博 士 論 文 の 内 容 の 要 旨

氏名	LUO ,YING
学位名	博士（工学）
学位授与年月日	2021 年 3 月 20 日
論文題目	Studies on the growth of $BaTaO_2N$ single crystals by flux method for photocatalytic H_2 evolution （フラックス法による水素発生用光触媒 $BaTaO_2N$ 結晶育成の研究）

（博士論文の内容の要旨）

Solar driven water splitting on particulate photocatalysts has gained considerable attention as a potential way to generate clean, renewable, and storable hydrogen energy. Although a lot of metal oxides with a suitable energy band have been reported for water splitting, most metal oxides have a wide band gap and can only respond the ultraviolet (UV) light. Since about half of the incident sunlight on the surface of earth is visible light, the development of photocatalysts with narrower band gap to effectively utilize the sunlight is indispensable. In the metal oxide photocatalysts, the conduction band mainly consist of transition-metal d orbitals which usually locates at a more negative potential than 0 V (*vs*. NHE), and the valence band consist of O 2p orbitals which locates a more positive potential than 3.0 V (*vs.* NHE), thereby these photocatalysts always have a band gap larger than 3.0 eV. Considering that the valence band potential of metal oxide photocatalysts is sufficient to oxidize H_2O to O_2 (1.23 V *vs.* NHE), many efforts began to introduce other elements to adjust the composition of valence band, such as S and N elements. The potential of S 2p and N 2p orbitals are higher than that of O 2p orbitals, which results in more negative valence band, thus producing a small band gap that can active visible light.

Barium tantalum (oxy)nitride ($BaTaO_2N$) as one of most promising photocatalyst with a narrow band gap of 1.9 eV has been demonstrated to produce both H_2 and O_2 under visible light irradiation in the presence of related sacrificial reagents due to its suitable energy band. Compared with metal oxide photocatalysts, however, the synthesis of $BaTaO_2N$ requires an ammonia flow and a high temperature, which severely limits the synthesis and development of $BaTaO_2N$. During the nitridation process, the anion vacancies and reduced tantalum species are easily introduced and formed due to the charge compensation caused by the replacement of O^{2-} ions and N^{3-} ions and the reducing ammonolysis atmosphere, which would act as trapping centers for photogenerated electrons and holes and thereby cause a low activity. Flux method, which utilizes a high-temperature molten salts (the flux) as the solvent, has been demonstrated to be a powerful method to synthesize the high-quality (oxy)nitride crystals during the high-temperature nitridation process. It has been reported that $BaTaO_2N$ prepared by one step process in which the raw materials were directly treated in the NH_3 flow exhibited a higher photocatalytic activity than that by two step processes because it avoids the dissolution and recrystallization of the corresponding oxide precursors. However, there are few reports on the control of crystallinity, surface, and morphology of $BaTaO_2N$ by flux method which have an extremely important effect on photocatalytic performance.

Therefore, in this thesis, the goal is to grow high crystalized $BaTaO_2N$ crystals with some special surface features by selecting or combining suitable fluxes to obtain an excellent photocatalytic activity for H_2 evolution.

In Chapter 1, attention is focused on the growth of $BaTaO_2N$ crystals with different exposure facets and investigating its effect on photocatalytic performance. Charge separation has been regarded as one of the most important factors affecting the activity of photocatalysts in solar light-driven water splitting. Some groups have reported that the exposure of anisotropic facets on photocatalysts is beneficial to the charge separation and results in higher activity. However, it is difficult to create the exposed facets that facilitate spatial charge separation on (oxy)nitride materials, because the crystal growth of (oxy)nitrides is usually uncontrollable during the conventional high-temperature nitridation procedure.

