



Metal loaded WO_3 particles for comparative studies of photocatalysis and electrolysis solar hydrogen production

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ABSTRACT

Striving for new solar hydrogen fuel, the water oxidation reaction based on photocatalyst suspension and photoelectrochemical (PEC) cell are currently the most important research for sustainable energy. Here, the effects of electrolyte pH, crystallinity and grain size of tungsten trioxide (WO_3) particles on photoconductivity are studied. Subsequently, a simple hydrothermal route was employed to synthesize Cs loaded WO_3 (Cs-WO_3) particles to further improve the photochemical reactivity. The photoanodes and photocatalyst based on the Cs-WO_3 reveals a different photoreactivity performance in the PEC and photocatalyst suspension systems. This important fundamental insight can assist in optimization of WO_3 particles photocatalyst and photoanode for future hybrid photocatalysis–electrolysis water splitting system. Based on the high photocatalytic capability demonstrated in this study, surface modified WO_3 particles are proven to be a promising candidate for efficient water-splitting catalyst.

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1. Introduction

The earth is well positioned to produce an unlimited supply of clean hydrogen fuel as there is ample supply of sunshine and water. The need for energy sustainable development without emitting carbon or contributing nuclear waste, compels scientist and engineers to develop clean energy solutions dependent on solar energy. In order to overcome the intermittency of sun radiation, it is essential to create a material to be able to capture, convert and store. Undoubtedly, the most attractive method for this solar conversion and storage is in the form of hydrogen energy carrier. Hydrogen is a clean energy carrier since the chemical energy stored is easily released when it combines with oxygen, yielding only water as the by-product. The added advantages of hydrogen are being transportable and storable for extended time.

During the last decades, a wide range of oxides is examined for use as anodes in photoelectrochemical cells for the conversion of solar energy into hydrogen [1–4]. TiO_2 [5–7], WO_3 [8,9] and Fe_2O_3 [10–12] are the most commonly studied metal oxides for photocatalytic and photoanode materials [2–12]. In addition, there are quite a number of papers that focus on WO_3 catalysts for photodegradation work [13–17]. These oxides possess physical and chemical resilience toward harsh environments such as continuous contact to water and solar irradiation. Moreover, they are relatively

abundance in nature. The theoretical solar-to-hydrogen (STH) efficiency under solar Air Mass 1.5 Global illumination taking into account of only the bandgaps, Fe_2O_3 (STH efficiency 15%, bandgap 2–2.2 eV), monoclinic WO_3 (10.6%, 2.5–2.9 eV) and anatase TiO_2 (2.9%, 3.2 eV) [18]. Although Fe_2O_3 has the lowest bandgap, it typically suffer from a large positive photocurrent onset potential (ca. 0.8 V versus the reversible hydrogen electrode), which requires the application of additional electric bias in water splitting reaction. In the case of WO_3 , sometimes expressed as WO_{3-x} ($x=0-1$), bandgaps ranging from 2.5 to 3.0 eV, depending on their stoichiometries, crystalline structures and defects. WO_3 is a promising candidate for stable visible-light driven photocatalyst, including a deeper valence band and strong absorption within the solar spectrum [19–21]. However, pure WO_3 has lower light energy conversion efficiency compared to TiO_2 since the reduction potential is relatively low [22]. Thus several strategies including surface and interface modification, composite materials, transition/noble metal doping, surface sensitization have been adopted to enhance the photocatalytic properties. In particular, the limitation of WO_3 as a photocatalyst can be compensated for by modifying the morphology and surfaces of the semiconductor. Metal–semiconductor modifications are used primarily to increase electron trapping, inhibit charge recombination and increase the selectivity of a particular product so as to improve efficiency of photocatalytic processes.

Here in this paper, we investigate the effect morphology and surface modification by annealing and metal loading of WO_3 particles on photocatalysis and photoelectrolysis performance.

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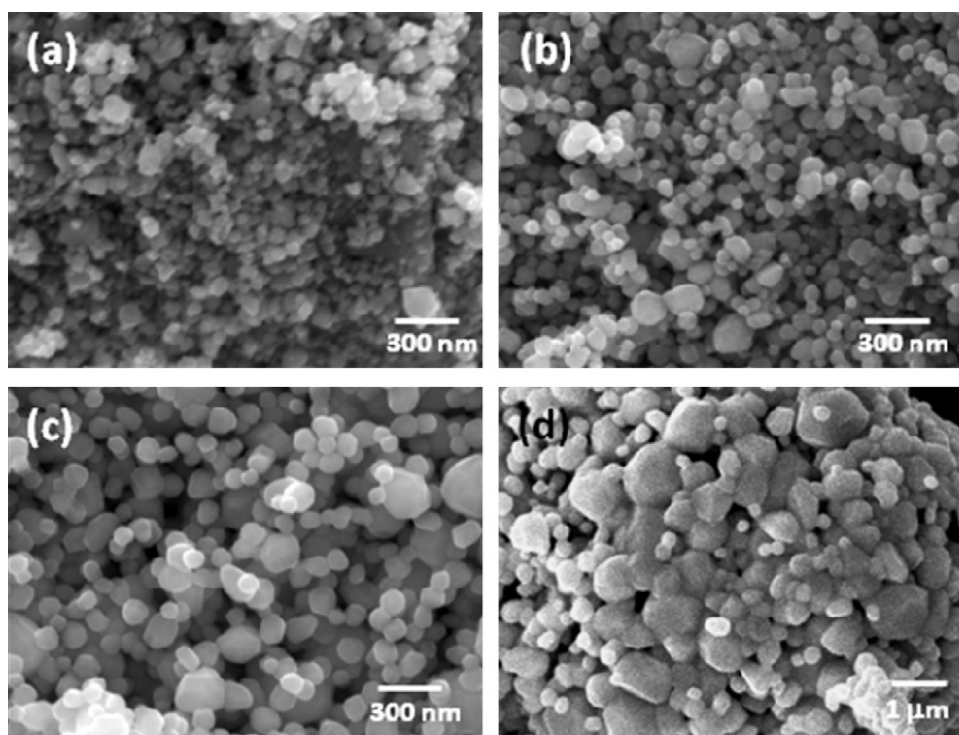


