Understanding the Reaction Mechanism of Photocatalytic Reduction of CO₂ with H₂O on TiO₂-Based Photocatalysts: A Review

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ABSTRACT

Recently, there has been an increasing interest in the research of photocatalytic reduction of CO₂ with H₂O, an innovative way to simultaneously reduce the level of CO₂ emissions and produce renewable and sustainable fuels. Titanium dioxide (TiO₂) and modified TiO₂ composites are the most widely used photocatalysts in this application; however, the reaction mechanism of CO₂ photoreduction on TiO₂ photocatalysts is still not very clear, and the reaction intermediates and product selectivity are not well understood. This review aims to summarize the recent advances in the exploration of reaction mechanism of CO₂ photoreduction with H₂O in correlation with the TiO₂ photocatalyst characteristics. Discussions are provided in the following sections: (1) CO₂ adsorption, activation and dissociation on TiO₂ photocatalyst; (2) mechanism and approaches to enhance charge transfer from photocatalyst to reactants (i.e., CO₂ and H₂O); and (3) surface intermediates, reaction pathways, and product selectivity. In each section, the effects of material properties are discussed, including TiO₂ crystal phases (e.g., anatase, rutile, brookite, or their mixtures), surface defects (e.g., oxygen vacancy and Ti³⁺) and material modifications (e.g., incorporation of noble metal, metal oxide, and/or nonmetal species to TiO₂). Finally, perspectives on future research directions and open issues to be addressed in CO₂ photoreduction are outlined in this review paper.

Keywords: TiO₂; CO₂ photoreduction; Surface Defects; Intermediates; Reaction Mechanism.

INTRODUCTION

The emissions of greenhouse gases, particularly carbon dioxide (CO₂), could result in the global climate change and unhealthful regional air quality (Roy et al., 2010). To reduce the emissions of CO₂ and to achieve a sustainable energy future, novel materials and new technologies have been developed that convert CO₂ into useful chemical compounds and fuels (Indrakanti et al., 2009; Dhakshinamoorthy et al., 2012; Kubacka et al., 2012). Besides the methods of solar thermo-chemical conversion and electrochemical reduction of CO₂ (Dubois and Dubois, 2009; Furler et al., 2012), solar-activated photocatalytic reduction of CO₂ with water at room temperature and atmospheric pressure (namely artificial photosynthesis) is attractive due to its relatively low cost (Roy et al., 2010; Dhakshinamoorthy et al., 2012). Towards this artificial photosynthesis, various semiconductors photocatalysts (CdSe, ZrO₂, TiO₂, Ga₂O₃, and ZnO) are investigated (Wang et al., 2010; Xi et al., 2011; Ashley et al., 2012; Dhakshinamoorthy et al., 2012; Liu et al., 2012b; Fan et al., 2013). Among them, TiO₂-based materials are most extensively studied for CO₂ photoreduction because of the stability, non-toxicity, and low cost of TiO₂. During the process of CO₂ photoreduction with H₂O, photo-illumination of the catalyst surface induces the generation of electron-hole (e−–h⁺) pairs in TiO₂. The excited electrons in the conduction band (CB) of TiO₂ could migrate to the surface and reduce CO₂ to solar fuels (e.g., CO, CH₄, CH₃OH, HCOOH). Meanwhile, the holes left in the valence band (VB) of TiO₂ could oxidize H₂O into oxygen. However, when H₂O is used as the reducing agent, the overall CO₂ photoreduction efficiency is typically very low.

The primary reasons for the limited efficiency of photocatalytic reduction of CO₂ with H₂O are as follows: (1) the highly unfavorable one-electron transfer to form CO₂ that requires a very negative reduction potential of −1.9 V_NHE; (2) the strong oxidation power of the photoexcited holes (or OH radicals) that induce backward reactions, i.e., oxidizing the intermediates and products converted from CO₂; (3) the fast recombination rate of e−–h⁺ pairs in TiO₂; and (4) the limitation in the harvest of visible light due to the wide band-gap of TiO₂ (3.2 eV for anatase). In order to overcome the above limitations, several approaches have been attempted to modify TiO₂, including the incorporation...
of TiO$_2$ with noble metals (Koci et al., 2010; Li et al., 2012; Wang et al., 2012b), metal oxides (Tseng et al., 2002, 2004; Slamet et al., 2005; Li et al., 2010; Zhao et al., 2012b; Liu et al., 2013b), and nonmetals (Varghese et al., 2009; Li et al., 2012; Zhang et al., 2011; Zhang et al., 2012), the dispersion of TiO$_2$ on high surface area supports (Li et al., 2010; Srinivas et al., 2011; Wang et al., 2011b; Zhao et al., 2012b), and the control of TiO$_2$ with different morphologies and crystal phases (DeSario et al., 2011; Jiao et al., 2012a; Li et al., 2008b; Liu et al., 2012b).

Besides the efforts to enhance the efficiency of CO$_2$ photoreduction with H$_2$O, much attention has been paid to clarify the reaction mechanism behind this reaction. In addition to theoretical calculations (Markovits et al., 1996; Pan et al., 2009; He et al., 2010; Indrakanti et al., 2011; Pipornpong et al., 2011; Rodriguez et al., 2012), various microscopic (e.g., scanning tunneling microscopy (STM)) (Lee et al., 2011; Sutter et al., 2011) and spectroscopic (e.g., diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), electron paramagnetic resonance (EPR)) (Schilke et al., 2012) have been conducted to understand the steps associated with CO$_2$ adsorption, activation, and dissociation. These steps are found to be significantly affected by crystal phases (e.g., rutile, anatase, surface acidic-basic sites (e.g., hydroxyl group), defect disorders (e.g., oxygen vacancy (V$_{O}$)), co-adsorbates (e.g., H$_2$O), and electronic structure (e.g., charge transport) of TiO$_2$.

Several reviews have described the strategies and challenges in the design of TiO$_2$-containing photocatalysts for CO$_2$ photoreduction (Indrakanti et al., 2009; Roy et al., 2010; Dhakshinamoorthy et al., 2012; Mori et al., 2012). For example, Dhakshinamoorthy et al. (2012) summarized the photocatalytic performance of TiO$_2$-based photocatalysts in correlation with the catalyst structure/properties. Indrakanti et al. (2009) analyzed photoinduced activation of CO$_2$ from surface state and surface sites on metal-doped TiO$_2$, dye-sensitized TiO$_2$, defective TiO$_2$, and isolated-Ti in porous materials. Unfortunately, the charge transfer mechanisms in TiO$_2$-based materials are seldom addressed in those literature reviews. In the recent few years, some novel oxygen-deficient TiO$_{2-x}$ materials and bicrystalline TiO$_2$ with controllable phase content have been applied for CO$_2$ photoreduction. Moreover, microscopic (e.g., STM) and spectroscopic techniques (e.g., DRIFTS, EPR) have been performed to explore the activation and dissociation mechanism of CO$_2$, to identify the reaction intermediates, and to probe the reaction pathways. Those new findings in the recent studies are not included in the past review papers. Hence, this review aims to summarize the recent research progress on mechanistic studies in CO$_2$ photoreduction in correlation with the material properties of TiO$_2$-based catalysts. There are three main sections in this review. The first section briefly describes CO$_2$ adsorption, activation and dissociation steps. The second section discusses the charge separation and transfer from TiO$_2$ to CO$_2$ and H$_2$O. The third section focuses on the surface intermediates and reaction pathways of CO$_2$ reduction. In each of the three sections, the reaction mechanism is discussed in the context of three factors including the crystal phase, defect disorders, and specific material modification of TiO$_2$. At the end of this review, we have summarized the research progresses and challenges and made recommendations for future research in the field of CO$_2$ photoreduction.

