Novel NiS cocatalyst decorating ultrathin 2D TiO₂ nanosheets with enhanced photocatalytic hydrogen evolution activity

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Abstract

In this paper, ultrathin 2D TiO₂ nanosheets which modified with ultrafine dispersions of NiS cocatalyst were successfully prepared via a low-cost and in-situ synthesis approach. The physical and chemical properties of the as-obtained NiS/TiO₂ nanosheets samples were investigated by a variety of analytical techniques. Cooperated with the photocatalytic hydrogen evolution tests and surface photovoltage spectroscopy (SPV) experiments, it can be deduced that the NiS is an efficient cocatalyst, which significantly limited the recombination of photogenerated electron-hole pairs in ultrathin 2D TiO₂ nanosheets and consequently improve the hydrogen evolution activity. The influence of different molar ratios of NiS on the photocatalytic activity was explored and the 5 mol% NiS/TiO₂ composite photocatalyst showed the highest photoactivity which the corresponding H₂-production rate was 313.6 μmol h⁻¹ g⁻¹ under the UV-vis light irradiation. The optimal H₂ evolution rate is 36 times as much as the value of pure TiO₂ nanosheets. The photocatalytic mechanism of NiS cocatalysts on the enhanced performance of the photocatalytic activity of TiO₂ nanosheets is proposed and confirmed by SPV results.

Keywords: NiS cocatalyst; TiO₂ nanosheets; Hydrogen evolution; Surface photovoltage spectroscopy.

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1. Introduction

As is known to all, solar energy is a kind of free and inexhaustible energy. So, photocatalytic hydrogen production by using semiconductor photocatalysts and solar energy is a green and environment friendly solution to address the current global energy and environmental issues. However, a few of photocatalysts have been applied for photocatalytic hydrogen production from water splitting, including g-C₃N₄ [1-4], TiO₂ [5-7], ZnO [8-10], CdS [11-13], F-Co₃O₄ [14] et al. In the past few decades, TiO₂ has been investigated and applied extensively because of its advantages, such as nontoxicity, chemical stability. However, its large band gap (3.2 eV) limits its practical application due to the high recombination rate photo-excited charge carriers and low light response range. Up to now, a significant amount of study has been carried out to improve the photocatalytic activity of TiO₂, for example, CdS [15-16], g-C₃N₄ [17], BiVO₄ [18], RGO [19], Cu(OH)₂ [20], FeOOH [21] and Ni(OH)₂ [22].

Besides, noble metal deposition (Pt, Au, PtAu, Cu, AuPd, Ag) [23-31] is also mentioned. In our previous work, AuPd/TiO₂ nanosheets photocatalyst was prepared and showed highly photocatalytic H₂ evolution activity [30]. It is urgent to explore economic cocatalysts to promote photocatalytic activity and practical applications for these noble metals are rare and high cost. So far, some cheap cocatalysts (Cu [28], NiO [32], Ni [33], NiS [34], et al) have been studied to enhance the photoactivity of TiO₂. As we know, NiS, which is low cost and high cocatalyst activity, has been selected to be cocatalyst for photocatalytic hydrogen evolution from water extensively although the pure NiS has no photocatalytic hydrogen production activity [34-38]. In addition, there is still limited report on this subject.

In this work, due to the higher specific surface area and the more reaction sites of TiO₂ nanosheets, we report the synthesis of ultrathin 2D TiO₂ nanosheets decorated by low cost cocatalyst NiS via in-situ solvothermal synthesis approach. The as-obtained NiS/TiO₂ nanosheets can be used directly for

efficient photocatalytic hydrogen evolution and the photocatalytic activity can be significantly improved by introducing NiS cocatalysts. The effects of NiS cocatalysts on the light absorption, electron-hole separation and hydrogen evolution activity were discussed in detail. For the first time, SPV is applied to explore the photocatalytic mechanism of NiS cocatalysts on the improvement of the hydrogen evolution activity of TiO₂ nanosheets. This work shows that low cost NiS is a promising substitute for noble metals (such as Pt, Au) in the photocatalytic H₂-production for application in solar energy utilization and conversion.

2. Experimental

2.1. Materials

Nickel nitrate (Ni(NO₃)₂·6H₂O), thiourea, ethylene glycol (EG), titanium isopropoxide (TTIP, Aladdin, 95%), concentrated HCl solution (37%), ethyl alcohol (EtOH, A.R.), polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO20-PPO70-PEO20, Pluronic P123) were used as received without further treatment. Distilled water was used in all the experiments.

