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Citation
Journal of materials chemistry A, 3(18), 9491-9501
https://doi.org/10.1039/c4ta05892e

Issue Date
2015-05-14

Doc URL
http://hdl.handle.net/2115/60969

Type
article (author version)

File Information

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP
In situ synthesis of ordered mesoporous Co-doped TiO$_2$
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the reduction of CO$_2$

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Abstract: Ordered mesoporous cobalt-doped titanium dioxide was successfully synthesized by a multicomponent self-assembly process. The doped Co species change the construction of the conduction band and valence band of TiO$_2$, leading to visible-light absorption for TiO$_2$. The designed cobalt-doped titanium dioxide performs a higher visible light activity for the reduction of CO$_2$ among the common reported photocatalysts. In addition, the selectivity of the reduction products is improved by optimizing the energy-band configurations of cobalt-doped titanium dioxide through varying the molar ratio of Co/Ti. When the content of doped cobalt species increases to some extent, Co$_3$O$_4$/Co-doped TiO$_2$ nanocomposites with oxygen vacancies were obtained, which markedly improve the generated rate of CH$_4$.

Keywords in situ synthesis, cobalt-doped titania, ordered mesoporous structure, cobalt oxide, photoreduction of carbon dioxide

1. Introduction

Reduction of CO$_2$ is an increasingly important research area because of the fossil fuel shortage and the global warming problem.$^{1-5}$ For decades, much effort has been devoted to the development of new technology for the reduction of CO$_2$, such as biological conversion,$^6$ thermal catalysis,$^7$ electrocatalysis,$^{8-10}$ artificial photosynthesis,$^{11, 12}$
photo-electrocatalysis\textsuperscript{13} and photothermal catalysis.\textsuperscript{14, 15} Compared with other technologies, the artificial photosynthesis is still a huge challenge due to the thermodynamic stability of CO\textsubscript{2}, and the sluggish formation of renewable hydrocarbon fuels (e.g. CO, CH\textsubscript{4}) which is generally less than tens of \(\mu\)mol per hour of illumination per gram of photocatalyst.\textsuperscript{11, 12} In artificial photosynthesis, the semiconductor should have appropriate conduction band minimum for the reduction half-reaction and valence band maximum for the oxidation half-reaction. Therefore, the main components of the common photocatalysts for CO\textsubscript{2} conversion are typically wide-band gap semiconductors, such as TiO\textsubscript{2},\textsuperscript{16-19} SrTiO\textsubscript{3},\textsuperscript{20, 21} NaNbO\textsubscript{3},\textsuperscript{22, 23} Gallate,\textsuperscript{24-26} germanate,\textsuperscript{27, 28} tantalate,\textsuperscript{29} which are photoactivated only under ultraviolet light. Since solar energy is composed of less than 10\% of ultraviolet range and the rest are visible and infrared wavelengths, it is necessary to develop a new photocatalyst which has a narrow band gap for the adsorption of visible light and improves the energy conversion efficiency. However, as demonstrated by the extensive researches on photocatalytic reduction of CO\textsubscript{2} with water, the common visible light active photocatalysts, such as oxynitrides,\textsuperscript{30, 31} sulfides,\textsuperscript{32, 33} phosphide\textsuperscript{13, 34-35} and metal-organic frameworks,\textsuperscript{36, 37} are quite difficult to promote the oxidation half-reaction, which leads to the generation of oxygen through the oxidation of water.

In recent years, the doping of various cations or anions into wide-band gap semiconductors has been extensively investigated to increase the visible-light adsorption for photocatalytic CO\textsubscript{2} reduction.\textsuperscript{38-42} Besides, photocatalysts with ordered
mesoporous structures have attracted growing interest due to their uniformly distributed porosity, ordered channels and high specific surface area.\textsuperscript{43-45} The highly ordered mesoporous structure develops a high-efficient CO\textsubscript{2} adsorption ability and improves the separation and transport of electron–hole. In addition, the active sites exist not only on the outside surface of mesoporous catalyst, but also exist on the inner surface of pores. Therefore, ordered mesoporous semiconductors with doping of ions have enormous potential for promoting CO\textsubscript{2} reduction under visible light region. Up to now, there are few researches report the doped semiconductor with ordered mesoporous structure for photocatalytic reactions.

