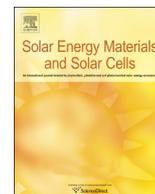




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10-fold enhancement in light-driven water splitting using niobium oxynitride microcone array films



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ABSTRACT

We demonstrate, for the first time, the synthesis of highly ordered niobium oxynitride microcones as an attractive class of materials for visible-light-driven water splitting. As revealed by the ultraviolet photoelectron spectroscopy (UPS), photoelectrochemical and transient photocurrent measurements, the microcones showed enhanced performance (~1000% compared to mesoporous niobium oxide) as photoanodes for water splitting with remarkable stability and visible light activity.

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1. Introduction

Owing to their exceptional stability, semiconducting properties, abundance and low cost, metal oxides have been extensively explored over the past few decades as photo electrodes for solar-driven fuel production in photo electrochemical cells (PEC) [1–6]. However, the long-standing bottleneck is the fact that metal oxides are wide band gap materials, with limited absorption activity to the ultraviolet spectral region, which contains only 3–5% of the incident solar energy. Thanks to the progress in the fabrication techniques, the precise control of the morphological and structural features of metal oxides that can enhance their optical and structural properties, rendering such structured materials useful in solar spectrum conversion devices [6,7]. However, the structured metal oxide systems demonstrated to date are still circumscribed by the minimal visible light absorption, which can be expounded predictably based on the fact that the valence bands of oxide semiconductor materials are mainly formed by O 2p orbitals, which are fixed at an extremely positive level of around 3.0 V vs. the normal hydrogen electrode (NHE) [8]. Moreover, the oxides with narrow band gaps (< 3.0 eV), for instance, Fe₂O₃ and WO₃, are either suffering from the stability

issues or the improper alignment of band levels necessary for water splitting and, therefore, require large external bias [2].

Due to the high potential energy of the metal–nitrogen bond compared to the metal–oxygen bond, transition metal oxynitrides [9–12], are identified as an alternative class of materials that can efficiently be used for solar energy conversion. This difference in bond energy results in narrower band gap energies in oxynitrides compared to their metal oxide counterparts. In addition, oxynitrides are ideal photoelectrodes for water splitting applications due to their stability in alkaline media [9–12]. Among all studied oxynitrides, niobium oxynitride (NbON) showed a significant promise as a visible light responsive material with suitable band-edge positions for water splitting [13,14]. To this end, Kanade et al. [15], showed that thermal ammonolysis of Nb₂Zr₆O₁₇ powder (3.1 eV) at 800 °C resulted in the formation of niobium zirconium oxynitride with a band gap of 2.14 eV. Moreover, Ruff et al. [13], fabricated NbON thin films via the annealing of niobium oxide films in ammonia at 450–600 °C for 5–60 min. The films annealed at 450 °C for 20 min engendered the highest photocurrent density (13 μA/cm² at 0.8 V) among other films treated at higher annealing temperatures and/or for longer times. However, those materials are either powders or thin films. Powders are not practical for a scalable photolysis process. Also, with thin films, the light absorption and carrier collection are in competition, i.e. while thick films are needed to harvest a reasonable amount of the solar

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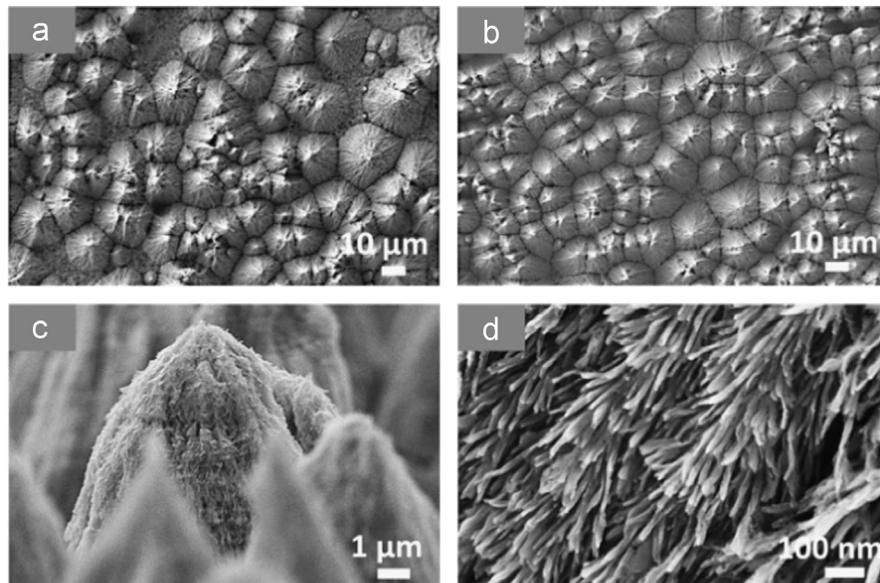


