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Metallic 1T-TiS₂ nanodots anchored on a 2D graphitic C₃N₄ nanosheet nanostructure with high electron transfer capability for enhanced photocatalytic performance

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Photocatalysis is one of the most promising technologies for solar energy conversion. With the development of photocatalysis technology, the creation of low-dimensional structure photocatalysts with improved properties becomes more and more important. Metallic 1T-TiS₂ nanodots with a low-dimensional structure were introduced into environmentally friendly two-dimensional g-C₃N₄ (2D-C₃N₄) nanosheets by a solvothermal method. It was found that the ultrathin TiS₂ nanodots were uniformly anchored on the surface of the 2D-C₃N₄. The effective suppression of electron–hole recombination was realized due to the addition of the intrinsic metallic property of 1T-TiS₂ in the prepared nanocomposite. The 5 wt% TiS₂/2D-C₃N₄ nanocomposite exhibited the best photocatalytic performance and the degradation rate towards RhB was ca. 95% in 70 min, which showed an improvement of ca. 30% in comparison with 2D-C₃N₄. The results indicate that the obtained TiS₂/2D-C₃N₄ nanocomposite is a promising photocatalyst for practical applications.

Introduction

With the increasing scarcity of conventional energy resources and the deterioration of the environment, the development and utilization of renewable energy becomes more and more important. Solar power can be converted by photocatalysts into chemical energy to degrade pollutants, which has attracted a lot of attention in the past decades. Numerous researchers have devoted themselves to creating efficient photocatalysts to take full advantage of the redox ability of photogenerated carriers. TiO₂ was reported to be used for hydrogen generation by capturing the full advantage of the redox ability of photogenerated carriers.

In recent years, researchers have found the dimension reduction of the photocatalysts can shorten the diffusion length of photogenerated carriers. Moreover, the introduction of conducting materials has been found to be able to suppress recombination of photogenerated electron (e)–hole (h) pairs of semiconductors, such as some noble metals (Ag, Au and Pt). Platinum (Pt) with the lowest Fermi level is the most effective accepter of photogenerated electrons for the photocatalytic reaction. However, its high material cost makes it uncompetitive for practical applications. Thus, the development of the substitute materials (noble metal-free) of the noble metals is very necessary, but still challenging to date.

Layered transition metal dichalcogenides (TMDs) such as MoS₂, WSe₂, TaS₂ etc., have received much attention owing to their excellent catalytic activity and low cost compared to noble metals. As a prototype of TMDs, 1T-TiS₂ is composed of metal Ti layer sandwiched between two S layers forming edge-sharing TiS₆ octahedra with strong covalent forces. The adjacent S–Ti–S layers are coupled to each other by weak van der Waals interactions, providing the practical feasibility for exfoliating the bulk TiS₂ to ultrathin two dimensional TiS₂ nanosheets. In addition, 1T-TiS₂ is a semimetal with excellent in-plane conductivities. It is noticeable that conductive 1T-TiS₂ can replace the noble metals to be used as the acceptor of the photogenerated electrons and improve the separation efficiency of the photoexcited carriers of semiconductors.

Graphitic carbon nitride (g-C₃N₄), a polymeric semiconductor with a low band gap of ~2.7 eV, has an appropriate band structure for photocatalysis. Two dimensional C₃N₄ (2D-C₃N₄) can be prepared according to our previous report. The two dimensional structure of g-C₃N₄ can contribute to the...
separation of photogenerated e-h pairs and then the carriers could handily transfer to the surface to suppress the recombination. However, the separation efficiency of the photoexcited carriers of 2D-C3N4 are still unsatisfactory in the absence of noble metals. To further improve the photocatalytic activity of 2D-C3N4, the introduction of some conductive materials is an effective method.