Herein, we employ a doping method to adjust the band structure of TiO\textsubscript{2} to promote the absorption of light in visible range and enhance the catalytic ability for oxidation half-reaction. Cobalt-based materials were discovered to be efficient catalysts for water oxidation at relatively low overpotentials,\textsuperscript{46-48} and even were able to carry out overall water splitting.\textsuperscript{49} Thus, in this paper, ordered mesoporous Co-doped TiO\textsubscript{2} was elaborately prepared by a multicomponent self-assembly process. The prepared ordered mesoporous Co-doped TiO\textsubscript{2} exhibited a much higher photocatalytic activity of CO\textsubscript{2} reduction under visible light owing to their regular porous structure and suitable band structure.

2. Experimental section

2.1 Synthesis of ordered mesoporous Co-doped TiO\textsubscript{2}: In a typical preparation, 2.0 g of triblock copolymer Pluronic F127 and a certain amount of cobalt acetate were poured
into 20.0 mL of anhydrous ethanol with vigorous stirring at 40 °C to obtain a clear solution. Then, 3.4 g of tetrabutyl titanate and 2.5 g of soluble resol were added with vigorous stirring for 2 h at 40 °C to obtain a homogeneous green solution. After evaporating the solvents at room temperature and thermo-polymerizing in an oven at 100 °C for 24 h, the resulting green film was pyrolyzed in a tubular furnace at 350 °C for 4 h under N₂ atmosphere with a heating rate of 1 °C min⁻¹ to get puce polymer-Co-TiO₂ composite. Finally, the puce composite was calcined at 400 °C for 5 h under air atmosphere to obtain ordered mesoporous Co-doped TiO₂. The samples were named as Co-OMT-x, where the corresponding molar ratios of Co/Ti in the synthetic process were shown in Table 1. When the addition of cobalt acetate is 0 g, the sample is named as OMT. The mesoporous Co₃O₄ was prepared by the same procedure, in which the amounts of cobalt acetate and tetrabutyl titanate were 2.49 and 0 g, respectively. The soluble resol (phenol-formaldehyde, Mw < 500, 20 wt% in ethanol) was synthesized according to the method reported by Dr. Zhao.⁵⁰

2.2 Characterization: X-ray diffraction (XRD) patterns were tested on an X-ray diffractometer (Rint 2000, Altima III, Rigaku Co. Japan,) using a Cu Kα source. Nitrogen adsorption-desorption isotherms were measured at 77 K using a BEL SORP-mini II (BEL Japan INC., Japan). The specific surface areas of the samples were calculated by utilizing the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were estimated by the Barret-Hoyner-Halenda (BJH) method by using the adsorption branch. Transmission electron microscopy (TEM) experiments were
conducted by a field-emission transmission electron microscope (2100F, JEOL Co.,
Japan) operated at 200 kV. Energy dispersive X-ray spectrum (EDX) installed in a
2100F was used to analyze the microzone composition (STEM-EDX mapping). The
scanning electron microscopy (SEM) images were recorded on a
field-emission-scanning electron microscope (S4800, Hitachi Co., Japan) with an
accelerating voltage of 10 kV. The diffuse reflection spectra were measured in an
ultraviolet-visible (UV-vis) recording spectrophotometer (UV-2600, Shimadzu Co.,
Japan) and were transformed to the absorption spectra according to the Kubelka-Munk
equation. Element chemical analysis and valence band of the samples were performed
by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, ULVAC-PHI Inc.,
Japan). TG/DTA were monitored by using a DTG-60H instrument (Shimadzu Co.,
Japan) from 25-800 °C under nitrogen or air with a heating rate of 1 °C min⁻¹. The
oxygen vacancies of the samples were investigated by ESR (Electron Spin Resonance)
using JEOL JES-FA-200 at 25 °C.

2.3 Photocatalytic measurements: All of the samples were treated at 400 °C in air for
4 h to remove organic adsorbates before the photocatalytic reaction. The photoreduction
of CO₂ was carried out in an airtight circulation system. A 300 W Xenon arc lamp with
a L-42 glass filter was used as the light source. 0.1 g of the sample was uniformly
dispersed on a porous quartzose film in the reaction cell, and 3 mL of the deionized H₂O
and 80 kPa pure CO₂ gas were added into the airtight system. The products were
measured by using a gas chromatograph (GC-14B, Shimadzu Co., Japan). The isotope
analysis of $^{13}$C was analyzed by using a gas chromatograph-mass spectrum (JEOL-GCQMS, JMS-K9 and 6890N Network GC system, Agilent Technologies).

