A novel visible light-driven TiO₂ photocatalytic reduction for hexavalent chromium wastewater and mechanism
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ABSTRACT
Titanium dioxide (TiO₂) photocatalyst was prepared with a sol-gel method and its characterizations were analyzed. TiO₂ photocatalytic reduction of Cr⁶⁺ was investigated in visible light irradiation and reduction mechanisms were calculated. Prepared TiO₂ is anatase with a bandgap of about 2.95 eV. Experimental results display that almost 100% of Cr⁶⁺ is removed by visible light-driven TiO₂ photocatalytic reduction after 120 min when Cr₂O₇²⁻ initial concentration is 1.0 mg·L⁻¹, TiO₂ dosage is 1.0 g·L⁻¹, and pH value is 3. In acidic aqueous solution, HCrO₄⁻ is the dominant existing form of Cr⁶⁺ and is adsorbed by TiO₂, forming a complex catalyst HCrO₄⁻/TiO₂ with an increase in wavelength to the visible light zone, demonstrated by UV–Vis diffuse reflection spectroscopy. Based on X-ray photoelectron spectroscopy data, it can be deduced that Cr⁶⁺ is adsorbed on the surface of TiO₂ and then reduced to Cr³⁺ in situ by photoelectrons. Self-assembly of HCrO₄⁻/TiO₂ complex catalyst and self-reduction of Cr⁶⁺ in situ are the key steps to start the visible light-driven TiO₂ photocatalytic reduction. Furthermore, TiO₂ photocatalytic reduction of Cr⁶⁺ fits well with pseudo-first-order kinetics and has the potential application to treat chemical industrial wastewater.

Key words | Cr³⁺, Cr⁶⁺, photocatalytic reduction, TiO₂, visible light

HIGHLIGHTS
- Cr(VI) is efficiently removed by visible light-driven TiO₂ photocatalytic reduction reaction.
- Photoinduced electrons are the major reductive substance for Cr(VI) removal.
- Adsorption, reduction in situ, and desorption are involved in reduction mechanism of Cr(VI).
- Photocatalytic reduction of Cr(VI) fits well with pseudo-first-order kinetics and rate constant is calculated.

GRAPHICAL ABSTRACT

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INTRODUCTION

Chromium pollutants mainly come from the industries of mining, metallurgy, electroplating, leather manufacture, bichromate, and chromium slag treatment (Zhang et al. 2017; Yang et al. 2018). However, they are used so widely that many tremendous environmental contaminations (Gheju & Balcu 2017; Ravindra & Mor 2019; Wang et al. 2020) are caused. Cr\(^{6+}\) is the dominant existing form of chromium compounds and is easily absorbed by bodies. Many international investigations have found that some serious pathological lesions occur not only in the skin (Yu et al. 2018) but also in other organs caused when people are exposed to Cr\(^{6+}\)-rich environment for a long time (Guo et al. 2016; Yoshinaga et al. 2018). There are some methods for wastewater containing Cr\(^{6+}\), such as adsorption or biosorption (Deveci & Kar 2013; Vendruscolo et al. 2017; Yao et al. 2017; Ayub et al. 2020), membrane separation (Habibi et al. 2015), electrolysis (Sarahaney et al. 2012), and chemical reagents (Sheikhmohammadi et al. 2019). Adsorption is a convenient way for Cr\(^{6+}\) removal (Gong et al. 2017), but the trace of absorbents should be noticed; otherwise, secondary pollution may be more serious. To avoid the potential risk of absorption, biosorption–biotransformation integrated processes where concentrated Cr\(^{6+}\) is reduced to non-toxic Cr\(^{3+}\) are developed (Jobby et al. 2018). However, the running environment and technical parameters are more strict than those of other technologies. Membrane separation can efficiently remove Cr\(^{6+}\) from wastewater; however, membrane assembly is easily contaminated or blocked, and so how to efficiently, safely, and economically remove Cr\(^{6+}\) becomes a research focus.

