Co-catalyst MoS2-nanosheets/TiO2 nanotubes for the enhancement of photocatalytic hydrogen production

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Abstract: The MoS2 nanosheets/TiO2 nanotubes heterojunctions are designed for enhancing photocatalytic hydrogen production. The results of XRD, SEM and TEM imply that the heterojunctions are successfully prepared via electrostatic spinning technology and hydrothermal co-deposition method. Besides, the results of UV and PL display that the MoS2 nanosheets enhance the absorption of visible light, drive the transfer of photo-electro and promote the separation of photo-generated carries. Further, compared with the pure TiO2 nanotubes, the heterojunctions exhibit excellent photocatalytic hydrogen production enhancement of about ~340.739μmol/g.h, which is about 7 times of pure TiO2 nanotubes.

1. Introduction
Now, with the sharply increasing of energy demand, the traditional non-renew energy, such as fossil fuel, could no longer meet the requirement. Therefore, the exploration of new renew energy has drew lots of attentions from different fields [1]. Due to properties of renew, sustainable and clean, solar energy is regarded as an effective solution for energy shortage, especially the photocatalytic spilling water hydrogen production. Among these previous works, the TiO2, including rutile phase and anatase phase [2-4], has been researched for over 40 years as a typical photocatalytic material [5-6]. Especially the various of morphologies, such as nanoparticle, nanosheet or nanofibers, are regarded as the unique advantages for the photocatalytic performances, and prepared via different methods, such as hydrothermal method, electrospinning technology [7-9], etc. There, the researches demonstrate that different morphologies and preparations could influence the photocatalytic hydrogen production observably. There, the TiO2 nanotubes are prepared via the electrospinning technology for enhancing the specific surface area.

On the other hand, due to the well transmission of electron, stability and easy synthesis, the MoS2 is usually regarded as the co-catalyst in photocatalyst filed [10-11]. According to previous reports, the MoS2, including different physical dimensions of 0D, 1D, and 2D, are widely employed in photocatalytic production hydrogen [12-14].

In this work, we prepared the TiO2 nanotubes via electrospinning technique for increasing the specific surface area, and the 2D MoS2 co-catalyst via the hydrothermal co-deposition method for promoting the photo-induced electron transmission and separation [15]. Further, the results manifest that the photocatalytic hydrogen production of the MoS2 nanosheets/TiO2 nanotubes heterojunctions exhibit a remarkable enhancement, and the mechanism of the photocatalytic enhancement is studied.
2. Experiment.

2.1 Materials
Tetrabutyl titanate (TBOT), acetic acid, ethyl alcohol, Polyvinylpyrrolidone (PVP), oil, ammonium molybdate ((NH₄)₆-Mo₇O₂₄H₂O), and thiourea (CH₄N₂S).

All the chemicals are analytical grade and purchased from Aladdin Industrial Corporation (shanghai, China).

2.2 The fabrication of TiO₂ nanotube
In the work, we employed the electrostatic spinning technology for preparing TiO₂ nanotube. Firstly, 1g TBOT, 0.35g PVP were dissolved in mixed solution, including 1.95g ethyl alcohol, 1.55g acetic acid, 1g oil and continuously string for composing precursor solution. And then the precursor solution was spined in 16.5 kv and rate of 0.05g/min. After spinning, the received sample was dried in 80 °C for 10 hours and annealed in 500 °C for 2 hours.

2.3 The fabrication of MoS₂ nanosheets/TiO₂ nanotubes heterojunctions (remarked as TM)
Firstly, different weight of (NH₄)₆Mo₇O₂₄H₂O and CH₄N₂S were dissolved in 35 ml of distilled water and stirred for 1 hour to form a homogeneous solution. And then, 100 mg TiO₂ nanotubes were added in pre-solution and continuously stirring for 1 hour. Following, the mix solution was transferred to a Teflon-lined stainless steel autoclave at 200 °C for 20 h. after cooling down to room temperature, the MoS₂ nanosheets/TiO₂ nanotubes heterojunctions (TM) was collected, washed with deionized water and ethanol, and dried at 80 C for 6 h. Here, we marked the samples with different ratios as TM-15%, TM-20%, TM-25% (the rate of MoS₂/TiO₂ are 15%, 20%, 25% respectively). The preparation of pure MoS₂ nanosheet is same as above.

