Physicochemical Properties of Tungsten Trioxide Photoanodes

Subjects: Others

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Advanced Oxidation Processes (AOPs) are widely regarded as the most effective method for rapidly degrading and oxidizing organic pollutants in water treatment, with chemical methods demonstrating high efficiency, especially for addressing organic wastewater.

Keywords: electrophotocatalysis ; tungsten trioxide ; photoanodes ; brick-and-mortar

1. Introduction

The urgent requirement to confront the pervasive pollution of groundwater, surface water, and drinking water by toxic and long-lasting organic chemicals stemming from industrial and domestic sources demands an increased emphasis on the development of wastewater treatment technologies [1][2]. Advanced wastewater treatment typically involves the use of physicochemical and combined physical and biological methods, which are categorized into three main groups: physical, chemical, and biological treatments [3][4]. Commonly used physical methods for water treatment include sedimentation, adsorption, and membrane separation [5]. Biological treatments can be an effective solution for removing organic matter from water, as conventional physical processes have limitations in this area. However, even though there have been advancements in membrane bioreactors, they have not yet been successful in removing micropollutants from wastewater. This is because the membrane components of these technologies become clogged with particles from previous processes, which hinders the separation process [6]. Advanced Oxidation Processes (AOPs) are widely regarded as the most effective method for rapidly degrading and oxidizing organic pollutants in water treatment, with chemical methods demonstrating high efficiency, especially for addressing organic wastewater [7].

Advanced oxidation processes possess several advantages, such as a high mineralization efficiency, rapid reaction rates, and minimal secondary pollution [8]. Organic products are highly susceptible to oxidation by hydroxyl radicals, which are generated by holes and other reactive oxygen species (ROS) that exist between electrons and molecular oxygen [9]. AOPs rely on efficient ROS generation and reduced mass transfer resistance to determine their oxidation capacity. Unlike other AOPs, electrochemical oxidation breaks down pollutants without producing secondary products at a relatively low cost. The anodic reaction is influenced by the organic compounds' affinity for the oxidant and results in the formation of active oxygen, which can lead to either the complete degradation or simplification of pollutants [7][8][10]. Photochemical AOPs offer a promising solution for both water treatment and energy production due to their capacity to break down persistent compounds using sunlight. Nevertheless, their relatively low efficiency in harnessing light energy and the rapid reunion of electron–hole pairs at the photocatalyst's surface present substantial obstacles to their practical implementation [11]. By integrating multiple advanced oxidation processes (AOPs), the oxidation efficiency of treating organic wastewater can be enhanced. This method aims to overcome the drawbacks and high operational costs of individual treatment technologies, by leveraging synergistic effects to improve the efficiency of organic degradation. PEC facilitates the separation of electron–hole pairs, thereby promoting the mineralization of organic pollutants in wastewater [8][9][12]. The conductivity of urban and industrial wastewater is adequate due to the presence of electrolytes [13]. The majority of PEC research has typically utilized synthetic wastewater composed of ultrapure water and electrolytes [12][14][15][16][17]. The process-specific parameters, system design, and water quality all play a role in determining the formation of radicals [4][18][19]. The efficiency of contaminant destruction in surface-based advanced oxidation processes (AOPs) is influenced by several factors, including radical scavenging, radical transfer, and hydrodynamics [8]. Optimal performance of a photocatalyst depends on effective morphology control, as it impacts the photocatalytic properties, specific surface area, quantum efficiency, and porosity [7]. Oxidation of these organic pollutants at the surface of photocatalyst is of the utmost importance [20]. The photocatalytic approaches have been the latest developments for the degradation of organic pollutants, based on semiconductor materials as catalysts in conjunction with the advanced oxidation processes (AOPs) under the irradiation of solar light [21].

In tungsten(VI) oxide (WO_3), the lower size of the bandgap starts at 2.6 eV, and photocatalysis can be excited by blue radiation of the visible spectrum, which has an edge for WO_3 over titania [22]. There are different mechanisms through which tungsten oxides act. One includes the bandgap value and band edge positions, allowing carrier generation in the healthcare system [23]. The energy of the bandgap can vary depending on the crystalline phase of the photocatalyst [24]. Photocatalysts face a significant challenge due to faster electron–hole recombination time, making it difficult in PEC cell activity [25][26][27]. The photoelectrochemical cell comprises a photoanode and a cathode immersed in an aqueous electrolyte, as shown in **Figure 1**. The smaller the photocatalytic particles, the greater the total number of charge separations [28][29][30]. Combining band structure engineering, geometric engineering, and heterostructure engineering may enhance the photocatalytic activity. The setup comprises a photoanode and a cathode immersed in an aqueous electrolyte, as shown in **Figure 1**. In the n-type photoanode, photogenerated holes move to the semiconductor interface to oxidize organic pollutants to carbon dioxide.

