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Crystalline/amorphous tungsten oxide core/shell hierarchical structures and their synergistic effect for optical modulation

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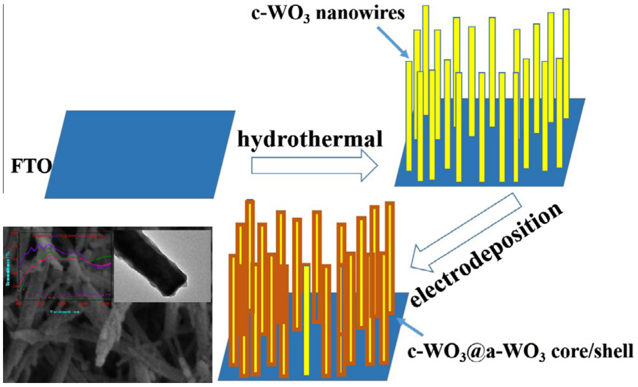
GRAPHICAL ABSTRACT



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ABSTRACT

High-performance electrochromic films with large color contrast and fast switching speed are of great importance for developing advanced smart windows. In this work, crystalline/amorphous WO_3 core/shell (c-WO_3@a-WO_3) nanowire arrays rationally are synthesized by combining hydrothermal and electrodeposition methods. The 1D c-WO_3@a-WO_3 core/shell hierarchical structures show a synergistic effect for the enhancement of optical modulation, especially in the infrared (IR) region. By optimizing the electrodeposition time of 400 s, the core/shell array exhibits a significant optical modulation (70.3% at 750 nm, 42.0% at 2000 nm and 51.4% at 10 μm), fast switching speed (3.5 s and 4.8 s), high coloration efficiency (43.2 $cm^2\ C^{-1}$ at 750 nm) and excellent cycling performance (68.5% after 3000 cycles). The crystalline/amorphous nanostructured film can provide an alternative way for developing high-performance electrochromic materials.

1. Introduction

Smart windows have the ability of modulating sunlight transmission upon a small external voltage based on the electrochromic phenomenon. They have a wide application in green buildings, vehicles and automobiles [1–10]. Currently, heavy research works

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have been focused on the optical changes in the visible spectrum, but less attention has been paid to changes in the infrared (IR) region [11–14]. It is well known that heat effect is mainly caused by the IR spectrum of sunshine. Rational control and use of IR energy is an important issue for constructing green building. Fortunately, electro chromic films are endowed with such a gift to modulate the light and heat flux through them [4,7,15–17]. To date a number of active materials (such as WO_3, Co_3O_4, MoO_3, V_2O_5, Nb_2O_5, NiO and TiO_2) have been explored as electrochromic layers [8,10,11,18–30]. Of these candidates, WO_3 has been considered as one of the most promising inorganic electrochromic materials due to its tender color change and large color contrast as well as facile synthesis [8,12,19,21]. Albeit these advantages, the electrochromic performance of dense WO_3 film is still not satisfactory because of its low diffusion coefficient and long diffusion length for ion insertion [31–33].

The electrochromic performance of WO_3 strongly depends on its crystal structure and architecture [34–36]. In the past decades, most of the studies have been focused on amorphous WO_3 (a-WO_3) thin films for their high coloration efficiency [37–39]. However, a-WO_3 thin films suffer from poor electrochromic stability due to their unstable chemical and structural properties. In contrast, crystalline WO_3 (c-WO_3) thin films are much more stable, but c-WO_3 has relatively low charge density and poor coloration efficiency [32,40,41]. Therefore, developing an WO_3 film with balanced electrochromic properties (both cyclic stability and optical modulation) are highly desirable. For example, Antonaia et al. [42] fabricated an amorphous/crystalline WO_3 with double layer structure, which showed a faster coloration response and a higher transmittance asymptotic value for the bleaching phase than the single amorphous or crystalline layer. Lin et al. [43] reported disordered porous semi-crystalline WO_3 films composed of WO_3 crystals surrounded by amorphous WO_3 layers, which showed fast switching kinetics and excellent durability. All these encouraging results demonstrate that the combination of amorphous and crystalline phase of WO_3 is favorable for the improvement of optical modulation.

Nanoporous structure has been proven as an effective strategy for constructing high-performance electrochrmomic films since this architecture provides fast ion/electron transfer path and large active surface, leading to improved optical modulation and fast response time. Typically, one-dimensional (1D) nanowire is desired for electrochromic application because of its large specific surface area and large porosity. Recently, Her and Chang [44] reported that the 1D crystalline/amorphous WO_3 core/shell structures fabricated by two-step hydrothermal process exhibited enhanced optical modulation. They suggested that the improved electrochromic properties were attributed to the rapid Li^+ ion intercalation/deintercalation into/from the a-WO_x shells, and high specific surface areas of the nanostructures.