Semiconductor photocatalytic reaction is valued for its powerful redox ability, whether oxidation of most organics (Zhao et al. 2016) or reduction of variable valence heavy metal ions. Titanium dioxide (TiO\(_2\)) photocatalytic reduction for trace Cr\(^{6+}\) has received researchers’ attention (Testa et al. 2004; Yang et al. 2006) for its favorable chemical property, high stability, and low cost (Hoffmann et al. 1995). The absorption bandgap of pure TiO\(_2\) (\(E_\text{g} = 3.2\ \text{eV}\)) lies in the ultraviolet light zone (\(\lambda = 1240/E_\text{g} = 385\ \text{nm}\)) (Fujishima et al. 2008), and it has no ability to oxidize or reduce pollutants in visible light irradiation. TiO\(_2\) modification is a good way to achieve the visible light-driven photocatalytic reaction because the spectrum scope of modified TiO\(_2\) transfers from the ultraviolet light region to the visible light zone. Modified TiO\(_2\) photocatalyst and its application in wastewater treatments have been greatly developed recently. Doping non-ions elements and constructing heterojunctions are both effective methods to achieve TiO\(_2\) photocatalytic performance in visible light irradiation. Chatterjee & Dasgupta (2005) discussed TiO\(_2\) visible light-assisted degradation of organic pollutants and mechanism, and there is more research into TiO\(_2\) photocatalytic degradation for organics in visible light irradiation. The bandgap of TiO\(_2\) doped with elements such as N, F, S, and Bi or anions such as OH\(^-\), SO\(_4^{2-}\), and ClO\(_4^-\) becomes narrow, producing a photoelectric response in visible light (Kerkez-Kuyumcu et al. 2015; Wang et al. 2017). Xu et al. (2019) prepared carbon dots (CDs)-modified N–TiO\(_2\)–x nanocomposite to reduce Cr\(^{6+}\) and obtained a satisfied efficiency in visible light irradiation. In addition, p–n junctions can also bring a red shift in the absorption spectrum, exhibiting a powerful visible light response. Magadevan et al. (2019) constructed a novel TiO\(_2–\)Cu\(_2\)(OH)PO\(_4\) heterojunction catalyst and found that the composite catalyst exhibited high reduction efficiency of Cr\(^{6+}\) because the bandgap narrowed from 3.2 eV to 2.6 eV. Dye-sensitized TiO\(_2\) also has photocatalytic reduction ability. Wu et al. (2015) prepared dye-sensitized TiO\(_2\) to reduce Cr\(^{6+}\) under visible light irradiation and found that Cr\(^{6+}\) was reduced by photo electrons that diffuse from the dye-sensitized zone to the TiO\(_2\) zone.

There are many investigations into reduction of Cr\(^{6+}\) with TiO\(_2\) ultraviolet photocatalysis (Zhou et al. 1995) or oxidation for organics with TiO\(_2\) or modified TiO\(_2\) (Asgari et al. 2021) or TiO\(_2\)-integrated process (Zhao et al. 2012, 2015, 2016); however, the study about direct reduction of Cr\(^{6+}\) with pure TiO\(_2\) in visible light is scarce. Our previous experiments have shown that in visible light irradiation, Cr\(^{6+}\) is reduced to Cr\(^{3+}\) by TiO\(_2\) prepared by a sol-gel method. To investigate TiO\(_2\) photocatalytic reduction of Cr\(^{6+}\), process reactions and reduction mechanisms are analyzed in this work.

EXPERIMENTAL

Reagents and chemicals

Titanium butoxide, H\(_2\)CrO\(_4\), C\(_2\)H\(_5\)OH, CH\(_3\)COOH, K\(_2\)Cr\(_2\)O\(_7\), HCl, NaOH, and methanol were all analytical degree reagents and purchased from Tianjin Chemical Reagent Co. (China). High pure water (18.2 M\(\Omega\)·cm\(^{-1}\)) was prepared via a water purification instrument (Unique-R20, Research Scientific Instruments Co. Ltd, China).
Synthesis of TiO₂

TiO₂ was prepared via a sol-gel method where titanium butoxide (Ti(OCH₂CH₂CH₂CH₃)₄) was used as the precursor. Detailed process is as follows: 100 mL ethanol and 10 mL precursor were mixed together for 20 min at room temperature, forming a homogeneous mixture; 15 mL H₂O and 4 mL CH₃COOH were simultaneously added into the above-mentioned mixture, stirred for 40 min at a constant speed to obtain a mixture with a pH of about 4. The mixture was put into the oven and dried for a set time at 105 °C to obtain the amorphous TiO₂. Finally, to reach the crystal phase transformation, amorphous TiO₂ was put into a box-type resistance furnace where a gradient temperature was preset. Temperature was raised from room temperature to 250 °C at a heating rate of 5 °C·min⁻¹ and kept for 1 h at 250 °C, and then increased from 250 °C to 600 °C at the same heating rate and maintained for 1 h at 600 °C.

