

A novel visible light-driven TiO₂ photocatalytic reduction for hexavalent chromium wastewater and mechanism

Baoxiu Zhao, Kaixin Zhang, Yue Huang, Qi Wang, Hao Xu, Yilin Wang, Jincheng Li, Tianwen Song, Wenxiang Xia and Jie Liu

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.

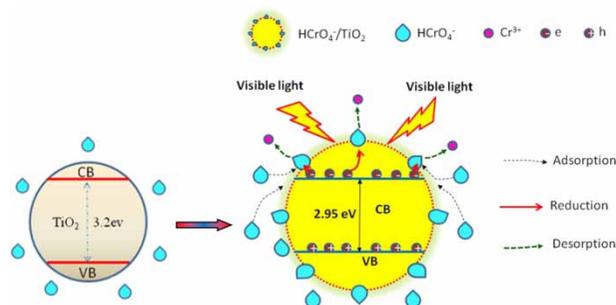
Key words | Cr³⁺, Cr⁶⁺, photocatalytic reduction, TiO₂, visible light

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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. Cr⁶⁺ 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 Cr⁶⁺-rich environment for a long time (Guo *et al.* 2016; Yoshinaga *et al.* 2018). There are some methods for wastewater containing Cr⁶⁺, 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 (Sarahney *et al.* 2012), and chemical reagents (Sheikhmohammadi *et al.* 2019). Adsorption is a convenient way for Cr⁶⁺ 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 Cr⁶⁺ is reduced to non-toxic Cr³⁺ 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 Cr⁶⁺ from wastewater; however, membrane assembly is easily contaminated or blocked, and so how to efficiently, safely, and economically remove Cr⁶⁺ 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 (TiO₂) photocatalytic reduction for trace Cr⁶⁺ 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 TiO₂ ($E_g = 3.2$ eV) lies in the ultraviolet light zone ($\lambda = 1240/E_g = 385$ nm) (Fujishima *et al.* 2008), and it has no ability to oxidize or reduce pollutants in visible light irradiation. TiO₂ modification is a good way to achieve the visible light-driven photocatalytic reaction because the spectrum scope of modified TiO₂ transfers from the ultraviolet light region to the visible light zone. Modified TiO₂ 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 TiO₂ photocatalytic performance in visible light irradiation. Chatterjee & Dasgupta (2005) discussed TiO₂ visible light-assisted degradation of organic pollutants and mechanism, and there is more research into TiO₂ photocatalytic degradation for organics in visible light irradiation. The bandgap of TiO₂ doped with elements such as N, F, S, and Bi or anions such as OH⁻, SO₄²⁻, and ClO₄⁻ 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 Cr⁶⁺ 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 TiO₂-Cu₂(OH)PO₄ heterojunction catalyst and found that the composite catalyst exhibited high reduction efficiency of Cr⁶⁺ because the bandgap narrowed from 3.2 eV to 2.6 eV. Dye-sensitized-TiO₂ also has photocatalytic reduction ability. Wu *et al.* (2013) prepared dye-sensitized TiO₂ to reduce Cr⁶⁺ under visible light irradiation and found that Cr⁶⁺ was reduced by photo electrons that diffuse from the dye-sensitized zone to the TiO₂ zone.

There are many investigations into reduction of Cr⁶⁺ with TiO₂ ultraviolet photocatalysis (Zhou *et al.* 1993) or oxidation for organics with TiO₂ or modified TiO₂ (Asgari *et al.* 2021) or TiO₂-integrated process (Zhao *et al.* 2012, 2015, 2016); however, the study about direct reduction of Cr⁶⁺ with pure TiO₂ in visible light is scarce. Our previous experiments have shown that in visible light irradiation, Cr⁶⁺ is reduced to Cr³⁺ by TiO₂ prepared by a sol-gel method. To investigate TiO₂ photocatalytic reduction of Cr⁶⁺, process reactions and reduction mechanisms are analyzed in this work.

EXPERIMENTAL

Reagents and chemicals

Titanium butoxide, H₂CrO₄, C₂H₅OH, CH₃COOH, K₂Cr₂O₇, HCl, NaOH, and methanol were all analytical degree reagents and purchased from Tianjin Chemical Reagent Co. (China). High pure water (18.2 MΩ·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 Quanta 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 Kα₁ 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 2θ of 25.31°, 36.97°, 37.86°, 38.63°, 48.11°, 53.93°, 55.14°, 62.23°, 62.72°,