2.4 Photoelectrochemical and electrochemical measurements: Photoelectrochemical and electrochemical measurements were carried in a quartzose beaker and an electrochemical station (ALS/CH model 650A) using three-electrode mode with a coated ITO as the working electrode, a platinum foil as the counter electrode, and Ag/AgCl electrode as the reference electrode in 0.5 M Na$_2$SO$_4$ aqueous solution. For working electrodes, 5 mg of photocatalyst and 10 μL of Nafion solution (5 wt%) were dispersed in 1 mL of ethanol to form a homogeneous turbid liquid and then 50 μL of turbid liquid was deposited on ITO conductive glass with an area of 1 cm$^2$. Photocurrent densities were measured at 0.4 V (vs. Ag/AgCl), and an AM 1.5 Solar simulator (PEC-L01, Pecell Co., Japan) with an L–42 glass filter as the light source. Mott–Schottky plots were obtained under direct current potential polarization with a potential step of 10 mV at a frequency of 1 kHz.

2.5 Theoretical calculations. Electronic structures of TiO$_2$ and Co-doped TiO$_2$ were investigated via the plane-wave-based density functional theory (DFT) using a standard Cambridge serial total energy package (CASTEP) code,$^{52}$ then the electronic exchange-correlation energy was analyzed within the frame-work of the local density approximation (LDA).

3. Results and discussion

3.1 Synthesis and characterization of ordered mesoporous Co-doped TiO$_2$
Fig. 1a describes the designed schematic route for in situ fabricating ordered mesoporous Co-doped TiO$_2$. Firstly, the triblock copolymer F127 used as a template, phenolic resol precursor act as a “binder” and metal salts co-assembled into rod-like micelles in ethanolic solution. The obtained green solution was poured into petri dish to evaporate the solvent and polymerized at 100 °C. Secondly, the dark green film was pyrolyzed at 350 °C under N$_2$ atmosphere to remove the template (Fig. S1a), and a puce polymer-Co-TiO$_2$ composite was obtained. Finally, well-crystallized Co-doped ordered mesoporous TiO$_2$ (Fig. 1(b,c)) was successfully synthesized by getting rid of “binder” through calcining the puce polymer-Co-TiO$_2$ composite at 400 °C in air (Fig. S1b).

Due to the ionic radius of Co$^{2+}$ and Ti$^{4+}$ are 65 and 60.5 pm,$^52$ the Co atom can take the place of Ti atom.$^{53,54}$ In general, Co-doped TiO$_2$ was prepared by conventional solid reaction by mixing the TiO$_2$ with CoO$_x$ or Co salts, which need a high calcined temperature in air. However, when the synthesis of Co-doped TiO$_2$ was carried out through mixing the Co$^{2+}$ and Ti$^{4+}$ in atomic scale, it only needs a low calcined temperature (~350 °C ) in air.$^{53,55}$ When the synthesis of Co-doped TiO$_2$ was carried out through mixing the Co$^{2+}$ and Ti$^{4+}$ in atomic scale, with a calcined temperature is 400 °C in air.

As shown in the elemental mapping images (Fig. 1d), the cobalt species are homogeneously doped throughout the TiO$_2$ framework, thus Co-doped ordered mesoporous TiO$_2$ is obtained. However, when the molar ratio of Co/Ti reaches to specific value (For example, Co/Ti = 0.2 in Co-OMT-7), lots of nanoparticles with a
diameter of 5–10 nm appear in the mesoporous structure, which are further proved to be cobalt oxides by the TEM image (Fig. 1e,f), elemental mapping images (Fig. 1g), STEM image (Fig. 1h), and the followed XRD analysis. The detailed discussion will be provided in the following parts. As a result, cobalt oxides/cobalt-doped ordered mesoporous TiO2 composites are prepared in the case of excess addition of cobalt species. As shown in Fig. 1i, series of Co-doped ordered mesoporous TiO2 with different colors are prepared by varying the mass ratio of cobalt source to titanium source during self-assembly process. The products are denoted as Co-OMT-x (x = 1–8), where the corresponding molar ratio of Co/Ti in the synthetic process is detailed illustrated in the Table 1. What is more, in order to obtain the doping levels of Co2+, we have removed the Co3O4 by using HCl treatment, as shown in Fig. S2. The molar ratios of Co/Ti in each samples before and after removing the Co3O4 are summarized in Table S1.

The morphologies and porous structures of the samples were directly observed by TEM and FE-SEM. As shown in Fig. 1b, Fig. 2, and Fig. S3, when the molar ratio of Co/Ti is lower than 0.05, the corresponding samples (OMT and Co-OMT-x (x=1–5)) present a well-ordered mesoporous structure with pore size of 2–4 nm. Nevertheless, the nanoparticles gradually appear and grow along with the increased addition of cobalt precursors, leading to the collapse of ordered mesoporous structure. The crystal lattice of the nanoparticles embedded in Co-OMT-8 are estimated to be 0.243 nm (shown in Fig. 2h), which corresponds to the crystalline Co3O4 (311) facet. For comparison, the
Co₃O₄ sample is prepared through a same process except the addition of Ti source. The TEM images in Fig. S4 revealed that Co₃O₄ sample is composed of nanoparticles with the size of 20-40 nm and the interplanar distances of Co₃O₄ (111) and (311) facets are respectively proved to be 0.468 and 0.243 nm by high resolution TEM images (Fig. S4c, d), which is in accordance with that of nanoparticles in Co-OMT-8.

