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Facile Fabrication of an Efficient Oxynitride TaON Photoanode for Overall Water Splitting into H_2 and O_2 under Visible Light Irradiation

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Abstract: The porous oxynitride TaON film electrode prepared on conducting glass (FTO) showed significantly high quantum efficiency (IPCE = ca. 76% at 400 nm at 0.6 V vs Ag/AgCl) in an aqueous Na_2SO_4 solution, after loading of $IrO_2 \cdot nH_2O$ nanoparticles as a cocatalyst for water oxidation. Overall water splitting into H_2 and O_2 under visible light was demonstrated using an $IrO_2 \cdot nH_2O$-loaded TaON photoanode combined with a Pt electrode under an externally applied bias (0.6−1 V).

Photocatalytic and photoelectrochemical water splitting using semiconductor materials have attracted considerable attention due to the potential for the clean production of H_2 from water utilizing abundant solar light.[1] The development of a stable semiconducting material that functions efficiently under visible light, which represents almost half of the available solar spectrum, is indispensable for the practical use of solar energy. The authors recently reported several oxynitrides of transition metals as potential candidates for visible light induced water splitting.[2] The conduction band edges of these oxynitrides consist predominantly of empty orbitals of the metal, resulting in similar energy levels to those of corresponding metal oxides. On the other hand, the valence bands of oxynitrides are more negative than those of oxides due to the hybridization of N 2p with O 2p orbitals. Consequently, some oxynitride materials possess appropriate band levels for water splitting, as well as a narrow band gap allowing visible light absorption. For example, tantalum oxynitride TaON (band gap: ca. 2.5 eV, corresponding to light absorption up to 500 nm) has conduction and valence band edges at ca. −0.3 and +2.2 V vs NHE, respectively, which are suitable for both water reduction and oxidation.[3] This implies that a TaON photoelectrode has the potential to produce H_2 and O_2 from water under visible light, even without an externally applied bias. In contrast, visible light-sensitive oxide semiconductor electrodes, such as WO_3, Fe_2O_3 and $BiVO_4$, require a considerable applied bias to produce H_2, because their conduction band levels are too low for water reduction.[4] Although there have been a few reports of the fabrication of n-type photoanodes based on metal oxynitrides, such as TaON or $LaTiO_2N$, their efficiencies were still low.[5] Furthermore, all these reports demonstrated only a photocurrent, without confirming appreciable O_2 evolution. In the present study, we attempted to fabricate an efficient tantalum oxynitride (TaON) photoelectrode on a conducting glass (FTO) support using a simple electrophoretic deposition method followed by a postnecking treatment.

TaON powder was prepared by heating Ta_2O_5 powder under NH_3 flow (20 mL min^{-1}) at 1123 K for 15 h. Electrophoretic deposition was carried out in an acetone solution (50 mL) containing TaON powder (40 mg) and iodine (10 mg). Two parallel FTO electrodes were immersed in the solution with a 8 mm separation, and a 10 V bias was applied between them for 3 min using a potentiostat. The TaON-coated area was fixed at ca. 1.5 cm × 4 cm, in which ca. 3 mg of TaON were included. This procedure resulted in the formation of a porous TaON layer with a relatively uniform thickness of ca. 2 μm, with good reproducibility (Figure S1). The as-prepared electrode was once calcined at 673 K for 30 min, dropped with 10 mM of $TaCl_5$ in methanol solution (50 μL), and then dried. After this process was repeated 5 times, the electrode was heated in air to 673 K for 30 min, followed by heating in NH_3 flow (10 mL min^{-1}) at 773 K for 30 min. The colloidal solution of $IrO_2 \cdot nH_2O$, which is known as an efficient O_2 evolution catalyst,[6] was prepared by hydrolysis of Na_2IrCl_6 in aqueous basic solution (pH 12) at 343 K. The TaON electrode was immersed into the prepared $IrO_2 \cdot nH_2O$ (will be denoted by IrO_2 hereafter) colloidal solution for 3 h, washed with distilled water, and then dried in air. The loaded amount of IrO_2 (ca. 0.3 wt %) was determined by the change in absorption spectrum of the colloidal solution. Detailed experimental conditions are described in the Supporting Information.

