

Article

Enhanced Visible Light Photocatalytic Reduction of Cr(VI) over a Novel Square Nanotube Poly(Triazine Imide)/TiO₂ Heterojunction

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Abstract: Hexavalent chromium Cr(VI) pollution makes has a harmful impact on human health and the ecological environment. Photocatalysis reduction technology exhibits low energy consumption, high reduction efficiency and stable performance, and is playing an increasingly important role in chromium pollution control. Graphite-phase carbon nitride has been used to reduce Cr(VI) to the less harmful Cr(III) due to its visible light catalytic activity, chemical stability and low cost. However, it has a low specific surface area and fast recombination of electron–hole pairs, which severely restrict its practical application. In this work, a TiO₂-modified poly(triazine imide) (PTI) square nanotube was prepared by the one-step molten salts method. The results showed the PTI had a square hollow nanotube morphology, with an about 100–1000 nm width and 60–70 nm thickness. During the formation of the PTI square tube, TiO₂ nanoparticles adhere to the surface of the square tube wall by strong adsorption, and eventually form a PTI/TiO₂ heterojunction. The PTI/TiO₂-7 wt% heterojunction exhibited very good Cr(VI) reduction efficiency within 120 min. The enhanced photocatalytic activity was mainly attributed to the efficient separation and transport of photo-induced electron–hole pairs and the high specific surface area in the heterojunction structure.

Keywords: poly(triazine imide); square nanotube; TiO₂; hexavalent chromium; visible light photocatalytic

1. Introduction

Chromium is a typical heavy metal pollutant from electroplating, leather tanning, and corrosion protection. In the chemical compound of chromium, hexavalent chromium Cr(VI) has the strongest toxicity and it is easily dissolved with the infiltration of rainwater, which could seriously pollute the soil, river and underground water sources of the surrounding environment [1,2]. Therefore, it is urgent for us to remove Cr(VI) from polluted wastewater. Compared with Cr(VI), the toxicity of Cr(III) is greatly reduced, and Cr(III) solution can be treated as solid waste by the precipitation method. Hence, it is feasible to reduce Cr(VI) to Cr(III) by a reduction process. Among various reduction processes, photocatalysis reduction technology exhibits low energy consumption, high reduction efficiency and stable performance, and plays an increasingly important role in chromium pollution control. Many semiconductor materials such as TiO₂ and ZnO have been used for photocatalysis Cr(VI) reduction [3,4]. However, the low utilization of visible light and high recombination rate of the photogenerated electron–hole pairs severely restrict its practical application. Therefore, the development of novel catalysts with visible light response has become a research hotspot in the field of photocatalysis Cr(VI) reduction.

Since 2009, it has been reported that graphite-phase carbon nitride (g-C₃N₄) has visible light catalytic properties, which has been widely valued by many researchers [4–6]. At present,

the photocatalysis of carbon nitride is faced with two major problems: its low specific surface area and the fast recombination of electron–hole pairs. These problems lead to its low quantum efficiency, which greatly limits its further application. The morphology of the material can be changed by different preparation methods, so that the specific surface area of the material was effectively improved. Recently, a crystalline species of carbon nitride, the poly(triazine imide) (PTI) nanotube, has been synthesized in LiCl/KCl molten salts [7]. Traditional heptazine-based g-C₃N₄ was usually obtained by thermal polymerization. PTI is a layered graphitic carbon nitride material based on stacked CN network layers consisting of imide-linked triazine (C₃N₃) units. The PTI nanotube obtained by the molten salts method exhibited a higher crystallinity and larger surface area [8–13].

In addition, it is necessary to reduce the combination of photogenerated electron–hole pairs to enhance the quantum efficiency of the catalyst. Many studies have shown that the semiconductor heterojunction structure could reduce the charge recombination and obviously enhance photocatalytic performance. Many semiconductors including TiO₂, ZnO, MoS₂ have been used to couple with g-C₃N₄, which can be effectively improve photocatalytic performance [14–17]. TiO₂, with many advantages such as high activity, good chemical stability, low cost and non-toxicity, was regarded as the most promising green photocatalyst [18,19]. At present, there have been very few reports on the preparation and pollution treatment of heavy metals Cr(VI) of the PTI nanotube/TiO₂ heterojunction.

Herein, a novel square nanotube PTI/TiO₂ heterojunction was synthesized by a molten salts method. The structure and morphology of the prepared PTI/TiO₂ heterojunction were characterized. The visible light photocatalytic characteristics of the heterojunction were evaluated by a Cr(VI) reduction experiment. The active species in the photocatalytic reaction can be determined by the capture experiment, and then the photocatalytic mechanism of the heterojunction was proposed.

