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The visible-light-sensitive titanate nanosheets were synthesized with Cr_2O_3 successfully loaded and well dispersed on (Cr(III)-TNSs) by one-step hydrothermal method for enhanced photocatalytic activity. As our previous reports, the asprepared samples obviously exhibited porous flake-like structure with large specific surface area (300-400 m²/g). Accompanied with the hydrothermal growth of TNSs, loaded Cr_2O_3 not only influenced the layered structure of TNSs, but also brought about remarkable enhancement on the visible-light response and the separation of photogenerated carriers. The XPS fitting results indicated that Cr ions mainly existed in trivalent forms and caused the change in binding states toward Ti and O. Based on the evaluation of photocatalytic activity, it was found that Cr(III)-TNSs obtained an significantly improvement for RhB and $K_2Cr_2O_7$ (Cr(VI)) degradation under visible-light irradiation, which was attributed to the retarding of charge recombination and the effective electron transfer from Cr_2O_3 to TNSs. The better photocatalytic activity was obtained with an optimal content (0.5 at.%) of Cr^{3+} , and the degradation rate (K_{app}) was 2.9-fold and 4.1-fold, respectively, as compared to TNSs. The samples were also evaluated by the photocatalytic R_{app} was 2.9-fold and 4.1-fold, respectively, as compared to TNSs. The results showed that the visible-light H₂ production rate of $Pt_{0.25}/Cr(III)$ -TNSs (0.25 wt.% of Pt) was observably enhanced under the efficient sacrificial agent/water system, giving a relatively high H₂ generation rate of 473 µmol $h^{-1} g^{-1}$ at 0.5 at.% of Cr^{3+} content. The cyclic tests demonstrated the nice stability and recycling performance of samples. The alternative mechanisms for the visible-light-sensitive photocatalytic activity were also proposed.

1. Introduction

TiO₂-based nanomaterials are well-known as an efficient photocatalyst owing to their great advantages containing low cost, strong oxidizing power, physicochemical stability and environmental friendliness.^{1,2} It has been commonly used in the researching fields of photocatalysis and solar energy conversion, especially in the removal of toxic pollutants from wastewater containing reactive dyestuff and heavy metal substances (e.g. Cr(VI), Pb(II), Hg(II) and As(III)) and the development of green power (e.g. hydrogen energy) in the case of global environment deterioration and energy crisis, which have been widely studied through lots of effort.^{3–5} As a typical researching object among these pollutants, dichromate (Cr(VI)) is highly water soluble in aquatic environment and has

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become a severe problem due to its toxicity, stubbornness and mutagenic nature, which can cause serious harm to human health such as carcinogenic disease and organic damage.^{6–8} X. Yuan et al. has reported the related work on the photocatalytic reduction of Cr(VI).^{9–11} By using the functionalized titanium metal-organic frameworks and decorated graphene composites as highly efficient photocatalysts, the visible-light assisted degradation of Cr(VI) as well as dye molecules was successfully achieved. When it comes to the photocatalytically splitting of water into H₂, many methods have been proposed and the deposition of noble metals as cocatalysts and the designing of composite semiconductors are commonly regarded as the effective and feasible ways for H₂ production.^{5,12}

However, it's difficult to utilize visible light due to its wide band gap of about 3.2 eV and the recombination of photoinduced electron and hole pairs is too fast in traditional TiO₂ materials.¹³ For this reason, much work has been done to improve its photocatalytic performance. Several ways, including design of nanostructure and morphology,¹⁴ coupling TiO₂ with sensitizing organic dyes or narrow band gap semiconductors,^{15,16} doping nonmetallic or metallic elements,^{17,18} and the modifications on the surface for TiO₂^{19,20} have been widely studied and paid to extend its photoresponse and improve its photoactivity. Although great

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enhancement has been made in visible-light response, improving the charge separation efficiency of TiO₂ still remains challenging. The fast recombination of photo-generated electrons and holes gives rise to the quenching of most of the excited charge carriers before they reach the surface and participate in the photocatalytic reaction. Based on the recent researches, it's noteworthy that some approaches of loading metal oxides or hydroxides on the surface of TiO₂ physically or chemically by introducing rare-earth or transition metal ions (Mn, Fe, Cr, Co, V, etc.) were regarded as the effective means for photocatalyst responding to visible light. These candidates are very promising for practical applications, especially for the photocatalytic degradation of organic or inorganic pollutants and the development of green energy under visible light irradiation.^{3,18,19} In contrast to a single component photocatalyst, the building of an interfacial heterostructure between supported semiconductor oxides and loaded metal oxide/hydroxide nanoparticles has shown a high separation efficiency of photogenerated charges and extensive light absorption by the approach of directly interface charge transfer (IFCT).^{21,23} According to some reports, the interfacial charge transfer efficiency is greatly dependent on the size of loaded particles.^{13,19,24} Hence, it's of great importance to develop the ways of loading appropriate-sized and highlydispersed metal oxide nanoparticles on TiO₂ photocatalyst for enhanced charge separation efficiency.

Among these 3d transitional metal ions (Cr, Mn, Fe, Co, V, etc.), chromium (Cr) appears to be a promising choose for TiO₂ owing to the unique properties for the supported chromium oxide species, including chemical states and coordination environment.^{25,26} There have been some reports clarifying the roles of these surface Cr oxide species during the redox reaction, particularly the decomposition of organic substrates.^{22,27} However, few researches are reported for supporting the degradation of pollutants and solar energy conversion under visible light irradiation. In addition, for chromium-modified materials, most of the work was supposed to incorporate chromium ions into the lattice using different methods, such as hydrothermal/solvothermal methods, chemical/physical vapor deposition, and ion implantation.^{28–30} In view of many reports regarding the substitution of metal ions for lattice sites, most of the photocatalysts are sensitive to visible light due to the localized narrow band newly-formed in their forbidden band, which originates from the d-orbitals of metal ions dopant.^{31,32} While the mechanism for obtained visible-light response by loading metal ions on the support surface is entirely different from that of doped materials. Irie et al.^{13,22} reported that the d-orbitals of grafted metal oxide species existed discretely on the TiO_2 surface, and it was proposed that the visible-light catalytic activity was arisen from directly interface charge transfer (IFCT) from d-orbital levels of metal ions to the conduction band (CB) of titania, as it was also demonstrated by the work group of Nolan.²⁴ This modified effect on the photocatalytic activity of TiO₂-based materials has been reported and exemplified combining DFT simulations and detailed experiments in their work. It had delivered a new coupling of molecule-scale metal oxides with

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TiO₂, as well as revealing the key effect of surface modification, which simultaneously promoted the absorption in visible-light region and charge separation. What's more, as the bimetallic compounds co-existing on the supported semiconductor have been studied to improve photocatalytic performance and facilitate water splitting successfully,^{33–36} it's spontaneously expected that the dispersion of a noble metal (Pt, Rh, Au) as cocatalyst on the basis of MO_x-loaded TiO₂ system (M = transition metal) would show a favorable performance in H₂ production by the synergistic effects of the photosensitizer (MO_x) and cocatalyst.

Herein, we reported a TiO₂-based titanate nanosheets (TNSs) loaded by trivalent chromium oxides (Cr₂O₃), which was prepared by a facile one-step hydrothermal treament in the alkaline environment. It had shown that the obtained TNSs, as two-dimensional (2D) nanosheets , possessed a large specific surface area, which was expected that more reactive sites were exposed and the introduced metal ions could spread easily and well disperse on the surface. Hence, more photogenerated electrons could fast transfer and reach the surface easily to involve in the photocatalytical reactions. In this work, we determined that the effects of the introduced Cr³⁺ ions and different amount of that on the visible-light response, separation of photo-generated carriers for Cr_2O_3 -loaded TNSs (Cr(III)-TNSs) by different characterizations. The enhancement on the photocatalytic redox activity by the degradation of Rhodamine B (RhB) and Cr(VI) in K₂Cr₂O₇ solution under visible light irradiation was demonstrated. Furthermore, it was also studied that the obtained TNSs photocatalysts combining Cr₂O₃ with Pt exhibited a synergistic effect for initiating the hydrogen evolution activated by visible light. The Pt/Cr(III)-TNSs in various proportions of Cr₂O₃ were fabricated by a simple photodeposition of Pt nanoparticles on the obtained sample surface. As Pt could serve as electron sink and active sites for proton reduction to H_2 ,³⁷ under the sacrificial agent/water system for this study, the Pt/Cr(III)-TNSs photocatalysts exhibited significantly enhancement on the efficiency of photocatalytic H₂ generation, which was due to the cooperation between the IFCT from photoactivated Cr₂O₃ and the electron sink of Pt. As mentioned above, it was demonstrated that Cr(III)/TNSs system functioned photocatalytically and exhibited excellent photocatalytic redox activity for its heterostructure formed at the interface. And it might find potential applications in water purification fields and efficient utilization and conversion of solar energy.

