Photocatalytic Reduction of CO\textsubscript{2} from Simulated Flue Gas with Colored Anatase

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Received: 29 December 2017; Accepted: 9 February 2018; Published: 13 February 2018

Abstract: Photocatalytic reduction with sunlight is an economical and promising advanced approach for reducing the excessive emissions of CO\textsubscript{2} from the combustion of fossil fuels. Aimed at practical applications, a type of inexpensive colored anatase material was used to evaluate CO\textsubscript{2} photoreduction performance on a platform with a continuous flow of gas mixtures (10 vol \% CO\textsubscript{2}, 90\% N\textsubscript{2}), which resembles realistic flue gas conditions. The results showed an enhanced photocatalytic activity compared with standard P25 and significant improvement over pristine anatase. Based on a series of characterization techniques, we propose that the oxygen vacancies and surface hydroxyl groups on colored anatase can reduce the bandgap and assist the binding of CO\textsubscript{2} molecules. Our results showed that photoreduction of CO\textsubscript{2} is feasible under practical conditions, and the efficiency could be improved through modification of catalysts.

Keywords: photocatalytic reduction; TiO\textsubscript{2}; anatase; CO\textsubscript{2}; flue gas

1. Introduction

The excessive emissions of CO\textsubscript{2} generated by the combustion of fossil fuels have a prolonged consequence on the global climate \cite{1}. For instance, as one of the major contributors to CO\textsubscript{2} emissions, thermal power stations emit 10–20 volume percent of CO\textsubscript{2} in their flue gas. Although major research efforts have been aimed at CO\textsubscript{2} capture and sequestration, direct conversion of CO\textsubscript{2} into useable chemicals is a desired, yet more challenging approach. Various chemical or electrochemical processes have been developed to reduce CO\textsubscript{2} to CO or hydrocarbon compounds \cite{2–4}; however, due to the chemical inertness of CO\textsubscript{2}, most strategies for CO\textsubscript{2} reduction can only be achieved at an unaffordable cost of energy or reagents. Alternatively, photocatalytic reduction of CO\textsubscript{2} with sunlight would be much more economical, and it is being actively researched \cite{5}. However, current photocatalytic processes either use strong ultraviolet light, or additional sacrificial agents, or conditions far from the industrial processes, while the development of solar-active photocatalysts is still at its early stage.

Till now, a great quantity of works has been endeavored to explore photocatalysts for selective CO\textsubscript{2} transformations \cite{6–9}. For instance, a novel molecular Ru(II)–Re(I) dinuclear complex photocatalytic system with high reduction ability of CO\textsubscript{2} and capture ability of CO\textsubscript{2} has been developed \cite{6}. Rosenthal et al. developed an inexpensive bismuth-carbon monoxide evolving catalyst (Bi-CMEC), which can selectively catalyze the conversion of CO\textsubscript{2} to CO without the need for a costly supporting electrolyte \cite{7}. BiFeO\textsubscript{3} and BiFeO\textsubscript{3}/single-walled carbon nanotubes (SWCNTs) were prepared by the sol-gel method, and the modification of the catalysts by single-walled carbon nanotubes not only greatly improved the response to visible light, but also doubled the catalytic reduction yield of...
CO\textsubscript{2} [8]. Among these, TiO\textsubscript{2}-based photocatalysts have been most widely studied as photocatalyst with different crystalline forms or modifications [10–13], and they show considerable prospect for the selective transformation of CO\textsubscript{2} to CO, HCOOH, CH\textsubscript{3}OH and CH\textsubscript{4} [14]. The P25 TiO\textsubscript{2} nanoparticles branded by Degussa, which have mixed phases of rutile and anatase, are the benchmark material with high photocatalytic performance. However, P25 is relatively expensive, which precludes its use on the scale required for fuel production. Alternatively, loading noble metals such as Pt, Au and Ag can enhance its activities of CO\textsubscript{2} photoreduction for commercial anatase or rutile materials, but the cost is also high. Therefore, the development of inexpensive photocatalysts that can promote the reduction of CO\textsubscript{2} to CO with high selectivity and efficiency is an important step for commercialization.