2. Results and Discussion

2.1. XRD Analysis

Figure 1a shows the XRD pattern of g-C₃N₄ and PTI. The pattern of heptazine-based g-C₃N₄ depicts diffraction peaks at 13.1° and 27.5°, which reflects different planes from (100) and (002). This is consistent with other studies [4]. Compared to g-C₃N₄, more diffraction peaks at 11.7°, 20.6°, 24.3°, 26.6°, 29.1°, 32.4°, 42.4° and 44.1° of PTI were observed in Figure 1a. The difference in XRD patterns mainly came from different structural units (as shown in Figure 1a). The results indicated that PTI had higher crystalline formation than that of g-C₃N₄. According to previous reports [20–22], the PTI phase is more stable than that of g-C₃N₄ in the molten salts system. The strongest XRD peak at 26.6° reflects planes from (002), which arose from an interlayer of the PTI phase. The XRD patterns of the TiO₂, PTI and PTI/TiO₂ heterojunction with different TiO₂ contents are shown in Figure 1b. It can be seen that the TiO₂ was mainly composed of two kinds of different crystalline TiO₂ (i.e., anatase and rutile phase). When the content of TiO₂ (3 wt%, 5 wt%, 7 wt%) was low in the heterojunction, the diffraction peak in Figure 1b mainly comes from PTI. With the increasing content of TiO₂ (10%), the (101) diffraction peaks of anatase TiO₂ can be observed in the heterojunction. There are no new diffraction peaks in the heterojunction. The results showed that the TiO₂ nanoparticles remained stable in the molten salts system.

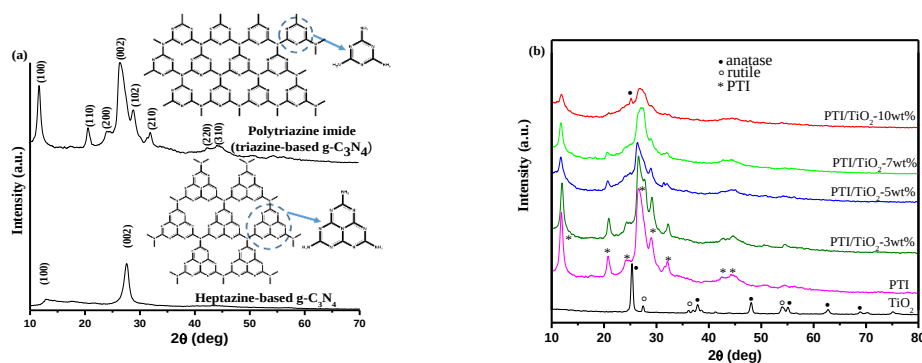


Figure 1. (a) XRD patterns of poly(triazine imide) (PTI), g-C₃N₄, (b) XRD patterns of TiO₂, PTI, PTI/TiO₂ heterojunction.

2.2. Morphology Analysis

The SEM image of the PTI/TiO₂-7 wt% heterojunction is shown in Figure 2a. The hollow tube morphology is observed clearly, and the tube is about a few micrometers to 10 micrometers long. An obvious square tube was observed in Figure 2b. The SEM image of the g-C₃N₄ is shown in Figure S1. It can be seen that the g-C₃N₄ had a layered structure and significantly agglomerated. The composition of the heterojunction was determined by energy dispersion spectrum (EDS). The C, N, Ti, O element signals were observed in Figure S2, which indicated the successful mixing of the heterojunction with TiO₂ and PTI. The elemental mapping image of the element on the PTI/TiO₂-7 wt% heterojunction (Figure 2c–f) further confirmed that the C, N, Ti and O were uniformly distributed in the heterojunction structure. The square hollow tube structure could be confirmed further by TEM imaging (Figure 2g). The nanotube is 100–1000 nm in width, and the thickness of the tube wall is about 60–70 nm. The TiO₂ nanoparticles can be clearly seen in the enlarged TEM image (Figure 2h), deposited on the surface of the tube wall.

