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Ni(OH)₂-Modified SrTiO₃ for Enhanced Photocatalytic Hydrogen Evolution Reaction

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Abstract:

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Strontium titanate (SrTiO₃) is a promising photocatalyst because of its high chemical stability and excellent photocatalytic activity. However, the requirement of near-ultraviolet (UV) irradiation for effective photocatalysis limits its practical application. In this work, we prepared a novel Ni(OH)₂-modified SrTiO₃ composite by a simple precipitation method and confirmed that the Ni(OH)₂ nanoparticles were successfully deposited on the SrTiO₃ surface rather than incorporated into the lattice. The optimal Ni(OH)₂ loading amount for high H₂ evolution was found to be 20%, giving a activation rate is up to 1.46 mmol h⁻¹ g⁻¹, which is ca. 15 times higher than that of the pure SrTiO₃. This significantly enhancement of activity could be ascribed to the lower recombination of electrons and holes in the presence of Ni(OH)₂, which was confirmed by Photo-luminescence spectroscopy (PL) and photo-current response property. The present finding could shed light on the design of efficient perovskite-type oxides based photocatalysts.

Key words: SrTiO₃; Ni(OH)₂; photocatalytic hydrogen production.

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1. Introduction

Photocatalytic hydrogen production is extremely important in exploring renewable energy conversion, storage technologies and solving environmental pollution problems¹⁻⁸. Modern photo-electrochemistry is traced back to 1972 which discovered by Fujishima and Honda⁹ that water splitting on TiO₂ electrode. Strontium titanate (SrTiO₃) has been proved to be catalytically active in photo-induced water splitting reactions¹³⁻¹⁶. However, the use of SrTiO₃ in the photocatalysis is limited by its wide band gap (3.2 eV)^{17, 18}, which results in less than 5% of sunlight absorption and requires UV photoexcitation. Moreover, the high recombination rate of electrons and holes^{19, 20} severely limits its practical application. Many studies have been dedicated to improve their photocatalytic performances by controlling their morphology²¹⁻²³, doping metals²⁴⁻²⁶ or non-metals²⁷, compounding other semiconductor materials^{28, 29}, intrinsically activation³⁰, and fabricating coordinated oxygen vacancies³¹.

Turing to the co-catalysts, some transition-metal oxides, sulfides, and hydroxides like CuO³²⁻³⁶, NiO³⁷⁻⁴², MoS²⁴³⁻⁴⁶, Ni(OH)⁴⁷⁻⁵¹ work well as co-catalysts to improve the photocatalytic hydrogen evolution reaction. Among them, Ni(OH)² has attracted much attention due to the high efficiency, low cost, and easy to synthesis. For example, Ran *et al.*⁵² synthesized CdS nanorods which modified with Ni(OH)² by a simple precipitation method, and induced an astonished influence on the H² production. Yu *et al.*⁵³ reported Ni(OH)²-modified TiO₂, which has a H²-production rate of 3056 µmol h⁻¹ g⁻¹ under UV light irradiation with the loading amount of 23%. Wang *et al.*⁵⁴ reported Ni(OH)²-modified g-C₃N₄ nano-composites, giving a H²-production rate of 7.6 mmol h⁻¹ g⁻¹. This activity is close to the optimal efficiency of 1.0 wt% Pt/g-C₃N₄, showing us the high potential of Ni(OH)² as an effective co-catalyst. For nickel compounds-modified SrTiO₃, Domen *et al.*⁵⁵ firstly reported the photocatalytic water splitting by NiO-SrTiO₃ catalyst, but the efficiency is low. All in all, these investigations provide evidence that the Ni(OH)² is an economical and efficient co-catalyst for hydrogen production from water splitting.

Herein we prepared Ni(OH)₂/SrTiO₃ composites for photocatalytic hydrogen/DON300771D evolution in aqueous methanol solution. Photo-luminescence spectroscopy (PL) and photo-current response property presented that the combination of Ni(OH)₂ with SrTiO₃ has effectively reduced the electrons and holes recombination, which contribute to the high performances. When the optimal Ni(OH)₂ loading amount was 20%, the hydrogen production of the composite catalysts showed the highest activity.

