Supporting Information

Reduced impurity-driven defect states in anodized nanoporous Nb₂O₅: the possibility of improving photoanodes' performance

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Materials and method of experiments

Niobium films sputtering: The initial material for fabricating the nanoporous Nb₂O₅ was niobium metal, which was deposited onto 2×1.5 cm of FTO using an RF sputtering system. A niobium target of 99.95% purity was placed at a distance of 65 mm from the substrate stage. The base pressure of the sputtering chamber was set to 1×10^{-5} Torr. The sputtering process was conducted in the presence of 100% argon at 2×10^{-2} Torr. During the deposition process, a constant RF power of 120 W was applied and the substrate temperature was set at 260 °C. A film thickness of ~2.4 µm niobium metal was formed on the FTO after 150 minutes of sputtering.

Anodization of niobium films: The anodization of niobium films was carried out in a two electrode configuration. The electrolyte for forming Nb₂O₅-EGAF was a combination of 0.25 g NH₄F (98 % purity, Sigma Aldrich), and 4 vol% deionized water in 50 ml ethylene glycol (98% purity, Sigma Aldrich). The electrolyte was kept at an optimum temperature of 50 °C during each experiment.^{S1} For forming Nb₂O₅-GLPP, the suggested experimental conditions for the electrolyte based on glycerol is 10 wt% K₂HPO₄ (98% purity, Sigma Aldrich) in 50 ml glycerol (99% purity, Sigma Aldrich) at an optimum temperature of 180 °C.^{S2} The anodization experiment for both electrolyte conditions was examined under different voltages of 10, 15 and 20 V. After anodization, the samples were carefully washed with deionized water and dried in a nitrogen gas stream. Then, Nb₂O₅-EGAF and Nb₂O₅-GLPP samples were annealed in air at temperatures of 430 and 500 °C for 60 minutes, respectively, with a slow ramp up and down rate of 2 °C/minute. The annealing temperatures were chosen as they produced the best crystal phases and structures. Annealing at higher temperatures causes deterioration of the films.

Structural characterization: The surface and cross-sectional morphology of the nanoporous Nb₂O₅ films were characterized using a FEI Nova NanoSEM scanning electron microscopy (SEM). The crystal structures of the Nb₂O₅ films were characterized by a D8 Advance Bruker AXS X-ray diffractometer with GADDS (General Area Detector Diffraction System) attachment fitted with a 50 µm spot size collimator, incorporating a High Star 2-dimensional detector and CuK α radiation ($\lambda = 0.1542$ nm) operating at 40 kV and 40 mA. The chemical compositions of the Nb₂O₅ films were conducted using a Thermo K-alpha X-ray Photoelectron Spectrometer (XPS). The analysis of the surface to volume ratios of the films was conducted using ImageJ.

Solar cell fabrication: The nanoporous Nb₂O₅ photoanodes were first immersed in a 0.3 mM Dyesol RuL₂(NCS)₂ (L = 2,2'-bipyr-idyl-4,4'-dicarboxylic acid) (N3 dye) ethanol solution and kept at room temperature for 24 hours. The counter-electrode was 10 nm thick platinum, sputtered on a FTO substrate (Delta Technologies). The electrolyte used was Dyesol high performance electrolyte (EL-HPE) with I^-/I_3^- as the redox species, inorganic iodide salt, organic iodide salt, and pyridine derivative as the additives dissolved in acetonitrile and valeronitrile. The dye-adsorbed Nb₂O₅ photoanodes and platinum counter-electrodes were assembled into a sandwich- type cell and sealed with a hot-melt Surlyn with a thickness of 25 µm (Dyesol). The Nb₂O₅ electrodes had dimensions of 5 × 5 mm (0.25 cm²).

Solar cell characterization: The dye loading measurements of the sensitized Nb_2O_5 photoanodes were established by desorbing the dye molecules from the photoanode in 10 mM KOH solution. UV-Vis absorption spectra of the desorbed dye were examined using a spectrophotometric system consisting of a Micropack DH-2000 UV-Vis-NIR light source and an Oceanoptics HR4000 spectrophotometer. Photovoltaic measurements were performed using an AM 1.5 solar simulator (ABET Technologies LS-120 solar light source fitted with an AM 1.5

filter). The power of the simulated light was calibrated to 100 mW.cm⁻² by using a reference silicon photodiode with a power meter (1835-C, Newport) and a reference silicon solar cell to reduce the mismatch between the simulated light and AM 1.5. A Keithly 2602 source meter was used to produce the *J*-*V* characteristics of the cells at a voltage ramping rate of 0.01 V s⁻¹, and a Labview program was used to interpret the *J*-*V* data generated. EIS spectra were measured in the dark and biased with the open circuit voltage value of the DSSC using a CHI 700 electrochemical workstation with an impedance analyzer in a two-electrode configuration. A 10 mV AC perturbation was applied ranging between 10 mHz and 100 kHz. Open-circuit photovoltage decay measurements were conducted by illuminated the DSSCs under simulated solar lamp for ~20 s and then the transient of the open circuit photovoltage was measured after the lamp was switched off. The velocity of the photovoltage decay is directly related to the electron lifetime by the following expression:^{S3,S4}

$$\tau_n = (-k_b T/e) (dV_{oc}/dt)^{-1}, \tag{1}$$

where k_bT is the thermal energy, dV_{oc}/dt is the derivative of open circuit voltage transient and *e* is the positive elementary charge.

