Fabrication and Photocatalytic Activity of Nanoporous WO\textsubscript{3} Film

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Nanoporous tungsten oxide (WO\textsubscript{3}) films with a thickness of 500 nm and pore size of about 80–100 nm are fabricated by chemical anodization of a W foil in a 1 M Na\textsubscript{2}SO\textsubscript{4} solution with 0.5 wt% NaF (pH 4.0) at 40 V. The effect of anodization voltage on the morphology of WO\textsubscript{3} films was investigated by evaluating the anodization current and the dissolution concentration of W in electrolyte during anodization process. The photoelectrochemical properties and photocatalytic activity of the nanoporous WO\textsubscript{3} films are investigated under visible light irradiation. The nanoporous WO\textsubscript{3} structure is a sensitive visible light photocatalyst that can be used to decompose contamination and our results show that the porous film has better photocactivity than a dense structure.

**Keywords:** Nanoporous, WO\textsubscript{3}, Photocatalysis, Photoconversion Efficiency, Anodization.

Semiconductor photocatalysts have attracted increasing interest because of their wide application in photoelectrochemical (PEC) water splitting and photocatalytic (PC) degradation of toxic chemicals in water and air.\textsuperscript{1–4} TiO\textsubscript{2} is currently the best known and most widely used photocatalytic material due to its low cost, non-toxicity, high stability, and high efficiency in degradation of pollutants.\textsuperscript{2–3} However, TiO\textsubscript{2} can be activated only by ultraviolet (UV) light because of the wide bandgap energies of the anatase (3.2 eV) and rutile (3.0 eV) phases. Since UV radiation only corresponds to less than 6% of the solar energy impinging the earth’s surface,\textsuperscript{2} many researchers have attempted to red-shift the absorption range in TiO\textsubscript{2} by doping or modification of TiO\textsubscript{2} or to develop new visible light sensitive photocatalysts in order to utilize the solar spectrum more efficiently.\textsuperscript{3,5} Tungsten oxide (WO\textsubscript{3}) is an important semiconductor with interesting optical and electrical properties that have promising applications in photoelectrochemical devices, photocatalysis, chemical sensors, and so on.\textsuperscript{6} Its lower bandgap of 2.4–2.8 eV also enables more efficient absorption of visible light. A nanoporous WO\textsubscript{3} film is an attractive photocatalyst because of its large surface and nanoporous structures that not only allow more effective absorption of incident photons but also can minimize the distance between the site of photon absorption and electron/hole redox reactions. These two factors result in enhanced photocatalytic activity. Porous WO\textsubscript{3} nanostructures have been synthesized by chemical vapor deposition,\textsuperscript{7–8} electrodepositions,\textsuperscript{9} and sol–gel method.\textsuperscript{10–11} Another possible route to fabricate nanoporous WO\textsubscript{3} films is electrochemical anodization of a W foil in a suitable electrolyte. Anodization is a commonly used surface treatment method especially pertaining to the formation of porous structures on the surface of metals such as Al, Ti, Ta, and Fe.\textsuperscript{12–15} Although there are several reports on the fabrication of porous WO\textsubscript{3} by anodization,\textsuperscript{16–21} the photocatalytic activity and photoelectrochemical properties of nanoporous WO\textsubscript{3} nanostructure have not been investigated in details.\textsuperscript{17} In this work, a regular nanoporous WO\textsubscript{3} film were fabricated on a W foil by electrochemical anodization of a W foil in a fluorine-containing electrolyte consisting of 1 M Na\textsubscript{2}SO\textsubscript{4} and 0.5 wt% NaF. The dissolution of WO\textsubscript{3} in the used electrolyte at different anodization voltages were investigated for the first time by measuring the W species concentration in the electrolyte. The morphology, structure, and composition of the nanoporous WO\textsubscript{3} film together with the photocatalytic activity and photoelectrochemical properties were determined. These nanoporous WO\textsubscript{3} films have potential applications in photocatalysis, chemical sensing, and photoelectrochemical devices.