2. Experimental Section

2.1 Synthesis of the Photocatalysts

All the chemicals used in this study are analytical grade without any further purification. Ni(OH)₂/SrTiO₃ photocatalysts were prepared by a simple precipitation method. Typically, 0.507g of SrTiO₃ powders (Tansoole Co. Ltd, Shanghai, China) were dispersed in 50 mL, 0.25 M NaOH aqueous solution. After 30 min of ultrasound, a certain volume of 0.05 M Ni(NO₃)₂ was added under rapid stirring. Then stirred the mixed solution at room temperature for 4 h. The precipitates were collected by centrifugation and washed with deionized water/ethanol for 6 times. Finally, the precipitates were dried at 60 °C overnight. Here, the nominal molar ratios of Ni(OH)₂ to SrTiO₃ were R = 0, 0.5, 5, 10, 20, 25 and 100 mol%, denoted as N0, N0.5, N5, N10, N20 and N25 respectively. Meanwhile, Pure Ni(OH)₂ sample was prepared under the same experimental conditions for comparison, which were labeled as N100. The actual chemical compositions of the prepared samples were measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Jena PQ9000) (Table S1).

2.2 Characterization

XRD patterns were recorded on a Bruker D8 advance X-ray diffractometer that used Cu-K α under 40 kV and 40 mA. DRS were measured in the range of 200–800 nm by a UV–vis spectrometer (UV-2600, Shimadzu, Japan) with the reference of BaSO₄. The PL (Photo-Luminescence) spectra were measured on Hitachi F-7000

fluorescence spectrophotometer, whose excitation wavelength is 325 nm. XPS Spectra/DONJ00771D

surveys were obtained on ESCALAB 250Xi system. TEM images (Transmission Electron Microscopy) and HRTEM images (High-Resolution Transmission Electron Microscopy) were performed on a JEOL JEM-2010F microscope operating at the voltage of 200 kV. The BET (Brunauer-Emmett-Teller) surface areas (S_{BET}) of the samples were achieved by a nitrogen adsorption (Micromeritics Tristar 3000 analyzer

2.3 Photocatalytic reactions

Photocatalytic H_2 evolution reactions were conducted in a Pyrex-top irradiation-type reaction vessel connected to a closed circulation system at room temperature. In a reaction vessel, 25 mg of the photocatalyst was dispersed in 40 mL (25%) methanol aqueous solution as sacrificial agent. Later this system was sealed and evacuated by a vacuum pump for 30 minutes. A 300 W xenon lamp was used as the light source. The outlet gas was analyzed online by gas chromatography (GC-7900 with a thermal conductivity detector and an nitrogen carrier gas, Shimadzu).

3. Results and discussions

3.1. Phase Structures and Morphology.

XRD patterns of the composite photocatalysts are shown in Fig. 1. Only SrTiO₃ phases were observed, both for pure SrTiO₃ (N0) and various Ni(OH)₂/SrTiO₃ composite photocatalysts (N0.5, N5, N10, N20, and N25). No Ni(OH)₂ peaks were observed, due to the low loading amount and poor crystallinity. Furthermore, there is no peak shift in the XRD patterns. This suggests that the deposited Ni(OH)₂ do not incorporate into the lattice of SrTiO₃. We further compared the XRD pattern of our synthesized Ni(OH)₂ with the standard card (Ni(OH)₂ JCPDS No. 14-0117), further demonstrating the successful synthesis of Ni(OH)₂ (Fig. S1).

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The morphology and microstructure of the composite compounds (N20 sample) were further identified by TEM. As shown in Fig. 2(a), the Ni(OH)₂ nanoparticles with ca. 10 nm were deposited on the surface of SrTiO₃. High-resolution TEM (HRTEM) image reveals the detailed information of N20. Fig. 2(b) exhibits fringes with a lattice spacing of 0.27 and 0.23 nm, which corresponding to the (110) plane of SrTiO₃ and (101) plane of Ni(OH)₂^{56, 57}. When the lattice spacing is 0.27 nm, two different crystal orientations can be observed, which is due to the stacked SrTiO₃⁵⁸.



Fig. 2. TEM (a), HRTEM images (b) of the N20 sample.

