

The Use of TiCl_4 Treatment to Enhance the Photocurrent in a TaON Photoelectrode under Visible Light Irradiation

Ryu Abe,* Tsuyoshi Takata,† Hideki Sugihara, and Kazunari Domen†

National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565

†Faculty of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

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A porous TaON photoelectrode was prepared on a conducting glass support, and the photocurrent based on water oxidation was investigated under visible light irradiation. The photocurrent was significantly increased by TiCl_4 treatment on the TaON electrode. The TiO_2 necking that formed between the TaON particles possibly improved the electron transport within the porous electrode.

Photocatalytic water splitting into H_2 and O_2 by semiconductors has received much attention because of the potential of the technology for the production of clean H_2 fuel from water using solar energy. The present authors have recently reported several stable nonoxide photocatalysts, (oxy)nitrides and oxysulfides, as potential candidates for visible-light-induced water splitting.¹⁻⁵ The valence bands of these materials are populated by N 2p and S 3p orbitals, respectively, mixed with O 2p, resulting in more negative valence band levels and smaller band gaps compared to oxide semiconductors. For example, oxynitride TaON with a band gap of 2.5 eV (adsorption edge at 500 nm) has conduction and valence band edges of ca. -0.3 and $+2.2$ V vs NHE (pH 0), respectively, sufficient for overall water splitting into H_2 and O_2 .⁵ (Oxy)nitride materials such as TaON are expected to be applicable, not only as photocatalysts, but also as visible-light-driven photoelectrodes.⁴⁻⁸ The present authors have previously reported the preparation of photoelectrodes of Ta_3N_5 and TaON on, respectively, Ta and Pt metal films.^{5,6} However, a simpler and less expensive method is desirable for the fabrication of photoelectrodes.

The present paper reports the preparation of a porous TaON photoelectrode on a conducting glass support. We found that the photocurrent in the porous TaON photoelectrode was significantly increased by TiCl_4 treatment. The fine TiO_2 particles that formed between the TaON particles possibly improved the electron transfer within the porous electrode, resulting in the increased photocurrent.

TaON powder was prepared by heating Ta_2O_5 powder under NH_3 flow (20 mL min^{-1}) at 850°C for 15 h. A porous electrode was prepared by spreading a viscous slurry of TaON particles on a glass plate coated with transparent conducting oxide (TCO, F-doped SnO_2 , Nippon Sheet Glass Co., $8\text{--}10 \Omega/\text{sq}$, transparency 80%). The slurry contained TaON particles, water, and small amounts of acetylacetone and surfactant (Triton X-100, Aldrich). The coated area was ca. 4 cm^2 ($1\text{--}4 \text{ cm}$). The TiCl_4 treatment was carried out as follows. The prepared electrode was immersed into a 1 mM aqueous TiCl_4 solution and kept at room temperature for 15 h in darkness. The TiCl_4 aq was prepared at 0°C to prevent precipitation of TiO_2 . It was then washed with distilled water, and heated in air or N_2 at 400°C for 30 min. The electrochemical cell (two-electrode type) used for photocur-

rent measurements consisted of a porous TaON electrode, a counter electrode (Pt wire), and an electrolyte (0.1 M aqueous Na_2SO_4 solution). The applied bias between the TaON electrode and the Pt counter electrode was controlled by a potentiostat. The three-electrode type measurements were also conducted using a Ag/AgCl as a reference electrode. The solution was purged with nitrogen for over 30 min before the measurements. The electrodes were irradiated through the conducting glass by a Xe lamp (300 W) fitted with a cut-off filter (Hoya L-42) to block light in the ultraviolet (UV) region. Photooxidation of H_2O into O_2 in the presence of an Ag^+ electron acceptor was performed as a test reaction to characterize the photocatalytic activity of the TaON powder after being heated at various temperatures in air or N_2 . The reaction conditions are the same as those in our previous report.¹

Figure 1a shows the rates of O_2 evolution over TaON powder photocatalysts after heat treatment at various temperatures in air or N_2 for 30 min. The rate of O_2 evolution decreased with increasing temperature from 300 to 500°C , especially after heating in air. TG-DTA and XRD measurements revealed the oxidation of TaON into Ta_2O_5 at above 400°C in air. The resultant Ta_2O_5 layer on the surface clearly prevented water oxidation to O_2 over the TaON photocatalyst, resulting in low O_2 evolution rates upon heat treatment above 400°C .

The photocurrents on TaON photoelectrodes after heat treatment are shown in Figure 1b. These measurements were made with a bias of $+0.4 \text{ V}$ under visible light irradiation ($\lambda > 420 \text{ nm}$). The observed photocurrent could be attributed to the photo-induced oxidation of water to O_2 as an analogy of photocatalytic O_2 evolution as shown in Figure 1a. The photocurrents over TaON electrodes increased somewhat with increasing tempera-

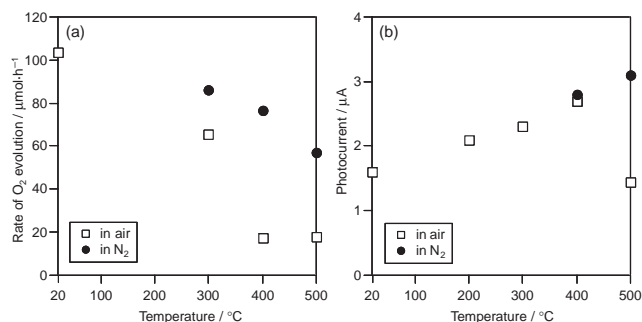


Figure 1. (a) Rates of O_2 evolution over a TaON photocatalyst in the presence of Ag^+ electron acceptor under visible light ($\lambda > 420 \text{ nm}$) after heat-treatment at various temperatures. (b) Anodic photocurrent in the TaON electrode at an applied bias of $+0.4 \text{ V}$ in a 0.1 M aqueous solution of Na_2SO_4 under visible light ($\lambda > 420 \text{ nm}$).