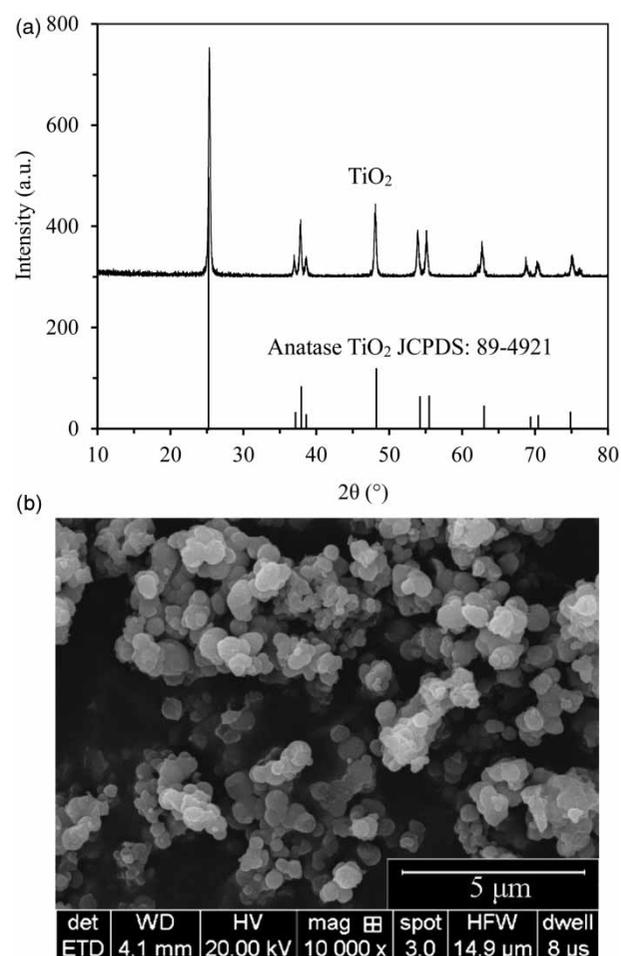


Figure 1 | (a) XRD pattern of TiO₂; (b) SEM image of TiO₂.

68.75°, 70.28°, 75.13°, and 76.15° correspond to (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), (215), and (301) planes of anatase phase, suggesting that as-prepared TiO₂ is clear and perfect, which is in accordance with the research reported by Wang *et al.* (2021). SEM images of as-prepared TiO₂ are shown in Figure 1(b). It seems that TiO₂ looks like some uniform microspheres. The average size of as-prepared TiO₂ is about 78 nm, according to Debye–Scherrer formula ($D = K\lambda/\beta\cos\theta$), where K is a constant of 0.59, λ is irradiation wavelength of 0.15406 nm, β is half-maximum of (101) obtained via XRD software, and θ is the diffraction angle. Furthermore, the surface of TiO₂ is not smooth but layered, which is good for the adsorption and photocatalytic reduction of Cr(VI), compared to the smooth surface.

Effects of TiO₂ dosage and Cr₂O₇²⁻ concentration

The effect of TiO₂ dosage on photocatalytic reduction of Cr⁶⁺ was investigated and results are displayed in Figure 2(a). It is observed that photocatalytic reduction of Cr⁶⁺ increases initially and then decreases with the enhancement of TiO₂, and the optimum is 1.0 g·L⁻¹. The reason is that when TiO₂ dosage is lower than 1.0 g·L⁻¹, more Cr⁶⁺ ions are adsorbed on the TiO₂ 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 Cr⁶⁺ aqueous solution receives light irradiation, resulting in low photocatalytic reduction efficiency.

The effect of Cr₂O₇²⁻ concentration on photocatalytic reduction of Cr⁶⁺ was studied and results are shown in Figure 2(b). It can be seen that reduction efficiency decreases with the enhancement of Cr₂O₇²⁻ concentration. Reduction of Cr⁶⁺ climbs to 98% at 90 min when Cr₂O₇²⁻ initial concentration is 0.5 mg·L⁻¹; however, it is only 24% when the Cr₂O₇²⁻ initial concentration is 5.0 mg·L⁻¹. The decline of reduction is mainly caused by light scattering. The higher the Cr₂O₇²⁻ initial concentration, the darker the aqueous solution becomes, and then the Cr₂O₇²⁻ anions participating in photocatalytic reduction reduces for the serious scattering of visible light.

Effect of pH

The effect of pH on photocatalytic reduction of Cr⁶⁺ was studied under visible light and results are displayed in