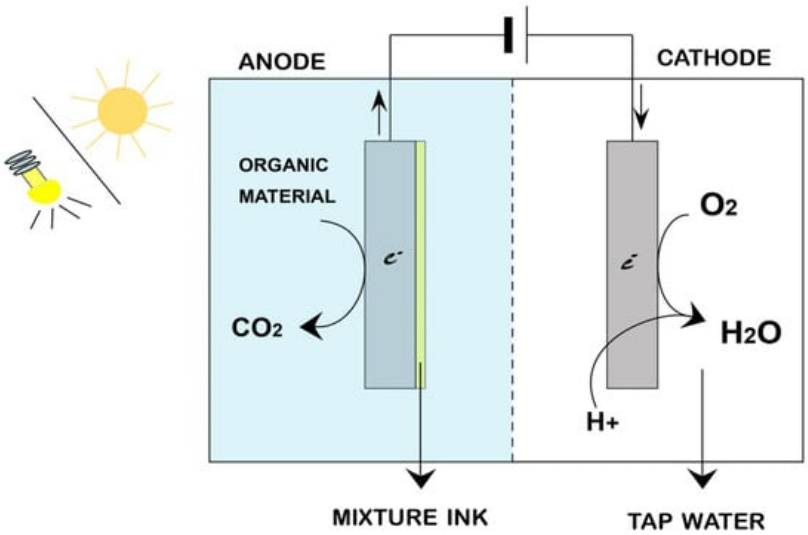

Figure 1. Schematic overview of photoelectrochemical cell.

The nanomaterial preparation can be divided into two basic procedures: top-down and bottom-up. In the top-down procedure, the bulk material is broken down into nanosized particles by different physical, chemical, and mechanical processes. Various synthetic methods can be utilized under this approach such as mechanical milling, laser ablation, and ion sputtering [31]. Mechanical mills of various types include planetary, attrition, vibration, low-energy ball, and high-energy ball mills [32]. Using the bottom-up procedure, larger layers can be prepared from soluble precursors and such processes include the sol–gel method. The precursors utilized in the sol–gel method are heated to a very high temperatures to achieve one of the immobilization conditions, namely, adhesion to the substrate [32].

2. Tungsten(VI) Oxide Layers Prepared by Top-Down Approach

Ball milling is commonly used in industrial mass production for ores, ceramics, and pigments [33]. The milling technique is quite suitable for morphological modifications of nanostructures and It comes with an advantage of low-cost preparation can use it at room temperature [34]. Ball milling is advantageous over laser ablation in terms of large-scale production [35]. Ball milling is a widely used technique for synthesizing amorphous materials [36]. A miller setup was designed to reduce WO_3 to metallic tungsten [37][38].

3. Tungsten(VI) Oxide Layers by Bottom-Up Approach

Different tungsten precursors were used in the literature for formation of tungsten(VI) oxide films via the sol–gel method. Suitable structure-directing agents and binders help in tailoring the morphology of WO_3 thin films. The peroxotungstic acid (PTA) derivatives are widely reported for casting tungsten(VI) oxide films in the sol–gel route. De Moura, D.S. et al. reported on a system to synthesize WO_3 powders via PTA and polyvinyl alcohol as precursor [39]. Fang, Y. et al. reported WO_3 films derived from the sol–gel synthesis of acetylated peroxotungstic acid (APTA), and polyethylene glycol layers deposited by spin coating [40]. Işık et al. reported the influence of tungsten(VI) oxide microstructures on the electrochromic properties obtained from tungsten peroxo complexes via the sol–gel method for the application of tungsten coatings [41]. The authors of article [36] published a study on the formation of thin oxide layers of modified tungsten chloride by the sol–gel method. Zhang et al. reported on the formation of thermally stable mesoporous tungsten oxide films by the sol–gel method using a surfactant [42].