3.2 Light Absorption Properties

The optical properties were investigated by UV-vis diffuse reflectance (DRS) (Fig. 3). It shown that the pristine $SrTiO_3$ exhibited an absorption edge at ~390 nm, which agrees with the band gap edge absorption of $SrTiO_3$ (3.2 eV). The composite photocatalysts shown absorption peaks in the range of 600–800 nm, which can be assigned to the d–d transition of Ni (II)⁵². In comparison to the pure $SrTiO_3$ (N0), no obvious changes in the absorption edge of the Ni(OH)₂/SrTiO₃ samples were observed. In order to further understand the mechanism, we compared the UV-vis diffuse reflectance spectra of N20 and N20* (after 3 hours of hydrogen production,

see Fig. S2). It can be seen that the N20* sample exhibits an obviously enhanced/DONJ00771D absorption in the 400–800 nm region, which can be ascribed to the formation of metallic Ni during HER⁵³.



Fig. 3. UV-vis diffuse reflectance spectra of the pristine SrTiO₃ and various Ni(OH)₂/SrTiO₃ samples.

Fig. 4 presents a comparison of PL spectra of N0–N25 in the wavelength of 350– 550 nm. PL emission peak around 410 nm is attributed from the photo-recombination of photo-generated charge carriers that from the VB (Valence Band) to the CB (Conduction Band). A fluorescence decrease (or quenching) is observed in the presence of Ni(OH)₂, indicating the Ni(OH)₂ nanoparticles lowering the recombination rate of electrons and holes under a UV irradiation. This could contributed to the presence of Ni(OH)₂ nanoparticles, that the excited electrons of SrTiO₃ can migrate more easier to the CB of Ni(OH)₂, which further prevents the direct recombination of electrons and holes.

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Fig. 4. Comparison of the PL spectra for various composite photo-catalysts.

Transient photo-current response experiments of N0 and N20 were measured to further confirm this proposed mechanism. As shown in Fig. 5(a), it shown that the photoelectric current density of N20 (~0.8 mA cm⁻²) is four times higher than that of N0 (~0.2 mA cm⁻²), implied that the charge separation in N20 was enhanced remarkably by reducing the recombination rate of electrons and holes. This is consistent with PL results.

Electrochemical impedance spectroscopy (EIS) curves of N0 and N20 were characterized. As shown in Fig. 5(b), with the modification of Ni(OH)₂ nanoparticles, the diameters of the semicircles in the plots decreased obviously. It is known that the smaller size of the arc in an EIS Nyquist plot means the smaller charge-transfer resistance on the electrode surface. Hence, the conduction of the photointroduced charges were enhanced in the presence of Ni(OH)₂ nanoparticles. The EIS results are in good agreement with the PL spectra. Therefore, the modification of Ni(OH)₂ could greatly improve the charge transportation of SrTiO₃, and enhance the photocatalytic activity.



Fig. 5. (a) Transient photocurrent responses of the samples N0 and N20; (b) Nyquist impedance plots N0 and N20; (c) Nitrogen adsorption-desorption isotherms of samples prepared at R = 0, 20; (d) the corresponding pore-size distribution curves of samples prepared at R = 0, 20 respectively.

3.3. BET Surface Areas and Pore Size Distributions.

We have also compared the BET results of various composite photocatalysts. Generally, a catalyst with high specific surface area and big pore volume is indispensable to the enhancement of catalytic performance. Fig. 5(c) and (d) show the nitrogen adsorption/desorption isotherms and the corresponding pore-size distribution curves of N0 and N20 (the relevant BET data of other samples can be seen in Fig. S3). It can be seen that the BET result of N20 is much larger both in the aperture and the surface area compared with that of N0. The surface area after Ni(OH)₂ modification was 14 times larger than the unmodified sample. This increases the contact area of the catalyst, which is an advantageous for accelerating the reaction rate and improving the photocatalytic efficiency of the catalyst. When the loading amounts of Ni(OH)₂ increased to 25%, the decrease in the H₂-production activity was

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observed. This is maybe due to the accumulation of Ni(OH)₂ particles $0^{\text{Wew Article Online}}$ resulting in the decreases of active sites *on the surface of SrTiO*₃.^{54,59}