**CO$_2$ PHOTOREDUCTION ON TiO$_2$-BASED MATERIALS: ACTIVATION AND DISSOCIATION**

The photoreduction of CO$_2$ is a multistep process involving the adsorption, activation of CO$_2$ and dissociation of C–O bond. The adsorption of CO$_2$ is the initial step during the photocatalytic reaction, but the importance of this step is often neglected in the literature. Another key step is the activation of CO$_2$ through the transfer of photogenerated electrons from photocatalyst surface to CO$_2$. At the gas-solid interface, the feasibility of electron transfer from TiO$_2$ to CO$_2$ depends on the electron affinity of gaseous CO$_2$ and the interaction of CO$_2$ with TiO$_2$ surface (Indrakanti et al., 2009). When CO$_2$ interacts with TiO$_2$ surface sites (e.g., Ti$^{3+}$) and gains electrons from TiO$_2$, CO$_2^{−}$ species could be formed. The linear structure of CO$_2$ is then transformed to a bent form, where the C–O bond is likely broken (Rasko and Solyomosi, 1994). Generally, the mechanism in the activation and subsequent reduction of CO$_2$ involves the participation of protons and electron transfer (one, two, or multiple electron process). Among them, CO$_2$ produced by one electron transfer to CO$_2$ is an important intermediate. In this section, one-electron induced activation and dissociation of CO$_2$ mechanism is discussed.

Theoretical and experimental studies consistently showed that the CO$_2$ adsorption, activation, and dissociation processes were significantly influenced by the crystal phase of TiO$_2$ and the defect disorders in TiO$_2$ (Pan et al., 2009; He et al., 2010; Liu et al., 2012b; Rodriguez et al., 2012). Adsorption of CO$_2$ on the perfect and oxygen-deficient rutile (110), anatase (101) and brookite (210) surfaces has been investigated using dispersion-corrected density functional theory (DFT) and first-principles calculations (Markovits et al., 1996; Schobert et al., 2008; He et al., 2010; Rodriguez et al., 2012). Compared with the defect-free surface, the presence of V$_O$ on the rutile (110), anatase (101) or brookite (210) surface induced the formation of new adsorption configurations, where CO$_2$ was bonded at the defect sites (He et al., 2010; Indrakanti et al., 2011; Pipornpong et al., 2011; Sutter et al., 2011; Rodriguez et al., 2012). Although the interactions of CO$_2$ with the brookite (210) surface and anatase (101) surface have similar energy, the defect-free brookite surface had negligible charge transfer to the CO$_2$ molecule. Once defect disorders such as V$_O$ were created on the surface, the binding of CO$_2$ with brookite and anatase was favorable (Rodriguez et al., 2012). Electrons stored in the V$_O$ could be spontaneously transferred to CO$_2$. Once the CO$_2^{−}$ radical was formed, it may decompose into CO through the occupation of one oxygen atom into the V$_O$ site. The overall reaction is written as follows: CO$_2$ + [TiO$_2$ + V$_O$] → CO + [TiO$_2$] (Pipornpong et al., 2011).
addition, the surface V₀ on anatase (101) and rutile (110) favors H₂O and O₂ adsorption and dissociation (Aschauer et al., 2010). Notably, H₂O, O₂ and CO₂ molecules may compete for the same V₀ sites. Since the binding energies of H₂O and O₂ molecules are 0.64 and 2.78 eV higher than that of CO₂ on the vacancy site (He et al., 2010), the adsorption of CO₂ can be hindered by H₂O and O₂.

The above theoretical studies indicated that the electrons originated from the defective TiO₂ itself induced the formation of CO₂⁻ and the subsequent dissociation of CO₂⁻ to CO in the dark. This electron-induced dissociation of CO₂ was experimentally confirmed by STM study (Lee et al., 2011), and the mechanism is shown in Fig. 1. The dissociation probability (P_diss) of CO₂ depended on the energy of the injected electrons from the STM tip. As shown in Fig. 1(A), the value of P_diss increased with increasing bias voltage, eventually reaching 1 at +2.2 V. In the dissociation process of CO₂, a metastable CO₂⁻ was formed through an electron attachment. This temporary CO₂⁻ can be formed only if the bias voltage is higher than \( V_{thres} = 1.7 \) eV, as shown in Fig. 1(B). Fig. 1(C) shows the scheme of CO₂ dissociation process. After a tunneling electron from the STM tip was successfully attached to CO₂, a negative CO₂⁻ was formed. Upon dissociation of the C–O bond, the fragment O atom of CO₂⁻ healed the V₀ sites on the rutile (110) surface. Subsequently, the CO fragment desorbed from the surface or moved away from the reaction site.

In situ DRIFTS studies also confirmed that CO₂ could be spontaneously dissociated into CO on reduced Rh/TiO₂-x (Rasko and Solymosi, 1994) or defective Cu(I)/TiO₂-x (P25) (Liu et al., 2012a) even in the dark. Fig. 2(a) shows the in situ DRIFTS spectra of CO₂ interaction with Cu(I)/TiO₂-x at 25°C in the dark. The exposure of the defective surface to CO₂ rapidly led to the generation of CO₂⁻ species (1673 and 1248 cm⁻¹) bonded with Ti⁴⁺. The formation of Ti⁴⁺–CO₂⁻ suggested that CO₂ can be activated in a way that excess electrons, being trapped at Ti⁷⁺/V₀ sites, migrate to adsorbed CO₂ spontaneously through a dissociative electron attachment process. Further prolong the time to 10 min resulted in the gradual decrease of CO₂⁻ intensity. In the meantime, a small peak at 2110 cm⁻¹ assigned to CO coordinated with Cu⁺ evolved, suggesting the formation of CO from the metastable CO₂⁻.

To confirm this dissociation of CO₂ to CO on the defective Cu(I)/TiO₂-x surface, an isotopic carbon-labeling experiment was conducted under the same condition. Fig. 2(b) shows the in situ DRIFTS spectra of \( ^{13} \)CO₂ interaction with Cu(I)/TiO₂-x, which follows a similar trend to that of \( ^{12} \)CO₂ in Fig. 2(a). \( ^{13} \)CO₂⁻ species (1217 cm⁻¹) were quickly formed and then gradually decreased after reaching its maximum at 10 min. A corresponding Cu⁺–\( ^{13} \)CO peak at 2064 cm⁻¹ appeared and reached it maximum at 10 min. The result of labeled carbon confirms that the produced CO bound to Cu⁺ site is indeed derived from CO₂ and that CO₂ is indeed activated and dissociated on defective Cu(I)/TiO₂-x, even in the dark at room temperature.

The spontaneous dissociation of CO₂ on Rh/TiO₂-x and Cu(I)/TiO₂-x in the dark is to a large extent associated with the surface V₀ that provide not only an electronic charge (Ti⁷⁺) but also the sites for the adsorption of oxygen atoms from CO₂. The formation of Cu⁺–CO or Rh–CO could be an additional driving force to promote the dissociation of CO₂. Furthermore, photoillumination could promote the dissociation of CO₂. Fig. 2(c) shows the in situ DRIFTS spectra acquired by sequentially exposing Cu(I)/TiO₂-x to CO₂ in the dark for 30 min and under photoillumination for another 30 min. After 30 min in the dark, CO₂ at 1248 cm⁻¹ and Cu⁺–CO at 2110 cm⁻¹ were not observed, although they

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Fig. 1. (A) Dissociation probability (P_diss) as a function of bias voltage; (B) The electron transfer process at the STM tip/CO₂/TiO₂ interface (above \( V_{thres} = 1.7 \) eV, the electrons start to tunnel into the negative-ion state of the adsorbed CO₂); (C) Schematics of an electron induced CO₂ dissociation process. Reproduced with permission from Ref. (Lee et al., 2011).
did appear upon the exposure to CO₂ at the beginning (See Fig. 2(a)). Subsequent photoillumination induced the presence of CO₂ and Cu⁺–CO species. The results obtained by IR study in Fig. 2(c) suggest that photoillumination significantly promotes the activation and dissociation of CO₂.

