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Synthesis and photocatalytic hydrogen production activity of the Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ hybrid layered perovskite

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ABSTRACT

The nickel-based complex Ni-CH₃CH₂NH₂-intercalated niobate layered perovskite Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ was synthesized via a facile in situ chemical reaction method. Using ultrathin H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ nanosheets and nickel acetate as precursors. The composition, structure, photophysical properties, and photocatalytic activity for H₂ production of Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ were studied systematically. The photocatalyst loaded with 0.5 wt% Ni exhibited the highest H₂ evolution rate of 372.67 μmol/h. This was 0.54 times higher than the activity of the H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ nanosheets. The activity of the optimized Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ was comparable to that of the Pt-loaded sample under the same reaction conditions. The photocatalytic activity of the Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ was mainly attributed to the excellent separation of photogenerated carriers, after formation of the intercalated complex Ni-CH₃CH₂NH₂. This study provides a facile strategy to synthesize a non-precious metal-loaded photocatalyst for H₂ production.

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1. Introduction

Photocatalytic hydrogen production from water is a green route to realize solar-to-hydrogen energy conversion [1–3]. Since the first report of hydrogen evolution through water splitting [4], various photocatalysts have been investigated for photocatalytic hydrogen evolution [5–8]. However, the activities of most photocatalysts for H₂ production are still low owing to the recombination of photoexcited electrons and holes [9,10]. Many approaches have been developed to overcome this problem, such as constructing p–n heterojunctions [11,12], using redox surfaces to spatially separate electrons and holes

[13,14], and inner electric field building [10,12,15].

Aurivillius-type layered perovskites with a formula of (Bi₂O₂)²⁺(A_{m-1}M_mO_{3m+1})²⁻ have been reported as promising photocatalysts for water splitting and the degradation of organic pollutants. This has been attributed to their lamellar structure, ability to tailor their elemental composition, and their charge transport and separation capabilities [16–18]. When layered perovskites are transformed into their protonated forms or exfoliated into ultrathin nanosheets, their photocatalytic properties are significantly enhanced. This is due to the increased specific surface area and improved charge separation ability of the catalyst [19,20]. However, the photogener-

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ated charge separation ability of these ultrathin nanosheets is still limited owing to the recombination of charges in the interlayer space, which limits the photocatalytic activity.

To improve the charge separation ability of the layered perovskite, guests such as noble metals or semiconductors have been intercalated into their interlayer nanospace via chemical reactions, to synthesize hybrid layered perovskites [21,22]. This strategy can allow the physical properties of the layered perovskite to be modulated over a wide range [23]. In hybrid layered perovskites, the guest in the interlayer provides active sites for proton reduction, and also promotes the diffusion of photoelectrons generated from the layered perovskite, thus enhancing the photocatalytic activity [24,25]. Ebina and co-authors reported RuO_2 -intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ for photocatalytic water splitting [21]. Highly-dispersed Pt nanocluster-intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets were reported by Oshima et al. [22]. Photocatalytic water splitting into H_2 and O_2 by the catalyst showed an eight-fold increase in activity under band-gap irradiation, compared with that of RuO_2 -intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ [21]. The introduced guests in these reports have typically been noble metals and semiconductors. The high cost and non-uniform distribution of these guests restricts their practical application. Non-precious metal nickel-based materials are attractive in that they are cost-effective, non-toxic, and stable. Because of this, Ni [26,27], NiO [27], Ni_2O_3 [28], NiS [29], NiS_2 [30], $\text{Ni}(\text{OH})_2$ [31–33] and $\text{Ni}(\text{OH})_x$ [34] have been widely used as co-catalysts for enhancing the photoelectrochemical performance of photoelectrodes or photocatalytic H_2 production ability of photocatalysts. Compared with solid inorganic materials, nickel-based molecular complexes that are efficient co-catalysts also provide the flexibility of tuning their properties by rational ligand design [35–37].

Herein, the nickel based complex $\text{Ni-CH}_3\text{CH}_2\text{NH}_2$ (Ni-EA)-intercalated layered perovskite, $\text{Ni-CH}_3\text{CH}_2\text{NH}_2/\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ (Ni-EA/HSN Ns) was fabricated via a facile in situ chemical reaction method. The ultrathin $\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ nanosheets (HSN Ns) are used as a host material for two reasons. First, the two-dimensional structure of the ultrathin HSN Ns provides a large specific surface area and high charge separation ability compared with its bulk form of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ platelets (SBN Ps), which are advantageous for photocatalytic hydrogen evolution. Second, the surface grafted ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$, minor) and interlayer protonated ethylamine ($\text{C}_2\text{H}_5\text{NH}_3^+$, major) [20] of the HSN Ns act as coordination sites for Ni^{2+} . Therefore, Ni-EA is readily formed in-situ during the photocatalytic process, without requiring the addition of extra ligands. Forming the Ni-EA complex significantly improves the charge transport and separation ability of the Ni-EA/HSN Ns, which enhances its photocatalytic ability for H_2 production.

