Enhancing photocatalytic CO₂ reduction by coating an ultrathin Al₂O₃ layer on oxygen deficient TiO₂ nanorods through atomic layer deposition

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Abstract

In this work, anatase nanorods (ANR) of TiO₂ with active facet {100} as the major facet were successfully synthesized, and reducing the ANR by NaBH₄ led to the formation of gray colored oxygen deficient TiO_{2-x} (ReANR). On the surface of ReANR, a thin layer of Al₂O₃ was deposited using atomic layer deposition (ALD), and the thickness of Al₂O₃ varied by the number of ALD cycles (1, 2, 5, 10, 50, 100, or 200). The growth rate of Al₂O₃ was determined to be 0.25 Å per cycle based on high-resolution TEM analysis, and the XRD result showed the amorphous structure of Al₂O₃. All the synthesized photocatalysts (ANR, ReANR, and Al₂O₃ coated ReANR) were tested for CO₂ photocatalytic reduction in the presence of water vapor, with CO detected as the major reduction product and CH₄ as the minor product. Compared with ANR, ReANR had more than 50% higher CO production and more than ten times higher CH₄ production due to the oxygen vacancies that possibly enhanced CO₂ adsorption and activation. By applying less than 5 cycles of ALD, the Al₂O₃ coated ReANR had enhanced overall production of CO and CH₄ than uncoated ReANR, with 2 cycles being the optimum, about 40% higher overall production than ReANR. Whereas, both CO and CH₄ production decreased with increasing number of ALD cycles when more than 5 cycles were applied. Photoluminescence (PL) analysis showed an ultrathin layer of Al₂O₃ (2 cycles of ALD) coating on the ReANR was able to reduce the charge carrier recombination rate, likely because of the passivation of surface states. On the other hand, a relatively thick layer of Al₂O₃ may act as an insulation layer to prohibit electron migration to the catalyst surface. This work gives valuable insights on the application of ALD coating on photocatalysts to promote CO₂ photoreduction to fuels.

Keywords:

ALD, CO₂ photoreduction, TiO₂, {100} facet, amorphous Al₂O₃, surface passivation

Introduction

Seeking solutions to reduce the emissions of greenhouse gases, particularly CO₂, has become one of the priority research topics in the field of energy and the environment. Besides the technologies of carbon capture and sequestration (CCS), photocatalytic CO₂ reduction with water assisted by photocatalysts has emerged as a possible and more attractive solution in recent years, since it aims to simultaneously utilize the emitted CO₂ and the abundant solar energy to produce value-added chemical and fuel products.¹ Among the variety of photocatalysts studied, TiO₂ is most frequently evaluated for the CO₂ photoreduction process because it is inexpensive and earth-abundant, chemically stable, and environmentally benign.²⁻⁴ Despite being widely used as a photocatalyst for CO₂ photoreduction, TiO₂ has limitations that include low light absorption in the visible range due to its large band gap (3.2 eV for anatase)⁵, low CO₂ adsorption capability⁶, and low quantum efficiency due to fast recombination of electrons and holes.^{7,8} Numerous approaches have been attempted to address those limitations, such as doping with metal⁹⁻¹¹ or nonmetal elements^{12,13}, tuning the exposed facets¹⁴, and engineering TiO₂ with oxygen vacancies (V_O)^{15,16}.