3.4. Photocatalytic Performance

The H₂-production from aqueous methanol solution under UV–vis irradiations was applied to evaluate the photo-catalytic performance of Ni(OH)₂/SrTiO₃ samples. Fig. 6(a) shown the H₂-production of various photocatalysts. The hydrogen production activity of the Ni(OH)₂-modified SrTiO₃ increases with the Ni(OH)₂ amount increase from 0.5 to 20 mol% and then decrease. When we look at 0.5 % Ni(OH)₂ loading sample, the activity was enhanced for ca. 6.5 times compared to the pure SrTiO₃, indicating the strong improvement effect of co-catalysts on SrTiO₃. Among all the samples, the optimal Ni(OH)₂ loading amount was found to be 20 mol%, the H₂-production rate is up to 1.46 mmol h⁻¹ g⁻¹ under UV–visible light irradiations, nearly 15 times higher than that of the pure SrTiO₃.



Fig. 6. (a) The efficiencies of hydrogen evolution over SrTiO₃ with different Ni(OH)₂ precipitation; (b) Hydrogen production cycle experiment of N20.

We have also concluded other works that on the basis of various SrTiO₃-based photocatalysts from the literature, as shown in Table S2. Among these works, the 20% Ni(OH)₂/SrTiO₃ in our work exhibits an extraordinarily high H₂-production activity compared to the exist SrTiO₃-based photocatalysts. Although they have different photo-catalytic reaction conditions, different light source and intensities (etc.), the H₂-production efficiency in term of specific H₂-production rate can be employed for

such comparison purpose. In order to determine the stability of the catalyst.¹⁰W@/DONJ00771D conducted a hydrogen production cycle experiment on N20. As shown in Fig. 6(b), the H₂-production result was quite similar, indicating the good stability of N20 after 4 cycles.



Fig. 7. High-resolution XPS spectra of Ni 2p of the samples (a) N20, (b) N20 after 3h photocatalytic hydrogen production from methanol aqueous solution under UV-LED irradiation.

The photocatalytic activity of SrTiO₃ have been enhanced significantly in the presence of Ni(OH)₂ nanoparticles. This is due to the Ni(OH)₂ obviously reduces the recombination of electrons and holes in the SrTiO₃. This recombination process is quite related to the state of nickel on the SrTiO₃. We hence need to identify the chemical status of nickel by XPS, the results are shown in Fig. 7. The as-prepared N20, the binding energies of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ are located at 855.9 and 873.3 eV, respectively. The Ni $2p_{3/2}$ peak at 855.9 eV indicates that the deposited nickel compound on the surface of SrTiO₃ nanorods was mainly Ni(OH)₂. However, after 3 hours photocatalytic reaction, we observed the binding energy of Ni $2p_{3/2}$ shifted to 855.5 eV. This suggests the formation of a small amount of NiO after/during the

photocatalytic reactions^{53, 54}. One possibility is that the photoinduced electrons in the photoinduced electrons is the photoinduced electron and the photoinduced electrons in the photoinduced electrons is the photoinduced electron and the phot conduction band (CB) of SrTiO₃ transfer to Ni(OH)₂ nanoparticles and partially reduce Ni²⁺ of Ni(OH)₂ to Ni⁰. Then the metallic Ni can be partially oxidized in air.

On the basis of XPS results and the band position of SrTiO₃ and Ni(OH)₂, the photocatalytic mechanisms are proposed and shown in Fig. 8. Without Ni(OH)₂, the pure SrTiO₃ shown a low H₂-production activity even the conduction band of SrTiO₃ is more negative than the reduction potential of H_2 . In the presence of Ni(OH)₂, the H₂-production activity of SrTiO₃ was improved a lot. This can be explained that the potential of $Ni^{2+}/Ni - 0.23 V^{52}$ (vs. SHE, pH = 0) is lower than the reduction potential of perovskite SrTiO₃ (CB level is about -0.76V). Therefore, the CB electrons of SrTiO₃ can be transfer to Ni(OH)₂, thus partially reduce Ni²⁺ to Ni⁰, this was confirmed by XPS results. The proton then transfer to the metallic Ni⁰ site to accept electrons come from SrTiO₃ and form hydrogen.



Fig. 8. Proposed mechanism graph of the Ni(OH)₂/SrTiO₃ composites as the photo-catalyst.

4. Conclusions

In summary, a facile precipitation method has been introduced to synthesis SrTiO₃ samples with different Ni(OH)₂ concentrations on their surfaces for

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgements

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