2. Experimental

2.1. Chemicals

The following materials and reagents were used as starting materials: strontium carbonate (SrCO_3 , 99%, Alfa), bismuth

oxide (Bi_2O_3 , A.R., Sinopharm Chemical Reagent Co. (SCRC)), niobium(V) oxide (Nb_2O_5 , A.R., SCRC), sodium chloride and potassium chloride (NaCl and KCl , A.R., Tianjin Bodi Chemical Industry Co., Ltd.), hydrochloric acid (HCl , 36–38 wt%, A.R., Sichuan Xilong Chemical Industry Co., Ltd.), ethylamine ($\text{C}_2\text{H}_7\text{N}$, 68.0–72.0 wt% in H_2O , Aladdin.) and nickel acetate tetrahydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Ni}\cdot 4\text{H}_2\text{O}$, A.R., Tianjin Zhiyuan Chemical Reagent Co., Ltd.).

2.2. Sample preparation

The Ni-EA/HSN Ns were fabricated by a facile in situ chemical reaction method, using HSN Ns and nickel acetate as precursors. The HSN Ns were fabricated via a protonated process using SBN Ps as a precursor, followed by liquid exfoliation in ethylamine solution [20].

2.2.1. Synthesis of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ platelets

The SBN Ps were prepared by the molten salt synthesis (MSS) method, which is a promising approach for fabricating Aurivillius-type oxides [38–40]. In detail, the starting materials of SrCO_3 , Bi_2O_3 , Nb_2O_5 , NaCl , and KCl were mixed stoichiometrically and ground for 40 min in a mortar. The $\text{NaCl}:\text{KCl}$ molar ratio was 1:1, and the SBN Ps:salt mass ratio was 1:1. The mixture was then transferred into an alumina crucible and calcined at 1000 °C for 3 h. The resulting SBN Ps were washed thoroughly with ultrapure water and then dried at 80 °C in an oven for 2 h.

2.2.2. Synthesis of $\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ platelets

The $\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ platelets (HSN Ps) were synthesized by protonation of the SBN Ps, which was carried out in 1 L of 3 mol/L aqueous HCl . Typically, 10 g of SBN Ps were added into the above acidic solution, and the resulting mixture was stirred at 25 °C for 3 d. The resulting HSN Ps were washed thoroughly with ultrapure water and then dried at 80 °C in an oven for 2 h.

2.2.3. Synthesis of $\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ nanosheets

The HSN Ns were fabricated by stirring the protonated material (HSN Ps, 3.0 g) in 0.1 mol/L aqueous ethylamine solution (1 L) for 5 d at 25 °C. The resulting mixture was separated by centrifugation, and the solid fraction washed with ultrapure water to remove residual ethylamine, before drying at room temperature. In this process, exfoliation of the HSN Ns and the connection of $\text{CH}_3\text{CH}_2\text{NH}_2$ on the HSN Ns were achieved simultaneously [20].

2.2.4. Synthesis of $\text{Ni-CH}_3\text{CH}_2\text{NH}_2/\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ hybrid layered perovskite

To synthesize the Ni-EA/HSN Ns, 50 mg of HSN Ns with the required amount of $\text{C}_4\text{H}_6\text{O}_4\text{Ni}\cdot 4\text{H}_2\text{O}$ (mass percentage of nickel was 0.05%, 0.1%, 0.3%, 0.5%, 0.8%, 1.0%, or 5.0%) were added in 100 mL of aqueous solution containing 30 vol% of methanol. The suspension was ultrasonicated for 5 min to uniformly disperse the sample. The system was evacuated to remove air, and then irradiated by a 300-W Xenon lamp without any opti-

cal filters. The vertical distance between the light source and liquid surface was about 17 cm. After 4 h of irradiation, the sample was separated by centrifugation, thoroughly washed with ultrapure water, and then dried at room temperature. The obtained sample is referred to as $x\%$ Ni-EA/HSN Ns, where $x\%$ indicates the mass percentage of Ni.

2.3. Characterization

The crystal structures of the samples were characterized using an X-ray diffractometer (XRD, Bruker D8 Advance) with $\text{Cu K}\alpha$ radiation at a scanning rate of $0.02^\circ/\text{min}$. A Nicolet-6700 spectrometer was used to acquire Fourier-transform infrared (FTIR) spectra, in the frequency range from 400 to 4000 cm^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific Escalab 250 system, to determine the chemical compositions and chemical states of the photocatalysts. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained on a JEM 2100 transmission electron microscope at an accelerating voltage of 200 keV. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) were recorded using a Thermo Scientific Evolution 220 spectrophotometer. Photocurrent measurements were carried out using a conventional three-electrode quartz cell on a CHI 760 electrochemical workstation. A 300-W Xenon lamp without any optical filters was used as a light source. An AUTOSORB-IQ-MP physical adsorption instrument was used to determine Brunauer-Emmett-Teller (BET) surface areas of the samples, by a multipoint BET method.

