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High efficiency photocatalytic conversion of CO₂ with H₂O over Pt/TiO₂ nanoparticles

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The objective of this research was to convert CO₂ to CH₄ using photocatalysis. In this investigation, well-crystallized anatase TiO₂ nanoparticles with diameters of ~18.4 nm and a BET surface area of 108.3 m² g⁻¹ were synthesized by a solvothermal method and then Pt/TiO₂ nanocomposites with high photocatalytic performance and stability were prepared by photoreduction. The average diameter of the well-dispersed Pt nanoparticles was 1.82 nm. The optimal TiO₂ calcination temperature was 500 °C, while Pt photodeposition time was 1 h. The photoluminescence (PL) spectra demonstrated that the efficiency of photogenerated charge transfer and separation of Pt/TiO₂ was better than that of Pt/P25. For the optimized Pt/TiO₂ photocatalysts, the CH₄ yield reached 60.1 μmol/(g_{cat} h), together with a H₂ yield of 87.5 μmol/(g_{cat} h) and an C₂H₆ yield of 2.8 μmol/(g_{cat} h) at 4 h of irradiation. The photocatalytic CO₂ conversion ability of Pt/TiO₂ was 3.7 times that of Pt/P25. Longer irradiation would result in an increase of H₂ output, but not the output of CH₄ or C₂H₆. With 10.0% CO₂, the CH₄ yield and H₂ yield reached 54.4 μmol/(g_{cat} h) and 80.2 μmol/(g_{cat} h), respectively. O₂ was detected and recorded for a systematic analysis of the relationship between CO₂ conversion and water splitting. In addition, the photogenerated electron–hole balance was calculated and an associated reaction mechanism was proposed.

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1. Introduction

The rapid increase in anthropogenic CO₂ emissions is of great concern, since fossil fuel consumption is not likely to cease in the foreseeable future,^{1–3} and one major CO₂ emission source is the flue gas from power plants.⁴ Although CO₂ capture and storage (CCS) have been suggested, the ability and environmental consequences of storing several billion tons of CO₂ per year are uncertain and costly.⁵ Another great challenge that has attracted high attention is the depletion of fossil fuels and the subsequent contribution to an energy crisis.⁶ One promising strategy for solving both issues is to develop new utilization methods for converting CO₂ into useful chemicals and clean fuels, which however is energy-intensive since CO₂ is very stable. A potentially cost-effective approach is to harness the nearly limitless energy available in sunlight by using efficient photocatalysts to perform these conversions.⁷ If CO₂ can be converted into useful products like CO, CH₄ or CH₃OH using

solar energy, it will serve to reduce atmospheric CO₂ concentrations while providing a renewable energy fuel compatible with our current energy infrastructure.⁸

Various attempts have been made at photocatalytic CO₂ conversion.^{9–11} Among the reported photocatalysts, TiO₂ has been investigated most frequently due to its robust reactivity, commercial availability and chemical stability. However, TiO₂ still has several disadvantages including the limit to only UV light absorption due to its wide band-gap, and low quantum efficiency resulting from the quick recombination of photo-generated electron–hole pairs.^{12–14} To resolve these issues and increase the photocatalytic efficiency of TiO₂, great endeavors have been made and they can be generally classified into two kinds. The first way to enhance the photoactivity of TiO₂ is through TiO₂ modification. Numerous modifications have been made, including metal or nonmetal ions doping, dye sensitization, semiconductor combination and noble metal loading.¹⁵ Noble metal loading refers to the loading of Ag, Au, Pt, Pd, *etc.* on the surface of TiO₂. The loaded noble metal has a higher work function than TiO₂, which induces the formation of a Schottky barrier in the TiO₂–metal region. Thus, the photo-generated electrons can migrate from TiO₂ conduction band (CB) to the metal phase, retarding the recombination of electron–hole pairs and subsequently increasing the photocatalytic activity.^{16,17} Among the noble metal loaded TiO₂ photocatalysts, Pt/TiO₂ has attracted much attention due to its much higher photoactivity than bare TiO₂. For example, Zhang *et al.* prepared

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Pt/P25 photocatalyst and used it to convert CO_2 to CH_4 through photocatalysis, and the CH_4 yield was $2.34 \mu\text{mol}/(\text{g}_{\text{cat}} \text{ h})$.¹⁸ Zhai and coworkers also tested the photoactivity of Pt/P25 to convert CO_2 , and the CH_4 yield was $11 \mu\text{mol}/(\text{g}_{\text{cat}} \text{ h})$, which was 9.2 times that of pure P25.¹⁹

The second way to enhance the photoactivity of TiO_2 is to improve the crystallinity and surface area of TiO_2 , so that the photogenerated charge carriers have better migration and separation ability. TiO_2 nanoparticles prepared with high crystallinity and large surface areas are widely utilized in organic decomposition and H_2 generation.^{20–23} Jiao *et al.* prepared TiO_2 hollow spheres with well-crystallized anatase phase and a large surface area of $104 \text{ m}^2 \text{ g}^{-1}$ to obtain high photocatalytic phenol degradation rates.²⁴ Yu and coworkers prepared Pt/ TiO_2 nanosheets with a surface area of $94 \text{ m}^2 \text{ g}^{-1}$ and used them in photocatalytic H_2 generation. The photocatalytic H_2 generation rates of the Pt/ TiO_2 nanosheets were 1.5 times higher than that of Pt/P25 ($S_{\text{BET}} = 41 \text{ m}^2 \text{ g}^{-1}$).²⁵ Nevertheless, the research of photocatalytic CO_2 conversion using TiO_2 with a large surface area is still scarce, and most research using Pt/ TiO_2 for photocatalytic CO_2 conversion only focuses on P25 with a surface area of around $50 \text{ m}^2 \text{ g}^{-1}$,²⁴ which largely limits the improvement of the photocatalytic ability of Pt/ TiO_2 systems. In order to further improve the photocatalytic CO_2 conversion ability of Pt/ TiO_2 photocatalysts, an effective synthetic method to produce TiO_2 with good crystallinity and a large surface area is needed.