Fig. 1. SEM images of niobium oxide microcones: (a) as-anodized, (b) after annealing in ammonia and (c) and (d) higher magnification of the microcones shown in (b).

spectrum, thicker films than the carrier diffusion length will result in poor carrier collection efficiency [7]. It is noteworthy mentioning that ordered nanostructured and/or microstructured niobium oxynitrides have been investigated. There is only one recent study on the use of ordered mesoporous nitrogen-doped Nb_2O_5 [14]. The authors reported an enhancement in the hydrogen production efficiency of 14.8 times over the nitrogen-doped TiO_2 (P25) counterparts prepared by the same method. The N-doped Nb_2O_5 resulted in a photocurrent of $7 \mu\text{A}/\text{cm}^2$ at 1.2 V compared to $3 \mu\text{A}/\text{cm}^2$ obtained for N-doped TiO_2 . This enhancement was attributed to the inherited ordered mesostructure of N-doped Nb_2O_5 that could offer more active sites for the photocatalytic reaction, thus accelerating the transfer of photo-generated charge carriers. Herein, we demonstrate, for the first time, the opportunity to fabricate niobium oxynitride (NbON) microcone arrays by a facile electrochemical method and investigate their performance as photoanode in photo-electrochemical water splitting cells.

2. Experimental details

Niobium foil (0.25 mm thick, purity 99.8%) was polished into portions and cleaned in acetone, ethanol and deionized water, respectively. Two-electrode electrochemical cell was used for anodization in which the Nb metal foil (positive electrode) and a platinum foil (negative electrode) were connected to a DC power supply at 40 V. The aqueous electrolyte contained 0.5 M NaF and 1.15 M HF (50%). All samples were anodized for 40 min at room temperature. After forming niobium oxide microcones by anodization, nitridation was carried in ammonia flow (200 sccm) at 450 °C. The heating and cooling rates were as low as 2 °C/min to preserve the morphology of the microcones and avoid their detachment. As a reference, niobium oxide microcones sample was annealed in air under the same conditions (450 °C and 2 °C/min for 1 h). The surface morphology was investigated by field-emission scanning electron microscope (FESEM-Zeiss SEM Ultra-60). X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) Omicron chamber equipped with a SPHERA U7 hemispherical energy analyzer, using X-ray photons with an incident kinetic energy of 1486.6 eV from a monochromatic Al K α X-ray source with a total energy resolution of 0.1 eV. The survey spectrum was acquired at a pass energy of

40 eV while the high-resolution core level peaks for the various elements were obtained at a pass energy of 20 eV. The SPHERA U7 hemispherical energy analyzer collected the photoelectrons, with a 7 channel MCD detector, in Constant Analyzer Energy (CAE) mode. For UPS measurements, the base pressure was maintained below 5×10^{-9} mbar. He I photons (21.2 eV) were used to acquire the spectra at normal emission. The photon line width was ≈ 250 eV and the minimum spot size was ≈ 1 mm. The crystal structure was studied using glancing angle X-ray diffractometer (GAXRD; Bruker thin film). Raman measurements were performed using a micro-Raman microscope with an excitation laser beam wavelength of 325 nm. The optical absorption of the samples was measured using a Cary 5000 UV-vis-NIR spectrophotometer. The J - V measurements were carried in a three-electrode electrochemical cell with reversible hydrogen electrode (RHE) as a reference, platinum foil as a counter electrode and the tested sample as the working electrode, immersed in 0.1 M Na_2SO_4 . A scanning potentiostat (CH Instruments, Model CHI 600B) was used to measure dark and illuminated currents at a scan rate of 10 mV/s. A 300 W ozone-free xenon lamp (Spectra Physics) was used as the light source, with an AM 1.5 G filter to simulate sunlight at $100 \text{ mW}/\text{cm}^2$.

3. Results and discussion

Fig. 1a shows an FESEM top-view image of the fabricated niobium oxide. The well-aligned, densely packed microcone arrays that are several microns long were formed and distributed uniformly with full coverage on the film surface. The average height of the microcones is estimated as $11.2 \pm 3 \mu\text{m}$. The morphology and structure of the microcones is preserved even after annealing in ammonia ambient for 1 h (Fig. 1b). Note that the microcone structure has not been affected by annealing. The higher magnification images in Fig. 1c and d show the wire-like nanostructure of the microcone thread. The average length of the wire-like nanostructure is 187 nm.

Fig. 2a shows the XRD patterns of the as-anodized microcones, the microcones annealed in air, and those annealed in ammonia for 1 h, revealing crystalline structures of niobium oxide. The diffraction peaks at $2\theta = 28^\circ$ and 50° are ascribed to orthorhombic Nb_2O_5 [16]. The as-anodized microcones are crystalline without

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