Herein, the exfoliated ultrathin TiS2 nanodots were introduced into 2D-C3N4. Anchoring metallic TiS2 nanodots on 2D-C3N4 nanosheets via solvothermal method facilitated the fast transfer of the photogenerated carriers. The high photocatalytic performance of the nanocomposite resulted from the effective suppression of the e-h recombination was tested by degrading Rhodamine B (RhB). In the nanocomposites, uniformly distributed TiS2 nanodots on surface of 2D-C3N4 nanosheets did serve as the accepter of the photogenerated electrons. Additionally, the photocatalytic mechanism was also studied in detail by electron spin resonance (ESR).

Experimental

1. Synthesis of ultrathin TiS2 nanodots

Ultrathin TiS2 nanodots were prepared via liquid phase exfoliation in a co-solvent (acetonitrile/IPA = 19 : 1, by volume). Specifically, 900 mg 1T-TiS2 powder (Sigma-Aldrich) was dispersed in 300 ml co-solvent and the solution was sonicated in an ultrasonic bath at 25 °C for 4 h. Then the mixture was centrifuged at 6000 rpm for 30 min to remove any unexfoliated bulk TiS2. The supernatant was further probe sonicated for another 4 h followed by centrifugation at 10 000 rpm for 30 min. The freeze-dried supernatant was named as TiS2 nanodots.

2. Synthesis of ultrathin g-C3N4 nanosheets

Ultrathin g-C3N4 was synthesized as below. 2 g melamine were calcined at 550 °C for 4 h with 2 °C min⁻¹ heating rate in the muffle furnace. The obtained sample was bulk g-C3N4. Then 400 mg bulk g-C3N4 was ground and heated at 550 °C for ~30 min in the muffle furnace. After that, the obtained samples were heated at 550 °C for another ~30 min in the muffle furnace. Finally, the obtained ultrathin g-C3N4 were white.

3. Synthesis of TiS2/2D-C3N4 nanocomposites

The TiS2/2D-C3N4 nanocomposite was prepared by solvothermal method in benzyl alcohol. An appropriate amount of ultrathin TiS2 nanodots and 70 mg 2D-C3N4 was dispersed in benzyl alcohol and sonicated for 20 min, respectively. Then a certain concentration of TiS2 nanodots was mixed with pure 2D-C3N4 and stirred for 2 h. After sonicating the mixture again for 20 min, the suspension was transferred to a stainless-steel autoclave and heated for 4 h at 140 °C. After natural cooling, the solution was washed by ethanol and water twice respectively. The washed powder was then freeze dried and used as catalyst. The TiS2/2D-C3N4 catalysts with different TiS2 content were named as x% TiS2/2D-C3N4, where “x” represent the mass percentage of TiS2 (x = 1, 3, 5, 10 wt%).

4. Material characterization

Scanning electron microscope (SEM) images of 5% TiS2/2D-C3N4 nanodots were taken on a JEOL-6500 scanning electronic microscope. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) images were recorded on a JEOL-2100F at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns of TiS2 nanodots and the nanocomposites were performed on D/MAX2500V with Cu-Kz radiation (λ = 1.54056 Å). Raman spectra of TiS2 nanodots, 2D-C3N4 and 5% TiS2/2D-C3N4 nanocomposite were acquired with a RENISHAW in Via Raman Microscope using a 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the presence of TiS2 in the nanocomposites at ambient temperature using PHI Quantera with Al-Kz X-ray source. Shimadzu UV-2450 ultraviolet-visible spectrophotometer was used to collect the UV-vis absorption spectra of TiS2/2D-C3N4 nanocomposites. Composition analysis of as-prepared materials was carried on fourier transforms infrared spectrometer (FT-IR) using Nicolet Nexus 470 spectrometer. The ESR spectra were conducted on a Bruker model ESR JES-FPA200 spectrometer. Photoluminescence (PL) spectroscopy experiments were conducted at excitation wavelength 377 nm using Jobin Yvon HORIBA NanoLog spectrofluorometer.

