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Photocatalytic Water Splitting Over a Protonated Layered Perovskite Tantalate $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$

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Abstract $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ was synthesized by treatment of $Bi_2SrTa_2O_9$ with 3 M hydrochloric acid for 96 h. The formation rate of H_2 from CH_3OH/H_2O solution under UV light irradiation is 57.67 mmol h^{-1} g^{-1} for $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ without co-catalyst. It also showed high activity for decomposition of pure water into H_2 and O_2 with the rates of 2.46 and 1.11 mmol h^{-1} g^{-1}, respectively.

Keywords Photocatalyst $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ · Water splitting

1 Introduction

Since the first photocatalyst titanium dioxide suitable for hydrogen evolution from water splitting was reported [1], photocatalytic water splitting into H_2 and O_2 with semiconductor photocatalysts [2–6] has attracted considerable interest because of its potential to obtain directly clean and high-energy containing H_2 from abundant H_2O. Although much work has been done to develop new photocatalysts responsive to UV and visible light irradiation, the number of effective photocatalysts for splitting of pure water into H_2 and O_2 is still limited. Layered compounds, such as $A_2SrTa_2O_7 \cdot nH_2O$ (A = H, K, and Rb) [7], $RbLnTa_2O_7$ (Ln = La, Pr, Nd, and Sm) [8] $Sr_2Nb_2O_7$ [9, 10], $KCa_2Nb_3O_{10}$ [11], $A_2La_2Ti_3O_{10}$ (A = K, Rb, Cs) [12–14], $A_4Nb_6O_{17}$ (A = K, Rb) [15], $PbBi_2Ta_2O_9$ [16, 17], $K_2Sr_{1.5}Ta_3O_{10}$ [18], and $H_2La_{2/3}Ta_2O_7$ [19], etc., have attracted special attention in the field of water splitting into H_2 and O_2 because of the availability of the interlayer space as reaction sites, where electron-hole recombination process could be retarded by physical separation of electron and hole pairs generated by photoabsorption [20]. However, for most of the photocatalysts, it is necessary to load transition metal co-catalysts for overall water splitting. The yield of hydrogen gas by these catalysts still settles in magnitude of μmol h^{-1} g^{-1}, which renders the overall process impractical. Therefore, it is still very important to find new photocatalytic materials with high photoactivity in order for the water splitting to become a viable method to provide clean and renewable source for hydrogen fuel in the future. In this paper, a novel photocatalyst, $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ (HST), was reported for pure water splitting without the assistant of co-catalysts. Because HST has the characteristic layered structure of perovskite, it would be interesting to examine photocatalytic properties of it.

2 Experimental

Polycrystalline sample of $Bi_2SrTa_2O_9$ (BST) was prepared by solid-state reaction method. Mixture of $SrCO_3$, Bi_2O_3, and Ta_2O_5 (1:1:1 mol ratio) were thoroughly ground and heated at 900 °C for 15 h, 1,000 °C for 15 h, and 1,200 °C for 24 h with intermittent grinding [21]. About 1 g of BST

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was dispersed in 200 mL of 3 M HCl for 96 h. The acid-treated product was centrifuged, washed with distilled water until free of Cl^- and dried at 30 °C. X-ray diffraction using a Rigaku D/max-2000 diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) was carried out for the sintered samples at room temperature. The amounts of metals were determined by inductively coupled plasma emission spectrometry (ICP; Perkin Elmer, Optima 5300DV) after the sample was dissolved by heating in a mixture of HNO_3, and HF at 50 °C for 48 h. Diffuse reflectance spectra were measured on a UV–vis spectrophotometer (TU-1900). The photocatalytic gas evolution was conducted in an outer irradiation quartz cell, which was connected to a closed gas-circulating system. A powder sample of $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ (0.1 g) was suspended in deionized H_2O (400 mL) or an aqueous CH_3OH/H_2O solution (20 mL CH_3OH, 400 mL deionized H_2O) in the cell by use of a magnetic stirrer. The reaction was carried out by irradiating the mixture with light from a 350 W Hg lamp. Gas evolution was analyzed by a gas chromatograph (Agilent 6820, TCD, Ar carrier).

