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Facile fabrication of bitter-gourd-shaped copper (II) tungstate thin films for improved photocatalytic water splitting

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ABSTRACT

Copper (II) tungstate ($CuWO_4$) has better light absorption and selectivity for a photochemical water-splitting reaction than those of its binary oxide counterpart. In this work, we report a facile single-step hydrothermal method to grow $CuWO_4$ with a bitter gourd shape directly on a transparent conductive substrate for the first time. $CuWO_4$ was synthesized via the condensation of a stable aqueous precursor solution of peroxopolytungstic acid and a copper precursor. The proposed method uniformly deposited $CuWO_4$ on fluorine-doped tin oxide with strong adhesion. The obtained $CuWO_4$ films showed a superior photocurrent density of 0.6 mA/cm^2 at 1.23 V vs. a reversible hydrogen electrode in a 0.1 M Na_2SO_4 electrolyte, which was relatively higher than the values recently reported for $CuWO_4$ photoanodes. The optimized $CuWO_4$ exhibited an incident photon-to-current conversion efficiency of 30% at 350 nm for the photoelectrochemical oxidation of water. An X-ray photoelectron spectroscopy valence band edge analysis revealed an increase in the valence band edge position in the $CuWO_4$, along with a decrease in the band gap compared to those in WO_3. The procedure proposed here provides a promising approach for the design of an efficient $CuWO_4$ photoanode for water splitting.

1. Introduction

A new viable approach is required for the production of alternative fuels because of the depletion of fossil fuel reserves [1]. As an alternate fuel, hydrogen (H_2) is regarded as one of the most promising clean energy carriers of the future, with zero emissions [2]. Among various methods of producing H_2, photoelectrochemical (PEC) water splitting is the most advanced and greenest method. The solar energy incident on the earth's surface is an inexhaustible and sustainable resource, which can potentially be harvested to produce H_2 through water splitting to meet our rising need for clean and renewable energy. Hence, this method offers the possibility of generating an essentially unlimited supply of clean-burning hydrogen fuel using sunlight and water [3,4]. It is of the utmost fundamental and technological importance to fabricate the photoelectrodes and photocatalysts employed in PEC water splitting using earth-abundant materials [5].

Photoelectrochemical water splitting based on semiconductor materials is a promising and environmentally friendly approach to hydrogen generation. In particular, employing metal oxide semiconductors for solar water splitting has become the most researched field because of their advantages, which include earth abundance, low cost, low toxicity, and relatively high stability in aqueous environments [6]. Various types of metal oxide semiconductors such as titanium dioxide (TiO_2) [7], ZnO [8], hematite (a-Fe_2O_3) [9], tungsten trioxide (WO_3) [10], and $BiVO_4$ [11] have been investigated for solar water-splitting applications. Although these materials show significant photoelectrochemical activity, some of them have limited utility because their band gap energies are poorly suited to capturing visible light photons, in which the bulk of solar spectrum energy lies. They are also prone to photocorrosion and have a short carrier path length and high charge carrier recombination [12–14]. Even though enormous effort has been invested in this area of research, the development of a high-efficiency water splitting PEC cell for solar-to-hydrogen fuel conversion remains a challenge. Therefore, it is important to research ways to exploit small band gap and stable semiconductors for efficient water splitting.

$CuWO_4$ is an n-type ternary metal oxide semiconductor and an attractive and promising photoanode for solar water splitting. It has a favorable band gap of 2.2–2.4 eV, leading to >10% theoretical solar-to-hydrogen (STH) conversion efficiency. It is also stable in aqueous media and has an environmentally benign composition [15–17]. $CuWO_4$ exhibits a small band gap property for water

