



Tuning of physical and electrochemical properties of nanocrystalline tungsten oxide through ultraviolet photoactivation

P.T.G. Gayathri ^{a, b}, S. Sajitha ^{a, b}, I. Vijitha ^{a, b}, S.S. Shaiju ^{a, b}, R. Remya ^{a, b}, Biswapriya Deb ^{a, b, *}

^a Photosciences and Photonics, Chemical Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, 695019, India

^b Academy of Scientific and Innovative Research (AcSIR), CSIR-NIIST, Thiruvananthapuram, 695019, India

ARTICLE INFO

Article history:

Received 30 December 2017

Received in revised form

5 March 2018

Accepted 3 April 2018

Available online 5 April 2018

Keywords:

Photoactivation

Tungsten oxide

Impedance spectroscopy

Mott-Schottky

Oxygen vacancy

Capping ligand

ABSTRACT

In this paper, we demonstrate the use of ultraviolet (UV, 365 nm) photoactivation to induce functional changes in the nanocrystalline tungsten oxide (n-WO₃) surfaces. n-WO₃ was initially synthesized by dissolving hydrated-WO₃ powder in 10% H₂O₂ with and without UV exposure. The photoactivation triggered homogeneous ligand-stripping in WO₃ seeds that transformed the random-shaped clusters observed in the unexposed solution into a mono-modal distribution of spherical aggregates. These aggregates were electrophoretically collected as a coating that exposed to a second installment of UV soaking to explore photoactivation effects in the film state. A significant network densification is observed as photo-decomposition of bridging ligands facilitated direct interactions of surface dipoles in those films. Experiments showed that the photodecomposition mechanism predominantly depends upon the discharge of oxygen atoms localized on the material surface that can also create donor type oxygen vacancies. Electrochemical studies showed that the photoactivation led up to ~2.8× enhancement in the surface donor density and considerably improved the interfacial charge transfer. The photo-activated electrodes exhibited up to ~33% increment in the areal capacitance (C_a) due to the increased number of active sites in the interface. Electrochromic (EC) response from the same electrodes produced ~57% improvement in the optical density (OD).

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

At nanometer length scale, the electrochemical responses of transition metal oxides (TMOs) become strongly dependent on their physicochemical properties like grain size/shape distribution, compositional divergence and effective free-surface etc. [1]. It is essential to develop inexpensive and facile processes that can manipulate nanoscale transport properties to extract preferred functionalities from these materials. The transport phenomena at nanoscale are predominantly surface dependent; therefore various surface modification schemes could be adopted for any desired application [2,3]. As a substitute to chemical alterations, UV-assisted modifications offer lower environmental footprint and

less physical hazard. Typically, UV photoactivation of the TMO surfaces leads to additional induced defects/states [4] that can have both beneficial and adverse effects depending on the selected usage. Among TMOs, WO₃ is particularly crucial for industries due to their widespread usage as functional electrodes in storage devices [5,6], photocatalytic water splitting systems [7–9], and gas sensing [10,11]; all of which are inherently related to their electrochemical functionalities. The amorphous (a-WO₃) and nanocrystalline (n-WO₃) phases are especially popular for exhibiting high contrast electrochromism; i.e. ability to reversibly change luminous transmittance triggered by electrically concerted charge carrier insertion/extraction [12]. Various chemical modifications schemes on WO₃ were explored and the effects of oxygen vacancies, moisture etc. were shown to be significantly affecting their photochemical performances [13–16]. Due to the high potency of n-WO₃ electrodes for solar technology usage, it is vital to inspect the effect of UV induced surface/interface modifications and their contribution to the electrochemical transformations in the films.

* Corresponding author. Photosciences and Photonics, Chemical Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Thiruvananthapuram, 695019, India.

E-mail address: biswapriya.deb@niist.res.in (B. Deb).

UV is frequently employed to clean oxide surfaces from organic residues by converting those into volatile substances, augmented by O₃ oxidation [17,18]. The treatment is known to change the hydrophilicity of the metal oxides (and polymer surfaces) that strongly influence their targeted applications. Dilpazir et al. [19] reported enhanced photocatalytic performance of TiO₂/PANI system resulting from UV-ozone treatment. For UV mediated modification studies, TiO₂ was frequently chosen as the test material. It is shown that UV irradiation could functionally control aggregation kinetics and photocatalytic activities of TiO₂ nanostructures [20]. A generic process based on deep-ultraviolet photochemical activation to form high-performing stable metal-oxide semiconductors at room temperature was developed and proposed for fabricating flexible and printed thin-film electronic devices [21]. The construction of three-dimensionally self-assembled network structures of TiO₂ nanoparticles on the solid surface by simple UV irradiation was reported by Kim et al. [22] Tebby et al. [23,24] demonstrated the UV-induced densification of the TiO₂ thin film network and resulting changes in their physicochemical properties. They also extended the approach to functionalize SnO₂ thin films. The effect of UV soaking on ZnO surface electronic structure is shown to be strongly dependent on the experimental conditions [25]. More recently, an improved photoelectrochemical activity of WO₃ photoanodes towards the oxygen evolution reaction has been obtained that was arising from the altered coating morphology due to UV exposure [26]. The activation process could also influence photocatalytic properties of oxide based insulators as shown by Dong et al. [27,28]. Therefore, UV photoactivation route has excellent prospective to be included in the fabrication protocol of industrial materials processing.