The solvothermal method has been gaining continuous interest because of its ease in controlling the size, crystal phase, size distribution and minimizing agglomeration.¹⁵ In this investigation, anatase TiO_2 nanoparticles with large surface areas were synthesized by a novel solvothermal method. Pt nanoparticles were deposited on the surface of TiO_2 through photoreduction. The influence of TiO_2 substrate and Pt deposition time were thoroughly studied. Although CH_4 , CO and CH_3OH were widely reported as photocatalytic CO_2 conversion products, the concentration change with reaction time hasn't been fully investigated. This doesn't facilitate the understanding of the reaction mechanism. 10.0% CO_2 with the balance gas of N_2 was used to mimic the flue gas and to test the photocatalytic CO_2 conversion efficiency as well. Although it is widely accepted that the photocatalytic CO_2 conversion is accompanied with water splitting, only reductive products, such as CH_4 , CH_3OH , H_2 , were reported in many investigations.^{8,26} The lack of O_2 might raise questions regarding the reliability of previous experimental data and generate confusion on the relationship of CO_2 conversion and water splitting. So in this work, a detailed analysis on CO_2 conversion together with water splitting was conducted. The balance of generated electrons and holes was calculated. This might provide some insight into understanding photocatalytic CO_2 conversion mechanisms.

2. Experimental

2.1 Materials preparation and characterization

All chemicals were purchased and directly used without any further purification. TiO_2 was prepared by a solvothermal method. First, 0.22 mol $\text{CH}_3\text{CH}_2\text{OH}$ (200 proof, Decon Labs),

0.28 mol CH_3COOH (glacial, Fisher-Scientific) and 0.12 mol deionized (DI) H_2O were mixed to form solution A. Then, 0.35 mol $\text{CH}_3\text{CH}_2\text{OH}$ and 0.04 mol titanium *n*-butoxide (reagent grade, 97%, Sigma-Aldrich) were mixed to form solution B. Next, solution A was dropped into solution B under stirring to make a homogeneous transparent yellowish sol. The final sol was stirred for 1 h before being introduced into a 200 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 180°C for 24 h. TiO_2 powder was obtained by centrifuging, washing with ethanol and DI water for several times, and then drying at 80°C for 24 h. Finally, the materials were heated with a temperature increase rate of 2°C min^{-1} and then calcined at 500°C for 2 h.

The Pt/ TiO_2 was prepared by the photoreduction method. First, 0.2 g TiO_2 was suspended in a mixture of 30 mL DI H_2O , 6 mL 1 mg mL^{-1} H_2PtCl_6 (8 wt% chloroplatinic acid solution, Sigma-Aldrich) and 10 mL 0.1 mol L^{-1} CH_3OH (HPLC grade, Fisher-Scientific). Then, the whole suspension was stirred for 0.5 h before being irradiated with a 500 W Xe lamp (Newport) for a certain time. Next, the Pt/ TiO_2 samples were separated by filtration, washed repeatedly with DI water, and finally dried at 80°C in a vacuum oven for 24 h. For comparison, Pt/P25 (Degussa) was also prepared by the same procedure.

UV-vis absorption spectra were obtained on a Cary 4000 UV-vis spectrophotometer (Varian), using MgO as reference (99+%, metals basis, Alfa Aesar). Photoluminescence (PL) spectra were measured by a Cary Eclipse fluorescence spectrophotometer (Varian). BET (Brunauer–Emmett–Teller) surface area was measured by a Quantachrome Autosorb IQ automated gas sorption analyzer with an outgas temperature of 180°C for 3 h and a N_2 adsorption–desorption isotherm. Scanning electron microscopy (SEM) images were obtained by an FEI Quanta 450 field emission scanning electron microscope with a Schottky field emission gun at an accelerating voltage of 20 kV. High resolution scanning transmission electron microscopy (HR-STEM) was taken by an FEI Tecnai G2 F20 S-Twin 200 kV transmission electron microscope. X-ray diffraction (XRD) data were collected using a Rigaku Smart Lab automated powder diffraction system. Runs were made with a scan range of $20\text{--}80^\circ$ at 5° min^{-1} with a step increment of 0.02° . X-ray photoelectron spectroscopy (XPS) analysis was performed using a Physical Electronics ESCA 5800 spectrometer. High-resolution XPS scans were performed with a pass energy of 23.5 eV and a step size of 0.1 eV. Adventitious carbon was used to determine the induced offset of the binding energy of the C1s peak (284.8 eV) due to surface charging effects. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was tested on a PerkinElmer Optima 8300 ICP-OES spectrometer.

2.2 Photocatalytic CO_2 conversion experiments

The experimental apparatus built for photocatalytic CO_2 conversion is shown in Fig. 1. It consists of three parts, including a light source unit, a photocatalytic reaction system, and online product measurement equipment. The photocatalytic CO_2 conversion was carried out in a 132 mL stainless steel reactor (4) with an inner Teflon liner and a quartz window

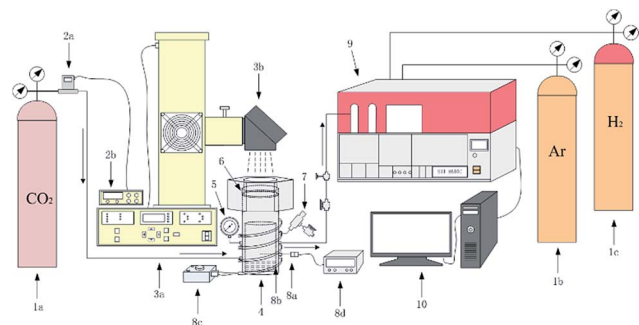


Fig. 1 Schematic diagram of the photocatalytic CO₂ conversion set up. (1a) CO₂ (1b) Ar (1c) H₂ (2a) mass flow meter (2b) mass flow controller (3a) light intensity controller (3b) light source (4) reactor (5) pressure gauge (6) quartz glass (7) pressure relief valve (8a) thermocouple (8b) heating tape (8c) temperature controller (8d) temperature display (9) gas chromatograph (10) computer.

on the top of the reactor. A 500 W Xe lamp (3b) was used for illumination. A heating tape (8b) with a temperature controller (8c) was used to regulate the reaction temperature when heating was needed. Typically, 0.02 g photocatalyst was placed on a Teflon catalyst holder in the upper region of the reactor and 5 mL DI water was pre-injected into the bottom of the reactor. Before reaction, CO₂ was used to purge the system for 1 h to completely remove the air inside the reactor. The pressure of CO₂ (laser grade, ~21 mmol in total) inside the reactor was regulated to 4 bar. Then the Xe lamp was turned on and the photocatalysts would react with the water vapor and CO₂ under illumination. After 4 hours of reaction, the Xe lamp was turned off and both the gas and liquid components were analyzed. An SRI 8610 C gas chromatograph with two FID detectors and one TCD detector was used to detect the gas component. The columns used were 6' MS-13X, 6' HAYESE-P and 60M MXT-1. The liquid component was detected by an Agilent Technologies 1260 Infinity high-performance liquid chromatograph (HPLC) with a Refractive Index Detector and Zorbax carbohydrate analysis column and Agilent 5975 C gas chromatography mass spectrometer (GC-MS) with a Triple-Axis Detector and an HP-5MS column.

