

Cite this: *RSC Adv.*, 2017, 7, 55269

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

Yang Liu,^{†ab} Xiaojie She,^{†c} Xiaoni Zhang,^c Chenglu Liang,^{ab} Jingjie Wu,^b Peng Yu,^a Yusuke Nakanishi,^b Banghu Xie,^a Hui Xu,^{id* c} Pulickel M. Ajayan^b and Wei Yang^{id* a}

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.

Received 30th September 2017
Accepted 27th November 2017

DOI: 10.1039/c7ra10826e

rsc.li/rsc-advances

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.¹ Solar power can be converted by photocatalysts into chemical energy to degrade pollutants, which has attracted a lot of attention in the past decades.² 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 *via* water splitting under ultraviolet light.^{3–6} Nevertheless, the challenges of photocatalytic degradation mainly lie in the following two points: (1) the wide light absorption range and (2) the efficient separation of photogenerated electrons and holes.^{7,8}

In recent years, researchers have found the dimension reduction of the photocatalysts can shorten the diffusion length of photogenerated carriers.^{9–16} 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).^{17–22} Platinum (Pt) with the lowest Fermi level is the most effective acceptor of photogenerated electrons for the photocatalytic reaction.²³ 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.^{24–30} 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.³ 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.^{31,32} In addition, 1T-TiS₂ is a semimetal with excellent in-plane conductivities.³³ 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.³⁴ Two dimensional C₃N₄ (2D-C₃N₄) can be prepared according to our previous report.^{35–37} The two dimensional structure of g-C₃N₄ can contribute to the

^aCollege of Polymer Science and Engineering, Sichuan University, State Key Laboratory of Polymer Materials Engineering, Chengdu 610065, Sichuan, China. E-mail: weiyang@scu.edu.cn

^bDepartment of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas 77005, USA

^cInstitute for Energy Research, Jiangsu University, Zhenjiang, 212013, P. R. China. E-mail: xh@ujs.edu.cn

[†] Authors contributed equally to this work.

separation of photogenerated e[−]–h⁺ pairs and then the carriers could handily transfer to the surface to suppress the recombination.^{38–43} 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 acceptor 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-Kα 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-Kα 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-FA200 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-C₃N₄ nanosheets clearly. It demonstrated that the hybridization of 2D-C₃N₄



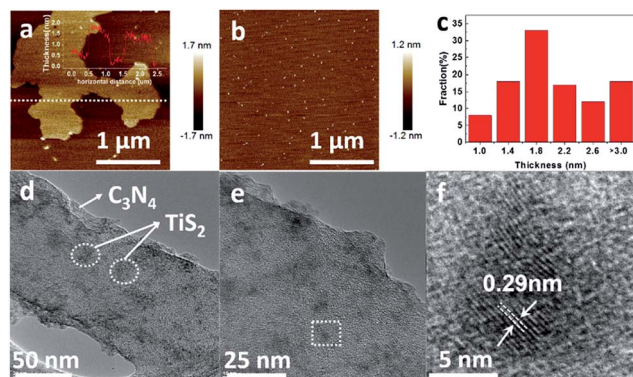


Fig. 1 (a) AFM image and thickness (inset) of 2D-C₃N₄; (b) AFM image of TiS₂ nanodots; (c) the statistics of thickness of TiS₂ nanodots; (d) and (e) TEM images and (f) HRTEM image of 5% TiS₂/2D-C₃N₄ composite.

nanosheets and TiS₂ nanodots did not disturb the crystal structure and morphology of TiS₂.