There are three naturally existing crystal phases of TiO₂, anatase, brookite, and rutile, which reveal different photocatalytic performance for CO₂ reduction with H₂O. Anatase is the most studied TiO₂ crystal phase because it is easier to synthesis compared to brookite and more active compared to rutile. A basic anatase crystal formed naturally has a truncated bipyramidal structure usually enclosed by eight {101} facets and two {001} facets, and because the surface energy of {001} is greater than {101}, the exposed facet of anatase is dominated by {101} at 94%.¹⁷ Recently, anatase nanomaterials with well-defined exposed facets have been successfully prepared and investigated for the facet-dependent photoactivity of TiO₂. Among the three low-index facets {100}, {001} and {101}, {100} facets was demonstrated to have a higher photocatalytic ability.^{18,19} Both {100} and {001} facets have higher surface energy than {101},²⁰⁻²² and have 100% fivefold coordinated Ti (Ti_{5C}). By contrast {101} facets have only 50% Ti_{5C} sites. Ti_{5C} sites are more active than Ti_{6C} sites due to unsaturated coordination of Ti_{5C}, and Ti_{5C} can act as the active sites for CO₂ activation and conversion.^{14,20} Meanwhile, both theoretical calculations and experimental results suggested that the {100} is more active than {001}.²³⁻²⁵ Pan *et al.* tested the photocatalytic H₂ evolution on TiO₂ with different dominant facets, and TiO₂-{100} showed the highest H₂ evolution.²⁰ In addition, the order of CO₂ photoreduction to methane on different anatase facets was reported as {100} > {101} > {001}.¹⁹ This is because the conduction band (CB) values for {100}, {101}, and {001} are -0.52eV, -0.49eV, -0.45eV, respectively, resulting in the driving force for CH₄ production ($E^0_{(\text{CO}_2/\text{CH}_4)} = -0.24 \text{ eV}$ vs. NHE, pH = 7.0) in the order of {100} > {101} > {001}. In this work, {100} is used to refer both {100} and {010} facets, since these two surfaces in anatase are isostructural.²⁶

In addition, oxygen deficient TiO_2 has shown better performance for CO_2 photoreduction compared to pristine TiO_2 because surface V_O can serve as the active sites for CO_2 adsorption^{27,28}, activation^{29,30}, and conversion^{29,31}. Also, the light absorption of TiO_2 can be improved due to the rising local states under the CB band minimum caused by the V_O .³² The promising results of combining the advantages of active facets and defect effects in our previous work¹⁴ have inspired on the design of novel TiO_2 material with high percentage {100} facets exposed and high density of surface oxygen vacancies.

However, as the concentration of the surface defects increases, the local surface states increase^{33,34}, which results in the formation of recombination centers near/on the defect sites. To suppress the recombination, a very thin layer (in ångström level) of metal oxide such as ZrO_2 ³⁵, Al_2O_3 ³⁶ and SnO_2 ³⁷ on the surface of semiconductors was applied by atomic layer deposition (ALD). Amorphous Al_2O_3 was popularly used as the surface passivation coating material on Si for solar cell application by two passivation mechanisms: chemical passivation by reducing the interface state density and field effect passivation caused by the fixed charges in the thin film.^{38,39} ALD is able to precisely control the thickness of the Al_2O_3 layer because of the self-limiting reaction of the dosed precursor gasses.^{40,41}

In this work, for the first time we report the amorphous Al_2O_3 passivated oxygen deficient single crystal anatase TiO_2 with {100} as the dominantly exposed facet for CO_2 photocatalytic reduction. The thickness of Al_2O_3 layer deposited on TiO_2 was controlled by ALD. The mechanism of the enhanced photocatalytic activity was proposed based on the materials characterization and activity test results. We have found that when the layer of Al_2O_3 was very thin, the surface passivation ability of Al_2O_3 over TiO_2 could enhance the photocatalytic activity, but a thick layer of Al_2O_3 as an insulator could hinder the electron transfer to the surface, thus lowering the rate of CO_2 photocatalytic conversion.

Experimental Section

Material Synthesis

Anatase nanorods (ANR) were prepared by a two-step hydrothermal method. Firstly, TiO_2 P25 (Evonik) was dispersed into a 10M NaOH solution, sealed in a Teflon-lined autoclave, and heated in an electric furnace at 140°C for 24 h to produce sodium titanates. The products were washed and centrifuged several times with D/I water till pH 10. Next, 2 g sodium titanates were mixed with D/I water and subject to a second hydrothermal process at 200 °C for 12 h. The resulting solids were separated from the liquid by centrifuge and washed with D/I water till pH 7. The anatase nanorods were obtained after drying the sample at 60 °C for 12 h.