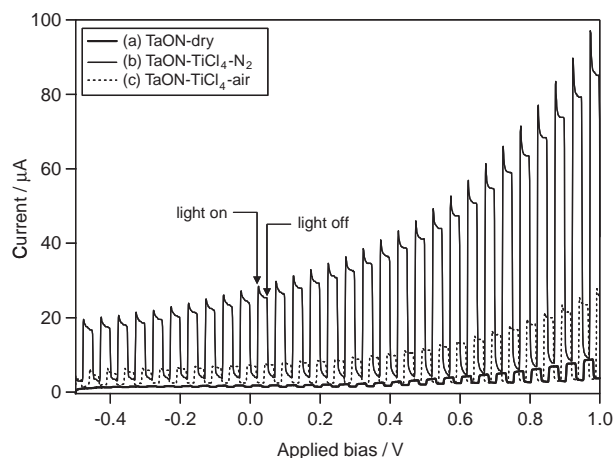


Figure 2. Dependence of current–bias on the TaON film electrodes (a) dried in air, (b) treated with an aqueous TiCl_4 solution and heated at 400°C in N_2 , and (c) treated with an aqueous TiCl_4 solution and heated at 400°C in air. The area of the TaON electrodes was ca. 4 cm^2 . The chopped visible light ($\lambda > 420\text{ nm}$) was generated by a Xe lamp (300 W) with a cut-off filter.

ture up to 400°C in both air and N_2 . This suggests that the TaON particles formed necks as a result of the heat treatment, which improved the electron transport between them. The photocurrent decreased dramatically upon heat treatment at 500°C in air because of the deactivation of TaON particles by surface oxidation, as suggested by the photocatalytic reaction (Figure 1a). The highest photocurrent was observed after the heat treatment at 500°C in N_2 (Figure 1b), but the increase in photocurrent was not as marked as in the case of the non-heat-treated electrode. These results indicate that a heat treatment at up to 500°C , which is the temperature limit for the conducting glass support, is not sufficient for fabricating an efficient photoelectrode. This is reasonable given that the preparation of TaON requires the relatively high temperature of 850°C .

Thus, we attempted to achieve necking between the TaON particles by using another semiconductor component, such as TiO_2 , to enhance electron transport. Some workers suggested that the TiCl_4 treatment on the porous TiO_2 film electrodes increased the necking between the TiO_2 particles of the film, thus facilitating the diffusion of electrons between particles.^{9–11} Figure 2 shows the current–bias dependence over the TaON electrodes before and after the TiCl_4 treatment under chopped visible light irradiation ($\lambda > 420\text{ nm}$) in the two-electrode type measurement. The photocurrent was greatly improved by the TiCl_4 treatment as shown in Figure 2: an approximately 30-fold increase in photocurrent (ca. $25\ \mu\text{A}$ at bias 0 V) was observed on the TaON electrode treated with TiCl_4 and heated in N_2 with respect to that observed on the non-heat-treated electrode (ca. $0.8\ \mu\text{A}$ at bias 0 V). The lower photocurrent in the electrode heated in air, rather than N_2 , was clearly due to deactivation by surface oxidation, as indicated by the results in Figure 1a. Similar trend was observed in the three-electrode type measurements. The photocurrent in the porous TiO_2 electrode was below $0.1\ \mu\text{A}$, even at an applied bias of 0.4 V , under the same conditions as in Figure 2. Thus, the photocurrent in the TaON elec-

trodes treated with TiCl_4 was undoubtedly based on the photoexcitation of TaON particles by the visible light. No obvious effect was observed on the photocurrent when the TaON electrodes were treated with other solutions, such as NbCl_5 , TaCl_5 , and ZnCl_2 .

From these results, we can conclude that the TiO_2 -necking that occurred between TaON particles was due to the TiCl_4 and heat treatments, and that the necking facilitated the transport of electrons between TaON particles. Consequently, a high photocurrent was observed in the TaON electrode treated by TiCl_4 . Although at present we have no clear evidence excluding the possibility that the observed photocurrent includes at least partly the oxidation of organic impurities in the film, it is clear that the photocurrent is enhanced by TiCl_4 treatment. As we reported previously, TaON possesses a conduction band level comparable to that of TiO_2 anatase (TaON: -0.3 V , TiO_2 -anatase: -0.2 V vs NHE at pH 0). Thus, it seems reasonable to suppose that the electrons generated in the conduction band of TaON are transferred through the conduction band of TiO_2 . The study on the TiO_2 structure is in progress. The TiO_2 -necking method would be useful for the low-temperature fabrication of efficient photoelectrodes composed of (oxy)nitrides or (oxy)sulfides on a conducting support, both of which are unstable at high temperature in air.

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