<table>
<thead>
<tr>
<th>項目</th>
<th>内容</th>
</tr>
</thead>
<tbody>
<tr>
<td>タイトル</td>
<td>論文・報告　可視光水分解用光アノードの高効率化を目的とした水の酸化助触媒の開発</td>
</tr>
<tr>
<td>著者</td>
<td>野口　輝 山中　雄太 富田　修 東　正信 阿部　竜</td>
</tr>
<tr>
<td>引用</td>
<td>ELCAS Journal (2016), 1: 70-72</td>
</tr>
<tr>
<td>発行日</td>
<td>2016-03</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/216478">http://hdl.handle.net/2433/216478</a></td>
</tr>
<tr>
<td>タイプ</td>
<td>Journal Article</td>
</tr>
<tr>
<td>言語版</td>
<td>publisher</td>
</tr>
</tbody>
</table>

京都大学
Development of Cocatalysts for Efficient Water Oxidation over a TaON Photoanode under Visible Light Irradiation

Hikaru Noguchi, Yuta Yamanaka, Osamu Tomita, Masanobu Higashi, and Ryu Abe

Abstract

Photoelectrochemical (PEC) water splitting using semiconductor materials have attracted considerable attention due to their potential for clean production of H2 from water by utilizing solar energy. TaON photoelectrodes have the potential to produce H2 and O2 from water under visible light, even without an externally applied bias. However, TaON is generally unstable under light irradiation in aqueous solution due to self-oxidative deactivation caused by photogenerated holes accompanied by the release of N3– anions. We have recently demonstrated stable water splitting on a CoOx-modified TaON photoanode, wherein the CoOx nanoparticles, acting as a catalyst for water oxidation, effectively scavenge the holes in TaON and suppress oxidative deactivation of the TaON surface. Loading of cocatalysts on oxynitrides improves stability and is required to achieve efficient PEC water splitting. Therefore, the development of cocatalysts for water oxidation is one of the most important subjects for achieving efficient PEC water splitting using such unstable oxynitrides as photoanodes. In the present study, we investigated the influence of various metal oxide species (Ni, Cu, Fe, Mn, Cr, and Ru) when loaded on a TaON electrode on the photocurrent generated under visible light irradiation. Ni, Cu, Fe, and Mn were found to improve the photocurrent stability of TaON.

Key words: Photoanode, Water splitting, Water oxidation, Oxynitride, cocatalyst

Introduction

Photoelectrochemical (PEC) water splitting using semiconductor materials has attracted considerable attention due to the potential for clean production of H2 from water by utilizing solar energy (1–3). The development of a stable semiconducting material that functions efficiently under visible light, which represents almost half of the available solar spectrum, is essential for the practical use of solar energy. It has been reported that certain oxynitrides (e.g., TaON) possess appropriate band levels for both H2 and O2 evolution, as well as narrow bandgaps for visible light absorption (4). This fact implies that photoelectrodes made of such oxynitrides have the potential to produce H2 and O2 from water using solar light, even without an externally applied bias. However, such oxynitrides are generally unstable under light irradiation in aqueous solution due to the occurrence of self-oxidative deactivation caused by photogenerated holes accompanied by the release of N3– anions from the surface region (2N3– + 6h+ → N2). We have recently demonstrated stable water splitting on a CoOx-modified TaON porous photoanode, wherein the CoOx nanoparticles, acting as a catalyst for water oxidation, effectively scavenge the holes in TaON and suppress oxidative deactivation of the TaON surface (6). Loading of cocatalyst on oxynitrides leads to improved stability and is required to achieve efficient PEC water splitting. Therefore, the development of cocatalysts for water oxidation is one of the most important subjects for achieving efficient PEC water splitting using such unstable oxynitrides as photoanodes. In the present study, we investigated the
influence of various metal species on the photocurrent generated by a TaON electrode under visible light irradiation.

