The MoS₂ Quantum Modified Hollow TiO₂ Nano-Heterojunction for Enhanced Hydrogen Evolution

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Abstract: A MoS₂ quantum dots modified hollow TiO₂ nanospheres heterojunction were prepared by a simple template method and annealing-impregnation deposition method. The structure and crystalline phase were proved by SEM, TEM and XRD. The photocatalytic water splitting performance of the MoS₂/TiO₂ nano-heterojunction exhibits an enhancement of 7.2 times 17.6 times than the pure TiO₂ and pure MoS₂, which could be ascribed to that the heterojunction between the TiO₂ and MoS₂ quantum dots could suppress the recombination of electron-hole pairs efficiently. What’s more, the hollow TiO₂ nanospheres and MoS₂ QDs with high specific surface area and pore diameter could supply plenty of active sites would be considered as another important reason.

1. Introduction

With the energy overusing, life and industry pollution deteriorating, the development of the renewable energy has attracted lots of attention in current researches. Especially hydrogen energy, as one of the new energy resources has become the scientist searchers hot point. Among such researches, the TiO₂, benefited by the unique band structure and high thermal stability[1,2], reveals excellent perform in photocatalytic water splitting into hydrogen and is wildly used in environmental conservation, maquillage, food and industrial application[3]. However, the low surface area and high recombination rate of photon-generated carriers restrict the anatase titania being applied in photocatalytic area. Thus, improving the surface area and decreasing the recombination would be efficient ways to improve the photocatalysis of the TiO₂.

Recently, the MoS₂, with itself narrow band gap and high charge mobility ratio on room temperature, has attracted plenty of attentions[4,5]. Especially the MoS₂ quantum dots, due to the distinctive “edge activity”[6] which is from the massive unsaturated Mo and S atoms on its edge that produced by S-Mo-S coordination in the crystal lattice, have been reported by series front works, such as photoelectric detection, photocatalytic, electrocatalysis, photovoltaic cell, and so on. In such works, with the introducing of the MoS₂ quantum dots, the formed heterojunction could separate the photon-generated carriers to improve the photocatalytic performance efficiently, which could prove researchers a remarkable view for design new heterojunction photocatalyst.

On the other hand, the specific surface area would be another important reason for the photocatalysis. For this issue, the morphological control or pore diameter would be an efficient way, and lots of literatures have reported, such as nanowires, nanosheets or nanotubes[7-9]. There, the hollow TiO₂ nanospheres[10,11] with sufficient specific surface area and smaller pore diameter are regarded as an ideal method, which could provide plenty of reaction sites for the photocatalysis and the deposition of the
MoS$_2$. In addition, the MoS$_2$ quantum dot with high specific surface area is another advantage for this structure.

In this work, we fabricated the MoS$_2$ modified TiO$_2$ hollow nanospheres via the template method. Compared with the pure TiO$_2$ nanospheres, the MoS$_2$/TiO$_2$ nanospheres exhibit obvious enhancement in photocatalytic hydrogen production. What’s more, the mechanism of the heterojunction was studied via the characterization of XRD, UV–vis absorption spectra, PL, SEM, TEM.

2. Material and Methods

2.1. Preparation of the SiO$_2$ nanospheres
SiO$_2$ nanospheres as template was prepared by classical Stöber method$^{[12]}$. 4ml of aqueous ammonia(32wt.%, Sigma-Aldrich), 98ml of ethanol and 10ml DI water were blended together. After stirring half an hour with constant speed at 30℃, add silicon source 5.6ml of TEOS (tetraethoxysilane, Sigma-Aldrich) and vigorously stir for 15 min. Waiting the mixture was left for 1 h, another 2 ml of TEOS and 2 ml of n-octadecyltrimethoxysilane (C18TMOS, Sigma-Aldrich) was dropped by drop with blending. Leaving without stirring for another 3 h at room temperature, monodisperse SiO$_2$ was gained after centrifuging, drying and annealing at 550℃.

2.2. Preparation of the SiO$_2$/TiO$_2$ nanospheres
0.2 g of SiO$_2$ template was add to 80 ml of isopropanol with ultrasound 15 min, then 0.4 ml Titanium(IV) isopropoxide(C12H28O4Ti Sigma-Aldrich) was poured into solution drop by drop with vigorously stirring. Leaving another 15 h, SiO$_2$/TiO$_2$ nanospheres was obtained by centrifuging, drying and annealing at 450℃(5℃/min) for 4 h in air$^{[13]}$.

2.3. Preparation of the MoS$_2$ QDs
By hydrothermal method$^{[14,15]}$, the MoS$_2$ QDs was synthesized. Briefly, 0.25 g sodium molybdate dihydrate (Na$_2$MoO$_4·2$H$_2$O Sigma-Aldrich) was dissolve in 25 ml DI water and 0.5 g of L-cysteine also added to 50 ml DI water. After waiting for 10 min ultrasonicati on, we poured L-cysteine solution into the other with stirring. The mixture was transferred into Teflon-lined stainless steel autoclave. Waiting for cooled naturally after 200℃ reaction for 24 h, the MoS$_2$ QDs supernatant was obtained by several time centrifuging for 5 min at 10000 rpm.

2.4. Preparation of the MoS$_2$/TiO$_2$ hollow nanospheres
Then, 0.1 g of TiO$_2$ hollow nanospheres, 5ml of MoS$_2$ QDs supernatant and 15 ml of DI water were blended for 12 h, the MoS$_2$/TiO$_2$ hollow nanospheres was obtained by centrifuging and drying.