2. Experimental

2.1 Materials

P25 (TiO₂, 70% anatase, 30% rutile) was the product of Degussa Co., Ltd. The NaOH, HCl, ethyl alcohol (C₂H₅OH), acetone (C₃H₆O), phosphoric acid (H₃PO₄), 1, 5– Diphenylcarbohydrazide (C₁₃H₁₄N₄O), Cr(NO₃)₃·9H₂O, Rhodamine B (RhB), potassium dichromate (K₂Cr₂O₇), isopropanol (IPA), tert–butyl alcohol (TBA), triethanolamine (TEOA), 1, 4–benzoquinone (BQ) and potassium persulfate

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 $(K_2S_2O_8)$ were obtained from Sinopharm Group Co., Ltd, and chloroplatinic acid (H_2PtCl_6) was provided by Sigma-Aldrich Co., LLC. All of the reagents were analytically pure and utilized without further purification. Deionized water was used in all experiments.

2.2 Preparation of photocatalysts

Cr₂O₃-loaded TNSs (Cr(III)-TNSs) with various contents were obtained by hydrothermal method. 0.8 g P25 was dispersed in 50 mL of 10 M NaOH solution with vigorous stirring. Precalculated content of chromium nitrate solution was added slowly into the suspension. Under vigorous stirring for 40 min, the mixture was then transferred into 100 mL Teflon-lined autoclave and treated at 130 °C for 3 h. After the reaction ended, the autoclave was immediately cooled down to room temperature using cold water. The resultant white powders were then rinsed with deionized water until neutral condition was obtained, followed by pickling with proton exchanging in 200 mL HCl solution (0.1 mol/L). Finally, the powders were washed and collected with deionized water for several times and then dried at 70 °C for 12 h. The obtained samples were denoted as x-Cr-TNSs, where x (x = 0.1, 0.25, 0.5, 0.75, 1.0, 1.5% and 2.0%) represented $Cr(NO_3)_3$ concentration in the precursor solution. For comparison, the bare titanate nanosheets (TNSs) sample was synthesized in the same process without adding chromium source and the pure Cr₂O₃ sample was also prepared by a similar procedure as mentioned above without adding P25.

2.3 Photodeposition with Pt on photocatalysts

The Pt_{0.25}/Cr(III)-TNSs and Pt_{0.25}/TNSs samples were prepared by the impregnation of above-prepared Cr(III)-TNSs and bare TNSs powders (0.5 g) in 100 mL isopropanol aqueous solution (10 vol.%), mixing with 625 μ L of H₂PtCl₆ aqueous solution (2 g/L) to load 0.25 wt.% of Pt (weight ratio of Pt:TNSs) on the surfaces of samples. Before irradiation, the suspensions were sonicated in an ultrasonic bath and degassed in a vacuum system for 30 min. Then the reaction mixture was irradiated by UV illumination (300 W Xe lamp) for 3 h under vigorous stirring. After that, the precipitates were collected by centrifuge and repeatedly washed with deionized water and ethanol for several times. The resultants were finally dried at 65 °C for 12 h.

2.4 Characterizations of photocatalysts

The morphology and compositions of the as-prepared samples was characterized using scanning electron microscope (SEM) (SIRION, FEI, Netherlands) and high-resolution transmission electron microscopy (HRTEM) taken on JEM–2010 FEM. The BET specific surface area was measured by N₂ adsorption-desorption isotherms at 77 K using the instrument (JW–BK122W, China). The X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer (Bruker D8 advance) using Cu K α radiation. The result was obtained with a step of 0.02° in the range (2 θ) from 20° to 80° for the determination of phase composition of the samples. The Raman spectra were collected using a Horiba Lab RAM HR Raman spectrometer

ARTICLE with an excitation wavelength of 448 nm. UV-Vis diffuse reflectance spectroscopy (UV-vis DRS) of the samples was recorded on a Shimadzu UV-2550 spectrometer equipped with a BaSO₄-coated integrating sphere, using BaSO₄ as reference. X-ray photoelectron spectroscopy (XPS, Thermo Electron VG Multilab2000) was performed to analyze the component and chemical states of samples. The binding energies were referenced to the C 1s peak at 284.6 eV. The spectra were analyzed by the XPS Peak software. The fluorescence emission spectra (FL) were examined by a Hitachi FL 4600 instrument to

2.5 Photoelectrochemical measurements of photocatalysts

determine the separation efficiency of photo-generated

The photocurrent of samples was measured on an electrochemical workstation (CHI-660C Instruments, Chenhua, China) with a standard three-electrode system using the sample-coated electrode as the working electrode with an active area of ca. 1.5 cm^2 , a Pt wire as the counter electrode, and a calomel electrode as a reference electrode. A 300 W Xe lamp was used as light source and a cutoff filter was utilized to provide visible light ($\lambda > 420 \text{ nm}$), and 0.1 M Na₂SO₄ aqueous solution was served as the electrolyte. The working electrode was prepared as following steps: 0.01 g of the sample was dispersed in 1 mL ethanol and sonicated to make a slurry. After that, the slurry was coated onto a 2 cm × 1 cm indium tin oxide film-coated glass (ITO glass) by the spin-coating method. Next, the electrode was dried in an oven. All working electrodes to be measured had a similar film thickness.

2.6 Photocatalytic performance of photocatalysts

2.6.1 Evaluation of RhB solution

electron and hole pairs.

The photocatalytic activities of samples were assessed by the oxidative degradation of RhB solution (20 ppm). The light source was a 300 W Xe lamp with a cut-off filter (λ > 420 nm). The distance between the light source and the solution was 15 cm. Prior to the reaction, 100 mg of sample was put into 100 mL RhB aqueous solution (20 ppm). The reaction apparatus was placed in water bath to maintain at room temperature. The solution was under stirring in darkness for 1 h to achieve the adsorption-desorption equilibrium before the photocatalytic reaction, and then was irradiated under light source. The reaction was continually processed for 40 min. Every 5 min, 1.6 mL solution was collected and centrifuged to obtain the supernatant liquor at 12000 r/min for 3 min. Then 0.8 mL of supernatant liquor was mixed with 2.4 mL of deionized water and tested to determine the concentration of RhB in the solution by the UV-Vis spectrometer. Blank experiment was conducted without any photocatalyst to verify the photo-stability of RhB molecules. The stability and reusability of samples was also evaluated by repeating photocatalytic experiment, and five consecutive cycles were tested, each lasting for 70 min.

2.6.2 Evaluation of K₂Cr₂O₇ (Cr(VI)) solution

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The photocatalytic reduction of aqueous Cr(VI) to Cr(III) was performed in a 200 mL quartz reactor containing 100 mg photocatalyst and 100 mL of Cr(VI) aqueous solution at 20 ppm. The initial pH value of reactant solution was adjusted to 3.0 by adding HCl. The solution was stirred in darkness for 1 h to reach the adsorption-desorption equilibrium, and then irradiated for 120 min under a 300 W Xe lamp with a cut-off filter (λ > 420 nm). For every 20 min, 2 mL of solution was collected and centrifuged for 3 min to obtain the supernatant liquor at 12000 r/min for 3 min. The final testing sample was obtained by 1 mL of supernatant liquor mixing with 2.2 mL of deionized water. The Cr(VI) concentration of the testing solution was analyzed colorimetrically at 540 nm using the diphenylcarbazide method (DPC) by UV-Vis spectrometer. Blank experiment was carried out without any photocatalyst to verify the stability of Cr(VI). The stability and reusability of samples was also evaluated by repeating photocatalytic experiment, and five consecutive cycles were tested, each lasting for 120 min.

