Catalysis Letters Vol. 110, Nos. 1–2, August 2006 (© 2006)
DOI: 10.1007/s10562-006-0101-3

Photocatalytic properties of a novel layered photocatalyst $CsLaSrNb_2NiO_9$

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Received 1 March 2006; accepted 17 May 2006

A new visible-light-driven photocatalyst $CsLaSrNb_2NiO_9$ based on the 2-D layered perovskite crystal structure was prepared by using the solid-state method. Photocatalytic H_2 evolution from the aqueous CH_3OH solution was achieved on the photocatalysts $CsLaSrNb_2NiO_9$ under UV or visible light irradiation. A possible electronic band structure of $CsLaSrNb_2NiO_9$ was proposed in regard to the complicated photocatalytic and photophysic properties.

KEY WORDS: photocatalysis; photocatalyst $CsLaSrNb_2NiO_9$.

1. Introduction

In the past several decades much attention has been paid to the photocatalytic decomposition of water into H_2 and O_2 over semiconductor materials, because of the promising future for providing a clean and renewable source of hydrogen fuel [1]. Several 2-D layered host materials containing TiO_6, NbO_6 or TaO_6 octahedral units have been reported as highly efficient photocatalysts for water splitting, such as $K_4Nb_6O_{17}$, $K_2La_2Ti_3O_{10}$, $KCa_2Nb_3O_{10}$, and $RbLaTa_2O_7$ *et al.*, among which $K_2La_2Ti_3O_{10}$ shows the best activity with an quantum efficiency higher than 30% at 300 nm light irradiation [2–5]. The structure of these layered materials are comprised of perovskite-like layers interleaved by the alkali cations. The photogenerated electron and hole pairs upon UV light irradiation were assumed to easily separate in the perovskite-like layers resulting in the higher photocatalytic activities of these layered photocatalysts for water splitting. However the reported layer photocatalysts are mainly limited to UV light response except the $RbPb_2Nb_3O_{10}$, which shows a low activity for H_2 evolution from aqueous methanol solutions under visible light irradiation (> 420 nm). Doping active semiconductors photocatalysts with 3d transition metals is one of efficient methods for developing new photocatalysts with visible light response. Our research group had reported several novel visible-light-driven photocatalysts for water splitting based on this method, for example $InTaO_4$ doped with Ni had been developed as one active photocatalyst for pure water splitting under visible light irradiation (> 420 nm) [6]. Most ion-exchangeable layered perovskites oxides are known containing d^0 cations such as Ti^{4+}, Nb^{5+}, and Ta^{5+} in the perovskite-like host layers of these oxides. It is of great interest to see whether new visible-light-driven 2-D layered perovskite photocatalysts can be prepared by doping extra 3d transition metals into the perovskite-like layers. In this paper we report a new kind of visible-light-driven photocatalysts $CsLaSrNb_2NiO_9$ crystallizing in 2-D layered perovskite structure similar to that of $CsCa_2Nb_3O_{10}$.

2. Experimental section

All the reagents such as Cs_2CO_3, La_2O_3, $SrCO_3$, Nb_2O_5 and NiO were used as receive without further treatment (Wako, 99.9% purity or higher). The $CsLaSrNb_2NiO_9$ was prepared according to the literature: [7] the stoichiometric mixtures of the starting oxides were ground and mixed thoroughly in an agate mortar. An excess amount of Cs_2CO_3 (40 mol%) was added to compensate for the loss due to the volatilization of the cesium component. The well-mixed powders were calcined at 1300 °C for 10 h. After the reaction, the powders were collected, washed and air-dried at room temperature. The crystal structure of the prepared samples was confirmed by the X-ray diffraction pattern (JEOL JDX-3500 Tokyo, Japan). UV–VIS diffuse reflectance spectra were recorded on a UV/VIS spectrometer (UV-2500, Shimadzu) and were converted from reflection to absorbance by the standard Kubelka–Munk method. The Photocatalytic H_2 evolution from an aqueous methanol solution was detected in a closed

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gas circulation system with a side window Pyrex cell. The light source was a 300 W Xe arc lamp attached with cutoff filters. The photocatalytic activity for the powders under UV light irradiation was examined using an inner irradiation type Pyrex cell with a 400 W high-pressure Hg lamp. The evolved gas was determined by a thermal conductivity detector (TCD) gas chromatograph (Shimadzu GC-8A), which was connected to the system with a circulating line. The 0.5 wt% Pt cocatalyst was photodeposited on the surface of the photocatalysts with the precursor of H_2PtCl_6 to introduce active sites.