The crystalline structure of the as-prepared TiS₂/2D-C₃N₄ nanocomposites with different content of TiS₂ 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-C₃N₄, respectively,^{44,45} many other peaks for intralayer crystal planes at 15.5, 34.2, 44.2, 53.9, 57.7 and 65.4° of TiS₂/2D-C₃N₄ nanocomposites were consistent with those of pure few layers of 1T-TiS₂.⁴⁶ Raman spectra of 5% TiS₂/2D-C₃N₄ nanocomposite, 2D-C₃N₄ and TiS₂ nanodots was taken to further demonstrate the presence of TiS₂ in the nanocomposites (Fig. 2c). The pure TiS₂ nanodots showed a peak at 227 cm⁻¹ assigned to E_g and a peak at 332 cm⁻¹ with a shoulder at 380 cm⁻¹ attributed to A_{1g} vibrational modes of 1T-TiS₂.⁴⁷ However, except for the significant peaks of 2D-C₃N₄, the peaks of TiS₂ were not very clear in 5% TiS₂/2D-C₃N₄ because of the low content of TiS₂ in the nanocomposites, which was in agreement with previous publications.⁴⁸ FT-IR spectra of pure 2D-C₃N₄ and TiS₂/2D-C₃N₄ nanocomposites were obtained as well. Because of the low detective sensitivity and low content of TiS₂ in the nanocomposites, FT-IR spectra of all hybrid only showed typical stretching mode of 2D-C₃N₄ heterocycles from 1250 to 1700 cm⁻¹ and the vibrational mode of N-H bond at 3147 cm⁻¹ respectively.⁴⁸

The chemical states and elemental compositions of TiS₂ nanodots, 2D-C₃N₄ and 5% TiS₂/2D-C₃N₄ nanocomposites were further examined by XPS, as shown in Fig. 3. The C 1s spectra of

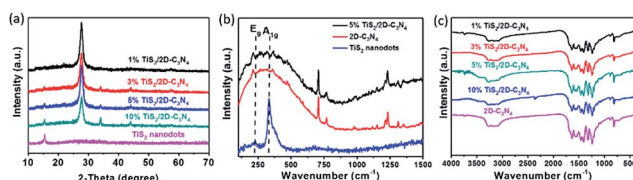


Fig. 2 (a) XRD patterns of TiS₂ nanodots and TiS₂/2D-C₃N₄ nanocomposites with different content of TiS₂; (b) Raman spectra of 2D-C₃N₄, TiS₂ nanodots and 5% TiS₂/2D-C₃N₄ nanocomposite; (c) FTIR of 2D-C₃N₄ and TiS₂/2D-C₃N₄ nanocomposites.

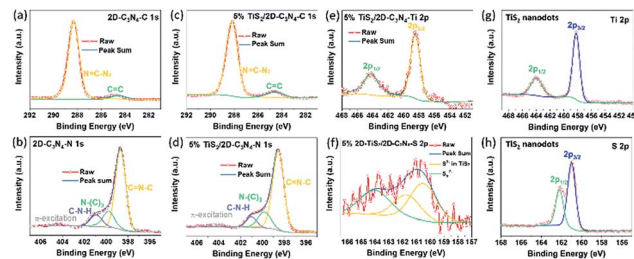


Fig. 3 XPS spectra of 2D-C₃N₄ and 5% TiS₂/2D-C₃N₄ nanocomposites. C 1s (a) and N 1s (b) of 2D-C₃N₄; C 1s (c), N 1s (d), Ti 2p (e) and S 2p (f) of 5% TiS₂/2D-C₃N₄ nanocomposite; (g) Ti 2p_{3/2}, 2p_{1/2} and (h) S 2p_{3/2}, 2p_{1/2} of TiS₂ QDs.