2.6.3 Evaluation of H_2 evolution

The photocatalytic H₂ evolution was carried out in a 500 mL top-irradiation quartz reaction vessel connected to an inclosed vitreous gas recirculation system. A 300 W Xe lamp was used as the light source and a cutoff filter was applied to generate visible light ($\lambda > 420$ nm). Typically, H₂ production was performed by dispersing 30 mg of catalyst in 50 mL aqueous solution of triethanolamine (TEOA) (10 vol.%) under magnetic stirring. Prior to the photoreaction, the system was vacuumized for 30 min to remove air and the dissolved oxygen completely. The reaction temperature was maintained at 6 °C through the cooling water circulation system and the accumulated amount of evolved gases was in situ monitored every 30 min interval using the gas chromatography equipped with a thermal conductive detector (TCD) (N₂ as the carrier gas, and 5 Å molecular sieve column).

3. Results and discussion

3.1 Structural characterization and morphology of photocatalysts

In this work, Cr₂O₃-loaded titanate nanosheets (Cr(III)-TNSs) heterostructural composites were synthesized by the facile hydrothermal strategy. To clarify the morphologies and microstructures of the as-synthesized samples, the SEM and high-resolution TEM (HRTEM) images of P25, bare TNSs and 2.0%Cr-TNSs were shown in Fig. 1. Compared with the granular structure of raw P25 materials, it was clearly observed that the samples displayed a flake-like and porous structure in Fig. 1 (bd). Raw P25 nanoparticles with high crystallinity could hardly be found in the SEM or HRTEM images (Fig. 1), revealing that most of the P25 nanoparticles had already transformed into titanate nanosheets during hydrothermal process at 130 °C for 3 h, which was in accordance with our previous reports.^{38,39} From Fig. 1 (e), it displayed the lattice fringes, which showed that the interplanar distance was ca. 0.54 nm and was corresponding to the (201) plane of H₂Ti₃O₇. Some researches suggested that the raw TiO_2 powders reacted with NaOH solution during the hydrothermal treatment and TiO_2 nanoparticles were stripped into thin lamellar fragments. With the exfoliation process developed, large amounts of Ti–O bonds were broken to form a highly disordered phase containing titanate nanocrystals. Then, the thin lamellar fragments jointed with each other and made larger planar nanosheets.^{40,41} As seen in Fig. 1 (e-f), the obtained

Cr(III)-TNSs did not possess well-developed lattice fringes and show other characteristic crystal clearly, indicating a very weak crystallinity. Only some low crystalline phases corresponding to chromium oxides could be found from the images of 2.0%Cr-TNSs. Some of them were overlapped with the H₂Ti₃O₇ phases. It was observed that these small quantity of fringes have spacings of 0.167 and 0.267 nm, which were in agreement with the spacings of the (116) and (104) planes of Cr_2O_3 , respectively,⁴² suggesting that the introduced Cr^{3+} ions were dispersed on the supporting TNSs surface in Cr₂O₃ forms with poor crystallinity due to the low proportion of Cr:TiO₂ and low temperature of treatment. The energy dispersive spectrometer (EDS) was measured to confirm the element compositions of samples. Besides Ti and O elements, Cr element was also observed from the EDS spectra (inset of Fig. 1 (d)), proving the existence of Cr element.

The effects of the Cr^{3+} ions on the specific surface area (S_{BET}) and pore structure of samples were measured by N_2 adsorption-desorption curves. Figure. 2 displayed the adsorption- desorption isotherms and pore size distribution plots for bare TNSs and x-Cr-TNSs (x = 0.1, 0.5%, 1.5%, 2.0%). It was clearly seen that all the samples exhibited a type-IV isotherm, indicating the existence of mesopores (2-50 nm) according to



Journal Name

Fig. 1. SEM images of (a) P25, (b-c) TNSs, (d) 2.0%Cr-TNSs; EDS spectra (inset) of (c) TNSs, (d) 2.0%Cr-TNSs; (e-f) HRTEM images of 2.0%Cr-TNSs.

the Brunauer-Deming-Deming-Teller (BDDT) classification. The corresponding hysteresis loops were type H3 at a relative pressure (P/P₀) range of 0.6-1.0, being representative for slit-shape pores.⁴³ The hysteresis loops was derived from the aggregation of flake-like titanate fragments. As seen from Table 1, the S_{BET} of bare TNSs was 375.6 m²/g using the Brunauer-Emmett-Teller (BET) method. Compared to the bare TNSs, the Cr(III)-TNSs samples possessed smaller surface area (S_{BET}), which decreased from 351.88 to 229.6 m²/g with the incremental Cr³⁺ content. Under the hydrothermal treatment, Ti–O–Na bonds in the alkali-treated specimen formed and then the proton



Fig. 2. The N₂ adsorption/desorption isotherms and the corresponding pore size distribution curves of x-Cr-TNSs (x = 0%, 0.1%, 0.5%, 1.5% and 2.0%).

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Table 1	The textual	properties a	and structural	parameters of a	samı
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Sample	S ^a BET (m ² /g)	D ^b _{Pore} (nm)	V ^c _{Pore} (cm ³ /g)	V ^d _{FWHM} (cm ⁻¹)
TNSs	375.60	10.81	1.05	16.37
0.1%Cr-TNSs	351.88	9.38	0.85	16.09
0.25%Cr-TNSs	311.18	9.42	0.76	15.21
0.5%Cr-TNSs	282.12	10.67	0.80	14.91
0.75%Cr-TNSs	291.98	11.12	0.85	14.48
1.0%Cr-TNSs	259.74	10.70	0.72	14.19
1.5%Cr-TNSs	273.25	10.06	0.71	14.04
2.0%Cr-TNSs	229.60	9.92	0.59	13.61

^a The specific surface area

^b The average pore diameter

^c The total pore volume

^d The FWHM of Raman peak (the predominant mode in anatase phase)

exchange of Na⁺ by H⁺ took place during the rinsing and acid pickling, thus resulting in flake-like particles, which were believed to be the layered titanate structures and each layer was connected by the edge-sharing octahedral $\text{TiO}_{6}^{.41}$ However,

the process might somewhat be influenced by the Cr^{3+} brought into the reaction system. On account of their high octahedral stabilization energy, the Cr³⁺ ions would be expected to occupy the octahedral sites.⁴⁴ Thus, it was assumed that a portion of the introduced Cr³⁺ ions had a chance to replace Ti⁴⁺ or occupy in the octahedral sites of TiO_6 and stabilize at the interface between the titanate layers and solution by forming Ti-O-Cr bonds. Notably, the hysteresis hoops observed in Cr(III)-TNSs showed a lower absorption than bare TNSs at higher range $(0.80 < P/P_0 < 0.99)$, indicating the decrease of the stacking pores and the piled nanosheets in Cr(III)-TNSs. Consequently, the junctions between the titanate layers were probably changed, which would promote the interlaminar connection and inhibit the exfoliation of the single nanosheets from the lamellar titanate, leading to the decrease in S_{BFT} of Cr(III)-TNSs. The result was also confirmed by the distribution curves of pore diameter and the pore volumes (Table 1). Meanwhile, all the samples exhibited an uniform average pore size with similar distribution (estimated using the adsorption branch of the isotherm). These results illustrated that the introduction of Cr³⁺ ions did not significantly change the textural properties of TNSs. Such open mesoporous architecture with large surface area and connected pore-system played an vital role for its being able to improve the transport of reactants and products.

The XRD patterns of bare TNSs and Cr(III)-TNSs were shown in Figure. 3. All the samples showed the observed diffraction patterns attributed to anatase-rutile mixed phase of TiO_2 (JCPDS No. 65-5714 and JCPDS No. 65-1119). The broadened shapes and relatively weak intensities of characteristic peaks revealed the poor crystallinity after treatment. During the hydrothermal process, the crystalline phase of P25 precusor was broken and subsequently a highly disorder structure was formed. From the XRD results, only relatively weak characteristic peaks of titania were observed, implying that few P25 powders were residual and most of them were transformed to titanate nanosheets (TNSs) with poor crystallinity. Notably, the titanate nanosheets



Fig. 3. XRD patterns of P25, TNSs and the spectra (inset) of x-Cr-TNSs (x = 0.0%, 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, 1.5% and 2.0%).

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were exfoliated under low reaction temperature (130 °C) before the transformation of layered titanate from nanosheet to nanotube. Comparing the positions and intensities of the diffraction peaks in all cases, it could be found that different concentrations of Cr^{3+} showed negligible influences on the phase structure of TNSs. Furthermore, no other peaks corresponding to chromium oxide or hydroxide species were found in Figure. 3 due to their low content and relatively weak crystallization. Thus, it was inferred that these Cr^{3+} ions were in amorphous oxide form and uniformly dispersed on the surface of TNSs.

