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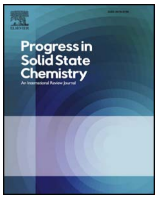

CO_2 reduction using oxynitrides and nitrides under visible light

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ABSTRACT

Reduction of CO_2 using a heterogeneous photocatalyst under visible light has been studied as a potential means to address the problems of global warming and the depletion of fossil fuels. Recently, hybrid photocatalysts constructed with a metal complex and a particulate semiconductor are of particular interest because of the excellent electrochemical (and/or photocatalytic) ability of the metal complexes for CO_2 reduction and the high efficiency of the semiconductors for oxidation reactions, where the ultimate target of oxidation reaction is water oxidation to form molecular O_2. This review article highlights our recent progress in the development of metal-complex/semiconductor hybrid materials for visible-light CO_2 reduction with a focus on oxynitride and nitride materials as the semiconductor component.

1. Introduction

1.1. Research background

It is generally believed that significant consumption of carbon resources and concomitant CO_2 emission have caused serious problems such as global warming and an energy shortage on Earth. The catalytic conversion of CO_2 into useful chemical feedstock is thus of significant interest in diverse areas of chemistry [1–5]. Among various reactions and schemes, photocatalytic CO_2 reduction using a semiconductor photocatalyst would be one of the most promising solutions because inexhaustible sunlight can be utilized as the energy input and water as the electron source. While photocatalytic H_2 production from water is another important subject of research [6–8], there still remains a difficulty in storing and transporting H_2. In contrast, photocatalytic CO_2 reduction is a potential means of directly producing transportable fuels or energy carrier such as alcohols and formic acid.

However, photocatalytic CO_2 reduction is generally very difficult because CO_2 is a chemically stable molecule that requires a high electrochemical potential for reduction ($E^\circ = -1.9$ V vs. NHE at pH 7):

$$CO_2 + e^- \rightarrow CO_2^{\bullet -} \qquad E^\circ = -1.9\ \mathrm{V} \tag{1}$$

In addition, the one-electron reduction product, $CO_2^{\bullet -}$, is so reactive that control of the product selectivity is also difficult. On the other hand, the reduction of CO_2 yields a variety of products, depending on how many electrons are involved. Equations (2)–(6) show that the potential (vs. NHE at pH 7) required for CO_2 reduction can be reduced if a multi-electron process through proton-coupled electron transfer is employed.

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \quad E^\circ = -0.61\ \mathrm{V} \tag{2}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad E^\circ = -0.53\ \mathrm{V} \tag{3}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad E^\circ = -0.48\ \mathrm{V} \tag{4}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^\circ = -0.38\ \mathrm{V} \tag{5}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad E^\circ = -0.24\ \mathrm{V} \tag{6}$$

For example, the two-electron reduction of CO_2 yields HCOOH and CO, both of which are useful compounds, one as a hydrogen storage material, and the other as an energy source for the Fischer-Tropsch reaction, with electrochemical potentials of −0.61 and −0.53 V (vs. NHE at pH 7), respectively. These potentials are approximately 1.3 V more positive than that required for one-electron reduction.

1.2. Basic principle of CO_2 reduction on semiconductor particle

The basic principle of CO_2 reduction on a semiconductor particle is illustrated in Fig. 1. Here, water oxidation is combined with CO_2 reduction as the oxidative half cycle of the entire reaction, while the reduction side is the formation of CO as an example. Under photoexcitation of a semiconductor photocatalyst with light energy greater than or equivalent to the band gap energy of the semiconductor, electrons in the valence band are excited into the conduction band, which leaves holes in the valence band. The photogenerated electrons and holes cause the reduction and oxidation reactions, respectively. To achieve CO_2 reduction combined with water oxidation to produce CO and O_2, the conduction band minimum (CBM) must be more negative than the reduction potential for CO_2 to CO (−0.53 V vs. NHE at pH 7),

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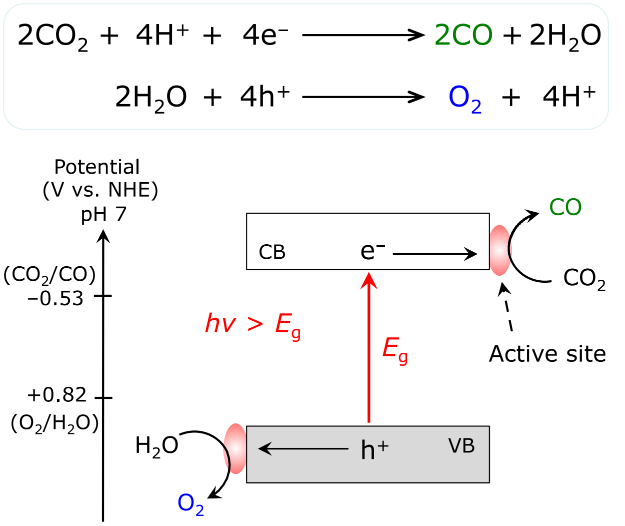

Fig. 1. Schematic energy diagram of CO_2 reduction and H_2O oxidation on a semiconductor photocatalyst. VB and CB denote the valence band and conduction band, respectively. E_g indicates the band gap energy for the semiconductor photocatalyst.

while the valence band maximum (VBM) must be more positive than the oxidation potential for H_2O to O_2 (+0.82 V vs. NHE). Therefore, the minimum photon energy that is thermodynamically required to drive photocatalytic CO_2 reduction and H_2O oxidation is 1.35 eV, which corresponds to a wavelength of ca. 920 nm. It is thus in principle possible to utilize the entire spectral range of visible light ($400 < \lambda < 800$ nm). However, there is an activation barrier for the charge transfer process between the solid photocatalyst and CO_2 molecules that requires a photon energy greater than the band gap of the photocatalyst to drive the overall reaction at a reasonable rate. More importantly, a cocatalyst is necessary to promote the multi-electron reduction of CO_2, and to control the reaction selectivity while suppressing the kinetically more favorable proton reduction, as described later. Reverse reactions of thermodynamically more oxidizable and reducible products (e.g., the reduction of O_2 and oxidation of CO), must be strictly suppressed, and the semiconductor photocatalyst itself must remain stable throughout the reaction.