both 2D-C₃N₄ and 5% TiS₂/2D-C₃N₄ nanocomposites showed two peaks at 284.7 eV and 288.2 eV assigned to the sp² C=C bonds and N=C-N₂ bonds, respectively (Fig. 3a and c). The N 1s spectrum of 5% TiS₂/2D-C₃N₄ nanocomposite with four peaks in Fig. 3b is similar with that of 2D-C₃N₄ in Fig. 3d. The peaks at 398.7 eV, 399.8 eV, 401.0 eV and 404.4 eV were ascribed to the sp²-hybridized nitrogen atoms in C=N-C, the tertiary nitrogen, the amino functions carrying hydrogen (C-N-H) and π -excitation, respectively.⁴⁹ The C 1s and N 1s signals confirmed the presence of 2D-C₃N₄ in 5% TiS₂/2D-C₃N₄ 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 S²⁻ 2p_{3/2} and 2p_{1/2} peaks emerging at 161.0 eV and 162.2 eV in 5% TiS₂/2D-C₃N₄ nanocomposite were similar with the peaks in TiS₂ nanodots, which agreed well with those of 1T-TiS₂.⁵⁰ It demonstrated the existence of TiS₂ nanodots in 5% TiS₂/2D-C₃N₄ composite.

The presence of TiS₂ nanodots in the nanocomposites was further studied by SEM images and corresponding EDS. The micro-morphology and element mapping of 5% TiS₂/2D-C₃N₄ nanocomposite were shown in Fig. 4. The 2D nanosheets could be seen clearly in Fig. 4a and d. Because TiS₂ nanodots and 2D-C₃N₄ nanosheets were self-assembled together, it was difficult to distinguish them from morphology. From the element mapping of 5% TiS₂/2D-C₃N₄ nanocomposite, it could be seen

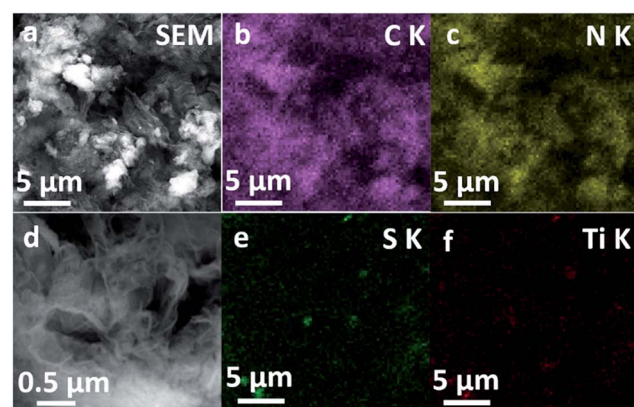


Fig. 4 SEM images and EDX mapping images of 5% TiS₂/2D-C₃N₄ nanocomposites. (a) SEM image; EDX mapping of C (b), N (c), S (e), Ti (f); (d) high amplification of SEM image.

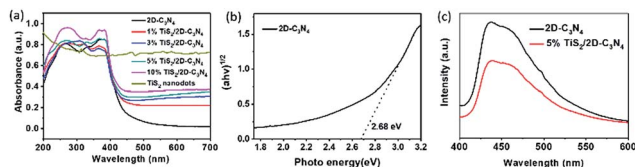


Fig. 5 (a) UV-vis absorption spectra of TiS_2 nanodots, 2D- C_3N_4 and $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites with different content of TiS_2 nanodots; (b) Tauc plot of pure 2D- C_3N_4 nanosheets from UV vis absorption. (c) Photoluminescence spectra of pure 2D- C_3N_4 and 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite.

that TiS_2 nanodots were dispersed in the soft nanosheets of 2D- C_3N_4 uniformly. Ti and S elements of TiS_2 nanodots were distributed in the matrix C and N elements of 2D- C_3N_4 in the nanocomposites, which was consistent with the TEM results. As the content of TiS_2 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 TiS_2 nanodots, 2D- C_3N_4 and as-prepared $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites were shown in Fig. 5a. The curve of 2D- C_3N_4 displayed a starting absorption at the edge of visible light blending into the ultraviolet, which corresponded to the band gap of 2D- C_3N_4 at 2.68 eV in Fig. 5b. And TiS_2 nanodots could absorb UV and visible light. $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites performed similar absorption width with 2D- C_3N_4 nanosheets but much higher absorption value attributed to the light absorption of TiS_2 , and the absorption intensity at the UV and visible light region were enhanced with increasing content of TiS_2 nanodots which indicated that $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites obtained more photogenerated e-h pairs at 200–700 nm. In order to investigate the influence of TiS_2 QDs on the separation efficiency of the photoexcited carriers in $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites, the PL spectroscopy measurements were carried out for 2D- C_3N_4 and 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites. As shown in Fig. 5c, the fluorescence intensity of emission peak at about 460 nm for 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite was much weaker than that of 2D- C_3N_4 due to the low recombination rate of photo-generated charge carriers.⁵¹ Because of the higher UV-vis absorption and lower fluorescence emission intensity, more photo-generated charge carriers in 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite were trapped by highly conductive TiS_2 nanodots on 2D- C_3N_4 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:

