WO_3 Nanostructures for Energy Storage

Subjects: Electrochemistry

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Electrochemical energy storage devices are one of the main protagonists in the ongoing technological advances in the energy field, whereby the development of efficient, sustainable, and durable storage systems aroused a great interest in the scientific community. Batteries, electrical double layer capacitors (EDLC), and pseudocapacitors are characterized in depth in the literature as the most powerful energy storage devices for practical applications. Pseudocapacitors bridge the gap between batteries and EDLCs, thus supplying both high energy and power densities, and transition metal oxide (TMO)-based nanostructures are used for their realization. Among them, WO_3 nanostructures inspired the scientific community, thanks to WO_3's excellent electrochemical stability, low cost, and abundance in nature.

energy storage | electrochemical characterization | WO3 | pseudocapacitor

1. Crystal Structure Properties

WO_3 is an *n*-type semiconductor with high electrochemical stability in acidic environments, and high intrinsic density (>7 g·cm^{-3}) [1]. Its energy storage performances strongly depend on the crystal structure, which can make the ions' intercalation easier in an electrochemical environment.

In its crystalline form, WO_3 is made of octahedra sharing corners and edges, where each W atom is linked to six O atoms, as **Figure 1** shows [2]. Thanks to the high coordination number, WO_3 possesses many crystalline phases, which depend on the rotation direction and tilting angles of the WO_6 octahedra (**Figure 1**a) with respect to the ideal cubic perovskite-like structure, whose stability depends on temperature [3]. The hexagonal phase is metastable, and it is turned into a monoclinic I phase when the temperature is higher than 400 °C [4][5]. A unique feature of h-WO_3 is that WO_6 octahedra share corner oxygen atoms in three- and six-membered ring arrangements along the (001) plane. This sharing forms three different types of tunnels in the W-O bulk structure, which are triangular and hexagonal cavities along the *ab* plane and square windows along the *c* axis, as shown in **Figure 1**b,c. According to the literature, these cavities can act as preferential ions intercalation channel for applications in electrochemical environment [3].

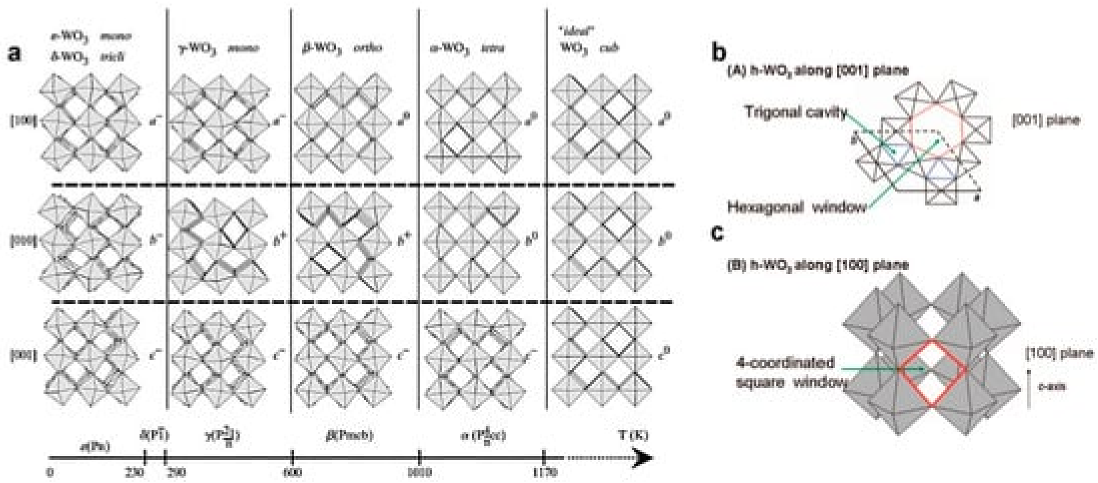

Figure 1. (**a**) Tilt patterns and stability temperature domains of the different polymorphs of WO_3; (**b**) the structure of h-WO_3 shown with the *c*-axis perpendicular and (**c**) parallel to the plane. Reproduced by [4].

2. WO_3 Nanostructure Synthesis Approaches

The nanotechnology advantages in a multitude of applications made the large-scale synthesis of nanostructures a crucial point for the development of new promising technologies. The electrochemical activity of WO_3 nanostructures towards energy storage strongly depends on the morphology and crystal structure, and consequently, on the synthesis techniques. WO_3 can be easily synthesized in a nanostructured form by different approaches, such as Vapor-Phase and Liquid-Phase Synthesis.

The Vapor-Phase Synthesis involves the condensation of a vaporized source material onto the substrate, using an expensive experimental setup [4]. Two types of deposition can be distinguished: Physical Vapor Deposition (or PVD) and Chemical Vapor Deposition (or CVD). Baek et al. [6], synthesized a dense WO_3 nanowire film on a W substrate by thermal evaporation (**Figure 2**a). Shankar et al. [7] synthesized WO_3 nanorods by using a hot filament chemical vapor deposition (HFCVD) with carbon nanotubes as a template (**Figure 2**b). For practical application, the low-cost, large-scale synthesis of nanostructures is necessary. In this scenario, Liquid Phase Syntheses, such as sol-gel, electrochemical anodization, and hydrothermal, are very attractive being characterized by simple equipment, low costs, and high reproducibility. Room temperatures are compatible with these processes, and good control and reproducibility can be achieved. Peroxotungstic acid ($H_2W_2O_{11}$) is generally used as a precursor for the WO_3 synthesis, thanks to its high stability at room temperature and in an acidic environment [4]. Yang et al. [8] synthesized mesoporous WO_3 film by using a simple sol-gel route (**Figure 2**c). Electrochemical anodization is widely used for the industrial synthesis of metal oxide films, thanks to its simplicity. Zheng et al. [9] synthesized a nanostructured WO_3 film by using a typical anodization route with a W foil as the anode (**Figure 2**d). Unfortunately, the high voltages required for the synthesis and the difficulty to achieve the desired nanostructured morphology make the anodization technique difficult to perform for the WO_3 nanostructure synthesis. The hydrothermal procedure represents one of the greenest, simplest, and most versatile procedures among all the Liquid Phase Synthesis methods viable for the synthesis of WO_3 nanostructures. It does not require any external potential and the preparation of the precursor solution occurs in just a few steps. Nanostructure formation can occur both in high and low temperature and pressure conditions. Moreover, the morphology and crystallinity of nanostructures strongly depend on precursor solution components, and on reaction time and temperature [10]. For example, Mineo et al. [11] synthesized WO_3 nanorods by using a simple hydrothermal route with NaCl as the capping agent (**Figure 2**e), which confines the growth along the *c*-axis.