Characterization of as-prepared TiO₂

X-ray diffraction (XRD) pattern was monitored by a D/max RB system (Cu Kα₁ irradiation, λ = 1.5406 Å, voltage = 40 kV, current = 30 mA, scanning rate = 0.01°·s⁻¹, scanning range = 10–80°). Scanning electron microscope (SEM) images were obtained using a Fei Qunta Feg 250 microscope (accelerating voltage = 10 kV). UV-Vis diffuse reflectance spectrum (UV-DRS) was obtained using a UV-Vis diffuse reflectance spectrometer (LAMBDA 750, PerkinElmer) and scanning wavelength range from 200 to 800 nm. X-ray photoelectron spectroscopy (XPS) was controlled by an ESCALAB 250 Xi instrument (ThermoFisher Scientific, Al Kα₂ irradiation, hν = 1486.6 eV, voltage = 12.5 kV, power = 250 W, pressure = 10⁻⁶–10⁻⁷ Pa).

TiO₂ photocatalytic reduction of Cr⁶⁺

TiO₂ photocatalytic reduction of Cr⁶⁺ was conducted in a cylindrical reactor equipped with a 150 W spherical xenon lamp (Shellett Photoelectric Technology Co. Ltd, China). A filter plate was used to remove ultraviolet light and 80 mW·cm⁻¹ irradiation intensity was measured using an illumination photometer. Then 200 mL of aqueous solution containing 1.0 mg·L⁻¹ Cr₂O₇²⁻ and 1.0 g·L⁻¹ TiO₂ powder was transferred into the reactor and stirred at a speed of 100 r·min⁻¹ for 60 min, to obtain Cr⁶⁺ adsorption equilibrium on the surface of TiO₂ and the inside of the reactor in a dark environment. After adsorption equilibrium, the light resource was turned on and photocatalytic reduction was started. Samples were removed from the same place in reactor at given time intervals and the concentration of Cr⁶⁺ was analyzed using diphenylcarbazide colorimetric method controlled by a UV-Vis spectrophotometer (UV-1900, Shimadzu). Total chromium was analyzed with a graphite furnace atomic absorption spectroscopy (AA4590, Shimadzu).

RESULTS AND DISCUSSION

Characterizations of TiO₂

To determine the crystal phase of as-prepared TiO₂, XRD pattern was performed and results are shown in Figure 1(a). Compared with the standard anatase TiO₂ (JCPDS: 89-4921), it is observed that the peaks at 20 of 25.31°, 36.97°, 37.86°, 48.11°, 53.95°, 55.14°, 62.23°, 62.72°,...
68.75\(^\circ\), 70.28\(^\circ\), 75.13\(^\circ\), and 76.15\(^\circ\) correspond to (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), (215), and (301) planes of anatase phase, suggesting that as-prepared TiO\(_2\) is clear and perfect, which is in accordance with the research reported by Wang et al. (2021). SEM images of as-prepared TiO\(_2\) are shown in Figure 1(b). It seems that TiO\(_2\) looks like some uniform microspheres. The average size of as-prepared TiO\(_2\) is about 78 nm, according to Debye–Scherrer formula 

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \(K\) is a constant of 0.59, \(\lambda\) is irradiation wavelength of 0.15406 nm, \(\beta\) is half-maximum of (101) obtained via XRD software, and \(\theta\) is the diffraction angle. Furthermore, the surface of TiO\(_2\) is not smooth but layered, which is good for the adsorption and photocatalytic reduction of Cr(VI), compared to the smooth surface.