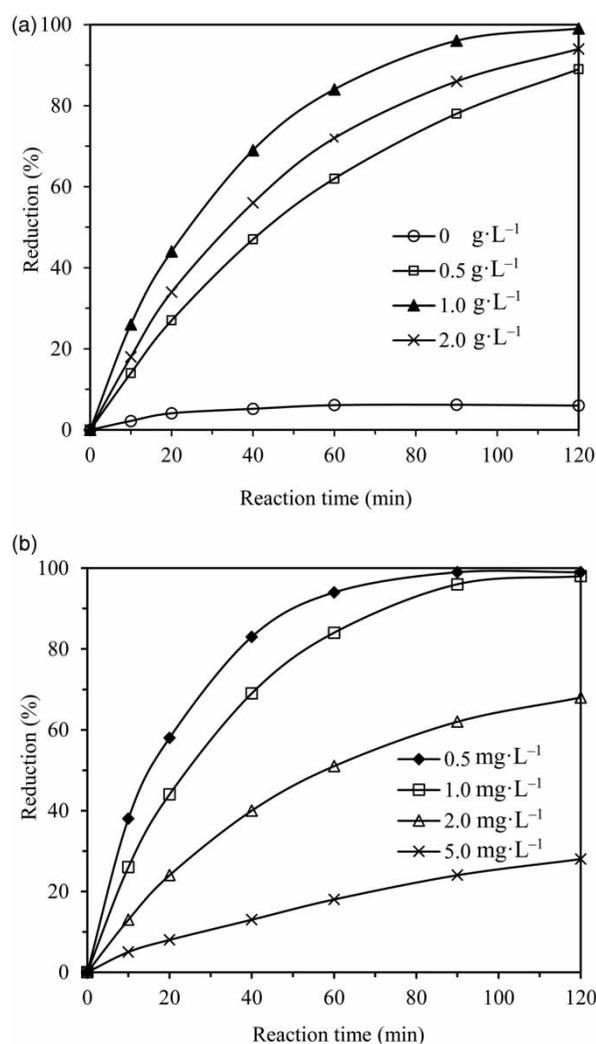


Figure 2 | (a) Effect of TiO₂ dosage on photocatalytic reduction of Cr⁶⁺ in the presence of air bubbles, where [Cr₂O₇²⁻] = 1.0 mg·L⁻¹, pH = 3, P = 150 W; (b) effect of Cr₂O₇²⁻ concentration on photocatalytic reduction of Cr⁶⁺ in the presence of air bubbles, where [TiO₂] = 1.0 g·L⁻¹, pH = 3.0, P = 150 W.

Figure 3(a). It is observed that photocatalytic reduction efficiency decreases with the enhancement of pH value. In TiO₂ photocatalytic reduction of Cr⁶⁺, pH not only affects the charge property of TiO₂ but also influences the existing form of Cr⁶⁺ species. Acharya *et al.* (2018) found that the existing form of Cr⁶⁺ strictly depends on pH value: H₂CrO₄ molecule (pH < 2), HCrO₄⁻ (2 < pH < 7) and Cr₂O₇²⁻ (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 TiO₂ was tested using an electrochemical method controlled by a zeta potentiometer and was found to be about 5. The surface of TiO₂ is positively charged when the pH value is lower than 5 and

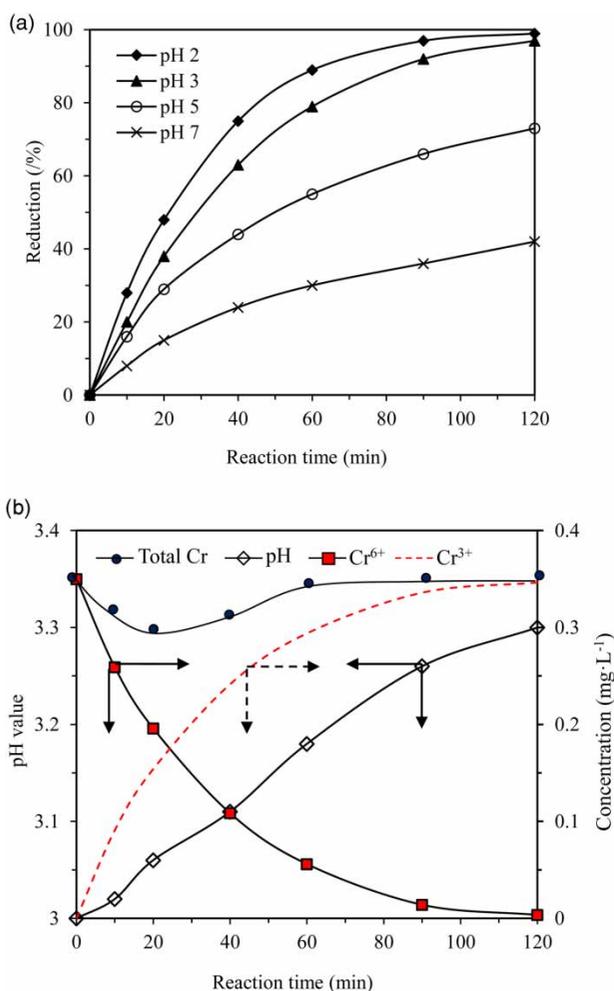


Figure 3 | (a) Effect of pH values on photocatalytic reduction of Cr⁶⁺ in the presence of air bubbles; (b) the changes of pH, concentration of Cr⁶⁺, and Cr³⁺ during photocatalytic reduction, where [TiO₂] = 1.0 g·L⁻¹, [Cr₂O₇²⁻] = 1.0 mg·L⁻¹, P = 150 W.

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:

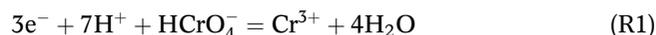


Figure 3(b) records the changes of pH value and Cr⁶⁺ concentration. From this figure, it can be seen that the pH value enhances from 3.0 to 3.3 and the Cr⁶⁺ concentration declines from 0.35 to 0.017 mg·L⁻¹ after 120 min. The concentration of generated Cr³⁺ ions is 0.35 mg·L⁻¹ at the same reaction time, 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 ($K_{sp} = 6.31 \times 10^{-31}$), as in the following chemical reaction:



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 $2/294 \times 10^{-3}$ 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 $2 \times 7/294 \times 10^{-3}$ mol·L⁻¹ according to Equation (R1), then the OH⁻ concentration increases to $10^{-14}/(10^{-3} - 2 \times 10^{-3} \times 7/294)$ mol·L⁻¹ according to the ion product constant of water. The product of Cr³⁺ and (OH⁻)³ is 7×10^{-39} , 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:



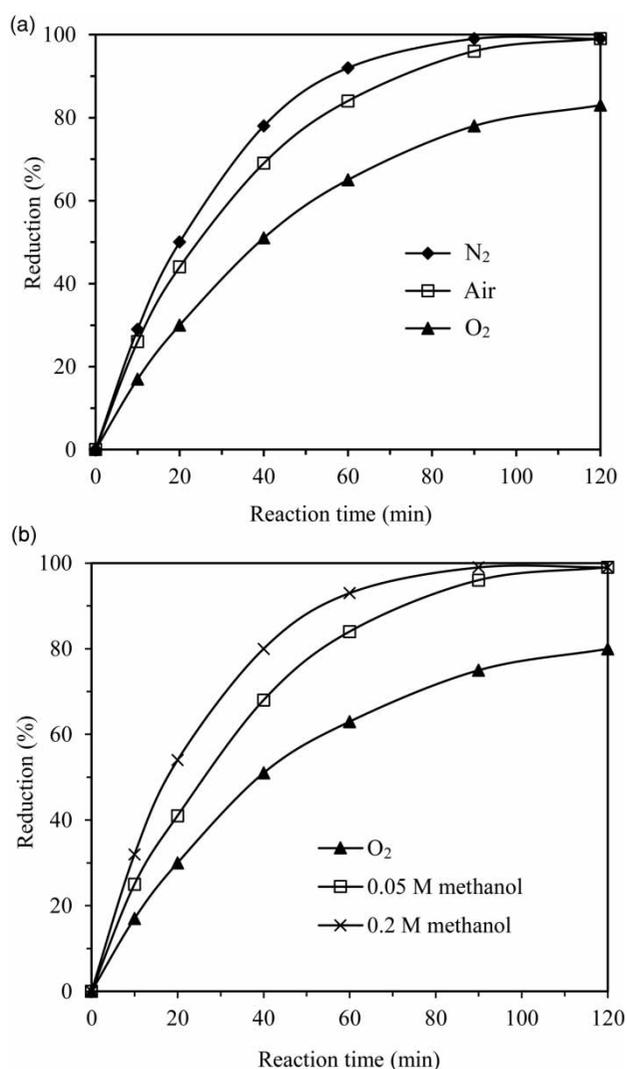


Figure 4 | (a) Effect of N₂, O₂, and air bubbles on photocatalytic reduction of Cr⁶⁺; (b) effect of scavengers on photocatalytic reduction of Cr⁶⁺, where [TiO₂] = 1.0 g·L⁻¹, [Cr₂O₇²⁻] = 1.0 mg·L⁻¹, pH = 3, P = 150 W.

The production of $\cdot\text{O}_2^-$ aggravates a tense competition between O₂ and Cr⁶⁺ with photoinduced electrons, and only some of the photoinduced electrons are involved in the reduction of Cr⁶⁺, inhibiting photocatalytic reduction efficiency. On the contrary, bubbling N₂ can greatly drive dissolved O₂ which is an effective photoinduced electron scavenger from aqueous solution, and as a result, more photoinduced electrons can take part in the reduction of Cr⁶⁺ in this situation, compared with those in O₂ or air atmospheres. In fact, oxidation–reduction is a concurrent reaction in the TiO₂ photocatalytic process. In this work, TiO₂ photocatalytic reduction conducted by photoinduced electrons was used to treat Cr⁶⁺. A partial oxidation reaction caused by photoinduced holes or hydroxyl radicals occurs, which consumes a

lot of photoinduced electrons if there is no additional scavenger of holes, leading to low photocatalytic 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 TiO₂ photocatalytic reduction was determined and the results are displayed in Figure 4(b). It is observed that the photocatalytic reduction efficiency of Cr⁶⁺ 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 Cr⁶⁺ instead of recombination of carriers, compared with those in the absence of methanol, which verifies that Cr⁶⁺ is removed via photocatalytic reduction channel.

Photocatalytic reduction mechanism

The HCrO₄⁻ anion is the dominant existing form when the pH is between 2 and 7. In this situation, adsorption of HCrO₄⁻ spontaneously happens on the surface of TiO₂, forming a narrow bandgap HCrO₄⁻/TiO₂ complex catalyst, which is proven by UV–Vis DRS analysis. Photoinduced electrons are generated on the HCrO₄⁻/TiO₂ conduction band in visible light irradiation and are involved in the reduction of Cr⁶⁺. 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 TiO₂ powder, named as TiO₂; the second is TiO₂ powder which is soaked in 1.0 mg·L⁻¹ Cr₂O₇²⁻ aqueous solution for 1 h in dark and then dried at 100 °C, named as TiO₂ before reaction; and the third is TiO₂ powder which is recovered from the reduction system after 120 min, named as TiO₂ after reaction. It is apparent that there are three characteristic peaks in the spectrum of TiO₂ with binding energies of 530.2 eV, 459.5 eV, and 285.7 eV, and they are assigned to O1s, Ti2p, and C1s elements, respectively. The peak of C1s is possibly caused by pollution. It is found that Cr2p intensity in the spectrum of TiO₂ before reaction (blue line) is stronger than that of TiO₂ (black line), suggesting that some HCrO₄⁻ ions are adsorbed onto the TiO₂ surface in dark conditions. However, it is surprising that the Cr2p peak almost disappears in the spectrum of TiO₂ after reaction (red line), revealing that adsorbed HCrO₄⁻ ions are reduced under visible light irradiation. Three continuous steps including adsorption, reduction, and desorption are involved in the reduction of Cr⁶⁺. These steps continue until almost all HCrO₄⁻ anions are reduced.