2.5. Photocatalytic activity
The photocatalytic property was evaluated by a typical process, 50 mg of the as-prepared sample was pour into 90 ml of DI water and 10 ml triethanolamine(TEOA) as sacrificial agent. Ultrasonic dispersion was carried out for 5 min to get a homogenous solution. The performance tested by a closed gas-circulation system and a gas chromatograph (GC-7900) with 300W light source. During the test progress, the temperature of the catalysator was maintained at 10℃ by cyclic water.

2.6. Characterization
The micromorphology was characterized by scanning electron microscopy (FESEM, Hitachi S-4800). The crystal structure and phase composition were determined by transmission electron microscopy (TEM, JEM-2100) and X-ray diffraction (XRD, Bruker D8 Discover). The UV–Vis diffuse reflectance spectra and photocatalytic degradation were obtained by a UV–Vis spectrophotometer (Hitachi-U3900). The PL spectra were recorded by a Hitachi F-7000 spectrofluorimeter.
3. Results and discussion

Fig. 1. SEM of MoS\textsubscript{2}/TiO\textsubscript{2} hollow nanospheres(a), TEM of MoS\textsubscript{2} QDs and MoS\textsubscript{2}/TiO\textsubscript{2} hollow nanospheres(b, c); HRTEM of MoS\textsubscript{2}/TiO\textsubscript{2}(d).

The hollow sphere structure of MoS\textsubscript{2}/TiO\textsubscript{2} can be seen in the Fig.1.a and c. In the Fig.1.c, we can see the TiO\textsubscript{2} nanospheres which comprised of plenty of TiO\textsubscript{2} nanoparticle. Because of the content and size of MoS\textsubscript{2} QDs, we cannot find the quantum on the surface of TiO\textsubscript{2}. As shown by Fig.1.b, we synthesize MoS\textsubscript{2} quantum. Through a simple pickling process MoS\textsubscript{2} QDs stuck to TiO\textsubscript{2} which can be seen in Fig.1.d which we measure the lattice spacing. There are 0.352 nm and 0.31 nm lattice spacing which could be ascribed to the (101) plate of TiO\textsubscript{2} and (004) plate of MoS\textsubscript{2}, proving the existence of MoS\textsubscript{2}/TiO\textsubscript{2} p-n type heterojunction. As we can see in the Fig.2.a, as result of the low content of MoS\textsubscript{2} QDs, we cannot see the symbol peak of MoS\textsubscript{2}.

![Fig. 2. XRD and UV–Vis diffuse reflectance spectra of TiO\textsubscript{2}, MoS\textsubscript{2} QDs/TiO\textsubscript{2} and MoS\textsubscript{2}](image)

From Fig.2.a, the as-prepared TiO\textsubscript{2} hollow nanospheres show XRD primary patterns at 25.3°, 37.8°, 48.0°, 53.9°, 55.1° which could be ascribed to the (101), (004), (200), (105), (211) plane of the TiO\textsubscript{2}(JSPDS-21-1272). Some patterns of pure MoS\textsubscript{2} are match with base peak, like (100) and (006) plane. There are not MoS\textsubscript{2} patterns on the blue line as a result of its low content. As shown in Fig.2.b, the absorption peak for the as-prepared MoS\textsubscript{2}/TiO\textsubscript{2} is located at approximately 386 nm, which present the complex substance have obvious shift than pure TiO\textsubscript{2}. Even slight MoS\textsubscript{2} QDs added, the absorption spectrum has a little increase in visible light.
Fig. 3. PL spectra of MoS$_2$ QDs at different excitation wavelength and PL spectra of TiO$_2$, MoS$_2$, MoS$_2$/TiO$_2$ at 325 nm.

As shown in Fig. 3.a, the emission peak is red-shifted from 430 to 480 nm with the excitation wavelength from 330 to 430 nm. As a result of the polydispersity and the hot fluorescence from the K point of the Brillouin zone, the red-shifted happened.

As shown in Fig. 3.b, the intensity of MoS$_2$/TiO$_2$ is lower than pure TiO$_2$. It means that the recombination between photogenic electron and hole has been decline due to the building of n-p type semiconductor.

Fig. 4. H$_2$ production of TiO$_2$, MoS$_2$, and MoS$_2$/TiO$_2$.

The photolysis of water performance of MoS$_2$/TiO$_2$ has been shown in Fig. 4. The MoS$_2$/TiO$_2$ hollow nanospheres catalyst has a remarkably superior photocatalytic activity than pure TiO$_2$. The hydrogen productivity has been increased by 7.2 times and 17.6 times than pure TiO$_2$ and pure MoS$_2$. The hydrogen productivity of MoS$_2$/TiO$_2$ reach 391.1 umol/g/h. The MoS$_2$ QDs located on the TiO$_2$ nanospheres increased plenty of active sites, and the “edge effect” may contribute to segregate electron-hole pairs.

In view of above reason, the MoS$_2$/TiO$_2$ hollow nanospheres present an unexceptionable photocatalytic performance.

4. Conclusions

In this work, we prepared a ternary catalyst MoS$_2$/TiO$_2$ by annealing-impregnation deposition method with SiO$_2$ as template. The semiconductor heterojunction between TiO$_2$ and MoS$_2$ QDs efficiently improve separation of electron and hole and increase the lifetime of the photon-generated electron-hole pairs.
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