In this report, we evaluated the CO\textsubscript{2} photoreduction performance on a platform with a continuous flow of gas mixtures (10 vol % CO\textsubscript{2}, 90% N\textsubscript{2} at 80 °C) that resembles realistic flue gas conditions. In such conditions, energy-intensive CO\textsubscript{2} separation processes [15] may be avoided. The conversion of CO\textsubscript{2} to CO can be achieved on titanium oxide catalysts with additional water under xenon light in the UV-visible or visible-only range. Carbon monoxide is a key chemical feedstock and a component of syngas, which can be further converted to liquid hydrocarbon fuels. In order to reduce the cost for large-scale application, a colored anatase (g-anatase) material has been prepared, which showed a comparable photocatalytic activity with standard P25 and significant improvement over pristine anatase. Based on characterizations by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), Fourier transforming infrared spectroscopy (FT-IR) and solid-state nuclear magnetic resonance (SSNMR), we propose that oxygen vacancies and surface hydroxyl groups on colored anatase can reduce the bandgap and assist the binding of CO\textsubscript{2} molecules. Our results showed that photo-reduction of CO\textsubscript{2} is feasible under flue gas conditions, and the efficiency could be improved through modification of catalysts.

2. Results and Discussion

2.1. CO\textsubscript{2} Photoreduction Performance

A number of photocatalysts has been reported for the conversion of CO\textsubscript{2} into CO under continuous flow conditions (Table 1) [11–13,16,17]. However, for flue gas, CO\textsubscript{2} concentration is around 10% in volume. If we used pure CO\textsubscript{2} for reduction, this would demand either intensive energy or special adsorbents for CO\textsubscript{2} separation [18]. For practical and economic considerations, we performed photocatalysis using low concentration CO\textsubscript{2} just like flue gas (i.e., 90% N\textsubscript{2} and 10% CO\textsubscript{2}). Other features of flue gas such as temperature and humidity have also been simulated [19]. The temperature of the reaction chamber was maintained at 80 °C, which also approximates the temperature of flue gas. A certain degree of humidity was maintained with added water, and the gas in the reaction chamber was internally cycled with a pump to assist the flow of flue gas. We used xenon light with either the UV or UV-visible range to excite anatase and colored-anatase samples. Under our experimental conditions, CO is the primary product that we detected through an on-line gas chromatography.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Light Source</th>
<th>CO$_2$ Concentration</th>
<th>CO Production (µmol/h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-x/exposed [001]/[101] facets (through NaBH$_4$ reduction)</td>
<td>UV: 100-W mercury vapor lamp; visible: 450-W Xe lamp (λ &gt; 400 nm)</td>
<td>4 mL/min CO$_2$ + H$_2$O continuous flow</td>
<td>UV: CO = 0.44, Vis: CO = 0.208</td>
<td>[13]</td>
</tr>
<tr>
<td>Brookite TiO$_2$-x (thermal treatment in He)</td>
<td>150-W solar simulator</td>
<td>2 mL/min, CO$_2$ + H$_2$O continuous flow</td>
<td>CO + CH$_4$ = 0.315</td>
<td>[11]</td>
</tr>
<tr>
<td>2.5 at% Co-TiO$_2$ (sol-gel method)</td>
<td>Visible light of 300-W Xe arc lamp with an L-42 glass filter</td>
<td>3 mL DI H$_2$O and 80 kPa CO$_2$ gas</td>
<td>CO = 0.194, CH$_4$ = 0.009</td>
<td>[16]</td>
</tr>
<tr>
<td>4% Cu@TiO$_2$ (annealing at 450 °C for 2 h in high vacuum)</td>
<td>Visible light of 500-W Xe lamp (λ &gt; 400 nm)</td>
<td>CO$_2$ generated from NaHCO$_3$/H$_2$SO$_4$ reaction</td>
<td>CO = 0.162, CH$_4$ = 0.027</td>
<td>[12]</td>
</tr>
<tr>
<td>10% I-TiO$_2$ hydrolysis of titanium isopropoxide (TTIP) in iodic acid solution followed by hydrothermal treatment</td>
<td>Visible light of 150-W solar simulator</td>
<td>CO$_2$ + H$_2$O mix gas</td>
<td>CO = 0.48</td>
<td>[17]</td>
</tr>
</tbody>
</table>
The production of CO (µmol/g) during a 6-h photo-illumination period was calculated, as shown in Figure 1. It can be seen that the CO production on colored-anatase greatly increased; the maximum CO production rate was up to 4.99 µmol g⁻¹ (i.e., a rate of 0.83 µmol g⁻¹ h⁻¹) under UV-visible light irradiation (the UV-vis column in Figure 1), which is circa 10.7-times that of anatase and higher than P25 [20]. If the UV light (wavelength smaller than 400 nm) was cut off, the overall production of CO decreased (the UV cut400 column in Figure 1), and this suggests that UV-light plays an important role in the catalyzing process. However, even with visible light, the colored anatase can still produce about 1.2 µmol g⁻¹ CO (i.e., a rate of 0.2 µmol g⁻¹ h⁻¹), which is ~20% higher than P25. Although such a conversion rate of CO₂ into CO does not seem so impressive compared to the literature, it should be pointed out that our experiments were performed with more stringent conditions at a much lower CO₂ concentration. As a proof of concept experiment, our results have confirmed the feasibility of direct photocatalytic conversion of CO₂ with flue gas for the first time. Our work also suggests that improvement of the existing catalysts can greatly benefit the conversion efficiency. Therefore, in the following section, we carried out further study on the colored anatase, which is also introduced in this work.