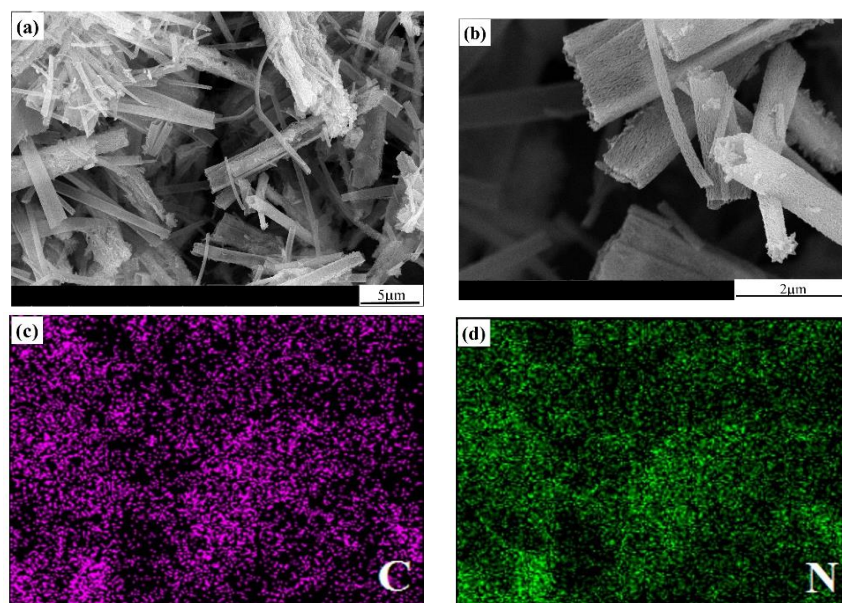


Figure 2. Cont.

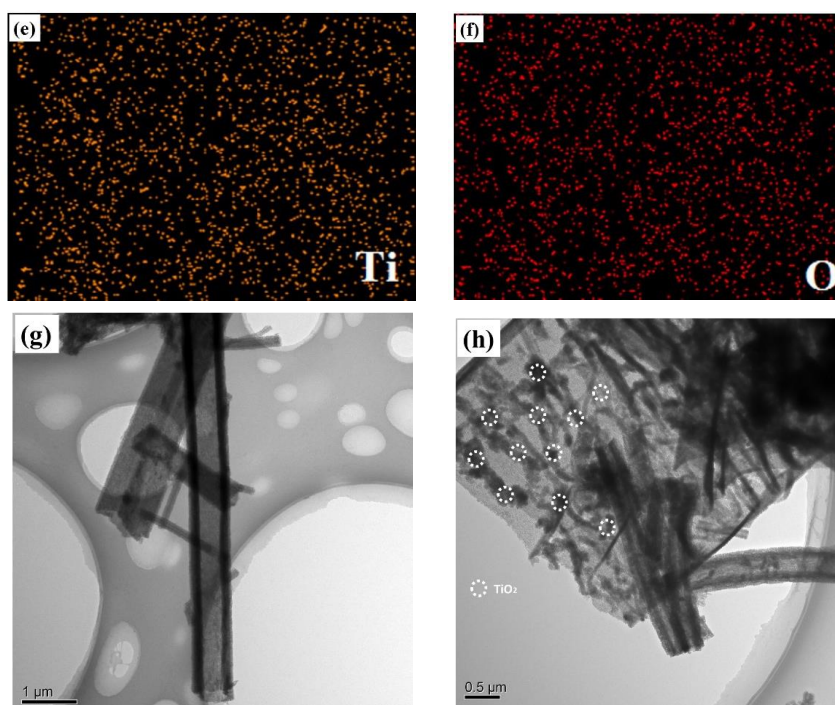


Figure 2. (a,b) SEM image, (c–f) EDS elemental mapping and (g,h) TEM image of the as-prepared samples.

2.3. UV-Vis DRS Analysis

Figure 3a shows the UV-vis diffuse reflectance spectrum (DRS) of PTI, TiO_2 and PTI/ TiO_2 heterojunction with different TiO_2 contents. As can be seen, single TiO_2 and PTI present strong absorption edges at about 390 and 460 nm, which are attributed to the intrinsic band gap absorption [23,24]. The absorption wavelength of the PTI/ TiO_2 heterojunction with different TiO_2 contents is similar to that of PTI. The results showed that the PTI square nanotube/ TiO_2 heterojunction still maintained strong visible light absorption. By using the Kubelka–Munk formula [25,26], $(\alpha h\nu)^n = A(h\nu - E_g)$, where α is the absorption coefficient, h is the Planck constant, ν is light frequency, A is a constant, E_g is the optical band gap energy and n is equal to 0.5 for PTI and TiO_2 , the band gap of samples could be calculated. As can be seen from this plot (Figure 3b), the band-gap energy of the as-prepared PTI/ TiO_2 -7 wt% heterojunction is roughly 2.64 eV, very close to that of PTI (about 2.60 eV). This result indicated that the TiO_2 nanoparticles in the heterojunction might simply be grown on the PTI nanotube wall without any doping effect.