2.4. Photocatalytic H_2 evolution

Photocatalytic H_2 production experiments were performed in a closed system. 50 mg of HSN Ns and the required mass of nickel acetate (mass percentage of nickel was 0.05%, 0.1%, 0.3%, 0.5%, 0.8%, 1.0%, or 5.0%) were dispersed in 100 mL of aqueous solution containing 30 vol% of methanol. Air in the system was removed by evacuating. The suspension was irradiated by a 300 W Xenon lamp without any optical filters, while being continuously stirred. The amount of H_2 produced was detected using an Agilent 7890A gas chromatography apparatus with a thermal conductivity detector.

3. Results and discussion

The photocatalytic activities of Ni-EA/HSN Ns compounds containing different mass ratios of nickel (0.05%, 0.1%, 0.3%, 0.5%, 0.8%, 1.0%, or 5.0%) were measured by water splitting. The 0.5% Ni-EA/HSN Ns shows the highest photocatalytic activity, so the rest of this study is focused on this sample. For comparison, data for the 5.0% Ni-EA/HSN Ns is also presented.

3.1. Crystal structures of the photocatalysts

XRD patterns of the as prepared HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns are shown in Fig. 1. The diffraction peaks of the three samples are almost the same in the range of

Fig. 1. XRD patterns of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

10° – 80° , indicating that the crystal structure of the HSN Ns does not significantly change after introducing Ni. The diffraction peak at $2\theta \approx 6.5^\circ$ is assigned to the (001) lattice plane (parallel to the perovskite layer) of the HSN Ns. However, the diffractions of the (001) lattice plane occur at $2\theta = 8.1^\circ$ and 8.5° for the 0.5% Ni-EA/HSN Ns and 5.0% Ni-EA/HSN Ns, respectively. Compared with the HSN Ns, the diffraction peaks corresponding to the (001) lattice plane of the 0.5% Ni-EA/HSN Ns and 5.0% Ni-EA/HSN Ns shift to larger angles, and the intensities of these (001) diffraction peaks are enhanced obviously. This indicates that the interlayer space of the HSN Ns is reduced, and that the crystallinity of the (001) lattice plane of the HSN Ns increases after introducing Ni. The reduction in the interlayer space of the 0.5% Ni-EA/HSN Ns and 5.0% Ni-EA/HSN Ns may be caused by the electrostatic interaction force between the negatively-charged perovskite layer ($\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$)^{1.78-} and positively-charged nickel complex Ni-EA. The increase of the intensity of the (001) diffraction peak may be due to the layer-by-layer self-assembly of the ultrathin HSN Ns along the [001] direction [41,42].

3.2. FTIR and XPS results

FTIR and XPS spectra were recorded to confirm the interaction between Ni and ethylamine. Fig. 2(a) shows FTIR spectra of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns. Enlargements of the 400 – 700 cm^{-1} region are shown in Fig. 2(b). In Fig. 2(a), the peaks at around 1195, 1393, 1543, and 3398 cm^{-1} for the HSN Ns are assigned to the C–C vibration, $-\text{CH}_2-$ bending vibration, N–H bending vibration, and N–H stretching vibration of ethylamine, respectively [20]. After introducing nickel, peaks emerge at around 415 and 480 cm^{-1} , as shown in Fig. 2(b). These are assigned to Ni–N vibrations [43], and their presence indicates the interaction between nickel and ethylamine.

Fig. 3 shows Ni 2p and N 1s core-level XPS spectra of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns. The bold red, pink and blue lines in Fig. 3(b) are the fitted curves for the N 1s XPS peaks of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns, respectively. As shown in Fig. 3(a), the

Fig. 2. FTIR spectra (a) and enlargement of the 400–700 cm^{-1} region (b) for the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

Fig. 3. Ni 2p (a) and N 1s (b) core-level XPS spectra of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

intensity of the Ni 2p XPS peaks increases with increasing amount of nickel, indicating that nickel has been introduced into the HSN Ns. The peaks at binding energies of 856.26 and 873.97 eV with two satellite peaks at 861.86 and 880.30 eV are assigned to the +2 oxidation state of nickel [37,44]. As shown in Fig. 3(b), the peaks at 395.38 and 401.27 eV for the HSN Ns are assigned to surface grafted amine ($-\text{NH}_2$) and protonated amine ($-\text{NH}_3^+$) in the interlayer space, respectively [20]. The intensities of the two peaks weaken gradually with increasing amount of nickel. When 5.0% Ni is introduced, the peak at 401.27 eV disappears. The weakening of the surface grafted amine ($-\text{NH}_2$) and protonated amine ($-\text{NH}_3^+$) peaks after Ni modification may be due to the formation of Ni-N, through the coordination of Ni ions with the lone electron pair of NH_2 in ethylamine. This is similar to the interaction between N and C in published studies [45], and is consistent with the FTIR results in Fig. 2(b). This result is strong evidence of the interaction between nickel and ethylamine.