**Materials & Methods**

TaON particles were prepared by heating Ta₂O₅ particles (High Purity Chemicals) at 1123 K for 24 h under NH₃ flow (20 mL min⁻¹). Nano-particulate metal oxide species (1 wt%, calculated as metal) were loaded on TaON particles by impregnation from an aqueous Ni(NO₃)₂, Co(NO₃)₂, Cu(NO₃)₂, Cr(NO₃)₃, Mn(NO₃)₂, Fe(NO₃)₃, or RuCl₃ solution, followed by heating at 673 K for 30 min in air. The resulting particles were deposited on Ti substrate by electrophoretic deposition (6–9). The coated area measured 1.5 × 4 cm². Post-necking was applied to enhance the conductivity among the TaON particles as well as between the TaON particles and the substrate, via trickle impregnation of methanolic TaCl₅ solution and subsequent heat treatment (6–9). The as-prepared electrodes had 50 μL of TaCl₅ methanol solution (10 mM) dropped on them before they were air-dried at room temperature. After performing this process five times, the electrode was heated under NH₃ flow (10 mL min⁻¹) at 723 K for 30 min. Unloaded TaON electrodes were fabricated using almost the same procedure as above, except that the NH₃ treatment temperature was 823 K.

The prepared samples were characterized by powder X-ray diffraction (XRD; MiniFLEX II, Rigaku) and UV-visible diffuse-reflectance spectroscopy (V-650, Jasco).

The electrochemical cell used for photocurrent measurements comprised a prepared TaON electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and a phosphate buffer solution (pH 8) as the electrolyte. The potential of the working electrode was controlled using a potentiostat (PARSTAT2263, Princeton Applied Research). The solution was purged with Ar gas for over 20 min prior to the measurement to exclude any dissolved air. The electrodes were irradiated with a 300-W Xe lamp (LX-300F, Cermax) fitted with a cut-off filter (L-42, Hoya) to block the emission of light in the ultraviolet region (λ < 400 nm). The irradiated area measured 6 cm² (1.5 × 4 cm²).

**Results & Discussion**

Fig. 1 shows the XRD pattern of the prepared TaON, along that of the Ta₂O₅ precursor for comparison. Only peaks corresponding to the baddeleyite phase were observed, which were in good agreement with those reported previously (10). No peaks assignable to an impurity phase (e.g., Ta₂O₅ and Ta₃N₅) were observed. As shown in Fig. 2, the absorption edge of the prepared TaON was approximately 520 nm, which was in good agreement with that reported previously (4).

Fig. 3 shows the current-potential relationship for various TaON electrodes in phosphate buffer solution under chopped visible light irradiation. Ni- and Cu-loaded TaON electrodes exhibited a higher photocurrent than an unloaded TaON electrode; in particular, the photocurrent was significantly higher at higher potentials (> 1.0 V vs. RHE). These results suggested that the Ni or Cu species loaded on to the TaON surface promote water oxidation. Fig. 4 shows the change in photocurrent generated on various TaON electrodes held at a fixed potential of 1.0 V vs. RHE over time under continuous visible light irradiation. The photocurrent of an unloaded TaON electrode decreased immediately, undoubtedly due to self-oxidative deactivation of the TaON surface by photogenerated holes, which reduce nitrogen content (7, 8). In contrast, the TaON electrodes loaded with either Ni or Cu exhibited a more stable photocurrent than the unloaded TaON electrode with only a gradual decrease with irradiation time. Loaded Ni or Cu species would scavenge the photogenerated holes in TaON, suppressing oxidative deactivation of the TaON surface. In the case of Fe and Mn loading, relatively stable but low photocurrents were observed during photoirradiation. It has been reported that Fe and Mn species work as cocatalysts for water oxidation (11, 12). In the present system, Fe and Mn species loaded on TaON facilitated water oxidation, suppressing oxidative deactivation of the TaON surface.

In the present study, we investigated the influence of various metal oxide species (Ni, Cu, Fe, Mn, Cr and Ru) loaded on a TaON electrode on the photocurrent under visible light irradiation. We found that Ni, Cu, Fe, and Mn improved the photocurrent stability of TaON, but not Cr or Ru.
References


Fig.3. Current-potential curves of various metal oxide species–loaded TaON electrodes in phosphate buffer (pH 8) under chopped visible light irradiation.

Fig.4. Change over time of the photocurrent on various metal oxide species–loaded TaON electrodes in phosphate buffer (pH 8) at +1.0 V vs. RHE under visible light irradiation.