![Figure 1](image_url)

**Figure 1.** The histogram of CO maximum output with 6 h using anatase, colored anatase and P25 as the catalysts. g-anatase, gray anatase.

### 2.2. Characterization of Colored Anatase

It has been demonstrated that a higher density of oxygen vacancies in colored TiO₂ could contribute to enhanced photocatalytic activity [21–23]. For example, black TiO₂ nanoparticles with a defective core/disordered shell structure exhibited a bandgap of only 1.85 eV, and the bandgap narrowing is dictated by the synergistic presence of oxygen vacancies and surface disorder [22]. Figure 2a shows the commercial anatase (white color) and the treated anatase powder (gray color, named g-anatase). This distinct change of color indicates that the band structure of anatase nanocrystals has been modified by the NaBH₄ reduction treatment. The XRD patterns in Figure 2b showed that the gray TiO₂ kept the anatase phase, suggesting this reduction treatment did not alter the crystalline core. The diffuse reflectance UV-Vis spectrum of colored anatase (Figure 2c) clearly shows a broad absorption from 400 nm to the near-infrared region. The relationship between absorbance (Absν)^(1/2) and photo energy (hν) is shown in Figure 2d, and the bandgap of g-anatase is calculated to be 2.04 eV (compared to 2.97 eV for pristine anatase), which allows the adsorption of a large part of visible light.
A photoluminescence (PL) experiment was used to track the recombination of charged carriers freed by photo excitation (325 nm) [24,25]. The PL intensity of colored anatase is much weaker compared to anatase, which indicates that the recombination rate of photo-generated electrons and holes had been reduced considerably (Figure 2e) [26]. Together, the UV-Vis and PL experiments explain the photoactivity of colored anatase in the visible and UV-visible range. In order to fully address the mechanism of its enhanced CO$_2$ reduction performance, we conducted further structural characterizations by TEM, EDX, XPS, IR, SSNMR, TG and CO$_2$ adsorption and desorption experiments.

TEM revealed that the average diameter of colored anatase nanocrystals is about 25 nm (Figure 3c), similar to pristine anatase (Figure 3a). Before the reduction treatment, TiO$_2$ nanocrystals exhibit a highly crystalline nature and well resolved lattice features throughout the whole particles (Figure 3b). However, after the reduction treatment, the anatase nanocrystals show a crystallized core with a disordered outer layer, which forms a shell of about 1.5 nm in thickness, as shown by the black arrows in Figure 3d, and this confirms that the obtained sample has a TiO$_2$@TiO$_2$–x core/shell structure feature [27]. The corresponding EDX spectrum (Figure 4) showed that there are only Ti and O elements existing in the g-anatase (C and Cu are from the supporting super-thin carbon-coated copper grid). In addition, the atomic ratio of Ti to O is below the stoichiometric ratio of two, which further proved the formation of the amorphous shell.

The high-resolution spectra of Ti2p XPS of commercial anatase and colored anatase are shown in Figure 5a. The Ti2p 3/2 and Ti2p 1/2 peaks centered at the binding energies of 460.5 and 466.2 eV are typical characteristics of the Ti$^{4+}$–O bonds in anatase. Such peaks shift nevertheless to lower binding energies of 460.0 and 465.9 eV in the colored anatase, which indicates that Ti$^{3+}$ species may have appeared in the colored anatase sample, as previously reported [28,29].

