

Electronic Supplementary Information

Study on Enhanced Visible-Light-Sensitive Photocatalytic Activity of Cr₂O₃-Loaded Titanate Nanosheets for Cr(VI) degradation and H₂ Generation

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Experimental Section

Sample reuse

After the adsorption-photocatalysis process, the sample used was separated by vacuum filtration using a 0.22 μm membrane from Cr(VI) solution at pH = 3. After dried in air, the separated sample of 0.2 g L⁻¹ was immersed in HNO₃ solution (0.5 M) for 8 h to desorb Cr³⁺, and then the desorbed sample were separated and washed with deionized water until the leachate to neutral. Finally, the desorbed sample was carried out by photocatalytic degradation to regenerate. In a typical regeneration treatment, about 0.1 g reduced product Cr-desorbed 0.5%Cr-TNSs (collected after the desorption experiments) was added into 50 mL of deionized water under intense stirring, and then 2 mL of 30% H₂O₂ solution was dropped into the suspension to accelerate the degradation of Cr(VI). After irradiated with a 300W high-pressure Xe lamp for 6 h, the photocatalyst was separated by centrifugation and used for the next photocatalytic cycle test. The whole process of photocatalysis adsorption, desorption, and regeneration was continuously run for 5 cycles, and conducted in triplicate. To investigate the reusability efficiency of the nanomaterial, 0.1 g L⁻¹ desorbed and regenerated materials were reused in the photoreduction of Cr(VI) experiments with an initial concentration of 20 ppm at pH = 3. In addition, the 0.5%Cr-TNSs sample was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectra for the confirmation of structure and component, after photocatalysis-adsorption followed by desorption and regeneration.

Regeneration and reuse of photocatalyst play an important role on its practical application. In the cyclic

test for the photoreduction of Cr(VI), 0.5%Cr-TNSs were carried out as a representative to evaluate the structure and photocatalytic activity after regeneration. The 0.5%Cr-TNSs after desorption (Des) and regeneration (Reg) process was reused during every cycle. After a series of processes of adsorption (Ads), desorption (Des) and regeneration (Reg), the structures and components of different-stage samples in the whole cycles were further characterized by XRD, Raman spectra (Fig. S1) and XPS analysis (Fig. S2). Almostly, there was no change of crystal phase for samples in the whole photocatalytic process. Due to the poor crystallinity of sample, the diffraction peaks of titanate were not well defined. The peak at $2\theta \approx 10^\circ$ ascribed to the interlayer diffraction of TNSs was chosen as a reference to investigate the structural change in the recycle process.^{1,2} This peak was slightly weakened after the adsorption of reduced product Cr^{3+} , suggesting that the adsorption process was only ion-exchange between Cr^{3+} and H^+ but would not affect the skeletal structure of titanate. However, the interlayer structure recovered after desorption with HNO_3 as the peak at 10° regained. After light irradiation treatment in the presence of H_2O_2 solution during regeneration process, the interlayer structure recovered and the 0.5%Cr-TNSs-Reg was obtained for efficient degradation. From Raman spectra, it was clearly observed that the peaks at 268 cm^{-1} and 456 cm^{-1} assigned to vibration modes of titanate were hardly changed after adsorption and desorption, respectively, indicating the stability of $[\text{TiO}_6]$ skeleton during the treatments.^{3,4} The spectrum of 0.5%Cr-TNSs-Reg was almost the same as that of pristine 0.5%Cr-TNSs-Raw, indicating the good regeneration of sample.

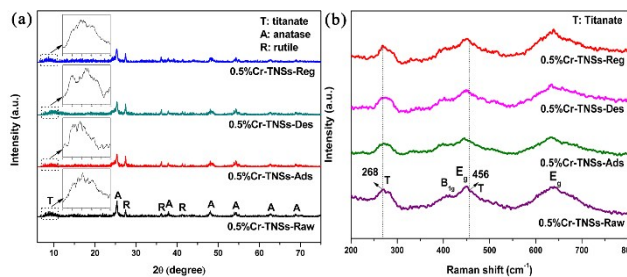


Fig. S1. (a) XRD patterns; (b) Raman spectra of 0.5%Cr-TNSs sample before and after different stages of adsorption, desorption and regeneration in the whole cycles.

Comparing the XPS spectra of 0.5%Cr-TNSs-Raw and 0.5%Cr-TNSs-Reg, it could be found that there was almost no difference in the Cr 2p spectra after regeneration for first and fifth cycle, suggesting the structure and component of as-prepared Cr_2O_3 -loaded TNSs were relatively stable.

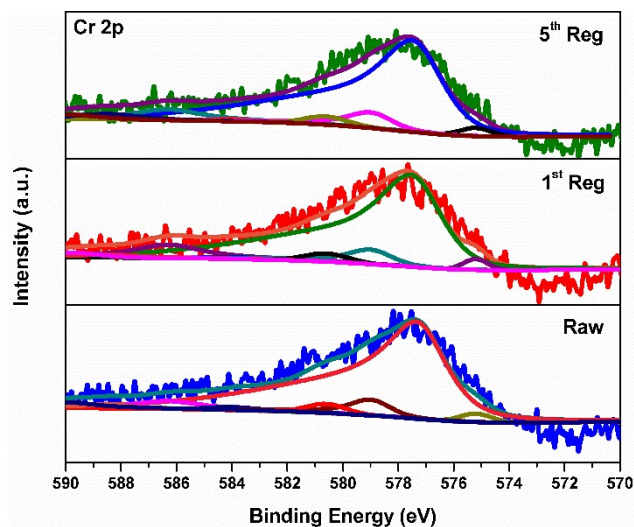


Fig. S2. The Cr 2p XPS spectra for 0.5%Cr-TNSs sample before and after regeneration in first and fifth cycle.