The impacts of doped amount of cobalt on the structures of the obtained samples were investigated by XRD and N₂ adsorption-desorption isotherms. The small-angle XRD patterns for the all of the samples are shown in Fig. 3A. It’s observable that pure OMT exhibit an unambiguous diffraction peak at two theta of 1.0°, indicating the ordered mesoporous structure. Whereas, the Co₃O₄ sample presents no diffraction peak, implying that it does not possess ordered porous structure. In the case of Co-doped TiO₂, the intensity of the well-resolved diffraction peaks at around 1.0° gradually decreases along with the increasingly doped amount of Co, suggesting the deterioration of long-range ordered porous structure in TiO₂. In the wide-angle XRD range (Fig. 3B), we can see that all Co-doped TiO₂ samples present anatase (JCPDS Card 21-1272), and the cubic Co₃O₄ phase (JCPDS Card 01-1152) started appearing in Co-OMT-x (x=6,7,8) when the molar ratio of Co/Ti exceeds 0.05. The electric state of Co in Co-OMT-x was investigated by X-ray photoelectron spectroscopy (XPS). The high resolution Co 2p spectra in OMT, Co-OMT-x and Co₃O₄ are shown in Fig. S5. As the doped amount of cobalt increases, the characteristic peaks of Co 2p are gradually enhanced. Thereinto,
two characteristic peaks with respect to $2p_{3/2}$ and $2p_{1/2}$ confirm the Co$^{2+}$ state in Co-doped TiO$_2$ materials.$^{56-58}$

N$_2$ adsorption–desorption isotherms give us more detailed structural information of the samples. As shown in Fig. 4A, Co-OMT-x and OMT samples exhibit type IV isotherms and type H1 hysteresis loops according to the IUPAC classification, generated from the capillary condensation in mesopores.$^{59}$ As the amount of cobalt increases, the pore size distribution of Co-OMT-x becomes wider due to the structural destruction (Fig. 4B). When we did not add the Ti salt, the obtained Co$_3$O$_4$ shows a non-porous structure. The specific structural parameters of the samples are concluded in Table 1. We can find that the surface areas and the pore volumes of Co-OMT-x trend to decline along with the increase of cobalt because of the deteriorated mesoporous structure, which is in accordance with the small-angle XRD result (Fig. 3A). Generally, the higher specific surface area, the more active sites.$^{43}$

UV-visible absorption spectra of the samples are shown in Fig. 5a,b. All of the samples except pure TiO$_2$, possess the optical absorption capability in the region of visible light. Moreover, with the gradual increase of Co, the absorption edges displayed a continuous red-shift, implying the narrowing of their band gaps. In the light of the corresponding Tauc plots (Fig. S6), their band gaps are shown in the Table 2. The result suggests that the band gaps of these samples can be tailored by changing the molar ratio of Co/Ti. Furthermore, the photoelectrochemical (PEC) test (Fig. 5c) was carried out to prove the photocurrent response of the samples under visible light. The photocurrent
densities of Co-doped TiO2 (0.3~0.4 \( \mu A \cdot cm^{-2} \)) are much higher than that of pure TiO2 (0.04 \( \mu A \cdot cm^{-2} \)).