The reduced anatase nanorods (ReANR) were prepared by mixing the ANR with NaBH_4 (1:1) in a mortar, and thermally treated in Ar at 300 °C for 30 min. The resulting mixed solids were washed with D/I water and centrifuged till pH 7. The ReANR was obtained after drying in the oven at 60 °C for 12 h. For comparison, pure anatase nanoparticles (ANP) were prepared by a simple hydrothermal method reported in our previous work.⁶ Briefly, titanium (IV) bis(ammonium lactato) dihydroxyde (TALH) was mixed with 0.1 M urea, and hydrothermally treated at 160 °C for 24 h. The sample was washed and dried using the same method as in the procedure for ANR. The ANP was finally calcined at 450 °C for 2 h to remove any possible organic residuals on the surface. The reduced ANP (ReANP) was also prepared using the same method as ReANR.

To obtain ALD coated Al_2O_3 on ReANR, a commercial ALD system (Savannah S200, Ultratech) was applied. For each coating process, ANR powders were loaded into a home-designed particle holder, which was placed in the middle of the reaction chamber of the ALD. To ensure adequate coating on porous materials, the ALD system was set in an “expo mode” assisted with a soft pump, which can prolong the time for precursor molecules to contact with the surface of ANR by slowing down the pressure decreasing rate. The pulse time of both the H_2O and Trimethylaluminum (TMA) was 0.03 s, and the reaction chamber was set at 200 °C. No external heater was applied to the TMA cylinder. The Al_2O_3 coated samples were denoted as xAl_ReANR, where x is the number of ALD cycles applied.

Material Characterization

X-ray diffraction (XRD, BRUKER D8) using Cu $K\alpha$ irradiation at 45 kV and 40 mA diffracted beam monochromator was applied to detect the crystal structures of the photocatalyst samples. The surface morphology was obtained by scanning electron microscopy (SEM, JEOL JSM7500F) equipped with a cold cathode UHV field emission conical. The Energy-dispersive X-ray spectroscopy (EDS, Oxford) associated with SEM was used for surface elemental mapping and quantitative elemental composition analysis. Transmission electron microscopy (TEM) and high resolution-TEM (HR-TEM) taken by an FEI Tecnai G2 F20 ST instrument with 0.24 nm point and 0.15 nm information limitation at 200 keV was used to obtain the lattice structure of ANR and identify the Al_2O_3 coating layer. UV–vis diffuse reflectance spectra were obtained by a Hitachi U4100 UV-Vis-NIR Spectrophotometer with Praying Mantis accessory. Photoluminescence (PTI QuantaMaster series Spectrofluorometer) was used to investigate the charge recombination emission using 360 nm incident light, scanning from 370 to 700 nm with scan rate 0.1nm/s. A 380 nm long pass filter was applied to the detector. X-ray photoelectron spectroscopy (XPS) was used to identify the chemical states of Ti, O and Al elements, using an Omicron

XPS system using Omicron's DAR 400 dual Mg/Al X-ray source. All region and components were calibrated using C 1s peak at 284.8 eV.

Photocatalytic activity test

Photocatalytic activity test for CO₂ photoreduction with water vapor was performed in a cylindrical quartz tube reactor. For each activity test, 10 mg catalyst was dispersed on a piece of glass fiber filter paper. The filter paper was placed in the middle of the reactor, with the catalyst side facing the light irradiation direction. CO₂ (99.999%, Airgas) continuously passed through a water bubbler and brought the mixed CO₂ and H₂O gas (2.3vol% of H₂O) into the reactor. The reactor was first purged at 100 ml/min for 1 h to eliminate air and then maintained at 4 ml/min (continuous-flow mode) for the whole photoreaction process. A 450 W Xe lamp (Newport) was used as the UV-vis source. The light intensity is about 267 mW/cm² in the range from 250 to 1050 nm, and 17 mW/cm² in the UV range (<390 nm). The spectrum of the light source was shown in **Fig. S1** in the Supporting Information. A 250 W infrared (IR) lamp was applied to keep the reactor at 100 °C, this is because a relatively higher reaction temperature can facilitate the desorption of the products and improve the activity of photo-activated TiO₂.⁴² In addition, Slamet *et al.*^{43,44} reported elevated CO₂ photocatalytic conversion to CH₄ by increasing the reaction temperature to 100 °C. The effluent from the reactor was analyzed continuously by a gas chromatograph (GC, Fuel Cell GC-2014ATF, Shimadzu) equipped with a thermal conductivity detector (TCD) and a methanizer assisted flame ionization detector (FID).