3. Results and discussion

The crystal structure of the prepared $CsLaSrNb_2NiO_9$ powders was confirmed by the X-ray diffraction patterns. In accordance with the previous paper [7], $CsLaSrNb_2NiO_9$ crystallized in a layered perovskite structure similar to that of $CsCa_2Nb_3O_{10}$. The color of the prepared $CsLaSrNb_2NiO_9$ powders is gray. Figure 1 shows the UV–VIS diffuse reflection spectrum of $CsLaSrNb_2NiO_9$ powders. There are three absorption edges in the UV–VIS absorption spectra. The main absorption edge was about ~388 nm (E_g: ~3.2 eV) for $CsLaSrNb_2NiO_9$ crystals. In addition, other two apparent absorption humps with absorption edge at ~484 nm (E_g: ~2.57 eV) and 857 nm (E_g: ~1.45 eV), respectively, were preliminarily assumed to the Ni 3d orbitals splitting in the octahedral field. Detail discussions will be given in the following sections.

Figure 2 shows the H_2 evolution from aqueous CH_3OH solution over $CsLaSrNb_2NiO_9$photocatalysts with 0.5 wt% Pt cocatalysts under UV light irradiation. In this case the final products of the reaction with positive holes for CH_3OH oxidization were mainly CO_2. As shown in figure 2, the rate of H_2 evolution was about 1242 μmol/h g_{catal}, and the activities were stable during the reaction. The activities of H_2 evolution over $KCa_2Nb_3O_{10}$, $CsCa_2Nb_3O_{10}$ and $KSr_2Nb_3O_{10}$ such 2-D layered photocatalysts with Pt cocatalysts had been reported smaller than 110 μmol/h g_{catal} under similar conditions [8]. It is interesting to find that the Ni^{2+} substituting does not reduce the activity of the layered structural photocatalyst for H_2 evolution. This is completely different from previous report that the dopant foreign ions could serve as an electron-hole recombination site and then resulting in the decrease of the photocatalytic activities. After evacuating the reaction system and re-running the experiment, almost identical gas production rate was achieved in the second time. Nearly 4000 μmol H_2 evolved during a course of 6.5 h experiment. The turnover number – the ratio of total amount of gas evolved to the photocatalyst (670 μmol in our system) – reaches to 6 after 6.5 h light irradiation. In terms of reacted electrons relative to the amount of Pt loaded on the surface of the photocatalysts, the turnover number exceeds 620 after the 6.5 h reaction, indicating the H_2 evolution from aqueous CH_3OH solution over $CsLaSrNb_2NiO_9$ powders is not caused by a photocorrosion but by a photocatalytic reaction. The XRD patterns of the $CsLaSrNb_2NiO_9$ photocatalysts have no changes before and after the H_2 evolution, indicating the crystal structure of the photocatalysts should be stable in the CH_3OH/H_2O solution under UV light irradiation.

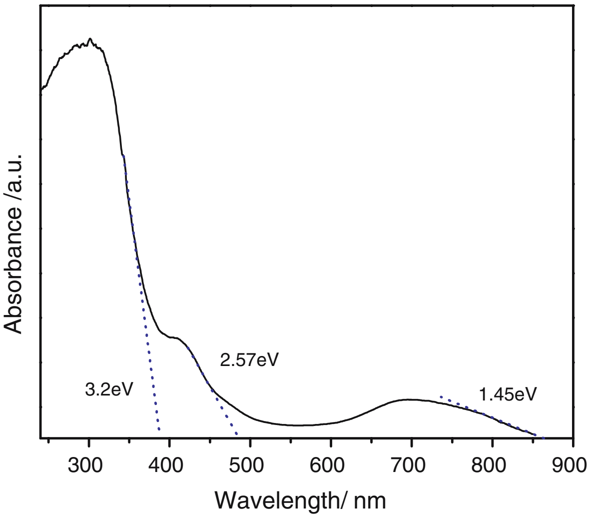

Figure 1. UV–absorption spectra of the prepared $CsLaSrNb_2NiO_9$ powders.

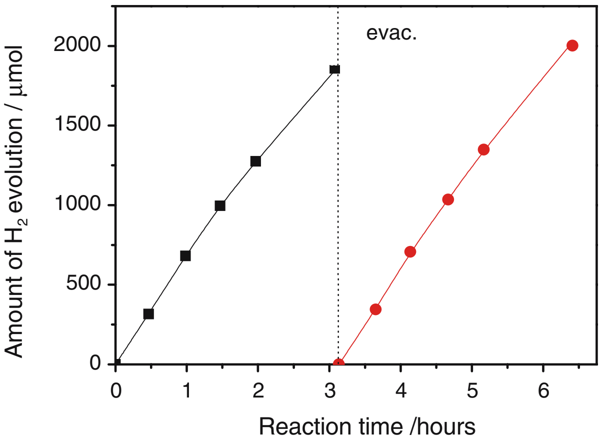

Figure 2. H_2 evolution from aqueous CH_3OH solution over $CsLaSrNb_2NiO_9$ photocatalysts with Pt cocatalysts. (Light source: 400 W Hg lamp; Catalysts: 0.5 g; Cocatalysts: 0.5 wt% Pt).