5. Photocatalytic activity measurements

For photocatalytic degradation experiment, the organic dye RhB was used as a model pollutant. In detail, 10 mg samples were added into 50 ml RhB (10 mg l⁻¹) in a Pyrex photocatalytic reactor with a circulating water system to maintain a constant temperature (30 °C). Before irradiation, the suspensions were magnetically stirred for 30 min in the dark to ensure that RhB could reach the absorption–desorption equilibrium on the photocatalyst surface. At a certain time intervals, 3 ml aliquots were sampled and centrifuged to remove the photocatalyst nanoparticles. Then the filtrates were analyzed by recording variations of the absorption band maximum (553 nm) in the UV-vis spectra of RhB using a UV-vis spectrophotometer. The air velocity was 2 l min⁻¹ and the photocatalytic reaction was performed under a 300 W Xe lamp with a 400 nm cutoff filter.

Results and discussions

The TiS2/2D-C3N4 nanocomposites with different content of TiS2 nanodots were prepared by solvothermal method in benzyl alcohol. The morphology of 2D-C3N4, TiS2 nanodots and the as-prepared 5% TiS2/2D-C3N4 nanocomposite were examined by AFM and TEM, as shown in Fig. 1. 2D-C3N4 nanosheets performed a micrometer-scale lateral size and thin thickness about 1–2 nm (Fig. 1a). The size and thickness of TiS2 nanodots were nanometer grade, 5–10 nm and 1–3 nm (Fig. 1b and c), respectively. Ultrathin and small TiS2 nanodots were uniformly anchored on the surface of thin 2D-C3N4 nanosheets without hard aggregations. From the HRTEM image, the lattice with spacing of 0.29 nm of TiS2 nanodots assigned to the [010] planes could be seen on the surface of 2D-C3-N4 nanosheets clearly. It demonstrated that the hybridization of 2D-C3N4...
The crystalline structure of the as-prepared TiS$_2$/2D-C$_3$N$_4$ nanocomposites with different content of TiS$_2$ nanodots were further characterized by XRD. In addition to the diffraction peaks at 12.5 and 27.7° attributed to the (100) and (002) crystal planes of 2D-C$_3$N$_4$, respectively, many other peaks for intralayer crystal planes at 15.5, 34.2, 44.2, 53.9, 57.7 and 65.4° of TiS$_2$/2D-C$_3$N$_4$ nanocomposites were consistent with those of pure few layers of 1T-TiS$_2$. Raman spectra of 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposite, 2D-C$_3$N$_4$ and TiS$_2$ nanodots was taken to further demonstrate the presence of TiS$_2$ in the nanocomposites (Fig. 2c). The pure TiS$_2$ nanodots showed a peak at 227 cm$^{-1}$ assigned to Eg and a peak at 332 cm$^{-1}$ with a shoulder at 380 cm$^{-1}$ attributed to A$_{1g}$ vibrational modes of 1T-TiS$_2$. However, except for the significant peaks of 2D-C$_3$N$_4$, the peaks of TiS$_2$ were not very clear in 5% TiS$_2$/2D-C$_3$N$_4$ because of the low content of TiS$_2$ in the nanocomposites, which was in agreement with previous publications. FT-IR spectra of pure 2D-C$_3$N$_4$ and TiS$_2$/2D-C$_3$N$_4$ nanocomposites were obtained as well. Because of the low detective sensitivity and low content of TiS$_2$ in the nanocomposites, FT-IR spectra of all hybrid only showed typical stretching mode of 2D-C$_3$N$_4$ heterocycles from 1250 to 1700 cm$^{-1}$ and the vibrational mode of N–H bond at 3147 cm$^{-1}$ respectively.