4. Fabrication of WO_3 Layers by Brick-and-Mortar Approach

The brick-and-mortar approach serves as a connection matrix, combining the two aforementioned methodologies, as shown in **Figure 2**. The authors of [43] used an innovative brick-and-mortar approach to prepare WO_3 nanoparticles and the photoanodes showed high photocurrents of 3.04 mA cm^{-2}.

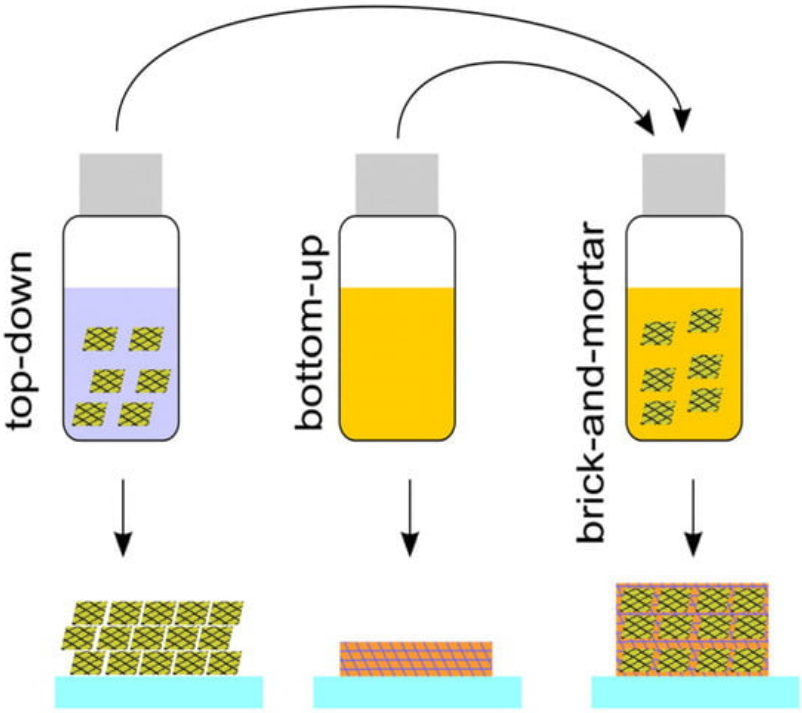

Figure 2. Illustration of top-down, bottom-up, and brick-and-mortar methods.

5. Wet Coating Techniques–Deposition of Liquid Formulations onto Substrates

Meyer rod coating is utilized in the production of the prepared inks for the larger electrodes to achieve uniform thickness, without the need for any additional processes. Ojeda, M. et al. reported on the fabrication of WO_3 thin films using a simple spin-coating route [44]. Sadale and Neumann-Spallart drop-casted WO_3 films to study the degradation of azo dyes [45]. Wang et al. [46] studied the deposition of tungsten trioxide films with photocatalytic and electrochromic properties by synthesizing a precursor solution with WO_3 powder in hydrogen peroxide. **Table 1** summarizes the comparative analysis of wet coating methods used for depositing liquid formulations on substrates.

Table 1. Presents a comparison of the advantages and disadvantages of using wet coating techniques for depositing liquid formulations.

S. No	Technique	Advantages	Disadvantages
1.	Screen Printer	Low cost [47][48]	One of the principal drawbacks of this method is the lack of flexibility in modifying the morphology and film thickness [49].
2.	Inkjet Printer	Inkjet printing offers several advantages, including non-contact, maskless, and combinatorial processing. It also consumes minimal materials and generates minimal waste [50][51].	Nozzle clogging, wetting behaviour, and film homogeneity [52][53][54][55][56].
3.	Spin Coater	A primary factor contributing to the popularity of spin coating is its ease of handling and rapid processing [57].	The utilization of spin-coating for automated fabrication is not feasible and lacks the capability to pattern substrates selectively. Furthermore, it has high material waste consumption [58][59].

S. No	Technique	Advantages	Disadvantages
4.	Meyer rod	The technique referred to as bar coating does not involve any additional processes such as pre-patterning of the substrate. Its purpose is to achieve a uniform, homogeneous coating with efficient processing [60].	The thickness of the laminating layer varies and depends on the range of possible bar diameters [61].

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