3. Results and discussions

3.1 Characteristics of catalysts

3.1.1 XRD analysis. The structure of photocatalysts was characterized by XRD. Fig. 2 shows the XRD patterns of TiO₂, Pt/TiO₂, used Pt/TiO₂, P25 and Pt/P25. It can be observed that the deposition of Pt did not generate any Pt peaks, which might result from the low loading amount of Pt (less than 1% of Pt/TiO₂) and the extremely small size of Pt nanoparticles (1–3 nm).¹⁸ Only typical anatase TiO₂ diffraction peaks of (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) were observed for Pt/TiO₂ samples. The average crystal size was calculated using Debye–Scherrer equation by peak (101), (004) and (200):

$$D = 0.89 \times \lambda / (\beta \cos \theta)$$

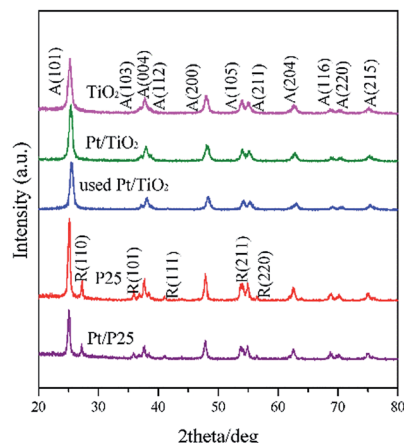


Fig. 2 XRD patterns of TiO₂, Pt/TiO₂, used Pt/TiO₂, P25 and Pt/P25.

where D is the crystal size, λ is the X-ray wavelength (1.54056 Å), β is the full-width at half maximum (FWHM) of the diffraction peak and θ is the diffraction angle.²⁷ The as calculated average crystal sizes are 13.9 nm for Pt/TiO₂, and 22.4 nm for Pt/P25.

3.1.2 SEM and STEM images. The shape and size of the nanoparticles are shown by SEM and STEM images. Fig. 3(a) shows a representative SEM image of the TiO₂ nanoparticles calcined at 500 °C. The average TiO₂ nanoparticle size is 18.4 nm, while that for P25 is 27.5 nm. Fig. 3(b) is a high-angle annular dark field (HAADF) STEM image of the Pt/TiO₂ nanoparticles. Ultrafine Pt with an average size of 1.82 nm (Fig. 3(c)) is evenly distributed on the surface of TiO₂. A smaller particle size usually indicates a larger surface area. The BET surface area

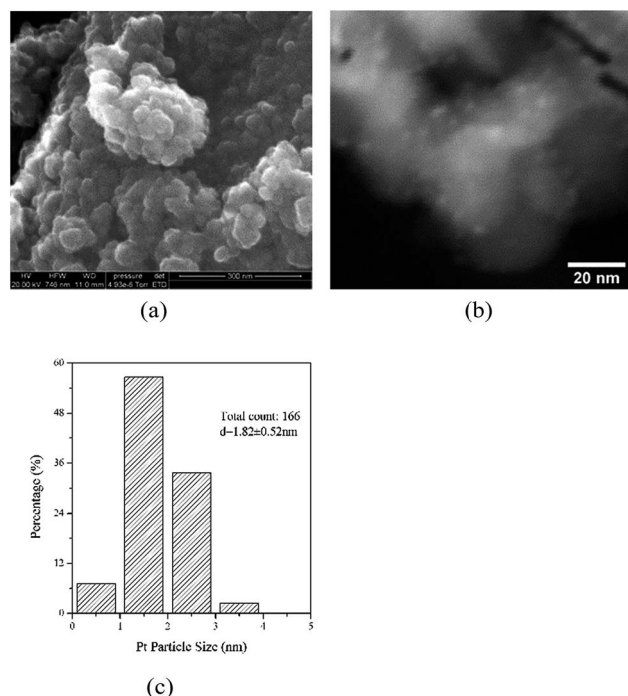


Fig. 3 (a) SEM image of TiO₂ (b) STEM image of Pt/TiO₂ (c) Pt particle size distribution for Pt/TiO₂.

of Pt/TiO₂ (110.4 m² g⁻¹) is much larger than that of Pt/P25 (59.7 m² g⁻¹), and this is one of the reasons for the high photoactivity of Pt/TiO₂.

3.1.3 XPS analysis. Compared with XRD, XPS is more sensitive for detection of surface species with low content. Hence, Pt/TiO₂ photocatalyst was investigated by XPS to verify the existence and oxidation states of Pt species. From Fig. 4, only part of the Pt species were fully reduced to metallic Pt. The most intense peaks at 71.3 eV and 74.4 eV are due to metallic Pt 4f core-level. The second set of doublets at 72.8 eV and 76.2 eV can be assigned to the photoemission of Pt²⁺ chemical states such as PtO and Pt(OH)₂. The third doublets of Pt at higher binding energies of 74.8 eV and 78.0 eV are assigned to Pt⁴⁺, such as PtO₂ or Pt(OH)₄.^{28–30} The ratio of platinum species, Pt⁰/Pt²⁺/Pt⁴⁺, was calculated with the peak areas of Pt 4f_{7/2}. Compared to used Pt/TiO₂, the Pt/TiO₂ and Pt/P25 peaks have a positive shift. Such a positive shift is postulated for highly dispersed and small size Pt.³¹ The negative shift from used Pt/TiO₂ may not only because of the Pt agglomeration, but also due to the fact that electrons transfer from TiO₂ to Pt because of a strong metal-support interaction (SMSI), which is based on the electronic and structural effects involving both the active metal and the support, and it may cause the rich electron states of Pt.^{31,32} The negative Pt would inhibit formation of Schottky barriers between P25 and metallic Pt, which increases the recombination of photo-induced electrons and holes and ultimately reduces the efficiency of CO₂ conversion.^{33,34} This is consistent with the fact that Pt nanoparticles grow bigger and partly explains the low efficiency of CO₂ conversion rate by used Pt/TiO₂.³⁵

3.1.4 UV-vis spectroscopy. The UV-vis light absorption is given in Fig. 5(a). The significant UV absorption below 390 nm is assigned to the intrinsic bandgap absorption of TiO₂ (~3.15 eV).