Two possible reasons could explain the enhanced CO₂ activation and dissociation by photoillumination. First, photoillumination induced a sustained electron transfer from the catalyst to the π orbital of adsorbed CO₂. This process makes CO₂ more anionic, and thus induced the cleavage of the C–O bond (Rasko and Solymosi, 1994). Second, photoillumination could induce the regeneration of surface VO₂. As illustrated in Fig. 1(c), the surface VO₂ is filled during the CO₂ dissociation process, which suggests the dissociation of CO₂ in the dark is likely stoichiometric rather than catalytic. However, photoillumination is capable of creating surface VO₂ in a way that surface oxygen atoms are oxidized to O₂ by photogenerated holes causing the formation of surface VO₂ (Wu and Huang, 2010). Similarly, partial regeneration of surface VO₂ on the Cu(I)/TiO₂-x catalyst may have occurred that accelerates the dissociation of CO₂ under the photoillumination (Liu et al., 2012a).
CO2 PHOTOREDUCTION ON TiO2-BASED MATERIALS: CHARGE TRANSFER MECHANISM

For photocatalytic reduction of CO2 with H2O, an important step is the generation of e–h+ pairs upon absorption of photons energy greater than or equal to the band gap of the photocatalyst (Dhakshinamoorthy et al., 2012). However, the recombination rate of e–h+ pairs is nearly two or three orders of magnitude faster than the rate of charge separation/transport (Fan et al., 2013). This is a main limiting factor for the low efficiency of CO2 conversion. Hence, any strategy that can inhibit the recombination of e–h+ or facilitate the charge separation and migration from the catalyst surface to reactants will enhance the efficiency of CO2 photoreduction. For TiO2-based photocatalysts, the charge separation and transfer process is closely related to TiO2 crystal phase, defect disorder in TiO2, and material modifications to TiO2.

Effect of Crystal Phase

TiO2 commonly occurs in three crystalline polymorphs: rutile, anatase, and brookite. TiO2 anatase, rutile or anatase-rutile mixed phase (e.g., Degussa P25 with a composition of 75% anatase and 25% rutile) has been frequently studied in photocatalytic reduction of CO2, using either bare TiO2 or with incorporation of metal, nonmetal or metal oxide species (Anpo et al., 1995; Tseng et al., 2004; Koci et al., 2009; Zhang et al., 2011; Wang et al., 2012a; Wang et al., 2012b). By contrast, the brookite phase or anatase-brookite mixed phase is much less studied as a photocatalyst for CO2 photoreduction, probably due to the previous difficulty in synthesizing high quality brookite nanocrystallites. The studies on pure phase TiO2 show that anatase phase is more photocatalytically active than rutile, possibly attributed to the combined effect of lower recombination rate of electron-hole pairs and higher surface adsorptive capacity (Hurum et al., 2003; Li and Gray, 2007; He et al., 2012). Recently, the much less studied brookite phase was found to have a catalytic activity similar to anatase but higher than rutile for CO2 photoreduction with H2O (Liu et al., 2012b).

Among the studies on the mixed-phase TiO2, anatase-rich anatase/rutile more active than pure anatase or pure rutile for CO2 photoreduction (Li et al., 2008b; Wang et al., 2012a). The enhanced activity of anatase/rutile mixture compared with single phase anatase or rutile was primarily attributed to the effective charge separation and transfer occurring between anatase and rutile. However, the findings in the charge transfer mechanism are not conclusive. Fig. 3 shows the two typical models of charge transfer between anatase and rutile. Some literature results (Bickley et al., 1991; Kawahara et al., 2002; Wang, Bai et al., 2012) suggested that photogenerated electrons tend to transfer from anatase to rutile, because the conduction band (CB) of anatase is more negative than that of rutile (Fig. 3(A)). The rutile phase acts as a passive electron sink hindering charge recombination in anatase. On the contrary, Gray and co-workers used EPR spectroscopy to monitor the direction of electron migration; they proposed a mechanism that electrons migrate from the higher-level rutile CB to the lower-level anatase lattice (Fig. 3(B)). In this case, the rutile phase serves as an antenna to extend the photoactivity into visible light range (Hurum et al., 2003; Li and Gray, 2007).

Besides anatase/rutile mixtures, TiO2 anatase/brookite mixtures have been applied for the photodegradation of organic compounds (e.g., methyl orange, rhodamine B) (Chiarello et al., 2011; Boppella et al., 2012; Gai et al., 2012; Jiao et al., 2012b; Zhao et al., 2012a), which exhibited higher activity than P25 and pure-phase anatase. Recently, bicrystalline TiO2 with controllable anatase/brookite phase content has been used as a photocatalyst for CO2 photoreduction with H2O (Zhao et al., 2013). The activity results showed that bicrystalline anatase-brookite was generally more active than single phase anatase and brookite. Analogous to the anatase/rutile mixture, the enhanced performance of anatase/brookite was primarily attributed to the interfacial electron transfer from brookite to anatase. Among the bicrystalline anatase-brookite mixtures, the anatase-rich mixture with a composition of 75% anatase and 25% brookite showed the highest activity, and was far more active than the anatase-rutile mixture with similar anatase fraction (i.e., P25). This may be due to the following reasons: (1) brookite itself is more active than rutile as a photocatalyst (Liu et al., 2012b), (2) brookite has a higher conduction band (CB) edge than rutile, which will promote the reaction of CO2 reduction with H2O that has a high reduction potential (Anpo et al., 1995), and (3) the excited electrons on brookite CB may transfer to anatase CB due to a slightly higher CB edge of brookite than anatase.

Effect of Defect Disorders

TiO2 is a nonstoichiometric compound, which contains defect disorders in terms of oxygen vacancies (V_O) and titanium interstitials (Nowotny et al., 2008). These defects...
can be created by photo-excitation in the presence of a hole scavenger (Panayotov et al., 2012), thermal removal of lattice oxygen with a reducing gas (Chen et al., 2011; Liu et al., 2013a), doping anions such as N and C (Gai et al., 2012; Hoang et al., 2012; Li et al., 2012), thermal treatment in vacuum (Xiong et al., 2012), or plasma treating (DeSario et al., 2011). The defects have been reported to play an essential role in photocatalytic degradation of organics and water splitting by TiO2 (Chen et al., 2011; Hoang et al., 2012; Xing et al., 2013). Three reasons can explain the importance of defects in TiO2. First, the creation of defects could introduce intermediate surface states that narrow the band gap and hence extending the photoresponse of TiO2 to visible light range (Chen et al., 2011). Second, the donor state located below the TiO2 CB promotes the charge separation and transfer (Nowotny et al., 2006). Third, Ti3+ and VO are considered to be important active sites for the adsorption and activation of reactants (Sutter et al., 2011). Fig. 4(a) shows the charge transfer mechanism in oxygen-deficient TiO2. Electrons could be excited from the VB to the defects donor state (red dashed line) under visible light illumination. The lifetime of electrons in the defects donor state is much longer than that on the CB (Lin et al., 2005; Xing et al., 2013), which facilitates the formation of superoxide radicals by attachment of electrons to oxygen. Meantime, the holes left in the VB accelerate the generation of free OH radicals. The superoxide and OH radicals are responsible for the enhanced activity of TiO2-x for the photodegradation of organic compounds (Xing et al., 2013).

Although oxygen-deficient TiO2-x is a promising candidate as a photocatalyst, only limited work has been done for CO2 photoreduction over TiO2-x. DeDario et al. (2011) fabricated defective anatase/rutile thin film by direct current magnetron sputtering and applied it as a photocatalyst for CO2 photoreduction. They demonstrated that the photocatalytic activity was influenced by the levels of oxygen deficiency in the films, which were controlled by adjusting the oxygen partial pressure during the film deposition process. They also suggested that VO likely had two competing roles: (1) VO could enhance visible light harvesting and act as active/adsorption sites, and (2) VO may serve as or induce the creation of active interfacial sites at certain concentrations. Beyond that level these sites may function as recombination centers to hinder the photoactivity.

The photoactivity of defective TiO2 was also influenced by its crystal phase (Liu et al., 2012b). The CO and CH4 production from CO2 photoreduction was in the order of brookite, anatase and rutile. Possible reasons for this superior activity of defective brookite include the facilitated formation of VOx, faster reaction rate of CO2 with adsorbed H2O or surface OH groups, and an additional reaction route involving an HCOOH intermediate (Pan et al., 2009; Liu et al., 2012b). It is noted that VOx generated from thermal treatment with inert gas under the atmospheric pressure, was not stable in an air environment and was consumed during the photoreaction process (Liu et al., 2012a, b). Further studies are necessary to develop more stable and more efficient TiO2-x for solar fuels production, and to better understand the specific roles of defects (i.e., VOx, Ti interstitial) and the dynamics of charges separation and transfer.