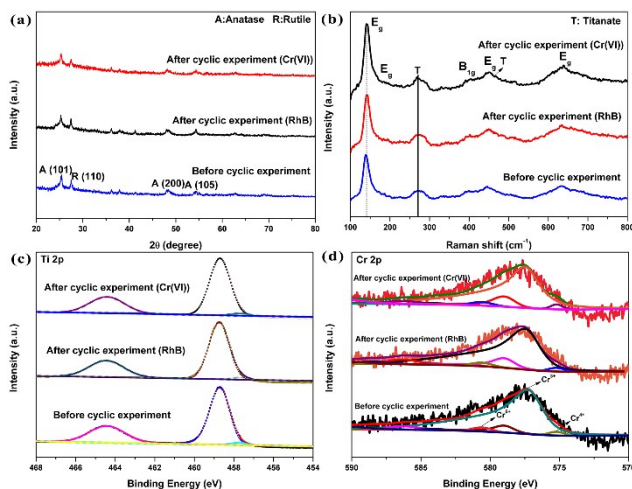


Fig. S3. (a) Ti 2p XPS spectra; (b) Cr 2p XPS spectra; (c) XRD patterns; (d) Raman spectra of Cr_2O_3 -loaded titanate nanosheets before and after cyclic experiments for the degradations of RhB and Cr(VI), respectively (0.5%Cr-TNSs was chosen as the testing sample).

To further confirmed the stability and reusability of synthetic photocatalyst, the leaching behavior of Cr and Ti was investigated after the five photocatalytic cycles for RhB and Cr(VI) degradations were performed, respectively. The photocatalyst was washed and collected for the following characterizations. Here 0.5%Cr-TNSs was chosen as the testing sample. The Ti and Cr 2p XPS spectra, XRD patterns and Raman spectra of the sample were investigated as shown below. And prior to the tests, the sample was also used as a contrast.

Table S1 The chemical states and contents of Cr and Ti obtained from the XPS analysis results for the Ti

and Cr 2p spectra of the samples before and after cyclic experiment

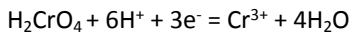
Sample 0.5%Cr-TNSs	BE ^a (eV)		Element content ^b (at. %)	
	Ti	Cr	Ti	Cr
	Before cyclic experiment	458.65	577.16	28.62
After cyclic experiment (RhB)	458.67	577.25	28.34	0.65
After cyclic experiment (Cr(VI))	458.64	577.23	28.46	0.67

^a The binding energy positions of the dominant 2p_{3/2} peaks for Ti and Cr XPS spectra, respectively

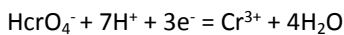
^b The molar ratios of Ti and Cr elements in the composite, respectively, from the XPS analysis results

From Fig. S3 (a-b), as compared to the pristine sample, the results showed 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 S3) from XPS spectra, the chemical states and contents of Cr and Ti almost retained constant after the photocatalytic reactions by turns. The results demonstrated the excellent stability and reusability of the synthetic photocatalyst in our work.

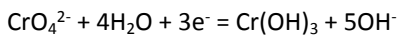
As it is well known that the photocatalytic reduction of Cr(VI) primarily depends on the solution pH, here the effect of the solution pH on the degradation efficiency of photocatalytic reduction of Cr(VI) was investigated for 0.5%Cr-TNSs sample. The photocatalytic reduction efficiency and reaction rate at different pH values under visible light were shown in Fig. S4 (a-b). It can be observed that the lower pH could significantly improve photocatalytic reduction of Cr(VI), and the higher reaction rate reached $19.89 \times 10^{-3} \text{ min}^{-1}$ at pH = 1. However, the reaction rate was only $0.82 \times 10^{-3} \text{ min}^{-1}$ at pH = 9. At lower pH values it was attributed to the main species H₂CrO₄, and photocatalytic reaction of Cr(VI) occurred in following ways^{5,6}:



or



As for alkaline medium, Cr(VI) mainly existed in the form of CrO₄²⁻, and the reaction process as:



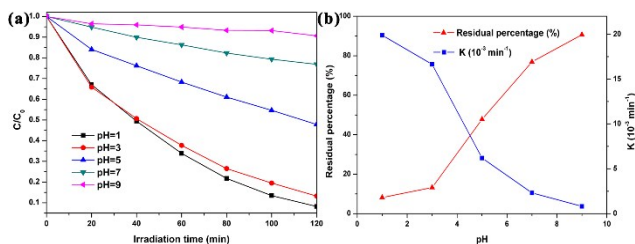


Fig. S4. (a) Photocatalytic reduction of Cr(VI) at various pH; (b) degradation efficiency and reaction rate of Cr(VI) at various pH for 0.5%Cr-TNSs sample.

It was apparent that the acid medium was beneficial to the photocatalytic reduction of Cr(VI) owing to the existence of abundant H^+ . Hence, higher efficiency of Cr(VI) would be expected at lower pH.

Reference

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