Results and Discussion

Crystal Structure

The crystal structure of the materials synthesized was characterized by XRD. **Fig. 1** shows the XRD patterns of the ReANR and 200Al_ReANR, both of which show characteristic peaks for anatase TiO₂ (tetragonal, space group I41/amd, JCPDS 21-1272). Peaks at 25.3, 37.1, 37.8, 38.9, 48.0, 53.9, and 55.0 degree can be assigned to (101), (103), (004), (112), (200), (105), and (211) crystal plane of anatase TiO₂, respectively. The full width at half maximum (FWHM) for peaks at 25.3, 37.8, and 48.0° was calculated to be 0.011, 0.006, and 0.012, which are indexed to crystal planes (101), (004) and (200), respectively. Compared with the FWHM of anatase nanocuboids (0.11, 0.26, 0.09) with 95% {100} exposed facet reported in the literature,⁴⁵ the ANR synthesized in this work with much smaller FWHM had better crystallinity. The peak intensity ratio I(101): I(004): I(200) was 100:14:40, while the standard ratio of anatase is 100:18:23,⁴⁵ suggesting that the preferential crystallographic orientation of anatase nanorod synthesized was along [100] direction. For ALD coated catalyst, there was a very broad peak at

20-50°, observed from the intensity difference between ReANR and 200Al_ReANR (inset of **Fig.1**). The broad peak matched the amorphous Al₂O₃ by ALD reported in the literature,⁴⁶ indicating the successful coating of amorphous Al₂O₃ layer on nanorods.

Fig. 1 XRD patterns of ReANR and 200Al_ReANR (inset figure is intensity by subtracting intensity of ReANR from 200Al_ReANR)

Morphology

The morphology of the photocatalysts was characterized by SEM in **Fig. 2**. The rod-shape ANR (**Fig. 2a**) and ReANR (**Fig. 2b**) have well-defined lateral facets with sharp edges, and the adjacent parallel facets {100} and {010} are perpendicular as boxed off in **Fig. 2d**. The rectangular shape has a width a of ~53 nm, and a depth b of ~58 nm, suggesting a is approximately equal to b . Thus, a geometry model of the ANR can be built based on the measurement in SEM, TEM, and HRTEM images, as shown in **Fig. 2e**. The exposed facets of ANR were composed by four {100}/{010} facets as the lateral planes,

two {001} as the end planes, and four {101} facet as the connecting planes. Although the anatase nanorods exhibited different lengths (along [001] direction), the aspect ratios of the rods are similar. The model parameters are estimated to be $a:b:c:H:h_1:h_2 = 1:1:0.3:10:9:0.5$. The percentage of {100} facets exposed was calculated to be 91.5% (see detailed calculations in the Supporting Information) using the method described in our previous work.¹⁴ As shown in **Fig. 2c**, after ALD coating of Al_2O_3 for 200 cycles on the surface of TiO_2 , the size of the nanorods became larger, and the edges became blurry, suggesting the successful coating of Al_2O_3 on ANR.

Fig. 2 SEM images of ANR (a), ReANR (b), 200Al_ReANR (c), the enlarged image of the circled area (d), and the simulated geometry model of ANR (e)

Lattice structure of ANR and identification of Al_2O_3 coating layer

The EDS mapping images and elemental analysis spectrum in **Fig. 3** further confirm the existence of the Al_2O_3 layer. In **Fig. 3a**, as the ALD cycle increased from 2 to 200, the size of nanorods increased. Moreover, the number of the green dots, which were corresponding to Al element, also increased with the increasing ALD cycle number. The surface quantitative elemental composition analysis (**Fig. 3b**) shows an even higher concentration of Al (21.69 wt.%) than Ti (15.01 wt.%) on 200Al_ReANR. All the above results demonstrate the successfully coating of an ALD layer of Al_2O_3 whose thickness increases with an increasing ALD cycle number. For the sample 2Al_ReANR, the presence of the ultrathin layer of Al_2O_3

was also demonstrated by XPS results in **Fig. 3c**. The broad peak at 74.75 eV represents typical characteristic of Al 2P (oxide).