2.4 Characterization
The micromorphology of MoS₂ nanosheets/TiO₂ nanotubes heterojunctions were obtained by the scanning electron microscopy (FESEM Hitachi S-4800), and transmission electron microscopy (TEM JEM-2100). The phase composition of the heterojunctions were detected by the X-ray diffraction (XRD, Bruker D8 Discover) using Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 40 mA. The UV–vis diffuse reflectance spectra were recorded by the UV–vis spectrophotometer (Hitachi-U3900). The PL spectra were collected by a Hitachi F-7000 spectrofluorimeter at the excitation wavelength of 330 nm.

2.5 Photocatalytic activity
Photocatalytic activity of the MoS₂ nanosheets/TiO₂ nanotubes heterojunctions were conducted by the photocatalytic hydrogen production using gas chromatograph (Techcomp GC-7900). A 300W Xe arc lamp was employed as light source. For the photocatalytic experiment, 50 mg samples were suspended in 100 mL solution (80 mL water and 20 mL triethanolamine as the sacrifice agented). Before the experiment, high purity Ar was transported 20 min for eliminating the dissolved oxygen from the reactor, and the suspension sample was ultrasonic bath for 20 min. In the whole process, the reaction was conducted at room temperature.
3. Result and Discussion

Figure 1. The XRD spectra of the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio. 

Figure 1 is the XRD spectra of the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio. As revealed, the peaks of the pure TiO$_2$ nanotube at 25.3, 37.6, 48.0, 54.5 and 62.8° are ascribed to the (101), (004), (200), (105) and (204) planes of the rutile phase TiO$_2$(PDF-21-1272), respectively. However, due to the low crystallinity of MoS$_2$, the typical peaks of MoS$_2$ could be observed only in the sample of TM-25%, where the peak appears at 44.15° corresponds to the (006) plane of the MoS$_2$(PDF-37-1492). Above results indicate that the sample compose of TiO$_2$ and MoS$_2$.

Figure 2. The SEM of the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio.

The micromorphology of MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio are displayed in the Figure 2. Figure 2a is pure TiO$_2$ nanotube, as shown, the diameter of the nanotube was about 400 nm. Then, the micromorphology of TM-15%, TM-20%, TM-25% were showed in Figure 2b, Figure 2c, Figure 2d respectively. It’s interesting that, the MoS$_2$ nanosheets on the surfaces of the nanotubes increase obviously with the concentration. It’s obvious the Figure.2 proved that the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions were prepared successfully via the electrostatic spinning technology and hydrothermal method.
According to the TEM of the sample (Figure 3a), it could be observed that the MoS$_2$ nanosheets grow on TiO$_2$ nanotubes. Further, as revealed in the HRTEM of TM-20% (Figure 3b), the lattice spaces of 0.347 nm and 0.611 nm are ascribed to the (101) of TiO$_2$ and (002) of MoS$_2$, respectively.

The Figure 4 shows the UV-vis absorption spectra of the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio. Black curve illustrates that the pure TiO$_2$ nanotube exhibits hardly absorbed in visible light. However, with the introducing of MoS$_2$ nanosheets, the absorption of the heterojunctions exhibit sharply enhancement in the area of visible light. Obviously, the MoS$_2$ nanosheets can promote the absorption in visible light.

The Figure 5 displays the PL of the MoS$_2$ nanosheets/TiO$_2$ nanotubes heterojunctions with different ratio under 330 nm excitation. As shown, the decreasing of the PL indicates the increased separation of the photo-induced electron-hole pairs. As revealed, the PL obtains a lowest value at TM-20%, which proved that the TM-20% obtains the best efficiency of the photo-induced electron-hole pairs separation.
Figure. 6. (a) the photocatalytic H₂ production of all samples (b) the rate of all samples

The Figure. 6 is the photocatalytic H₂ production performance of the sample with different ratio. As revealed, the pure TiO₂ obtains a photocatalytic H₂ production performance of about ~46.29 μmol/g·h. Further, with the increasing of the MoS₂, the photocatalytic HER performance of the samples are 82.817, 340.739 and 134.867 μmol/g·h, respectively. It’s obvious that the MoS₂ without obvious photocatalytic HER performance and the TM-20% exhibits the optimal photocatalytic HER performance, which indicate that the MoS₂ nanosheets could act as the co-catalyst in this system and the suitable MoS₂ nanosheets could improve the photocatalytic HER performance efficiently.