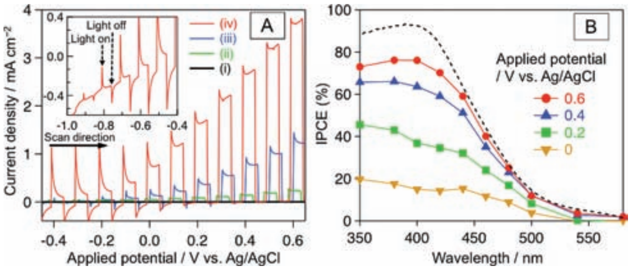

Figure 1. (A) Current−potential curves in aqueous 0.1 M Na_2SO_4 solution (pH 6) under chopped visible light irradiation ($\lambda > 400$ nm) for TaON electrodes as-prepared (i), treated by $TaCl_5$ (ii), heated in NH_3 (iii), and loaded with IrO_2 (iv). (B) Incident photon to current efficiency (IPCE) spectrum of IrO_2−TaON electrode with various applied potentials (1 M Na_2SO_4, pH 6) and absorption spectrum of TaON (dashed line).

Figure 1A shows the current−potential relationship for TaON electrodes under chopped visible light irradiation ($\lambda > 400$ nm). Over the TaON electrode prepared by electrophoretic deposition and subsequent calcination at 673 K (i), the photocurrent was negligibly low. Heat treatment after electrophoresis in air, N_2, or NH_3 at up to 773 K (the temperature limit of FTO) resulted in a slight improvement in the photocurrent but was insufficient to substantially improve the contact among the TaON particles, which had a rigid surface formed at a high temperature (1123 K). However, the $TaCl_5$ treatment followed by calcination at 723 K in air afforded a clear increase in photocurrent (ii). (SEM images of electrode before and after the treatment are shown in Figure S2.) The improvement in photocurrent in this case, however, was undoubt-

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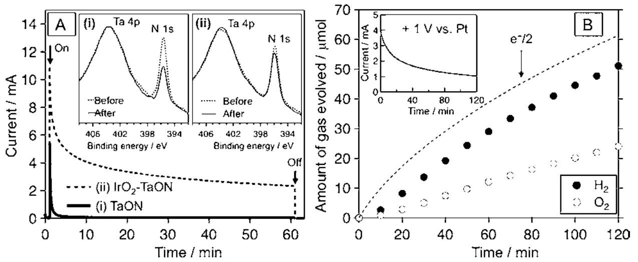

Figure 2. (A) Current−time evolution for TaON and IrO_2−TaON electrodes (6 cm^2) at +0.6 V (vs Ag/AgCl) and XPS spectra of electrodes before and after 1 h of irradiation (inset). (B) Time course of gas evolution in two-electrode system of IrO_2−TaON and Pt-wire with 1 V of applied bias. All reactions were carried out in aqueous 0.1 M Na_2SO_4 solution (pH 6) under visible light irradiation.

