Growth of rod-like Ta_3N_5 single crystal on $KTaO_3$ towards visible-light-driven overall water splitting

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Abstract: We have found that Ta_3N_5 nano-crystals grown on $KTaO_3$ by short-time nitridation have a remarkable photocatalytic ability for overall water splitting to produce H_2 and O_2 under visible light ($\lambda \geq$ 420nm) irradiation in the presence of co-catalysts such as Rh/Cr_2O_3. The specific active structures are discussed.

Keywords: Ta_3N_5 nanorod, single crystal, water splitting.

1. Introduction (11-point boldface)

Direct decomposition of water into hydrogen and oxygen using one particulate photocatalyst is the simplest and most cost-effective means to solar energy-driven hydrogen production. Tantalum nitride (Ta_3N_5) photocatalyst with a small band-gap energy of 2.1 eV and simple composition is one of the promising candidates and has extensively been studied as a H_2 or O_2 evolving photocatalyst in the half reactions, Z-schemed water splitting, and a photoanode in the photoelectrochemical water splitting.[1-3] However, it has not yet been applicable for overall water splitting. In this study, we have found that Ta_3N_5 nanorods epitaxially grown on cubic potassium tantalate ($KTaO_3$) exhibits a remarkable photocatalytic activity for overall water splitting under visible light irradiation when Rh/Cr_2O_3 cocatalyst is deposited.

2. Experimental (or Theoretical)

$KTaO_3$ prepared by a conventional solid state reaction method was subject to short-term nitridation under NH_3 gas flow at 1173 K, which yielded Ta_3N_5 maintaining the $KTaO_3$ phase (Ta_3N_5/$KTaO_3$). A Rh/Cr_2O_3 core-shell co-catalyst was formed on Ta_3N_5/$KTaO_3$ surfaces by the successive photodepositions of Rh and Cr_2O_3.[4] The prepared photocatalysts were characterized by XRD, UV-vis DRS SEM and HR-STEM.

Photocatalytic reactions were carried out in a Pyrex reaction vessel connected to a closed gas-circulation system. 300 W Xe lamp (L42, $\lambda \geq 420$ nm) and solar simulator (AM 1.5G) were used as a light source. The evolved gas products were analyzed by the on-line TCD-GC equipped with a Molecular Sieve 5A column.

3. Results and discussion

The XRD patterns showed that short-time (0.05 ~ 0.5h) nitridation of $KTaO_3$ caused small peaks assigned to Ta_3N_5 phase and no other impurity phase like TaON structure was formed, indicating the formation of Ta_3N_5 in the presence of $KTaO_3$. SEM images exhibited rod-like Ta_3N_5 crystals were grown at the edges of $KTaO_3$ particulates. With the increase of nitridation time from 0.5h to 4 h, the number density of Ta_3N_5 nanorods and the length increased. The HR-STEM demonstrated that the nanorods were Ta_3N_5 single crystals selectively grown on the (110) facets of $KTaO_3$ rather than on (100) faces. In addition, the UV-vis DRS of Ta_3N_5/$KTaO_3$ showed similar absorption feature to that of conventional Ta_3N_5 in the longer wavelength range and the absorption backgrounds of Ta_3N_5/$KTaO_3$ samples were much lower as compared with the conventional Ta_3N_5, indicating the less defect density in the Ta_3N_5 nanorod single crystals. In the photodeposition of Rh under visible light ($\lambda \geq 420$ nm) on $Ta_3N_5/KTaO_3$, Rh metal particles were selectively formed on the Ta_3N_5 nanorod crystals without the deposition on the surface of $KTaO_3$. The Rh/Cr_2O_3 core-shell cocatalyst on $Ta_3N_5/KTaO_3$ exhibited the best photocatalytic activity for overall water splitting, as compared with other core-shell-structured metal/Cr_2O_3 cocatalysts, such as Pt, Ir and Ru. The optimum loading amount of Rh on $Ta_3N_5/KTaO_3$ varied for $Ta_3N_5/KTaO_3$ samples with the different nitridation durations, because of the variable density of Ta_3N_5 structure in different $Ta_3N_5/KTaO_3$ samples. Fig. 1 shows time course of the H_2 and O_2 evolution for overall water splitting under visible light ($\lambda \geq 420$ nm). The simultaneous evolution of H_2 and O_2 occurred in nearly the same ratio as the stoichiometry of 2 : 1. The repetition of the reaction by evacuating the gas phase shows nearly the same evolutions of H_2 and O_2, which clearly demonstrates that Rh/Cr_2O_3-loaded $Ta_3N_5/KTaO_3$ is very stable for the decomposition of water under visible light ($\lambda \geq 420$nm). The quantum efficiency measured using a band pass filter was 0.22% at 420 nm(±10nm). Furthermore, stable H_2 and O_2 production was also obtained under simulated sunlight (AM 1.5G) irradiation over Rh/Cr_2O_3-loaded $Ta_3N_5/KTaO_3$. The photocatalytic performance of the Ta_3N_5 is attributed to the formation of well-crystallized single crystals with no grain boundary.

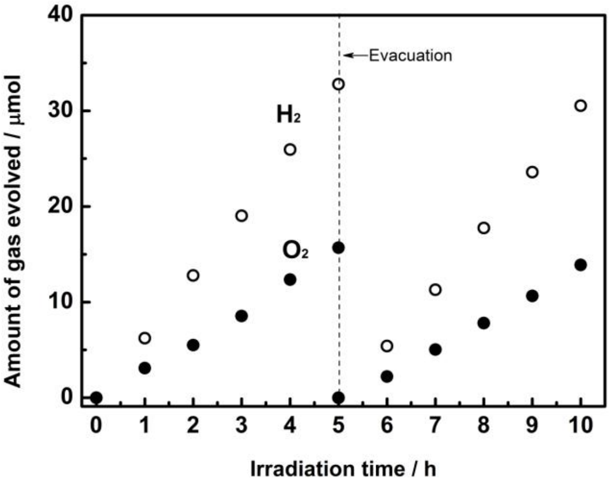

Figure 1. Time courses of H_2 (○) and O_2 (●) evolutions in overall water splitting over Rh/Cr_2O_3-loaded $Ta_3N_5/KTaO_3$ under visible light (300W Xe lamp, $\lambda \geq 420$ nm) irradiation.

4. Conclusions

In summary, we succeed to fabricate a rod-like Ta_3N_5 single crystal through a simple epitaxial growth process. By controlling the nitridation of cubic $KTaO_3$ powders for short duration, the Ta_3N_5 nanorod single crystals are selectively grown on the edges of $KTaO_3$ cubes. The high-crystalline Ta_3N_5 nanorods on $KTaO_3$ modified with Rh/Cr_2O_3 cocatalyst are very active for the overall water splitting under visible light irradiation.

References

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