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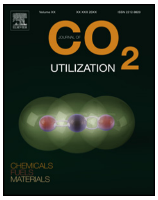

Photocatalytic reduction of CO_2 over a hybrid photocatalyst composed of WO_3 and graphitic carbon nitride (g-C_3N_4) under visible light

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) has attracted much attention as a metal-free semiconductor having visible light absorption and relatively high chemical stability. g-C_3N_4 can reduce CO_2 to organic fuels such as methanol (CH_3OH), formic acid (HCO_2H), and methane (CH_4) under visible light irradiation. However, oxidation potential of g-C_3N_4 is not enough for water oxidation. Therefore, we focused on hybridization of g-C_3N_4 and tungsten(VI) oxide (WO_3) which has high oxidation potential for water oxidation. In this study, we examined CO_2 reduction by composite photocatalyst of g-C_3N_4 and WO_3, which was prepared by three methods (mixture using an agate mortar, impregnation and planetary mill). As a result, composite photocatalyst prepared with planetary mill showed the highest photocatalytic activity.

Photodeposition of silver or gold nanoparticles only on g-C_3N_4 of the hybrid photocatalyst induced an increase in CH_3OH because the loaded metal nanoparticles play an important role in multi-electron reduction of CO_2. Photocatalytic activity of the Au-loaded hybrid photocatalyst composed of g-C_3N_4 and WO_3 was 1.7-times higher than that of the hybrid photocatalyst without Au loading.

In addition, we investigated photocatalytic reaction mechanism of composite photocatalyst by double-beam photoacoustic spectroscopy. This result revealed Z-scheme reaction proceeds in the composite photocatalyst to maintain high oxidation ability of WO_3 and high reduction ability of g-C_3N_4, resulting in high photocatalytic activity.

Introduction

Carbon dioxide (CO_2) is one of the major compounds responsible for global warming, which has now become a global environmental issue because fossil fuel consumption will cause a monotonical increase in the atmospheric CO_2 concentration in the future [1]. Therefore, CO_2 conversion or energy-oriented use is a priority subject of investigation throughout the world. Effective utilization of clean and abundant solar energy for CO_2 conversion will be a promising solution not only for energy issues due to the consumption of natural energy sources but also for many problems caused by greenhouse gases [2]. In order to efficiently utilize solar energy, photocatalytic CO_2 reduction to produce useful fuels under visible light, mimicking artificial photosynthesis, is one possible solution. Actually, photocatalytic reaction over semiconductor photocatalysts has the potential to reduce CO_2 into hydrocarbons using water as an electron donor. For instance, Inoue and coworkers first reported photocatalytic CO_2 reduction in a semiconductor aqueous suspension to produce hydrocarbon fuels such as formaldehyde (HCHO), formic acid (HCOOH), methanol (CH_3OH), and methane (CH_4) [3]. In addition, metal oxide semiconductor photocatalysts including titanium(IV) oxide (TiO_2) can produce formic acid (HCOOH), formaldehyde (HCHO), methanol (CH_3OH), and methane (CH_4) [3–16]. However, quantum yields for photocatalytic CO_2 reduction have been low. The carbon source of the products is not clear. However, most of the photocatalytic CO_2 reductions using metal oxide semiconductor photocatalysts are carried out under UV-light irradiation, and the synthetic process and recipe of the photocatalysts are complicated. Therefore, visible-light-driven materials with high efficiency and stability represent a central challenge in the field of photocatalytic CO_2 conversion for energy-oriented use.

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Recently, a visible light-responsive graphitic carbon nitride (g-C_3N_4) photocatalyst with high reduction ability was attracted much attention since hydrogen evolution over g-C_3N_4 had reported to proceed from water under visible-light irradiation in the presence of sacrificial reagents [17]. Since Wang and co-workers first reported polymeric graphitic carbon nitride (g-C_3N_4) as a novel photocatalyst that exhibited photoactivity for H_2 production under visible-light irradiation [18], many efforts have been made to synthesize g-C_3N_4 through thermal treatment of some nitrogen-rich organic precursors, such as cyanamid, dicyanamide, triazine and heptazine derivatives [19–26]. Band gap and flat-band potential of g-C_3N_4 were reported to be 2.67 eV and −1.42 V, respectively (versus Ag/AgCl, pH 6.6) [27]. Although, oxidation ability of g-C_3N_4 is low enough for efficient oxidation of water, it has high reduction ability because of the high conduction band potential. Moreover, g-C_3N_4 can be synthesized by a simple and low-cost route and it has relatively high stability under light irradiation in water solution as well as in acid or base solutions due to the strong covalent bonds between carbon and nitride atoms [28]. g-C_3N_4 photocatalysts are mainly applied to pollutant degradation or H_2 production, and there are only a few reports on the application to photocatalytic CO_2 reduction. Very recently, Dong and coworkers reported that g-C_3N_4 can reduce CO_2 to CO in the presence of water vapor under visible-light irradiation [29]. In addition, Mao et al. [30] directly heated urea or melamine to produce two kinds of g-C_3N_4 photocatalysts that can reduce CO_2 to methanol and ethanol. However, as mentioned above, the photocatalytic activity of g-C_3N_4 for CO_2 reduction is relatively low in most cases because of low efficiency of the counter reaction, which is oxidation of water. In order to overcome this problem, we focused on a hybrid of two semiconductors to improve photocatalytic activity for CO_2 reduction under visible-light irradiation. Some studies have suggested that a charge transfer with charge separation model [31–34] or Z-scheme model [18,35,36] proceeds at the interface between two kinds of semiconductors in a hybrid photocatalyst, resulting in an increase in photocatalytic activity.