$$C/C_0 = -kt + b$$

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

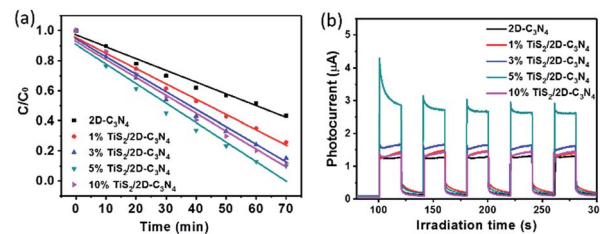


Fig. 6 (a) Photocatalytic activity of RhB in the presence of the 2D- C_3N_4 and $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites with different content of TiS_2 nanodots under visible light. (b) Transient photocurrent response of pure 2D- C_3N_4 and $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites.

matched well with the obtained data.⁵² So, the degradation behaviour surely followed the zero-order kinetic process. The degradation rate constant of 2D- C_3N_4 was 0.00783 min^{-1} . Compared with blank 2D- C_3N_4 , all the $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites exhibited higher photocatalytic degradation rate under the same condition. The addition of TiS_2 nanodots to 2D- C_3N_4 enhanced the photocatalytic activity obviously. As the amount of TiS_2 nanodots increase, the degradation rate of RhB was enhanced significantly. 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite performed the highest degradation rate among all the catalysts (0.0128 min^{-1}). When the loading amount of TiS_2 nanodots reached to 10 wt%, the photocatalytic degradation of RhB decreased as too much TiS_2 nanodots blocked the photo absorption of 2D- C_3N_4 . The as-prepared 10% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ has higher b value than 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite because of weaker absorption ascribed to too high loadings of TiS_2 nanodots. The highest degradation rate of $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposites was ca. 95% in 70 min, which got an improvement of ca. 30% in comparison with that of 2D- C_3N_4 . The photocurrent experiment was carried out to explore the charge separation and transfer efficiency (Fig. 6b). The measurements clearly showed that the introduction of TiS_2 nanodots enhanced the photocurrent of 2D- C_3N_4 , in which the 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite exhibited the highest value. The photocurrent for 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ was about 2.5 times higher than that given by bare 2D- C_3N_4 . The results above suggested that the introduction TiS_2 nanodots enhanced the charge separation greatly and suppressed the recombination of e-h pairs, thus an improving the photocatalytic performance.

Besides the high photocatalytic degradation efficiency, the 5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$ nanocomposite showed high stability after five times of cyclic experiments (Fig. 7a). In addition, the nanocomposite still preserved the chemical structure of 2D-

Table 1 The k , b and R^2 value following zero-order kinetic process of catalytic degradation

Sample	b	$k \text{ (min}^{-1}\text{)}$	R^2
2D C_3N_4	0.96	0.00783	0.982
1% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$	0.97	0.0105	0.992
3% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$	0.94	0.0120	0.985
5% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$	0.90	0.0128	0.990
10% $\text{TiS}_2/\text{2D-C}_3\text{N}_4$	0.97	0.0125	0.986