Visible-light-induced activities of the prepared $CsLaSrNb_2NiO_9$ for photocatalyic H_2 evolution were examined with CH_3OH sacrificial materials (> 420 nm). As shown in figure 3, a course of 10 h light irradiation is needed for H_2 evolution, which can be attributed to the photoreducing time for Pt loading onto the surface of the photocatalysts and serving as active sites. Further experiments show that the H_2 evolution can be achieved without the induced time under the same conditions, when using the recycled $CsLaSrNb_2NiO_9$ (after the H_2

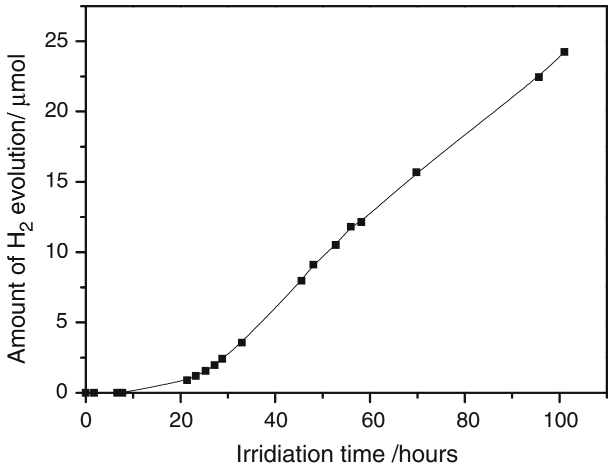

Figure 3. H_2 evolution from aqueous CH_3OH solution over $CsLaSrNb_2NiO_9$ photocatalysts under visible light irradiation. (Light source: 300 W Xe lamp with 420 nm filter; Catalysts: 0.5 g; Cocatalysts: 0.5 wt% Pt).

evolution from CH_3OH/H_2O solution with Pt (0.5 wt%) under UV light irradiation) as the photocatalyst. The rate of H_2 evolution from aqueous CH_3OH solution over $CsLaSrNb_2NiO_9$ photocatalysts was about 0.6 μmol/h g_{catal} under visible light iradiation. It is found that the activities for H_2 evolution were stable during a prolonged 100 h light irradiation and the XRD patterns of the used photocatalysts have no different before and after the photocatalytic reactions, suggesting the photocatalysts is stable upon the visible-light-induced photocatalytic reactions. The possibility of H_2 evolution from aqueous methanol solution with $CsLaSrNb_2NiO_9$ photocatalysts under UV or visible light irradiation indicates the potential of the bottom of the conduction band should be more negative than the redox potential of H^+/H_2 (0 V versus SHE, PH = 0). The electronic structure of the transition metal oxides with perovskite structures is generally defined by the d-level of the transition metal and the 2p-level of the O atoms, when comprised of d^0 transition metals, such as Ti^{4+}, Nb^{5+} and Ta^{5+}. However, for a metal oxide containing transition metals with the d orbitals partly occupied, the electronic structure should be strongly influenced by those transition ions with partly occupied d orbitals. For example, in NiO oxides the 3d orbitals of Ni^{2+} were thought to form an electron donor level at a more negative potential than the O 2p band [9]. Different with $NaLaSrNb_2NiO_9$ oxides that crystallizing in a 3-D perovskite, the $CsLaSrNb_2NiO_9$ was crystallized in a 2-D layered perovskite structure because of the large tolerance factor [7]. It is reported that the layered perovskite $CsLaSrNb_2NiO_9$ consists of perovskite-like slabs of composition $[LaSrNb_2NiO_9]$ interleaved by the large Cs cations. The Nb and Ni metal ions occupy the octahedral sites at random with some oxygen vacancies in ordered or disordered distributing around [7]. Previous studies of Ni-doping on the photocatalytic properties of TiO_2 and $SrTiO_3$ showed that an occupied level was created in the center of the band gap due to the Ni 3d band splitting in the oxides [10], indicating the important role of Ni 3d band in deciding the visible-light-induced photocatalytic activities. In the case of $CsLaSrNb_2NiO_9$, in which the Ni^{2+} cations reside in the center of Ni–O octahedrons with partly oxygen vacancies, the Ni 3d orbitials would be split into two part, an lower energy level of 6-fold degenerate t_{2g} orbitals and a 4-fold higher energy level of e_g orbitals. The distorted Ni–O octahedrons for the random oxygen vacancies make it possible for the further splitting of the e_g and t_{2g} orbitals. The higher energy level e_g will be split into a higher energy b_{1g} orbital and a lower-energy a_{1g} orbital, and the t_{2g} orbitals with 6-fold degenerate will be further split into a higher energy b_{2g} orbital and a lower 4-fold degenerate e_g orbitals. The split Ni 3d-t_{2g} and Ni 3d-e_g orbitals must play important roles in constructing the band structure and the photocatalytic activities, especially the properties under visible light irradiation.

