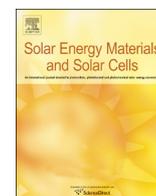




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Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

WO₃/TiO₂ core–shell nanostructure for high performance energy-saving smart windows

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ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form

2 November 2014

Accepted 3 November 2014

Keywords:

WO₃/TiO₂

Core–shell

Photodegradation

Electrochromic

Photoinduced hydrophilicity

ABSTRACT

The electrochromic, photodegradation, and photoinduced hydrophilicity properties of the WO₃/TiO₂ core–shell nanostructure as a smart building material for energy-saving are investigated. The core–shell nanostructure exhibits a highly reduced ion intercalation capacity with good reversible electrochemical cycling of intercalation–deintercalation, and shows a higher coloration efficiency (110.8 cm² C^{−1}), faster switching speed (0.7 s and 2.9 s) and better cycling performance than as-deposited WO₃ nanowires (NWs). The TiO₂ shell layer greatly enhanced the photocatalytic oxidation activity of WO₃ NWs, increasing the photoinduced hydrophilic conversion. The enhanced photocatalytic reaction by the core–shell structure was attributed to the multi-electron reduction in the interlayer, caused by the electrons injected from the conduction band of the WO₃ NWs. These results suggest that the WO₃/TiO₂ core–shell nanostructure enhances the electrochromic, photodegradation, and photoinduced hydrophilicity properties due to the increased density of charge separated electron–hole pairs aided by the TiO₂ and WO₃ interlayer. The WO₃/TiO₂ core–shell structure was found to possess superior properties giving it good potential for use in energy-saving smart windows.

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1. Introduction

Smart building materials have attracted considerable research and development interest due to potential applications such as smart building glazing, self-cleaning exterior tiles, and anti-fogging mirrors [1–4]. Among transition metal oxides, tungsten trioxide (WO₃) and titanium dioxide (TiO₂) exhibit excellent electrochromic properties, environmental purification, and self-cleaning properties [2,5,6]. TiO₂ is an effective photocatalyst under ultraviolet (UV) irradiation for decomposing volatile organic compounds. It is also super-hydrophilic and potentially useful in smart windows. However, TiO₂ has three disadvantages that restrict itself from being widely adopted in practical applications: (1) the rapid recombination of photogenerated electron–hole (E–H) pairs that significantly reduces photocatalytic efficiency [7], (2) long coloration time and low electrochromic efficiency [8], and (3) its light response region is located in the UV wavelength, which accounts for only ~5% of the energy of sunlight. When TiO₂ is combined with WO₃, the spectral of absorption increases due to the band gap of WO₃ (2.8 eV, λ = 443 nm) being smaller than that of TiO₂ (3.2 eV, λ = 388 nm). This allows light with λ ≤ 443 nm to be absorbed by the heterogeneous structure, and the photocatalytic activity can be

extended to a large spectral range [9,10]. The WO₃ can act as an electron scavenger and can pull the photo generated conduction band electrons of TiO₂ to its own conduction band, thus keeping the E–H pairs apart longer to improve overall photocatalytic performance [11]. In addition, the WO₃ has been intensively studied because of its superior electrochromic properties such as stability, low power consumption, good coloration effect, and high contrast [12,13].

The present work develops a WO₃/TiO₂ core–shell nanowire (NW) structure for smart building materials such as electrochromic windows, and surfaces which feature photodegradation and photoinduced hydrophilicity. The TiO₂ shell layer uniformly covers the WO₃ NWs. By combining TiO₂ and WO₃ through this fabrication method, we are able to enhance the coloration efficiency, reduce the photodegradation time, and increase the photoinduced hydrophilicity stability of the core–shell structure through the extension of the absorption range, the charge separation, and an optimized interfacial area between the materials. The effect of different TiO₂ shell layer thicknesses on WO₃ NWs for smart building material properties is discussed.

2. Experimental

Indium tin oxide (ITO) glass substrates were cleaned in an acetone bath for 15 min with ultrasonic agitation then rinsed in DI water for 15 min and finally etched by air plasma for 20 min. The

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tungsten (W) films were first deposited on an ITO glass substrate by reactive DC magnetron sputtering system. The deposition was carried out under an argon flow rate of 20 sccm, under DC power of 15 W for 15 min. The thickness of the deposited W film was about 80 nm. The samples were subsequently subjected to thermal annealing in a quartz tube furnace at 550 °C in nitrogen ambient (99.5% purity) for 60 min under 50 Torr. The core structure tungsten oxide NWs formed on the ITO glass. Different thicknesses (40, 50, 60, 70, and 80 nm) of titanium films were separately deposited on the as-deposited samples. The WO_3/TiO_2 core-shell nanostructure was finally synthesized by annealing Ti/ WO_3 films at 550 °C in nitrogen and oxygen atmosphere with 100 sccm of each for 1 h under 50 Torr.