To further investigate the surface structure of Cr(III)-TNSs, Raman spectra were tested. As shown in Figure. 4, all samples displayed similar peak positions. The predominant peaks identified at 146 cm⁻¹ (E_g), broad bands around 400 cm⁻¹ (E_g), 510 cm⁻¹ (E_g) and 640 cm⁻¹ (E_g) were corresponding to vibration modes of anatase phase, while a broad band around 448 cm⁻¹ (E_g) was assigned to rutile phase.⁴⁵ The overlapped vibration peaks of 456 cm⁻¹ and the Raman peaks at 268 cm⁻¹ were attributed to the broken symmetry in the bent TiO₆ layers and the presence of the 2D lepidocrocite-type TiO₆ octahedral layers, respectively, suggesting the presence of titanate.¹

As can be seen from the spectrum, with increasing amounts of Cr³⁺ from 0% to 2.0%, obvious enhancement and decreased FWHM could be observed at 146 cm⁻¹ as the dominating vibration mode of anatase structure. The result indicated that the introduction of Cr³⁺ had a non-negligible impact on the Ti-O lattice of TNSs. Considering the results from N₂ adsorption/desorption measurement and XRD analysis, it was deduced that the newly-formed Cr_2O_3 were loaded on the surface of TNSs by Ti-O-Cr bonds during the hydrothermal treatment, inducing a possible change in polarization of the Ti-O lattice, leading to the enhancement of Raman peaks.⁴⁶ From the main peaks 147 cm⁻¹ (anatase phase), it was also proved by the slightly shift of vibrational frequency with the attachment of Cr₂O₃ to the TNSs surface by Ti–O–Cr bonds.^{35,47} For the samples with 0.1-2.0 mol.% of Cr³⁺, Raman spectra didn't show any peak ascribed to Cr-O bending or stretching modes owing to the much smaller quantity and size of Cr_2O_3 than those of TNSs, indicating that the loaded Cr₂O₃ was welldispersed on the surface. The results were also consistent with electron microscope and XRD analysis.



Fig. 4. Raman spectra of x-Cr-TNSs (x = 0.0%, 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, 1.5% and 2.0%).

The surface chemical compositions and bonding states of x-Cr-TNSs (x = 0.5% and 2.0%) samples were systematically investigated by XPS analysis and compared with those of bare TNSs. The fully scanned spectra (Fig. 5 (a)) for Cr(III)-TNSs showed that Cr element existed in the samples besides Ti, O and C elements, while the C element should be assigned to impurities from air and the C 1s peak around 284.6 eV was used for calibration. The XPS results with the areas corresponding to the binding energies for the Ti 2p, O 1s and Cr 2p regions were analyzed. From Fig. 5 (c), the Ti 2p core level spectra for bare TNSs displayed two spin-orbit splitting peaks observed at ~458.5 eV and ~464.2 eV, which were assigned to $Ti^{4+} 2p_{3/2}$ and $Ti^{4+} 2p_{1/2}$, respectively, while for 2.0%Cr-TNSs (or 0.5%Cr-TNSs), the asymmetric Ti 2p spectra showed similar peak positions of Ti⁴⁺ compared with those for bare TNSs and could be fitted into two components of Ti³⁺ (457.5 eV and 463.1 eV) and Ti⁴⁺ (458.5 eV and 464.1 eV). It could be observed that the loading of Cr₂O₃ caused the generation or distinct increase of Ti³⁺. Since XPS was a measurement technique mainly for surface characterization, it could be deduced that most of Ti³⁺ might distribute in the surface layers of TNSs. And Ti³⁺ was regarded as the favorable state for the photocatalytical performance.⁴⁸ During the hydrothermal treatment, the reduction of Ti⁴⁺ probably happened in the delamination and growth process of titanate nanosheets, accompanied with the loading of Cr³⁺ and the formation of Cr_2O_3 , implying that the local chemical states of external titanium ions were slightly influenced by the Cr³⁺ ions attached to the surface layers of TNSs. As shown in Fig. 5 (c), the broad and asymmetric O 1s signals for both bare TNSs and Cr(III)-TNSs were fitted into one peak centered at ~530 eV assigned to O²⁻ ion of Ti–O bonds within TNSs, and a shoulder located at ~531 eV, illustrating the presence of plentiful surface hydroxyl groups or chemisorbed H₂O molecules.⁴⁹ When trivalent chromium species hybridized with superficial reactive



Fig. 5. XPS spectra for (a) survey spectrum; (b) Ti 2p region; (c) O 1s region; (d) Cr 2p region of TNSs, 0.5%Cr-TNSs and 2.0%Cr-TNSs.

sites of TNSs, the O 1s core level spectra for Cr(III)-TNSs exhibited two new peaks at ~529 eV (Cr-O) and ~530.5 eV (Ti-O-Cr), suggesting that the Cr³⁺ ions mainly existed on the surface as oxides by the attachment of Ti-O-Cr bonds to the interface between TNSs and chromium oxides.⁵⁰ Fig. 5 (d) showed that the XPS spectra of Cr 2p regions for Cr(III)-TNSs (0.5%Cr-TNSs and 2.0%Cr-TNSs). Compared to individual Cr₂O₃ as reference, the Cr(III)-TNSs samples exhibited a similar trend for Cr 2p core level spectra. For the Cr(III)-TNSs samples, the dominant peaks at around 577 and 586.5 eV should be ascribed to Cr $2p_{3/2}$ and Cr $2p_{1/2}$, respectively, indicating the presence of Cr³⁺ loaded as Cr₂O₃ structure.⁵¹ In addition to a slight amount of hexavalent chromium ions (~580.3 eV) found in Cr(III)-TNSs by curve fitting in the Cr 2p spectra, a wide shoulder peak located at lower binding energies (~578.6 eV) was clearly observed, suggesting that a trace of chromium ions existed with one or more valence states which were higher than the valence of Cr³⁺. Thus, it was concluded that some Cr³⁺ might mostly transform into higher valence and remain excited states by releasing the photo-induced electrons through the Ti-O-Cr bonds. Through this interfacial charge transfer approach, the change in the electronic states of Cr³⁺ consequently caused the broadening and a shift to the higher binding energy of Cr³⁺ 2p signal peaks. As Cr₂O₃ and CrO₂ were both regarded as the thermodynamically stable oxides, the peak of Cr 2p_{3/2} observed at ~575 eV should be assigned to a tetravalent chromium ion in CrO₂ chemical environment.⁵²

3.2 Optical response and photochemical properties of bare TNSs and $\rm Cr_2O_3\mathchar`-loaded$ TNSs samples

As the optical absorption properties were very important to photocatalytical activity, bare TNSs and Cr(III)-TNSs were tested by the diffuse reflectance UV-Vis spectroscopy. As can be seen from the Fig. 6, bare TNSs showed only the absorption in UV region with a cutoff wavelength at ~400 nm which corresponded to the interband transition of TiO₂. As for Cr(III)-TNSs, the spectra exhibited the absorption from 620 nm to 800



Fig. 6. UV-Vis diffuse reflectance spectra of reference Cr_2O_3 , as-prepared bare TNSs, and Cr_2O_3 -loaded TNSs with various molar ratio of Cr^{3+} .

nm and one absorption shoulder at ~450 nm, as well as the onset of absorption at ~400 nm. As a reference, the similar trend of Cr_2O_3 absorption was also consistent with the previous study.²⁶ Besides the intrinsic band of Cr₂O₃, the broad absorption band in the range of 600~800 nm was assigned to the ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ d–d transition of Cr³⁺ in an octahedral surroundings. For individual Cr2O3, the large absorption peak at ~450 nm could be assigned to ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ of Cr³⁺ in an octahedral environment.²² Note that, as for all the Cr(III)-TNSs samples, the newly-formed dominant peaks were exhibited by Cr₂O₃ except for the absorption from interband transition of TiO_2 . And with increased loading amount of Cr_2O_3 , the absorption intensity at these new regions enhanced and the initial absorption edge at ~480 nm was gradually bathochromic shift to ~540 nm (inset) for the absorption of Cr₂O₃ aroused by the charge transfer from 3d sub-band of Cr₂O₃ to the conduction band (CB) of TNSs. The formation and tailing of new adsorption shoulder demonstrated that the excited electrons of Cr^{3+} were transferred to the CB of TiO₂ via the approach of direct IFCT (Interface Charge Transfer) during the photocatalytic reaction. The newly-formed and extended absorbance of samples in the visible region suggested that the visible-light photoactivity of Cr(III)-TNSs could be remarkably improved.