Fig. 4. Schematic illustration of charge transfer mechanism in (a) defective TiO2-x, (b) N-doped TiO2, (c) noble metals or metal oxides-modified TiO2, and (d) graphene coupled-TiO2. Adapted from (Liang et al., 2011; Li et al., 2012; Wang et al., 2012b; Xing et al., 2013).
Effect of Materials Modification

The discussions in sections 3.1 and 3.2 suggest that charge transfer in TiO$_2$ can be promoted by tailoring its phase content and engineering defect disorders on the surface. In this section, we discuss another three main strategies to enhance charge transfer by modifying TiO$_2$ with some other elements or species. First, doping TiO$_2$ with nonmetal elements (e.g., N and I) could narrow the band gap of TiO$_2$ and/or create impurity energy levels above the VB (Zhang et al., 2011; Li et al., 2012). The excited electrons by visible light are transferred from the impurity state to TiO$_2$ CB. Second, electron transfer could be promoted in the direction from TiO$_2$ CB to external trappers or carriers. The electron trappers can be noble metals (e.g., Pt, Pd, Au, Ag) (Sasirekha et al., 2006; Iizuka et al., 2011; Yui et al., 2011; An et al., 2012; Uner and Oymak, 2012; Wang et al., 2012b) or metal oxides (e.g., CuO, FeO$_2$, CeO$_2$) (Tseng et al., 2004; Qin et al., 2011; Srinivas et al., 2011; Wang et al., 2011b; Truong et al., 2012; Zhao et al., 2012b), and the electron carriers are often carbon materials (e.g., graphene) (Li et al., 2011, 2012; Tu et al., 2012). Third, the incorporation of TiO$_2$ with another semiconductor, i.e., photo-sensitizer (e.g., AgBr, CdSe, PbS) (Wang et al., 2010; Asi et al., 2011; Wang et al., 2011a; An et al., 2012) or n-type semiconductor (e.g., ZnO) (Xi et al., 2011), promotes electron transfer between the CB of the second semiconductor and the CB of TiO$_2$.

Electron Transfer from the Impurity State to TiO$_2$ CB

The photocatalytic efficiency of TiO$_2$ for CO$_2$ photoreduction under visible light is very low due to its large band gap of 3.0–3.2 eV. It was found that doping of TiO$_2$ with nonmetal elements improved the visible light activity, depending on the type and the concentration of nonmetal dopants. Among the various nonmetal dopants, N-doped TiO$_2$ is widely used in photooxidation of organics (Lin et al., 2005; Chen and Burda, 2008; Gai et al., 2012) and in CO$_2$ photoreduction as well (Varghese et al., 2001; Fan et al., 2011; Zhang et al., 2011; Li et al., 2012; Peng et al., 2012; Zhang et al., 2012). However, the origin of the visible light activity of N-doped TiO$_2$ has long been debated. One general mechanism is shown in Fig. 4(b). Doped N gives rise to an impurity state above the TiO$_2$ VB. The mixing of N 2p orbital and the TiO$_2$ VB narrows the band gap of TiO$_2$ and extends the photoresponse of TiO$_2$ to the visible light region (Lin et al., 2005; Chen and Burda, 2008; Li et al., 2012). Visible light irradiation will induce the electron transfer from the nonmetal impurity state to the CB, while the photogenerated holes left in the impurity state may oxidize H$_2$O to O$_2$ or OH groups to OH$^-$ radicals. This impurity state is regarded as the highest occupied N 2p orbital. XPS analysis by Li et al. (2012) indicated that the oxidation state of doped N is molecularly chemisorbed N$_2$ or NO/NO$_2$ species. Similarly, Asahi et al. (2001) attributed the visible light sensitivity of N-doped TiO$_2$ to the substitutional N atoms. By contrast, Noda et al. (1986) concluded that the visible light activity of N-doped TiO$_2$ was due to V$_0$, rather than the N impurity state. The electron transfer thus follows the mechanism illustrated in Fig. 4(a) rather than in Fig. 4(b). Other studies made similar conclusions that visible light activity of N-doped TiO$_2$ was ascribed to V$_0$, which induced donor states located below the CB, while substitutional N acted as an inhibitor for $e^-\rightarrow h^+$ recombination (Justicia et al., 2002; Ihara et al., 2004). This controversy makes it necessary to decouple the contributions of V$_0$ and N-doping in TiO$_2$ in future studies.

Recently, a new type of visible light responsive catalyst, iodine-doped TiO$_2$ (I-TiO$_2$), has been explored for CO$_2$ photoreduction, and the electron transfer mechanism in I-TiO$_2$ is similar to that of N-TiO$_2$ illustrated in Fig. 4(b) (Zhang et al., 2011, 2012). The iodine doping resulted in a reduced crystal size of TiO$_2$ and a red-shift of the TiO$_2$ absorption edge to the visible region. Moreover, titanium ions (i.e., Ti$^{IV}$) were partially substituted by iodine ions (i.e., I$^-$) and consequently, Ti$^{IV}$ was generated for charge balance. The Ti$^{IV}$ sites may trap photoinduced electrons and inhibit charge recombination, which is an advantage of the iodine dopant over other nonmetal dopants. I-TiO$_2$ demonstrated significant enhancement in CO$_2$ photoreduction to CO compared with undoped TiO$_2$ under both visible light and UV-vis irradiation. The concentration of the iodine dopant could affect the visible light and UV-vis light activities of I-TiO$_2$. For iodine doping higher than 10 wt%, the activity of I-TiO$_2$ under UV-vis irradiation was not superior to that seen under visible light. The formation of recombination centers at high doping levels could account for this phenomenon.

Electron Transfer from TiO$_2$ CB to Trapping Sites

Fig. 4(c) shows the electron transfer mechanism on the noble metals or metal oxides modified TiO$_2$. Photogenerated electrons on TiO$_2$ can be easily trapped by the noble metal nanoparticles, because the Fermi energy levels of noble metals are typically lower than that of TiO$_2$. Such separation process leads to the formation of Schottky barrier at the interface of metal-semiconductor, which can retard the recombination of $e^-\rightarrow h^+$ pairs. The noble metal particles also sever as co-catalysts by providing active sites for the activation and dissociation of H$_2$O and CO$_2$. The two functions of noble metals can enhance the activity of TiO$_2$ towards CO$_2$ photoreduction. The promotional effects of noble metals on the separation and transport of carriers depend on the type, state of dispersion, particle size, and valence state of noble metals. Li et al. (2012) found that Pt-modified TiO$_2$ showed a higher activity than Au and Ag-coupled TiO$_2$, likely due to the higher work function of Pt (5.65 eV) than Au (5.1 eV) and Ag (4.26 eV). Wang et al. (2012) demonstrated that either too small or too large Pt particles exhibited lower production rate of CH$_4$. It was proposed that the energy for band separation of the smaller Pt particles was higher due to the quantum confinement, thus preventing electron transfer from TiO$_2$ CB to Pt. Yui et al. (2011) suggested that the addition of Pd to TO$_2$ induced the reduction of CO$_2$ to CH$_4$, while the oxidation of Pd to PdO caused the catalyst deactivation. The above studies indicate the importance of choosing an appropriate noble metal, tailoring the particle size in an appropriate range, and avoiding the oxidation of noble metal to metal oxide.