Anodized nanoporous Nb₂O₅ at different applied voltage.

Practically, the surface morphology and thickness of the nanoporous Nb_2O_5 can be controlled by varying fluoride content, applied voltage, water content and temperature during the anodization process. Since the electrolyte composition and the setup temperature have been optimized in the previous studies,^{S1,S2} here, we only optimized the anodization of nanoporous Nb_2O_5 by varying the applied voltage.

As can be seen in Fig. S1 and S2, increasing the applied voltage to up to 20 V enlarges the pore size due to the enhancement of the chemical dissolution effect on the porous structure. It is observed that the pore openings on the surface of the nanoporous Nb₂O₅ become wider at higher voltages, while the widths of the walls of the remaining oxide decrease. Furthermore increasing the applied voltage, it also increases the thickness of the nanoporous films. Three different film thicknesses ranging from ~3.5 to ~6.8 μ m, which are are obtained at 10, 15 and 20 V are shown in Fig. S1 and S2.



Fig.S1. SEM images of top view (a-c) and cross-sectional view (d-f) of Nb₂O₅-EGAF prepared at different anodization voltages, (a,d) 10 V, (b,e) 15 V, and (c,f) 20 V in the electrolyte of 50 ml ethylene glycol with 0.25 g NH₄F and 4 vol% H₂O at 50 °C.



Fig.S2. SEM images of top view (a-c) and cross-sectional view (d-f) of Nb₂O₅-GLPP prepared at different anodization voltages, (a,d) 10 V, (b,e) 15 V, and (c,f) 20 V in the electrolyte of 50 ml glycerol with 10 wt% K₂HPO₄ at 180 °C.

XRD patterns

The crystal phase of annealed nanoporous Nb₂O₅, anodized in the presence of Nb₂O₅-EGAF and Nb₂O₅-GLPP electrolytes were determined by X-ray diffraction (XRD. Fig.S3 shows the diffraction pattern of annealed nanoporous Nb₂O₅-EGAF and Nb₂O₅-GLPP. From these data, the diffraction pattern of the nanoporous Nb₂O₅-EGAF, contains a dominant orthorhombic Nb₂O₅ phase (ICDD30-0873), as indicated by peaks appearing at 22.6, 28.5, 37, 45, 46.3, 50.5, and 55.5° 2-theta.^{S5, S6} The XRD pattern also indicate that the nanoporous Nb₂O₅-GLPP has an orthorhombic (ICDD 30-0873) Nb₂O₅ phase.^{S5, S6}



Fig. S3. XRD patterns of annealed nanoporous (a) Nb_2O_5 -EGAF (blue line) and (b) Nb_2O_5 -GLPP (red line). Orthorhombic Nb_2O_5 (ICDD30-0873) is denoted by ,* while FTO is denoted by

■.

Dye loading measurement

Measurement of dye coverage has been conducted by desorbing the adsorbed dye from the photoanode into the 10 mM KOH solution and measuring the absorbance of the solution. According to the UV-Vis absorption spectra in Fig.S4, the calculated dye loading amounts for the Nb₂O₅-EGAF and Nb₂O₅-GLPP photoanodes were 63.6 and 74.8 nmol/cm² at 534 nm, respectively.



Fig.S4. UV-Vis absorption spectra of N3 dye desorbed from Nb_2O_5 -EGAF (blue line) and Nb_2O_5 -GLPP (red line) photoanodes.

EIS spectra measurement

EIS spectra of Nb₂O₅ DSSCs were measured in the dark at an applied bias of $-V_{oc}$, using a CHI 700 electrochemical workstation with an impedance analyzer in a two-electrode configuration. A 10 mV AC perturbation was applied ranging between 100 kHz and 10 mHz. The EIS measurements of the DSSCs are presented by Nyquist plots and Bode phase plots in Fig.3d and Fig.S5, respectively. According to Fig.3d, the two well-defined semicircles of the Nyquist plots represent the charge transfer for the redox reaction of I^-/I_3^- at the Pt counter electrode/electrolyte interface (in the kHz range) and the electron transfer/charge recombination at the photoanode/dye/electrolyte interface (1-100 Hz), respectively. It is suggested that the radius of the second semicircles define the charge-transfer resistance of the DSSCs.^{S7,S8} The graph shows that the semicircles radius of the Nb₂O₅-EGAF DSSC are 3-fold larger than that of Nb₂O₅-GLPP DSSC, indicating lower electron recombination with the tri-iodide ions in the Nb₂O₅-EGAF DSSC due to the high charge-transfer resistance. In addition, the Bode phase plots in Fig.S5 also demonstrate that the Nb₂O₅-EGAF DSSC has a longer electron lifetime, since it has a lower frequency peak position in comparison to Nb₂O₅-GLPP DSSC.



Fig. S5. Bode phase plots of the impedance spectra. Electrochemical impedance spectra of the DSSCs fabricated using Nb₂O₅-EGAF (blue line) and Nb₂O₅-GLPP (red line) photoanodes with thicknesses of $\sim 5 \,\mu$ m.

Sample	V_{oc} (V)	J_{sc} (mA)	Fill Factor	Efficiency, η (%)
Nb ₂ O ₅ -EGAF	0.635	8.72	0.625	3.45
Nb ₂ O ₅ -GLPP	0.670	6.91	0.468	2.20

Table S1. Photovoltaic properties of Nb₂O₅-EGAF and Nb₂O₅-GLPP DSSCs.

References (Supporting information)

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