**Effects of TiO\(_2\) dosage and Cr\(_2\)O\(_7^{2-}\) concentration**

The effect of TiO\(_2\) dosage on photocatalytic reduction of Cr\(^{6+}\) was investigated and results are displayed in Figure 2(a). It is observed that photocatalytic reduction of Cr\(^{6+}\) increases initially and then decreases with the enhancement of TiO\(_2\), and the optimum is 1.0 g·L\(^{-1}\). The reason is that when TiO\(_2\) dosage is lower than 1.0 g·L\(^{-1}\), more Cr\(^{6+}\) ions are adsorbed on the TiO\(_2\) surface with the enhancement of catalyst dosage, resulting in high reduction; however, when the dosage is higher than 1.0 g·L\(^{-1}\), the homogeneous solution becomes murky with the increase in catalyst dosage, leading to a reflection of light, meaning that only the surface layer Cr\(^{6+}\) aqueous solution receives light irradiation, resulting in low photocatalytic reduction efficiency.

The effect of Cr\(_2\)O\(_7^{2-}\) concentration on photocatalytic reduction of Cr\(^{6+}\) was studied and results are shown in Figure 2(b). It can be seen that reduction efficiency decreases with the enhancement of Cr\(_2\)O\(_7^{2-}\) concentration. Reduction of Cr\(^{6+}\) climbs to 98\% at 90 min when Cr\(_2\)O\(_7^{2-}\) initial concentration is 0.5 mg·L\(^{-1}\); however, it is only 24\% when the Cr\(_2\)O\(_7^{2-}\) initial concentration is 5.0 mg·L\(^{-1}\). The decline of reduction is mainly caused by light scattering. The higher the Cr\(_2\)O\(_7^{2-}\) initial concentration, the darker the aqueous solution becomes, and then the Cr\(_2\)O\(_7^{2-}\) anions participating in photocatalytic reduction reduces for the serious scattering of visible light.

**Effect of pH**

The effect of pH on photocatalytic reduction of Cr\(^{6+}\) was studied under visible light and results are displayed in Figure 3(a). It is observed that photocatalytic reduction efficiency decreases with the enhancement of pH value. In TiO\(_2\) photocatalytic reduction of Cr\(^{6+}\), pH not only affects the charge property of TiO\(_2\) but also influences the existing form of Cr\(^{6+}\) species. Acharya et al. (2018) found that the existing form of Cr\(^{6+}\) strictly depends on pH value: H\(_2\)CrO\(_4\) molecule (pH <2), HCrO\(_4^-\) (2 < pH < 7) and Cr\(_2\)O\(_7^{2-}\) (pH > 7). The isoelectric point of photocatalyst varies depending on preparation conditions, and is particularly affected by pH value (Gumy et al. 2006). The isoelectric point of as-prepared TiO\(_2\) was tested using an electrochemical method controlled by a zeta potentiometer and was found to be about 5. The surface of TiO\(_2\) is positively charged when the pH value is lower than 5 and...
negatively charged when the pH value is higher than 5. In TiO₂ photocatalytic reduction, the main form of Cr⁶⁺ is HCrO₄⁻ when the pH value ranges from 2 to 5. In this situation, the TiO₂ surface is positive, and more HCrO₄⁻ anions are adsorbed onto the TiO₂ surface due to coulomb attraction forces when the pH value declines gradually. The adsorbed HCrO₄⁻ ions are then reduced to Cr³⁺ in situ by reductive substances. When the pH value increases from 5 to 7, the dominant existing form of Cr⁶⁺ is still HCrO₄⁻; however, the negative charge property of the TiO₂ surface becomes stronger, which results in the adsorption of HCrO₄⁻ anions on the catalyst surface and so the photocatalytic reduction declines. Adsorption is a key step for photocatalytic reactions – the stronger the adsorption, the higher the photocatalytic reduction efficiency.