2.2. Synthesis of the photocatalysts

In this paper, a literature method with a slight modification was used to prepare the ultrathin 2D TiO₂ nanosheets sample [39]. 3.15 g TTIP was dissolved in 2.22 g concentrated HCl (labeled as solution A) and kept stirring. Briefly, solution B was prepared by adding 0.6 g Pluronic P123 into 9.0 g ethanol. After stirring for 20 min, the solution B was added slowly to the solution A under stirring. Then, 40 ml EG and 5 ml the above mixed solution were transferred into a 100 ml Teflon-inner-liner stainless steel autoclave. The autoclave was heated at 150 °C for 40 h. After the process of solvothermal treatment, the produced solid materials were filtered and washed several times by ethanol and distilled water. Finally, the white powders were dried at 80 °C for 12 h and collected for further study.

The method for NiS/TiO₂ nanosheets composite photocatalysts is shown as follows: 0.3 g ultrathin

2D TiO₂ nanosheets was put into a beaker with 70 mL glycol, and under sonication for 1h, then 0.0545 g Ni(NO₃)₂·6H₂O and 0.0286 g thiourea (Ni/Ti =5%, Ni/S=1:2, mole ratio) were dissolved into above solution with stirring at room temperature. The final mixed solution was transferred into a 100 mL Teflon-inner-liner stainless steel autoclave and then reacting at 180 °C for 12 h. After the reaction process, the final sample was washed by ethanol/water for several times, and then dried at 60 °C for 12 h in vacuum oven. Furthermore, the samples with different molar ratios of (Ni/Ti) were also synthesized under the same condition with fixed Ni/S mole ratio (1:2). The nominal mole ratios of Ni to Ti were 0%, 3%, 5%, 7%, 9% and 11 %, respectively. At the same time, the pure NiS sample was synthesized under the same condition without TiO₂ nanosheets.

2.3 Characterization

X-ray diffraction (XRD) test was performed on an X-ray diffraction (XRD; Bruker D8 Advance, X-ray diffractometer), which use Cu K α radiation at a scan rate of 4° min⁻¹ in the 2 θ range from 20° to 70°. The acceleration voltage was 40 KV and the applied current was 40 mA. A JEM-2100 electron microscope (JEOL, Japan) was applied to investigate transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), and the accelerating voltage was 200 kV. UV-Vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-4100 spectrophotometer, and the reflectance standard was BaSO₄. A PHI 5300 ESCA system was used to measure the X-ray photoelectron spectroscopy (XPS). The beam voltage was 3.0 eV, and the energy of Ar ion beam was 1.0 keV. The adventitious carbon at 284.8 eV was used to normalize the binding energies.

2.4. Evaluation of photocatalytic performance

The photocatalytic H₂ evolution tests were carried out in a 300 ml quartz reactor, which was connected to a low-temperature thermostat bath to keep it at 4 °C. The light source was a PLS-SXE 300

UV Xe lamp (UV-visible, $\lambda > 300$ nm), which was positioned at 10 cm away from the reactor to trigger the photocatalytic reaction. In the photocatalytic H_2 evolution test, there were 50 mg photocatalyst powder, 75 ml water and 25 ml sacrificial agent (methanol). During photocatalytic test, the reaction system should maintain vacuuming and anaerobic conditions. The gas chromatography (Beifen 3420 A, TCD, high purity Argon as a carrier gas and 5 Å molecular sieve column) equipped with a thermal conductivity detector was applied to analyze the products from the reaction system.

2.5. SPV measurements

The surface photovoltage (SPV) spectroscopy and corresponding phase spectra measurements were carried out based on a lock-in amplifier. The measurement system consists of a source of monochromatic light, a lock-in amplifier (SR830, Stanford research systems, inc.) with a light chopper (SR540, Stanford research systems, inc.) and a sample chamber. The monochromatic light is provided by passing light from a 500 W Xenon lamp (CHFXQ500 W, global Xenon lamp power) through a grating mono-chromator (Omni-5007, No.09010, Zolix), which chopped with a frequency of 23 Hz. SPV measurements were carried out at room temperature by scanning monochromatic light from 600 to 300 nm.

