Photocatalytic reduction of Cr(VI) within mesoporous TiO$_2$ templated and confined with chlorophyll

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Abstract
Biomimetic light-harvesting architecture has been proposed as an alternative for existing solar conversion systems. Chlorophyll-sensitized TiO$_2$ have been identified as promising catalyst for photocatalytic reduction system, but it is largely limited to complicated process for purification of chlorophyll and adding extra hole scavenger in system. In sharp contrast to conventional photosensitization methods in which the organic dyes were often adsorbed after photosensitization, herein mesoporous TiO$_2$ incorporated with chlorophyll extract was synthesized in situ (TiO$_2$/Chl). Interestingly, TiO$_2$ incorporated with chlorophyll exhibited two distinct absorption bands around 407 and 668 nm which are closed to the characteristic absorption peak of chlorophyll. TiO$_2$ incorporated with chlorophyll kept at 185$^\circ$C for 1.5 hours (TiO$_2$/Chl-185) achieved a high photoreduction rate of 86.1% for the photocatalytic reduction of Cr(VI), which was approximately 29 and 20 times higher than that of TiO$_2$ and TiO$_2$ adsorbing chlorophyll (TiO$_2$/ads Chl), respectively. The significant enhancement was due to the confinement of chlorophyll. This demonstrates that mesoporous TiO$_2$ templated and confined with chlorophyll could offer a new approach for synergistic photoreduction of Cr(VI).

KEYWORDS
chlorophyll composite, mesoporous TiO$_2$, nanoscale confinement, photocatalytic reduction of Cr(VI), visible-light photocatalysis

1 | INTRODUCTION

Photocatalytic reduction has been emerged as a promising method for treatment of Cr(VI), one of the most toxic pollutants in water. A variety of TiO$_2$ catalysts such as commercial TiO$_2$, organic acid modified TiO$_2$, TiO$_2$-coated cellulose acetate, polymer-sensitized TiO$_2$ and TiO$_2$/activated carbon have been used for photocatalytic reduction of Cr(VI). However, the photocatalytic reduction of Cr(VI) over TiO$_2$ has been largely limited to adding extra hole scavenger under acidic condition.

Photosensitization of TiO$_2$ by organic dyes is a convenient way to extend absorption from UV to visible light region. For example, as a key molecule for
photosynthesis, chlorophyll is well known photosensitizers for fabrication of ZnO photo-anode \cite{4} and TiO$_2$ photocatalysts.\cite{5} Nevertheless, these dye-sensitized photocatalysts suffered from poor photo-and thermal-stability. Therefore, surfactants and suitable temperature are frequently used to stabilize the photosensitive function of photocatalysts. For instance, methods for incorporating dyes into the mesoporous materials such as SBA-15,\cite{6} MCM-48 \cite{7} and MCM-41 \cite{8} to generate photosensitive functional materials with applications in the fields of optics and photonics were developed.\cite{9} In sharp contrast to conventional photosensitization methods in which the original organic dyes were often adsorbed after photosensitization, our group has successfully synthesis the mesoporous TiO$_2$ by using the used chrome azurol S, natural food coloring agents and even commercial synthetic dyes as templates.\cite{10} Meanwhile, chlorophyll entrapped in silica gel nano matrix could be resistant to the degradation of chlorophyll in water.\cite{11} In most cases, pure chlorophyll or complicated process for purification of chlorophyll are often required to prepare chlorophyll-nanomaterial composites. Therefore, development of feasible approaches to prepare chlorophyll-TiO$_2$ composite is still a challenging topic.

On the other hand, nanoscale confinement is an effective way to enhance chemical reactivity due to the locally enriched concentration of reactant molecules within the nanoscale confinement reactor.\cite{12} However, the application of this approach is limited to carbon nanomaterials, mesoporous silica and zeolites.\cite{13} Compared with these traditional nanoscale confinement reactors, porous TiO$_2$ have also been regarded as a promising candidate for nanoscale confinement. For example, the dehydrogenation properties of LiBH$_4$ are significantly enhanced after LiBH$_4$ was incorporated into anatase TiO$_2$ micro-tubes, due to the effect of nanoscale confinement of TiO$_2$.\cite{14} Such great successes encouraged us to further explore the nanoscale confinement effects and design chlorophyll-TiO$_2$ composite photocatalysts. Furthermore, comparing with traditional materials, mesoporous materials are show high surface areas and uniform and controllable morphologies. In addition, aerogels are high surface area/low density materials consisting of open and highly porous structure derived from the supercritical drying of highly cross-linked inorganic or organic gels.\cite{15} These properties make mesoporous materials and aerogels very promising materials for nanoscale confinement reactor.