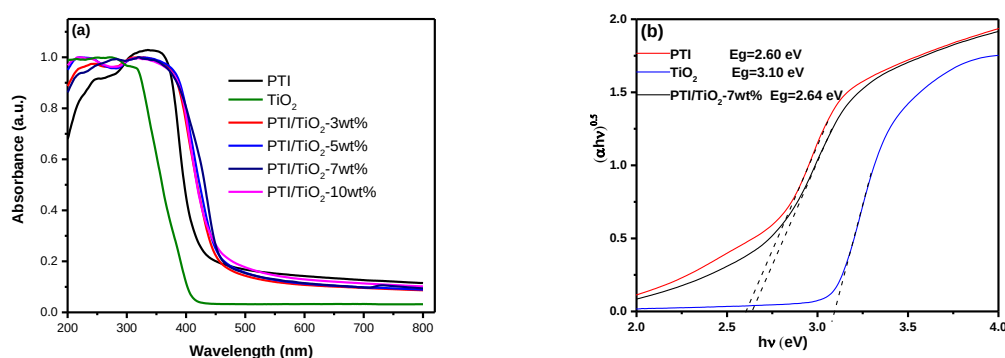


Figure 3. (a) UV-vis diffuse reflectance spectrum (DRS) of PTI, TiO_2 and PTI/ TiO_2 heterojunction with different TiO_2 content. (b) estimated band gap energies of PTI, TiO_2 and PTI/ TiO_2 -7 wt% heterojunction.

2.4. Photoluminescence Spectroscopy Analysis

Figure 4 shows the photoluminescence (PL) spectra of the different as-prepared samples. The fluorescence emission intensity of the PTI/TiO₂ heterojunction sample is remarkably suppressed compared to that of the PTI sample. The results showed that photo-induced electrons and holes in the PTI/TiO₂ heterojunction were separated rapidly, and the recombination of photo-induced electrons and holes was inhibited significantly.

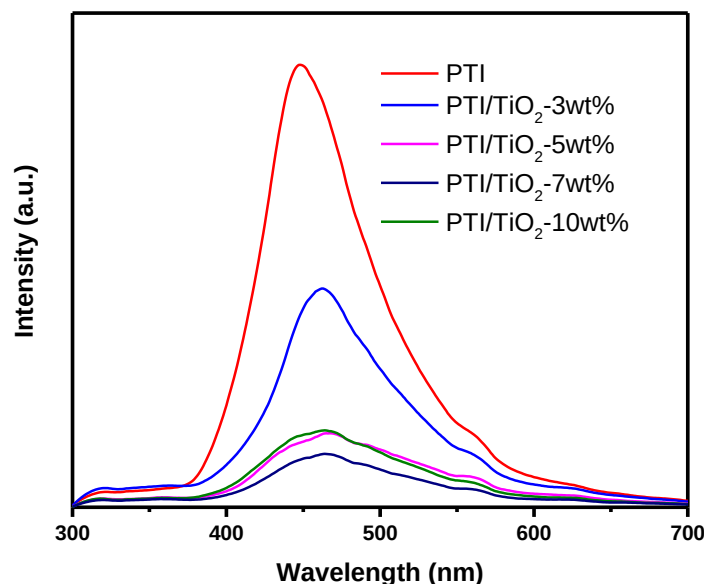


Figure 4. Photoluminescence spectra of as-prepared samples.

2.5. N₂ Adsorption/Desorption Isotherms

Figure 5a depicts the N₂ adsorption/desorption isotherms of the PTI square nanotube, g-C₃N₄ and PTI/TiO₂-7 wt% heterojunction. The bulk g-C₃N₄ shows a type II isotherm with no hysteresis loop, which indicates its non-porous layered structure. As shown in Figure 5b, there is no pore-size distribution peak in g-C₃N₄. A type IV isotherm with hysteresis loop were observed in the PTI square nanotube and PTI/TiO₂-7 wt% heterojunction. According to the results of pore-size distribution curves (Figure 5b), macroporous structures were found in the PTI square nanotube and PTI/TiO₂-7 wt% heterojunction. This is consistent with the SEM and TEM results. In addition, the pore-size distribution peak centered at 8.1 nm in the PTI/TiO₂-7 wt% heterojunction can be attributed to the constructed mesoporous structures by the accumulation of TiO₂ nanoparticles. Using the adsorption data, the Brunauer–Emmett–Teller (BET) surface area can be calculated. The values for the PTI square nanotube, g-C₃N₄ and PTI/TiO₂-7 wt% heterojunction were 140.37 m²g^{−1}, 22.24 m²g^{−1} and 160.09 m²g^{−1}, respectively. The results manifested that PTI square nanotube had a higher specific surface area than that of g-C₃N₄ materials. The increase of specific surface area mainly resulted from the square nanotube morphology. The specific surface area of the heterojunction with different TiO₂ contents was shown in Table S1. The results showed that the specific surface area of all heterojunction was slightly higher than that of the PTI square nanotube. It reveals that the heterojunction still retains a high specific surface area; moreover, mesoporous structures by the accumulation of TiO₂ nanoparticles can contribute to the further improvement of the specific surface area of heterojunction.