1.3. Oxynitrides and nitrides as visible-light-absorbing semiconductors

The development of a semiconductor photocatalyst that works efficiently under visible light ($\lambda > 400$ nm) to reduce CO_2 is highly desirable with respect to solar energy conversion. Such a photocatalyst should meet the following three requirements:

(1) a band gap smaller than 3 eV (an absorption edge shorter than 400 nm)
(2) band-edge potentials suitable for CO_2 reduction and H_2O oxidation
(3) stability throughout the photocatalytic reaction

Several metal oxides have already been reported to act as active photocatalysts for CO_2 reduction and water oxidation [9–12]. For example, Kudo et al. reported that Ag-loaded $ALa_4Ti_4O_{15}$ (A = Ca, Sr, and Ba) with a layered perovskite structure and a band gap of 3.79–3.85 eV exhibited photocatalytic activity for CO_2 reduction to form CO and the oxidation of water into O_2 [9]. However, these photocatalysts only work under UV irradiation due to their large band gaps (> 3 eV). The relatively large band gaps of metal oxides originate from the VBM, which is formed by O 2p orbitals and is more positive than 3 V [13]. Therefore, if a metal oxide meets the thermodynamic requirement for CO_2 reduction and H_2O oxidation, then the band gap of the metal oxide inevitably becomes larger than 3 eV, which is too wide to absorb visible light. Nevertheless, the difference between the oxidation potential for H_2O into O_2 (1.23 V vs. NHE at pH 0) and the VBM (ca. 3 V vs. NHE) suggests that metal-oxide photocatalysts have sufficient potential to oxidize water.

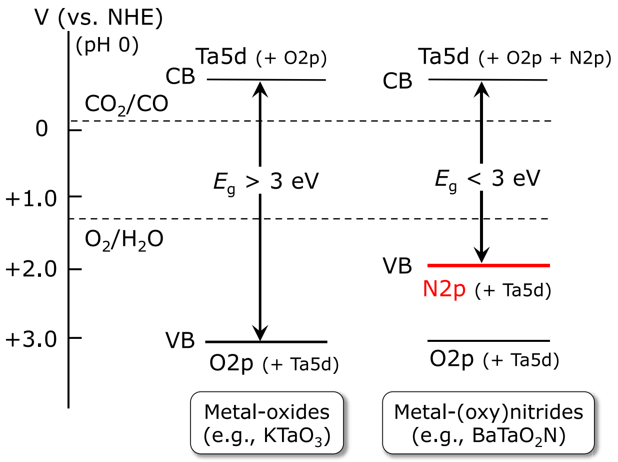

Fig. 2. Schematic band structures of a metal oxide ($KTaO_3$) and metal (oxy)nitride ($BaTaO_2N$).

The N 2p orbital has a higher potential energy than the O 2p orbital, which suggests it would be of interest to apply a metal nitride or oxynitride as a photocatalyst [6–8]. Typical examples of metal oxide ($KTaO_3$) and oxynitride ($BaTaO_2N$) band structures, both of which have the same perovskite structure, are schematically shown in Fig. 2. The VBM for $KTaO_3$ consists of O 2p orbitals. When N atoms are partially or fully substituted for O atoms in a metal oxide, the VBM for the material is expected to shift higher than the corresponding metal oxide, while the CBM potential is basically maintained. Density functional theory (DFT) calculations for $BaTaO_2N$ have indicated that the VBM consists of hybridized N 2p and O 2p orbitals, whereas the CBM is mainly composed of empty Ta 5d orbitals [6].

In 2000, Jansen and Letschert reported that some particulate (oxy)nitrides containing early transition-metal cations are stable, non-toxic inorganic pigment alternatives to metal chalcogenides [14]. Domen et al. have since been developing (oxy)nitrides as photocatalysts for water splitting under visible light [6]. Fig. 3 shows UV–visible diffuse reflectance spectra of some (oxy)nitrides that have absorption bands in the range of 500–750 nm, which correspond to band gaps of 1.7–2.5 eV as estimated from the onset wavelengths of the absorption spectra. To date, GaN:ZnO solid solutions [15,16], ZrO_2-modified TaON [17],

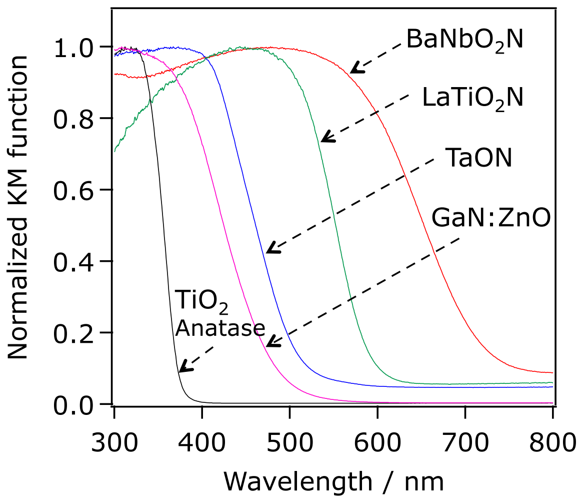

Fig. 3. UV–visible diffuse reflectance spectra for anatase TiO_2, GaN:ZnO (Zn/Ga = 0.22 by mole), TaON, $LaTiO_2N$, and $BaNbO_2N$. KM means the Kubelka-Munk function.