Fig. 3 EDS mapping images of ReANR with different cycles of ALD Al₂O₃ coating (a), the EDS elemental analysis spectrum of 200Al_ReANR (b), and the XPS for 2Al_ReANR (c)

TEM and HRTEM were applied to obtain crystal structure information and verify the surface Al₂O₃ coating layer. **Fig. 4** compares the morphology of 2Al_ReANR and 200Al_ReANR. The rod-shaped structure shown in **Fig. 4a** and **4c** agrees well with the SEM observation and literature report^{18,21,22}. The lattice spaces of TiO₂ are measured to be 0.48, 0.35, and 0.35 nm in **Fig. 4b** and **4d** based on the inset fast Fourier transform (FFT) images, corresponding to the (002), (101), and (10 $\bar{1}$) facets, respectively.^{47,48} For 2Al_ReANR in **Fig. 4b**, the fuzzy edges may be attributed to the ultra thin layer of Al₂O₃ on the surface of TiO₂. The amorphous layer of Al₂O₃, which is outlined by dashed lines, can be observed clearly in **Fig. 4d**. The amorphous Al₂O₃ gave the circle signal in the inset FFT image (**Fig 4d**). The thickness of the Al₂O₃ from the edges of the nanorod to the dashed lines was estimated to be 5 nm for the 200Al_ReANR sample, which also matches the average thickness measured in **Fig. 4c**. Therefore, the growth rate of the Al₂O₃ overlayers estimated to be ~0.25 Å per cycle.

Fig. 4 TEM and HRTEM images of 2Al_ReANR (**a** and **b**) and 200Al_ReANR (**c** and **d**)

Optical and charge transfer property

Based on the UV-vis absorption result (**Fig. 5a**) and the Tauc plot (**Fig. 5b**), the band gap of ANR was calculated to be 3.12 eV, while ReANR had a slightly reduced band gap, 3.04 eV. This agrees with the color change from white to grey after the reduction treatment by NaBH_4 due to the formation of V_O , which was confirmed by XPS shown in **Fig. S3**.⁴⁹ According to the O 1s XPS spectra in **Fig. S3a**, the oxygen vacancy peak (~ 532.0 eV) of ReANR and 2Al_ReANR was higher than that of ANR, suggesting

more oxygen vacancies were formed after reduction.^{50,51} Also, quantitative analysis of Ti^{3+} is given in **Table S1** in terms of the $\text{Ti}^{3+}/\text{Ti}^{4+}$ fraction. It was found that after reduction, the $\text{Ti}^{3+}/\text{Ti}^{4+}$ fraction increased from 0.35 (ANR) to 0.48 (ReANR). The increased formation of Ti^{3+} is another evidence of Vo formation.⁵² With 2 cycles of Al_2O_3 ALD coating, the band gap was slightly increased to 3.08 eV, compared to uncoated ANR, which may be because the surface Vo were partially consumed by H_2O during the ALD pulsing process.

Fig. 5 UV-vis absorption spectra (a) and band gap measurement using Tauc plot (b)

The charge recombination property of the photocatalysts was characterized by photoluminescence. Promoted charge separation lowering the rate of radiative or non-radiative recombination leads to the quenching of the photoluminescence intensity.⁵³ According to the photoluminescence results (**Fig. 6**), the reduced sample ReANR had a much lower intensity of emission peak around 550 nm than ANR, suggesting a reduced charge recombination on ReANR. This is likely because the ReANR had more surface V_O , which can generate donor states below the conduction band (CB), promoting the charge separation and transportation.⁵⁴ After the surface of ReANR was coated with 2 or 200 cycles of Al_2O_3 ALD, the height of the 550 nm emission peak of 2Al_ReANR and 200Al_ReANR was further lowered, indicating the coated overlayer further helped to suppress the surface charge recombination. The photoluminescence intensities of 2Al_ReANR and 200Al_ReANR were quite close to each other, indicating the ultrathin layer of Al_2O_3 coating in the range from 0.5 Å to 5 nm was capable to promote the charge separation. This is consistent with existing literature reports that the thickness of Al_2O_3 for the surface passivation effect varies from several tenths of Å to tens of nm.⁵⁵⁻⁵⁷

