



Hydrogen bonds in heterojunction photocatalysts for efficient charge transfer



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ABSTRACT

A hydrogen bond-based heterojunction photocatalyst, g-C₃N₄/melamine-cyanurate (gMC), was synthesized by a facile alkaline hydrothermal approach. The hydrogen bonds between the two substrates (N–HO=C) provide not only an ultrafast pathway (hundreds of femtoseconds) but also an inner electric field for hole transfer from g-C₃N₄ to melamine-cyanurate. Although only the g-C₃N₄ moiety acts as a photocatalyst, the optimized composite presents approximately 5.4, 3 and 2.5 times higher photocatalytic activity than bulk g-C₃N₄ in the decomposition of acetaldehyde and 2-propanol and the generation of H₂ by water splitting, respectively. In this paper, we demonstrate that hydrogen bonds can not only lower the interfacial barrier and separate redox sides but also control the direction of charge transfer, which enables the design of the photocatalytic mechanism.

1. Introduction

The development of heterojunction composite photocatalysts is one of the most effective ways to harvest energy from the visible-light region and to improve the photocatalytic activity [1–3]. The interfacial barrier between two substances in a heterojunction photocatalyst is the bottleneck for charge transfer, both in the Z-scheme and charge separation mechanisms, which are most used in heterojunction photocatalysis. The van der Waals force is not strong enough at such distance to lower the interfacial barrier to efficiently transfer charge. Several strategies have been reported to lower the interfacial barrier, such as loading noble metals or graphene between two substances [4,5], the formation of p-n heterojunctions [6], and the introduction of ions in solution as a redox agent [7].

Here, we present a novel method to lower the interfacial barriers, namely, through hydrogen bonding. Hydrogen bonding is a type of force with a strength between the van der Waals force and a chemical bond that widely exists in nature [8]. Research into hydrogen bonding can be easily found in many branches of science [9]. Although electron transfer through a hydrogen bond in a single DNA base pair and a better conduction in a hydrogen bond as compared to that in a covalent σ bond have been reported [10,11], very limited reports about the hydrogen bonding can be found in photocatalysis until recently [12,13].

These reports have examined the hydrogen bonds between the photocatalyst and organic compounds (such as benzylalcohol) to explain the mechanism of the improved photocatalytic activity of photodecomposition. Since many new types of strong and unconventional hydrogen bonds have been identified in the liquid phase as well as the solid state [8,14], the aim of this study is to suggest a hydrogen bond is perhaps an excellent constitution for development of composite photocatalysts.

Melamine-cyanurate (MC) contains oxygen in its frame and is constituted by melamine and cyanuric acid. MC is commonly used as a precursor for synthesizing g-C₃N₄ samples with unique architecture, such as hollow spheres, sheets and tubes [15,16].

In this paper, we report a facile hydrothermal method and the successful synthesis of g-C₃N₄/melamine-cyanurate (gMC), which has high photocatalytic activity towards the photodecomposition of gaseous organics as well as water splitting for H₂ generation under visible-light irradiation. gMC reveals a higher photocatalytic activity than bulk g-C₃N₄ under visible-light irradiation, although it has a low specific surface area and a blueshifted light absorption. In the gMC complex, the hydrogen bonds between g-C₃N₄ and melamine-cyanurate play a key role in the improvement of the photocatalytic activity. The two ends of the N–HO=C hydrogen bonds provide the driving force for the transfer of photoexcited electrons from MC to g-C₃N₄. This behavior is

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analogous to Z-scheme, in which photoexcited holes transfer from the valence band to a deeper band. Moreover, since the oxidation site changes from the nitrogen of $g\text{-C}_3\text{N}_4$ to the oxygen of melamine-cyanurate, the redox sites are separated, which reduces the recombination of photoexcited electrons and holes.

2. Experimental procedures

2.1. Materials

Melamine (Wako Pure Chemical Industries, Ltd.), ammonia solution (25%) (Wako Pure Chemical Industries, Ltd.), dimethyl sulfoxide (DMSO) (Wako Pure Chemical Industries, Ltd.) and cyanuric acid (98%) (Sigma-Aldrich) were used as received without further treatment.

2.2. Characterization

Characterization was performed by using an X-ray diffractometer (Rigaku, MiniFlex II) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Morphology of the prepared samples were observed by a field emission scanning electron microscope (FE-SEM; JEOL, JSM-6701FONO) and a transmission electron microscopy (TEM; Hitachi H-9000NAR). Diffuse reflectance spectra (DRS) were measured using a UV-vis spectrophotometer (Shimadzu, UV-2600) equipped with an integrating sphere unit (Shimadzu, ISR-2600 Plus). Specific surface area (S_{BET}) and porosity/volume were determined with a surface area analyzer (Quantachrome, Nova 4200e) by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) method. Functional group vibrations were confirmed by using a Fourier transform infrared spectrometer (FTIR; JASCO, FT/IR 4200) with a diffuse reflectance accessory (JASCO, DR-81), and the in-situ FTIR was performed by FTIR (VERTEX 70v) with a high temperature and pressure cell (Specac). Fluorescence spectrophotometer (Edinburgh Instruments FLS-920; 365 nm as incident light source) was used to determine photoluminescence and the time-resolved fluorescence decay. Surface chemical states were investigated by X-ray photoelectron spectroscopy (XPS) measurement with Thermo Scientific ESCALAB 250Xi system by Al K α radiation and adventitious C1s peak (284.6 eV) as the reference. Fluorescence spectrophotometer (Edinburgh Instruments FLS-920; 405 nm as incident light source) was used to determine photoluminescence and the time-resolved fluorescence decay. Thermogravimetric (TG) analysis was measured by using Rigaku TG-TDA-8120H. Solid-state NMR studies were performed with a Bruker AvanceII spectrometer operating at 400 MHz ^1H Lamor frequency. The ^1H spectra were recorded using a standard Bruker 4 mm double-resonance MAS probe. The samples were rotated with a spinning frequency of 14 kHz. For ^1H single pulse MAS experiments, the 900 pulse length was 2.5 μs , and the recycle delay was 25 s.