For transition metal oxides modified TiO$_2$ composites
(Fig. 4(c)), the most popular photocatalyst is probably CuOx/TiO2, where CuOx indicates copper oxides that are either Cu2O or CuO. Take CuO/TiO2 as an example, light irradiation induces the photoexcited electrons transfer from TiO2 to the dispersed CuO. The electrons trapped by CuO are consumed by reducing CO2 into CH4 and CO; meanwhile, the holes oxidize H2O into O2. To evidence the direct electron transfer between Cu2+ and TiO2, X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS) were employed to identify the chemical state and environment of Cu2+ before and after irradiation (Irie et al., 2009). The results demonstrated that for Cu2+-grafted TiO2, Cu2+ was incorporated in a distorted amorphous CuO-like structure, which could form clusters and attach to TiO2 surface. Photoinduced electrons were directly transferred from TiO2 to Cu2+ that led to the formation of Cu+, while the produced Cu2+ could be oxidized back to Cu2+ by O2. The enhanced charge separation by CuOx is greatly influenced by its concentration, dispersion, and valence state. The addition of too high a concentration of CuOx beyond the optimum value would lead to decreased photocatalytic efficiency. It is possibly because of (1) the shading effect of CuOx that reduces the light absorption of TiO2 and (2) CuOx acting as charge recombination centers at high concentrations (Li et al., 2008a; Irie et al., 2009).

The effect of Cu valence in CuOx is still controversial. Highly dispersed surface Cu+ species is reported to be more active than Cu2+ and Cu0, probably because Cu+ has the highest positive reduction potential value (Cu+/Cu0 = 0.52 V). However, Slamet et al. (2005) suggested that Cu2+ was more active than Cu+ and Cu0 obtained by H2 reduction. They argued that due to the strong interaction between TiO2 and Cu+ implanted in the vacant sites of TiO2, the trapped electrons by Cu+ are difficult to be transformed to the adsorbed species on the catalyst surface. As a result, Cu+ may play a negative role as an electron-hole recombination center. Qin et al. (2011) demonstrated that it was the heterojunctions between CuO and TiO2 that contributed to the promotion of the photoactivity. Only one study in the literature (Hirano et al., 1992) indicated that metallic Cu deposited on TiO2 enhanced the photoefficiency of CO2 reduction, where Cu metal played the roles as an effective co-catalyst for the reduction of CO2 and as a reducing species to react with the positive holes simultaneously. On the contrary, Tseng et al. (2004) pointed out that the presence of Cu0 on Cu/TiO2 obtained by H2 reduction decreased the production of methanol product from CO2.

The above controversies in the literature on the effect of Cu valence partially resulted from the uncertainties in the identification of Cu valence because of the typically very small concentration of Cu, the amorphous nature of dispersed Cu, and potential Cu valence change during material handling and characterization. Heat treatment in a reducing atmosphere (e.g., H2) is usually applied to tailor the Cu valence from as-prepared Cu/TiO2 samples. However, the Cu valence on a H2-reduced Cu/TiO2 samples may have changed when exposed to air environment before XPS analysis or before activity measurement, thus making it difficult and inaccurate to explore which Cu species are most active. Hence, it is very important to use in situ analytical instrumentation and experimental approaches to accurately identify the Cu valence and measure its activity in CO2 photoreduction. Noticeably, when preparing Cu/TiO2 in a reducing atmosphere to form Cu+ or Cu0 species, defects such as V0 and Ti3+ on TiO2 were most likely created concurrently due to the oxygen loss (Chen et al., 2011; Xiong et al., 2012; Liu et al., 2013a). However, the effect of these defects or the potential synergies between Cu and the defects were often neglected.

In a recent study, Liu et al. (2013) engineered Cu/TiO2 composites with different Cu valences plus V0/Ti3+ sites by heat treatment in H2 or He, applied in situ XPS and DRIFTS to characterize the Cu valence, and measured their photocatalytic activities immediately after in situ thermal pretreatment. The results demonstrated that the unpretreated, He-pretreated, and H2-pretreated Cu/TiO2 surfaces were dominated by Cu+, Cu0, and Cu/Cu0, respectively. The mixture of Cu+/Cu0 induced by H2-reduction was more active in charge separation than Cu+ species alone induced by He-pretreatment. This work also indicated the existence of the synergy between Cu species (particularly Cu+/Cu0 mixture) and surface oxygen vacancies on TiO2, which facilitate the separation of electron-hole pairs and promote electron transfer to adsorbed CO2.

Carbon materials such as two-dimensional graphene sheets have been used to couple with TiO2 due to the graphene’s unique carrier mobility, high flexible structure, and large surface area. As shown in Fig. 4(d), the deposition of TiO2 on graphene sheets promotes the electron transfer from TiO2 to graphene, and extends the light absorption to the visible range. The visible light response of TiO2/graphene is attributed to the chemical bonding between TiO2 and the specific sites of carbon that leads to the narrowing of TiO2 band gap (Zhang et al., 2010). To date, only a few studies have been conducted on TiO2/graphene for CO2 photoreduction (Liang et al., 2011; Liang et al., 2012; Tu et al., 2012). The defects in graphene and the contact between graphene and TiO2 will significantly affect the charge transfer and determine the activity and selectivity of CO2 conversion. Since the defects in graphene serve as the recombination centers of charge carriers, minimizing the defects in graphene decreased the charge recombination rate (Liang et al., 2011). Moreover, increasing the contact between graphene and TiO2 favors fast electron transfer from TiO2 to graphene. The electrons on graphene diffused very quickly due to its larger surface area, which restrained the accumulation of electrons and decreased the local electron density. Consequently, the process of two-electron reduction of CO2 to CO was facilitated as compared with the process of eight-electron reduction of CO2 to CH4 (Tu et al., 2012).

Electron Transfer from Photosensitizer CB to TiO2 CB

Another approach to enhance visible light activity is to couple TiO2 with quantum dots (QDs) photosensitizers (e.g., CdSe, PbS, AgBr) that have a narrow band gap and absorb visible light (Wang et al., 2010; Asi et al., 2011; Wang et al., 2011a). Generally, these QDs sensitzers have

Liu and Li, Aerosol and Air Quality Research, 14: 453–469, 2014
a higher conduction band edge than TiO$_2$. A larger difference between the CBs of QDs and TiO$_2$ will cause a higher driving force of electron injection from QDs CB to TiO$_2$ CB. This electron transfer process facilitates the e$^-$–h$^+$ separation and improves the visible light activity. If coupling electron trappers (e.g., Pt, Cu) with QDs/TiO$_2$, the electron transport can be further enhanced in the direction from QDs to TiO$_2$ and to Pt or Cu. The generation and transfer of charge carriers are closely associated with the dispersion and particles size of the QDs sensitizers. Wang et al. (2011) applied PbS QDs to sensitize Cu/TiO$_2$ for CO$_2$ photoreduction, and proposed a charge transfer mechanism in PbS/Cu/TiO$_2$, as shown in Fig. 5(a). Although the CB edge of bulk PbS was slightly lower than that of TiO$_2$, the CB edge of the smaller PbS particles shifted to a higher energy level due to the quantum confinement, enabling the injection of electrons from 3 or 4 nm PbS to TiO$_2$. As a result, PbS-(Cu/TiO$_2$) catalysts showed three times higher activity than Cu/TiO$_2$ under white-light irradiation.

**Electron Transfer between Heterojunctions**

A heterojunction, like a diode, is created when two different layers of crystalline semiconductors are placed in conjunction or layered together with alternating or dissimilar band gaps. Both semiconductors in the heterojunctions are photoexcited to generate e$^-$–h$^+$ pairs. The energy bias between the two sides will result in the electrons and holes transfer between them. The electrons could transport from the semiconductor with a higher CB to the one with a lower CB. Meanwhile, the holes could transport from the semiconductor with a lower VB to the one with a higher VB. In this respect, the separation and transfer of charge carriers are enhanced, leading to a higher photocatalytic efficiency. Xi et al. (2011) developed a nanoporous “French-fires”-shaped TiO$_2$-ZnO composite, which demonstrated a six times higher activity than P25 for CO$_2$ photoreduction. Fig. 5(b) shows the charge transfer mechanism in the TiO$_2$-ZnO heterojunction for CO$_2$ photoreduction. The photogenerated electrons migrated from ZnO CB to TiO$_2$ CB, since the CB of ZnO (−0.31 V) was higher than that of TiO$_2$ (−0.29 V). In the meantime, the holes migrated from TiO$_2$ VB (2.91 V vs. NHE) to ZnO VB (2.89 V vs. NHE). This literature result demonstrated the significant role of heterjunctions in enhancing photocatalytic performance of TiO$_2$ by accelerating the charge separation.