Here, $BaTaO_2N$ crystals exposed with sole {100} facets and co-exposed with anisotropic {100} and {110} facets were fabricated by using the one-pot NaCl or KCl-assisted nitridation approach, respectively. When

modified with Pt as a H_2 evolving cocatalyst, the photocatalytic activity for H_2 production on $BaTaO_2N$ with co-exposed {100} and {110} facets is nearly tenfold over those on $BaTaO_2N$ with only {100} facets or irregularly shape. The enhanced activity is attributed to the efficient spatial charge separation, that is, the accumulation of photogenerated electrons and holes on the {100} and {110} facets of $BaTaO_2N$, respectively.

In Chapter 2, attention is focused on the selection of more suitable flux to obtain $BaTaO_2N$ crystals with better crystallinity to further improve the activity. $BaTaO_2N$ is an important oxynitride photocatalyst for the splitting of water under visible light. However, the preparation of $BaTaO_2N$ crystals with low defect densities and high crystallinities is challenging via ammonolysis at high temperatures. Although NaCl and KCl fluxes were used for assisting the growth of $BaTaO_2N$ in the above chapter, no other chloride fluxes were examined for the synthesis of $BaTaO_2N$ crystals.

Thus, the effects of the flux type (RbCl, CsCl, and $BaCl_2{\cdot}2H_2O$) on the morphology, crystallinity, and photocatalytic performance of the $BaTaO_2N$ crystals were studied initially. It was found that the $BaTaO_2N$ crystals grown using a RbCl flux exhibited a significantly higher photocatalytic H_2 evolution rate than those grown using the other two fluxes because of the lower defect density and higher crystallinity. Subsequently, the effects of the source ratio, solute concentration, reaction temperature and time on the crystallinity and morphology of the $BaTaO_2N$ crystals grown using a RbCl flux were studied systematically to gain insight into the $BaTaO_2N$ crystal growth mechanism.

In Chapter 3, attention is focused on the selection of more suitable flux to obtain $BaTaO_2N$ crystals with better crystallinity to further improve the activity. Shape-controlled syntheses of inorganic single crystals play a crucial role in the determination of their physical and chemical properties. Nevertheless, the main shape of $BaTaO_2N$ is still cubic because $BaTaO_2N$ belongs to the cubic system and has a highly symmetric lattice. It has been reported that the plate-like structure of photocatalyst materials could decrease the charge carrier diffusion distance from the bulk to the surface, thus promoting the photo-excited charge separation and transfer towards efficient photocatalytic reactions. Therefore, plate-like structured $BaTaO_2N$ crystals that are well crystallized are expected to be explored and so are their photocatalytic performances for H_2 evolution.

Herein, highly crystalline $BaTaO_2N$ crystal with a plate-like structure from K_2CO_2–KCl binary flux under a nitridation atmosphere were fabricated. The fabricated platy $BaTaO_2N$ was characterized and the results as well as formation mechanism were discussed accordingly. Owing to the generation of oxo-complex $[TaO_3]^-$ by the assistance of CO_3^{2-} and the lattice match of the $BaTaO_2N$ (111) plane with the $Ba_5Ta_4O_{15}$ (001) plane, the platy $BaTaO_2N$ crystals with well-developed {111} facets were formed via the simultaneous formation and transformation of $Ba_5Ta_4O_{15}$. Upon optimizing the molar ratio of K_2CO_3 and KCl, an excellent photocatalytic performance for H_2 evolution was obtained at the molar ratio of 20/80 due to the plate-like structure and high crystallinity of the $BaTaO_2N$ photocatalyst.

In this thesis, $BaTaO_2N$ co-exposed with {100} and {110} facets is developed to facilitate spatial charge separation, a higher crystallinity $BaTaO_2N$ with low defects is fabricated to reduce the generation of recombination centers, and a platy $BaTaO_2N$ is obtained to decrease the migration distance of photogenerated electrons and holes. All these positive features resulted in an enhanced activity of $BaTaO_2N$. Therefore, the design and discovery of photocatalysts with desirable shape and high crystallinity is an important strategy to further improve the photocatalytic water splitting performance on (oxy)nitrides via refinement of the fabrication procedure and the use of various flux species. It provides a facile approach to the development of efficient (oxy)nitride photocatalysts for solar energy conversion.