Tungsten foils (0.5 mm thick, 99.6% purity) were purchased from Baoji Nanrong Company (Baoji, China). Nanoporous WO\textsubscript{3} films were fabricated by anodizing W foils and the detailed procedures have been described.
previously. In brief, the W foils were mechanically polished by SiC sandpapers and then anodized in an alkali electrolyte under low voltage to remove the oxide layer. The electrochemical cell had the conventional two-electrode configuration with the tungsten sheet as the working electrode and a graphite foil as the counter electrode (1 cm separation). Anodization of W substrate with the area of 1.5 cm² was carried out at different voltages (20–60 V) and a temperature of 298 K for 2 hours in a 100 mL aqueous electrolyte containing 1 M Na₂SO₄ and 0.5 wt% NaF (pH = 4.0). In the process of anodization, the anodized current was recorded by the computer connect with the DC supply power (ITECH IT6123). After anodization, the samples were rinsed with a diluted HF solution and deionized water several times and then dried in air. The nanoporous WO₃ films initially had an

![Fig. 1. Effect of anodization voltage on the morphology of WO₃ nanoporous films. (a) 20, (b) 40, (c) 60 V, respectively. The insets in (a)–(c) are the corresponding SEM images with enlarged magnification and the scale bar in the insets is 500 nm. (d) side-view SEM image of nanoporous films shown in (b), the inset is the EDX spectroscopy. (e) side-view image of non-porous flat WO₃ film formed in non-fluorine ions electrolyte.](image-url)
amorphous structure and could be crystallized by annealing at 723 K in air for 3 h at a heating rate of 10 K·min⁻¹. For comparison, non-porous WO₃ films were also prepared in 1 M Na₂SO₄ without fluoride under the same anodization conditions.

The morphologies of the anodized samples were characterized by field emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano). The thickness of the nanoporous film was estimated directly from the cross-sectional SEM image. The as-anodized and subsequent annealed samples were determined by X-ray diffraction with CuKα radiation (λ = 1.5416 Å) (XRD, Philips X'Pert Pro), X-ray photoelectron spectroscopy (XPS Physical Electronics 5600), energy-dispersive X-ray spectroscopy (EDS, Oxford INCA 200) and UV-Vis-NIR Spectrophotometer (Lambda 750 UV/Vis/NIR, PerkinElmer). The W-containing species concentration in the electrolyte resulting from the dissolution of WO₃ during anodization was detected by Inductive Coupled Plasma Emission Spectrometer (IRIS Advantage ER/S).

The photocatalytic (PC) activities of the nanoporous and non-porous WO₃ films were evaluated using methyl orange (MO) in an aqueous solution as the probing molecule. A sample with dimensions of 1 × 1 cm² was immersed in 20 ml of the MO aqueous solution with an initial concentration of 10 mg/L. The solution was stirred in dark for 2 hrs to saturate the photocatalyst with MO. The photodegradation experiments were performed at the natural pH of the MO dye. The solution was aspirated continuously with air during the PC reaction. A Xe-lamp (500 W) was used as the visible light irradiation source and the distance between the light source and samples was maintained at about 10 cm. The change in the MO concentration versus PC time was monitored using a UV-Vis spectrophotometer (TU-1810SPC, Beijing PGENERAL, Beijing, China) at a wavelength of 464 nm and using a standard quartz cuvette of 1 cm.

The PEC characteristics of the nanoporous WO₃ films were evaluated using a three electrode PEC cell with the same Xe lamp. The samples were insulated with epoxy resin leaving an open area of 1 × 1 cm² as the working photoanode. An Ag/AgCl electrode served as the reference electrode and a platinum foil was the counter electrode. All the photocurrent experiments were performed on a CHI650c potentiostat (CH Instruments Inc. Shanghai, China) by means of linear sweep voltammetry at a scanning rate of 0.01 V/s and a 0.5 M Na₂SO₄ solution was used as the electrolyte.