HCrO₄⁻ ions are reduced to Cr³⁺ in TiO₂ photocatalytic reduction, consuming lots of hydrogen ions, as the following equations demonstrates:

\[ 3e^- + 7H^+ + HCrO_4^- = Cr^{3+} + 4H_2O \]  

(R1)

Figure 3(b) records the changes of pH value and Cr⁶⁺ concentration. From this figure, it can be seen that the pH value enhances from 3.0 to 3.3 and the Cr⁶⁺ concentration declines from 0.35 to 0.017 mg·L⁻¹ after 120 min. The concentration of generated Cr³⁺ ions is 0.35 mg·L⁻¹ at the same reaction time, theoretically. In fact, the actual Cr³⁺ may be lower than the theoretically concentration because some produced Cr³⁺ is still adsorbed on the TiO₂ surface, as shown by XPS analysis. On the other hand, dissolved Cr³⁺ may be precipitated to Cr(OH)₃ by OH⁻ anions if the mathematical product of Cr³⁺ and (OH⁻)³ is higher than the solubility of Cr(OH)₃ (K_sp = 6.31 × 10⁻³¹), as in the following chemical reaction:

\[ Cr^{3+} + 3OH^- \rightleftharpoons Cr(OH)_3 \]  

(R2)

In this experiment, it is presumed that all HCrO₄⁻ ions are reduced to Cr³⁺ and released into solution, the maximum concentration of Cr³⁺ reached is at 2/294 × 10⁻³ mol·L⁻¹ (initial concentration of K₂Cr₂O₇ is 1.0 mg·L⁻¹). At the same time, if the H⁺ ions are assumed to be about 2 × 7/294 × 10⁻³ mol·L⁻¹ according to Equation (R1), then the OH⁻ concentration increases to 10⁻¹⁴/(10⁻³ − 2 × 10⁻³ × 7/294) mol·L⁻¹ according to the ion product constant of water. The product of Cr³⁺ and (OH⁻)³ is 7 × 10⁻⁵⁹, which is much lower than 6.31 × 10⁻³¹. This means that Cr³⁺ cannot be precipitated in the form of Cr(OH)₃ in this experiment.

**Effect of atmospheres and scavengers**

Effects of N₂, O₂, and air bubbles on TiO₂ photocatalytic reductions were studied and the results are shown in Figure 4(a). It is observed that the order of reduction ability of Cr⁶⁺ is N₂ > air > O₂, suggesting that N₂ is positive for reduction and O₂ is negative for it. This is probably because the amount of O₂ molecules consume photoinduced electrons to produce a superoxide radical ·O₂, displayed in the following reaction:

\[ O_2 + e^- \rightarrow \cdot O_2 \]  

(R3)
The production of \(-\text{O}_2\) aggravates a tense competition between \(\text{O}_2\) and \(\text{Cr}^{6+}\) with photoinduced electrons, and only some of the photoinduced electrons are involved in the reduction of \(\text{Cr}^{6+}\), inhibiting photocatalytic reduction efficiency. To inhibit the recombination of photoinduced carriers and deduce photocatalytic reduction pathway, methanol acting as a scavenger of holes was added to system. The influence of methanol on \(\text{TiO}_2\) photocatalytic reduction was determined and the results are displayed in Figure 4(b). It is observed that the photocatalytic reduction efficiency of \(\text{Cr}^{6+}\) increased and it increases with an increase in methanol dosage. Well known, photoinduced holes are easily captured by methanol (Gumy et al. 2006), hence more photoinduced electrons can participate in the reduction of \(\text{Cr}^{6+}\) instead of recombination of carriers, compared with those in the absence of methanol, which verifies that \(\text{Cr}^{6+}\) is removed via photocatalytic reduction channel.