4. Conclusion
In this work, the electrostatic spinning technology and hydrothermal co-deposition method are employed for the preparation of the MoS₂ nanosheets/TiO₂ nanotubes heterojunctions. Further, the photocatalytic HER performance of the samples are evaluated, there, the TM-20% exhibits remarkable photocatalytic HER performance of about ~340.739 μmol/g·h, that is about ~7 folds than the pure TiO₂, which is ascribed to the co-catalyst MoS₂ nanosheets obtains well electro transmission could restrained the recombination of photo-induced electron-hole pairs, and the nanotubes and nanosheets could increase the specific surface area for increasing the photocatalytic HER performance. Thus, the MoS₂ nanosheets/TiO₂ nanotubes heterojunctions exhibits an excellent HER performance and provide a new path for designing the novel energy materials.

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Reference
[1] Chen W T , Jovic V , Sun-Waterhouse D , et al. (2013) The role of CuO in promoting photocatalytic hydrogen production over TiO2.J. International Journal of Hydrogen Energy. 38(35):15036-15048.
[2] Yu H , Zhao Y , Zhou C , et al. (2014) Carbon quantum dots/TiO2 composites for efficient photocatalytic hydrogen evolution.J. Journal of Materials Chemistry A. 2.
[3] Xiang Q , Yu J , Jaroniec M .(2011) Tunable photocatalytic selectivity of TiO2 films consisted of flower-like microspheres with exposed {001} facets J. Chemical Communications. 47.
[4] Zhang H , Song Y , Sheng Y , et al.(2015) EDTA-assisted fabrication of TiO2 core–shell microspheres with improved photocatalytic performance.J. Ceramics International.41(1):247-252.
[5] Nyamukamba P , Tichagwa L , Greyling C.(2012) The Influence of Carbon Doping on TiO2
Nanoparticle Size, Surface Area, Anatase to Rutile Phase Transformation and Photocatalytic Activity. J. Materials Science Forum. 712:49-63.

[6] Zhang, Yuyuan, Chen, et al. (2010) Preparation and Photocatalytic Performance of Anatase/Rutile Mixed-Phase TiO2 Nanotubes. J. Catalysis Letters. 139(3-4):129-133.

[7] Gupta S M, Tripathi M. (2011) A review of TiO2nanoparticles. J. Chinese Science Bulletin. 56(16):1639-1657.

[8] Yu J, Fan J, Lv K.(2010) Anatase TiO2 nanosheets with exposed (001) facets: improved photoelectric conversion efficiency in dye-sensitized solar cells. J. Nanoscale. 2(10):2144-2149.

[9] Zhan S, Chen D, Jiao X, et al. (2006) Long TiO 2 Hollow Fibers with Mesoporous Walls: Sol–Gel Combined Electrospun Fabrication and Photocatalytic Properties. J. The Journal of Physical Chemistry B. 110(23):11199-11204.

[10] Ren X, Qi X, Shen Y, et al. (2016) 2D co-catalytic MoS2 nanosheets embedded with 1D TiO2 nanoparticles for enhancing photocatalytic activity. J. Journal of Physics D Applied Physics. 49(31):315304.

[11] Han W, Zang C, Huang Z, et al. (2014) Enhanced photocatalytic activities of three-dimensional graphene-based aerogel embedding TiO2 nanoparticles and loading MoS2 nanosheets as Co-catalyst. J. International Journal of Hydrogen Energy. 39(34):19502-19512.

[12] Zong X. (2010) Photocatalytic H2 Evolution on MoS2/CdS Catalysts under Visible Light Irradiation. J. Journal of Physical Chemistry C. 114(4):1963-1968.

[13] Lin H, Li Y, Li H, et al. (2017) Multi-node CdS hetero-nanowires grown with defect-rich oxygen-doped MoS2ultrathin nanosheets for efficient visible-light photocatalytic H2evolution. J. Nano Research. 10(4):1377-1392.

[14] Bai S, Jiang W, Li Z, et al. (2015) Surface and Interface Engineering in Photocatalysis. J. ChemNanoMat. 1(4):223-239.

[15] Liu J, Fang W, Wei Z, et al. (2018) Metallic 1T-LixMoS2 Co-catalyst Enhanced Photocatalytic Hydrogen Evolution over ZnIn2S4 Floriated Microspheres under Visible Light Irradiation. J. Catalysis Science & Technology. 8(5).