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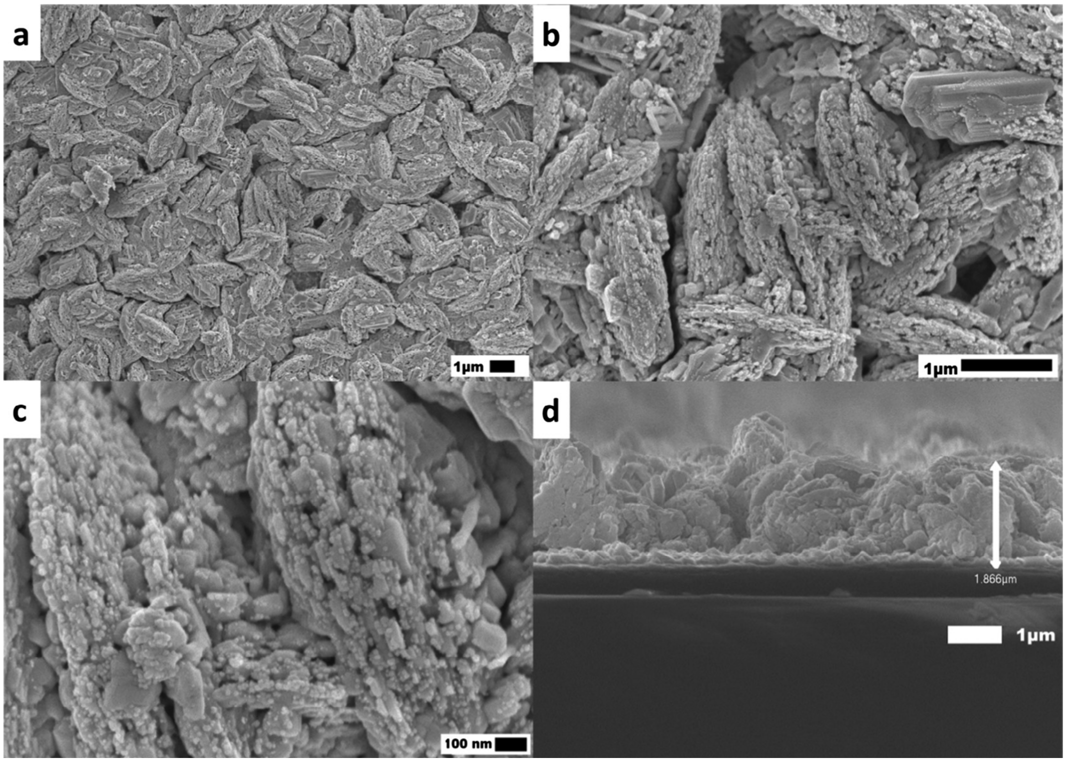

Fig. 1. Low-resolution (a) and high-resolution (b, c) top view SEM images of $CuWO_4$ on FTO surface annealed at 500 °C. (d) Cross-sectional SEM image of $CuWO_4$ on FTO.

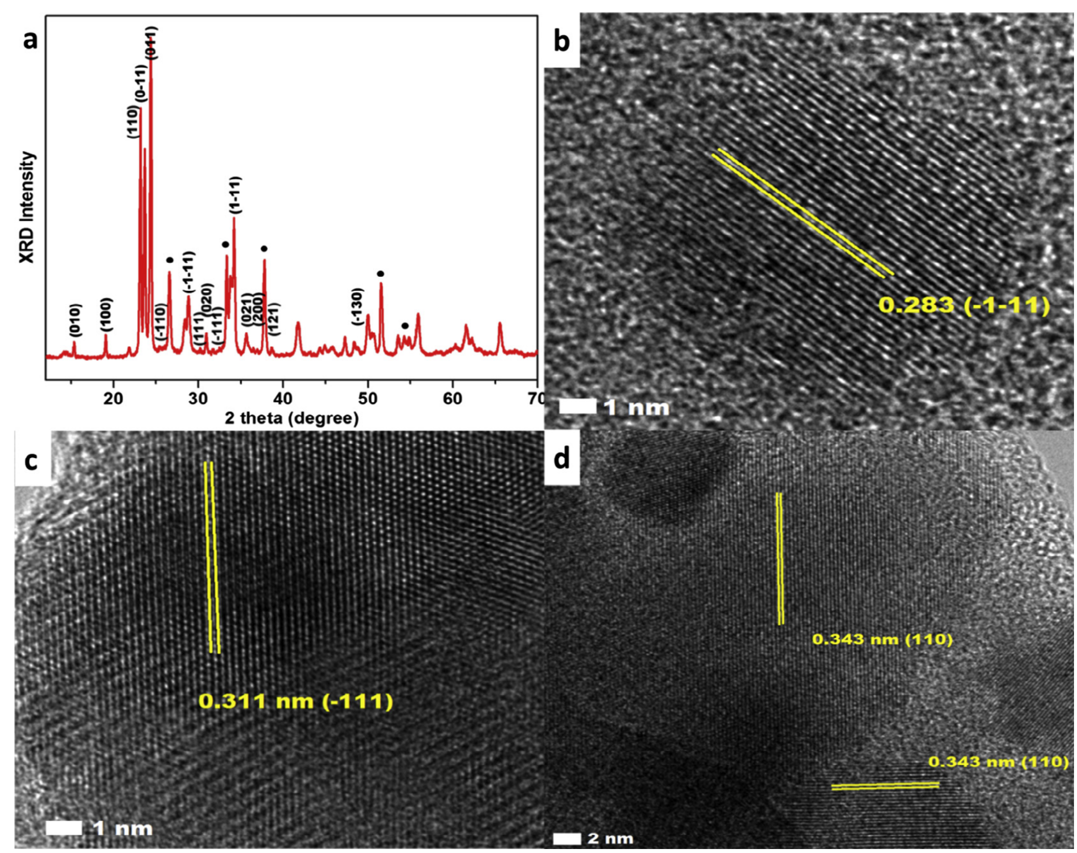

Fig. 2. (a) XRD patterns of $CuWO_4$ annealed at 500 °C for 2 h. (b–d) shows typical HRTEM images with corresponding *d*-spacings of $CuWO_4$.