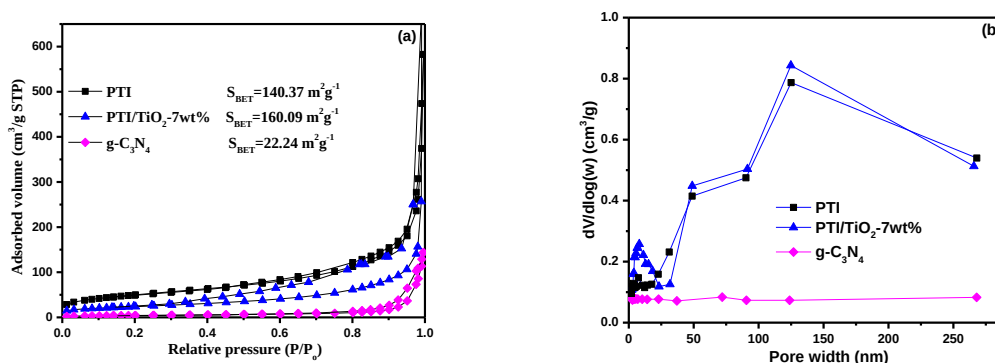


Figure 5. N₂ adsorption/desorption isotherms (a) and corresponding pore-size distribution curves (b) of as-prepared samples.

2.6. Photocatalytic Activity Analysis

Figure 6a shows the photocatalytic reduction of Cr(VI) under visible light irradiation with g-C₃N₄, PTI, PTI/TiO₂ photocatalysts. Only 23% of Cr(VI), 44% of Cr(VI) were reduced under visible light irradiation for 120 min by g-C₃N₄ and the PTI square nanotube, respectively. It is worth noting that the Cr(VI) reduction efficiency is significantly improved in PTI/TiO₂ heterojunction. The Cr(VI) reduction ratio of PTI/TiO₂-3 wt%, PTI/TiO₂-5 wt%, PTI/TiO₂-7 wt%, PTI/TiO₂-10 wt% reached 60%, 73%, 97%, 88%, respectively. Among them, PTI/TiO₂-7 wt% exhibited the most excellent photocatalytic performance.

As displayed in Figure 6b, the kinetic curves of Cr(VI) reduction showed a linear relationship between $-\ln(C/C_0)$ and reaction time, suggesting that the reaction followed pseudo-first-order kinetics. The rate constant was calculated from the slope k of the linear regression line. The kinetic constants of the Cr(VI) reduction of g-C₃N₄, PTI, PTI/TiO₂-3 wt%, PTI/TiO₂-5 wt%, PTI/TiO₂-7 wt% and PTI/TiO₂-10 wt% are 0.00135 min⁻¹, 0.00259 min⁻¹, 0.00623 min⁻¹, 0.00929 min⁻¹, 0.02549 min⁻¹, 0.01486 min⁻¹, respectively. Apparently, the PTI/TiO₂-7 wt% heterojunction possesses the highest k value. The kinetic constant value of the heterojunction is about 10 times that of the PTI nanotube.

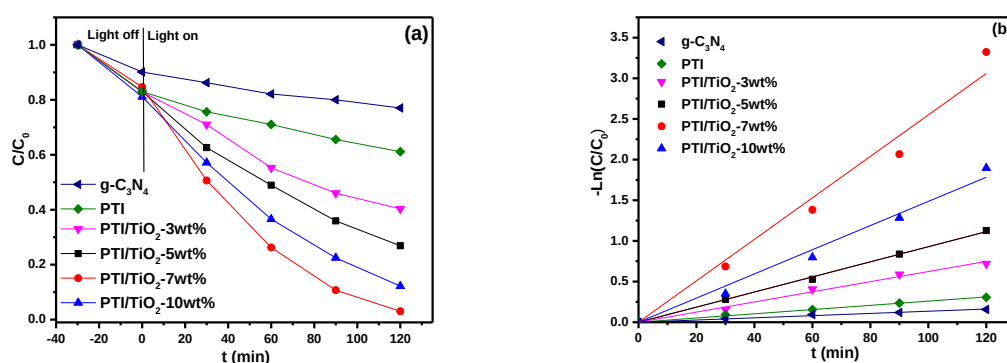


Figure 6. (a) Photocatalytic reduction of Cr(VI), (b) kinetic plot of the samples under visible light irradiation.

