



Electrochromic properties of self-assembled nanoparticle multilayer films

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ABSTRACT

Hexagonal tungsten bronze (HTB) nanocrystal and TiO₂ nanoparticles were assembled into thin films by layer-by-layer self-assembly method. HTB nanocrystals were synthesized by hydrothermal route at 155 °C. UV–Vis spectra showed that the HTB/TiO₂ films exhibit a linear increase in film thickness with assembly exposure steps. The electrochromic property of the film was carefully investigated. Cyclic voltammetry indicated that the redox peak was around −0.5 V. The electrochromic contrast, coloration efficiency, switching speed, stability and optical memory were carefully investigated. The films vary from white to blue and finally dark brown. The electrochromic contrast is 63.9% at 633 nm. The coloration efficiency of the films is relatively high. The response time is less than 3 s.

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1. Introduction

In recent years, one of the promising methods to fabricate well-defined thin film is to deposit nanomaterials on substrate [1,2,3]. Many techniques have been developed and studied, such as electrodeposition [4,5], Langmuir–Blodgett technique [6,7], sol–gel chemistry-based deposition [8], templates synthesis [9,10] and layer-by-layer (LBL) assembly. LBL assembly is a convenient and inexpensive approach. By this method, two or more nanomaterials could be assembled into thin films with a precise size on the nanoscale.

Electrochromic (EC) compounds are defined as materials whose optical properties can be reversibly changed by applying an external voltage [11,12]. Film devices with electrochromic property have been widely studied in these years. Many nanomaterials have been used as electrochromic components, such as poly(3,4-ethylenedioxythiophene), polyaniline, polyoxometalate, Prussian blue and so on [13–15]. Some researchers have studied its preparation and properties; however the material's disadvantages, such as short lifetime, long response time, cost-intensive production process and high price, limit its application in devices.

In this paper, we present a convenient way to incorporate hexagonal tungsten bronze (HTB) nanorods and TiO₂ nanoparticles into an ultra thin multilayer film by LBL technique. The color of the [HTB/TiO₂]_n film varies from white, light blue to dark blue and finally dark brown. Its properties of contrast, color range, response time, coloration efficiency and operation potential were developed to meet

the requirements for developing flexible displays and electrochromic devices.

2. Experimental details

2.1. Materials

The Indium Tin Oxide (ITO) coated glass substrates were obtained from the Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. The TiO₂ nanoparticles were purchased from JingYing chemical reagent company, Shanghai. The branched polyethylenimine (PEI), was purchased from Aldrich. The PEI was dissolved in deionized (DI) water. The pH of the PEI solution was adjusted to 7 by diluted HCl aqueous. All other reagents were of reagent grade. UV–Vis spectra were recorded on a 756CRT UV–visible spectrometer. Cyclic voltammetry, double-potential steps and other electric chemistry measurements were undertaken on a CHI 660 electrochemical workstation with conventional three-electrodes: the working electrode, Ag/AgCl and Pt. TEM photographs were gathered on a JEM-2010F TEM (transmission electron microscope) with 100 kV operating voltage.

2.2. Nanoparticle synthesis and dispersion

The HTB nanorods were prepared according to the methodology of Griffith and Luca [16]. Simply, Na₂WO₄ solution (10 g, 1.0 M) was acidified with HCl (1.0 M) within pH range 1.65–1.75. Hydrothermal treatment (155 °C, 30–48 h) of the resultant solution was undertaken in Teflon-lined Parr acid digestion bombs to afford a pale blue-green solid that was washed with deionized water until the pH of the eluant was neutral and then dried to constant weight at 75 °C in air. The TEM

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photographs and XRD patterns of the HTB nanorods are shown in Fig. 1. The XRD patterns indicate that the crystalline structure of the as-synthesized HTB nanorods is tetragonal crystal phase.

2.3. Preparation of the film

The quartz and ITO substrates were cleaned by immersing into a Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7:3$ v/v) for a few minutes, followed by rinsing thoroughly with DI water and drying under nitrogen gas. The HTB suspension was prepared as follows: HTB nanorod was dispersed in DI water. The pH was adjusted to 1.5–2.0 by HCl solution. HTB nanorods absorb the negative ion in the solution and formed a stable hydrosol. The TiO_2 suspension was prepared as follows: commercial TiO_2 was used as the starting material. The TiO_2 nanoparticles were dispersed in DI water. HNO_3 was added as a stabilizer to maintain anatase nanoparticle. The pH values of the TiO_2 suspensions were adjusted to 1.5 by HNO_3 solution. TiO_2 nanoparticles absorb the positive ion in the solution. TEM observations revealed that the suspension contains monodispersed anatase nanoparticle with dimensions of 40–50 nm. Both the HTB nanorods and TiO_2 nanoparticles in suspension have sufficient charges to maintain well dispersed state for LBL [17].