Different from the above works, we develop a facile method to fabricate crystalline/amorphous WO_3 core/shell nanowire arrays on FTO glass substrates. Previous works have demonstrated the advantages of using WO_3 nanowires as the core for constructing core/shell nanostructures [45,46]. The electrodeposited amorphous WO_3 shell is intimately coated on the crystalline WO_3 core nanowire forming crystalline/amorphous WO_3 arrays. As electrochromic film electrodes, the optical modulation both in the visible and IR region is thoroughly investigated. The c-WO_3@a-WO_3 core/shell hierarchical structures exhibit fast coloration/ bleaching responses and excellent cyclic stability. The proposed electrode design strategy should potentially be able to extend to prepare other high-performance electrochromic films.

2. Experimental section

2.1. Preparation of WO_3 nanowires

Typically, the FTO-coated glass (2 × 4 cm^2 in size, sheet resistance $R_s = 10\ \Omega$ and surface roughness $R_a = 25$ nm) was washed with acetone, then ethanol, and finally de-ionized water in an ultrasonic bath for 10 min, respectively. A WO_3 sol was deposited on the FTO-coated glass through spin coating according to a literature method [47]. The spin coating process was performed at 3000 rpm for 40 s and repeated 4 times. Subsequently, the WO_3 sol-coated substrates were heated at 400 °C in air for 60 min to obtain the FTO-coated glass with a WO_3 seed layer.

WO_3 nanowire arrays were fabricated by a sulfate-assisted hydrothermal method. Briefly, 3.29 g of $Na_2WO_4{\cdot}2H_2O$ was dissolved in 76 ml of de-ionized water, and then 3 M HCl was added to the aqueous solution to adjust the pH value to 2.0. Afterwards, 3.30 g of $(NH_4)_2SO_4$ was added to the resulting solution to control the morphology of the WO_3 product. After stirring for 1 h, the solution was transferred into a Teflon-lined stainless autoclave. Then the FTO-coated glass with the WO_3 seed layer was placed vertically in the autoclave, and the autoclave was sealed and heated at 190 °C for 4 h. The obtained nanowire array films were washed with de-ionized water three times and dried in a vacuum oven at 60 °C for 12 h.

2.2. Preparation of c-WO_3@a-WO_3 core/shell nanowire arrays

The c-WO_3@a-WO_3 core/shell nanowire arrays were prepared by cathodic electrodepositing an a-WO_3 thin layer onto the surface of WO_3 nanowires. Before the electrodeposition, Na_2WO_4 salt was dissolved in de-ionized water (concentration: 12.5 mM) to form the solution. Then hydrogen peroxide was added to above solution maintaining a concentration ratio of 3 with sodium tungstate, according to the literatures [48,49]. The pH value of the resulting solution was adjusted down to 1.2 by adding perchloric acid. The solution is very stable at room temperature and argon was bubbled for 5 min in the cell before the deposition. The electrodeposition was performed with a CHI660E electrochemical workshop in a three-electrode cell at room temperature with the WO_3 nanowire array-coated FTO glass as the working electrode, an Ag/AgCl as the reference electrode and a platinum foil with a size of 2 × 2 cm^2 as the counter electrode. The electrodeposition was conducted at a potential of −0.7 V (vs. Ag/AgCl) for 200 s, 400 s and 600 s, and corresponding named as c-WO_3@200a-WO_3, c-WO_3@400a-WO_3 and c-WO_3@600a-WO_3, respectively. After the electrodeposition, the samples were thoroughly washed with methanol and water alternately two times, and finally dried in air. An a-WO_3 film on an FTO substrate was also electrodeposited for 400 s with the same parameters for comparison.

2.3. Characterization

The structure and morphology of the films were characterized using X-ray diffraction (XRD, RIGAKU D/MAX 2550/PC with Cu Kα radiation), field emission scanning electron microscopy (FESEM, Hitachi SU-70), transmission electron microscopy (TEM, JEOL 2100F) and X-ray photoelectron spectroscopy (XPS, AXIS UTLTRADLD equipped with a dual Mg Kα–Al Kα anode for photo excitation). The films were scratched from the FTO substrate and re-dispersed in ethanol solution for the TEM analysis. The transmission spectra of these WO_3 films in the fully bleached and fully colored states were measured using a SHIMADZU UV-3600 spectrophotometer in the wavelength range from 400 to 2100 nm. The