Besides ZnO-coupled TiO$_2$, other semiconductors such as CuO, Cu$_2$O, and FeTiO$_3$ have been paired with TiO$_2$ for CO$_2$ photoreduction (Mor et al., 2008; Roy et al., 2010; Qin et al., 2011; In et al., 2012; Truong et al., 2012). These semiconductors have a narrow band-gap ($E_g = 1.8–2.5$ eV) and relatively high absorption coefficient in the visible region. Consequently, the heterojunctions formed between these semiconductors and TiO$_2$ may enhance the separation of charge carriers and the response of visible light simultaneously. It should be noted that in section 3.3.2, we have discussed that CuO and Cu$_2$O, incorporated on TiO$_2$, can act as electron trapping sites to enhance electron transfer from TiO$_2$ to CuO$_x$. A key factor that determines the function of CuO$_x$ in a CuO$_x$-TiO$_2$ composite catalyst system is the concentration and crystal structure of CuO$_x$. When the

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**Fig. 5.** (a) Band alignment between TiO$_2$ and PbS QDs with different particles size, and the schematic diagram of the photocatalytic process for CO$_2$ photoreduction under visible light irradiation. Adapted from (Wang et al., 2011a). (b) Schematic illustration of the band structure and charge separation in the hybrid TiO$_2$/ZnO composites. Adapted from (Xi et al., 2011).
concentration of CuOx is small (e.g., 0.1 to 2%), CuOx is typically amorphous and highly dispersed on the surface of TiO2. In this case, the dispersed Cu2+ or Cu+ species trap electrons from TiO2, undergoing redox processes of Cu2+/Cu+ or Cu+/Cu0 (Slamet et al., 2005). When the concentration of CuOx is very high (close or more than the TiO2), CuOx usually exists as crystalline particles and behaves as a semiconductor. In this case, when CuOx is coupled with TiO2, the heterojunction effect occurs. Because the TiO2 CB edge and CuO VB edge are close to each other, photoexcited electrons in the TiO2 CB could recombine with holes produced in the CuO VB, while higher energy electrons left in the CuO CB reduce CO2 to hydrocarbons and the holes left in the TiO2 VB oxide H2O to O2 (Roy et al., 2010; Qin et al., 2011; Fan et al., 2013). This charge transfer mechanism at the CuOx/TiO2 heterojunction is different from that at the ZnO/TiO2 heterojunction previous described.

CO2 PHOTOREDUCTION ON TiO2-BASED MATERIALS: REACTION PATHWAYS

For the photocatalytic reduction of CO2 with H2O over TiO2-based materials, the reaction pathways generally includes the following steps, i.e., the adsorption of reactants on the catalyst, activation of the adsorbed reactants by the photogenerated charge carriers, formation of surface intermediates, conversion of intermediates to products, desorption of products from catalyst surface, and regeneration of the catalyst. Each of these steps determines the dynamics of the reaction process and affects the final products from CO2 conversion. In addition, organic Ti-precursors (e.g., titanium isopropoxide), organic solvents (e.g., ethanol), and chloride-containing chemicals (e.g., CuCl2 and H2PtCl6) are often used to prepare the photocatalysts. Even after calcination, a certain amount of organic residues (e.g., carbon or hydrocarbons) or inorganic ions (e.g., Cl–) may still be present on the catalyst surface. These surface contaminants could react with CO2 and H2O under photo-irradiation, interfering with the photoinduced reactions and influencing product selectivity. The steps of adsorption/activation of CO2 and charge transfer from the catalyst to CO2 have been discussed in Sections 2 and 3. In this section, the rate limiting step, reaction intermediates, product selectivity, and interferences by the surface contaminants are discussed.

Rate Limiting Step

Only a few studies have been conducted on the investigation of the kinetic models for CO2 photoreduction, where there are two views about the rate limiting step. The first view is that the activation of CO2 or H2O through charge transfer is the rate limiting step. Lin et al. (2004) proposed that for CO2 photoreduction with H2O, CO2 reduction and H2O splitting proceeded competitively at the same Ti-O sites. Uner and Oymak (2012) indicated that the activation of both CO2 and H2O through charge transfer is the two important steps in the photocatalytic reduction of CO2 with H2O vapor over Pt/TiO2. The adsorption and accommodation of CO2 is not limiting the rate of CH4 formation, while the production of protons and electrons, or the production of hydrogen atoms from H2O splitting is the rate limiting step in the overall process. Rasko and Solymosi (1994) suggested that the most important step in any reaction of CO2 is the activation of rather inert and stable CO2 involving an electron transfer to CO2.

The second view is that the rate limiting step in CO2 photoreduction is determined by the dynamics of reactant adsorption and product desorption. Lo et al. (2007) found that the photoreduction rate of CO2 increased linearly with the initial CO2 concentration. They suggested that CO2 photoreduction could be a pseudo-first-order reaction, and the adsorption of CO2 on TiO2 was the rate limiting step. Slamet et al. (2005) reported that the desorption of products was the rate limiting step in the formation of CH3OH from CO2 photoreduction over Cu/TiO2. In addition, Salatin and Alxneit (1997) demonstrated that the reaction rate of CH4 formation from CO2 photoreduction increased when the temperature increased from 25 to 200°C. Their kinetic model indicated that at lower temperatures, the desorption of products was the rate limiting step, while at high temperatures, the adsorption of reactants was the rate limiting step. Similarly, in situ DRIFTS analysis in a recent work confirmed that the activities and stabilities of TiO2 and MgO/TiO2 were temperature-dependent and associated with the equilibrium of reactants adsorption/intermediates desorption at the catalyst surface (Liu et al., 2013b). The disagreement in the rate limiting step in the literature warrants further studies to advance the understanding of the reaction kinetics of CO2 photoreduction, involving CO2 and H2O adsorption, activation, dissociation and desorption steps at a wider range of temperatures.

Surface Reaction Intermediates

Several studies have been conducted to explore the surface reaction intermediates in the CO2 photoreduction over bare TiO2, micro- and meso-porous titanosilicates, and modified TiO2 (as mentioned in Section 3.3). The photocatalysts, reaction media, reaction intermediates, and products are summarized in Table 1. Table 1 shows that there are a variety of possible reaction intermediates, largely depending on the reaction media. In a solid-gas reaction system involving CO2 and H2O vapor, CO2•, C•, CO, HCOOH, and HCOO are the primary intermediates. CO• and HCOOH can be converted to CO2 while C•, CO and HCO• are considered as the intermediates for the production of hydrocarbons (e.g., CH4, C2H6, C3H8). In a solid-liquid reaction system involving dissolved CO2 in water, CO2•, CO2–, CO3–, HCOOH•, and HCHO are the common intermediates, which can be transformed into CH4, CH3OH, HCOOH and CH3CH2OH.

The type and nature of active sites of the catalyst may also affect the intermediate species and final products. Isolated Ti-sites incorporated into various porous silica materials (e.g., MCM-41, SBA-15, 5A sieves) have been fabricated and applied to CO2 photoreduction (Lin et al., 2004; Ulagappan and Frei, 2000; Srinivas et al., 2011; Yang et al., 2011; Zhao et al., 2012b). The reaction mechanisms on these supported TiO2 materials were also investigated. Anpo et al. (1995) proposed a mechanism for CO2
In addition, the reduction of CO2 and the decomposition of H2O proceeded competitively on the same Ti3+–O–* sites, inducing the formation of H radicals, OH radicals, and carbon species. These intermediate radicals combine with each other to form CH4 and CH3OH. The intermediates and reaction pathways for CO2 photoreduction were related to the crystal phase and defects in TiO2 as well. In situ DRIFTS studies have been done to explore the surface intermediates and reaction mechanism of CO2 photoreduction on defective and defect-free TiO2 (Liu et al., 2011), three hydrocarbons (i.e., CH4, C2H4, and C2H6) were produced from photocatalytic reduction of CO2 with H2O over Ti-SBA-15. For the formation mechanism of the hydrocarbons, Ti-OH serves as the active site for the adsorption of CO2 and H2O, where CO and hydroperoxo (Ti–OOH) intermediates are generated and subsequently photo-activated H2O; two HCHO combined to form C2H4, and the reaction of two HCHO with each other to yield C2H6, and the reaction of two HCHO with one H2O led to the formation of C2H6.