At the beginning, we tried to use chlorophyll as templates as we did to synthesize mesoporous TiO$_2$. We also tried to make some modification to prepare TiO$_2$ aerogel instead of conventional mesoporous TiO$_2$ by using chlorophyll as templates. By chance, we unexpectedly obtained mesoporous TiO$_2$ entrapped with chlorophyll with an autogenous pressure instead of the supercritical condition. The obtained crystalline mesoporous TiO$_2$ incorporated with chlorophyll exhibited efficient photocatalytic reduction of Cr(VI) under visible light irradiation without adding any extra hole scavenger at a neutral pH.

\section*{RESULTS AND DISCUSSION}

\subsection{Syntheses, N$_2$ sorption and X-ray powder diffraction (XRD) measurements}

In the preparing process we developed, spinach extracts was extracted from fresh spinach leaves without further purification. Figure 1 shows the corresponding photos of spinach extract and TiO$_2$/Chl-185, indicating that their colors change from deep green to yellow. In Figure 2, spinach extracts exhibits the absorption peaks at wavelength ca. 410 and ca.664 nm which suit well with the characteristic absorption peaks of chlorophyll.\cite{4} The samples synthesized at 185$^\circ$C, 205$^\circ$C, and 245$^\circ$C were denoted as TiO$_2$/Chl-185, TiO$_2$/Chl-205 and TiO$_2$(AG)-245, respectively. Obviously, all the three samples exhibited broad absorption from UV to visible-light region. Interestingly, it is also seen that TiO$_2$/Chl-185 and TiO$_2$/Chl-205 exhibited the two distinct absorption bands around ca. 407 and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Photographs of spinach extract and TiO$_2$/Chl-185}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{UV-vis DRS spectra of different samples and spinach extract}
\end{figure}
668 nm which are close to the characteristic absorption peak (ca. 410 and 664 nm) of chlorophyll.[4] Thus, chlorophyll has been successfully incorporated into TiO$_2$. In contrast to TiO$_2$/Chl-185 and TiO$_2$/Chl-205, TiO$_2$(AG)-245 exhibited very weak absorption at ca. 407 nm. This blue shift from ca. 410 to ca. 407 nm clearly indicated the changed band gap of the samples.[16] For further comparison, TiO$_2$ (TiO$_2$/ctrl) or Degussa P25 TiO$_2$ (P25) was mixed with spinach extract dried at 90°C for 12 hours, the samples were denoted as TiO$_2$/adsChl and P25/adsChl. Moreover, the above mixtures of TiO$_2$/ctrl or P25/adsChl were also transferred into a standard autoclave under nitrogen atmosphere and also kept at 185°C for 1.5 hours, which denoted as TiO$_2$/adsChl-185 and P25/adsChl 185, respectively. Different from TiO$_2$/Chl-185 and TiO$_2$/Chl-205, those samples prepared by adsorption with chlorophyll show broader absorption in the visible region without significant peak at ca. 410 and 664 nm of chlorophyll (Figure S2). The broader absorption in the visible regions was probably due to the absorption of spinach extracts.[4] By contrast, TiO$_2$/ctrl and TiO$_2$/Chl-185 sample was calcined at 400°C (TiO$_2$/Chl [calcined]) only exhibited significant absorption in the UV region though the absorption edges of TiO$_2$/ctrl are clearly red shifted (to 450-800 nm) compared with P25 (Figure S2). These observations imply that the characteristic absorption peaks of chlorophyll were successfully reserved by only one-pot synthesis of TiO$_2$ incorporated with chlorophyll at low temperature. This also justifies why it can be potentially good candidate for performing photocatalytic reactions under visible light.

Using the preparing process we developed, TiO$_2$ incorporated with chlorophyll from spinach extract, such as TiO$_2$/Chl-185 was light-green in color with BET surface area of 136.2 m$^2$ g$^{-1}$, pore volume of 0.2 cm$^3$ g$^{-1}$ and pore diameter of 8.3 nm. The $N_2$ adsorption/desorption isotherms of prepared materials are shown in Figure S1. Typical IV adsorption/desorption isotherms are observed in samples, a characteristic of TiO$_2$ type mesoporous materials. The specific BET surface areas, pore volumes, and pore sizes of samples are summarized in Table S2. With an increasing temperature, the pore diameter and pore volume of as-prepared TiO$_2$ samples gradually increase. As an aerogel, the pore volume and pore diameter of TiO$_2$(AG)-245 were 0.5 cm$^3$ g$^{-1}$ and 18.1 nm, respectively.