In this study, we hybridized g-C_3N_4 with WO_3, which are specialized for reduction of CO_2 and for oxidation of water, respectively. WO_3 is known to exhibit visible-light absorption and show photocatalytic activity for oxidation of organic compounds or water under visible light [37–39]. Recently, there have been several reports on hybrids of g-C_3N_4 with TiO_2 [40], TaON [41], and poly(3-hexylthiophene) [42]. However, a charge separation mechanism was employed in these photocatalysts and explanation of the mechanism was not sufficient. In the present study, we also elucidated the reaction mechanism of the hybrid photocatalyst using DB-PAS measurement.

Experimental

Materials

g-C_3N_4 powders were prepared by heat treatment of melamine (Wako Pure Chemical Industries, Ltd., 99%). Thirty grams of melamine in an alumina pot was heated at 550 °C for 4 h with a temperature rising rate of ca. 9 °C min^{-1} in a muffle furnace [43]. WO_3, silver nitrate, deuterium oxide, and chloroauric acid were purchased from Wako Pure Chemical Industries, Ltd. $^{13}CH_3OH$ was obtained from ISOTEC. Other chemicals were obtained from commercial sources as guaranteed reagents and were used without further purification.

Preparation of hybrid photocatalysts

g-C_3N_4 and WO_3 were hybridized in appropriate ratios between 100:0 and 0:100 (wt:wt) by a planetary mill method. The samples which were prepared in g-C_3N_4 and WO_3 at the ratio of 1:2, 1:1 and 2:1 with a planetary mill, were referred to GW12, GW11 and GW21, respectively. Hybrid photocatalysts of WO_3 and g-C_3N_4 at the ratio of 1:1 were also prepared by an agate mortar method and sonication method. For the agate mortar method, two kinds of powders were ground by an agate mortar for ca. 20 min. For the sonication method, two kinds of powders were suspended in 20 mL of ion-exchanged water by sonication for 30 min and subsequently stirred for 3 h. Then the sample was separated by filtration, washed with ion-exchanged water several times, and dried in a vacuum drying oven at 60 °C overnight. For the planetary mill method, 1.5 g of each kind of powders and 20 mL of ion-exchanged water were added to a 50 mL agate bowl containing 50 g of yttrium-stabilized zirconia grinding beads (Nikkato Co., Ltd., $\Phi = 0.6$ mm). Then the bowl was placed on a planetary mill (Fritsch Japan Co., Ltd., Planetary Micro Mill pulverisette 7) and the planetary mill was operated at 750 rpm for 10 min. After removing the beads by screening, the sample was separated by filtration, washed with ion-exchanged water several times, and dried in a vacuum drying oven at 60 °C overnight. Denotation of samples names and the hybrid methods are summarized in Table 1.

Au or Ag co-catalyst-loaded hybrid photocatalysts (co-catalysts mainly deposited on g-C_3N_4)

For preparation of Au loaded hybrid photocatalysts, we used a photodeposition method as follows. Firstly, a hydrogen tetrachloroaurate(III) was dissolved in 50 mL of iron-exchange water. Secondly, g-C_3N_4 particles (500 mg) were suspended in 50 mL of an ethanol aqueous solution (10 vol%) containing an appropriate amount Au precursor and the solution was applied ultrasonic treatment for 10 min. After N_2 bubbling for 30 min, an aqueous suspension was irradiated by using light-emitting diode (Nichia, NCCU033) at a wavelength of ca. 365 nm and an intensity of 0.3 mW cm^{-2} for 24 h with vigorous magnetic stirring. For photodeposition of Ag, an aqueous suspension consisting of g-C_3N_4 particles (500 mg) and 50 mL of ion-exchanged water containing an appropriate amount of silver nitrate was photoirradiated under the same conditions. After irradiation, photodeposited samples were obtained by filtration, washing with ion-exchanged water several times, and drying in a vacuum drying oven at 60 °C overnight. The net amounts of Au and Ag compounds on the surface of g-C_3N_4 were estimated by analysis of the filtrate with inductively coupled plasma optical emission spectroscopy (ICPOES; Shimadzu, ICPS-8000). ICP analysis revealed that the net molar amounts of Au and Ag compounds photodeposited on g-C_3N_4 were more than 99% of the provided molar amounts of Au and Ag. Co-catalyst-loaded hybrid photocatalysts composed of WO_3 and Au or Ag-loaded g-C_3N_4 at the ratio of 2:1 were also prepared by the planetary mill.

Characterization of prepared samples

Crystal structures of the particles were confirmed by using an X-ray diffractometer (Rigaku, MiniFlex II) with Cu Kα radiation ($\lambda = 1.5405$ Å). A diffuse reflectance spectrum was measured using a UV–vis spectrophotometer (Shimadzu, UV-2550 and 2600)

Table 1
Abbreviations and S_{BET} of hybrid photocatalyst prepared by three kinds of process and their original compound.

Name	Sample	Treatment	S_{BET} ($m^2 g^{-1}$)
g-C_3N_4	g-C_3N_4	No treatment	10
WO_3	WO_3	No treatment	7
Milled g-C_3N_4	g-C_3N_4	Planetary mill	21
Milled WO_3	WO_3	Planetary mill	10
a-CW	g-C_3N_4, WO_3	Agate mortar	8
s-CW	g-C_3N_4, WO_3	Sonication	8
p-CW	g-C_3N_4, WO_3	Planetary mill	17