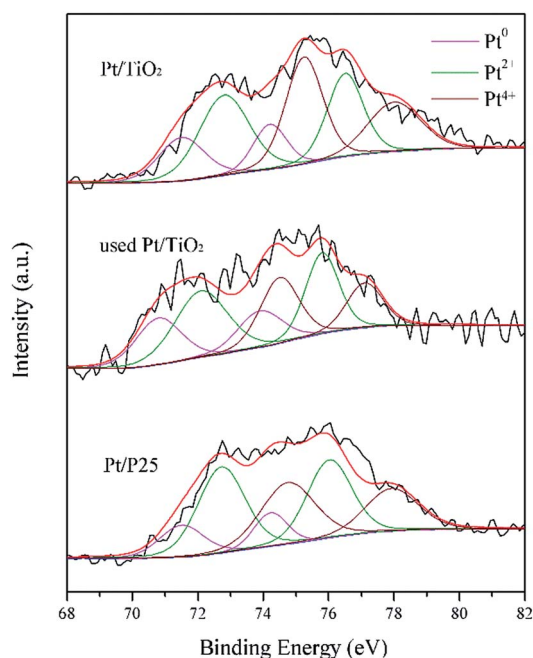
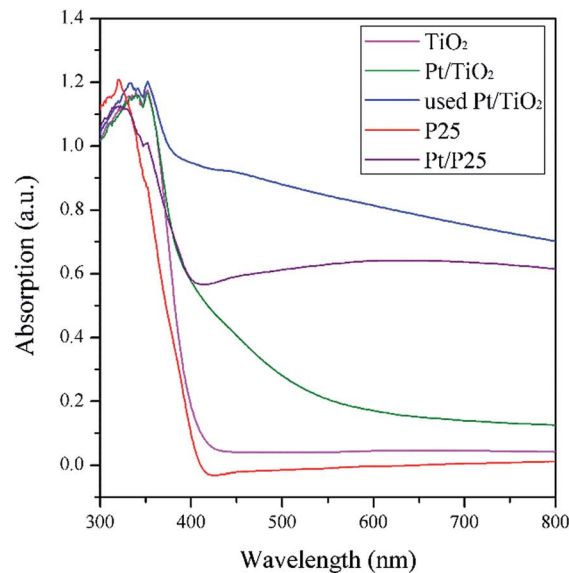
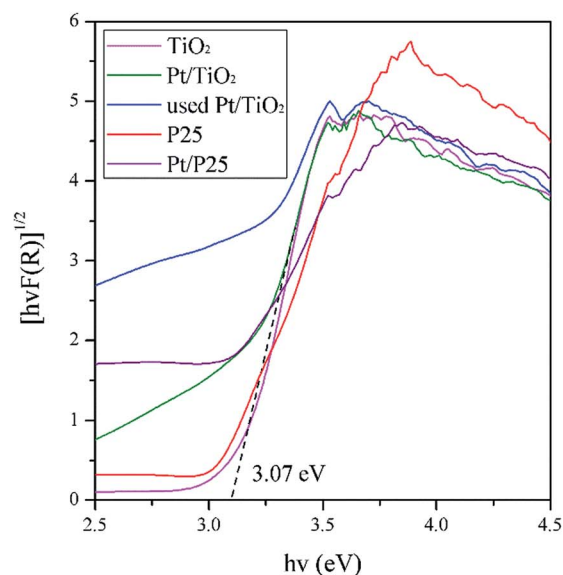


Fig. 4 XPS spectra of Pt 4f level of Pt/TiO₂, used Pt/TiO₂ and Pt/P25.



(a)



(b)

Fig. 5 (a) UV-vis absorption spectra of TiO₂, Pt/TiO₂, used Pt/TiO₂, P25 and Pt/P25 (b) Corresponding plot of transformed Kubelka–Munk function versus the energy of the light.

The deposition of Pt on TiO₂ or P25 increases its visible light response ability.²⁵ Secondly, PtO/Pt(OH)₂ and PtO₂/Pt(OH)₄ on the surface also contribute to the visible light absorption.³⁶

The corresponding diffuse-reflectance UV-vis spectra in Fig. 5(b) were obtained according to the Kubelka–Munk function: $F(R) = (1 - R)^2 / 2R$, in which R is the reflectance (%). The Kubelka–Munk function was then applied to the Tauc equation $(hvF(R))^{1/n} = A(hv - E_g)$, where hv is the photo energy, E_g is the bandgap and A is a constant. For indirect allowed transition, $n = 2$, since the fundamental absorption of TiO₂ possesses an

indirect transition between bands. If $(h\nu F(R))^{1/2}$ is plotted against $h\nu$ and a tangent line is drawn from the inflection point on the curve, the intersection of the tangent line with the horizontal axis is the bandgap.³⁷ As calculated, the bandgap of the Pt/TiO₂ is 3.07 eV.

3.1.5 PL spectroscopy. The PL emission results from the recombination of photogenerated electrons and holes, and a lower PL emission intensity usually indicates a decrease in radiative recombination and better separation of photogenerated electrons and holes.³⁸ To understand the efficiency of photogenerated charge transfer and separation of the Pt/TiO₂ photocatalyst, PL tests were carried out. Fig. 6 presents a comparison of the PL spectra of several representative samples. For all the samples, two main emission peaks appear around 391 nm and 453 nm, which are equivalent to 3.17 and 2.74 eV, respectively. The 391 nm peak is due to the bandgap transition emission with the energy of emission light approximately equal to the bandgap energy of TiO₂.³⁴ The PL signals at about 430–500 nm mainly result from excitonic PL, due to surface oxygen vacancies and defects of the TiO₂ samples. The PL peak at 453 nm is attributed to band edge free excitons.³⁹ Two small peaks at 472 nm and 486 nm result from bound excitons.⁴⁰ As shown in Fig. 6, the TiO₂ bandgap emission is lower than P25, indicating the electron–hole recombination rate through radiative combination is lower than that of P25. The photodeposition of Pt nanoparticles generates considerable fluorescence quenching, which indicates the transfer of electrons from TiO₂ to Pt and the favorable contact between them. In addition, it should be noted that the PL peak of Pt/TiO₂ is weaker than that of Pt/P25, suggesting its lower electron–hole recombination rate through radiative combination. Under UV light irradiation, the electrons from the valence band of TiO₂ will be excited to the conduction band and then migrate rapidly to Pt nanoparticles, decreasing the direct recombination of charge carriers and finally contributing to the high photocatalytic performance.²⁵

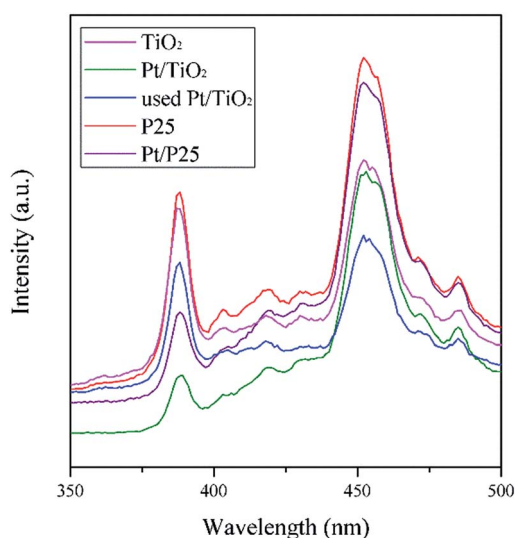


Fig. 6 PL spectra of TiO₂, Pt/TiO₂, used Pt/TiO₂, P25 and Pt/P25.