Introduced nickel usually exists as nickel or nickel oxide nanoparticles [46,47]. However, the FTIR and XPS analyses suggest that the state of Ni in the present study differs from that in previous reports, likely because of the presence of ethylamine. The layered perovskite formed from stacked layers of opposing charge exhibits ion exchange in the interlayer space [19,20]. Therefore, Ni^{2+} is easily introduced into the in-

terlayer of the HSN Ns, and the protons combined with ethylamine molecules would be substituted by the Ni^{2+} cations. The coordination of ethylamine (through the NH_2 lone pair) with Ni ions gives rise to the complex Ni-EA [48]. The surface morphologies of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns were investigated by TEM. No extra nanoparticles are observed in the HRTEM images in Fig. 4(a)–(c), only lattice figures belonging to the HSN Ns. This observation is consistent with the FTIR and XPS results which show that the state that nickel exists in is the Ni-EA complex.

3.3. Formation process of the Ni-EA/HSN Ns hybrid layered perovskite

Based on the above results, the proposed formation process of the Ni-EA/HSN Ns hybrid layered perovskite is shown schematically in Fig. 5. We previously proposed an evolution process for the ultrathin HSN Ns [20]. In detail, the crystal structure of the SBN Ps starting material can be described as the alternate stacking of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $(\text{SrNb}_2\text{O}_7)^{2-}$ perovskite-type layers, as shown in Fig. 5(a). First, the $(\text{Bi}_2\text{O}_2)^{2+}$ layers are selectively removed, and protons are simultaneously introduced into the interlayer space when SBN Ps are treated with 3 mol/L HCl. This forms the protonated layered perovskite of the HSN Ps (Fig. 5(b)). Subsequently, the HSN Ps are

Fig. 4. HRTEM images of the HSN Ns (a), 0.5% Ni-EA/HSN Ns (b), and 5.0% Ni-EA/HSN Ns (c). Higher magnification images of the regions marked by yellow squares in (a), (b), and (c) are shown inset.

exfoliated into HSN Ns with a thickness of several nanometers, by treating the HSN Ps in ethylamine solution (Fig. 5(c)). The interaction between the $(\text{SrNb}_2\text{O}_7)^{2-}$ perovskite-type layers weakens when ethylamine is introduced into the interlayer, which is essential for obtaining the ultrathin nanosheets of HSN Ns. Finally, the HSN Ns are transformed into Ni-EA/HSN Ns via an intercalation process. HSN Ns are two-dimensional ultrathin nanosheets which contain surface grafted ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$, minor) and interlayer protonated ethylamine ($\text{C}_2\text{H}_5\text{NH}_3^+$, major). When nickel acetate is added to aqueous solutions containing HSN Ns, Ni^{2+} reacts with the $\text{C}_2\text{H}_5\text{NH}_2$ and $\text{C}_2\text{H}_5\text{NH}_3^+$ moieties of the HSN Ns to form the positively charged complex $(\text{Ni}-\text{C}_2\text{H}_5\text{NH}_2)^{2+}$ (Ni-EA). Owing to the electrostatic interaction force between the positively charged complex Ni-EA and negatively charged perovskite layer $(\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7)^{1.78-}$, the interlayer space of the HSN Ns decreases and the ultrathin nanosheets of HSN Ns self-assemble perpendicular to the perovskite layer. This forms the Ni-EA complex intercalated composite layered perovskite Ni-EA/HSN Ns, as shown in Fig. 5(d). Thus, well-dispersed Ni-EA complexes on HSN Ns can be prepared using this in situ method. The high dispersion of the Ni-EA complexes may provide abundant reactive sites for photocatalytic reaction, which will benefit the activity of the photocatalyst.

3.4. Optical properties of the photocatalysts

The optical properties of the HSN Ns, 0.5% Ni-EA/HSN Ns,

Fig. 5. Formation process of the Ni-EA/HSN Ns hybrid layered perovskite. (a) SBN Ps; (b) HSN Ps; (c) HSN Ns; (d) Ni-EA/HSN Ns.

and 5.0% Ni-EA/HSN Ns were measured by UV-vis DRS, as shown in Fig. 6. The reflection intensity was transformed into absorbance intensity using the standard Kubelka-Munk method. As shown in Fig. 6, the light absorption edges of the three samples occur at 362, 380, and 401 nm, respectively. The corresponding bandgaps for the three samples calculated from the onsets of the absorption edges are 3.43, 3.26, and 3.09 eV, respectively. The red shift of the light absorption edge of the catalyst after Ni modification may be due to the visible light absorption of the Ni-EA complex.

3.5. Photocatalytic activities

Fig. 7 shows the time dependent photocatalytic H_2 production abilities of the as synthesized samples. As shown in Fig. 7(a), the photocatalytic activity of the 0.5% Ni-EA/HSN Ns is correlated with the solution pH, and optimized photocatalytic activity is observed at pH of about 8.0. At higher pH ($\text{pH} \geq 9.0$), H_2 generation becomes less thermodynamically favorable, which results in a decrease in the photocatalytic activity [49,50]. At lower pH ($\text{pH} \leq 7.0$), the adsorption of reactant molecules (methanol) on the surface of the photocatalyst is restrained, which also leads to a lower reaction rate [51]. As shown in Fig. 7(b), the optimum amount of introduced Ni is 0.5