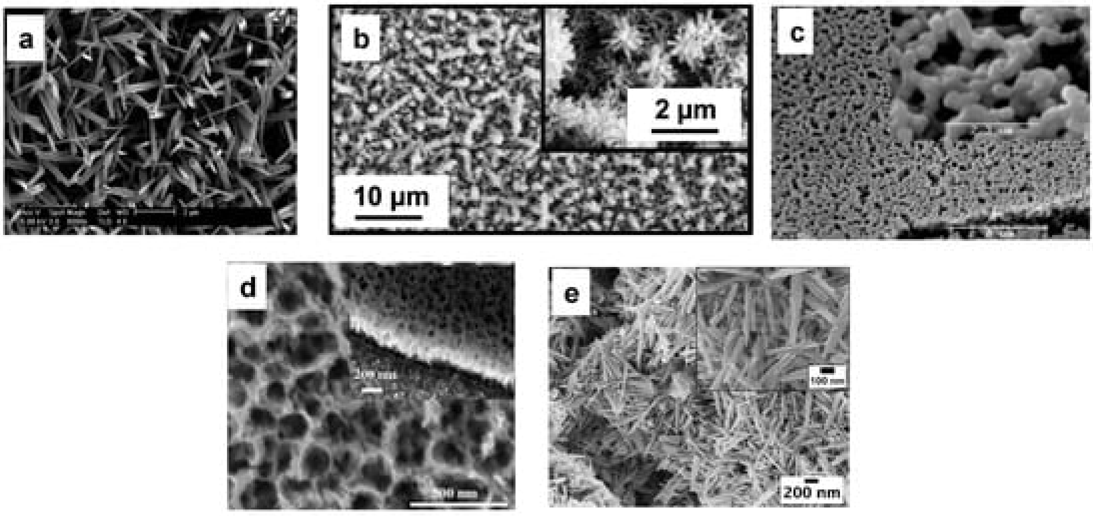

Figure 2. SEM images of WO_3 nanostructures (nanowires, nanorods, mesoporous and nanostructured film, nanospheres, and nanorods, respectively) synthesized (**a**) by thermal evaporation [6]; (**b**) by hot wire CVD [7]; (**c**) by sol-gel method [8]; (**d**) by electrochemical anodization [9]; and (**e**) by hydrothermal synthesis [11]. Reproduced with permission.

3. Affinity of WO_3 for Energy Storage Applications

WO_3 nanostructures possess structural flexibility, stability in an acidic environment, and resistance to electrochemical corrosion, which makes it a suitable candidate for electrochemical energy storage. The electrochemical reactions occur at the electrode surface and involve electron and ion transfer, so high exposed surface and good conductivity are preferable and the optimization of several factors, such as specific surface area and mass loading, affect the energy storage activity of WO_3. Unfortunately, stoichiometric WO_3 is characterized by poor electron conductivity, which can be improved by properly tailoring the morphology and crystallinity of WO_3-based nanostructures, or by using carbon-based nanocomposites during the electrode preparation [12],[13],[14],[15],[16]. It was demonstrated that in comparison to other polymorphisms, 1D hexagonal WO_3 nanostructures possess the highest energy storage performances, thanks to the presence of triangular and hexagonal cavities and square windows in the crystal structure (**Figure 1**b). These tunnels can provide accommodation sites for many cations during the electrochemical process, by facilitating electrolyte ion insertion and storage in the WO_3 matrix thanks to its multiple oxidation states [3].

State-of-the-art research on WO_3 demonstrates that it exhibits a pseudocapacitor behavior with quasi-rectangular cyclic voltammetry (CV) curves [11],[13],[15],[17],[18]. According to Dunn et al. [19] the charge storage mechanism in

WO_3 can be described in terms of surface and diffusion-limited contributions and occurs at the electrode–electrolyte interface. Surface-limited contributions are related to the adsorption/desorption of charge on the surface, while diffusion-limited contributions result from redox reactions that occur at the surface during which the W oxidation state changes as follows [20]:

$$\mathrm{WO_3 + xM^+ + xe^- \rightleftharpoons M_x WO_{3-x}} \quad (1)$$

in which M^+ represents the cation of the used electrolyte (H^+, Na^+, Li^+).

WO_3 is characterized by many oxidation states, which promote redox reactions at the active material surface. The high theoretical capacitance and the possibility to easily tailor the morphological and crystal properties of WO_3 make it a suitable candidate for the development of an efficient anode in energy storage devices, such as symmetric and asymmetric supercapacitors. These WO_3 features have aroused a great interest in the scientific community, and many efforts have been made to pave the way to the development of very efficient WO_3-based energy storage devices.

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