Scanning electron microscopy (SEM) reveals that these samples have no regular morphology and different degrees of aggregated (Figure 3). As an aerogel, TiO$_2$(AG)-245 (Figure 3D) has loose porosity compared with the other samples. TEM images presented in Figure 4 shows the size of TiO$_2$/Chl-185 with about 11 nm in diameter. It exhibited the irregular aggregates, which was also in agreement with SEM image. The High-resolution transmission electron microscopy (HRTEM) image reveals TiO$_2$/Chl-185 of the lattice spacing of 0.35 nm, which correspond to the (101) crystallography planes. This also confirmed the successful preparation of anatase TiO$_2$ even at 185°C.

XRD patterns (Figure 5) show the diffraction peaks of all the samples which are matched well with anatase TiO$_2$ (JCPDS card No.21-1272) and the corresponding miller indices were indexed, reveals that these samples...
were highly crystallized. Hence, TiO$_2$/ctrl, TiO$_2$/Chl-185, TiO$_2$/Chl-205, TiO$_2$(AG)-245 and TiO$_2$/Chl-1 have anatase crystalline phase. According to (101) diffraction, the crystalline size of TiO$_2$/Chl-185 was 11.8 nm, which was also in agreement with HRTEM measurement.

### 2.2 XPS analyses for samples

TiO$_2$/Chl-185 was examined by X-ray photoelectron spectroscopy (XPS). The binding energy spectra of Ti, O and C are shown in Figure 6. The atomic percentage of elements is also shown in Table S3. The binding energies of Ti 2p and O 1s are appeared at approximately 457 and 529 eV, respectively. The O 1s spectra of TiO$_2$/Chl-185 show the contributions of two components: the major peak at 529.0 eV is ascribed to Ti-O, the second peak at 530.9 eV may be caused by adsorbed water.[1] The two peaks of TiO$_2$/Chl-185 at 457.9 and 463.5 eV can be assigned to Ti$^{4+}$ in anatase TiO$_2$, which shift toward lower binding energy than those of TiO$_2$/ctrl (Figure S5). From the C 1s spectra, the major peak at 284 eV is related to carbon atoms which was carbon contamination adsorbed from the ambient environment.[17] The binding energies around 287.9 and 285.6 eV were assigned to C = C and C-O bonds, respectively, which indicates substitution of lattice titanium ions to form Ti-O-C bonding.[18] Furthermore, TiO$_2$/Chl-185 exhibited broad peak centered at 399.2 eV which was ascribed to Ti-N-O [19] and TiO$_2$/ctrl exhibited broad peak centered at 400.2 eV (Figure S3). The N 1s peaks at binding energies at 400 to 402 eV might be due to the signals of the absorbed molecular nitrogen species.[19] In the case of TiO$_2$/Chl-185, the N 1s peak was 1 eV shifted to lower binding energy further demonstrates the successful forming the Ti-N-O structure.[19,20] The amount of N atom in TiO$_2$/Chl-185 were higher than TiO$_2$/ctrl (Table S3), indicating an increase in the density of N atom in TiO$_2$/Chl-185.[19]