3. Results and discussion

3.1. Characterization of NiS/TiO₂ nanosheets samples

Fig.1 shows the XRD results of the NiS/TiO₂ nanosheets samples with different Ni/Ti molar ratio. All the composite samples show the diffraction peaks ($2\theta = 24.9^\circ, 48.4^\circ, 27.6^\circ$), which are corresponding to (101), (200) planes of anatase (JCPDS, No.71-1169) and (110) planes of rutile (JCPDS, No.88-1169), respectively. As presented in Fig.1(b-f), it can be clearly seen that there is no obvious phase change in ultrathin 2D TiO₂ nanosheets during the glycol solvothermal process, and some new peaks corresponding to NiS species can be clearly detected. The diffraction peaks, which are located at 30.1° ,

34.6°, 45.8°, 53.5°, are assigned to (110), (101), (102) and (110) facets of NiS phase (JCPDS, No.77-1624). The peak intensities of NiS increase gradually with the increasing NiS content in the composite sample.

The obtained TEM images of pure TiO₂ nanosheets are presented in Fig.2(a-c). From the TEM images Fig.2(a-b), it can be clearly observed that the TiO₂ nanosheets with rolled up edges were formed, and the size of TiO₂ nanosheets were about 200 nm. Based on the result of HRTEM image Fig.2c, the measured lattice spacing ultrathin 2D TiO₂ nanosheets is $d=0.351$ nm, which is assigned to (101) plane of anatase phase (JCPDS, No.71-1169). Fig.2(d-f) shows the TEM results of NiS/TiO₂ composite sample. Based on the result of Fig.2d, the introduced NiS is deposited on the surface of ultrathin 2D TiO₂ nanosheets and there is no obvious change in the microstructure of ultrathin 2D TiO₂ nanosheets. In Fig.2(e-f), the lattice fringes with spacing of $d=0.298$ nm and $d=0.26$ nm which calculated from the line profile can be indexed to the (100) and (101) planes of NiS phase (JCPDS, No.77-1624), respectively. The TEM results illustrate that the NiS decorating 2D TiO₂ nanosheets prepared via in-situ synthesis process show heterostructures with intimate interfaces. Fig.3(a) shows a TEM image of NiS/TiO₂ at low magnification. Fig.3(b-e) displays the elemental distribution maps (O, Ti, S and Ni respectively) determined by energy-filtered TEM technique through the nanostructure in Fig.3(a). It is found that O, Ti, S and Ni elements distribute almost uniformly in the surface of NiS/TiO₂, which further confirmed the NiS/TiO₂ composite photocatalysts was prepared successfully.

The UV-vis-diffuse reflection spectra of the NiS/TiO₂ nanosheets photocatalysts with different molar ratio of NiS, together with those of pure TiO₂ nanosheets and pure NiS, were studied and presented in Fig.4. The pure TiO₂ nanosheets show absorption around 387 nm, corresponding to the band gap of 3.2 eV for TiO₂. After introducing NiS species, the NiS/TiO₂ composite samples present similar absorption edge in the visible light region as comparison to pure TiO₂ nanosheets. The

absorption intensity of NiS/TiO₂ composite enhanced with increasing amount of NiS in visible light region from 400 to 550 nm, which is in good agreement with the color of the composite samples varying from white to gray. The absorption of NiS phase leads to such an additional broad band ($\lambda > 400$ nm), and then improving photocatalytic activity.

The presence of NiS on the surface of TiO₂ nanosheets is further investigated by XPS, and the existence of Ti, O, Ni, S elements is indicated in the XPS survey spectrum Fig.5(a). Besides, because of the banding energy is calibrated with C 1s in the XPS test process, the carbon peak is also observed. In order to identify the chemical states of different elements, the XPS spectra of O 1s, Ti 2p, S 2p and Ni 2p are conducted and presented in Fig.5(b-e). There are two O 1s peaks (530.6 eV and 531 eV) in Fig.5b, and the O 1s peaks are in accordance with the reference value for TiO₂ [15]. The Ti 2p_{3/2} peak at 458.5 eV and the Ti 2p_{1/2} peak at 464.5 eV [15, 40-41] are presented in Fig.5c, and the results indicate that binding energy of Ti 2p is about 1 eV lower than the corresponding stoichiometric bulk crystals [42]. As previous reports shown, the lower binding energy for surface atoms may be due to the electron gain (reduction) of Ti atoms from the surrounding oxygen atoms [43]. The S 2p_{1/2} peak at 161.5 eV, shown in Fig.5d, is in accordance with the reference value for NiS. The Ni 2p_{3/2} peak at 852.6 eV and the Ni 2p_{1/2} peak at 854.9 eV are depicted in Fig.5e, which correspond with that of NiS.