3.2 Photocatalytic reduction of CO2 over ordered mesoporous Co-doped TiO2

In order to evaluate the impact of cobalt content and porous structure of the samples for CO2 photoreduction under visible light, we carried out the photocatalytic reaction in a gas-closed circulation system in the presence of water vapor and CO2. The basic schematic of photocatalytic process over Co-doped TiO2 is illustrated in Fig. 6a. Generally, in the gas–solid system, CH4, CO or other organic products and H2 are the main reduction products, O2 is the main oxidation product. According to the previous research, the ordered porous structure and high specific surface area are beneficial to improve the stability and activity of the catalysts. Based on the small-angle XRD (Fig. 3A), N2 adsorption-desorption isotherms analysis (Fig. 4A) and UV-vis spectra (Fig. 5a,b), we concluded that the structural ordering, specific surface areas and pore volumes of Co-OMT-x trend to decline along with the increased doping of cobalt, but the band gap also decreases to adsorbing more light. Thus, after carefully adjusting and controlling the structure and components in Co-doped TiO2 by changing the molar ratio of Co/Ti, we can successfully find out the best ratio for CO2 photoreduction. As shown in Fig. 6b,c, the pure order mesoporous TiO2 were not able to reduce CO2 under visible light, and the activities of Co-OMT-x (x=1~5) for CO2 reduction rises firstly, then decreases along with the increased content of doped cobalt. The best catalyst is Co-OMT-4, in which the theoretical molar ratio of Co/Ti is 0.025.
As demonstrated by TEM (Fig. 2) and XRD (Fig. 3B), the Co species are doped into the TiO₂ frameworks when the molar ratio of Co/Ti was controlled less than 0.1 in Co-OMT-x (x=1~5) samples. In this case, we infer that ordered mesoporous structure and band gap are the dominant factors contribute to activity and stability. When the ratio of Co/Ti exceeds 0.1, Co₃O₄ nanoparticles appear in Co-OMT-x (x=6~8) samples. It is observable from Fig. 6d,e that the evolution rate of CO decreases as the cobalt continues to increase in Co-OMT-x (x=6~8), whereas the evolution rate of CH₄ is significantly enhanced. Nevertheless, according to the previous analysis, the structural ordering of Co-OMT-8 is worse than Co-OMT-7 and Co-OMT-4, leading to the poorer stability (Fig. S7). In this situation, the dispersed Co₃O₄ nanoparticle in ordered mesoporous framework is prevailing reason for activity and stability, and the best theoretical molar ratio of Co/Ti is 0.15.

The H₂ and especially O₂ are detected in the productions, and the evolution rates of different products are presented in Table 2. It is noteworthy that the photocatalytic performance shown in this study under visible light is significantly higher or comparable in comparison with the previously reported photocatalytic systems under visible light, even under UV-vis light (Table S2). However, due to the different experimental conditions (such as light intensity, illumination area, photocatalysts dosage) in these photocatalytic systems, the direct comparison is not appropriate. Therefore, we also compared our materials with some typical semiconductors or composites (including N-doped TiO₂, Au/TiO₂, C₃N₄, WO₃, P25)
measured in the same reactor system. The experimental details, characteristics and performances of these materials are shown in supporting information (Fig. S8 and Table S2). We can see that the ordered mesoporous Co-doped TiO$_2$ materials show the optimal photocatalytic activity for CO$_2$ reduction under visible light (Fig. 6f). In addition, the major products under UV-vis light are also CO and CH$_4$ for Co-OMT-4, and the corresponding photocatalytic activity (Table S2) is higher than that of pure ordered mesoporous TiO$_2$. In this study, the porous structure properties and energy-band configurations in the ordered mesoporous Co-doped TiO$_2$ material can be easily adjusted by tuning the molar ratio of Co/Ti, thus, superior photocatalytic performance can be optimized successfully. Co-OMT-4 shows the best photocatalytic activity, which is 0.09 μmol g$^{-1}$ h$^{-1}$ (CH$_4$) and 1.94 μmol g$^{-1}$ h$^{-1}$ (CO). The corresponding quantum efficiency of Co-OMT-4 for the photoreduction is 0.031%. Combined Co-doped TiO$_2$ with Co$_3$O$_4$, we can enhance the selectivity of products, and Co-OMT-8 shows the best activity, which is 0.258 μmol g$^{-1}$ h$^{-1}$ (CH$_4$).

A necessary investigation was performed to confirm whether the products were from CO$_2$ by using $^{13}$CO$_2$. As shown in the GC-MS spectrum (Fig. S9a), the peak with the retention time 02:07 is confirmed to be the main product $^{13}$CO (named as M) for Co-OMT-4. The intensity ratio of M$^+$ and (M-13)$^+$ of $^{13}$CO (m/z = 29, 16) matches that of $^{12}$CO (m/z = 28, 16). In the case of Co-OMT-7 (Fig. S9b), the base peak with the retention time 02:20 is determined to be the parent peak of $^{13}$CH$_4$ (named as M'). The intensity ratio of M$^+$, (M'-1)$^+$ and (M'-2)$^+$ of $^{13}$CH$_4$ (m/z = 17, 16, 15) matches that of
$^{12}$CH$_4$ (m/z = 16, 15, 14). Therefore, the main organic product $^{13}$CO or $^{13}$CH$_4$ is verified to be generated from the reduction of $^{13}$CO$_2$.