3.1.6 Characteristics of Pt/TiO₂ with TiO₂ calcined at different temperatures. With the exception of the representative photocatalysts, the Pt/TiO₂ photocatalysts with TiO₂ calcined at different temperatures were also characterized. The results are shown in Table 1. It is obvious that with the increasing of calcination temperature, the TiO₂ particle size is increasing together with the decreasing of BET surface area. Meanwhile, with the same deposition time, the surface Pt atomic percentage first increased and then decreased with a further increasing calcination temperature from 500 °C. No metallic Pt was observed on Pt/TiO₂-650 °C, which agrees with Fig. 8 that the photocatalytic activity decreased rapidly over this sample. While at 650 °C, the bandgap still decreased to 2.89 eV; this is probably due to the growing amount of PtO/Pt(OH)₂ and PtO₂/Pt(OH)₄ on the surface of TiO₂. After reaction, the surface Pt amount decreased, together with an increase in average Pt size (~1.98 nm), and this agrees with the experiment results of Bai *et al.*⁴¹

3.2 Factors affecting the performances of photocatalysts

3.2.1 Preparation conditions of photocatalysts. TiO₂ calcined under different temperatures were used to synthesize Pt/TiO₂ and then used for photocatalytic CO₂ conversion. As shown in Fig. 7, with the increase in calcination temperature from 400–500 °C, the photocatalytic CO₂ conversion ability kept increasing, and reached a maximum value at 500 °C. The CH₄ yield was 277.2 ppm [60.1 μmol/(g_{cat} h)] after 4 h of illumination, together with a H₂ concentration of 389.2 ppm [87.5 μmol/(g_{cat} h)] and an C₂H₆ concentration of 12.4 ppm [2.8 μmol/(g_{cat} h)]. The increase in photoactivity is mainly due to the improved crystallization of anatase TiO₂, an appropriate surface Pt percentage (shown in Table 1), and an ultrafine Pt size (shown in Fig. 3). When the calcination temperature was higher than 550 °C, a sharp decrease in photoactivity was observed, which could be ascribed to bigger and agglomerated TiO₂,⁴² a low Pt content and a decrease of Pt⁰ state (shown in Table 1).

In addition to the effect of TiO₂ calcination temperature, the influence of Pt deposition time was investigated. Fig. 8 shows the photocatalytic activity of P25, Pt/P25 and Pt/TiO₂ samples. Pure TiO₂ had a better photocatalytic activity than that of P25, with a CH₄ production of 12.4 ppm and a H₂ production of 68.3 ppm, while P25 could only produce 3.8 ppm CH₄, 11 ppm CO and 23.7 ppm H₂. The homemade TiO₂ preferentially produced CH₄, rather than CO, and had a higher photocatalytic water splitting ability. The Pt loading greatly promoted the photocatalytic activity of both TiO₂ and P25. As can be seen in Fig. 8, with the increase of Pt deposition time, the photocatalytic performance first sharply increased and then decreased slowly. The optimal photodeposition time was 1 h under the given experimental conditions. Considering that Pt was deposited on TiO₂ by photoreduction, the variation of the photocatalytic performance of Pt/TiO₂ might be due to different Pt nanoparticle content. With a short deposition time, not enough Pt was reduced. From ICP-OES test results, with a deposition time of 0.25 h, Pt counts for only 4.48‰ of the catalyst weight. It is accepted that Pt has a good ability to trap photogenerated electrons, but if not enough Pt was deposited, insufficient sites

Table 1 Characteristics of Pt/TiO₂ with TiO₂ calcined at different temperatures

Samples	Structure ^a	Bandgap ^b (eV)	TiO ₂ particle size ^c	Pt particle size ^c	Pt weight percentage ^d	Pt ⁰ : Pt ²⁺ : Pt ⁴⁺ ratio ^d	BET (m ² g ⁻¹)
Pt/TiO ₂ -400 °C	Anatase	3.10	14.8 ± 4.3	1.6 ± 0.5	5.38% ₀₀	18 : 56 : 26	128.5
Pt/TiO ₂ -450 °C	Anatase	3.09	15.5 ± 5.6	1.7 ± 0.6	8.02% ₀₀	19 : 52 : 29	124.6
Pt/TiO ₂ -500 °C	Anatase	3.07	18.4 ± 7.1	1.8 ± 0.5	10.87% ₀₀	21 : 40 : 39	110.4
Pt/TiO ₂ -550 °C	Anatase	3.03	19.9 ± 7.7	2.2 ± 0.8	8.87% ₀₀	21 : 49 : 30	49.7
Pt/TiO ₂ -600 °C	Anatase	2.97	24.5 ± 8.9	4.6 ± 2.0	6.15% ₀₀	15 : 40 : 45	37.7
Pt/TiO ₂ -650 °C	Anatase	2.89	37.5 ± 11.8	N/A	3.02% ₀₀	N/A	12.1
Used Pt/TiO ₂ -500 °C	Anatase	2.83	18.4 ± 7.1	1.9 ± 0.7	10.63% ₀₀	26 : 43 : 31	108.9

^a Obtained by XRD. ^b Calculated from UV-vis spectra. ^c Measured from TEM images. ^d Analyzed from ICP-OES.