Therefore, from the results of XRD, TEM and XPS, it can be seen that the NiS clusters are successfully deposited on the surface of ultrathin 2D TiO₂ nanosheets with high dispersibility, and the intimate interfaces between NiS and TiO₂ are formed.

3.2. Photocatalytic H₂ evolution activity

Photocatalytic H₂ evolution activity of the various samples were evaluated under UV-visible light ($\lambda > 300$ nm) irradiation and methanol which served as sacrificial reagents, and the results are presented in Fig.6. The photocatalytic H₂ production rate is negligible when pure TiO₂ alone is used as

photocatalyst due to fast recombination of photo-generated electron-hole pairs, indicating that pure TiO_2 is not active for photocatalytic hydrogen production. At the same time, the pure NiS shows no photocatalytic H_2 evolution activity. All the NiS/ TiO_2 composite samples show the enhanced activity of photocatalytic H_2 -generation after introducing NiS cocatalyst. The higher photocatalytic activity of NiS/ TiO_2 sample may be attributed to the reason that the interfaces between NiS and TiO_2 can effectively inhibit recombination of photo-generated electron-hole pairs. The rate of H_2 evolution over NiS/ TiO_2 composite samples with different NiS contents are illustrated in Fig.7. After loading NiS on the ultrathin 2D TiO_2 nanosheets, the H_2 evolution activity is significantly improved. The photocatalytic H_2 -production of TiO_2 increases from 250.4 to 313.6 $\mu\text{mol h}^{-1} \text{g}^{-1}$ with increasing the NiS contents from 3 mol% to 5 mol%, and the maximum photocatalytic H_2 -production rate is observed when the NiS content is 5 mol%. However, a further increase of NiS content leads to a decrease of H_2 evolution activity. The phenomena may be attributed to the reason that high loading content of NiS leads to a decrease in the surface active sites of TiO_2 nanosheets or excess NiS covered on the surface of TiO_2 nanosheets may shield the incident light, thus preventing the generation of electrons from the inside of TiO_2 nanosheets. As the result, a suitable content of NiS is crucial to enhance the photocatalytic activity of NiS/ TiO_2 nanosheets. To further prove the high photocatalytic H_2 -production activity of NiS/ TiO_2 , which was prepared via the in-situ synthesis approach, the photocatalytic H_2 -production activity of the mechanical mixing NiS and TiO_2 nanosheets (the molar ratio in the mixture is the same as that of NiS/ TiO_2 -5%) was evaluated under the same condition. The result of Fig.8 presents that mechanical mixing NiS on TiO_2 nanosheets can slightly enhance the photocatalytic H_2 -production activity, but far less than that of NiS/ TiO_2 prepared via the in-situ synthesis approach.

Based on above results, the NiS is a cheap and effective cocatalyst for the application of TiO_2 in photocatalytic hydrogen evolution.

3.3. Photocatalytic mechanism discussion

Fig.9 presents the proposed photocatalytic H₂-production mechanism in the NiS/TiO₂ nanosheets composite sample. Electron-hole pairs are excited from ultrathin 2D TiO₂ nanosheets after absorbing photons under UV-visible light irradiation. It is well-known that the photo-generated electron-hole pairs in the pure TiO₂ tend to recombine rapidly without any cocatalyst. The results of TEM and HRTEM show that the intimate contact is formed between NiS and TiO₂ nanosheets, and then the photo-generated electrons in the conduction band of TiO₂ can be easily transferred to the surface of NiS, which can inhibit the recombination of electron-hole pairs. After trapping electrons by NiS, the intermediate HNiS was generated by absorption-reduction of an H⁺ at first, and then electrochemically releases H₂ with the reduction of another H⁺. Some previous work have proved the mechanism of forming such a hydride-NiS intermediate of NiS in many hydro-treating processes [34-35]. The photo-induced holes in the VB of TiO₂ can oxidize the sacrificial agent (methanol) to products, such as CO₂, H₂O et al. Therefore, the separated electrons will have longer time to reduce H⁺ to H₂ on the NiS surface, resulting in obvious improvement of H₂ production for the NiS/TiO₂ photocatalysts.