The chemical states and elemental compositions of TiS$_2$ nanodots, 2D-C$_3$N$_4$ and 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposites were further examined by XPS, as shown in Fig. 3. The C 1s spectra of both 2D-C$_3$N$_4$ and 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposites showed two peaks at 284.7 eV and 288.2 eV assigned to the sp$^2$ C=C bonds and N=C–N$_2$ bonds, respectively (Fig. 3a and c). The N 1s spectrum of 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposite with four peaks in Fig. 3b is similar with that of 2D-C$_3$N$_4$ in Fig. 3d. The peaks at 398.7 eV, 399.8 eV, 401.0 eV and 404.4 eV were ascribed to the sp$^2$-hybridized nitrogen atoms in C=N–C, the tertiary nitrogen, the amino functions carrying hydrogen (C–N–H) and π-excitation, respectively. The C 1s and N 1s signals confirmed the presence of 2D-C$_3$N$_4$ in 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposite, which is consistent with the results in FT-IR. The binding energies of Ti 2p peaks (458.5 eV for 2p$_{3/2}$ and 463.3 eV for 2p$_{1/2}$) and the weak binding energies of S 2p$_{3/2}$ and 2p$_{1/2}$ peaks emerging at 161.0 eV and 162.2 eV in 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposite were similar with the peaks in TiS$_2$ nanodots, which agreed well with those of 1T-TiS$_2$. It demonstrated the existence of TiS$_2$ nanodots in 5% TiS$_2$/2D-C$_3$N$_4$ composite.

The presence of TiS$_2$ nanodots in the nanocomposites was further studied by SEM images and corresponding EDS. The micro-morphology and element mapping of 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposites were shown in Fig. 4. The 2D nanosheets could be seen clearly in Fig. 4a and d. Because TiS$_2$ nanodots and 2D-C$_3$N$_4$ nanosheets were self-assembled together, it was difficult to distinguish them from morphology. From the element mapping of 5% TiS$_2$/2D-C$_3$N$_4$ nanocomposite, it could be seen...
that TiS₂ nanodots were dispersed in the soft nanosheets of 2D-C₃N₄ uniformly. Ti and S elements of TiS₂ nanodots were distributed in the matrix C and N elements of 2D-C₃N₄ in the nanocomposites, which was consistent with the TEM results. As the content of TiS₂ nanodots in composite was 5%, the signals of Ti and S were much lower than those of C and N.

The UV-vis absorption of pure TiS₂ nanodots, 2D-C₃N₄ and as-prepared TiS₂/2D-C₃N₄ nanocomposites were shown in Fig. 5a. The curve of 2D-C₃N₄ displayed a starting absorption at the edge of visible light blending into the ultraviolet, which corresponded to the band gap of 2D-C₃N₄ at 2.68 eV in Fig. 5b. And TiS₂ nanodots could absorb UV and visible light. TiS₂/2D-C₃N₄ nanocomposites performed similar absorption width with 2D-C₃N₄ nanosheets but much higher absorption value attributed to the light absorption of TiS₂, and the absorption intensity at the UV and visible light region were enhanced with increasing content of TiS₂ nanodots which indicated that TiS₂/2D-C₃N₄ nanocomposites obtained more photogenerated e–h pairs at 200–700 nm. In order to investigate the influence of TiS₂ QDs on the separation efficiency of the photoexcited carriers in TiS₂/2D-C₃N₄ nanocomposites, the PL spectroscopy measurements were carried out for 2D-C₃N₄ and 5% TiS₂/2D-C₃N₄ nanocomposites. As shown in Fig. 5c, the fluorescence intensity of emission peak at about 460 nm for 5% TiS₂/2D-C₃N₄ nanocomposite was much weaker than that of 2D-C₃N₄ due to the low recombination rate of photo-generated charge carriers. Because of the higher UV-vis absorption and lower fluorescence emission intensity, more photo-generated charge carriers in 5% TiS₂/2D-C₃N₄ nanocomposite were trapped by highly conductive TiS₂ nanodots on 2D-C₃N₄ nanosheets.