Fig. 6. UV-vis DRS of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

Fig. 7. Amounts of H_2 evolved with increasing reaction time. (a) 0.5% Ni-EA/HSN Ns at various pHs; (b) various contents of Ni, pH = 8.0±0.2; (c) 0.5% Ni-EA/HSN Ns and 0.5% Pt/HSN Ns, pH = 8.0±0.2; (d) 0.5% Ni-EA/HSN Ns, pH = 8.0±0.2, durability test.

wt%. The photocatalytic H_2 production rate of the 0.5% Ni-EA/HSN Ns is 372.67 $\mu\text{mol/h}$ in solution at pH of about 8.0, which is 0.54 times higher activity than that of the HSN Ns (241.58 $\mu\text{mol/h}$). Fig. 7(c) shows the time dependent photocatalytic activities of the 0.5% Ni-EA/HSN Ns and 0.5% Pt/HSN Ns in solution at pH of about 8.0. The 0.5% Ni-EA/HSN Ns (372.67 $\mu\text{mol/h}$) show comparable activity to that of the 0.5% Pt/HSN Ns (465.23 $\mu\text{mol/h}$). This indicates that Ni can satisfactorily replace the noble metal Pt in the photocatalyst. Fig. 7(d) shows the time dependent activity for the 0.5% Ni-EA/HSN Ns. The amount of H_2 during 8 h of reaction increases linearly with time, indicating that the hybrid photocatalyst is stable under light-irradiation.

3.6. Mechanism of the enhanced photocatalytic activity

The activity of a photocatalyst is affected by many factors, such as its light absorption ability, charge separation efficiency, and amount of surface active sites. Fig. 6 shows that the light absorption of the Ni-EA/HSN Ns samples extends into the visible range, in contrast to that of HSN Ns. Light absorption by the 5.0% Ni-EA/HSN Ns is clearly higher than that of the 0.5% Ni-EA/HSN Ns, however the photocatalytic H_2 production activity of the former sample is much lower. Therefore, the enhanced photocatalytic activity of the Ni-EA/HSN Ns cannot be attributed to enhanced light absorption.

Fig. 8 shows photocurrent transient responses of the HSN

Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns. The photocurrent transient responses of the samples were recorded during four on-off cycles of intermittent UV-vis irradiation. Each light opened-closed interval is 50 s. The transient photocurrent responses of the three samples are fast and stable during each switch-on and switch-off event. As shown in Fig. 8, the photocurrents of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns are 8.64, 13.17, and 10.80 $\mu\text{A}/\text{cm}^2$, respectively. This indicates that the separation ability of photogenerated carriers by the HSN Ns is improved after modification with Ni. The Ni-EA complex in the interlayer space can promote the

Fig. 8. Photocurrent transient responses of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

Fig. 9. Nitrogen adsorption-desorption isotherms of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

diffusion of photogenerated electrons from the layered perovskite to the guest complex [24,25], thus enhancing the separation ability of the sample. Considering the photocatalytic activities and photocurrents of the photocatalysts, the improved separation ability of photogenerated carriers may be one factor for the higher photocatalytic activity.

The specific surface area is also an important factor affecting the photocatalytic activity of a photocatalyst, because the photocatalytic reaction occurs on the catalyst surface. Fig. 9 shows N_2 adsorption-desorption isotherms of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns. The N_2 isotherms of the three samples all show type IV adsorption curves with type H3 hysteresis loops, indicating the presence of mesopores [52]. Table 1 shows the BET specific surface areas (A_{BET}) of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns. Compared with the HSN Ns, the specific surface areas of the 0.5% Ni-EA/HSN Ns and 5.0% Ni-EA/HSN Ns decrease from 9.056 to 7.845 and 8.037 m^2/g , respectively. These decreases may be due to the partial agglomeration of the nanosheets of HSN Ns, as a result of the layer-by-layer assembly process. Therefore, the specific surface area does not contribute to the enhanced photocatalytic properties of the photocatalyst. Based on the above analysis, it is concluded that efficient charge separation plays a major role in the improved photocatalytic activity of the Ni-EA/HSN Ns.

A possible mechanism for the enhanced photocatalytic activity of the Ni-EA/HSN Ns is shown in Fig. 10. Under UV-light irradiation, electrons (e^-) in the valence band (VB) of the Ni-EA/HSN Ns are excited to the conduction band (CB), leaving behind holes (h^+) in the VB. These charge carriers recombine easily if no suitable active sites are located at the catalyst surface [53,54]. In the Ni-EA/HSN Ns, the Ni-EA complex acts as an

Table 1

BET specific surface areas of the HSN Ns, 0.5% Ni-EA/HSN Ns, and 5.0% Ni-EA/HSN Ns.

Photocatalyst	A_{BET} (m^2/g)
HSN Ns	9.056
0.5% Ni-EA/HSN Ns	7.845
5.0% Ni-EA/HSN Ns	8.037

Fig. 10. Diagram showing the proposed mechanism for the enhanced photocatalytic activity.

active site for photocatalytic H_2 production. The Ni-EA complex is located in the interlayer space. This promotes the diffusion of photogenerated electrons from the layered perovskite to the guest complex, which in turn promotes the separation of photogenerated charge carriers. As a result, the photocatalytic H_2 production activity is enhanced. Meanwhile, the holes are mainly consumed by methanol molecules.