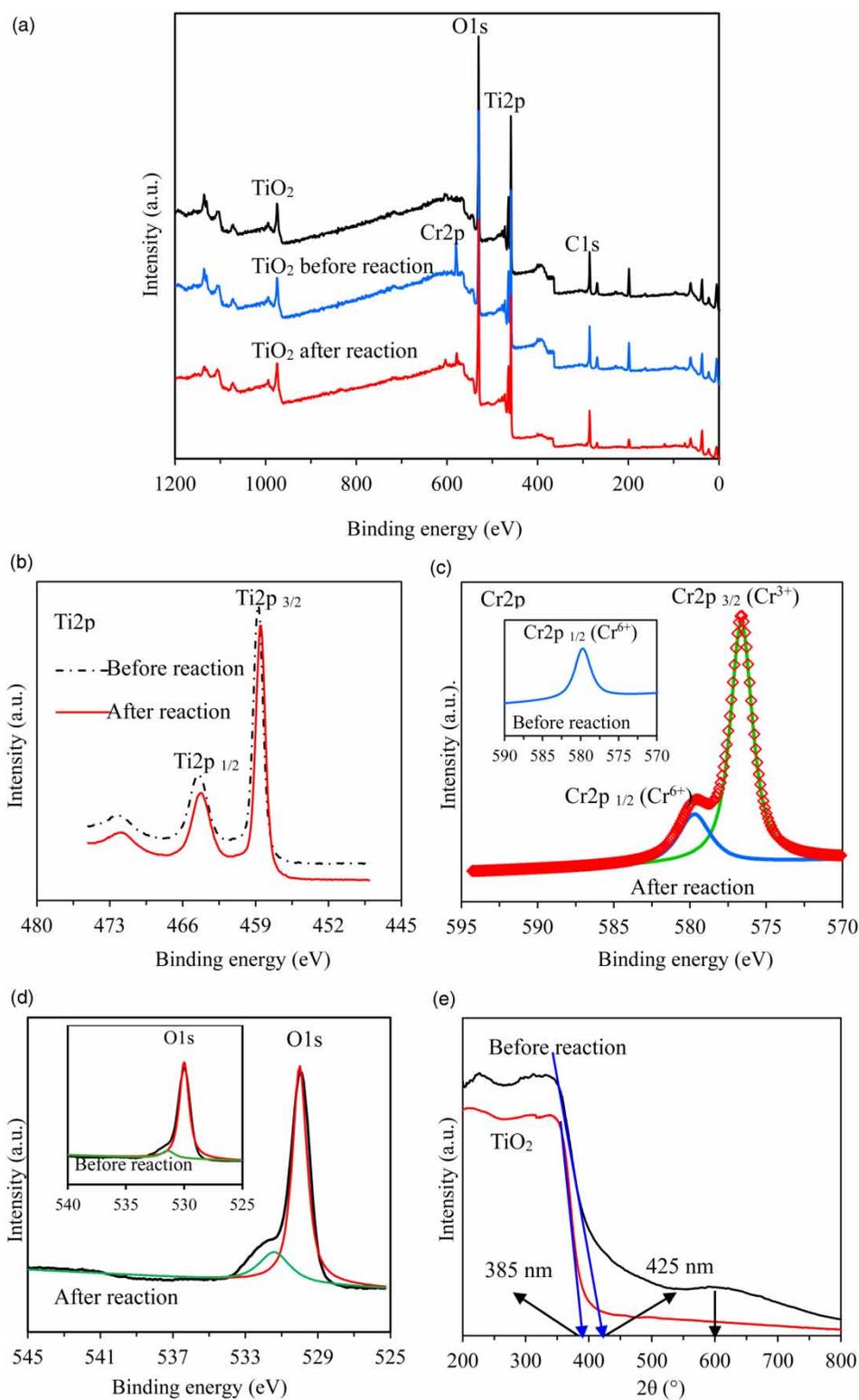


Figure 5 | (a) XPS spectra of three samples (TiO₂, TiO₂ before, and TiO₂ after reaction); (b) Ti2p XPS spectrum and separation peak at the binding energy of 459.5 eV for two samples (TiO₂ before and TiO₂ after reaction); (c) Cr2p XPS spectrum and separation peak at the binding energy of 579.7 eV for the sample (TiO₂ after reaction), and the inset is the Cr2p XPS spectrum of the sample (TiO₂ before reaction); (d) O1s XPS spectra and separation peak at the binding energy of 530.2 eV for two samples of TiO₂ after reaction and TiO₂ before reaction (the inset picture); (e) UV-Vis diffuse reflectance spectra of TiO₂ and TiO₂ 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 Ti2p_{1/2} and the other appears at 458.8 eV which is caused by Ti2p_{3/2}. 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 spectra marked with green and blue curves, respectively. The blue line represents the spectrum of Cr2p_{1/2} and it belongs to Cr⁶⁺ with a characteristic peak at 579.7 eV. The green line