### 2.3 Photocatalytic activity

Before investigating the effect of as-prepared TiO$_2$ samples on synergistic removal of Cr(VI) under visible light, the effect of adsorption in darkness was examined. The adsorption yield in darkness of Cr(VI) over the as-prepared TiO$_2$ samples were summarized in Table S4. It is clear that TiO$_2$/Chl-185 exhibits the highest adsorption yield of Cr(VI) (35%) in darkness. As expected, those samples without incorporating chlorophyll such as TiO$_2$/Chl(calcined), TiO$_2$/ads Chl, P25, P25/ads Chl and P25/ads Chl-185 exhibited negligible adsorption yield of Cr(VI) (<10%). While TiO$_2$/Chl-205, TiO$_2$/Chl-245 and TiO$_2$/ads Chl-185 showed adsorption yield were 26.1%, 27.4% and 16.1%, respectively. Figure 7 shows the photocatalytic activities for the photoreduction of Cr(VI) under visible irradiation. Obviously, TiO$_2$/ctrl and P25 exhibited negligible photoreduction yield of Cr(VI). The photoreduction yield of Cr(VI) by chlorophyll alone increased with time and the removal yield was only approximately 20%. By contrast, TiO$_2$/Chl-185 achieved a very high photoreduction yield of 86.1% while the calcined sample TiO$_2$/Chl (calcined) only exhibited negligible photoreduction yield of Cr(VI) because of the absence of the two characteristic absorption peak (ca. 407 and ca. 668 nm) of chlorophyll. This strongly suggests that chlorophyll plays an important role in the reduction of Cr(VI) under visible irradiation. The full XPS survey spectra of TiO$_2$/Chl-185 and recycled TiO$_2$/Chl-185 were displayed in Figure S6. The Cr spectrum of recycled TiO$_2$/Chl-185 can be fitted to two peaks of 2p$^3/2$ and 2p$^1/2$ (578.6 and 586.3 eV, respectively), which is corresponded to the spectra characteristics of Cr(VI). A pair of peaks at 576.6 and 585 eV represented Cr$^{3+}$ 2p$^3/2$ and Cr$^{3+}$ 2p$^1/2$, respectively.[21] The presence of strong signal of Cr(III) is attributable to the photocatalytic reduction of Cr(VI) by TiO$_2$/Chl-185. This indicates that TiO$_2$/Chl-185 has both the photoreduction capability of Cr(VI) and the adsorption ability of Cr(III).
The effect of the different treatment temperature of TiO$_2$ on the photocatalytic of Cr(VI) was also studied (Figure 7). It is seen that TiO$_2$/Chl-205 showed lower activity (59%) than TiO$_2$/Chl-185. Interestingly, even the aerogel photocatalyst (TiO$_2$/Chl-245) prepared in the supercritical condition exhibited much lower activity than TiO$_2$/Chl-185 and TiO$_2$/Chl-205.

Moreover, we note that the photoreduction activity of those samples prepared by adsorbing chlorophyll was negligible. The photoreduction yield of Cr(VI) by TiO$_2$/adsChl and P25/adsChl were only 4% and 3.2%, respectively. After kept at 185°C for 1.5 hours, the photoreduction yield of Cr(VI) of these two samples were increased to 22.8% and 30.4%, respectively. Obviously, the photoreduction activity of TiO$_2$ incorporated with chlorophyll in situ was much higher than that of TiO$_2$ adsorbed chlorophyll. This also implies that the significant enhancement was due to the confinement of chlorophyll though further research is needed to understand the details.

2.4 Possible reasons for the enhancement of the visible-light performance

It would be interesting to evoke some reasons why the prepared TiO$_2$ incorporated with chlorophyll exhibited significant activities for the synergistic reduction of Cr(VI) under visible irradiation. A probable mechanism of synergistic reduction of Cr(VI) over TiO$_2$ incorporated with chlorophyll has been proposes as follows (Figure S7): Firstly, chlorophyll incorporated in TiO$_2$ acted as a photosensitizer [17,26] and enhanced the absorption of light under visible light irradiation. Chlorophyll majorly absorbs light energy to excite electron from a ground state to an excited state and the electron can be easily released and transferred to TiO$_2$. The excited chlorophyll synchronously was converted to its cationic form which may be regenerated back to chlorophyll by receiving electron from decomposed compounds from spinach extract.[5] Secondly, the prepared TiO$_2$ samples acted as a reaction platform to confine chlorophyll and Cr(VI). Meanwhile, the adsorption of both chlorophyll and Cr(VI) into TiO$_2$ may also be beneficial for the photoreduction of Cr(VI). At the same time, the neighbouring chlorophyll also facilitated efficient energy transfer and electron-hole charge separation.[22] Therefore, the confined catalyst is able to deliver a high activity.

3 CONCLUSIONS

In summary, we have demonstrated for the first time that TiO$_2$ incorporated with chlorophyll synthesized by a facile one-pot method significantly increased the photocatalytic reduction activity of Cr(VI). The prepared TiO$_2$ sample acted as a reaction platform for confinement environment of chlorophyll and Cr(VI). The chlorophyll incorporated in TiO$_2$ enhanced absorption of light under visible light irradiation, which acted as a photosensitizer and donates electrons to TiO$_2$. TiO$_2$/Chl-185 achieved a high photoreduction rate of 86.1% for the photocatalytic reduction of Cr(VI), which was approximately 29 and 20 times higher than that of TiO$_2$ and TiO$_2$/adsChl, respectively. The present research not only provides a novel method of incorporation chlorophyll in TiO$_2$ but also opens a promising platform for nanoscale confinement reactor in the treatment of polluted water.