Figure. 7 showed the fluorescence (FL) emission spectroscopy of bare TNSs and x-Cr-TNSs samples (x = 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, 1.5%, 2.0%). It could be observed that the intensities of FL emission peaks for Cr(III)-TNSs samples were lower than that for bare TNSs (Fig. 7 (a)). In addition, with the increase in loading amount of Cr₂O₃, the FL emission intensity initially declined, and then increased instead when reaching the minimum value for 0.5%Cr-TNSs (Fig. 7 (b)). It was reported that the FL emission spectrum was the result from the recombination of photo-generated electron-hole pairs, the lower FL emission intensity indicated a lower recombination rate ⁵³. Therefore, the decline in FL intensities for Cr(III)-TNSs samples was attributed to the decreased number of recombination of electron-hole pairs, indicating the enhanced separation efficiency for photo-induced carriers. The

ARTICLE

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 Cr_2O_3 -loaded TNSs led to the effective quenching of the photoluminescence with different efficiencies. Consequently, it was deduced that the Cr_2O_3 loaded on TNSs surface with appropriate amount would act as traps to capture the photo-induced electrons, and thus enhanced the charge separation efficiency, which suggested the enhancement of photocatalytic activity; whereas excess loading Cr_2O_3 would result in agglomeration and serve as recombination centers during the reactions, leading to the decrease of photocatalytic efficiency.



Fig. 7. (a) Fluorescence spectra of TNSs and Cr_2O_3 -loaded TNSs using an exicitation of 300 nm; (b) fluorescence intensity at 452 nm and 468 nm as a function of loaded amount.

The photocurrent transient measurement method was used to further examine the photoelectrochemical properties of the samples and the results were shown in Figure 8. According to the photocatalytic evaluation and PL results, it was found that the promotion effects of Cr₂O₃ on the photo-activity of TNSs were quite evident. Steady-state photocurrent responses of Cr(III)-TNSs exhibited higher current density than that of bare TNSs (Fig. 8 (a)), implying that the enhanced visible-lightharvesting abilities and higher charge transfer efficiency in Cr(III)-TNSs.⁵⁴ When the introduced content of Cr³⁺ was 0.5 at.%, the current density was improved dramatically, which was in agreement with the high photocatalytic degradation rates of the 0.5%Cr-TNSs for RhB and Cr(VI). When a contrast was made between the Cr₂O₃-loaded TNSs and mechanical mixed Cr₂O₃&TNSs samples, the Cr₂O₃-loaded TNSs samples displayed a much higher current density (Fig. 8 (b)), suggesting that the loaded Cr₂O₃ was well dispersed on the TNSs with superior interfacial contact.



Fig. 8. Surface photocurrent curves for the photoelectric behavior of (a) TNSs and Cr_2O_3 -loaded TNSs; (b) Cr_2O_3 -loaded TNSs and Cr_2O_3 -TNSs mixed samples (the Cr:TiO₂ ratios of 0.5% and 1.0% were chosen).

3.3 Evaluation of visible-light photocatalytic activities

3.3.1 Photocatalytic degradation of RhB and Cr(VI)

The visible light photocatalytic activities of all samples were evaluated by the degradation of RhB (20 mg/L) and Cr(VI) (20

mg/L) aqueous solutions, respectively, as shown in Fig. 9. The blank tests without any catalysts showed that RhB and Cr(VI) were relatively stable and the photolysis process was negligible. It could be clearly observed that the degradation efficiencies of TNSs for RhB and Cr(VI) were both greatly enhanced after loading with Cr₂O₃. When the loading amount of Cr^{3+} was relatively low (≤ 0.5 at.%), the degradation rate continually enhanced with the increase of loading amount, and 0.5%Cr-TNSs showed the best photocatalytic efficiency and activity among these samples. However, with further increase in the Cr³⁺ content, the degradation efficiency decreased instead. For RhB degradation, the reaction curves and reaction rate histograms corresponding to the first-order kinetic equation $(\ln(C_t/C_0) = -K_{app}t)$ were directly observed from Fig. 9 (a) and Fig. 9 (c), respectively, where $K_{\mbox{\tiny app}}$ was the apparent rate constant, C_{0} was the initial concentration of solution, \boldsymbol{t} was the reaction time, and C_t was the concentration of solution at the reaction time of t. The visible-light degradation rate (K_{app}) of 0.5%Cr-TNSs was 2.9-fold as compared to bare TNSs.

Moreover, the photocatalytic reduction of toxic Cr(VI) in K₂Cr₂O₇ aqueous solution was also investigated as typical heavy metal pollutants under visible light irradiation. It was well known that the pH value of reaction medium also play a crucial role in the photo-reduction of Cr(VI). The effect of the solution pH on the photocatalytic reduction of Cr(VI) was investigated for 0.5%Cr-TNSs sample and the photocatalytic reduction efficiency and reaction rate at different pH values under visible light were shown in Fig. S4 (a-b). It could be observed that the lower pH could significantly improve photocatalytic reduction of Cr(VI), and the higher reaction rate reached 19.89×10^{-3} min⁻¹ at pH = 1, while the reaction rate was only 0.82×10^{-3} min⁻¹ at pH = 9. Thus, the higher efficiency in Cr(VI) degradation would be expected at lower pH due to the existence of abundant H⁺.³ Here the photocatalytic activities of various Cr₂O₃-loaded TNSs were evaluated by controlling the initial pH = 3 in the solution. From Fig. 9 (a) and Fig. 9 (c), similarly, the reaction curves and reaction rate histograms for Cr(VI) degradation were conform to the first-order kinetic equation $(\ln(C_t/C_0) = -K_{app}t)$. Under visible light irradiation, the photo-degradation rate (K_{app}) of 0.5%Cr-TNSs was 4.1-fold as compared to bare TNSs. Thus, for both the photocatalytic oxidation of RhB and the reduction of Cr(VI), it was confirmed that appropriate loading amount of Cr₂O₃ definitely enhanced the photocatalytic activity of TNSs a lot, whereas when the excess amount was introduced, at the least, the photodegradation rate declined, which was unfavourable for the enhancement of photocatalytical

8 | J. Name., 2012, 00, 1-3

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Fig. 9. Visible-light photocatalytic performance evaluation of TNSs and Cr_2O_3 -loaded TNSs: photocatalytic degradation of (a) RhB and (b) Cr(VI); reaction kinetics (ln (C/C_0) = $-K_{app}t$) of (c) RhB and (d) Cr(VI); reaction rate constant (K_{app}) values of (e) RhB and (f) Cr(VI) under visible-light irradiation. The initial concentrations of RhB and Cr(VI) were both 20 ppm. The initial pH of RhB and Cr(VI) solution were 7.0 and 3.0, respectively.

performance. It could be ascribed to the agglomeration of Cr₂O₃, leading to the decrease of interfacial charge transfer efficiency. The photocatalytic performance was just consistent with the result from the FL emission and photocurrent spectra. Furthermore, for Cr(III)-TNSs system, the formed heterostructure of binary oxides was much more favorable for the degradation of pollutants and the enhancement on visiblelight catalytic activity as compared to single semiconductor oxides. Meanwhile, as shown in Fig. 10, the photo-degradation of RhB and Cr(VI) were both monitored over five cycles by using 0.5%Cr-TNSs sample for evaluating the photocatalytic stability under the same conditions. Since regeneration and reuse of photocatalyst played an important role on its practical application, the sample after the adsorption-photocatalysis process was treated with desorption and regeneration for the reuse of next cycle test during the every cycle of Cr(VI) reduction. In a series of processes of adsorption (Ads), desorption (Des) and regeneration (Reg), Fig. S1 and S2 showed the further characterization of different-stage samples in the whole cycles by XRD, Raman and XPS analysis. And the results exhibited the good stability of recovered sample. The sample reused for the cycle test of RhB degradation was also treated by the regeneration step. The photodegradation rates almost retained constantly and didn't exhibit any significant decline during the five consecutive cycles. Even after the cyclic performance tests for the degradations of RhB and Cr(VI), the Ti and Cr 2p XPS spectra, XRD patterns and Raman spectra of the testing sample were also investigated, respectively. As

shown in Fig. S3 (a-b), as compared to the pristine sample, it could be clearly observed that the sample remained almost the same structure even after the five cyclic photocatalytic tests, and the influence on the structure of the sample was negligible during the reaction. In addition, confirmed by the fitting results (Fig. S3 (c-d)) and the elemental analysis (Table S1) from XPS spectra, the chemical states and contents of Cr and Ti almost retained constant after the photocatalytic reactions by turns, demonstrating that the as-prepared Cr_2O_3 -loaded TNSs photocatalyst possessed excellent photocatalytic stability and reusability under visible



Fig. 10. Cyclic performance testing for RhB solution (a); Cr(VI) solution (b) in the Cr_2O_3 -loaded TNSs system. The recycle stability of photocatalytic efficiency for RhB solution and Cr(VI) solution was tested using the 0.5%Cr-TNSs sample.

light irradiation.