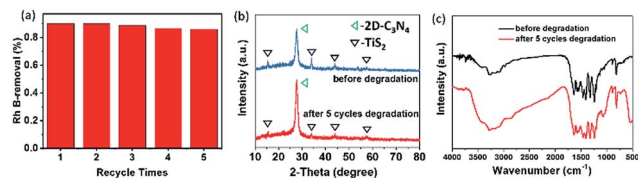


Fig. 7 (a) Cycling runs for the photodegradation of RhB in the presence of 5% $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ nanocomposite. The chemical and crystal structure of 5% $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ nanocomposite before and after 5 cycles photodegradation of RhB, XRD pattern (b) and FT-IR spectra (c).

C_3N_4 and TiS_2 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 $2\text{D-C}_3\text{N}_4$ and many other peaks at $15.5, 34.2, 44.2$ and 57.7° for intralayer crystal planes of TiS_2 were consistent with nanocomposite before cycling. FT-IR spectra of $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ nanocomposites before and after cycling was similar as well.

As discussed above, the metallic TiS_2 nanodots in the system played a crucial role in the migration of electrons excited by the $2\text{D-C}_3\text{N}_4$ 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 $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ nanocomposite were employed as photocatalyst, both $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ could be generated under visible light irradiation. According to previous reports, the top of valence band (TVB) potential of $2\text{D-C}_3\text{N}_4$ was 1.79 V vs. RHE .^{53,54} The band gap was calculated to be 2.68 eV (Fig. 5b), thus the bottom of conduction band (BCB) potential of $2\text{D-C}_3\text{N}_4$ was -0.89 V vs. RHE . Apparently, the potential energy of the photo-excited electrons at BCB potential was higher than that of $\text{O}_2^{\cdot-}/\text{O}_2$ (-0.046 eV), thus the electrons possessed the ability to combine with O_2 into $\text{O}_2^{\cdot-}$. For the generation of $\cdot\text{OH}$, the holes at the TVB of $2\text{D-C}_3\text{N}_4$ cannot oxidize H_2O or OH^- into $\cdot\text{OH}$ due to the lower TVB position in comparison with $\text{OH}^-/\cdot\text{OH}$ (1.99 eV) and $\text{H}_2\text{O}/\cdot\text{OH}$ (2.38 eV). The $\cdot\text{OH}$ may be generated by the further reactions of strong reduction $\text{O}_2^{\cdot-}$ through an intermediate of $\cdot\text{OOH}$.⁵⁵⁻⁵⁷

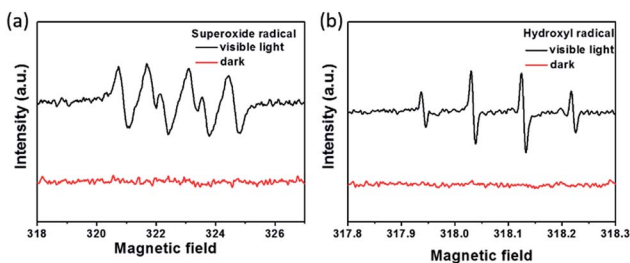


Fig. 8 (a) ESR spectra of $\text{DMPO-O}_2^{\cdot-}$ (a) and $\text{DMPO-}\cdot\text{OH}$ (b) adducts in $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ aqueous dispersion systems under visible light irradiation or in the dark.

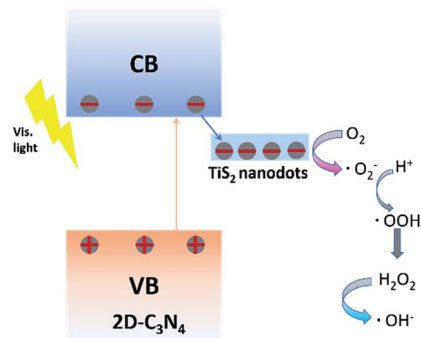


Fig. 9 The degradation of mechanism of as-prepared $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ composites.