### Photocatalytic reduction mechanism

The \(\text{HCrO}_4^-\) anion is the dominant existing form when the pH is between 2 and 7. In this situation, adsorption of \(\text{HCrO}_4^-\) spontaneously happens on the surface of \(\text{TiO}_2\), forming a narrow bandgap \(\text{HCrO}_4^-/\text{TiO}_2\) complex catalyst, which is proven by UV–Vis DRS analysis. Photoinduced electrons are generated on the \(\text{HCrO}_4^-/\text{TiO}_2\) conduction band in visible light irradiation and are involved in the reduction of \(\text{Cr}^{6+}\). To verify this hypothesis, XPS and UV–Vis DRS were both conducted and the results are shown in Figure 5. Figure 5(a) displays the XPS spectra of three samples. The first sample is as-prepared \(\text{TiO}_2\) powder, named as \(\text{TiO}_2\); the second is \(\text{TiO}_2\) powder which is soaked in \(1.0 \text{ mg·L}^{-1} \text{ Cr}_2\text{O}_7^{2-}\) aqueous solution for 1 h in dark and then dried at 100°C, named as \(\text{TiO}_2\) before reaction; and the third is \(\text{TiO}_2\) powder which is recovered from the reduction system after 120 min, named as \(\text{TiO}_2\) after reaction. It is apparent that there are three characteristic peaks in the spectrum of \(\text{TiO}_2\) with binding energies of 530.2 eV, 459.5 eV, and 285.7 eV, and they are assigned to \(\text{O}_1s\), \(\text{Ti}_2p\), and \(\text{C}_1s\) elements, respectively. The peak of \(\text{C}_1s\) is possibly caused by pollution. It is found that \(\text{Cr}_2p\) intensity in the spectrum of \(\text{TiO}_2\) before reaction (blue line) is stronger than that of \(\text{TiO}_2\) (black line), suggesting that some \(\text{HCrO}_4^-\) ions are adsorbed onto the \(\text{TiO}_2\) surface in dark conditions. However, it is surprising that the \(\text{Cr}_2p\) peak almost disappears in the spectrum of \(\text{TiO}_2\) after reaction (red line), revealing that adsorbed \(\text{HCrO}_4^-\) ions are reduced under visible light irradiation. Three continuous steps including adsorption, reduction, and desorption are involved in the reduction of \(\text{Cr}^{6+}\). These steps continue until almost all \(\text{HCrO}_4^-\) anions are reduced.
Figure 5 | (a) XPS spectra of three samples (TiO$_2$, TiO$_2$ before, and TiO$_2$ after reaction); (b) Ti$_2$p XPS spectrum and separation peak at the binding energy of 459.5 eV for two samples (TiO$_2$ before and TiO$_2$ after reaction); (c) Cr$_2$p XPS spectrum and separation peak at the binding energy of 579.7 eV for the sample (TiO$_2$ after reaction), and the inset is the Cr$_2$p XPS spectrum of the sample (TiO$_2$ before reaction); (d) O$_1$s XPS spectra and separation peak at the binding energy of 530.2 eV for two samples of TiO$_2$ after reaction and TiO$_2$ before reaction (the inset picture); (e) UV-Vis diffuse reflectance spectra of TiO$_2$ and TiO$_2$ before reaction.
The peak of Ti2p binding at 459.5 eV was fitted using XPS software and results are shown in Figure 5(b). One peak appears at the binding energy of 464.4 eV which is caused by Ti2p1/2 and the other appears at 458.8 eV which is caused by Ti2p3/2. It is found that Ti4+ is the only chemical form during the whole photocatalytic reduction, demonstrating that TiO2 keeps a good structural stability. The fitting of Cr2p binding at 579.7 eV was also analyzed and results are shown in Figure 5(c). The spectrum of Cr2p marked with red diamonds is divided into two individual curves marked with green and blue curves, respectively. The blue line represents the spectrum of Cr2p1/2 and it belongs to Cr6+ with a characteristic peak at 579.7 eV. The green line represents the spectrum of Cr2p3/2 and is assigned to Cr3+ with the characteristic peak at 576.6 eV. It is concluded that Cr3+ is the only reductive product. At the same time, the fitting of Cr2p in the spectrum before photocatalytic reaction was simulated, but there is only one Cr2p1/2 peak caused by Cr6+, shown in Figure 5(c). This shows that HCrO4- is initially adsorbed on the surface of TiO2 before photocatalytic reaction and is then reduced in situ to Cr3+ in visible light irradiation. The quantities of Cr6+ and Cr3+ adsorbed on the TiO2 surface are calculated and exported using software. Molar ratio of Cr6+:Cr3+ is about 1:4, indicating that HCrO4- is reduced to Cr3+ and that Cr3+ ions still adsorb on the surface of TiO2 catalyst. Figure 5(d) displays the fitting of O1s spectra in two samples of TiO2 after and before reaction (inset figure), respectively. It is observed that O1s binding at 530.2 eV can be divided into two peaks. One peak binding at 530.0 eV (red curve) is assigned to the lattice oxygen coming from TiO2 and HCrO4-. It is found that TiO2/HCrO4- is intitially adsorbed on the surface of TiO2 before reaction, proving that O2 or OH− or produced ·O2 adsorbs on the TiO2 surface during photocatalytic reduction. Figure 5(e) shows the absorption bandgap of pure TiO2 and TiO2 before photocatalytic reaction. The absorption of pure TiO2 focuses on the ultraviolet zone and that of TiO2/HCrO4- increases to visible light scope, proving that TiO2/HCrO4- can produce photoinduced carriers irradiated by visible light.

