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Flame synthesis of WO_3 nanotubes and nanowires for efficient photoelectrochemical water-splitting

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Abstract

Tungsten trioxide (WO_3) is a technologically important material for photoelectrochemical (PEC) water-splitting for the solar production of hydrogen fuel from water. For PEC water-splitting, high aspect ratio WO_3 nanostructures such as nanowires (NWs) and nanotubes (NTs) are superior to planar WO_3 films because they orthogonalize the directions of light absorption (along the long axis) and charge transport (across the short radius), leading to both efficient light absorption and charge carrier collection. However, PEC water-splitting requires the growth of WO_3 on delicate transparent conducting oxide (TCO) substrates that cannot tolerate high temperature processing. To date, the large-scale, rapid, economical synthesis of high aspect ratio WO_3 nanostructures on these delicate TCO substrates remains a major challenge. Previously, we synthesized WO_3 NW arrays by a rapid, atmospheric and scalable flame vapor deposition (FVD) method, in which a flame oxidizes and evaporates tungsten metal to produce tungsten oxide vapors that condense onto a colder substrate in the form of NWs. Nevertheless, at substrate temperatures low enough to ensure the health of the TCO, the growth of WO_3 NW arrays was non-uniform and sparse due to limitations of the experimental design. Herein, we significantly improve the FVD design to grow uniform and densely packed WO_3 nanostructures on TCO substrates, thereby enabling the application of these WO_3 nanostructures to PEC water-splitting. The morphology of the nanostructures varied from densely packed multi-shell NTs and single-shell NTs to NWs as we increased the substrate temperature in the range 530–700 °C. Importantly, the WO_3 NTs synthesized by FVD had higher areal number density and longer length than state-of-the-art WO_3 NW photoanodes grown by chemical vapor deposition and hydrothermal methods, resulting in stronger light absorption and superior PEC water-splitting performance. Thus, in addition to being scalable, rapid and economical, the FVD method also synthesizes materials of high quality.

Keywords: Flame synthesis; Tungsten oxide; Nanowire; Nanotube; Photoelectrochemical water-splitting

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1. Introduction

Tungsten trioxide (WO_3) is an earth abundant and chemically stable n-type semiconductor with an optical bandgap of 2.7 eV and good charge transport properties [1,2]. WO_3 has already found wide commercial applications in chemical sensors [3] and electrochromic windows [4], for which it is commonly used in the form of polycrystalline thin films, or packed particle films. However, by reducing the size of WO_3 crystals to the nanoscale and shaping them into anisotropic one-dimen-

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sional (1-D) structures such as nanowires (NWs) and nanotubes (NTs), the functionality of WO_3 can be greatly enhanced. For instance, WO_3 NW chemical sensors [5,6] have better detection limits and lower power requirements than those of particle films because they have a large surface area for the adsorption of analyte molecules and a radius that is comparable to the resulting depletion width, without having the interparticle resistances that are present in particle films. In the case of electrochromic films, arrays of oriented WO_3 NWs [7] grown perpendicularly onto a planar conductor have shorter switching times, lower voltage requirements and improved stability compared to nanoparticle films because of the facile ion transport across the short radial NW dimension, direct electron conduction path to the current collector along the NW axis, and improved fracture resistance and mechanical connection of the NWs to the planar conductor. Moreover, WO_3 is also a promising photoanode material for photoelectrochemical (PEC) water-splitting technologies used to produce hydrogen fuel by splitting water with sunlight [1,2,8–10]. Here, 1-D WO_3 NWs orthogonalize the directions of light absorption (along the long NW axis) and charge transport (across the short NW radius), leading to both efficient light absorption and charge carrier collection [9,10].

These technologically important WO_3 NWs and NTs are typically synthesized either by vapor deposition (usually thermal or chemical vapor deposition, CVD) [8,11–13] or by solution phase growth (usually hydrothermal method) [10]. CVD produces WO_3 NWs/NTs of high crystallinity and purity, but the growth is expensive due to the need for vacuum chambers and pumps and is difficult to scale up [14]. Hydrothermal growth is scalable and inexpensive, but it is self-limiting because of a finite supply of reactants, typically has low growth rates, and produces materials of low purity and crystallinity [15]. The flame synthesis, or flame vapor deposition (FVD) method [14–17] overcomes many of the above limitations and is an attractive and versatile method for growing 1-D nanomaterials. Flame synthesis has several distinct advantages: (1) rapid growth rates due to the high temperature achievable by flames, (2) high material crystallinity and purity, (3) low-cost and scalability due to the atmospheric condition, volumetric chemical heat generation, and continuous operation, and (4) great flexibility in tuning the oxidation states and morphologies of as-grown nanostructures by varying various flame synthesis parameters [14,15].

With FVD, we previously synthesized 1-D $W_{18}O_{49}$ and WO_3 NWs using a co-flow diffusion burner [14]. Briefly, the flame oxidizes and evaporates a W mesh to produce WO_x vapors that condense onto a colder substrate in the form of NWs. The major limitation of the previous method was that significant amounts of WO_x vapors were absorbed by cooling meshes that were inserted between the W mesh and the substrate to cool the substrate. Consequently, the substrate temperature could not be reduced without an accompanying reduction in the tungsten oxide vapor concentration, so NWs could not be grown uniformly and densely over a large substrate area at low substrate temperatures [14]. The low substrate temperature is essential for the health of the delicate, temperature-sensitive transparent conducting oxide (TCO) substrates that are needed for applications such as PEC water-splitting. Hence, our previous FVD method could not be used to grow WO_3 NWs with sufficient areal number density on TCO substrates for PEC applications. Herein, we present an improved version of FVD that decouples the substrate temperature and WO_x vapor concentration, and opens up a new regime of fast, uniform and dense growth of NWs and NTs at low substrate temperatures. Under these new FVD conditions, we have synthesized a spectrum of novel, high-aspect ratio tungsten oxide nanomaterials ranging from previously unseen multi-shell NTs composed of thin NWs at low substrate temperatures, to individual NWs at higher substrate temperatures. Moreover, with the uniform and dense growth of WO_3 NTs/NWs on TCO substrates at the centimeter scale, we can directly test the performance of the NTs/NWs for the PEC water-splitting application. Significantly, the WO_3 NTs grown by FVD were found to have superior PEC water-splitting performance compared to state-of-the-art 1-D WO_3 photoanodes grown by hydrothermal [10] or CVD methods [8,9].

2. Experimental specifications

2.1. Overview of the synthesis method and characterization of 1-D WO_3 nanostructures

Although the objective is to grow 1-D WO_3 nanostructures, the nearly cubic WO_3 crystal tends to grow as an isotropic 3-D structure instead of an anisotropic 1-D structure. Consequently, anisotropic 1-D WO_3 nanostructures were grown by a two-step approach that takes advantage of the intrinsically anisotropic growth of $W_{18}O_{49}$: FVD of 1-D $W_{18}O_{49}$ ($WO_{2.72}$) nanostructures, followed by air annealing to oxidize the sub-stoichiometric $W_{18}O_{49}$ to stoichiometric WO_3. The 1-D $W_{18}O_{49}$ nanostructures were synthesized by our previously reported FVD method [14] but with greatly improved experimental design. For FVD in general, the flame provides the heat and reactants to generate metal oxide vapors from a metal wire precursor, and these vapors then deposit onto a colder substrate further downstream to form the desired metal oxide nanostructures. In