3.3.2 Photocatalytic H₂ generation

It was commonly recognized that the nanosize metal as cocatalyst, such as Pt, Au and Pd, promoted the catalytic efficiency due to the build-up Mott-Schottky barrier, which faciliated the charge transport and had the lower overpotential for hydrogen-production reaction kinetics.^{36,55} Here the as-prepared TNSs were employed as the supporting material for Pt loading by photodeposition in this work.

Since Pt was known as the most effective cocatalyst in achieving water splitting, the effect of Pt depositing on TNSs was investigated. Fig. 11 (a-b) exhibited the photocatalytic hydrogen evolution test over TNSs and Cr(III)-TNSs with Pt (0.25 wt.%) via in-situ photodeposition. As expected, when 0.25 wt.% of Pt was loaded on the bare titanate nanosheets, the activity of the metal/nanosheets for photocatalytic hydrogen evolution showed an unnegligible enhancement. Compared with the Pt_{0.25}/TNSs, the samples with the identical content of Pt (Pt_{0.25}/x-Cr-TNSs, x = 0.1%, 0.25%, 0.5%, 0.75%, and 1.0%) exhibited a remarkable enhancement on the H_2 generation rate, and $Pt_{0.25}/0.5\%$ Cr-TNSs showed the relative high performance, giving the H_2 evolution rate of ~473 µmol h g^{-1} . When the loading content of Cr_2O_3 further increased, the H_2 production efficiencies of the samples ($Pt_{0.25}/x$ -Cr-TNSs, x = 1.5% and 2.0%) decreased instead. Nevertheless, the Ptdeposited Cr(III)-TNSs



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Journal Name

ARTICLE

Fig. 11. Visible-light photocatalytic H₂ evolution of platinized TNSs and Cr₂O₃-loaded TNSs: (a) accumulative amount of H₂ evolution; and (b) H₂ evolution rate of Pt_{0.25}/TNSs and Pt_{0.25}/x-Cr-TNSs (x = 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, 1.5% and 2.0%); (c) Cyclic performance tests for H₂ evolution were conducted using Pt_{0.25}/0.5%Cr-TNSs sample.

with an appropriate proportion of Cr₂O₃ still could bring about a significant enhancement on the H₂ generation rate compared with the $Pt_{0.25}$ /TNSs, which implied that the optical response of Cr₂O₃ in the TNSs must play a crucial role in the photocatalytic H₂ production. It was demonstrates that the loaded Cr₂O₃ was a good photosensitizer with a slight amount of Pt deposited as the co-catalyst for the design of high-performance photocatalysts. In addition, the photocatalytic stability of Pt_{0.25}/0.5%Cr-TNSs was also demonstrated for H₂ evolution (Fig. 11 (c)). In each cycle, the system was deaerated by evacuation before the next test to make sure there was no residual gas, and the process was same as the photocatalytic H₂ evolution mentioned above. In the first two run, there was a slight decline in the total ${\rm H}_2$ production, which was 40.4 μmol and 39.1 $\mu mol,$ respectively, a little less than that of original materials (42.6 µmol). However, even after five cycles, the high photocatalytic performance was mostly retained at around 38.5 μ mol in the total H₂ production, demonstrating a good stablility and reusablity. As the catalyst was repeatedly used for cyclic test, the decrease of H₂ evolution rate might be mainly due to the consumption of sacrificial reagents and the influence of intermediate products during the reaction. Compared with some catalysts using organic and organometallic molecules as photosensitizers, the Pt/Cr-TNSs resulted from the loading of Cr₂O₃ as photosensitizer was superior in terms of stability, and the nice reusability of platinized Cr(III)-TNSs (0.25 wt.% Pt) indicated a firm attachment of Pt nanoparticles to the TNSs surface.

4. Discussion on the mechanism for the enhanced photocatalytic activity of Cr₂O₃loaded TNSs

4.1 Photocatalytic degradation of RhB and Cr(VI)

In order to get insights into the photocatalytic mechanism of heterostructural Cr(III)/TNSs system, capture experiments were conducted by introducing different trapping agents to investigate the reactive radicals involved in the reaction process of RhB and Cr(VI) degradation, respectively. The detailed experiments were the same as the photo-degradation experiments mentioned above. In the experiments, tert-butyl alcohol (TBA), triethanolamine (TEOA) and 1, 4-benzoguinone (BQ) were employed as the hydroxyl radical (OH \cdot), hole (h⁺) and superoxide radicals (O_2) scavengers for RhB degradation, respectively. And triethanolamine (TEOA) and potassium persulfate $(K_2S_2O_8)$ were used as hole (h^+) and electron (e^-)



Fig. 12. Capture experiments by introducing dif photocatalytic degradation process of RhB (a); and C system. The capture experiments were performed usir

scavengers for Cr(VI) degradation, r displayed the results of the capture e TNSs sample. It was clearly photodegradation of RhB was almost presence of TBA, suggesting that OH· v specie. While with the addition of BQ the degradation efficiencies of RhB bo And it further displayed that the photo was most greatly suppressed in the scavenger. This revealed that O_2^- a dominant active species in the p determining photoactivity for the vis based titanate nanosheets with loaded the reduction of Cr(VI), the addition o could significantly enhance the phot 0.5%Cr-TNSs sample, while the degr decreased with the addition of elect Since the presence of TEOA as a hole the recombination of photogenerated an electron scavenger could consum electrons, which inhibited the photo results confirmed that the photoger dominated in the photocatalytic reduct

To explain the enhancement of the activity and better understand the structures of Cr₂O₃ and TNSs were inv absorption and XPS valence band sp possible energy level diagram for the transfer of Cr₂O₃/TNSs heterostructure



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Fig. 13. (a) Tauc plots of as-prepared bare TNSs, x-Cr-TNSs (x = 0.5% and 2.0%) and (inset) Cr₂O₃ for the estimation of optical band gap. The intercepts of the linear part well fit to the experimental data (α = 0) gave the values of the fundamental band gap and the transition band gap; (b) XPS valence-band spectra recorded for the as-prepared bare TNSs and Cr₂O₃. The intercepts of the linear part well fit to the experimental data gave the valence band positions.