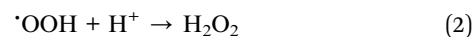


Fig. 9 is a schematic illustration of the synergistic effect of the photocatalytic process. In a typical photocatalytic degradation process, the $2\text{D-C}_3\text{N}_4$ nanosheets could photogenerated e-h pairs under visible light firstly. Afterwards, the electrons kept at conduction band would be efficiently trapped by metallic TiS_2 nanodots as co-catalyst. The high concentration of electrons could react with O_2 to form active radicals $\text{O}_2^{\cdot-}$. Due to the strong reduction of the photogenerated electrons, the formed $\text{O}_2^{\cdot-}$ also possessed very strong reduction which led to the further reactions and formation of $\cdot\text{OH}$ radicals through an intermediate of $\cdot\text{OOH}$ as listed from reaction (1) to (3). The radicals $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ were well known as effective radicals for water pollutant treatment. In addition, the hole at valence band of $2\text{D-C}_3\text{N}_4$ could oxidize pollutant directly. The metallic nature of TiS_2 nanodots and the construction of tight interface between the two components were beneficial for the separation and transfer of photo-excited carriers. Therefore, high concentration of photogenerated electrons could converge for photocatalytic reactions at TiS_2 nanodots instead of recombination at $2\text{D-C}_3\text{N}_4$ nanosheets.

Conclusion

We utilized a simple exfoliation synthesis to get ultrathin TiS_2 nanodots and the $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ was synthesized by a temperate solvothermal method. The TiS_2 nanodots were tightly anchored on the surface of $2\text{D-C}_3\text{N}_4$ nanosheets and the inherent metallic nature of 1T-TiS_2 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 TiS_2 nanodots in the prepared complex played a role in the RhB photocatalytic degradation. The 5% $\text{TiS}_2/2\text{D-C}_3\text{N}_4$ 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 $2\text{D-C}_3\text{N}_4$ nanosheets. So, the combination of ultrathin metallic TMDs with 2D graphitic C_3N_4 yields a promising photocatalyst for practical application.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is financially supported by the National Natural Science Foundation of China (NNSFC Grant No. 51422305, 21476097).