Table 1. The comparison of the reaction intermediates, products and reaction media for CO2 photoreduction with H2O on the different photocatalysts from the literature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction intermediates</th>
<th>Products</th>
<th>Reaction Media</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2-anatase</td>
<td>H+, CH3, OH*</td>
<td>CH4, CH3OH</td>
<td>NaOH solution</td>
<td>(Koci et al., 2009)</td>
</tr>
<tr>
<td>TiO2-brookite</td>
<td>CO2, HCOOH</td>
<td>CO, CH4</td>
<td>H2O vapor</td>
<td>(Liu et al., 2012b)</td>
</tr>
<tr>
<td>TiO2-P25</td>
<td>CO2*</td>
<td>CH4</td>
<td>H2O solution</td>
<td>(Dimitrijevic et al., 2011)</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>O*, OH*</td>
<td>CO</td>
<td>H2O vapor</td>
<td>(Lin et al., 2004)</td>
</tr>
<tr>
<td>Ti-SBA-15</td>
<td>CO, HCOH</td>
<td>CH4, C2H4, C2H6</td>
<td>H2O vapor</td>
<td>(Yang et al., 2011)</td>
</tr>
<tr>
<td>Cu/Ti/SiO2</td>
<td>CO2*, COOH*, CH3OH</td>
<td>CH4, CH3OH, CH3COOH, COOH-COOH</td>
<td>Alkaline solution</td>
<td>(Srinivas et al., 2011)</td>
</tr>
<tr>
<td>Cu/Ti/SiO2</td>
<td>CO2*, COOH*, CH3OH</td>
<td>CH4, CH3OH, CH3COOH, COOH-COOH</td>
<td>Alkaline</td>
<td>(Srinivas et al., 2011)</td>
</tr>
<tr>
<td>Pt/TiO2</td>
<td>HCOO−</td>
<td>CH4</td>
<td>H2O vapor</td>
<td>(Uner and Oymak, 2012)</td>
</tr>
<tr>
<td>Au/TiO2</td>
<td>C residue</td>
<td>CH4, C2H6, HCHO, CH3OH</td>
<td>H2O vapor</td>
<td>(Hou et al., 2011)</td>
</tr>
<tr>
<td>Pd/TiO2</td>
<td>CO2−, CO2(aq), H2CO3</td>
<td>CH4, C2H6, C2H4</td>
<td>Na2CO3 solution</td>
<td>(Dubois and Dubois, 2009)</td>
</tr>
<tr>
<td>N-TiO2</td>
<td>CH3, HCOO−</td>
<td>HCHO, CH3OH, CH3OH, CH3O2−</td>
<td>H2O vapor</td>
<td>(Peng et al., 2012)</td>
</tr>
<tr>
<td>FeTiOx/TiO2</td>
<td>H2CO3, HCO2*, HCOOH</td>
<td>CH3OH</td>
<td>NaHCO3 solution</td>
<td>(Truong et al., 2012)</td>
</tr>
<tr>
<td>CuO/TiO2</td>
<td>CO2−, HCOOH, HCHO</td>
<td>HCOOH, CH3OH</td>
<td>CH3OH solution</td>
<td>(Qin et al., 2011)</td>
</tr>
<tr>
<td>CuO/TiO2</td>
<td>CO2−, HCOO−</td>
<td>CO, CH3</td>
<td>H2O vapor</td>
<td>(Liu et al., 2012a)</td>
</tr>
<tr>
<td>AgBr/TiO2</td>
<td>CO2−, C•, CH3•</td>
<td>CH4, CH3OH, CO, CH3CH2OH</td>
<td>KHC03 solution</td>
<td>(Asi et al., 2011)</td>
</tr>
<tr>
<td>Pt-Cu/TiO2</td>
<td>CO, OH•</td>
<td>CH3, CH2, olefin, branched paraffin, alkanes</td>
<td>H2O vapor</td>
<td>(Varghese et al., 2009)</td>
</tr>
<tr>
<td>Ag/Al₄TiO₇ (A: Ca, Sr, Ba)</td>
<td>C residue</td>
<td>CH4, HCOOH, H2, O2</td>
<td>H2O vapor</td>
<td>(Izuka et al., 2011)</td>
</tr>
<tr>
<td>Cu-I/TiO2</td>
<td>H+, CO−, C•</td>
<td>CO, CH3, CH3Cl</td>
<td>H2O vapor</td>
<td>(Zhang et al., 2012)</td>
</tr>
<tr>
<td>Ni-N/TiO2</td>
<td>CH3OH</td>
<td>NaOH, Na2SO3 solution</td>
<td>(Fan et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>M-N/TiO2</td>
<td>CH4</td>
<td>H2O vapor</td>
<td>(Li et al., 2012)</td>
<td></td>
</tr>
</tbody>
</table>

Subsequently under photo-illumination, no CO2− or other new species were formed on defect-free TiO2, and the adsorbed H2O was stable. By contrast, CO2 was favourably formed on the defective TiO2 anatase. Fig. 6 shows the IR spectra of CO2 and H2O interaction with the defective anatase in the dark and under the photoillumination. At 5 min, the early stage of adsorption, CO2− species (1670 and 1247 cm−1) were formed even in the dark (Fig. 6(a)). Although it disappeared by prolonging the adsorption time to 15 min, subsequent photo-illumination induced the reappearance of CO2−, the intensity of which increased with the irradiation time (Fig. 6(b)). The re-presence of CO2− is an evidence that the photoexcited electrons that were trapped in the defect sites transferred to the adsorbed CO2 on the defective surface. In the case of brookite, CO2− was formed on the defective brookite in the dark but was not represent under photoillumination in the presence of H2O. This is likely due to the faster reaction of CO2− with H• (generated from H2O) on brookite.

Table 2 shows the tentative mechanism for CO and CH4 formation on the defective anatase and brookite (Liu et al., 2012b). CO2− and HCOO− were formed on both the defective anatase and brookite (Reactions 2 and 3), CO2 could be reduced to CO via reaction with H• (Reaction 4), self-transformation (Reaction 5), or direct dissociation by healing the VC sites (Reaction 6). A unique intermediate, HCOOH, was only formed on the defective brookite (Reactions 8 and...
Scheme 1. Schematic representation of the photocatalytic reduction of CO$_2$ with H$_2$O on the anchored titanium oxide. Reproduced with permission from (Anpo et al., 1995).

Fig. 6. In situ DRIFTS spectra of CO$_2$ and H$_2$O interaction with defective anatase (i.e., TiA(He)) (a) in the dark, and (b) subsequently irradiated by UV-visible light as a function of time. Reproduced with permission from (Liu et al., 2012b).

Table 2. The possible reaction pathways for the formation of CO and CH$_4$ from CO$_2$ photoreduction with H$_2$O vapor on oxygen-deficient TiO$_2$ anatase and brookite phases. Reproduced with permission from (Liu et al., 2012b).