In order to certificate the above analysis, the SPV and corresponding phase spectroscopy of pure TiO₂ nanosheets, pure NiS and NiS/TiO₂ was measured to fully understand the behaviors of charge carriers, and the results were shown in Fig.10. From the results we can see that there are no SPV response from pure TiO₂ and pure NiS, which may be attributed to the low crystallinity and the rapid recombination of photo-excited electrons and holes in the semiconductors. After loading the NiS clusters on the TiO₂ nanosheets, the sample shows two obvious responses in the 370 nm to 500 nm region. It is well known that the band gap of TiO₂ is 3.2 eV, and the corresponding photo-excited wavelength is about 390 nm. Based on the above results, the band to band transitions of TiO₂ may be the reason for the SPV response ranging from 370 nm to 420 nm. And the other SPV response ranging

from 420 nm to 500 nm arises from sub-band transition, which probably is due to presence of Ti^{3+} in the TiO_2 nanosheets [44], as discussed in XPS.

It is well-known that the pure TiO_2 is n-type semiconductor, and the photo-excited electrons transfer from the conduction band of TiO_2 to the bulk, while the photo-excited holes transfer from the valence band of TiO_2 to the outer surface [45]. Fig.10(b) shows the corresponding phase spectroscopy of NiS/TiO_2 , and the phase angles in the both response region (370 nm ~ 500 nm) are in the range of -130° to -110° . Because the valence band of NiS is more positive than that of TiO_2 , and the conduction band of NiS is more negative than TiO_2 , the above phenomenon means that the photo-generated electrons transfer from the CB of TiO_2 to the acceptor states NiS [45], which is deposited on the surface of ultrathin 2D TiO_2 nanosheets with high dispersibility, while the TiO_2 bulk get the holes. The above results imply that the introduced NiS accelerate the separation of photo-generated electrons and holes in TiO_2 , and lead to obvious enhancement of H_2 production for the NiS/TiO_2 photocatalysts. Most importantly, the results of SPV and corresponding phase spectroscopy are consistent with the mechanisms described in Fig.9.

4. Conclusions

Novel NiS nanoparticles decorating ultrathin 2D TiO_2 nanosheets photocatalysts are successfully prepared with an in-situ solvothermal synthesis approach. The introduced NiS clusters did not affect the morphology and crystal structure of ultrathin 2D TiO_2 nanosheets. The composite photocatalysts exhibit enhanced photocatalytic activity and the optimal loading content of NiS is determined to be 5 mol% for TiO_2 nanosheets, and the corresponding H_2 -production rate is $313.6 \mu\text{mol h}^{-1}\text{g}^{-1}$ under UV-visible light irradiation. The NiS could increase the interfacial charge transfer and inhibit the recombination of electron-hole pairs in TiO_2 . The photocatalytic mechanism is proposed based on the experimental results, and the mechanism is supported by the results of SPV. Therefore, the low cost NiS clusters decorating

2D TiO₂ nanosheets is a promising cheap material which can be potentially used for new energy conversion field.

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Figure Captions:

Fig.1 XRD patterns of NiS/TiO₂ composite photocatalysts.

Fig.2 TEM images of ultrathin 2D TiO₂ nanosheets (a-c) and NiS/TiO₂ composite (d-f).

Fig.3 TEM image of NiS/TiO₂ at low magnification (a); elemental distribution mapping of (b) O, (c) Ti, (d) S and (e) Ni.

Fig.4 DRS spectra of the NiS/TiO₂ composite samples with different NiS contents.

Fig.5 XPS spectra of NiS/TiO₂ sample: (a) survey spectrum of Ni/TiO₂; (b) O 1s; (c) Ti 2p; (d) S 2p; (e) Ni 2p.

Fig.6 Photocatalytic H₂ evolution over NiS/TiO₂ composite samples with different NiS contents under UV-visible light: 0 mol% NiS, 3 mol% NiS, 5 mol% NiS, 7 mol% NiS, 9 mol% NiS, 11 mol% NiS, pure NiS.

Fig.7 Rate of H₂ evolution over NiS/TiO₂ composite samples with different NiS contents under UV-visible light: (a) 0 mol% NiS; (b) 3 mol% NiS; (c) 5 mol% NiS; (d) 7 mol% NiS; (e) 9 mol% NiS; (f) 11 mol% NiS, (g) pure NiS.

Fig.8 The comparison of H₂ evolution rate over different samples: (a) pure NiS; (b) 0 mol% NiS; (c) mechanical mixture (NiS/TiO₂=5 mol%); (d) 5 mol%NiS.

Fig.9 The schematic illustration of the proposed mechanism for charge transfer and H₂ evolution in NiS/TiO₂ composite under UV-visible light irradiation.

Fig.10 SPV spectra of pure TiO₂ nanosheets, pure NiS and NiS/TiO₂, and (b) corresponding phase spectra of NiS/TiO₂.

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Graphical Abstract