4. Conclusions

We fabricated a hybrid layered perovskite Ni-EA/HSN Ns, via a facile in situ chemical reaction method using HSN Ns and nickel acetate as precursors. The formed Ni-EA complex significantly enhances the charge transport and separation abilities of the HSN Ns, therefore improving its photocatalytic ability. After optimizing the photocatalytic reaction conditions, the 0.5% Ni-EA/HSN Ns exhibit the highest activity for H_2 evolution, which is 0.54 times higher than that of the HSN Ns. The photocatalytic hydrogen evolution rate of the 0.5% Ni-EA/HSN Ns is comparable to that of the 0.5% Pt/HSN Ns. This indicates that Ni can satisfactorily replace noble metal Pt in this system. The enhanced activity is attributed to the improved separation of photogenerated carriers, which arises upon introducing Ni-EA into the HSN Ns.

References

- [1] Y. X. Li, G. Chen, C. Zhou, J. X. Sun, *Chem. Commun.*, **2009**, 2020–2022.
- [2] Y. X. Li, G. Chen, Q. Wang, X. Wang, A. K. Zhou, Z. Y. Shen, *Adv. Funct. Mater.*, **2010**, 20, 3390–3398.
- [3] J. X. Low, J. G. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [4] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [5] X. B. Chen, S. H. Shen, L. J. Guo, S. Mao, *Chem. Rev.*, **2010**, 110, 6503–6570.
- [6] T. T. Wu, X. D. Kang, M. W. Kadi, I. Ismail, G. Liu, H. M. Cheng, *Chin. J. Catal.*, **2015**, 36, 2103–2108.
- [7] H. N. Cui, J. Y. Shi, H. Liu, *Chin. J. Catal.*, **2015**, 36, 969–974.
- [8] Y. J. Cui, Y. X. Wang, H. Wang, F. Cao, F. Y. Chen, *Chin. J. Catal.*, **2016**, 37, 1899–1906.
- [9] J. Z. Chen, X. J. Wu, L. S. Yin, B. Li, X. Hong, Z. X. Fan, B. Chen, C. Xue, H. Zhang, *Angew. Chem. Int. Ed.*, **2015**, 127, 1226–1230.
- [10] J. Li, L. J. Cai, J. Shang, Y. Yu, L. Zhang, *Adv. Mater.*, **2016**, 28, 4059–4064.
- [11] S. Ida, A. Takashiba, S. Koga, H. Hagiwara, T. Ishihara, *J. Am. Chem.*

Graphical Abstract

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Synthesis and photocatalytic hydrogen production activity of the $\text{Ni-CH}_3\text{CH}_2\text{NH}_2/\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ hybrid layered perovskite

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The photocatalytic hydrogen production activity of $\text{H}_{1.78}\text{Sr}_{0.78}\text{Bi}_{0.22}\text{Nb}_2\text{O}_7$ nanosheets is greatly enhanced by inserting nickel(II) ions in the interlayer space, and is comparable to that of the platinum-loaded sample.