<table>
<thead>
<tr>
<th>Phase</th>
<th>CO$_2$ photoreduction with H$_2$O vapor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defective TiO$_2$</td>
<td></td>
</tr>
<tr>
<td>anatase and brookite</td>
<td></td>
</tr>
<tr>
<td>H$_2$O + h$^+$ → H$^+$ + OH$^.$</td>
<td>(1)</td>
</tr>
<tr>
<td>OH$^.$ + CO$_2$ → HCO$_3^.$</td>
<td>(2)</td>
</tr>
<tr>
<td>CO$_2^-$ + CO$_2^-$ → CO + CO$_3^-$</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>CO$_2^-$ + Ti$^{3+}$ + e$^-$ → CO + OH$^-$</td>
</tr>
<tr>
<td></td>
<td>CO$_2^-$ + [Ti$^{3+}$-O$_2$-Ti$^{4+}$] → CO + [Ti$^{4+}$-O$_2$-Ti$^{3+}$]</td>
</tr>
<tr>
<td></td>
<td>CO$_2^-$ + OH$^.$ + H → CH$_2$OH</td>
</tr>
<tr>
<td></td>
<td>CO + H$_2$O → CH$_4$</td>
</tr>
<tr>
<td>Defective TiO$_2$</td>
<td></td>
</tr>
<tr>
<td>brookite</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + 2e$^-$ → HCOOH</td>
<td>(8)</td>
</tr>
<tr>
<td>HCOOH → CO + H$_2$O</td>
<td>(9)</td>
</tr>
<tr>
<td>CO$_2$ + 2H$^+$ + e$^-$ → HCOOH</td>
<td>(10)</td>
</tr>
<tr>
<td>CO, HCOOH → e$^-$H$^+$ → CH$_4$</td>
<td>(11)</td>
</tr>
</tbody>
</table>

9) and could be dissociated to CO subsequently (Reaction 10). Table 2 shows that CO$_2$ photoreduction to CO probably undergoes different mechanisms on defective anatase and brookite through different surface intermediates (e.g., CO$_2^-$ on anatase; CO$_2^-$ and HCOOH on brookite). For CH$_4$ formation, possible intermediates are CO, HCO$_3^-$, and HCOOH, which may be converted to CH$_4$ via a multi-electron transfer process, once dissociated hydrogen atoms are available (Reactions 7 and 11).

Product Selectivity

Table 1 clearly demonstrates the variety of possible products from CO$_2$ photoreduction, such as H$_2$, O$_2$, CO, CH$_4$, CH$_3$OH, HCOOH, HCHO and other hydrocarbons, indicating the lack of control of product selectivity in CO$_2$ conversion over TiO$_2$-based photocatalysts. Table 1 also shows that the product selectivity is dependent on the types of reaction media and catalyst composition. In the gas phase reaction environment, CO and CH$_4$ are reported as
the major C1 chemicals; while in the aqueous environment, alcohols (e.g., CH₃OH, CH₃CH₂OH) are mainly produced. In addition, the incorporation of metals or metal oxides to TiO₂ facilitated the production of hydrocarbons such as CH₄ and CH₃OH.

As shown in Table 1, CO, CH₄, and CH₃OH are the three most common products from CO₂ photoreduction. Scheme 2 illustrates the possible reaction pathways to form those three products. CO can be formed via the intermediates of CO₂⁻ and HCOOH, respectively. The CO₂⁻ anions can be converted to CO via the reaction with H⁺ radical, self- transformation, or dissociation on the oxygen vacancy sites (Scheme 2(a)). Another route for CO formation is the photocatalytic formation of HCOOH (Scheme 2(b)). The generated CO can serve as the intermediate for the subsequent formation of CH₄ and CH₃OH through deoxygenation (Scheme 2(c)). In this process, the oxidation states of carbon decrease from +IV (CO₂), to +II (CO), to 0 (HCHO), to –II (CH₃OH), and then to –III (CH₃•). The CH₃• can either combine with OH• radical to form CH₃OH or with H⁺ radical to form CH₄. Another pathway for CH₃OH and CH₄ formation is the hydrogenation of CO₂ with H atoms through the HCOOH intermediate (Scheme 2(d)). In this route, the oxidation states of carbon change from +IV (CO₂), to +II (HCOOH), to 0 (HCHO), to –I (CH₃OH), and then to –III (CH₃•). The CH₃• can either combine with OH• radical to form CH₃OH or with H⁺ radical to form CH₄.

As shown in Scheme 2(c), the formation of CH₃OH on Cu/TiO₂ due to the migration of H⁺ with trapped electrons. The H-Cu sites promote the hydrogenation of the intermediates to generate CH₃OH. Anpo et al. (1997) reported a unique role of Pt metal on Ti/Y-zeolites for CO₂ photoreduction, besides the conventional role of Pt in promoting charge transfer. They found that carbon radicals and H atoms were generated on the same Pt metal sites, and thus CH₄ formation was facilitated by Pt. Because the OH• radicals were formed at different sites from where the carbon radicals were formed, the presence of Pt metal suppressed the formation of CH₃OH.

Interference of Surface Contaminants

Recently, Yang et al. (2010) raised a concern on the interference of surface contaminants on the catalyst such as carbon residues that may participate in the CO₂ photoreduction and affect the activity and selectivity. The surface contaminants are possibly originated from the Ti-precursors and the solvents during the catalyst synthesis process. As suggested by Yang et al. (2010), the carbon residues were derived from the use of Ti-alkoxides and organic solvents. Calcination in air environment could not completely remove these carbon residues, while exposure of the catalyst to H₂O vapor and UV-irradiation was effective to clean the catalyst surface. Through the DRIFTS analysis using ^13^C labelled CO₂, Yang et al. (2010) demonstrated that carbon residues can react with CO₂ and H₂O to form CO over Cu-promoted TiO₂, i.e., CO₂ + ^13^C → ^13^CO + ^13^CO and H₂O + ^12^C → ^12^CO + H₂.

Other surface contaminants like chlorine species may interfere with the CO₂ photoreduction. A recent work reported that an undesirable product (i.e., CH₃Cl) was formed during CO₂ photoreduction on copper and iodine co-modified TiO₂ when a chlorinated Cu-precursor was used (Zhang et al., 2010). The path to CH₃Cl formation is likely through the reaction of a methyl radical (CH₃•) and a chlorine radical (Cl•), the latter of which is generated by Cl ions reacting with photoexcited holes. The generation of CH₃Cl indirectly confirms that methyl radicals, likely derived from surface adsorbed carbon species, is a reaction intermediate for CO₂ photoreduction. The above studies on the effect of surface contaminants can provide two insights in the field of CO₂ photoreduction. First, it is important for the researchers to choose the right chemical precursors or methods to prepare catalysts to avoid or remove surface contaminants and to ensure the accuracy of their results. Second, if properly applied, intentionally contaminated surfaces can be useful to help explore and decouple the complex reaction mechanism.

CONCLUSIONS AND FUTURE PROSPECTS

In this review, we have summarized the literature results on the mechanism of CO₂ photoreduction with H₂O using TiO₂-based photocatalysts, including CO₂ adsorption/dissociation, charge transfer mechanism, and reaction pathways/product selectivity. Three primary factors, TiO₂ crystal phase, surface defects, and material modifications, are reviewed. The literature has demonstrated that (1) CO₂ activation and dissociation process can be promoted by creating defect disorders on TiO₂ surface (e.g., Ti^{4+} and oxygen vacancy), (2) the charge separation and transfer
can be enhanced by tailoring the crystal phase of TiO₂ (e.g., mixture of anatase/brookite or anatase/rutile), engineering the defects in TiO₂, and incorporating modifiers with TiO₂ (e.g., metals, metal oxides, graphene, quantum dot sensitizers), and (3) the crystal phase, active sites, modifiers, and reaction media all affect the types of surface reaction intermediates and final products. One has to be aware that several challenges still exist in this field. First, there is a great need to promote the CO₂ conversion efficiency by orders of magnitude, since the current efficiency is very low and far from practical applications. Second, there is lack of detailed experimental evidences for the charge transfer directions and dynamics. Third, the surface intermediates, reaction pathways, and reaction kinetics for CO₂ photoreduction have not been clearly understood. It is also difficult to control or even rationalize the product selectivity.

In light of this review, we suggest that future research can be conducted in the following directions to extend the understanding in the CO₂ photoreduction mechanism and to design more efficient photocatalysts: (1) Taking the advantages of the combined effects of mixed crystal phase, defect-defects, and material modifications to rationally design an efficient, selective, long-term stable, and regenerative TiO₂-based photocatalysts; (2) Studying the direction of electron transfer in TiO₂-based materials by EPR or in situ EPR (particularly the interfacial electron transfer between two phases or between TiO₂ and modifiers), and correlate it with materials properties and photocatalytic activities; (3) Applying in situ FTIR to monitor the surface reaction intermediates and to investigate the strategies to control product selectivity; (4) Investigating the rate limiting step and the dynamics of the reactant adsorption/product desorption process by conducting photocatalytic reactions at different temperatures.

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