Fig. 1. SEM images of WO_3 particles (a) as prepared, (b) 600, (c) 700 and (d) 800 °C. The diameters of the particles increase with annealing temperature.

The comparative results clearly suggest a different charge transport mechanism present in the two photoreactivity systems. This important fundamental insight can assist in optimization of WO_3 particles photocatalyst and photoanode for future hybrid photocatalysis–electrolysis water splitting.

2. Experimental procedure

WO_3 nanopowder (<100 nm), cesium carbonate (Cs_2CO_3), polyethylene glycol (PEG) $M_w = 20,000$, potassium hydroxide (KOH) pellets were purchased from Sigma–Aldrich. All of the chemicals are of analytically grade purity and were used without further purification. WO_3 particles were transferred into Teflon-lined autoclaves with de-ionized (DI) water and 2.43 mM Cs_2CO_3 aqueous solution. The hydrothermal treatment was conducted at 120 °C for 12 h before the suspension was rinsed and dried for further use. Scanning Electron Microscope (SEM) micrographs of the particles were obtained using a JEOL JSM-7001F at 10 kV. Structural characterizations were obtained by X-ray diffraction (XRD) on Philips X-ray diffractometer with $\text{CuK}\alpha$ radiation. The absorption spectra of the films were recorded using a Shimadzu UV-3600 spectrophotometer.

All the photoactivities were performed from a side-window quartz tube. A 250 W mercury lamp with wavelength illuminator at 365–550 nm was employed for UV to visible light irradiation with the samples placed 50 mm away from the lamp. The photoelectrochemical measurements of the films were carried out using WO_3 particles as the photoanode and Pt as the counter electrode. Various treated WO_3 particles were mixed with PEG at 1:1 mass to form a smooth paste. Thin films were doctor bladed on SnO_2 :F-coated conducting glass as the photoanodes. The coated films were annealed in air at 450 °C for 1 h. The counter-electrodes used were Pt coated SnO_2 :F conducting glass. As for the photocatalyst suspension system, the photocatalyst powder (0.01 g) was dispersed in 10 ml of $\text{Fe}_2(\text{SO}_4)_3$ aqueous solution. Photocatalytic decomposition of water through a new reaction mechanism, similar to the

Z-scheme reaction was carried out using WO_3 particles catalyst and Fe ion redox system. The suspension was stirred vigorously using a magnetic stirrer to ensure homogeneous mixture. Next, all the experiments involved purging of the reactor quartz tube with N_2 for 15 min before illumination of light. The amount of evolved H_2 was determined using gas chromatography HP 6890 Series G1530A, thermal conductivity detector with N_2 carrier.

3. Results and discussion

Fig. 1 shows morphologies of the WO_3 particles at different annealing temperatures. The particles are generally spherical in shape and have a fairly tight size distribution. The average diameter of the particles increases with annealing temperature. The average diameter for the as-prepared particles is ~80 nm (**Fig. 1a**). Annealing the samples increases the mean particle size to 130, 190 and 900 nm for 600, 700 and 800 °C (**Fig. 1b–d**). A huge increase in mean particle diameter is observed between 700 and 800 °C. The primary particles appear to have agglomerated and sintered to form large crystallites, some are more than 1 μm in diameter. The surfaces of these large crystallites appear smooth and fairly faceted. The sintering and interconnection of the WO_3 particles is considered a desirable aspect for enhanced electron conductivity.

The XRD patterns for WO_3 films annealed at different temperatures are shown in **Fig. 2**. The diffraction peaks indicated the presence of monoclinic WO_3 phase, according to JCPDS data (JCPDS 43-1035). The monoclinic WO_3 phase exhibits three characteristic peaks at $2\theta = 23.3$, 23.8, and 24.6° and is the most stable phase at room temperature. These peaks of the various spectra are relatively similar in intensity which suggests no preferential crystal growth direction. However, there is a distinct increase in intensity and sharpening of diffraction peaks with increase annealing temperature, most likely attributed to the improved crystallinity. The full-width-half-maximum (FWHM) of the (001) crystal plane of monoclinic WO_3 decreases with increasing annealing temperature. The decrease of FWHM is in coherent with the

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