RhB and Cr(VI) was schematically illustrated in Scheme 1 (a). The intrinsic band gap energy for TNSs (n-type semiconductor) was found to be 3.17 eV from the absorption edge of TNSs (Fig. 13 (a)). The valence band edge measured from the XPS spectra for TNSs was positioned at about 2.98 eV (Fig. 13 (b)) and the conduction band edge of TNSs was consequently determined at -0.19 eV. While Cr_2O_3 was a p-type extrinsic semiconductor at low temperature,⁵⁸ and the predominant d-d transition band gap was valued at ~2.35 eV except for the intrinsic band of Cr₂O₃. According to the XPS valence band spectra, the E_{VB} level for Cr_2O_3 standed at ~2.33 eV (vs. NHE), which was in good agreement with that as reported.⁵⁸ While the potential of the Cr^{III}/Cr^{IV} redox couple (E⁰) was reported to be 2.1 eV.²² Thus, the energy gap (E_g) between the TNSs E_{CB} and the $Cr_2O_3 E^0$ was 2.29 eV, corresponding to the light energy of wavelength (λ = 540 nm) by the equation: λ = $1240/E_g$. And it was in good agreement with the result of photocurrent action on the significant enhancement under visible light with wavelength above 420 nm (≤ 540 nm). This indicated that the high energy electrons of Cr₂O₃ could be induced at wavelength shorter than 540 nm and then transfered thermodynamically to the CB of TNSs. Hence, the visible-light ranged from 420 to 540 nm wavelength was beneficial to the directly interfacial transfer of high energy electrons from the d-orbital energy level (E^0) of Cr₂O₃ to the CB of TNSs. Interestingly, the similar effect of surface modification on the photocatalytic activity of TiO₂-based materials had been reported and exemplified with the combination of theoretical simulations and detailed experiments by the group of M. Nolan.²⁴ This report had delivered new coupling of molecular scale metal oxides and TiO₂, as well as revealing the key effect of surface modification aroused by the formation of new interfacial Metal-O-Ti bonds, e.g., band gap modification and charge carrier localization, which would promote both the visible-light response and charge separation. The new routes of charge transfer would be generated by the dispersed 3d orbitals of Cr₂O₃ forming new bonds (Ti-O-Cr) to the surface of TNSs in the status of heterostructure, resulting in strong electronic coupling. In general, it could be deduced that when the heterostructure was formed between TNSs and Cr₂O₃, an electric field tended to form at the interface. In the equilibrium state of the hetero-structural interface, negative charges appeared on the side of p-type Cr₂O₃ while positive ones aggregated on the n-type TNSs caused by the formed interfacial electric field. Thus, it could be deduced that the photo-induced high energy electrons produced from the 3d sub-band of Cr₂O₃ could transfer thermodynamically to the CB of TNSs through interface electric field. However, for single Cr_2O_3 , these visible-light excited electrons in the Cr^{IV} excited state were easily relaxed to the ground state (Cr^{III}) in extremely short period, leading to the high recombination rate for photogenerated carriers. Hence, in the present of $Cr_2O_3/TNSs$ system, the charge separation and photocatalytic activity were remarkably enhanced, which was consistent with the PL spectra and photocurrent results.

Under visible light irradiation, these photo-excited electrons transferred from 3d-orbital energy level of Cr₂O₃ nanoparticles into the CB of TNSs, and then the redox of Cr^{III} - Cr^{IV} occurred [Eqs. (1)-(2)]. Combined with the results of trapping experiments, as the Cr^{IV} excited state with highly active holes (h⁺) generated by IFCT contributed to oxidation, it was deemed that the more negative the redox potential of the reductant, the more active for its oxidation. Thus, the newly-formed Cr^{IV} possessing strong oxidative ability were supposed to oxidize substrates and return to the initial and stable ground state Cr^{III}. Simultaneously, by the approach to direct IFCT, these activated electrons gathering in the CB of TNSs were captured by O₂ molecules, or involved in the fast reduction reaction with substrates directly [Eqs. (3)]. The majority of them were directly reduced to form O_2^{-1} radical anions through oneelectron reduction; only few O_2 molecules accepted more electrons and then, •OH radicals generated during a series of reactions [Eqs. (4)-(6)]. Subsequently, these reactive species with strong oxidative ability participated in the degradation of pollutants (e.g. RhB) [Eqs. (7)-(9)]. In general, the photogenerated holes (h^+) and superoxide radicals ($\cdot O_2^-$), as highly reactive species, both played a significant role in the photocatalytic oxidation of dye molecules, while the photogenerated electrons (e) participated in the reduction of heavy metal pollutants (e.g. Cr(VI)). In addition to the fast reaction with absorbed substrates, the slight holes left in the motivated Cr₂O₃ nanoparticles might oxidize OH⁻ groups to create ·OH radicals as well [Eqs. (10)]. Notably, the tetravalent chromium ions (Cr4+) in the composites also played a role during the photocatalytic process though the content of Cr⁴⁺ was extremely low. When involving in the photocatalytic reactions, it was deemed that these concomitant Cr4+ could assist the oxidizing reaction with adsorbed substrates during the photocatalytic process. Via directly reacting with pollutants (e.g. RhB) or oxidizing the surface hydroxyl groups (OH) into hydroxyl radicals (·OH), the Cr⁴⁺ could accept electrons and then was reduced to Cr^{3+} , thus separately accelerating the oxidation process and the generation of reactive species, which was definitely beneficial to the reactions during the photocatalytic process.

In the oxidation of absorbed organic substrates (RhB molecules) over bare TNSs under visible light irradiation, the self-photosensitized oxidation of surface-adsorbed RhB molecules possibly happened and injected electrons into the CB of TNSs.⁵³ Since the DRS result of bare TNSs showed no response in the visible-light region, its visible-light catalytical ability was majorly from the self-sensitive decomposition of RhB molecules. When it comes to Cr_2O_3 -loaded TNSs, the excited RhB molecules would inject electrons into the CB of TNSs [Eqs. (11)-(12)] or directly involve in the oxidative reactions [Eqs. (7)-(9)]. Then these electrons in the CB of TNSs could participate in the photoreaction processes mentioned above as well [Eqs. (3)-(6)]. Thus, the generation of superoxide

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ARTICLE

anion $(\cdot O_2)$ and photogenerated holes (h^{\dagger}) were accelerated via interfacial charge transfer (IFCT) during the degradation process and beneficial for photocatalytic degradation caused by their strong oxidizability. Cr^{III} h⁺)/TNSs Cr₂O₃/TNSs hv e + (Vis) (1) Cr^{III*} Cr^{IV}(h⁺)/TNSs h⁺)/TNSs (e (e⁻) (2) $\cdot O_2^{-}_{ads}$ or H_2CrO_4 $4H_2O$ \mathbf{O}_{2ads} 3e⁻ + 6H¹ Cr³⁺ (3) H_2O_2 20H 2e $2H_2O$ (4) $H_2O_2 + O_2^{-} \rightarrow OH_{ads} + OH^{-} + O_2$ (5) ·OH_{ads} H_2O_2 e \rightarrow OH_ (6) Pollutants (e.g. RhB) + h^+ (Cr^{IV}) \rightarrow Degradation products + Cr^{III} (7) Pollutants (e.g. RhB) + $\cdot O_2^{-}_{ads} \rightarrow$ Degradation products (8) Pollutants (e.g. RhB) + $\cdot OH_{ads} \rightarrow Degradation products$ (9) $OH_{ads}^{-} + h^{+} (Cr^{IV}) \rightarrow OH_{ads} + Cr^{III}$ (10)RhB + hv (Vis) $\rightarrow RhB^* + e^-$ (11) $RhB^* + e^- + TNSs \rightarrow RhB^* + TNSs(e^-)$ (12)

4.2 Photocatalytic H₂ evolution

With noble metal Pt photodeposited on the surface of samples, participating in the photocatalytic water splitting, the synergistic effect between Cr₂O₃ and Pt was also considerable in the process of H₂ evolution under visible-light irradiation for Cr(III)-TNSs.



Fig. 14. XPS analysis spectra of Pt 4f for (a) $Pt_{0.25}/TNSs$; (b) $Pt_{0.25}/0.5\%Cr$ -TNSs; (c) Pt_{0.25}/2.0%Cr-TNSs. The Pt_{0.25}/TNSs, Pt_{0.25}/0.5%Cr-TNSs and Pt_{0.25}/2.0%Cr-TNSs were obtained by photodepositing Pt with the same weight ratio (Pt:TNSs) at 0.25 wt.%

Fig. 14 showed the XPS analyses for Pt/TNSs and Pt/x-Cr-TNSs (x = 0.5% and 2.0%). The Pt:TNSs weight ratio for all samples was theoretically at 0.25 wt.%. From the fitting spectra of the samples, no appreciable difference in peak positions was identified for the Pt 4f spectra. And for these samples, the Pt 4f spectra showed a similar trend and the proportions of Pt:Ti and Pt⁰ (Pt-O_{ads}):Pt were calculated by their peak areas in Table 2. The peaks at ~70.8 and ~74.4 eV were attributed to $4f_{7/2}$ and $4f_{5/2}$ electrons of Pt⁰ (metallic Pt), respectively. In addition, the $4f_{7/2}$ peak, observed at ~72.4 eV, had a lower BE than that associated with Pt^{II}O species (ca. 73.4 eV). Thus the two minor peaks could be assigned to Pt with an

adsorbed oxygen (Pt-O_{ads}).⁵⁹ In the case of adding isopropanol to the suspension, the large amount of unsaturate surface atoms on the photoreduced Pt might partially bond with oxygen atoms, forming $Pt-O_{ads}^{60}$ However, the $4f_{7/2}$ peaks assigned to Pt^{0} and $Pt-O_{ads}$ were located at higher bingding energies than those of the Pt foil (ca. 70.2 and 71.5 eV, respectively) as reported. This shift was attributed to the decrease in the polarization energy with smaller size of the Pt particle compared to that of bulk Pt and the loaded Pt species on TNSs were easier to become somewhat electrondeficient.³⁷ And it should be noted that the broadened peaks for Pt species were possibly the result from the non-uniformly distribution of Pt paticles and the formation of Pt agglomerates on the TNSs in this work.⁶¹