represents the spectrum of Cr2p_{3/2} 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 Cr2p_{1/2} 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⁻, and the other binding at about 531.4 eV (green curve) probably belongs to hydroxyl oxygen coming from the chemical adsorption of oxygen, which is in accordance with the conclusion by Yang *et al.* (2006). It is obvious that the hydroxyl oxygen is higher on the TiO₂ surface after the reaction than 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 ultra-violet zone and that of TiO₂/HCrO₄⁻ increases to visible light scope, proving that TiO₂/HCrO₄⁻ can produce photo-induced 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

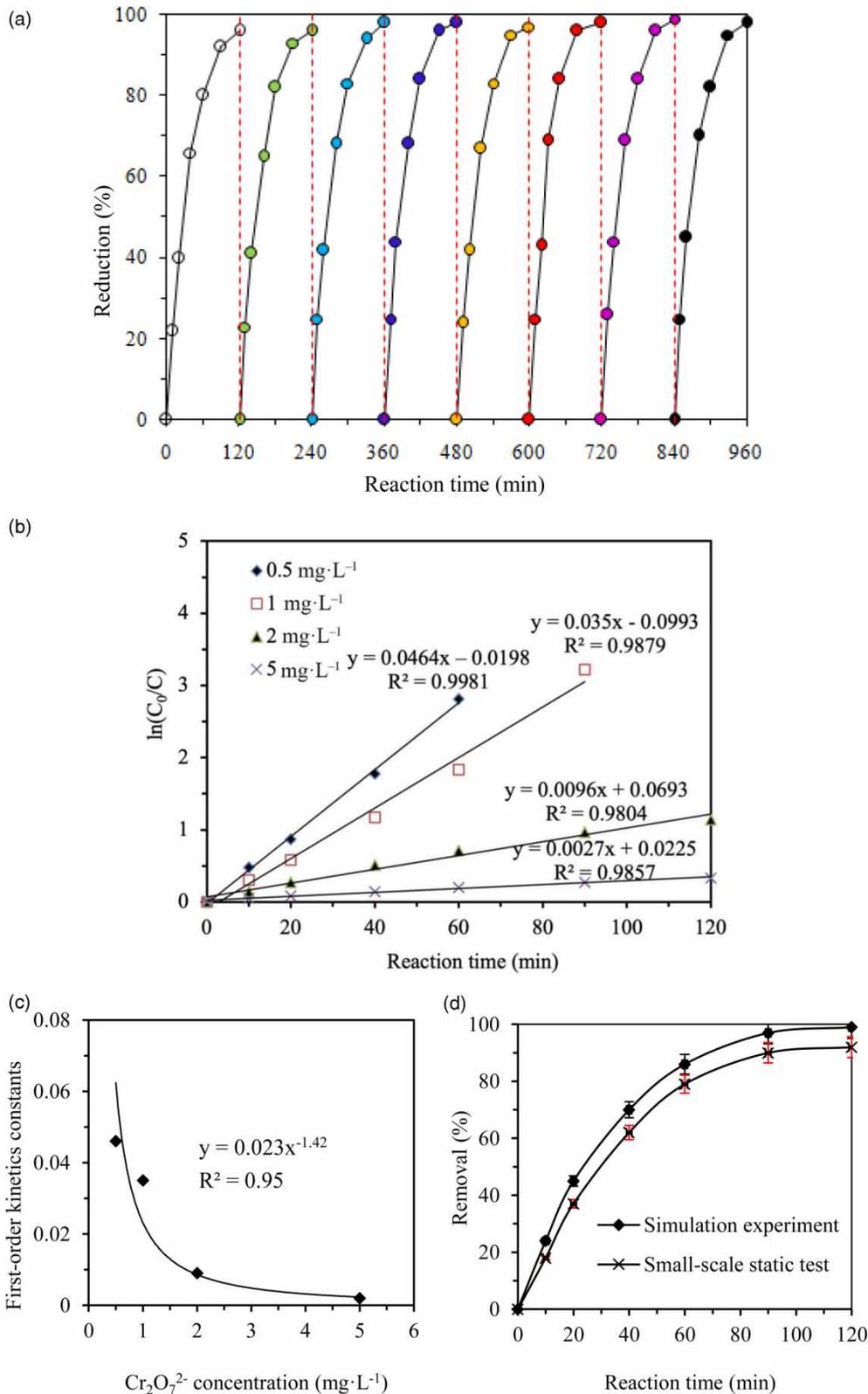


Figure 6 | (a) Life span of TiO₂ photocatalyst of Cr⁶⁺; (b) relationship between $\ln(C_0/C)$ and reaction time; (c) effect of Cr₂O₇²⁻ initial concentration on first-order kinetics constants; (d) removal of Cr⁶⁺ in simulation experiment and small-scale static test under the same experiment conditions.