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Figure 2. (a) Images of anatase (top) and colored anatase (bottom), (b) XRD patterns, (c) diffuse reflectance UV-Vis spectra, (d) relationship between (Ahv)$^{1/2}$ and hv and (e) photoluminescence (PL) spectra of anatase and colored anatase.
From Figure 5b, there is an obvious signal at $g = 2.058$ for the g-anatase sample, which can be attributed to oxygen vacancy [30]; therefore, the defects probed from slow negative annihilation can be considered to be related vacancy, which is consistent with XPS results. Oxygen-related vacancy defects. From Figure 3b, there is an obvious signal at $g = 2.058$ for the g-anatase sample, which can be attributed to oxygen vacancy [30]; therefore, the defects probed from slow negative annihilation.

The EPR technique was further employed to analyze the Ti$^{3+}$-related vacancy defects. From Figure 5b, there is an obvious signal at $g = 2.058$ for the g-anatase sample, which can be attributed to oxygen vacancy [30]; therefore, the defects probed from slow negative annihilation
spectroscopy may be considered to be oxygen-related vacancy, which is consistent with the XPS results. Oxygen-related vacancy defects mainly exist in the bulk (or surface) lattice of the TiO₂ samples after reduction treatment. Raman spectroscopy (Figure 5c) reveals that the strongest vibration mode area (Eg) at 144 cm⁻¹ had a significant peak broadening and blue shifting after reduction treatment, compared with commercial anatase. The peak broadening effect and shift have been observed in several recent studies on hydrogenated TiO₂ [22,30–32], which are attributed to the presence of lattice disorder resulting from phonon confinement or nonstoichiometry as the result of oxygen vacancy (VO) doping.

FT-IR spectra (Figure 6a,b) of both white and colored anatase were recorded to investigate light absorption in the mid-infrared light region, from 400 cm⁻¹–4000 cm⁻¹. This allowed gaining further insight into the molecular-level alterations induced by the hydrogenation process. Similar absorption features can be detected in the two samples, namely the OH of H₂O bands near 1635 cm⁻¹ and 3400 cm⁻¹ and the characteristic wide band in the region 510–650 cm⁻¹, which is due to the symmetric stretching vibrations of the Ti–O bonds of the TiO₄ tetrahedra. The differences between spectra (Figure 6b) reveal that hydrogenation leads to additional absorption peaks at 3648, 3672, and 3691 cm⁻¹, which can be associated with tetrahedral coordinated vacancies and designated as Ti⁴⁺–OH [33]. Moreover, hydrogenation leads to another new absorbance at 3710 cm⁻¹, corresponding to terminal OH groups [34], which could be attributed to the hydrogen atoms embedded in the TiO₂ network.

Ultra-fast magic-angle spinning (MAS) solid-state NMR spectroscopy is a crucial tool for the effective characterization of the hydrogen species present on nanocrystals. We performed ¹H NMR measurements of anatase and colored anatase at an MAS rate of 60 kHz, as shown in Figure 6c. The dominant peaks at 5.5 and 4.8 ppm in anatase and colored anatase, respectively, can be assigned to the isolated water molecules trapped in anatase crystal defects. Such sharp ¹H peaks, which were also observed at the lower spinning speed of 12 kHz, are features of weak ¹H–¹H dipolar coupling. It is unlikely to be mobile water, however, as the sample has been treated in vacuum at elevated temperatures. Different from anatase, the colored anatase showed also a relatively broad signal at 6.7 ppm corresponding to bridging (i.e., non-terminal) surface hydroxyl groups (marked in Figure 6c as OH₈), which is consistent with the 3648 cm⁻¹ FT-IR signal [35].

CO₂ adsorption and desorption curves of anatase and colored anatase are shown in Figure 7a. One can find that both CO₂ adsorbed and desorbed capacities detected at the low pressure range (P/P₀ < 0.2) on g-anatase nanocrystals are higher than those on anatase nanocrystals; this feature is probably closely related to the more exposed alkaline sites, namely Ti³⁺ vacancies on g-anatase nanocrystals, which can absorb more CO₂ molecules [36]. The TGA curve reported in Figure 7b shows that the continuous weight losses of the anatase and g-anatase samples are 2.36 and 3.65% before 350 °C, which can be ascribed to the adsorbed water evaporation. Obviously, the greater weight loss of g-anatase indicates that more water molecules are adsorbed on the surface of the crystals, which is probably closely associated with the amorphous shell of colored anatase [37].
3. Experimental Section