Figure 1 displays the SEM images of the tungsten oxide films anodized at different voltages and the morphology changes according to the anodization voltage. At 20 V, very little etching can be observed and some nonporosified patches are still visible. With the anodization voltage increased to 40 V, a regular nanoporous structure is formed on the entire surface of W foil. However, a higher anodization voltage of 60 V leads to an over-etched layer and the pores tend to “grow” together. The highly organized nanoporous film formed at 40 V has an average pore size of 80–100 nm and wall thicknesses of 6–12 nm. The thickness of the nanoporous film is about 500 nm as indicated by the side-view SEM image in Figure 1(d). EDS suggests that the nanoporous film mainly consists of W and O (Fig. 1(d), inset). For comparison, a non-porous WO₃ film is also prepared by anodization of a W foil for 30 min in 1 M Na₂SO₄ without fluoride at the same anodization voltage and the side-view image reveals that the thickness of the non-porous film is about 450 nm (Fig. 1(e)).

The effect of anodization voltage on the morphology of WO₃ films was also investigated by evaluating the anodization current and the dissolution concentration of W species in electrolyte during anodization process by ICP analyses. Figure 2 shows that the anodization current (j) versus time (t) under different anodization voltages, exhibiting a classic characteristic shape including the dip-rise-gradual fall that has been observed for the formation of nanoporous or nanotube arrays of metal oxide via anodization. Initially the current density transient of the flat W surface decreased rapidly due to the formation of a barrier oxide film on the W metal and then the slightly increases in current density stem from the solubility of oxides in electrolytes containing F ions, resulting in the formation of a partially porous structure. The current density increased again beyond the minimum value as a consequence of the thinning barrier oxide layer at the pore bottom. After that, a steady current density was attained by maintaining an equilibrium state between the oxide formation rate and the dissolution rate of the grown oxide. The overall current density observed in j–t plots increased with elevation of anodization voltages. This may be attributed to an accelerated dissolution of the formed tungsten oxide as soluble fluoride-complexes with the higher voltage. Figure 3 shows the concentration of the dissolved tungsten in electrolyte versus anodization voltage with the reaction time.
Fig. 3. The dissolved concentration of W species versus different voltage after anodization of W foil for 2 h in a 100 mL electrolyte.

of 2 h. It is clearly seen that the concentration of W increase with the anodization voltage. The W concentration in a 100 mL electrolyte for anodization of 2 h under 20 V is 40.3 mg/L, which increased to 41.52 mg/L under 40 V. At 60 V, the W concentration in 100 mL electrolyte is 48 mg/L. The dissolve W species in electrolyte is believed to the dissolution of tungsten oxide on surface of W foil. The increase of W species in electrolyte with the voltages suggests that the dissolution of the formed tungsten oxide as soluble fluoride-complexes accelerated with the elevation of voltage. Thus over-etching occur at higher voltage due to the faster dissolution of the formed oxide layer and the irregular nanoporous nanostructures are formed at higher voltage such as 60 V in this paper.

Figure 4 depicts the XRD patterns of the anodized tungsten oxide films before and after annealing in air at 723 K for 3 h. Before annealing, only peaks corresponding to the W substrate are apparent revealing that the anodized nanoporous film is amorphous (curve 1). After annealing, the XRD patterns of the nanoporous film (curve 2) can be indexed to a monoclinic phase of WO₃ (JPCD card, No. 43-1035). XPS is further used to confirm the WO₃ composition. Figure 5(a) shows the survey XPS results acquired from the annealed nanoporous WO₃ film. No F or Na contamination can be detected. The double peaks for W 4f(1/2) and 4f(3/2) at 35.7 and 37.7 eV (Fig. 5(b)) and one peak for W 5p(3/2) at 41.2 eV could be seen, respectively correspond to W (VI) in WO₃. The O peaks could be fitted to two peaks centered at 531.1 and 531.7 eV by Lorentzian-Gaussian curve fitting, which could be attributed to W–O and W–OH, respectively (Fig. 5(c)). This result suggested that the nanoporous WO₃ has good hydrophilic performance.
The UV-Vis absorption of nanoporous WO$_3$ was also investigated and shown in Figure 6. The as-anodized sample has an absorption edge at around 380 nm corresponding to a band gap of 3.2 eV. Annealing at 723 K for 3 h results in the absorption edge red-shifted to longer wavelength (lower energy) of around 480 nm (2.6 eV) and a higher absorption in the region of visible light could also be observed. It is suggested that the crystalline WO$_3$ shows better photoresponse in visible region.