As we all know, the electronic structure of a semiconductor plays an important role in the level of the conduction band and the valence band, which subsequently influence the photocatalytic performance. The theoretical calculation of electronic structures for pure TiO$_2$ and Co-doped TiO$_2$ were calculated by Density Functional Theory (DFT), which provides guidance toward understanding the variation of photocatalytic properties. The electronic calculation presented in Fig. S10 illustrated that pure TiO$_2$ and Co-doped TiO$_2$ present indirect gaps. In order to obtain more insight into the band gap narrowing for the Co-doped TiO$_2$ compared with TiO$_2$, we further investigated their total and projected partial densities of states (DOS). For TiO$_2$ (Fig. 7a), the states at the valence band (VB) maximum are composed of O 2p and the states at the conduction band (CB) minimum are composed of Ti 3d. Whereas, the states at the VB maximum of Co-doped TiO$_2$ (Fig. 7b) are composed of O 2p, Co 3d, and the states at the CB minimum are composed of Ti 3d, Co 3d, O 2p. It is clear that doping of Co species in TiO$_2$ will change both the VB and CB of TiO$_2$, and narrow the band gap of the TiO$_2$, thus leading to an enhanced photocatalytic performance in visible region. Moreover, the doped Co$^{2+}$ ions (Co-O) in the surface of TiO$_2$ and the Co$_3$O$_4$ would enhance the water oxidation, due to their partially similar constitution (Co 3d and O 2p) in VB.$^{46-49,71}$ Generally, O$_2$ is difficult to be detected in CO$_2$ photoreduction, due to the incidental O$_2$ reduction. However, in this study, we can detect the O$_2$ in CO$_2$ reduction over Co-doped TiO$_2$. 

14
Therefore, the doping of Co species in TiO$_2$ probably increases the ability for water oxidation of TiO$_2$.

What are the reasons for the selective CO$_2$ conversion on Co-doped TiO$_2$ materials? A lot of properties, including the reduction potential, electronic structure, the level of conduction band and valence band of a semiconductor, should be taken into consideration. Firstly, the relative positions of the VB maximum of the samples were investigated by comparing their VB X-ray photoelectron spectroscopy (XPS) spectra. As show in Fig. S11, the VB maximum of Co-OMT-1, Co-OMT-4, Co-OMT-6 and Co-OMT-7 are, respectively, 0.19, 1.06, 1.32 and 1.38 eV higher than that of pure TiO$_2$. Furthermore, the Fermi level and CB can be roughly estimated by flat band potential obtained from the Mott-Schottky plots (Fig. S12). On the basis of the Fermi levels, valence band of XPS, and band gaps, the potentials of VB and CB of the samples could be drawn in the Fig. 7c. The potential at the bottom of the conduction band of Co-doped TiO$_2$ is higher than that at the bottom of the conduction band of TiO$_2$. This may be due to the ionic radius of Co$^{2+}$ (65 pm) is bigger than the ionic radius of Ti$^{4+}$ (60.5 pm), which would lead to the varying octahedral ligand field in TiO$_2$. Then, a resulting stress in the distortion of lattice contributes to the lifting of Fermi energy and the energy of the bottom of the conduction band.$^{72}$ The results of Mott-Schottky plots in Fig. S12 prove the lifting of the Fermi level of TiO$_2$ after doping Co, which is consistent with the previous reports.$^{73-75}$ It is observable from Fig. 7c that the CB minimum of pure TiO$_2$ and Co-doped TiO$_2$ are negative enough to reach the reduction potential of CO$_2$ to
produce CO \( \text{(CO} + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}, -0.07 \text{ V vs. NHE at pH=0) or CH}_4\text{(CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}, 0.17 \text{ V vs. NHE at pH=0). It is worth noting that pure TiO}_2 \) and Co-doped TiO\(_2\), also can reduce H\(_2\)O to H\(_2\) \( (2\text{H}^+ + 2e^- \rightarrow \text{H}_2, 0 \text{ V vs. NHE at pH=0}), \) which compete with CO\(_2\) reduction, while the Co\(_3\)O\(_4\) is only able to reduce CO\(_2\) to CH\(_4\). However, as the doped content of cobalt (Co\(^{2+}\)) increases, it will promote the formation of oxygen vacancies, as shown in UV-vis absorption spectra (500–700 nm).\(^{76}\) As we know, electron spin resonance (ESR) measurement is a common technique to detect the spin polarized charge state of defective TiO\(_2\) nanostructures.\(^{77-79}\) In order to further prove the existence and increase of oxygen vacancies in Co-doped TiO\(_2\), we have supplemented the ESR experiments of the samples and showed the signal induced by oxygen vacancies. As shown in Figure 7d, Co\(_3\)O\(_4\) and undoped TiO\(_2\) show no signals except the signals of Mn\(^{2+}\) which are used as the reference, while the symmetrical ESR peaks with \( g=2.002 \) was observed, which can be assigned to single-electron-trapped oxygen vacancy.\(^{80,81}\) It was found that, the concentration of single-electron-trapped oxygen vacancy of Co-doped TiO\(_2\) increased with the content of doping Co. This implies that doping Co into TiO\(_2\) would promote the forming the oxygen vacancy in TiO\(_2\), agreed with the literatures.\(^{54,82}\) According to the Tanc plots (Fig. S6b), we deduced that the levels of oxygen vacancies are near around -0.05 V (vs. NHE at pH=0) for Co-OMT-6 and Co-OMT-7, which cannot reduce CO\(_2\) to CO, as shown in Fig. 7c. In these cases, some excited electrons would transfer to the levels of oxygen vacancies
from CB, which only reduce CO₂ to CH₄. Thus, it is promising to improve the selective production of CH₄ by introducing cobalt species into TiO₂.