3 Results and Discussion

Figure 1 shows the XRD patterns of BST and its protonated form, HST. The X-ray diffraction pattern of BST (Fig. 1a) was indexed on an orthorhombic cell with $A2_1am$ space group (PDF#49-0608). The acid-treated product showed broad peaks (Fig. 1b), which can be indexed on the basis of a tetragonal cell [21, 22]. The Bi:Sr:Ta metal composition ratio was found to be 0.19:0.81:2.0 after the acid treatment by ICP. So, protonation of the BST resulted in $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ (HST). Tsunoda et al. have also reported that protonation of BST resulted in the formation of $H_{1.8}Sr_{0.8}Bi_{0.2}Ta_2O_7$ [21]. The bismuth oxide sheets in $Bi_2SrTa_2O_9$ were selectively leached and that protons were introduced into the interlayer space to form a protonated layered perovskite, $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$. The remaining bismuth and the loss of a corresponding amount of strontium should be ascribed to cation disorder (Bi↔Sr) [21]. Crystal structure of HST has been investigated by HREM observations and diffraction results (XRD and ED) [21], which clearly revealed that HST retained the structure of the perovskitelike-slabs in BST.

UV–vis diffuse reflectance spectra of BST and HST are shown in Fig. 2. The reflectivity spectrum was transformed to absorbance intensity through Kubelka–Munk method. As shown in Fig. 2, the absorption for the HST was significantly blue shifted compared with that for BST crystal, in good agreement with the previous report [22]. Consequently, the band gap of HST is also wider than that of BST. The band gap energies of BST and HST samples were estimated to be about 3.64 and 3.88 eV from the onsets of UV–vis diffuse reflectance spectra, respectively.

The sacrificial reagent CH_3OH was employed to evaluate the photocatalytic activity of the photocatalyst. When the photocatalytic reaction is carried out in aqueous solutions including easily oxidizable reducing reagents such as CH_3OH and SO_3^{2-}; photogenerated holes irreversibly oxidize the reducing reagents instead of water. This makes the photocatalyst electron rich and a H_2 evolution reaction is enhanced [23]. Figure 3 shows a time course of gas evolution for the photocatalytic decomposition of the CH_3OH/H_2O solution (20 mL CH_3OH, 400 mL H_2O) over HST (0.1 g) without any catalyst pretreatment. After the first

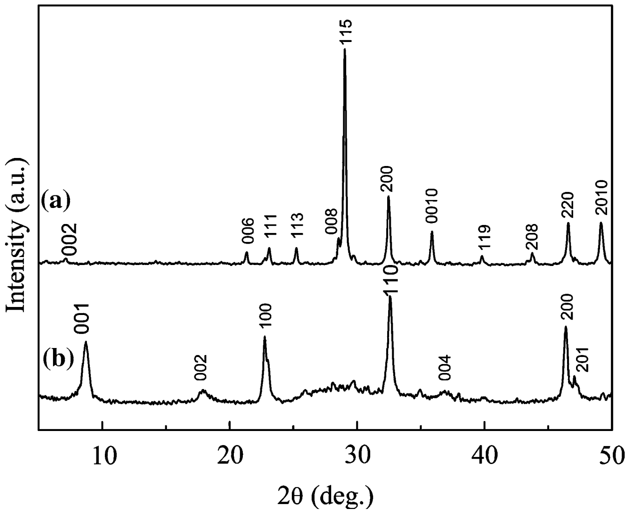

Fig. 1 XRD patterns of (**a**) $Bi_2SrTa_2O_9$ and (**b**) acid-treated $Bi_2SrTa_2O_9$