Figure 7(a) exhibits the photocurrent density as a function of applied potential (vs. Ag/AgCl) measured from the annealed nanoporous and non-porous WO$_3$ films in a 0.5 M Na$_2$SO$_4$ solution under Xe lamp irradiation. The average photon intensity reaching the sample surface is measured to be about 5.0 mW/cm$^2$ and the anodic bias potential is scanned from $-0.3$ to $+1.5$ V at a rate of 10 mV/s. The dark current without Xe lamp irradiating is close to zero and negligible, but the photocurrents measured from the nanoporous WO$_3$ photoanode increase dramatically with anodic potential when the bias potential exceeds 0.2 V and the photocurrent density reaches 0.48 mA/cm$^2$ at 1.5 V bias potential. This value is about three times that observed from the non-porous WO$_3$ film. The corresponding photoconversion efficiency ($\eta$) of light energy to chemical energy in the presence of an external applied potential could be calculated as follows:

$$\eta(\%) = \left(\frac{\text{total power output} - \text{electrical power output}}{\text{light power input}}\right) \times 100\% = \frac{j_p(E_{\text{rev}}^0 - |E_{\text{app}}^0|)}{I_0} \times 100\%$$

where, $j_p$ is the photocurrent density (mA/cm$^2$), $I_0$ is the intensity of the incident light in mW/cm$^2$, $E_{\text{rev}}^0$ is the standard reversible potential which is 1.23 V NHE$^{-1}$, $j_p(E_{\text{rev}}^0)$ is the total power output, and the electrical power output is $j_p|E_{\text{app}}^0|$. $E_{\text{app}} = E_{\text{meas}} - E_{\text{ocp}}$. $E_{\text{meas}}$ is the electrode potential (vs. Ag/AgCl) of the working electrode at which the photocurrent is measured during illumination and $E_{\text{ocp}}$ is the electrode potential (vs. Ag/AgCl) of the same working electrode under open circuit conditions and the same illumination in the same electrolyte. The $E_{\text{ocp}}$ values of the self-assembled nanoporous WO$_3$ and the non-porous WO$_3$ films are measured to be 0.102 and 0.054 V, respectively. The curves of the photoconversion efficiency as a function of bias potential for the nanoporous and non-porous WO$_3$ are shown in Figure 7(b). A maximum photoconversion efficiency of 2.81% is obtained at 0.74 V versus SCE from the nanoporous film, whereas it is 0.42% at 0.9 V versus SCE for the WO$_3$ film. The high photoconversion efficiency may be attributed to the large area and improved light absorption due to photo multi-scattering in the pores of the nanoporous films.

The PC activity of the nanoporous WO$_3$ film is also investigated by studying the degradation in the MO solution under Xe lamp irradiation with a filter to remove UV radiation. MO is a non-biodegradable dye used in the textile industry and often considered the standard dye in the determination of PC activity. The photodegradation experiments are performed at the natural pH of MO and the
Fig. 8. (a) MO Concentration (C) as a function of illuminating time (t) under Xe-lamp with porous and flat WO3. (b) Curves of ln(C/C₀) versus irradiation time. The photocatalytic activity of MO in the presence of the nanoporous WO3 film is obviously enhanced. The PC degradation rate constant, k, values calculated from the nanoporous and non-porous WO3 are listed in Table 2, which demonstrate the magnitude of the overall photodegradation rate. The k value of the nanoporous WO3 is about 4 times larger than that of the non-porous one disclosing that the nanoporous WO3 films have better photocatalytic activity than the non-porous one.

Regular self-assembled nanoporous WO3 films have been produced by simple anodization of W foils in a fluorine-based electrolyte. The effect of anodization voltage on the morphology of WO3 films was investigated by evaluating the anodization current and the dissolution concentration of W in electrolyte during anodization process. The self-assembled nanoporous WO3 film that possesses a large surface area and porous structure exhibits higher photocatalytic activity and better photoelectrochemical performance than the non-porous WO3 film.

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References and Notes


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