The stability of the photocatalyst is one of the key factors to limit the application of photocatalytic technology. Figure 7a shows that the Cr(VI) reduction rate of the PTI/TiO₂-7 wt% heterojunction reached about 90% after 5 cycles. Besides this, no change of the crystal structure and morphology could be found, on the basis of the XRD results of catalysts before/after the cycling test and SEM image after the cycling test in Figure 7b. The results showed that the heterojunction had a high photocatalytic stability for the Cr(VI) reduction. The high stability of the photocatalyst is mainly due to the rapid and effective separation of electrons and holes in the heterojunction [27–29].

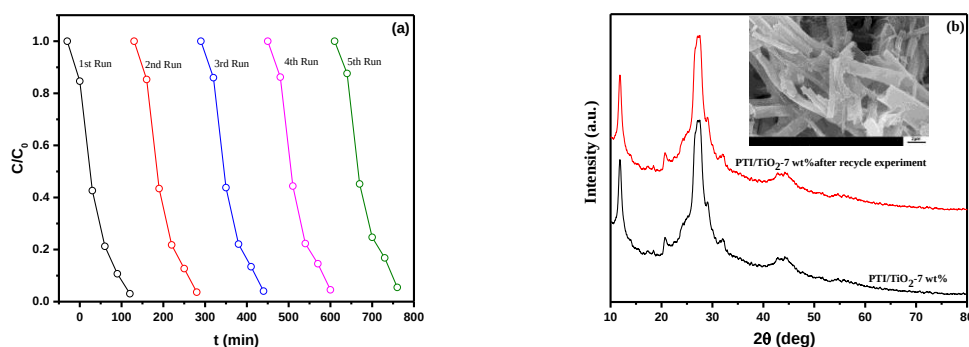


Figure 7. (a) Recycle experiments of PTI/TiO₂-7wt% for reduction of Cr(VI), (b) XRD pattern before and after the recycle experiment.

2.7. Photocatalytic Mechanism Analysis

The trapping experiment of photocatalysts can determine the active species in the photocatalytic reaction. It is very helpful for us to understand the catalytic mechanism of the PTI/TiO₂ heterojunction. The benzoquinone (BQ), ammonium oxalate (AO), and AgNO₃ were used as scavengers for reactive species of $\bullet\text{O}_2^-$, h^+ and e^- , respectively. As can be seen from Figure 8, the reduction rate of Cr(VI) within 60 min was 74% without any scavengers. Obviously, the reduction rate of Cr(VI) was reduced to 50% with the addition of AgNO₃. Many studies showed that Ag^+ were easily reduced by photo-generated electrons, resulting in the number of photo-generated electrons decreasing during the photocatalytic process [30–33]. Therefore, the reduction rate of Cr(VI) was greatly inhibited. The reduction rate of Cr(VI) increased to 87% with the addition of AO. The enhancement of photocatalytic activity results from suppressing the excited electron–hole pair recombination because of decreasing the number of holes. The reduction rate of Cr(VI) still remained unchanged with the addition of BQ. The results showed that photo-generated electrons played an important role in Cr(VI) reduction.

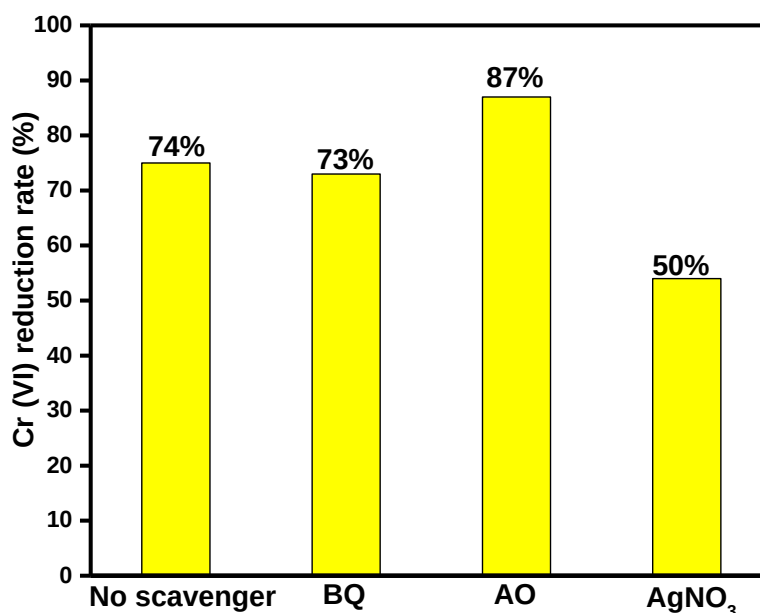


Figure 8. The reduction rate of Cr(VI) in the presence of different scavengers under visible light irradiation within 60 min.