The fabrication of the multilayer film was carried out as follows: the pre-cleaned substrate was exposed to TiO_2 suspension for 10 min. Water rinsing and nitrogen drying steps were performed after the adsorption. Then the coated substrate was immersed in HTB dispersion for 10 min, followed by water rinsing and drying under nitrogen gas. UV-Vis spectroscopy was used after each bilayer deposition to

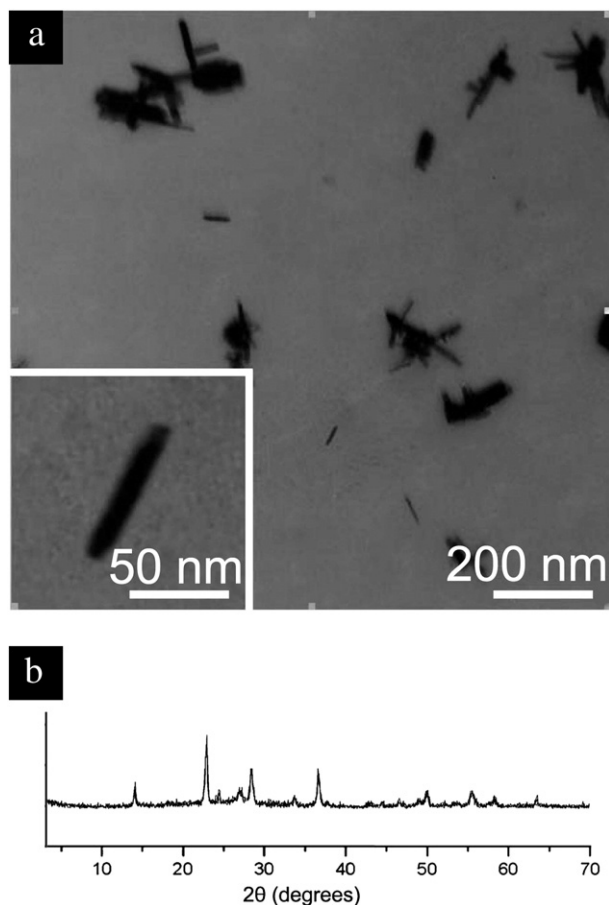


Fig. 1. (a) TEM image of the HTB nanorods; (b) XRD spectrum of as synthesized HTB sample.

monitor the layer-by-layer assembly. Following this process, the layer of the nanoparticle films grew nearly linearly as shown in Fig. 2.

2.4. Electrochemistry and electrochromic characterization

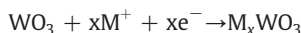
Electrochemical measurements were conducted in a standard buffer solution (pH 6.8) containing 0.1 M CH_3COONa and CH_3COOH . The working electrode, the counter-electrode, and the reference electrode were $[\text{HTB}/\text{TiO}_2]_2$ coated ITO glass, platinum wire, and Ag/AgCl , respectively.

Double-potential experiments that cooperated with UV-Vis spectroscopy were used to characterize the electrochromic property of the $[\text{HTB}/\text{TiO}_2]_2$ films. Electrochromic contrast, coloration efficiency, switching speed, stability and optical memory were characterized. All data about electrochromic property averaged from five samples and each sample have worked for 50 cycles.

3. Results and discussion

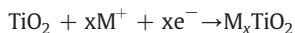
3.1. Electrochemistry—cyclic voltammetry

Fig. 3 shows the cyclic voltammogram of the $[\text{HTB}/\text{TiO}_2]_2$ (a), the monolayer HTB (b) and the monolayer TiO_2 film (c). The peak of HTB and TiO_2 integrated into one redox peak around -0.5 V. HTB displays a color change from white to blue when reduced, which is affected by the number of ions inserted into the oxide matrix, through the process [18]



where M^+ could be H^+ , Li^+ , K^+ , and so forth. When an electron injects (or removes) into (or from) the conduction band, a cationic ion will move into the structure to compensate for the charge [19].

TiO_2 is a semiconductor and its oxidation wave was observed between -1.0 V and -0.5 V depending on size and morphology [20]. The electrochromic process of TiO_2 films is [21]:



where M^+ could be H^+ , Li^+ , K^+ , and so forth. Previous studies reported that cationic polarization causes electrons to accumulate in the semiconductor film [22]; thus, charge compensation is accomplished by proton intercalation. However, this reaction is reversible. An oxidation current could be observed when the voltage is scanned in a positive mode. The result was consistent with the Nernst equation, and shows that the redox process preceded proton diffusion [23].

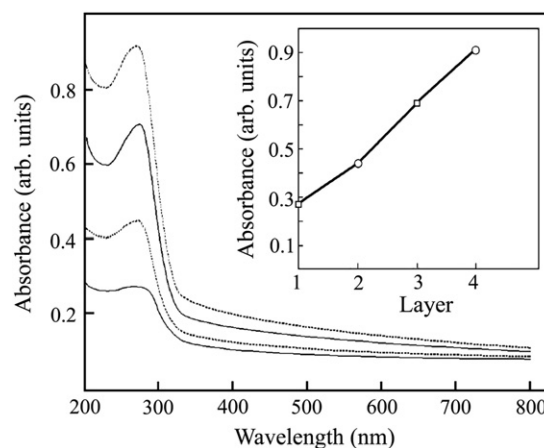


Fig. 2. UV-visible absorbance spectra of the $[\text{HTB}/\text{TiO}_2]_2$ films, the insert figure was the absorbance vs. layer number at 280 nm.

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