The morphology of the films was characterized by a field emission scanning electron microscope (FESEM, JEOL JSM-6500F) and a high resolution transmission electron microscope (HRTEM,

Philips Tecnai F20 G2). X-ray diffraction (XRD) measurements were conducted using $\text{CuK}\alpha$ radiation (Bruker D8 phaser). Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were performed in 1 M lithium perchlorate (LiClO_4) using a propylene carbonate (PC)–water mixture as the electrolytes, a platinum plate as the counter electrode, tungsten oxide as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. Optical transmittance spectra were recorded on a JASCO V-560 ultraviolet–visible (UV–vis) spectrophotometer. Contact angle measurement was conducted on three points for each sample and the experimental error for each point was within $\pm 2^\circ$. The UV-lamp used in the experiment had a wavelength of 369 nm using a 4 W black light bulb with an intensity of 0.1 mW/cm². The chemical binding of oleic acid on the samples was investigated by Fourier-transform infrared (FTIR) spectrometry (BomemDA8.3).

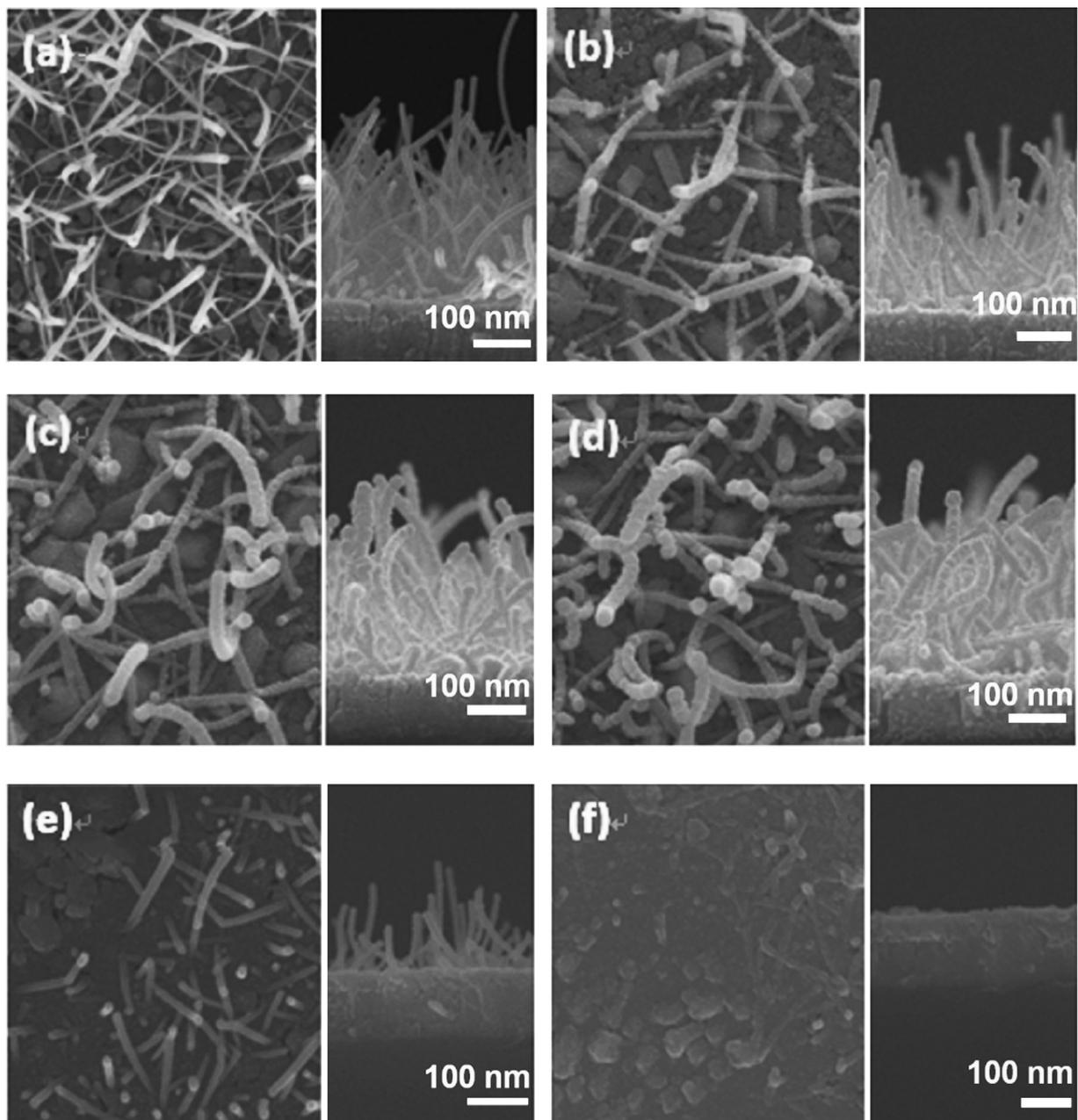


Fig. 1. SEM images of the cross-section and plain-view of the (a) as-deposited WO_3 NWs (W1) and WO_3/TiO_2 core-shell structure with the different Ti thicknesses of (b) WT1, (c) WT2, (d) WT3, (e) WT4, and (f) WT5.

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