Fig. 6 Photoluminescence spectra of anatase nanorod photocatalysts

Photocatalytic Activity for CO₂ photoreduction with H₂O under UV-Vis irradiation

The photocatalytic activity of the synthesized photocatalysts for CO₂ photoreduction was tested by UV-vis light irradiation for 4 h with continuous CO₂ and H₂O vapor feeding. Two control experiments were conducted: (1) in the dark with the photocatalyst, and (2) under light irradiation without photocatalyst. In both cases, no CO₂ reduction products were detected. Under light irradiation in the presence of photocatalysts, CO and CH₄ were detected as the major products of CO₂ photoreduction with H₂O.

Fig. 7 The production of CO and CH₄ during a 4 h UV-vis irradiation period by anatase nanorods and nanoparticles

The production of CO and CH₄ from CO₂ photoreduction with H₂O within 4 h was compared among ANR, ReANR, ANP and ReANP, as shown in **Fig. 7**. Even though ANP had a larger surface area than ANR due to the much smaller particle size of ANP (5-10 nm, as shown in **Fig. S4 a-b**, which was also reported in our previous work⁶) than ANR (a few hundred nm in length as shown in **Fig. 2**), ANP produced 50% less amount of CO (8.2 μmol/g) than ANR (17.1 μmol/g). There are two possible reasons for the higher CO production on ANR over ANP. First, ANR has a very high percentage (91.5%) of exposed ⁵⁸{100} facet that has 100% active Ti_{5C} sites; by contrast, ANP has zero percent {100} facet. Second, the anisotropic structure of ANR may also enhance charge separation between different facets.

The reduced sample ReANR had 50% higher CO production and 10 times higher CH₄ production than ANR. The improvement by ReANR can be attributed to the enhanced light absorption and formation of surface oxygen vacancies. The light adsorption of ReANR was enhanced as evidenced by the narrowed band gap of 3.04 eV, compared with 3.12 eV for ANR. In addition, ReANR prepared by reducing ANR with NaBH₄ had Vo created on the surface rather than in the bulk.⁵⁹ The Vo in the bulk is believed to be recombination centers for electrons and holes,⁶⁰ whereas, Vo on the surface facilitates CO₂ adsorption and activation^{27,28}, and promote electron transfer. The promoted CH₄ production was attributed to the

increased local electron density by V_O , since CH_4 formation involves 8 electrons, while only 2 electrons are required for CO formation. When comparing the activity of ReANR and ReANP, one can find that the production of both CO and CH_4 were higher by ReANR and the overall production of CO and CH_4 by ReANR was 22% higher than ReANP. The results reveal the superior photocatalytic activity of ReANR that takes the advantages of the active exposed facet and surface defect effects. However, it can also be noticed that the activity difference between nanoparticles and nanorods became smaller after reduction. It may be because ReANP may have more V_O formed than ReANR due to the high surface area of ReANP. In addition, the band gap of anatase nanoparticles was reduced from 2.95 eV to 2.85 eV after $NaBH_4$ reducing treatment (**Fig. S4 c-d**). The further narrowed band gap of ReANP compared to ReANR (3.04 eV) leads to higher light absorption capability of ReANP, which may be another reason for the less difference in activity between the reduced nanorods and nanoparticles.