4 EXPERIMENTAL SECTION

4.1 Instrumentation and chemical

Titanium(IV) isopropoxide (98%), Methanol (99.5%) and Ethanol(99.5%) were obtained from Innochem. Nitric acid (65%) was from Xilong Scientific CO.LTD. The data of
XRD experiments were recorded in the $2\theta$ range 10°-90° at a scan rate of 10° per minute (D/max-3B spectrometer with Cu Kα irradiation). The Brunauer-Emmett-Teller (BET) surface areas were measured by the nitrogen adsorption/desorption measurements (NOVA 2000e gas sorption analyzer Quantachrome Crop). Before the test, the samples were degassed in vacuum at 90°C for 4 hours. SEM operated at an accelerating voltage of 10 kV (Quanta 200 scanning electron microscope) and HRTEM images were carried out on a JEM-2100 operated at 200 kV. UV-Vis diffuse reflectance spectra were measured on a Shimadzu UV-2401PC photometer over the range from 200 to 800 nm at room temperature. The base pressure of XPS measurements was about 10⁻⁷ Pa (PHI5500ESCA analyzer with 200 W Mg Kα radiation). The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

4.2 | Preparation of natural spinach extract

Natural spinach extract was extracted from fresh spinach leaves. Fresh spinach leaves were cleaned using distilled water and sliced into small pieces dried at room temperature for a night. The small pieces of 100 g were extracted in 200 mL ethanol for 7 days. Then, solid residues were filtrated out to obtain clear spinach extract solutions and dried at 60°C for an hour. The thick spinach extract was kept in tube for further use.

4.3 | Preparation of titania incorporated with chlorophyll (TiO₂/Chl)

TiO₂/Chl was synthesized with a process (Figure 8) modified from refs. Spinach extract of 0.2 g was dissolved in methanol (80 mL), titanium isopropoxide (10 mL), 0.1 mL nitric acid and deionized water (4 mL) were mixed and stirred for 30 minutes. The final mixture was then transferred into a standard autoclave under nitrogen atmosphere and kept at 185°C, 205°C, and 245°C for 1.5 hours, respectively. Then the pressure was quickly released by venting of solvent vapor. The sample was flushed again with nitrogen for 15 minutes and allowed to cool down in nitrogen to room temperature.

To remove the spinach extract, the TiO₂/Chl-185 sample (TiO₂/Chl(calcined)) was calcined at 400°C in air for 6 hours. Table S1 (see Supporting Information) summarizes these designations of various samples.

4.4 | Preparation of titania adsorbed by spinach extract (TiO₂/ads Chl)

0.5 g TiO₂/ctrl or Degussa P25 TiO₂(P25) was mixed with 0.08 g spinach extract in 10 mL methanol and then stirred for 24 hours at room temperature. The mixtures were dried at 90°C for 12 hours. For further comparison, the above mixtures of TiO₂/ctrl or P25 with spinach extract were also transferred into a standard autoclave under nitrogen atmosphere and kept at 185°C for 1.5 hours.

4.5 | Evaluation of photocatalytic activity

The photoreduction yield were carried out in a quartz photoreactor containing 50 mL 20 ppm Cr(VI) aqueous solution and 50 mg of photocatalyst without any additives. The suspensions were stirred in the dark for 1 hour to attain adsorption-desorption equilibrium. The Cr(VI) adsorption yield was obtained using as follows: the adsorption yield of Cr(VI) = (C₀ - Cₙ) / C₀ × 100%, where C₀ and Cₙ are the initial and the equilibrium Cr(VI) concentrations, respectively.

After being stirred for 1 hour in the dark, the suspensions were irradiated by 800 W Xe lamp, in which a glass filter (>420 nm) was used to allow emission of visible radiation above 420 nm only. The solutions were stirred during the reaction process with a magnetic stirrer. During illumination, about 5 mL of suspension was filtered to separate the catalyst. The Cr(VI) content was determined at 540 nm using the 722 UV-vis spectrophotometer. The determined absorbance intensities at different illumination times were transformed to the concentration of Cr(VI). Photoreduction yield was defined as follows: Photoreduction yield of Cr(VI) = (Cₙ - Cᵣₙ) / Cₙ × 100%, where Cₙ and Cᵣₙ are the concentration after photoreduction when illuminated for 0 and t minutes, respectively.
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DATA AVAILABILITY STATEMENT
Research data are not shared.

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