Based on the above analysis, visible light-driven TiO2 photocatalytic reduction of Cr6+ was explored. The mechanism involves four major pathways: (1) adsorption of HCrO4- on the surface of TiO2; (2) production of photoinduced electrons under visible light irradiation; (3) reduction of Cr6+ to Cr3+ by photoinduced electrons; and (4) desorption of Cr3+. The cycle of adsorption → reduction → desorption continues until almost all the HCrO4- is reduced.

**Life span, kinetics and application**

TiO2 was reused eight times under the same experimental conditions and the results are shown in Figure 6(a). It is observed that the TiO2 photocatalytic reduction efficiency does not decrease with recycled times, showing that TiO2 has a satisfied structural stability and a potential application for use in wastewater treatment. Photocatalytic reduction kinetics of Cr6+ with TiO2 was investigated and results are shown in Figure 6(b) and 6(c). The photocatalytic reduction fits well with pseudo-first-order kinetics when Cr2O72− initial concentration ranges from 0.5 to 5.0 mg L−1, and rate constants decrease with the enhancement of Cr2O72− initial concentration. The functional relationship between first-order kinetic rate constants and Cr2O72− initial concentration was simulated and shown in Figure 6(c). Pseudo-first-order kinetics constant (k) can be described as: $k = 0.023 C^{-1.42}$, where C is the Cr2O72− initial concentration. Hence, we can obtain the corresponding k value at a certain Cr2O72− initial concentration according to this simulation.

To investigate the application of TiO2 photocatalytic reduction in real industrial wastewater containing Cr6+, a small-scale static test was carried out in the same reactor. Properties, including Cr2O72− initial concentration and pH of chemical wastewater, are listed in Table 1, and experimental results are shown in Figure 6(d). It is observed that removal efficiencies of Cr6+ in the simulation experiment and small-scale static test are 100% and 93%, respectively, suggesting that TiO2 photocatalytic reduction can be used to treat wastewater containing Cr6+. The slight decline of Cr6+ removal may be caused by co-existing ions in chemical wastewater.

**CONCLUSIONS**

Almost 100% of Cr6+ is reduced to Cr3+ in situ by visible light-driven TiO2 photocatalytic reduction under the optimal experimental conditions. Photoinduced electrons are the major reductive substance of Cr6+, and the mechanism involves adsorption of HCrO4-, reduction of Cr6+, and desorption of Cr3+. The TiO2 photocatalyst has a reliable lifespan for reduction Cr6+ under visible light irradiation and its
Figure 6 | (a) Life span of TiO₂ photocatalyst of Cr⁶⁺; (b) relationship between ln (C₀/C) and reaction time; (c) effect of Cr₂O₇²⁻/C₀ initial concentration on first-order kinetics constants; (d) removal of Cr⁶⁺ in simulation experiment and small-scale static test under the same experiment conditions.
photocatalytic reduction reaction fits well with pseudo-first-order kinetics.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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### Table 1 | Properties of wastewater

| Cr₂O₇²⁻ | pH | Turbidity | Temp. | Conductivity | Ca²⁺ | Na⁺ | NO₃⁻ | Cl⁻ |
|--------|----|-----------|-------|--------------|------|-----|------|-----|
| 1 mg·L⁻¹ | 5  | 4         | 20 °C | 160 m·sm⁻¹   | 10⁻³ mg·L⁻¹ | 10⁻³ mg·L⁻¹ | 3 mg·L⁻¹ | 10⁻³ mg·L⁻¹ | 10⁻³ mg·L⁻¹ |
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