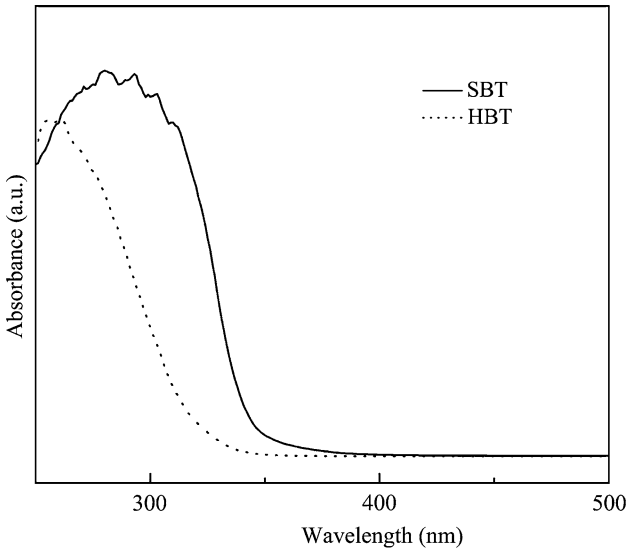

Fig. 2 UV–vis diffuse reflectance spectra of $Bi_2SrTa_2O_9$ and $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$

run, the system was evacuated, and the reaction was repeated using the same reaction mixture. In the second and third runs, splitting of water occurred with almost the same rate as the first run, which demonstrates a high durability of the catalyst. As shown in Fig. 3, the rate of H_2 evolution over HST reached 57.67 mmol h^{-1} g^{-1}. The result showed that the H_2 evolution rate was quite high upon light irradiation.

The turnover number (TN) is usually defined as a ratio of the number of molecules reacted or produced to the number of the active sites on the surface of a catalyst. However, it is difficult to determine the number of active sites that actually work for heterogeneous photocatalysts. Therefore, the turnover numbers were calculated by adopting the total amount of the catalyst as the number of active sites to ensure the reliability of the evaluation. The turnover number is enough to prove that the reaction is photocatalysis, not a photocorrosion [24]. As shown in Fig. 3, the photocatalyst presented a high activity for H_2 evolution when irradiating with a high-pressure Hg lamp and the turnover number reached 412.6 after only 4.5 h of reaction time. This result contains important evidence for indicating the reaction occurs catalytically.

The reactions using sacrificial reagents are regarded as half reactions and are often employed for test reactions of photocatalytic H_2 or O_2 evolution. However, one should realize that the results do not guarantee a photocatalyst to be active for overall water splitting into H_2 and O_2 in the absence of sacrificial reagents. So, photocatalytic H_2 and O_2 evolution from water containing no sacrificial reagents was investigated to evaluate the possible thermodynamic potential of HST without co-catalyst for overall water splitting. Figure 4 shows the time course of H_2 and O_2 evolution over HST. Both H_2 and O_2 were produced starting at the onset of the reaction in proportion nearly equal to irradiation time. The formation rates of the H_2 and O_2 evolution from pure water under UV light irradiation were 2.46 and 1.11 mmol h^{-1} g^{-1}, respectively. It is noteworthy that the photocatalyst shows such high activity without co-catalysts such as platinum. The ratio of the turnover number of electrons reacted to the total amount of the HST catalyst used was 17.6 after 6 h of reaction time, suggesting that the reaction proceeded photocatalytically. But hydrogen evolution was not observed from pure water in this experiment using $Bi_2SrTa_2O_9$ after 4 h of reaction time. The H^+-exchanged forms are known to be easily hydrated [7, 12, 19, 25, 26]. The marked improvement of the photocatalytic activity of HST may be due to the migration of the reactant H_2O into the interlayer spaces [25]. The photogenerated electrons and holes can be effectively transferred to the interlayer water, and this results in the effective photocatalytic water splitting in the hydrated layered tantalates [19].