The photocatalytic performance of the nanocomposites was mainly evaluated by photo-degradation of RhB, because RhB is a typical organic dye which is a common water pollutant and could cause long-term environmental toxicity and short-term public health damage. Fig. 6a showed the evolution of the degradation rate of RhB along with time. All the curves had a similar linear downtrend which seemed to be zero-order kinetic process. Hence, the data points were fitted according to the zero-order kinetic process:

\[
\frac{C}{C_0} = -kt + b
\]

where \(k\) is the degradation rate constant, and \(b\) represents the residual composition at 0 min. The \(k\), \(b\) and \(R^2\) values of the fitted curves for all the samples were listed in Table 1. According to \(R^2\) values of the samples (higher than 0.982), the fitted curves matched well with the obtained data. So, the degradation behaviour surely followed the zero-order kinetic process. The degradation rate constant of 2D-C₃N₄ was 0.00783 min⁻¹. Compared with blank 2D-C₃N₄, all the TiS₂/2D-C₃N₄ nanocomposites exhibited higher photocatalytic degradation rate under the same condition. The addition of TiS₂ nanodots to 2D-C₃N₄ enhanced the photocatalytic activity obviously. As the amount of TiS₂ nanodots increase, the degradation rate of RhB was enhanced significantly. 5% TiS₂/2D-C₃N₄ nanocomposite performed the highest degradation rate among all the catalysts (0.0128 min⁻¹). When the loading amount of TiS₂ nanodots reached to 10 wt%, the photocatalytic degradation of RhB decreased as too much TiS₂ nanodots blocked the photo absorption of 2D-C₃N₄. The as-prepared 10% TiS₂/2D-C₃N₄ has higher \(b\) value than 5% TiS₂/2D-C₃N₄ nanocomposite because of weaker absorption ascribed to too high loadings of TiS₂ nanodots. The highest degradation rate of TiS₂/2D-C₃N₄ nanocomposites was ca. 95% in 70 min, which got an improvement of ca. 30% in comparison with that of 2D-C₃N₄. The photocurrent experiment was carried out to explore the charge separation and transfer efficiency (Fig. 6b). The measurements clearly showed that the introduction of TiS₂ nanodots enhanced the photocurrent of 2D-C₃N₄, in which the 5% TiS₂/2D-C₃N₄ nanocomposite exhibited the highest value. The photocurrent for 5% TiS₂/2D-C₃N₄ was about 2.5 times higher than that given by bare 2D-C₃N₄. The results above suggested that the introduction TiS₂ nanodots enhanced the charge separation greatly and suppressed the recombination of e–h pairs, thus improving the photocatalytic performance.

Besides the high photocatalytic degradation efficiency, the 5% TiS₂/2D-C₃N₄ nanocomposite showed high stability after five times of cyclic experiments (Fig. 7a). In addition, the nanocomposite still preserved the chemical structure of 2D-

\[
\text{Table 1 \ The } k, b \text{ and } R^2 \text{ value following zero-order kinetic process of catalytic degradation}
\]

| Sample                  | \(b\)     | \(k\) (min⁻¹) | \(R^2\) |
|-------------------------|-----------|---------------|---------|
| 2D-C₃N₄                | 0.96      | 0.00783       | 0.982   |
| 1% TiS₂/2D-C₃N₄        | 0.97      | 0.0105        | 0.992   |
| 3% TiS₂/2D-C₃N₄        | 0.94      | 0.0120        | 0.985   |
| 5% TiS₂/2D-C₃N₄        | 0.90      | 0.0128        | 0.990   |
| 10% TiS₂/2D-C₃N₄       | 0.97      | 0.0125        | 0.986   |

Fig. 5 (a) UV-vis absorption spectra of TiS₂ nanodots, 2D-C₃N₄ and TiS₂/2D-C₃N₄ nanocomposites with different content of TiS₂ nanodots; (b) Tauc plot of pure 2D-C₃N₄ nanosheets from UV vis absorption; (c) Photoluminescence spectra of pure 2D-C₃N₄ and 5% TiS₂/2D-C₃N₄ nanocomposite.