Fig. 8 The production of CO and CH_4 during a 4 h UV-vis irradiation period by Al_2O_3 coated ReANR with different ALD cycles

The CO_2 photocatalytic reduction with H_2O was also conducted on Al_2O_3 coated ReANR with varied thickness of Al_2O_3 coating layer. **Fig. 8** compares the CO and CH_4 production on ReANR with

different cycles (0-200) of ALD coated Al_2O_3 . By applying less than 5 cycles of ALD, the Al_2O_3 coated ReANR had enhanced overall ($\text{CO}+\text{CH}_4$) production than uncoated ReANR, with 2 cycles being the optimum, about 40% higher overall production ($45.2 \mu\text{mol/g}$ in total with $40.8 \mu\text{mol/g}$ CO and $4.4 \mu\text{mol/g}$ CH_4) than ReANR($32.1 \mu\text{mol/g}$ in total). A thin layer of Al_2O_3 deposited on the surface can passivate the trapping states caused by the surface oxygen vacancies, and consequently reduce the recombination of electrons and holes, as revealed by the photoluminescence results. The electrons can still reach to the surface by tunneling or other effects and react with the gas molecules to produce CO and CH_4 when the layer of Al_2O_3 coating is very thin. Due to the passivation effect of Al_2O_3 , the surface recombination was suppressed, resulting in the enhanced CO production, and the increase of the overall electron involved. At the same time, the surface electron density was decreased, which can explain the decline of CH_4 selectivity. However, both CO and CH_4 production decreased with increasing number of ALD cycles when more than 5 cycles were applied. When more than 100 cycles of ALD was applied, the overall production was reduced to $\sim 12 \mu\text{mol/g}$ with negligible amount of CH_4 . The insulating property of a thick layer of Al_2O_3 may have decreased the surface electron density, which leads to an overall low product yield and low selectivity of CH_4 . Future studies will continue to focus on the application of ALD on the design of innovative photocatalyst, and the effect of varied coating materials on the performance of TiO_2 .

To investigate wavelength dependence of the photocatalyst activity, 2Al_ReANR was tested for CO_2 photoreduction with H_2O under 365 nm UV light at an intensity of 13 mW/cm^2 . The result is compared with that under UV-vis irradiation from the 450 W Xe lamp, as shown in **Fig. S5**. The result suggests both UV and visible lights contributed to the production of CO and CH_4 while the activity under visible light was superb and higher than that under UV.

Finally, the stability of the photocatalyst was investigated. The sample of 2Al_ReANR, which has the optimal thickness of Al_2O_3 coating layer, was undergone 5 cycles (8 h/cycle) of activity tests. After each 8 h cycle test, the photocatalysts were wetted by DI water and dried at 60°C prior to the next cycle test. The cycling performance results are presented in **Fig. S6**. It shows the total production of $\text{CO}+\text{CH}_4$ after 5 cycles maintained $\sim 80\%$ of the initial value, suggesting a relatively high stability of 2Al_ReANR. In addition, the color of ReANR and Al_2O_3 coated ReANR remained the same gray color for months, which also indicates the prepared materials are very stable.

Conclusions

Three materials innovations have been applied in this work to synthesize a unique nanostructured photocatalyst (TiO₂ anatase nanorods with over 90% exposed {100} facet, oxygen-deficient surface, and ALD coated Al₂O₃ overlayer), which demonstrated significantly enhanced capability for CO₂ photoreduciton with H₂O to produce CO and CH₄. ANR with dominating {100} facets, despite a smaller surface area, was much more active than ANP. Reduced ANR facilitated CO₂ adsorption and activation due to surface oxygen vacancies. However, the density of surface states increased with increasing oxygen vacancies, which may be detrimental to photocatalytic reactions. An ultrathin overlayer of Al₂O₃ deposited by ALD demonstrated the ability to passivate the surface states of reduced ANR and thus further enhanced the yield of CO₂ photoreduction. The thickness of the Al₂O₃ coating is found to be critical to the photocatalytic performance of TiO₂. Two cycles of ALD coating or approximately 0.5 Å Al₂O₃ corresponded to the optimum CO and CH₄ production. However, when more than five ALD cycles was applied, the CO and CH₄ production decreased, likely because the relatively thick overlayer inhibited electron transfer to the catalyst surface, although the surface passivation effect was still in effect. The strategy of ALD coating of a surface passivation layer can be applied to other photocatalysts beyond TiO₂ and other engineered surfaces and nanostructures, which may lead to the discovery of efficient, stable photocatalysts for CO₂ photoreduction with H₂O.

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