Notes and references

- 1 S. Cao, J. Low, J. Yu and M. Jaroniec, *Adv. Mater.*, 2015, **27**, 2150–2176.
- 2 H. Xu, L. Liu, X. She, Z. Mo, Y. Xu, L. Huang, Y. Song and H. Li, *RSC Adv.*, 2016, **6**, 80193–80200.
- 3 C. M. Fang, R. A. de Groot and C. Haas, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **56**, 4455–4463.
- 4 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
- 5 M. Zhu, C. Zhai, L. Qiu, C. Lu, A. S. Paton, Y. Du and M. C. Goh, *ACS Sustainable Chem. Eng.*, 2015, **3**, 3123–3129.
- 6 I. Hwang, I. Jeong, J. Lee, M. J. Ko and K. Yong, *ACS Appl. Mater. Interfaces*, 2015, **7**, 17330–17336.
- 7 H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri and J. Ye, *Adv. Mater.*, 2012, **24**, 229–251.
- 8 J. Li, X. Zhang, F. Raziq, J. Wang, C. Liu, Y. Liu, J. Sun, R. Yan, B. Qu, C. Qin and L. Jing, *Appl. Catal., B*, 2017, **218**, 60–67.
- 9 J. Shen, Y. He, J. Wu, C. Gao, K. Keyshar, X. Zhang, Y. Yang, M. Ye, R. Vajtai, J. Lou and P. M. Ajayan, *Nano Lett.*, 2015, **15**, 5449–5454.
- 10 M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh and H. Zhang, *Nat. Chem.*, 2013, **5**, 263–275.
- 11 Q. Lu, Y. Yu, Q. Ma, B. Chen and H. Zhang, *Adv. Mater.*, 2016, **28**, 1917–1933.
- 12 Y. Sang, Z. Zhao, M. Zhao, P. Hao, Y. Leng and H. Liu, *Adv. Mater.*, 2015, **27**, 363–369.
- 13 S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 2452–2456.
- 14 Y. Zhou, Y. Zhang, M. Lin, J. Long, Z. Zhang, H. Lin, J. C. Wu and X. Wang, *Nat. Commun.*, 2015, **6**, 8340.
- 15 J. Low, S. Cao, J. Yu and S. Wageh, *Chem. Commun.*, 2014, **50**, 10768–10777.
- 16 P. Yang, H. Ou, Y. Fang and X. Wang, *Angew. Chem.*, 2017, **129**, 4050–4054.
- 17 V. Subramanian, E. E. Wolf and P. V. Kamat, *Langmuir*, 2003, **19**, 469–474.
- 18 K. Awazu, M. Fujimaki, C. Rockstuhl, J. Tominaga, H. Murakami, Y. Ohki, N. Yoshida and T. Watanabe, *J. Am. Chem. Soc.*, 2008, **130**, 1676–1680.
- 19 S. Sakthivel, M. Shankar, M. Palanichamy, B. Arabindoo, D. Bahnemann and V. Murugesan, *Water Res.*, 2004, **38**, 3001–3008.
- 20 C. Han, Y. Lu, J. Zhang, L. Ge, Y. Li, C. Chen, Y. Xin, L. Wu and S. Fang, *J. Mater. Chem. A*, 2015, **3**, 23274–23282.
- 21 R.-B. Wei, P.-Y. Kuang, H. Cheng, Y.-B. Chen, J.-Y. Long, M.-Y. Zhang and Z.-Q. Liu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 4249–4257.
- 22 M. Sun, J. Hu, C. Zhai, M. Zhu and J. Pan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 13223–13230.
- 23 X. Pan and Y.-J. Xu, *J. Phys. Chem. C*, 2013, **117**, 17996–18005.
- 24 V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano and J. N. Coleman, *Science*, 2013, **340**, 1226419.
- 25 X. Huang, C. Tan, Z. Yin and H. Zhang, *Adv. Mater.*, 2014, **26**, 2185–2204.
- 26 H. Li, J. Wu, Z. Yin and H. Zhang, *Acc. Chem. Res.*, 2014, **47**, 1067–1075.
- 27 Z. Zeng, C. Tan, X. Huang, S. Bao and H. Zhang, *Energy Environ. Sci.*, 2014, **7**, 797–803.
- 28 C. Tan, Z. Zeng, X. Huang, X. Rui, X. J. Wu, B. Li, Z. Luo, J. Chen, B. Chen, Q. Yan and H. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 1841–1845.
- 29 P.-Y. Kuang, Y.-Z. Su, K. Xiao, Z.-Q. Liu, N. Li, H.-J. Wang and J. Zhang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 16387–16394.
- 30 D. Chu, C. Zhang, P. Yang, Y. Du and C. Lu, *Catalysts*, 2016, **6**, 136.
- 31 J. Chen, S. L. Li and Z. L. Tao, *J. Am. Chem. Soc.*, 2003, **125**, 5284–5285.
- 32 G. Guelou, P. Vaqueiro, J. Prado-Gonjal, T. Barbier, S. Hebert, E. Guilmeau, W. Kockelmann and A. V. Powell, *J. Mater. Chem. C*, 2016, **4**, 1871–1880.
- 33 U. Gupta, B. G. Rao, U. Maitra, B. E. Prasad and C. N. Rao, *Chem.-Asian J.*, 2014, **9**, 1311–1315.
- 34 W. Cui, J. Li, W. Cen, Y. Sun, S. C. Lee and F. Dong, *J. Catal.*, 2017, **352**, 351–360.
- 35 X. She, L. Liu, H. Ji, Z. Mo, Y. Li, L. Huang, D. Du, H. Xu and H. Li, *Appl. Catal., B*, 2016, **187**, 144–153.
- 36 X. She, H. Xu, Y. Xu, J. Yan, J. Xia, L. Xu, Y. Song, Y. Jiang, Q. Zhang and H. Li, *J. Mater. Chem. A*, 2014, **2**, 2563.
- 37 X. She, H. Xu, H. Wang, J. Xia, Y. Song, J. Yan, Y. Xu, Q. Zhang, D. Du and H. Li, *Dalton Trans.*, 2015, **44**, 7021–7031.
- 38 Q. Han, B. Wang, J. Gao, Z. Cheng, Y. Zhao, Z. Zhang and L. Qu, *ACS Nano*, 2016, **10**, 2745–2751.
- 39 H. Wang, Y. Su, H. Zhao, H. Yu, S. Chen, Y. Zhang and X. Quan, *Environ. Sci. Technol.*, 2014, **48**, 11984–11990.
- 40 G. Zhang, Z. A. Lan and X. Wang, *Angew. Chem., Int. Ed.*, 2016, **55**, 15712–15727.
- 41 Y. Cui, Y. Tang and X. Wang, *Mater. Lett.*, 2015, **161**, 197–200.
- 42 M. Zhu, C. Zhai, M. Sun, Y. Hu, B. Yan and Y. Du, *Appl. Catal., B*, 2017, **203**, 108–115.
- 43 Y. Wang, H. Wang, F. Chen, F. Cao, X. Zhao, S. Meng and Y. Cui, *Appl. Catal., B*, 2017, **206**, 417–425.
- 44 Y. Shang, X. Chen, W. Liu, P. Tan, H. Chen, L. Wu, C. Ma, X. Xiong and J. Pan, *Appl. Catal., B*, 2017, **204**, 78–88.
- 45 T. Y. Ma, Y. Tang, S. Dai and S. Z. Qiao, *Small*, 2014, **10**, 2382–2389.
- 46 S. Jeong, D. Yoo, M. Ahn, P. Miró, T. Heine and J. Cheon, *Nat. Commun.*, 2015, **6**, 5763.
- 47 S. J. Sandoval, X. K. Chen and J. C. Irwin, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **45**, 14347–14353.
- 48 X. Lu, Y. Jin, X. Zhang, G. Xu, D. Wang, J. Lv, Z. Zheng and Y. Wu, *Dalton Trans.*, 2016, **45**, 15406–15414.
- 49 J. Liu, H. Xu, Y. Xu, Y. Song, J. Lian, Y. Zhao, L. Wang, L. Huang, H. Ji and H. Li, *Appl. Catal., B*, 2017, **207**, 429–437.