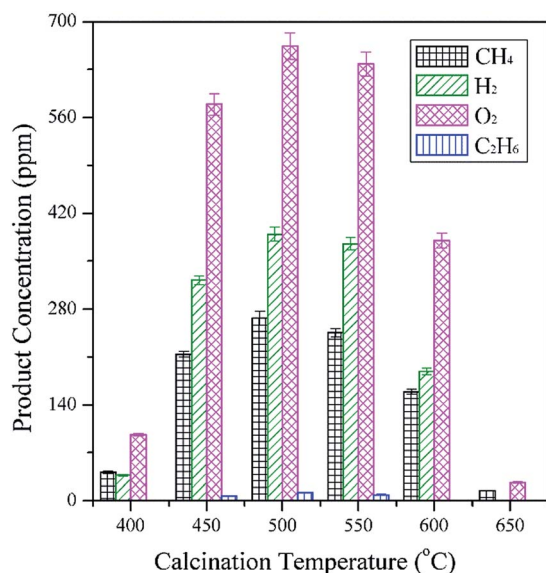


Fig. 7 Effect of TiO₂ calcination temperature on the concentrations of products resulting from photocatalytic CO₂ conversion over Pt/TiO₂ (catalyst weight: 20 mg; water volume: 5 mL; CO₂ pressure: 4 bar; temperature: 80 °C).

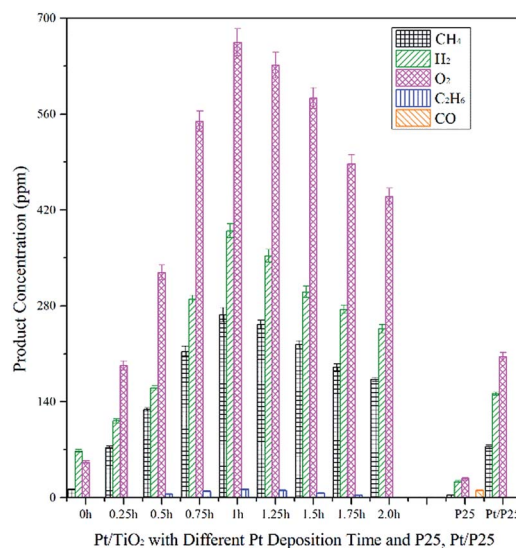


Fig. 8 Comparison of photocatalytic performances of P25, Pt/P25 and Pt/TiO₂ with different Pt deposition time (catalyst weight: 20 mg; water volume: 5 mL; CO₂ pressure: 4 bar; temperature: 80 °C).

would not trap enough electrons for CO₂ conversion.⁴³ The increase in photodeposition time improved the Pt content, promoting the photocatalytic activity. At the optimum Pt deposition time of 1 h, Pt weight percentage was 10.87%₀₀ of the catalyst weight. At a Pt deposition time of 2 h, the Pt weight percentage was 13.92%₀₀ of the catalyst weight. When the deposition time was beyond the optimum, too much Pt was deposited on the surface of TiO₂, which might block the light to the active sites on TiO₂ and retard the conversion of CO₂.^{25,44} For comparison, Pt/P25 was also prepared by the photodeposition method for 1 h under the same conditions. After photodeposition, the Pt weight percent was 11.21%₀₀ of the catalyst weight, similar to that of Pt/TiO₂. The selectivity of P25 was changed after photodeposition. CO could not be detected. The production of CH₄ was 74 ppm [16.6 μmol/(g_{cat} h)] while H₂ was 151.4 ppm [34.0 μmol/(g_{cat} h)], much smaller than that of Pt/TiO₂.

3.2.2 Effects of reaction conditions. In addition to the photocatalyst itself, the reaction conditions also show great effect on the photocatalytic reaction. Hence, the influence of

reaction time, reaction temperature and CO₂ concentration on the photocatalytic performance of the optimized Pt/TiO₂ samples were investigated. Fig. 9 is a plot of the product concentration under different reaction time. The products include CH₄, CO, H₂, C₂H₆ and O₂. As can be seen in Fig. 9, for the first 4 h, CH₄ concentration kept increasing and reached a peak of 277.2 ppm. Under longer irradiation, the concentration of CH₄ did not grow anymore, which might be due to the deterioration of the photocatalyst, resulting from the saturation of adsorption sites on the Pt/TiO₂ surface with intermediate products.⁴⁵ This can be proved by repeated use of Pt/TiO₂ photocatalysts. After removing the intermediate products, Pt/TiO₂ photocatalyst still had 88.6% of its original activity. In the first 3 h CO was detected with a peak concentration of 25.9 ppm, and then it disappeared. After longer reaction time, CO diminished when more photogenerated electrons were created; this phenomenon can be attributed to the further conversion of CO to CH₄, since CH₄ formation is an 8-electron photoreduction process, while the formation of CO only needs 2 electrons.⁴⁶ The diminishment of CO can also be explained by the electrochemical potential, -0.53 V per NHE (normal hydrogen

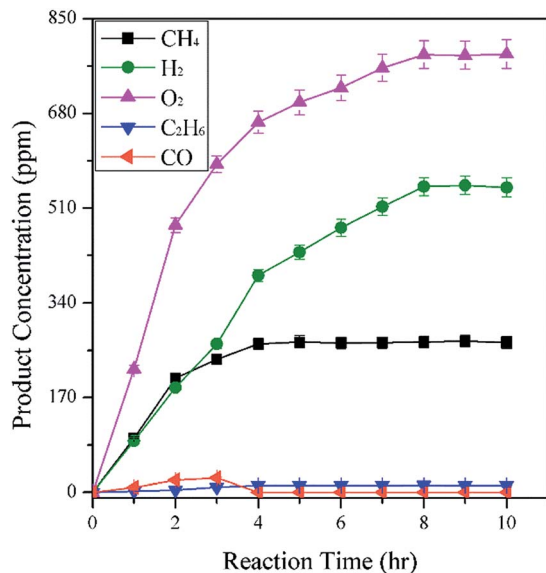


Fig. 9 Effect of reaction time on the concentrations of products resulting from photocatalytic CO₂ conversion over Pt/TiO₂ (catalyst weight: 20 mg; water volume: 5 mL; CO₂ pressure: 4 bar; temperature: 80 °C).

electrode) for CO and -0.24 V per NHE for CH₄, which indicates that CH₄ is more stable than CO.²⁶ In addition to CH₄ and CO, C₂H₆ was detected and reached its highest concentration (12.3 ppm) at 4 h. This value remained unchanged at longer irradiation. The generation of C₂H₆ occurs when the system has an abundance of photogenerated electrons, and can't provide enough 'H for 'CH₃, since 'H has participated in H₂ production.⁴⁷ Output of H₂ kept increasing during 8 h of irradiation, reaching 548.8 ppm. This demonstrated the photocatalytic water splitting ability of Pt/TiO₂ to form 'H, which is in accordance with the report of Nada, in which H₂O is an electron acceptor and competes with CO₂ to accept electrons.⁴⁵ The high H₂ yield may be partly due to enough water coverage on the catalyst surface, which contributes to the generation of 'H and the transport of 'H to CO₂.⁴⁸ The different increases of CH₄ and H₂ demonstrate a difference in the intermediate balance concentration and further different reaction active sites.⁴² Along with the reduction products, O₂ was detected in our system. After reaction, the liquid was carefully analyzed by Agilent 1260 Infinity HPLC and Agilent 5975 C GC-MS, but potential products such as CH₃OH, CH₂OH and HCOOH were not detected.