4. Conclusion

In summary, we have developed a novel visible-light-driven photocatalyst based on the ordered mesoporous Co-doped TiO₂. The highly ordered mesoporous structure effectively improves the photocatalytic activity and stability, and the doping of Co species increases the visible-light absorption and the ability for water oxidation of TiO₂. The optimal molar ratio of Co/Ti is 0.025, which shows the best activity of 0.09 µmol g⁻¹ h⁻¹ (CH₄) and 1.94 µmol g⁻¹ h⁻¹ (CO). Furthermore, an important observation is that the selectivity of products can be controlled by adjusting the molar ratio of Co/Ti in Co-doped TiO₂. When the molar ratio of Co/Ti increases to 0.2, the generated rate of CH₄ reaches to 0.258 µmol g⁻¹ h⁻¹, due to the formation of oxygen vacancies in Co-doped TiO₂ nanocomposites. This study opens a new strategic approach to develop the visible light active photocatalysts for selectively catalyzing CO₂ reduction.

Acknowledgements

This work received financial support from the World Premier International Research Center Initiative (WPI Initiative) on Materials Nanoarchitectonics (MANA), MEXT, Japan, and National Basic Research Program of China (973 Program, 2014CB239301).

Footnote
Electronic supplementary information (ESI) available: Additional TG/DTA, SEM images, ESR, X-ray photoelectron spectroscopy, the Tauc plots, GC-MS spectra, electronic structures, Valence band XPS spectra, and Mott-Schottky plots of the samples. See DOI:

