration. To make it clear, we have modified the original descript to “For the fabrication of EC devices, bare amorphous and crystalline WO₃ nanorods, as well as crystalline/amorphous WO₃ core-shell heterostructures were dispersed in methanol, respectively, to form a suspension with a WO₃ concentration of 0.03 g/l.” [Please see Page 2, lines 57-61]

(4) The resultant products are the as-synthesized products obtained from the hydrothermal processes. To make it clear, we have changed “the resultant products” to “the as-synthesized products”. [Please see Page 2, line 71]

(5) We have added the reference, which is the same as ref. 16. [Please see Page 3, line 20]

(6) We have changed “uniform” to “conformal”. [Please see Page 3, line 35]

(7) The transmittance measurement of the EC device is conducted by inserting our samples into the standard sample compartment and no sample is inserted into the reference side. To make it clear, we have modified the original descript to “In situ coloration/bleaching switching characteristics of the as-fabricated EC devices were recorded by monitoring the variation in transmittance at a wavelength of 550 nm using a SHIMADZU UV-VIS spectrophotometer (UV-1601PC). The coloration and bleaching potentials were kept constant at -3.0 V and +1.5 V, respectively, using a programmable potentiostat. It should be noted that the transmittance measurements were conducted by inserting the EC devices into the standard sample compartment and no reference sample was inserted into the reference side.” [Please see Page 2, lines 81-90]

(8) \[ \Delta \text{OD} = \log \left( \frac{T_b}{T_c} \right) \] where \( T_b \) and \( T_c \) are the transmittance in the bleached and colored states, respectively. Actually, \( T_b \) and \( T_c \) are obtained from the variations in transmittance of different EC devices during the coloration process (Fig.3). Because our EC device with an active area of 1 cm x 1 cm is fixed by the sample holder and the beam dimensions of the Shimadzu spectrophotometer are 1 mm x 10 mm (WxH) at center of sample compartment, we can only measure the transmittance at the central line of the sample so that the OD data in Fig.4(b) obtained from the in situ coloration/bleaching
switching responses of each EC device in Fig.3 is just single point data. Actually, we prepared several samples for each EC device and recorded their in situ coloration/bleaching switching responses. The data in Figs. 3 and 4 are the representative data.

(9) We have carefully checked the manuscript and some typographical errors have been corrected. In addition, the manuscript has also been revised by a native speaker to polish the English and make our statement more concise.
List of changes

(CE-ART-03-2014-000430)

<table>
<thead>
<tr>
<th>Page</th>
<th>line</th>
<th>Major changed</th>
<th>Note</th>
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<tr>
<td>2</td>
<td>48~57</td>
<td>For the purpose of comparison, amorphous WO₃ nanorods were also prepared by a similar hydrothermal process. The precursor solution, contained in a Teflon-lined stainless steel autoclave was the same as that for amorphous WO₃ shells. The autoclave was heated to 110 °C for 24h. Typical FESEM and TEM bright-field images of the as-grown amorphous WO₃ nanorods are shown in figures S1(a) and (b). The highly dispersed selected area electron diffraction (SAED) patterns confirm that the as-grown nanorods are of a completely amorphous state.</td>
<td>Added</td>
</tr>
<tr>
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<td>48~51</td>
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<td>Modified</td>
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<tr>
<td>2</td>
<td>71</td>
<td>The morphologies and crystalline structures of the as-synthesized products were examined and characterized …</td>
<td>Modified</td>
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<tr>
<td>2</td>
<td>82~84</td>
<td>In situ coloration/bleaching switching characteristics of the as-fabricated EC devices were recorded by monitoring the variation in transmittance at a wavelength of 550 nm using a SHIMADZU UV-VIS spectrophotometer (UV-1601PC).</td>
<td>Modified</td>
</tr>
<tr>
<td>2</td>
<td>86~90</td>
<td>It should be noted that the transmittance measurements were conducted by inserting the EC devices into the standard sample compartment and no reference sample was inserted into the reference side.</td>
<td>Revised</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>It is also believed that the capping action of Na⁺ ions is responsible for the preferential growth of h-WO₃ nanorods along the c-axis.</td>
<td>Added</td>
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<tr>
<td>3</td>
<td>35</td>
<td>It can be seen that the morphologies of the nanostructures remained a rod-like shape, indicating that conformal a-WO₃ shells have been grown on the surfaces of the h-WO₃ nanorods.</td>
<td>Modified</td>
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<tr>
<td>5</td>
<td>112</td>
<td>As cations and electrons are inserted into crystalline tungsten oxide films, …</td>
<td>Revised</td>
</tr>
<tr>
<td>7</td>
<td>1~25</td>
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