In this paper, we demonstrate that UV-soaking can significantly affect both morphological and chemical parameters such as film compactness, roughness, surface state/trap density and interfacial energy level alignment etc. In the application side, we especially emphasized the electrochromic (EC) and charge storage performances as these are the two most industrially relevant technologies for n-WO₃. A few prototype electrochromic devices (ECDs) and asymmetric capacitors were fabricated using electrodes with and without photoactivation. Both applications showed enhancements in their functionalities owing to the increased number of active sites for electrochemical reactions. The obtained results offer valuable insights on the underlying mechanism and could find generic use as a surface functionalization scheme for metal-oxide nanostructure based applications.

2. Experimental

2.1. Materials

H₂O₂ (7722-84-1), Tungsten powder (7440-33-7) and methanol (67-56-1) were obtained from Alfa-Aesar. PMMA (CAS# 9011-14-7), PC (108-32-7) and LiClO₄ (7791-03-9) were procured from Sigma-Aldrich for the preparation of electrolytes.

2.2. Preparation of the precursor solutions

Fluorinated Tin Oxide (FTO) electrodes were cleaned by step-wise ultrasonication using detergent, distilled water, acetone, and isopropanol (15 min with each solution, in respective order). The materials synthesis required a two step process. Initially, 5 g of W powder was dissolved in 60 ml of H₂O₂ (20%) under constant stirring for 24 h in an ice bath. The solution was then filtrated that results in a colorless clear liquid. The excess hydrogen peroxide was decomposed by stirring the solution for 4 h at 80 °C that changes the solution color to deep yellow. Subsequent drying of this

solution produced yellow colored hydrogen tungsten oxide hydrate (H₂WO₄·H₂O) powder (XRD spectrum of this powder is presented in Fig. S1). In the second step, two sets of precursors were prepared by dissolving 1 g of H₂WO₄·H₂O in 30 ml H₂O₂ (10%). One set was kept in the normal ambient conditions and another inside the UV chamber. In the reaction vessel, H₂WO₄·H₂O decomposes to WO₃ and the reaction progress can be visually monitored by observing gas-bubbles formation resulted from catalytic decomposition of H₂O₂ that continues for almost ~2 h. Any excess H₂O₂ is thereafter decomposed by overnight stirring at 80 °C [29,30].

2.3. Fabrication of n-WO3 films

n-WO₃ films were electrophoretically coated on the FTO substrates (4×5 cm) from each of the aforementioned stocks. These two film sets were used as the reference samples (hereon R1 is used for the standard and R2 for the UV-activated solution derived films). The film sets T1 and T2 were obtained by UV-soaking R1 and R2 respectively for 1 h. The actual deposition area were 4×4 cm with masking for power connectors. For the depositions, a galvanostatic source current of 5 mA was applied. Thicknesses of the films were controlled by controlling the deposition time. Fig. 1 schematically illustrates the fabrication steps involved in the thin film deposition process.

2.4. Materials characterization and electrochemical measurements

A precision source meter (Keithley 2450) was used to source current for the electrophoretic deposition. UV treatment was carried within a Rayonet photochemical reactor (RPR-100, 365 nm, 6 lamps-16 W each). The particle size and correlation coefficient were measured from Dynamic light scattering (DLS) using Zetasizer nanoseries (Zeta Nano-ZS, Ms. Malvern Instruments). Structural and compositional identification of the samples were performed using X-ray diffraction (XRD, Bruker D8 ADVANCE) and Fourier transform infrared spectroscopy (FTIR, Shimadzu IR Prestige-21). For the morphological studies, we used tapping-mode AFM (Bruker Multimode AFM-3COCF) and High resolution transmission electron microscopy (HRTEM) (FEI-Tecna G 2 -30 with EDAX). EC performance assessments were done using a combined system of UV-Vis spectrometer (Ocean Optics USB4000-XR) and an electrochemical workstation (Metrohm micro-Autolab μ3AUT070904) integrated with NOVA software. Electrochemical and impedance measurements were performed with Metrohm Autolab PGSTAT302 N. The thickness of films was measured by a Dektak XT profilometer. Kelvin probe (KP) data were recorded under ambient conditions using a NTEGRA (NT-MDT). X-ray photoelectron spectroscopy (XPS, PHI5000 Versa Probe II) measurements were done at room temperature using Al K_α source (1486.7 eV). The C 1s line at 284.8 eV was used as an internal energy reference.

3. Results and discussion

Along with the storage applications, the electrochemistry of WO₃ has practical importance for its electrochromism [31] as discussed in the introduction. It is established that a substoichiometry in oxygen content is critical for obtaining a characteristic chromic response from the material [12]. Therefore, the entire photoactivation experiments were done using 365 nm wavelength as deep UV illumination can promote ozone formation and subsequent oxidation of the near surface states. In the photoactivation chamber, the temperature can reach up to ~50–60 °C. To avoid any unwanted noise from thermally-induced transformations, the reference samples covered with metallic foils were also placed in the UV chamber during exposure. This step ensured that all

Download English Version:

<https://daneshyari.com/en/article/6603148>

Download Persian Version:

<https://daneshyari.com/article/6603148>

[Daneshyari.com](https://daneshyari.com)