The photocatalytic properties of the $CsLaSrNb_2NiO_9$ photocatalysts for pure water splitting were examined under UV light irradiation with 0.3 wt% RuO_2 cocatalysts. For loading of RuO_2, $CsLaSrNb_2NiO_9$ was impregnated up to incipient wetness with a ruthenium carbonyl complex, $Ru_3(CO)_{12}$, in THF, dried in air and calcined at 673 K for 5 h to convert the ruthenium species to RuO_2. It was found that a small amount of H_2 could be evolved under UV light irradiation, whereas no O_2 evolution was detectable. These phenomena can be related to the physisorbed or chemisorbed of O_2 molecules on the surface of the photocatalyst particles, just as that found on TiO_2 [11, 12]. Taking into the band gap energy accounted from the UV–VIS diffuse reflectance spectrum, the band structure of $CsLaSrNb_2NiO_9$ was proposed and schematically illustrated in figure 4. For Ni^{2+} with the electronic configurations $3d^8$ in the photocatalysts, the following electronic occupying states are expected: the split Ni 3d-t_{2g} orbitals were fully occupied, while the split Ni 2d-e_g orbitals should be partially occupied. With Ni 2d-e_g orbitals further splitting into two parts for the distortion of the Ni–O octahedrons, the lower energy band a_{1g} orbitals were assumed to fully occupation to better consist with the photophysical and photocatalytic properties of the photocatalysts. As suggested in figure 4, the main absorption band at 388 nm was attributed to the direct band gap of the photocatalysts from the valence band (formed by Ni3d + O2p) to the conduction band (Nb 4d + Ni 3d-b_{1g}). The other two observed apparent absorption humps with absorption edge at ~484 nm (E_g: ~2.57 eV) and 857 nm (E_g: ~1.45 eV) were assumed to the formed Ni 3d-b_{2g} and Ni 3d-a_{1g} orbitals, respectively, by the further splitting of Ni 3d orbitals in the octahedral field. More experiments are necessary to reveal the exact band structure of the $CsLaSrNb_2NiO_9$ photocatalysts. At the present stage the photocatalytic

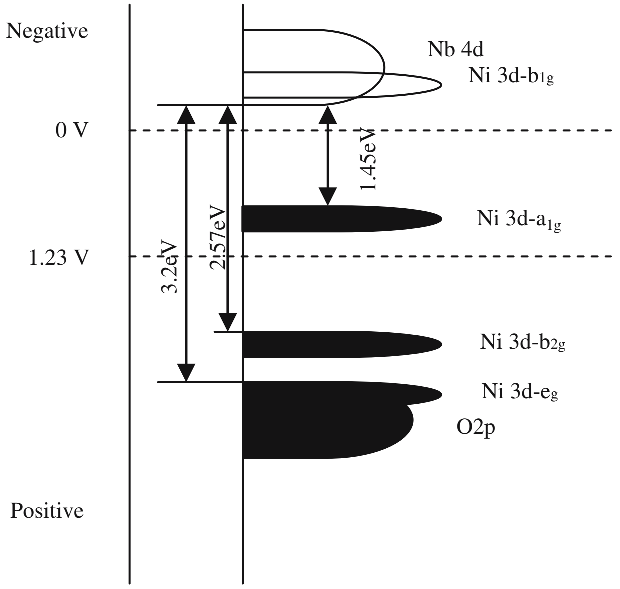

Figure 4. Suggested band structure for the CsLaSrNb$_2$NiO$_9$ photocatalysts.

activity of the layered photocatalyst CsLaSrNb$_2$NiO$_9$ for H_2 evolution under visible light irradiation is still low. While a most promising advantage of the layered photocatalysts is the possibility of modifying their chemical composition as well as microstructure by means of ion exchange, intercalation, or pillaring, this is helpful for developing novel efficient photocatalysts. Further experiments to improve the activity of the new 2-D layered photocatalysts CsLaSrNb$_2$NiO$_9$ are in progress.

In summary, one novel visible-light-driven photocatalyst CsLaSrNb$_2$NiO$_9$ crystallizing in a 2-D layered perovskite structure was developed by doping extra transited element (Ni^{2+}) into the perovskite-like oxide sheets in the layered oxides. The photophysical and photocatalytic properties of the prepared photocatalytic under visible light irradiation were assumed to the Ni 3d orbitals splitting in the octahedral field.

Acknowledgments

One of the authors thanks the Japan Society for the Promotion of Science (JSPS) for financial support. This work was supported by a Grant-in-Aid for scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

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