Notes and references


3 N. S. Lewis and D. G. Nocera, P. Natl. Acad. Sci. USA., 2006, 103, 15729–15735.


Fig. 1 (a) Schematic illustration of the formation process of ordered mesoporous Co-doped TiO$_2$. TEM images and elemental mapping images of (b,c,d) Co-OMT-1 and (e,f,g) Co-OMT-7. (h) STEM image of Co-OMT-7. (i) The photos of the samples.
Fig. 2 TEM images of (a) OMT, (b) Co-OMT-2, (c) Co-OMT-3, (d) Co-OMT-4, (e) Co-OMT-5, (f) Co-OMT-6 and (g,h) Co-OMT-8.
Fig. 3 (A) Small-angle XRD and (B) wide-angle XRD patterns of the samples: (a) OMT, (b) Co-OMT-1, (c) Co-OMT-2, (d) Co-OMT-3, (e) Co-OMT-4, (f) Co-OMT-5, (g) Co-OMT-6, (h) Co-OMT-7, (i) Co-OMT-8, (j) Co$_3$O$_4$. 
Fig. 4  (A) $N_2$ adsorption-desorption isotherms and (B) pore size distribution of the samples: (a) OMT, (b) Co-OMT-1, (c) Co-OMT-2, (d) Co-OMT-3, (e) Co-OMT-4, (f) Co-OMT-5, (g) Co-OMT-6, (h) Co-OMT-7, (i) Co-OMT-8, (j) $Co_3O_4$. 
Fig. 5 (a,b) UV-vis absorption spectra and (c) photocurrent response in 0.5 M Na$_2$SO$_4$ solution at 0.4 V (vs. Ag/AgCl) of the samples.
Fig. 6 (a) Schematic illustration of basic mechanism of TiO$_2$ photocatalytic process. CH$_4$ (b,d) and CO (c,e) evolution over various samples under visible light. (f) Comparison of photocatalytic activity of the samples with common photocatalysts under visible light, calculated according to the mounts evolved in 6 h.
Fig. 7 DOS of (a) anatase TiO$_2$ and (b) Co$_x$Ti$_{1-x}$O$_2$ (x=0.0625). (c) schematic illustration of the band structures of the samples. (d) ESR spectra of the samples, and Mn$^{2+}$ is used as position correction.
Table 1 Molar ratio and structural parameters of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio (Co:Ti)</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)$^a$</th>
<th>$V_{total}$ (cm$^3$ g$^{-1}$)$^b$</th>
<th>$P$ (nm)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMT</td>
<td>0</td>
<td>246</td>
<td>0.31</td>
<td>2.7</td>
</tr>
<tr>
<td>Co-OMT-1</td>
<td>0.002</td>
<td>231</td>
<td>0.29</td>
<td>2.4</td>
</tr>
<tr>
<td>Co-OMT-2</td>
<td>0.005</td>
<td>222</td>
<td>0.27</td>
<td>2.1</td>
</tr>
<tr>
<td>Co-OMT-3</td>
<td>0.01</td>
<td>214</td>
<td>0.26</td>
<td>2.1</td>
</tr>
<tr>
<td>Co-OMT-4</td>
<td>0.025</td>
<td>201</td>
<td>0.23</td>
<td>2.1</td>
</tr>
<tr>
<td>Co-OMT-5</td>
<td>0.05</td>
<td>173</td>
<td>0.23</td>
<td>2.1</td>
</tr>
<tr>
<td>Co-OMT-6</td>
<td>0.1</td>
<td>148</td>
<td>0.21</td>
<td>2.4</td>
</tr>
<tr>
<td>Co-OMT-7</td>
<td>0.15</td>
<td>154</td>
<td>0.26</td>
<td>2.4</td>
</tr>
<tr>
<td>Co-OMT-8</td>
<td>0.2</td>
<td>97</td>
<td>0.21</td>
<td>4.6</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>-</td>
<td>20</td>
<td>0.05</td>
<td>-</td>
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$^a$ $S_{BET}$ is calculated by BET equation; $^b$ $V_{total}$ (pore volume) is calculated at $p/p_0=0.950$–0.995; $^c$ Peak of pore size ($P$) is calculated by BJH method.
Table 2 Activities and selectivities of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ratio (Co: Ti)</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>Band gap (eV)</th>
<th>Products (( \mu \text{mol g}^{-1} \text{ h}^{-1} ))</th>
<th>CH(_4)</th>
<th>CO</th>
<th>CH(_4)/ (CH(_4)+CO)</th>
<th>H(_2)</th>
<th>O(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMT</td>
<td>0</td>
<td>246</td>
<td>3.20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co-OMT-1</td>
<td>0.002</td>
<td>231</td>
<td>3.08</td>
<td>0.015</td>
<td>0.23</td>
<td>6.1%</td>
<td>trace</td>
<td>trace</td>
<td>trace</td>
</tr>
<tr>
<td>Co-OMT-2</td>
<td>0.005</td>
<td>222</td>
<td>3.01</td>
<td>0.031</td>
<td>0.72</td>
<td>4.1%</td>
<td>0.052</td>
<td>0.128</td>
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<tr>
<td>Co-OMT-3</td>
<td>0.01</td>
<td>214</td>
<td>2.32</td>
<td>0.053</td>
<td>1.64</td>
<td>3.1%</td>
<td>0.54</td>
<td>0.156</td>
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<tr>
<td>Co-OMT-4</td>
<td>0.025</td>
<td>201</td>
<td>2.29</td>
<td>0.090</td>
<td>1.94</td>
<td>4.4%</td>
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<td>0.133</td>
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<tr>
<td>Co-OMT-5</td>
<td>0.05</td>
<td>173</td>
<td>2.21</td>
<td>0.046</td>
<td>0.79</td>
<td>5.5%</td>
<td>1.89</td>
<td>0.119</td>
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<tr>
<td>Co-OMT-6</td>
<td>0.1</td>
<td>154</td>
<td>2.20</td>
<td>0.140</td>
<td>0.33</td>
<td>29.8%</td>
<td>0.45</td>
<td>0.108</td>
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<tr>
<td>Co-OMT-7</td>
<td>0.15</td>
<td>148</td>
<td>2.15</td>
<td>0.180</td>
<td>0.34</td>
<td>34.6%</td>
<td>0.029</td>
<td>0.072</td>
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<tr>
<td>Co-OMT-8</td>
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<td>2.19</td>
<td>0.258</td>
<td>0</td>
<td>100%</td>
<td>0</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>-</td>
<td>20</td>
<td>1.44</td>
<td>0.060</td>
<td>0</td>
<td>100%</td>
<td>0</td>
<td>0.071</td>
<td></td>
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</table>