- 50 R. J. Toh, Z. Sofer and M. Pumera, *J. Mater. Chem. A*, 2016, **4**, 18322–18334.
- 51 G. Dong, Y. Zhang, Q. Pan and J. Qiu, *J. Photochem. Photobiol., C*, 2014, **20**, 33–50.
- 52 X. Liu, N. Chen, Y. Li, D. Deng, X. Xing and Y. Wang, *Sci. Rep.*, 2016, **6**, 39531.
- 53 X. She, J. Wu, H. Xu, J. Zhong, Y. Wang, Y. Song, K. Nie, Y. Liu, Y. Yang, M.-T. F. Rodrigues, R. Vajtai, J. Lou, D. Du, H. Li and P. M. Ajayan, *Adv. Energy Mater.*, 2017, **7**, 1700025.
- 54 J. Yi, X. She, Y. Song, H. Xu, P. Zhang, Z. Mo, L. Liu, D. Du and H. Li, *RSC Adv.*, 2016, **6**, 112420–112428.
- 55 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96.
- 56 S. Yan, Z. Li and Z. Zou, *Langmuir*, 2010, **26**, 3894–3901.
- 57 Y. Cui, J. Huang, X. Fu and X. Wang, *Catal. Sci. Technol.*, 2012, **2**, 1396–1402.