Transient photocurrent response analysis is helpful to determine the separation efficiency of photoelectron–hole pairs in photocatalysts. As shown in Figure 9, compared to PTI, a stronger

photocurrent intensity existed in the PTI/TiO₂-7 wt% heterojunction. This showed that the separation efficiency of photo-generated electrons and holes in the heterojunction has been significantly improved.

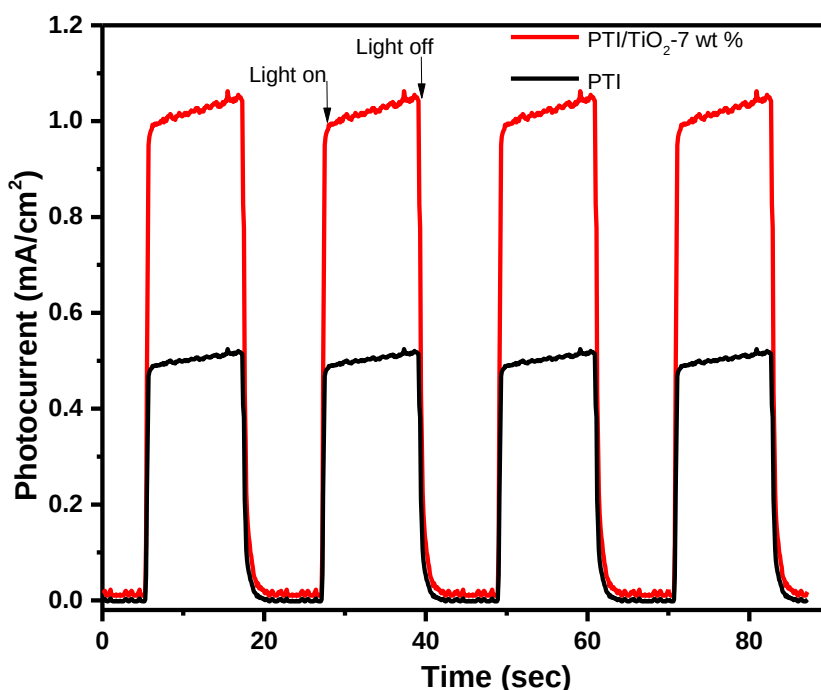


Figure 9. Transient photocurrent response of the PTI and PTI/TiO₂-7wt% heterojunction.

According to the above results, the possible mechanism of the PTI square nanotube/TiO₂ heterojunction is illustrated in Figure 10. A possible mechanism for Cr(VI) reduction over the PTI square nanotube/TiO₂ heterojunction was proposed based on the energy-band theory (Figure 10). As we can see in the schematic diagram, PTIs are excited by visible light irradiation to generate electrons and holes; however, TiO₂ cannot be excited because of the wide band-gap. The CB edge potentials of TiO₂ are more positive than that of PTI. The electrons in the valance band (VB) of PTI would rapidly transfer into the CB of TiO₂ through the interfacial heterojunction. Then, the interfacial transfer improved electron–hole pairs separation, which enhanced the photocatalytic reduction Cr(VI). The holes stored in the VB of PTI could oxidize water to form O₂, further promoting the photocatalytic performances of PTI/TiO₂ heterojunction. This is in good agreement with the literature [34–37].

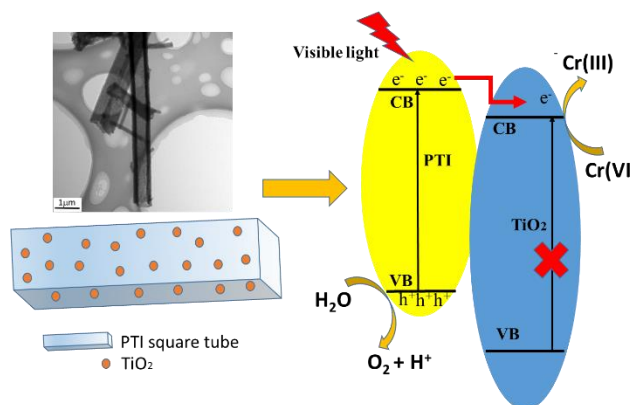


Figure 10. Schematic diagram of possible mechanisms in the PTI square nanotube/TiO₂ heterojunction.

3. Materials and Methods

3.1. Materials

Sodium chloride (NaCl), potassium chloride (KCl), lithium chloride (LiCl), melamine, TiO₂ nanoparticles were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All the chemicals were of analytically pure grade and used without further purification.