Fig. 6 (a) Photocatalytic activity of RhB in the presence of the 2D-C₃N₄ and TiS₂/2D-C₃N₄ nanocomposites with different content of TiS₂ nanodots under visible light; (b) Transient photocurrent response of pure 2D-C₃N₄ and TiS₂/2D-C₃N₄ nanocomposites.
C₃N₄ and TiS₂ after five cycles degradation shown by the XRD and FTIR spectra in Fig. 7b and c. The diffraction peak at 27.7° for the (002) crystal plane of 2D-C₃N₄ and many other peaks at 15.5, 34.2, 44.2 and 57.7° for intralayer crystal planes of TiS₂ were consistent with nanocomposite before cycling. FT-IR spectra of TiS₂/2D-C₃N₄ nanocomposites before and after cycling was similar as well.

As discussed above, the metallic TiS₂ nanodots in the system played a crucial role in the migration of electrons excited by the 2D-C₃N₄ semiconductor, which could efficiently suppress the recombination of e–h pairs. To gain a further insight into the photocatalytic degradation process, ESR analysis was carried out to explore the active radicals using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trapping, as shown in Fig. 8. Obviously, the ESR results showed that, when TiS₂/2D-C₃N₄ nanocomposite were employed as photocatalyst, both O₂⁻ and ‘OH could be generated under visible light irradiation. According to previous reports, the top of valence band (TVB) potential of 2D-C₃N₄ was 1.79 V vs. RHE. The band gap was calculated to be 2.68 eV (Fig. 5b), thus the bottom of conduction band (BCB) potential of 2D-C₃N₄ was –0.89 V vs. RHE. Apparently, the potential energy of the photo-excited electrons at BCB potential was higher than that of O₂⁻/O₂ (–0.046 eV), thus the electrons possessed the ability to combine with O₂ to form O₂⁻. For the generation of ‘OH, the holes at the TVB of 2D-C₃N₄ cannot oxidize H₂O or OH⁻ into ‘OH due to the lower TVB position in comparison with OH⁻/OH⁻ (1.99 eV) and H₂O/OH⁻ (2.38 eV). The ‘OH may be generated by the further reactions of strong reduction O₂⁻ through an intermediate of ‘OOH:

\[
\text{OOH} + \text{H}^+ \rightarrow \text{H}_2\text{O}_2
\]

\[
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{‘OH} + \text{OH}^- \quad (3)
\]

Fig. 8 (a) ESR spectra of DMPO-O₂⁻ (a) and DMPO-‘OH (b) adducts in TiS₂/2D-C₃N₄ aqueous dispersion systems under visible light irradiation or in the dark.

Fig. 9 The degradation of mechanism of as-prepared TiS₂/2D-C₃N₄ composites.

Conclusion

We utilized a simple exfoliation synthesis to get ultrathin TiS₂ nanodots and the TiS₂/2D-C₃N₄ was synthesized by a temperate solvothermal method. The TiS₂ nanodots were tightly anchored on the surface of 2D-C₃N₄ nanosheets and the inherent metallic nature of 1T-TiS₂ improved the photocatalytic degradation activity due to the effective suppression of the e–h recombination and the higher light absorption. Noteworthy, the content of the TiS₂ nanodots in the prepared complex played a role in the RhB photocatalytic degradation. The 5% TiS₂/2D-C₃N₄ exhibited the best photocatalytic performance and the degradation rate towards RhB was ca. 95% in 70 min, which got an improvement of ca. 30% in comparison with pure 2D-C₃N₄ nanosheets. So, the combination of ultrathin metallic TMDs with 2D graphitic C₃N₄ yields a promising photocatalyst for practical application.
Conflicts of interest
There are no conflicts to declare.

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