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$TiN_{0.07}O_{1.93}$ Semiconductor Electrodes for Photoassisted Oxidation of Water†

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Synopsis. As a new anode for the photoassisted oxidation of water, the $TiN_{0.07}O_{1.93}$ semiconductor electrode is proposed. Its photoanodic behavior in 0.1 M Na_3PO_4 was similar to those of n-type TiO_2 electrodes, but the photocurrent response was a little extended toward the long wavelength region. The electrode stability under the irradiation with ultraviolet light was good.

Much recent attention has been paid to the application of semiconductor electrodes to the photolysis of water and the direct conversion of solar to electrical energy. The n-type TiO_2 has been intensively studied as one of the most promising anode materials for such systems.[1-23] However, the n-type TiO_2 has a relatively wide band gap of *ca.* 3 eV[1,2,6] and thus makes inefficient use of solar energy. In addition, a certain deterioration of the photoanode characteristics of n-type TiO_2 under the irradiation from an artificial light source has been reported recently,[16,17] in opposition to the notion that the n-type TiO_2 electrode is chemically stable. Titanium nitride oxide $TiN_{0.07}O_{1.93}$, proposed here, is a novel photoanode material with the n-type semiconductivity. As shown by the formula of $TiN_{0.07}O_{1.93}$, this non-stoichiometric compound is one of the modified forms of TiO_2; it is easily prepared by the thermal treatment of metallic titanium substrate in a N_2–O_2 atmosphere. The idea of doping nitrogen together wtih oxygen into a titanium substrate is based on the fact that the titanium nitride TiN_x shows both good electronic conductivity and chemical stability, and on the possibility that the interstitial permeation of nitrogen atoms into the TiO_2 structure might produce some oxygen vacancies.

Experimental

Electrode Preparation. Commercial titanium plate (20 mm × 15 mm, 0.5 mm in thickness) with a short sleeve for the electrical connection to a leading wire was heated in a nitrogen gas atmosphere containing 0.5 vol % oxygen gas at 1100 °C for 3 h. Most electrodes thus obtained had a grayish appearance with a metallic luster. Prior to the measurement of the current-potential characteristics, the surface of the electrode was investigated by means of X-ray diffraction and ESCA (DuPont Model 650B) techniques. A copper lead wire was tied tightly around the sleeve of the electrode after the sleeve was scratched by a fine emery paper to expose the titanium substrate. The apparent working area for the photoanode was $1 \times 1\ cm^2$ and the remaining portion was coated with solid paraffin.

Measurements of Current-potential Characteristics. The apparatus, comprising a light source, photoelectrochemical cell, and recording equipment, is shown in Fig. 1. A monochromatic light source was prepared by attaching an interference filter (Koshin Optics Ltd.) to a xenon lamp. The accelerated life testing for inspecting the stability of the electrode was performed under the ultraviolet irradiation from a 440 W high pressure mercury lamp.

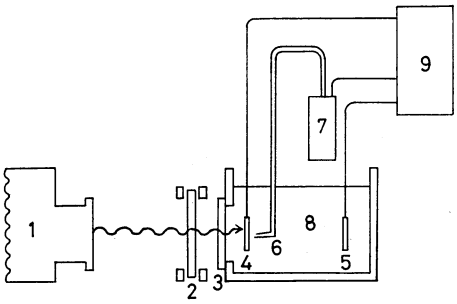

Fig. 1. Schematic representation of the experimental arrangement.
1: 450 W xenon lamp, 2: interference filter, 3: quartz window (3 mm thick), 4: working electrode, 5: Pt counter electrode, 6: Luggin capillary, 7: SCE reference electrode, 8: 0.1 M Na_3PO_4 (pH=6), 9: potentiostat and recorder.

Results

The X-ray diffraction analysis of the electrode surface gave mixed diffraction profiles of rutile, anatase, and titanium substrate. The ESCA spectra showed the presence of N, O, and Ti atoms in the thin surface layer of the electrode. The emission peaks of N 1s, O 1s, Ti 2p3/2, and Ti 2p1/2 electrons were observed at binding energies of 395.5 and 399.3, 529.1 and 531.3, 457.7, and 463.7 eV, respectively. From the summation of the corresponding peak areas on the ESCA spectra and the atomic sensitivity corrections for the photoelectron emission, the chemical composition of the outer surface layer of the electrode was estimated to be $TiN_{0.07}O_{1.93}$. Among a number of TiN_xO_y electrodes prepared under various atmospheric and thermal conditions, an electrode having a surface composition near $TiN_{0.07}O_{1.93}$ was found by a preliminary test to perform best as a photoanode.

The current-potential characteristics of the electrode in 0.1 M Na_3PO_4 (adjusted to pH 6 by addition of a small quantity of concd H_3PO_4) are shown in Fig. 2. From the comparison of curves A and B in Fig. 2, it is obvious that the electrode behaves as a photoanode. In addition, gas evolution at the electrode surface was

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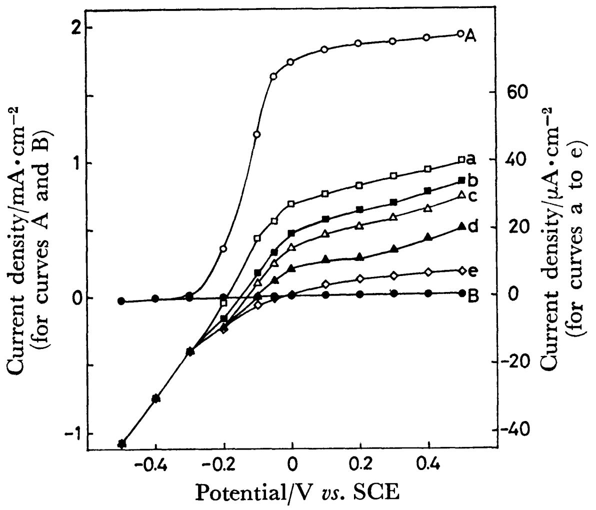

Fig. 2. Current-potential characteristics of TiN$_{0.07}$O$_{1.93}$ electrode in 0.1 M Na$_3$PO$_4$ (pH=6).
A: Under irradiation without interference filter, B: dark, a: under irradiation through a 400 nm interference filter, b: 440 nm, c: 420 nm, d: 450 nm, e: ≥460 nm.

observed in response to the passage of photocurrent. As shown by the curves a to e in Fig. 2, the electrode responded to the monochromatic light at wavelengths shorter than 460 nm, which corresponds to a band gap of *ca.* 2.7 eV. A small maximum of photocurrent at around 440 nm was a new feature of the electrode.

The accelerated stability test of the electrode was conducted in the following manner. Strong ultraviolet irradiation was directed, by use of a high pressure mercury lamp, onto the photoanode. This was short-circuited with the counter platinum cathode for 12 h and then operated with a constant anodic current density of 3.5 mA/cm^2 for 14 h. No significant change in the photocurrent-potential relation or in the electrode appearance was detected. These results demonstrate the stability of TiN$_{0.07}$O$_{1.93}$ electrode under ultraviolet irradiation.

Finally, the selection of Na$_3$PO$_4$ solution as electrolyte was due to its high pH-buffer action and its ability to detach the evolved bubbles from the electrode surface and move them into the bulk. In fact, the use of 0.1 M Na$_2$SO$_4$ as electrolyte caused a rapid decrease of the photocurrent with time.

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