Control experiments were carried out to rule out possibilities of carbon contamination during the preparation process, such as incomplete reaction of titanium *n*-butoxide, or from CH₃OH during Pt photodeposition. When He (5.0 UHP, 99.999%) was used as the carrier gas instead of introducing CO₂ into the reactor, while all the other condition remained the same, no CH₄/C₂H₆ was detected, suggesting that all the CH₄ and C₂H₆ came from CO₂ conversion. Also, without light illumination, no product was detected, demonstrating light illumination is the driving force and CO₂ conversion is a photocatalytic process.

Fig. 10 shows the effect of reaction temperature on the photocatalytic performance of Pt/TiO₂. It is known that the photocatalytic efficiency mainly depends on the photogenerated electron-hole pair separation and reaction, but a higher temperature can increase the diffusion rate and collision frequency.⁴ As shown in Fig. 10, the concentration of C₂H₆ increased slightly with an increase in temperature, while CH₄ output increased 8.7%, with a concentration change from 258.4 ppm at 30 °C to 280.9 ppm at 175 °C. Output of H₂ increased 19.0%, with a concentration change from 358.4 ppm at 30 °C to 426.5 ppm at 175 °C. The increased temperature speeded up the desorption process during the heterogeneous photocatalytic reaction, resulting in a higher reaction rate.⁴⁹ Hence, the output of products was increased. Meanwhile, it can be noticed that the reaction temperature had a stronger influence on H₂ production than on CH₄. This phenomenon may be attributed to an improved concentration of water vapor with the increased temperature, which is beneficial for water splitting.

In addition to the effects of reaction time and temperature, the influence of CO₂ concentration on the photoactivity was also investigated. For these tests, 1.0% and 10.0% concentration of CO₂ diluted with N₂ were used. From Fig. 11, the CH₄ production of 1.0% CO₂ was 167.9 ppm, accounting for 60.8% of the CH₄ yield of pure CO₂. For the 10.0% CO₂, the CH₄ production was 251 ppm, accounting for 90.5% of the CH₄ yield of pure CO₂ and demonstrating the potential ability to photocatalytically convert flue gas into CH₄. As can be seen, the H₂ production with diluted CO₂ was even higher than the H₂ production with pure CO₂, which may be because there was more 'H bonded to form H₂, instead of reacting with 'CH₃, due to the decreased CO₂ content.⁵⁰ No C₂H₆ was observed with diluted CO₂ since there was enough 'H and all 'CH₃ bonded with 'H instead of 'CH₃.

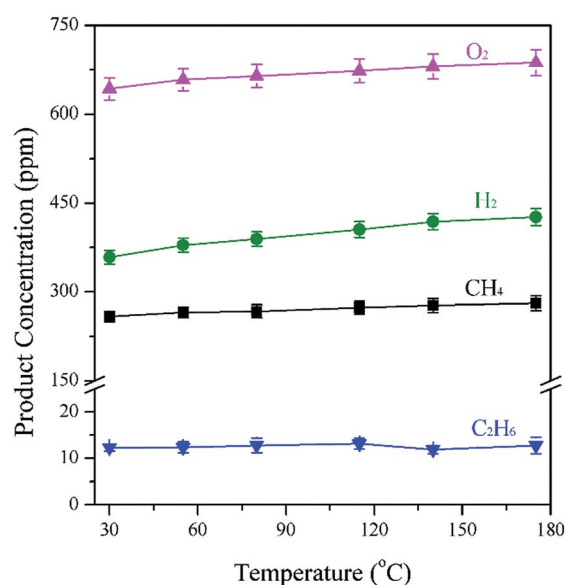


Fig. 10 Effect of temperature on the concentrations of products resulting from photocatalytic CO₂ conversion over Pt/TiO₂ (catalyst weight: 20 mg; water volume: 5 mL; CO₂ pressure: 4 bar).

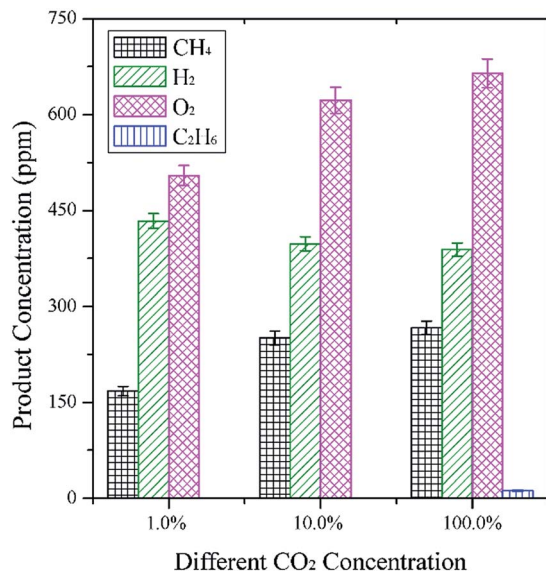


Fig. 11 Effect of CO₂ concentration on the concentrations of products resulting from photocatalytic CO₂ conversion over Pt/TiO₂ (catalyst weight: 20 mg; water volume: 5 mL; total pressure: 4 bar; temperature: 80 °C).

