



Enhancement of visible-light-driven O₂ evolution from water oxidation on WO₃ treated with hydrogen



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ABSTRACT

The photocatalytic O₂ evolution from water oxidation was investigated over a series of WO₃ materials treated with hydrogen at different temperatures. The activity of WO₃ treated with hydrogen at 200 °C can be enhanced to 2.3 times of that of pristine WO₃. The surface WO₃ layer is partially reduced during the hydrogen treatment, forming a kind of H_xWO₃-WO₃ composite material. The H_xWO₃ phase possesses high electrical conductivity and plays as a reduction cocatalyst for WO₃ in the photocatalytic process. Formation of suitable amount of H_xWO₃ could facilitate the transfer of electrons, leading to efficient charge separation of WO₃ and resulting in the enhancement of the photocatalytic O₂ evolution activity under visible light irradiation. Fabrication of semiconductor and conductor nanocomposite might be a useful strategy for the development of efficient water-splitting photocatalysts.

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1. Introduction

Photocatalytic water splitting with semiconductor-based photocatalysts is an attractive reaction due to its potential contribution to the sustainable energy development [1–6]. Water-splitting reaction is composed of two half reactions, water oxidation (2H₂O → 4H⁺ + O₂ + 4e⁻) and proton reduction (2H⁺ + 2e⁻ → H₂) [7–9]. Water oxidation is the most critically challenging step in water splitting, which involves a four-electron transfer process and accompanies with a largely positive change in the Gibbs free energy [10,11]. Understanding the factors affecting water oxidation reaction for designing more efficient photocatalysts for overall water splitting is highly desirable [12–14].

Among various metal oxide semiconductor photocatalysts, tungsten oxide (WO₃) is an n-type semiconductor with a bandgap of ca. 2.6 eV [15,16]. It is chemically stable in acid condition and has been demonstrated to be active for visible-light-driven O₂ evolution from water oxidation [17]. Many efforts have been devoted to developing new strategies for further improving the photocatalytic activity of WO₃ [18–20]. For example, Xie et al. found that forming boron oxynitride nanoclusters on the surface of WO₃ could improve the photocatalytic O₂ reaction [18]. They proposed that boron oxynitride acts as a cocatalyst promoting electron-hole

separation and transfer. Waller et al. reported that photocatalytic water oxidation efficiency could be slightly improved by forming single-crystal WO₃ nanosheets [19]. Our recent work showed that WO₃ dispersed on silica support forming highly dispersed nanoparticles also exhibits a higher visible-light-driven O₂ evolution activity than that of the bulk WO₃ [20].

Modification of semiconductor photocatalysts with hydrogen treatment has arisen interest recently [9,21]. In this work, we found that the photocatalytic activity of WO₃ for water oxidation can be significantly enhanced by treatment with hydrogen at elevated temperatures. It was found that reduced highly electrical conductive H_xWO₃ phase on WO₃ plays as a reduction cocatalyst in the photocatalytic process, which facilitates efficient charge transfer and separation, hence enhancing the photocatalytic O₂ evolution activity under visible light irradiation.

2. Experimental

2.1. Preparation of the catalysts

WO₃ was prepared by the calcination of ammonium metatungstate in air at 500 °C for 3 h. The obtained WO₃ was treated in pure H₂ flow (60 mL min⁻¹) at elevated temperatures for 30 min. The resulting materials were denoted as WO₃-HT, where T is the treatment temperature (T = 100, 200, 300, 400, and 500 °C).

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Table 1

O₂ evolution activities, specific surface areas and electronic properties of WO₃ and hydrogen-treated WO₃ samples.

Samples	O ₂ evolution ^a (μmol h ⁻¹)	S _{BET} (m ² g ⁻¹)	R _s (ohm sq ⁻¹)
WO ₃	32.6	6.1	1.7 × 10 ⁷
WO ₃ -H100	65.1	6.3	–
WO ₃ -H200	75.3	6.5	4.6 × 10 ⁶
WO ₃ -H300	55.9	6.0	–
WO ₃ -H400	43.9	6.0	3.6 × 10 ⁴
WO ₃ -H500	0	5.4	2.7

^a Reaction condition: catalyst, 0.2 g; reactant solution: 100 mL 0.01 M AgNO₃ aqueous solution; light source: 300 W Xe lamp with cutoff filters (λ > 420 nm).