- Soc.*, **2014**, 136, 1872–1878.
- [12] X. X. Xu, T. T. Lu, X. X. Liu, X. L. Wang, *Chem. Eur. J.*, **2015**, 21, 14638–14647.
- [13] M. Y. Xing, B. C. Qiu, M. M. Du, Q. H. Zhu, L. Z. Wang, J. L. Zhang, *Adv. Funct. Mater.*, **2017**, 27, 1702624.
- [14] J. K. Zhang, Z. B. Yu, Z. Gao, H. B. Ge, S. C. Zhao, C. Q. Chen, S. Chen, X. L. Tong, M. H. Wang, Z. F. Zheng, Y. Qin, *Angew. Chem. Int. Ed.*, **2016**, 128, 1–6.
- [15] D. Y. Fan, R. F. Chong, F. T. Fan, X. L. Wang, C. Li, Z. C. Feng, *Chin. J. Catal.*, **2016**, 37, 1257–1262.
- [16] Y. X. Li, G. Chen, H. J. Zhang, Z. H. Li, J. X. Sun, *J. Solid State Chem.*, **2008**, 181, 2653–2659.
- [17] Y. X. Li, G. Chen, H. J. Zhang, Z. S. Lv, *Int. J. Hydrogen Energy*, **2010**, 35, 2652–2656.
- [18] H. Q. He, J. Yin, Y. X. Li, Y. Zhang, H. S. Qiu, J. B. Xu, T. Xu, C. Y. Wang, *Appl. Catal. B*, **2014**, 156–157, 35–43.
- [19] Y. X. Li, G. Chen, C. Zhou, Z. H. Li, *Catal. Lett.*, **2008**, 123, 80–83.
- [20] B. Zhang, Y. X. Li, J. M. Luo, H. Zhao, J. Zhao, G. H. Dong, Y. Q. Zhu, C. Y. Wang, *Appl. Surf. Sci.*, **2017**, 391, 499–506.
- [21] Y. Eina, N. Sakai, T. Nagasaki, *J. Phys. Chem. B*, **2005**, 109, 17212–17216.
- [22] T. Oshima, D. Lu, O. Ishitani, K. Maeda, *Angew. Chem. Int. Ed.*, **2015**, 54, 1–6.
- [23] H. L. Gao, S. C. Yan, J. J. Wang, Y. A. Huang, P. Wang, Z. S. Li, Z. G. Zou, *Phys. Chem. Chem. Phys.*, **2013**, 15, 18077–18084.
- [24] J. H. Wu, Y. H. Cheng, J. M. Lin, Y. F. Huang, M. L. Huang, S. C. Hao, *J. Phys. Chem. C*, **2007**, 111, 3624–3628.
- [25] J. S. Jang, S. H. Choi, D. H. Kim, J. W. Jang, K. S. Lee, J. S. Lee, *J. Phys. Chem. C*, **2009**, 113, 8990–8996.
- [26] B. Fan, Z. L. Chen, Q. Liu, Z. G. Zhang, X. M. Fang, *Appl. Surf. Sci.*, **2016**, 370, 252–259.
- [27] G. G. Zhang, G. S. Li, X. C. Wang, *ChemCatChem*, **2015**, 7, 2864–2870.
- [28] X. P. Chen, W. Chen, P. B. Lin, Y. Yang, H. Y. Gao, J. Yuan, W. F. Shangguan, *Catal. Commun.*, **2013**, 36, 104–108.
- [29] J. D. Hong, Y. S. Wang, Y. B. Wang, W. Zhang, R. Xu, *ChemSusChem*, **2013**, 6, 2263–2268.
- [30] F. Chen, H. Yang, X. F. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.
- [31] J. R. Ran, J. Zhang, J. G. Yu, S. Z. Qiao, *ChemSusChem*, **2014**, 7, 3426–3434.
- [32] P. Wang, Y. G. Lu, X. F. Wang, H. G. Yu, *Appl. Surf. Sci.*, **2017**, 391, 259–266.
- [33] J. G. Yu, S. H. Wang, B. Cheng, Z. Lin, F. Huang, *Catal. Sci. Technol.*, **2013**, 3, 1782–1789.
- [34] K. L. He, J. Xie, X. Y. Luo, J. Q. Wen, S. Ma, X. Li, Y. P. Fang, X. C. Zhang, *Chin. J. Catal.*, **2017**, 38, 240–252.
- [35] Y. An, Y. Y. Liu, P. F. An, J. C. Dong, B. Y. Xu, Y. Dai, X. Y. Qin, X. Y. Zhang, M.-H. Whangbo, B. B. Huang, *Angew. Chem. Int. Ed.*, **2017**, 129, 1–6.
- [36] Y. Xua, R. Xu, *Appl. Surf. Sci.*, **2015**, 351, 779–793.
- [37] J. F. Dong, M. Wang, X. Q. Li, L. Chen, Y. He, L. C. Sun, *ChemSusChem*, **2012**, 5, 2133–2138.
- [38] Y. X. Li, L. Zang, Y. Li, Y. Liu, C. Y. Liu, Y. Zhang, H. Q. He, C. Y. Wang, *Chem. Mater.*, **2013**, 25, 2045–2050.
- [39] Y. X. Li, B. R. Bunes, L. Zang, J. Zhao, Y. Li, Y. Q. Zhu, C. Y. Wang, *ACS Nano*, **2016**, 10, 2386–2391.
- [40] Y. X. Li, L. Zang, D. L. Jacobs, J. Zhao, X. Yue, C. Y. Wang, *Nat. Commun.*, **2017**, 8, 14462.
- [41] J. L. Gunjekar, T. W. Kim, H. N. Kim, I. Y. Kim, S. J. Hwang, *J. Am. Chem. Soc.*, **2011**, 133, 14998–15007.
- [42] L. Li, R. Z. Ma, Y. Ebina, K. Fukuda, K. Takada, T. Sasaki, *J. Am. Chem. Soc.*, **2007**, 129, 8000–8007.
- [43] Y. Bai, H. N. Chen, S. Xiao, Q. F. Xue, T. Zhang, Z. L. Zhu, Q. Li, C. Hu, Y. Yang, Z. C. Hu, F. Huang, K. S. Wong, H. L. Yip, S. H. Yang, *Adv. Funct. Mater.*, **2016**, 26, 2950–2958.
- [44] J. Matienzo, L. I. Yin, S. O. Grim, W. E. Swartz Jr., *Inorg. Chem.*, **1973**, 12, 2762–2769.