Table 1 | Properties of wastewater

Cr ₂ O ₇ ²⁻	pH	Turbidity	Temp.	Conductivity	Ca ²⁺	Na ⁺	NO ₃ ⁻	Cl ⁻
1 mg·L ⁻¹	5	4	20 °C	160 m·sm ⁻¹	10 ⁻³ mg·L ⁻¹			

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.

REFERENCES

- Acharya, R., Naik, B. & Parida, K. 2018 Cr(VI) remediation from aqueous environment through modified-TiO₂-mediated photocatalytic reduction. *Beilstein Journal of Nanotechnology* **9**, 1448–1470.
- Asgari, E., Sheikhmohammadi, A., Nourmoradi, H., Nazari, S. & Aghanaghad, M. 2021 Degradation of ciprofloxacin by photocatalytic ozonation process under irradiation with UVA: comparative study, performance and mechanism. *Process Safety & Environmental Protection* **147**, 356–366.
- Ayub, S., Siddique, A. A., Khurshed, M. S., Zarei, A., Alam, I., Asgari, E. & Changani, F. 2020 Removal of heavy metals (Cr, Cu and Zn) from electroplating wastewater by electrocoagulation and adsorption processes. *Desalination & Water Treatment* **179**, 263–271.
- Chatterjee, D. & Dasgupta, S. 2005 Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **6** (2–3), 186–205.
- Deveci, H. & Kar, Y. 2013 Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis. *Journal of Industrial & Engineering Chemistry* **19** (1), 190–196.
- Fujishima, A., Zhang, X. T. & Tryk, D. A. 2008 TiO₂ photocatalysis and related surface phenomena. *Surface Science Reports* **63** (11), 515–582.
- Gheju, M. & Balcu, I. 2017 Assisted green remediation of chromium pollution. *Journal of Environmental Management* **203**, 920–924.
- Gong, Y., Gai, L., Tang, J., Fu, J., Wang, Q. & Zeng, E. Y. 2017 Reduction of Cr(VI) in simulated groundwater by FeS-coated iron magnetic nanoparticles. *Science of the Total Environment* **595**, 743–751.
- Gumy, D., Morais, C., Bowen, P., Pulgarin, C., Giraldo, S., Hajdu, R. & Kiwi, J. 2006 Catalytic activity of commercial of TiO₂ powders for the abatement of the bacteria (*E. coli*) under solar simulated light: influence of the isoelectric point. *Applied Catalysis B Environmental* **63** (1–2), 76–84.
- Guo, S. H., Liu, Z. L., Li, Q. S., Yang, P., Wang, L. L., He, B. Y., Xu, Z. M., Ye, J. S. & Zeng, E. Y. 2016 Leaching heavy metals from the surface soil of reclaimed tidal flat by alternating seawater inundation and air drying. *Chemosphere* **157**, 262–270.
- Habibi, S., Nematollahzadeh, A. & Mousavi, S. A. 2015 Nano-scale modification of polysulfone membrane matrix and the surface for the separation of chromium ions from water. *Chemical Engineering Journal* **267**, 306–316.
- Hoffmann, M., Martin, S. T., Chio, W. & Bahnemann, D. W. 1995 Environmental applications of semiconductor photocatalysis. *Chemical Reviews* **95**, 69–96.
- Jobby, R., Jha, P., Yadav, A. K. & Desai, N. 2018 Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: a comprehensive review. *Chemosphere* **207**, 255–266.
- Kerkez-Kuyumcu, Ö., Kibar, E., Dayioğlu, K., Gedik, F., Özkara-Aydınoglu, Ş., Gedik, F., Akin, A. N. & Zkara-Aydınoglu, S. Ö. 2015 A comparative study for removal of different dyes over M/TiO₂ (M = Cu, Ni, Co, Fe, Mn and Cr) photocatalysts under visible light irradiation. *Journal of Photochemistry & Photobiology A Chemistry* **311**, 176–185.
- Magadevan, D., Dhivya, E., Mundari, N. D. A., Mishra, T. & Aman, N. 2019 Development of novel TiO₂-Cu₂(OH)PO₄ heterojunction as nanophotocatalyst for improved Cr(VI) reduction. *Journal of Environmental Chemical Engineering* **7** (2), 102968.
- Ravindra, K. & Mor, S. 2019 Distribution and health risk assessment of arsenic and selected heavy metals in groundwater of Chandigarh, India. *Environ. Environmental Pollution* **250**, 820–830.
- Sarahney, H., Mao, X. & Alshawabkeh, A. N. 2012 The role of iron anode oxidation on transformation of chromium by electrolysis. *Electrochimica Acta* **86**, 96–101.
- Sheikhmohammadi, A., Mohseni, S. M., Hashemzadeh, B., Asgari, E., Sharafkhani, R., Sardar, M., Sarkhosh, M. & Almasiane, M. 2019 Fabrication of magnetic graphene oxide