As shown in Fig. 15, to further investigate the photoabsorbance properties, the UV-vis diffuse reflectance spectra (DRS) of bare TNSs and Cr(III)-TNSs before and after photodeposition of Pt were analyzed. Compared with bare TNSs,

Table 2 Pt 4f data and their valence states obtained from the XPS analysis spectra for $Pt_{0.25}/TNSs$ and $Pt_{0.25}/x$ -Cr-TNSs (x = 0.5% and 2.0%) at the 0.25 wt.% level of photodeposition with Pt

Sample	BE ^a (eV)		Pt/Ti ^b	Pt^δ/Pt^c (%)	
Sample	Pt ⁰	Pt-O _{ads}	(%)	Pt ⁰	Pt-O _{ads}
TNSs	70.74	72.41	0.96	73.17	26.83
0.5%Cr-TNSs	70.81	72.53	0.93	72.60	27.40
2.0%Cr-TNSs	70.78	72.45	0.97	72.73	27.27

^a The binding energies of Pt 4f_{7/2}

^b The XPS peak area ratios for Pt 4f relative to that for Ti 2p

^c The XPS peak area ratios for Pt⁰ and Pt-O_{ads} 4f relative to that for Pt 4f

except for the transition band and characteristic absorption band in Cr(III)-TNSs, the optical absorption of Pt_{0.25}/TNSs and Pt_{0.25}/Cr(III)-TNSs in the visible light region both increased, owing to the localized surface plasmon resonance (LSPR) of Pt nanoparticles on the pore-wall of TNSs.^{55,59} In addition, from Fig. 15 (a), the results for both $Pt_{0.25}/0.5\%$ Cr-TNSs and Pt_{0.25}/2.0%Cr-TNSs showed the broad absorption from 620 nm to 800 nm and the absorption shoulder at ~450 nm, which was in accordance with the DRS results for Cr(III)-TNSs except for a slight decrease in absorbance. According to Fig. 15 (b), the transient photocurrent of the Pt-deposited samples were improved obviously. Photocurrent responses of Cr(III)-TNSs showed higher current densities than that of bare TNSs, suggesting the higher charge separation efficiency for Pt/Cr(III)-TNSs. When the introduced content of Cr^{3+} was 0.5 at.%, the current density was readily improved, which was consistent with the high photocatalytic activity of H₂ evolution for Pt_{0.25}/0.5%Cr-TNSs sample.

These results proved, when Pt nanoparticles were loaded on the surface of TNSs as cocatalyst, the LSPR effect accelerated the separation of photo-generated carriers and extended the range of photoabsorption.^{55,59} Moreover, upon visible light excitation, the surface 3d sub-band electrons on Cr₂O₃ tended

Journal Name

to be excited to high-energy level and transfer into the CB of TNSs through the Cr(III)/TNSs interfaces for the surface protonic

reduction reaction [Eqs. (13)-(14)]. The remaining holes in Cr_2O_3 could be occupied by electrons in the presence of appropriate electron donors, such as TEOA in the current study for H₂ production. Subsequently, the sacrificial reagent reacted with photo-generated holes (h⁺) to promote the separation of electrons-hole pairs and more electrons (e⁻) enriched in the CB of TNSs could react with H⁺ deriving from the ionization of H₂O to produce H₂ through metallic Pt which served as active sites [Eqs. (15)-(17)]. However, trace H₂ evolved was observed during the photocatalytic tests for Cr(III)-TNSs samples with the absence of Pt, due to the large H₂ evolution over-potential on TNSs surface and the fast backward reaction of H₂ with dissolved O₂ in the solution. As TiO₂-based materials, the result



Fig. 15. (a) UV-Vis diffuse reflectance spectra of as-prepared bare TNSs and Cr_2O_3 -loaded TNSs before (inset) and after photodepositing Pt ($Pt_{0.25}/TNSs$, $Pt_{0.25}/x$ -Cr-TNSs (x = 0.5% and 2.0%)); (b) Surface photocurrent curves for the photoelectric behavior of $Pt_{0.25}/TNSs$ and $Pt_{0.25}/x$ -Cr-TNSs (x = 0.5%, 1.0% and 2.0%).

was common in most of the studies.55,62 Therefore, an alternative mechanism should be attributed to the IFCT at the Cr(III)/TNSs interface, which could promote the electron-hole separation of Cr₂O₃ under visible light irradiation (Scheme 1 (b)). This would allow a longer lifetime for photo-induced electrons to diffuse toward metallic Pt, which served as electron-sink and active sites for proton reduction to H₂ by lowering the over-potential under sacrificial agent/water system in the present study,⁵⁵ and favorably suppressed the H₂ back-oxidation derived from its weak adsorption and motivation ability to O_2 and H_2 molecules. In brief, the overall high photocatalytic activity of Pt/Cr₂O₃ decorated TNSs in H₂ production can be ascribed to the synergy between the visiblelight sensitization of Cr_2O_3 and the electron-sink effect of Pt nanoparticles. And furthermore, compared to traditional bulk TiO₂ materials, the unique structure of titanate nanosheets with large surface area could strengthen the light harvesting ability and increase the contact between the Pt/Cr(III)-TNSs and the reagent, which might be in favor of solar-to-fuel conversion.

Cr(III)/TNSs + hv (Vis) → Cr^{III*} (e^{-} + h^{+})/TNSs (13) Cr^{III*} (e^{-} + h^{+})/TNSs → Cr^{IV} (h^{+})/TNSs (e^{-}) (14) TNSs (e^{-}) → TNSs + Pt (e^{-}) (15) 2H⁺ + 2e⁻ → H₂ (16) TEOA + h⁺ (Cr^{IV}) → TEOA⁺ + Cr^{III} (17)

5. Conclusions

The visible-light-sensitive titanate nanosheets with loaded Cr₂O₃ was synthesized via a simple one-step hydrothermal method for improving the visible-light photocatalytic activity. These chromium oxide species were well-dispersed on the surface of TNSs and preferably proposed to exist as Cr₂O₃-like structure with low crystallinity by forming Ti-O-Cr bonds. The as-prepared samples showed obviously flake-like structure, possessing high specific surface area $(300-400 \text{ m}^2/\text{g})$. Accompanied with the loading of Cr₂O₃, the layered structure of nanosheets was influenced during the hydrothermal growth of TNSs. And the newly-formed heterostructure (Ti-O-Cr) at the interface was demonstrated to expand the visible-light absorption region for TNSs and achieve the efficient separation and transport of photo-induced carriers via interfacial charge transfer (IFCT). Based on the comparison of degradation efficiencies, it turned out that the Cr₂O₃-loaded TNSs (Cr(III)-



Scheme 1. Schematic diagram for the charge separation and transfer of the photocatalysts of Cr_2O_3 -loaded TNSs in the process of degradation of RhB and Cr(VI) (a); and in the process of H₂ evolution (b) under visible-light irradiation.

TNSs) with the appropriate content exhibited an significantly improved photocatalytic activity for oxidation of RhB and reduction of Cr(VI) under visible light irradiation, which could be attributed to the retarding of the charge recombination and the effective electron transfer from Cr_2O_3 to TNSs. In addition,

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Journal Name

ARTICLE

the result obtained from Cr(III)-TNSs for visible-light photocatalytic H₂ generation (0.25 wt.% Pt deposited as co-catalyst) also demonstrated the favorable synergistic effect between Cr₂O₃ (photosensitizer) and metallic Pt (electron sink) that readily enhanced H₂ evolution rate. The nice stability and reusability of Cr(III)-TNSs was confirmed and the alternative mechanism for the visible-light-sensitive photocatalytic activity was also proposed.

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 Cr_2O_3 -loaded titanate nanosheets with large surface area shows excellent visible–light catalytic activity for Cr(VI) degradation and H_2 generation.