edly limited by the inefficiency of the interface between TaON and Ta_2O_5 particles. Subsequent heating of the same sample under NH_3 achieved a significant increase in photocurrent (iii). The atomic ratio of oxygen to nitrogen (O/N) in samples (ii) and (iii) determined by XPS analysis were 2.07 and 1.03, respectively, assuming the ratio in sample (i) was unity (O/N = 1). NH_3 treatment resulted in the most Ta_2O_5 bridges to TaON, greatly facilitating electron transport between the large TaON particles in the electrode. The loading of IrO_2 colloid (ca. 0.3 wt %), which is known as an effective catalyst for water oxidation,[6] onto the TaON electrode further improved the photocurrent (iv). The onset potential of IrO_2−TaON (inset of Figure 1A) was observed at approximately −0.8 V vs Ag/AgCl, which corresponds to −0.25 V vs RHE, agreeing with our previous report.[3] The action spectra of the IrO_2-loaded TaON electrode are shown in Figure 1B, in which high incident photon-to-current conversion efficiencies (ca. 76% at 400 nm at 0.6 V vs Ag/AgCl) were obtained. This is the highest IPCE ever reported for an oxynitride or nitride semiconductor photoelectrode. The IrO_2 loading was also found to improve the stability of TaON electrodes during photoirradiation. As shown in Figure 2A, the photocurrent of a bare TaON electrode immediately decreased and became negligibly low within 10 min, with an obvious decrease in nitrogen content indicated by XPS (inset). This was undoubtedly due to the self-oxidative decomposition of TaON, whereby nitrogen anions were oxidized to N_2 by photogenerated holes ($2N^{3-} + 6\,h^+ \rightarrow N_2$). IrO_2 loading noticeably suppressed the decreases in both photocurrent and N content. IrO_2 loading most likely resulted in hole scavenge to the IrO_2 particles, preventing self-oxidation of the TaON surface. The number of electrons passing through the outer circuit in 1 h (11.72 C, corresponding to 121.5 μmol of electrons) exceeded the molar amounts of both TaON (ca. 14.2 μmol) and IrO_2 (ca. 0.04 μmol) contained in the electrodes. This indicates that most of the photocurrent resulted from photocatalytic water oxidation, not merely the self-oxidative decomposition of the TaON material itself.

However, the decreases in both photocurrent and N content indicated that self-oxidation was not entirely suppressed by the loading of IrO_2 cocatalyst. STEM images of IrO_2-loaded TaON particles peeled from the electrode (Figure S3) indicated that most of the IrO_2 colloids were aggregated on a relatively small fraction of the TaON surface, leaving large portions of the TaON surface uncovered. These results suggest that the naked TaON surfaces were oxidized during photoirradiation, resulting in a decrease in photocurrent, even with IrO_2 loading. Although the stability of IrO_2-loaded TaON electrodes must be improved further, these electrodes should be expected to split water to H_2 and O_2 under visible light irradiation with the appropriate applied bias. Figure 2B shows time courses of gas evolution over an IrO_2-loaded TaON electrode under visible light irradiation with 1 V of applied bias between the TaON electrode and Pt wire counter electrode (with no reference electrode). H_2 and O_2 were evolved in a nearly stoichiometric ratio. The amounts of gases evolved in 2 h (H_2, 51.3 μmol; O_2, 24.0 μmol) exceeded that of TaON (ca. 14.2 μmol). The amount of H_2 evolved was slightly less than half of the electrons passing through the outer circuit ($e^-/2$, shown as a broken line), possibly due to the water formation from H_2 and O_2 on the Pt electrode. The evolved O_2 amount was less than the stoichiometric value certainly because of hole (h^+) consumption by the self-oxidation of the TaON surface in the initial period. We confirmed that the simultaneous evolution of H_2 and O_2 could occur, even under a lower applied bias (0.8 or 0.6 V), although the amounts of gases evolved were smaller than those under 1.0 V (Figure S4).

This is the first demonstration of photoelectrochemical water splitting on an oxynitride photoanode with an appreciable production of O_2, in addition to a measured anodic photocurrent. Although IrO_2−TaON electrodes require further improvement in their stability, the present study demonstrates the possible application of oxynitride photoanodes for water splitting, utilizing visible light under a low applied bias. Furthermore, the simple and inexpensive preparation of the oxynitride electrode described (electrophoretic deposition followed by postnecking treatment) enables the possibility of large-scale application of oxynitride photoelectrodes for the practical splitting of water under solar light.

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Supporting Information Available: Detailed experimental conditions, SEM and STEM images of TaON electrode, and photoelectrochemical water splitting results. This material is available free of charge via the Internet at http://pubs.acs.org.

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