3.3 Photocatalyst stability

Although Pt/TiO₂ photocatalyst demonstrates high photocatalytic performance in CO₂ conversion, its stability is still very important for practical applications. Repeated uses of Pt/TiO₂ on photocatalytic CO₂ conversion were conducted to explore the Pt/TiO₂ stability. These experiments were tested every 4 h for ten times. Each time, after one round, the reacted gas was evacuated and new CO₂ and DI water were introduced. As can be seen in Fig. 12, after one cycle, the CH₄ output dropped to 245.6 ppm, accounting for 88.6% of its original photocatalytic ability, while

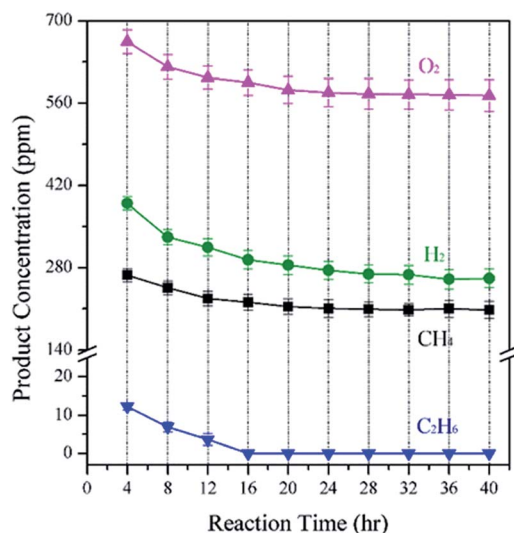


Fig. 12 Time course of photocatalytic CO₂ conversion over Pt/TiO₂ (catalyst weight: 20 mg; water volume: 5 mL; CO₂ pressure: 4 bar; temperature: 80 °C).

the H₂ output decreased from 389.2 ppm to 332.1 ppm. Subsequently, Pt/TiO₂ gradually became stable and the CH₄ evolution didn't change after five rounds of reaction. After three rounds of reaction, there was no C₂H₆ produced, due to the deterioration of photocatalysts. After 10 rounds of reaction, the CH₄ concentration was 207.9 ppm and the H₂ was 257.8 ppm, demonstrating 75.8% of the original CH₄ output; this was still 2.8 times that of Pt/P25. In comparison, the CH₄ concentration over Pt/P25 dropped to 60.2 ppm only after one cycle, accounting for 81.4% of its original photocatalytic ability and was lower than that of Pt/TiO₂.

3.4 Reaction mechanism

The generation of electron-hole pairs upon UV irradiation and the migration of the charges on Pt/TiO₂ photocatalyst are obvious. The photoexcited electrons generated by TiO₂ are trapped by the Pt nanoparticles and the surface reduction process takes place on Pt nanoparticles, while the holes stay on TiO₂ to oxidize H₂O to O₂. However, the photocatalytic CO₂ conversion process is not clear. Based on previous literature and the data obtained in this research, photocatalytic CO₂ conversion might occur according to the following process: CO₂ is first reduced to CO at the Pt sites, while at the same time 'H' is formed from water splitting. Then the as-formed CO reacts with 'H' to form CH₄ and C₂H₆.^{46,51} Formation of O₂ was detected. For example, over the Pt/TiO₂ catalyst and a reaction time of 4 h, the O₂ concentration reached 664.4 ppm, the CH₄ concentration reached 277.2 ppm, together with a H₂ concentration of 389.2 ppm and an C₂H₆ concentration of 12.4 ppm. From the concentration of the reductive products, the stoichiometric formation of O₂ was calculated by assuming that the oxidation of water to form O₂ is the only source to provide electrons. The O₂ calculated concentration (O_{2,c}), based on the quantities of measured H₂, CH₄, and C₂H₆, can be estimated as follows:

$$O_{2,c} = 0.5H_{2,m} + 0.5CO_{m} + 2CH_{4,m} + 3.5C_{2}H_{6,m}$$

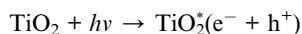
where H_{2,m}, CO_m, CH_{4,m} and C₂H_{6,m} refer to the measured concentration of H₂, CO, CH₄ and C₂H₆, respectively. The calculated O₂ concentration and the measured O₂ formation concentration (O_{2,m}) under different reaction time are listed in Table 2. The errors between them are listed. Considering the actual O₂ formation is similar to the calculated stoichiometric

Table 2 Calculated O₂ concentration vs. measured O₂ concentration

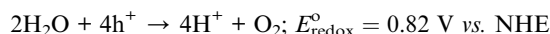
Time (h)	O _{2,m} (ppm)	O _{2,c} (ppm)	Error ^a (%)
1	221.2	252.8	12.50f
2	479.7	529.75	9.45
3	589.1	656.35	10.25
4	664.4	783.4	15.19
5	699.6	798.15	12.35
6	725.7	815.95	11.06
7	761.4	837.15	9.05
8	785.3	859.2	8.60

^a Error was calculated by (O_{2,c} – O_{2,m})/O_{2,c}.

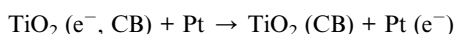
O₂ formation value, the following reaction pathways at pH = 7 are proposed:^{19,26}



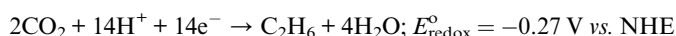
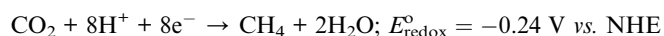
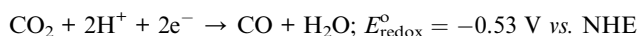
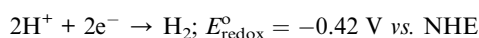
Valance band (photooxidation)



Conduction band (electrons transfer)



Pt surface (photoreduction)



4. Conclusions

In summary, well-crystallized anatase TiO₂ nanoparticles with a high surface area and a diameter of ~18.4 nm were prepared by a solvothermal method at 180 °C. Pt/TiO₂ nanocomposites with an average Pt nanoparticle size of 1.82 nm were then prepared by photoreduction and used for photocatalytic CO₂ conversion. XPS analysis indicated that only part of the Pt species were reduced to metallic Pt. The Pt/TiO₂ nanocomposites had a bandgap of 3.07 eV, and the photogenerated electron-hole recombination rate was lower than that of Pt/P25. Pt photodeposition time and TiO₂ calcination temperature had a significant impact on the photoactivity of Pt/TiO₂, and the optimal TiO₂ calcination temperature and Pt photodeposition time were 500 °C and 1 h, respectively. The optimized Pt/TiO₂ presented a photoactivity 3.7 times higher than that of Pt/P25 and 18.7 times higher than that of P25. Reaction temperature had a slight influence on the photocatalytic CO₂ conversion process. By using 10.0% CO₂ diluted in N₂, the CH₄ yield was 90.5% that of pure CO₂. Moreover, The Pt/TiO₂ nanocomposites were more stable than Pt/P25 and could be used repeatedly. In addition, O₂ was detected and recorded for a systematic analysis of the relationship between photocatalytic CO₂ conversion and water splitting, and the balance between the photogenerated electrons and holes were calculated. It is proposed that CO and 'H were formed at first and then the as-formed CO reacted with 'H to form CH₄ and C₂H₆.

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