Oxygen-doped Ta_3N_5 modified with a Ru(II) binuclear complex having the ability to reduce CO_2 under a wide range of visible light

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Abstract: A hybrid photocatalyst constructed with Ta_3N_5 and a binuclear ruthenium(II) complex had the ability to reduce CO_2 into HCOOH with very high selectivity (>99%) under a wide range of visible light ($\lambda >$ 500 nm). In particular, Ta_3N_5/SiO_2 prepared from Ta_2O_5, which was loaded on SiO_2 by a sol-gel method, showed 4–6 times higher activity than the bulk type Ta_3N_5. UV-vis diffuse reflectance spectra showed that the background absorption of the Ta_3N_5/SiO_2 spectrum, which is attributed to tantalum reduced species, was reduced, compared to the bulk Ta_3N_5. The decrease of the defect density contributed to the suppression of the charge recombination, resulting in higher activity of Ta_3N_5/SiO_2.

Keywords: CO_2 fixation, (Oxy)nitride, Metal complex.

1. Introduction

There are many reports on tantalum nitride (Ta_3N_5) for photocatalytic or photoelectrochemical water splitting, because Ta_3N_5 has wide range of visible light absorption property and suitable band edge position for water splitting.[1] However, there is no report on application of Ta_3N_5 for photocatalytic CO_2 reduction. In order to enhance the photocatalytic activity, it is well known that in the synthesis of Ta-based oxynitrides, suppressing the Ta reduced species is important, which acts as a recombination center of charge carrier.[2] Herein we report that Ta_3N_5 can reduce CO_2 to HCOOH when combined with a Ru(II) binuclear complex (**RuRu'**) under the irradiation of visible light (λ > 500 nm). In particular, we focused on interfacial interaction between anion (in particular oxygen) and Ta_3N_5 by using composite of Ta_2O_5 loaded on SiO_2 as a precursor, which is considered to have interaction between oxygen within SiO_2 and Ta.[3,4] This method is based our previous report, in which ZrO_2-modified TaON showed higher activity by utilizing interaction between the two components, resulting in suppression of reduced Ta species.[5] In this work, we successfully suppressed the production of the undesirable reduced Ta species in Ta_3N_5, thereby improving photocatalytic CO_2 reduction activity.

2. Experimental (or Theoretical)

In this work, Ta_3N_5-loaded SiO_2 (Ta_3N_5/SiO_2) was synthesized by thermal ammonolysis of Ta_2O_5/SiO_2, which was in prior prepared by a sol-gel method, with dry annmonia.[3,4] Powders of bulk Ta_3N_5 and nanoparticulate Ta_3N_5 were also synthesized as references according to the methods reported previously.[5] These reference samples are represented hereafter as bulk-Ta_3N_5 and nano-Ta_3N_5, respectively. Each nitride sample was characterized by X-ray diffraction (XRD), UV-visible diffuse reflectance spectra (DRS), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and transmission electron microscope (TEM). Prior to CO_2 reduction, the as-prepared Ta_3N_5 samples were modified with both Ag nanoparticles and a **RuRu'**, which work as an electron-transfer promoter and a photocatalytic unit having a high ability to reduce CO_2, respectively.

3. Results and discussion

XRD and DRS showed that the single phase Ta_3N_5 was produced in each nitrided sample. To investigate the possible incorporation of oxygen into the lattice of Ta_3N_5, XPS measurements were conducted. The Ta $4f_{7/2}$ peak positions in Bulk-Ta_3N_5 and Nano-Ta_3N_5 (24.6 eV) were in good agreement with previous reports.[6] On the other hand, the peak position in Ta_3N_5/SiO_2 (25.0 eV) is located between the Ta_3N_5 references (24.6 eV) and TaON (25.2 eV), which is intermediate product between Ta_2O_5 and Ta_3N_5. This result clearly indicates that there is much more contribution of Ta–O bondings in Ta_3N_5/SiO_2 than those in pure Ta_3N_5 samples.

The incorporation of oxygen into Ta_3N_5 was found to alter the optical absorption profile of Ta_3N_5. Figure 1 shows the DRS of each Ta_3N_5 sample. The absorption edge position of Ta_3N_5 is consistent with the previous report[6]. However, the absorption edge of Ta_3N_5/SiO_2 is located at ca. 580 nm, 20 nm blue-shifted compared to other Ta_3N_5 samples. This is primarily attributed to the higher oxygen concentration in Ta_3N_5/SiO_2 than the others, as indicated by XPS. The absorption at wavelength regions longer than 600 nm, attributed to reduced tantalum species,[2] is different from each other. The fact that Ta_3N_5/SiO_2 has the weakest absorption in the longer wavelength region compared to Bulk-Ta_3N_5 and Nano-Ta_3N_5 indicates that formation of anionic defects during nitridation is most effectively suppressed in Ta_3N_5/SiO_2.

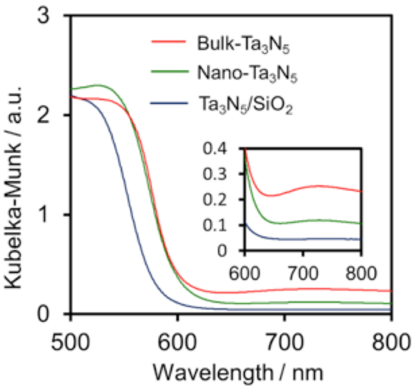

Figure 1 UV-visible diffuse reflectance spectra for Ta_3N_5 samples

Using as-prepared Ta_3N_5 and **RuRu'**, CO_2 reduction was conducted. All Ta_3N_5 samples were capable of reducing CO_2 into HCOOH under visible light with high selectivity (~99%) (Table 1). In particular, Ta_3N_5/SiO_2 showed 4–6 times higher activity than the other Ta_3N_5 samples. As mentioned above, Ta_3N_5/SiO_2 has the weakest absorption in the longer wavelength region than band gap transition, which is derived from reduced tantalum species (i.e., anionic defects). The lower density of defects in Ta_3N_5/SiO_2 is most likely to contribute to suppression of electron–hole recombination, leading to higher activity. In addition, an increase in the driving force for reduction/oxidation processes that resulted from the blue-shift of the absorption edge (see Figure 1) might be responsible to higher activity as well.

Table 1. Results of CO_2 reduction by **RuRu'**/Ag (1.5 wt%)/Ta_3N_5[a]

Sample	Amount of product / nmol (TON)			$Selectivity_{HCOOH}$ / %
	HCOOH	CO	H_2	
Bulk-Ta_3N_5	738 (41)	N.D.	7	99
Nano-Ta_3N_5	1080 (60)	N.D.	13	99
Ta_3N_5/SiO_2	4320 (240)	N.D.	7	>99

[a] Reaction conditions: photocatalyst, 4.0 mg (Ag 1.5 wt%); solution, a mixture of MeCN and TEOA (4:1 v/v) 4.0 mL; light source, 400 W high pressure Hg lamp (SEN) with a K_2CrO_4 solution filter. Reaction time: 15 h. **RuRu'** loaded was 4.5 μmol g^{-1}.

4. Conclusions

In this work, we could apply Ta_3N_5 to visible-light CO_2 reduction with the aid of **RuRu'**. When using Ta_2O_5/SiO_2 as a precursor oxide, we could suppress the production of anion defects of Ta_3N_5/SiO_2 during the nitriding reaction, resulting in higher activity of Ta_3N_5/SiO_2. It is also suggested that appropriate amount of oxygen doping into Ta_3N_5 is effective for enhancing photocatalytic activity.

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