3.1. Surface Defective Anatase Preparation

Anatase (99.8%, 25 nm), NaBH₄ (98%) and ethanol (AR) were purchased from Aladdin Reagent Comp. (Shanghai, China) and used without purification. The surface defective anatase preparation process is reported elsewhere [20]. Typically, 2.40 g of anatase powder and 0.90 g of NaBH₄ were mixed thoroughly with 20 min if grinding. The mixture was then placed into a porcelain capsule inside a tubular furnace in Ar atmosphere and heated from ambient temperature with a rate of 10 °C/min until it reached 400 °C, then maintained at this level for 120 min. After self-cooling to ambient temperature, the obtained gray powder was washed seven times alternately with deionized water and ethanol to remove unreacted NaBH₄, then dried at 60 °C in air.

3.2. Sample Characterization

Diffraction patterns were collected using an X-ray diffractometer (XRD) (Bruker AXS D8 Focus, Karlsruhe, Germany) with Cu Ka radiation (λ = 1.54056 A). The UV-Vis absorption spectra were recorded on a Shimadzu UV 2600 UV/Vis spectrophotometer (SHIMADZU Corporation, Kyoto, Japan). Transmission electron microscope (TEM) images were taken using a JEOL 2100 operating at 200 kV (Japan Electron Optics Laboratory Co., Ltd., Kyoto, Japan). X-ray photoelectron spectra (XPS) analyses were recorded using an ESCALABMKII spectrometer with an AlKa (1486.6 eV) achromatic X-ray source (VG Scienta, East Sussex, UK). The EPR spectra were acquired using a Bruker EMX-8 spectrometer at 9.36 GHz at 298.5 K (Karlsruhe, Germany). Raman spectra were collected on a thermal dispersive spectrometer using laser light with an excitation wavelength of 532 nm at a laser power of 10 mW. ¹H SSNMR experiments were conducted at a probe temperature of 302 ± 1 K on an AVANCE 600-MHz wide bore spectrometer (Bruker, Karlsruhe, Germany) operating at 14.1 T (the Larmor frequency was 599.80 MHz for the proton) and equipped with a 1.3-mm triple-resonance magic angle spinning (MAS) probe. Free induction decays (FIDs) were not multiplied by an exponential anodization function before Fourier transformation. The spectrum of an empty NMR rotor was collected under the same conditions and subtracted to eliminate the contribution from background signals [35,38,39]. Chemical shifts were measured relative to secondary standard adamantane as an external reference [40,41].

3.3. The Gas-Solid Reaction System

The gas-solid reaction measurement is designed as shown in Scheme 1. A 300-W Xe lamp was used as the light source and eventually filtered to remove its UV part. As a preliminary step, we tested with GC/TCD-FID the eventual background level of carbon-containing products of a mixture of H₂O and He passing through the catalyst with the lamp on. This confirmed that CO₂ was indeed...
the only carbon source. The production of CO during a given period was calculated by measuring its concentrations at the reactor outlet.

**Scheme 1.** Diagram of the photocatalytic equipment. (1) Quartz boat for the loading of the TiO$_2$ catalyst, (2) external heating sleeve, (3) Petri dish containing deionized water, (4) main device constituted by a high-permeability quartz tube and stainless seal flanges, (5) xenon light source, (6) needle valve for the control of the gas flow rate, (7) air gauge displaying the pressure variation in the reaction device. The arrows indicate the flow direction.

4. Conclusions

In summary, we firstly prepared the core/shell structure of the TiO$_2@$TiO$_2$-x sample by mildly reducing commercial anatase. Such a colored anatase showed comparable photocatalytic activity towards CO$_2$ reduction under a simulated flue gas system. The enhanced activity is attributed to the formation of oxygen vacancies and Ti$^{3+}$ on the amorphous surface shell, which promotes CO$_2$ activation under photo-illumination. Our work represents a further step to utilize post-combustion CO$_2$ in a sustainable manner, i.e., using sunlight and without further processing. Further refinement of reaction conditions and catalytic supports is still possible in order to improve the overall efficiency of photocatalysis.

Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (No. 41402037, 21573197) and the State Key Laboratory of Chemical Engineering No. SKL-ChE-16D03.

Author Contributions: X.K., Y.G. and M.X. conceived and designed the experiments; Y.G., M.X. and W.C. performed the experiments; M.X. and A.M. analyzed the data; H.G. and X.M. contributed reagents/materials/analysis tools; Y.G. and X.K. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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