2.3. Synthesis of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{melamine-cyanurate}$ and melamine-cyanurate

$g\text{-C}_3\text{N}_4$ powders were synthesized by heating 30 g of melamine at 823 K with a heating rate of 9 K min^{-1} and kept for 4 h. The products were collected and grounded into powders. The sample is denoted as bulk $g\text{-C}_3\text{N}_4$.

$g\text{-C}_3\text{N}_4/\text{melamine-cyanurate}$ was synthesized by hydrothermal treatment of $g\text{-C}_3\text{N}_4$ in alkaline solution as follows. Ammonia solution (Wako 25%, 2 ml, 5 ml and 10 ml) was added in 50 ml deionized-water, respectively. One gram of $g\text{-C}_3\text{N}_4$ was dispersed in above solution by ultrasonication for 10 min and stirring of 1 h. Then it was heated in Teflon-lined autoclave at $200 \text{ }^\circ\text{C}$ for 6 h. Light yellow powder was obtained after filtration and evaporation. The samples were denoted as gMC2, gMC5 and gMC10 corresponding to the added volume of ammonia solution 2 ml, 5 ml and 10 ml, respectively.

Melamine-cyanurate was fabricated as follows. Five hundred

milligram of melamine and 500 mg of cyanuric acid were dissolved in 20 ml and 10 ml of dimethyl sulfoxide, respectively, with sonication. Both solutions were mixed together for 10 min to give white precipitates. Subsequently, the sample was filtered and washed with ethanol several times, followed by evaporation.

2.4. Performance analysis

2.4.1. Photodecomposition of acetaldehyde and 2-propanol

Before evaluation of the photocatalytic activity, each sample was irradiated with UV light using black light (UVP, XX-15BLB) in order to remove organic contaminants on the sample. The photocatalytic activity of the sample was evaluated by CO_2 liberation from photodecomposition of acetaldehyde. One hundred milligrams of powder, which has complete extinction of incident radiation, was spread on the bottom of glass dish, and the glass dish was placed in a Tedlar bag (AS ONE Co. Ltd.). Then 125 cm^3 artificial air containing 500 ppm of acetaldehyde was injected into the bag. Photoirradiation was performed at room temperature after the acetaldehyde had reached adsorption equilibrium. A light-emitting diode (LED; Epitex, L435-30M32L, ca. 435 nm, 3.0 mW cm^{-2}) was used as a light source. The concentrations of acetaldehyde and CO_2 were collected by on-line gas chromatography (Agilent Technologies, 3000A Micro-GC, TCD detector) equipped with OV1 and PLOT-Q columns as a function of irradiation time. Photodecomposition of 2-propanol was evaluated by the same procedure as acetaldehyde.

2.4.2. Photocatalytic hydrogen generation from water splitting

The photocatalytic activities were evaluated by photocatalytic generation of H_2 from water splitting with $\lambda \geq 420 \text{ nm}$ light (Xenon lamp, CEAULIGHT, CEL-HXF300; optical filter CEAULIGHT, CEL-UVIRCUT420). Reactions were carried out in a Pyrex top-irradiation reaction vessel connected to a closed glass gas system (CEAULIGHT, CEL-SPH2N). Typically, 10 mg of samples were dispersed in 100 ml deionized water, which contains 10 vol % of triethanolamine (TEOA) and 3 wt% (respect to Pt) $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. The solution was irradiated by the light with the intensity of 100 mW cm^{-2} after the air was completely removed in the system. The temperature of the solution was maintained at $12 \text{ }^\circ\text{C}$. The evolved gases were analyzed by gas chromatography (CEAULIGHT, GC-7920) using N_2 as the carrier gas.

2.4.3. Photoelectrochemical measurements

The sample was fabricated on FTO substrates by an electrophoresis method. 10 mg of the sample and a spot of iodine were ultrasonically dispersed in 20 ml acetone solution. Two FTO conducting glasses were placed in the solution as the anode and the cathode. A bias of 15 V was applied between two electrodes using a direct current power supply for 3 min (3 times). Sample loaded FTO was then dried. Linear sweep voltammetry and chronoamperometry measurements were carried out by using an automatic polarization system (HSV-100, Hokuto Denko Co.) with a three-electrode system, in which the prepared electrode, a Pt and a Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively. 0.5 M Na_2SO_4 solution was used as the electrolyte. The light source was an AM 1.5 G solar-simulated system (PEC-L15, Peccell Tech., Inc.). The light intensity of the solar-simulated light was adjusted to 100 mW cm^{-2} by utilizing a thermopile power meter (ORION-TH). The linear sweep voltammogram (LSV) was scanned in the anodic direction at a scan rate of 10 mV s^{-1} .

3. Results and discussion

Direct evidence for the formation of MC can be confirmed in the XRD patterns and FTIR spectra shown in Fig. 1a and b. It can be determined that with a higher concentration of ammonia solution, both the XRD patterns and FTIR spectra become more similar to that of MC. Fig. 1a shows the XRD patterns of the samples. After hydrothermal

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