3.2. Synthesis of Photocatalyst

Ternary LiCl-NaCl-KCl in a weight ratio of 32:34:34 with a eutectic point of around 400 °C was used as the reaction media. A total of 15 g of the LiCl-NaCl-KCl, 1 g melamine and a certain amount of TiO₂ nanoparticles were manually ground and mixed in an agate mortar. The crucible containing the mixed salts was then placed in alumina crucible. Then, the crucible was heated to 550 °C with a heating rate of 10 °C min⁻¹ for 4 h in a muffle furnace. After cooling to ambient temperatures, the powders were collected after centrifugation five times with deionized water at a speed of 5000 rpm and vacuum drying at 80 °C. The real TiO₂ mass content was determined by the thermogravimetry method. The detailed procedure is provided in Supplementary Information. These samples were marked as PTI/TiO₂-3 wt%, PTI/TiO₂-5 wt%, PTI/TiO₂-7 wt% and PTI/TiO₂-10 wt%, respectively. For comparison, the heptazine-based g-C₃N₄ was prepared by the thermal polymerization according to [4].

3.3. Characterization of the Prepared Photocatalyst

X-ray diffraction (XRD) patterns were recorded in a Bruker D8 Advance X-ray diffractometer (Karlsruhe, Germany) with Cu K α radiation source. Scanning electron microscopy (SEM) analysis and transmission electron microscopy (TEM) analysis were conducted by using a FEI Nova Nano SEM 450 (Hillsboro, OR, USA) and a FEI Tecnai G20 (Hillsboro, OR, USA), respectively. UV-visible diffuse reflectance spectra were obtained by using the dry-pressed disk samples recorded in a UV-visible spectrophotometer (UV-3660, Shimadzu, Kyoto, Japan). BaSO₄ was used as a reflectance standard in the experiment. Photoluminescence (PL) spectra were recorded on a HORIBA Fluorolog-3 type fluorescence spectrophotometer (Paris, France). The excitation wavelength of the fluorescence spectrum is 325 nm. The photocurrent response was measured on an electrochemical workstation (CHI 660D, Chenhua Instrument, Shanghai, China), where the electrolyte used in the measurement was 0.5 M Na₂SO₄ aqueous solution. The three-electrode structure is adopted, including the working electrode (sample preparation), counter-electrode (platinum wire) and reference electrode (Ag/AgCl). The light source was a low-power LED (3 W, 365 nm). The 30 mg sample and 2 ml ethanol were grinded into slurry and coated on FTO glass to form a working electrode. The electrodes were dried in an oven at 80 °C for 30 min. The Brunauer–Emmett–Teller (BET) specific surface areas of the powders were measured by nitrogen adsorption–desorption at 77 K in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (Micromeritics Instrument Co., Norcross, GA, USA).

3.4. Photocatalytic Activity Experiment

The reduction experiments of the Cr(VI) solution were investigated under a 300 W Xe lamp equipped with a $\lambda > 400$ nm glass filters. Twenty milligrams of the photocatalyst powder was ultrasonically suspended to 100 mL of K₂Cr₂O₇ aqueous solution with a Cr(VI) concentration of 10 mg/L. The solution was placed in a glass beaker and stirred by a magnetic stirrer for 30 min in the dark to establish the adsorption–desorption equilibrium. The vertical distance between the 300 W Xe lamp and the solution was 20 cm. At certain time intervals, a small amount of solution was collected and centrifuged. The concentration of Cr(VI) in the solution was measured by the diphenylcarbazide method.

4. Conclusions

In this study, we reported the synthesis of a square nanotube PTI/TiO₂ heterojunction via the molten salt method. The PTI/TiO₂ heterojunction exhibited enhanced photocatalytic activity for the reduction of Cr(VI) under visible light irradiation. The kinetic constant of the reduction reaction with PTI/TiO₂-7 wt% heterojunction (0.02549 min⁻¹) is about 10 times as high as that of the PTI (0.00259 min⁻¹). More photocatalytic reaction active sites and the efficient separation of electron-hole pairs were the main reasons for the enhanced heterojunction photocatalytic performance. The PTI/TiO₂ heterojunction has significant photocatalytic activity and stability, which means that it is very possible to apply this new catalyst to the detoxification of Cr(VI) in actual water pollution.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/1/55/s1>, Figure S1: SEM image of heptazine-based g-C₃N₄, Figure S2: EDS spectra of PTI/TiO₂-7 wt% heterojunction, Table S1: BET surface area of the as-prepared samples.

Author Contributions: Data curation, X.Y. and G.N.; Formal analysis, P.Z.; Methodology, X.Y. and G.N.; Writing—original draft, X.Y.; Writing—review & editing, X.Y. and P.Z.

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Conflicts of Interest: There is no conflict of interests existing in the manuscript submission, and it is approved by all of the authors for publication. All the authors listed have approved the manuscript to be enclosed.

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