- nanocomposites functionalized with a novel chelating ligand for the removal of Cr(VI): modeling, optimization, and adsorption studies. *Desalination & Water Treatment* **160**, 297–307.
- Testa, J. J., Grela, M. A. & Litter, M. I. 2004 Heterogeneous photocatalytic reduction of chromium(VI) over TiO₂ particles in the presence of oxalate: involvement of Cr(V) species. *Environmental Science & Technology* **38** (5), 1589–1594.
- Vendruscolo, F., Ferreira, R. G. L. & Filho, N. R. A. 2017 Biosorption of hexavalent chromium by microorganisms. *International Biodeterioration & Biodegradation* **119**, 87–95.
- Wang, Q., Yang, C., Hang, G. Z., Hu, L. & Wang, P. 2017 Photocatalytic Fe-doped TiO₂/PSF composite UF membranes: characterization and performance on BPA removal under visible-light irradiation. *Chemical Engineering Journal* **319**, 39–47.
- Wang, X., Fu, R., Li, H., Zhang, Y., Xiong, Y., Lu, M., Xiao, K., Zhang, X., Zheng, C. & Xiong, Y. 2020 Heavy metal contamination in surface sediments: a comprehensive, large-scale evaluation for the Bohai Sea, China. *Environmental Pollution* **260**, 113986.
- Wang, X., Zhang, L., Bu, Y. & Sun, W. 2021 Interplay between invasive single atom Pt and native oxygen vacancy in anatase TiO₂ (101) surface: a theoretical study. *Applied Surface Science* **540**, 148357.
- Wu, Q., Zhao, J., Qin, G., Wang, C., Tong, X. & Xue, S. 2013 Photocatalytic reduction of Cr(VI) with TiO₂ film under visible light. *Applied Catalysis B Environmental* **142–143**, 142–148.
- Xu, L., Bai, X., Guo, L., Yang, S. & Yang, L. 2019 Facial fabrication of carbon quantum dots (CDs)-modified N-TiO_{2-x} nanocomposite for the efficient photoreduction of Cr(VI) under visible light. *Chemical Engineering Journal* **357**, 473–486.
- Yang, S., Zhu, W., Jiang, Z., Chen, Z. & Wang, J. 2006 The surface properties and the activities in catalytic wet air oxidation over CeO₂-TiO₂ catalysts. *Applied Surface Science* **252** (24), 8499–8505.
- Yang, Q., Li, Z., Lu, X., Duan, Q., Huang, L. & Bi, J. 2018 A review of soil heavy metal pollution from industrial and agricultural regions in China: pollution and risk assessment. *Science of the Total Environment* **642**, 690–700.
- Yao, W., Wang, J., Wang, P., Wang, X., Yu, S., Zou, Y., Hou, J., Hou, J., Hayat, T., Alsaedi, A. & Wang, X. 2017 Synergistic coagulation of GO and secondary adsorption of heavy metal ions on Ca/Al layered double hydroxides. *Environmental Pollution* **229**, 827–836.
- Yoshinaga, M., Ninomiya, H., Al Hossain, M. M. A., Sudo, M., Akhand, A. A., Ahsan, N., Alim, M. A., Khalequzzaman, M., Iida, M., Yajima, I., Ohgami, I. N. & Kato, M. 2018 A comprehensive study including monitoring, assessment of health effects and development of a remediation method for chromium pollution. *Chemosphere* **201**, 667–675.
- Yu, X., Yu, R. Q., Gui, D., Zhang, X. & Wu, Y. 2018 Hexavalent chromium induces oxidative stress and mitochondria-mediated apoptosis in isolated skin fibroblasts of Indo-Pacific humpback dolphin. *Aquatic Toxicology* **203**, 179–186.
- Zhang, C., Xia, F., Long, J. & Peng, B. 2017 The pollution of chromium in wet-end process of leather manufacture. *Journal of Cleaner Production* **154**, 276–283.
- Zhao, B., Lv, M. & Zhou, L. 2012 Photocatalytic degradation of perfluorooctanoic acid with beta-Ga₂O₃ in anoxic aqueous solution. *Journal of Environmental Science* **24** (4), 774–780.
- Zhao, B., Li, X., Li, W., Yang, L., Li, J., Xia, W., Zhou, L. & Zhao, C. 2015 Degradation of trichloroacetic acid by an efficient Fenton/UV/TiO₂ hybrid process and investigation of synergetic effect. *Chemical Engineering Journal* **273**, 527–533.
- Zhao, B., Wang, X., Shang, H., Li, X., Li, W., Li, J., Xia, W., Zhou, L. & Zhao, C. 2016 Degradation of trichloroacetic acid with an efficient Fenton assisted TiO₂ photocatalytic hybrid process: reaction kinetics, byproducts and mechanism. *Chemical Engineering Journal* **289**, 319–329.
- Zhou, X., Korenaga, T., Takahashi, T., Moriwake, T. & Shinoda, S. 1993 A process monitoring/controlling system for the treatment of wastewater containing chromium (VI). *Water Research* **27** (6), 1049–1054.

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