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2500/PC (40 kV, 100 mA) using Ni-filtered Cu Kα radiation source. Raman spectra were recorded on a home-assembled Raman spectrograph using a Jobin-Yvon T64000 triple-stage spectrograph with spectral resolution of 2 cm⁻¹. The laser line at 532 nm of an Ar laser was used as an excitation source. N₂ adsorption–desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2000 analyzer. Scanning electron microscopy (SEM) images were taken on a Hitachi S-5500. High-resolution transmission electron microscopy (HRTEM) images were taken on a Tecnai G² F30 S-Twin (FEI Company) with an acceleration voltage of 300 kV. The ultraviolet–visible (UV–vis) diffuse reflectance spectra were obtained using a VARIAN Cary 5000 spectrophotometer. Elemental analysis was performed on a VARIO ELCHN analysis meter. The sheet resistances were obtained with a HL5550 LN2 Hall effect measurement. X-ray photoelectron

spectra (XPS) were recorded on a Thermo Escalab 250 Xi with a monochromatic Al Kα X-ray source.

2.3. Photocatalytic activity measurements

The photocatalytic O₂ evolution reactions in an aqueous solution with AgNO₃ (0.01 M) as a sacrificial reagent were carried out in a closed gas circulation system. The catalyst powder (0.2 g) was dispersed by a magnetic stirrer in the aqueous solution (100 mL) in a reaction cell made of Pyrex glass. The reaction temperature was maintained at 10 °C. The reactant solution was

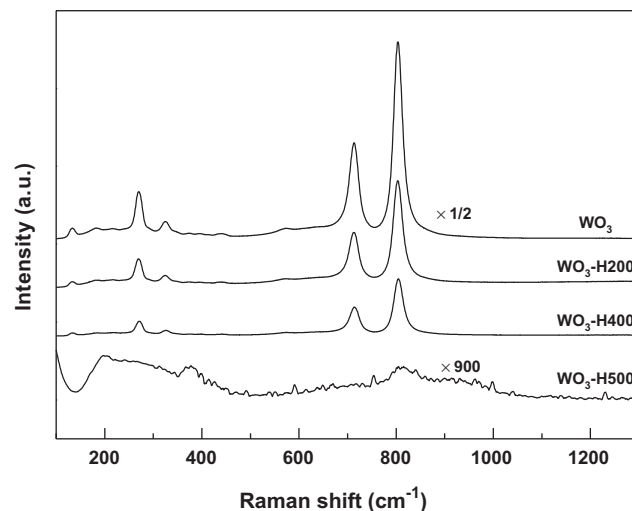


Fig. 3. Raman spectra of pristine WO₃ and hydrogen-treated WO₃ samples.

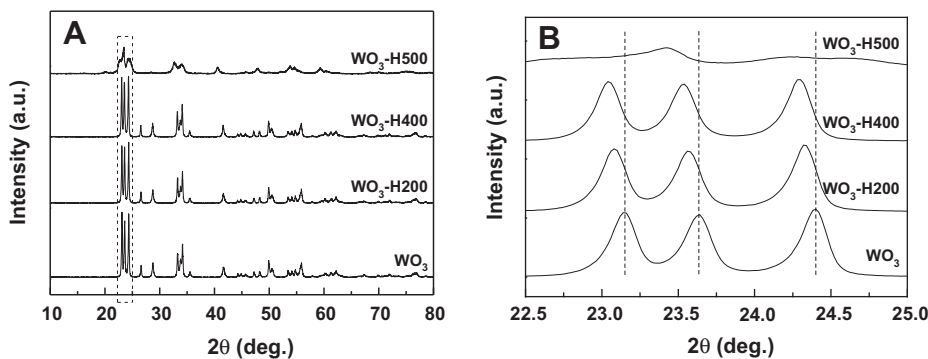


Fig. 1. (A) XRD patterns of WO₃ and hydrogen-treated WO₃ and (B) magnified peaks in 2θ range from 22.5° to 25° (scan speed: 0.2° min⁻¹).

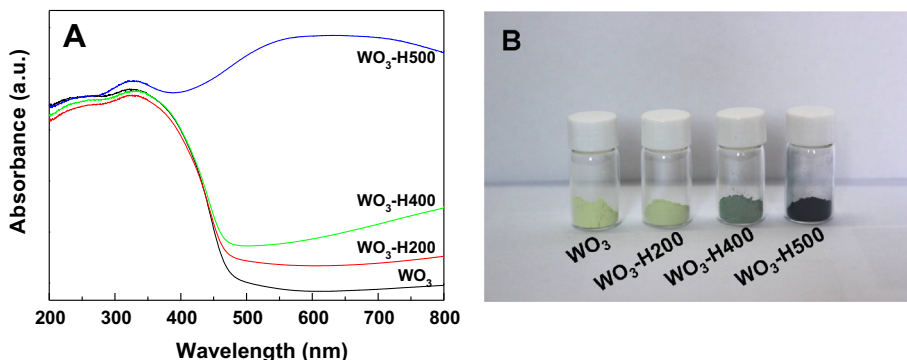


Fig. 2. (A) UV–vis diffuse reflectance spectra and (B) photographs of WO₃ and hydrogen-treated WO₃ samples.

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