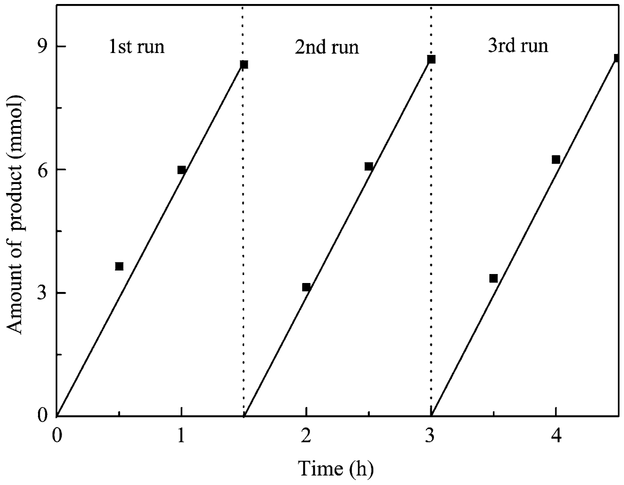

Fig. 3 Amount of H_2 evolution according to reaction time of $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ (0.1 g catalyst, 400 mL H_2O + 20 mL CH_3OH, 350 W Hg lamp)

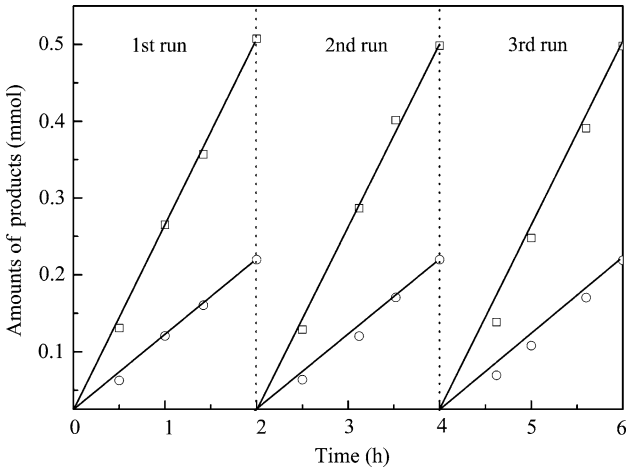

Fig. 4 Amounts of H_2 and O_2 evolution according to reaction time of $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ (0.1 g catalyst, 400 mL pure water, 350 W Hg lamp)

Kudo and co-workers have found various tantalates which show high activities for photocatalytic water splitting under UV light irradiation [27–31]. In particular, $NaTaO_3$ with a perovskite structure is most active among these tantalates [32]. We also studied the reaction over the non-hydrous perovskite tantalate, $NaTaO_3$, which was synthesized by solid-state reaction method [32]. Photocatalytic water splitting over HST and $NaTaO_3$ was carried out under otherwise identical reaction conditions and the rates of H_2 and O_2 evolution for $NaTaO_3$ were about 0.82 and 0.40 mmol h^{-1} g^{-1}, respectively. $NaTaO_3$ showed quite high activity for H_2 evolution, though the rate of H_2 evolution was lower than that of HST. This result supports the above proposal that the presence of hydrated interlayer space is important for improving the photocatalytic activity of

Ta-based catalysts. The above result also indicated that the HST semiconductor has suitable band structure for the reduction of H^+ to H_2 and oxidation of H_2O to O_2, respectively.

4 Conclusion

In summary, $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ with the layered perovskite structure has been synthesized via acid treatment of $Bi_2SrTa_2O_9$ and the crystal structure, optical absorption and photocatalytic activity for water splitting have been investigated. The band gap of $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ was estimated to be about 3.88 eV. Under UV light irradiation, the photocatalyst shows favorable photocatalytic activity in splitting pure water into H_2 and O_2 even without the assistance of co-catalysts. The high photocatalytic activity of $H_{1.81}Sr_{0.81}Bi_{0.19}Ta_2O_7$ in the present article may imply a series of stable layered oxides as candidates for highly efficient photocatalysts.

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