- [45] J. W. Jang, C. E. Lee, S. C. Lyu, T. J. Lee, C. J. Lee, *Appl. Phys. Lett.*, **2004**, 84, 2877–2879.
- [46] M. Zhukovskiy, P. Tongying, H. Yashan, Y. X. Wang, M. Kuno, *ACS Catal.*, **2015**, 5, 6615–6623.
- [47] C. T. Dinh, M. H. Pham, F. Kleitz, T. O. Do, *J. Mater. Chem. A*, **2013**, 1, 13308.
- [48] S. T. Oyama, X. Q. Wang, R. Radhakrishnan, *Stud. Surf. Sci. Catal.*, **2002**, 145, 347–350.
- [49] Z. J. Han, W. R. McNamara, M.-S. Eum, P. L. Holland, R. Eisenberg, *Angew. Chem. Int. Ed.*, **2012**, 51, 1667–1670.
- [50] S. Cao, C. J. Wang, X. J. Lv, Y. Chen, W. F. Fu, *Appl. Catal. B*, **2015**, 162, 381–391.
- [51] W. C. Lin, W. D. Yang, I. L. Huang, T. S. Wu, Z. J. Chung, *Energy Fuels*, **2009**, 23, 2192–2196.
- [52] Y. Y. Xie, J. Wang, M. Z. Wang, X. W. Ge, *J. Hazard. Mater.*, **2015**, 297, 66–73.
- [53] K. Chang, Z. W. Mei, T. Wang, Q. Kang, S. X. Ouyang, J. H. Ye, *ACS Nano*, **2014**, 8, 7078–7087.
- [54] Y. H. Hu, *Angew. Chem. Int. Ed.*, **2012**, 51, 12410–12412.

Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇复合层状钙钛矿的合成及光催化分解水产氢性能

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摘要: 自从分解水产氢被首次报道以来, 许多光催化剂被开发出来并用于光催化分解水产氢。然而, 由于光生电子和空穴的复合率普遍较高, 大部分的光催化剂分解水产氢效率都很低。因此, 开发新型高效的光催化材料至关重要。具有(Bi₂O₂)²⁺(A_{m-1}M_mO_{3m+1})²⁻通式的Aurivillius相层状钙钛矿材料因具有独特的层状结构、元素可调性以及优异的电荷传输和分离能力而广泛应用于光催化分解水和去除有机污染物。此外, 当该类层状钙钛矿被剥离成超薄纳米片时, 其光催化性能进一步提高。

为了进一步提高层状钙钛矿的载流子分离能力, 将客体(如贵金属, 半导体等)通过化学反应的途径插入到层状钙钛矿的层间区域, 从而合成出复合层状钙钛矿被广泛发展和应用。然而, 引入的客体主要是贵金属和半导体, 这类客体的高成本和不均匀分布制约了其进一步的应用。由于廉价、无毒和稳定等优点, 镍基材料如Ni, NiO, Ni₂O₃, NiS, NiS₂, Ni(OH)₂和Ni(OH)_x等被广泛用作增强电极材料的光电性能和催化剂的光催化分解水产氢性能的助催化剂。

本文采用简单的原位化学反应法制备出镍基配合物Ni-CH₃CH₂NH₂ (Ni-EA)插层的Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇ (Ni-EA/HSN Ns)复合层状钙钛矿; 然后采用X-射线衍射(XRD)、傅立叶变换红外光谱(FTIR)、X-射线光电子能谱(XPS)、紫外-可见漫反射光谱等手段对Ni-EA/HSN Ns光催化剂进行了系统的研究。XRD结果表明, 引入Ni²⁺后, HSN Ns层间距减小并且平行于钙钛矿层的晶面结晶度增强, 证明HSN Ns沿垂直于钙钛矿层的方向出现了层层组装。FTIR和XPS结果表明, 引入的Ni²⁺与HSN Ns层间和表面的乙胺分子之间存在较强的相互作用, 结合高分辨透射电镜图可知, Ni的存在形态可能为配合物Ni-EA。由此可见, 当向HSN Ns中引入Ni²⁺时, Ni²⁺和HSN Ns层间和表面的乙胺分子反应生成带正电的配合物Ni-EA, 由于Ni-EA与HSN Ns的钙钛矿层带有异种电荷, 两者之间存在较强的静电相互作用力, 从而引起钙钛矿纳米片HSN Ns的层层组装, 最后形成Ni-EA/HSN Ns复合层状钙钛矿。光催化分解水产氢性能测试结果表明, 当引入0.5 wt% Ni时, 复合层状钙钛矿表现出最优的光催化性能。与HSN Ns(241.58 μmol/h)相比, 0.5% Ni-EA/HSN Ns的光催化分解水产氢速率(372.67 μmol/h)提高了0.54倍, 表现出与0.5% Pt/HSN Ns可比拟的光催化活性, 可见, 非贵金属Ni具有替代贵金属Pt的能力。进一步的研究表明, 镍基配合物Ni-EA显著增强了催化剂的光生载流子的传输和分离能力, 从而提高了其光催化分解水产氢性能。该文为光催化分解水产氢提供了一种简便的合成非贵金属配合物助催化剂的方法。

关键词: Ni-CH₃CH₂NH₂/H_{1.78}Sr_{0.78}Bi_{0.22}Nb₂O₇; 插层; 光催化; 产氢; 纳米片

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