



Decomposition of methyl orange using C₆₀ fullerene adsorbed on silica gel as a photocatalyst via visible-light induced electron transfer

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ABSTRACT

Visible-light induced electron transfer reactions of C₆₀ fullerene adsorbed on silica gel (C₆₀/SiO₂ powder) to methyl orange in water have been studied. The C₆₀/SiO₂ powder was simply prepared by mixing a toluene solution of the C₆₀ fullerene with silica gel followed by evaporating the toluene. Irradiation by visible light (>420 nm) of the methyl orange aqueous solution (25 μM) in the presence of the C₆₀/SiO₂ powder and ascorbic acid resulted in the decomposition of the methyl orange. These results showed that the degradation conversion reached 96% after a 25-min visible light irradiation. The reaction also occurred by the irradiation of sunlight. The reductive products of methyl orange, *N,N*-dimethyl-*p*-phenylenediamine and sulfanilic acid, were ascertained and monitored by liquid chromatography/mass spectrometry (LC/MS). The reaction did not occur in the dark and in the absence of C₆₀/SiO₂ or ascorbic acid. The possible mechanism of the reaction is discussed. Furthermore, the C₆₀/SiO₂ powder was applied to a continuous flow system for the photodecomposition of methyl orange. C₆₀/SiO₂ powder was packed in a glass tube. The methyl orange solution was pumped into the glass tube, and the tube was irradiated by visible light or sunlight. The continuous decomposition of methyl orange was achieved by this method.

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1. Introduction

C₆₀ fullerene has attracted special interest since its structure and properties are very unique [1,2]. In particular, the photoreactivity of C₆₀ fullerene has received much attention because of its electron acceptability and broad absorbance in visible light region [3–5]. Intensive studies using C₆₀ fullerene as a photocatalyst have been reported [6–9]. However, there are very few studies on the photoreaction of fullerene in water, because the compound shows a very low solubility in water (the aqueous solubility of C₆₀: 2.6–8.0 ng/L) [10].

It is very important for aquatic conservation to develop a visible-light induced reaction system, which can be applied to the decomposition of chemicals in water. There are several examples about the photoreaction of pollutants using C₆₀ derivatives by the irradiation of visible light [11]. However, there are very few examples of useful reactions for water clean-up using C₆₀ as a photocatalyst to the best of our knowledge [12].

In this report, we describe a novel photoreaction of methyl orange using C₆₀ fullerene adsorbed on silica gel (C₆₀/SiO₂) and ascorbic acid via visible-light induced electron transfer. The surface of fullerene is hydrophobic, and C₆₀ powder cannot disperse in an aqueous solution without several treatments, such as the evaporation of the tetrahydrofuran (THF)/water solution of C₆₀ and hydroxylation of the surface [13,14]. C₆₀ adsorbed on silica gel powder could disperse using a stirrer in the aqueous solution.

It has been reported that C₆₀ adsorbed onto silica gel acts as a photocatalyst for the oxidation of olefins in acetonitrile [15,16]. However, to the best of our knowledge, there are no examples that C₆₀ adsorbed onto silica gel has been applied to a visible light-activated photocatalyst for the decomposition of environmental pollutants in water. In addition, the photo-degradation of furfuryl alcohol in water by C₆₀ immobilized on silica gel by amine–fullerene covalent binding has been reported [12]. It is well-known that the functional groups of fullerene affect the redox potential and reactivity of fullerene [17], and the photoreactivity of fullerene without functional groups in water has aroused considerable interest.

Methyl orange is one of the azo dyes, and it has been widely used as a model compound for the research of photoreactions [18]. Many

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researchers have reported the decomposition of methyl orange using TiO_2 as a photocatalyst under ultraviolet irradiation [19–21]. However, there are few examples concerned with the decomposition of methyl orange by visible light irradiation [22]. In this study, we discuss the utility and mechanism of the degradation of methyl orange using $\text{C}_{60}/\text{SiO}_2$ as a visible light-activated photocatalyst. Furthermore, the $\text{C}_{60}/\text{SiO}_2$ powder was used in a continuous flow system for the photodecomposition of methyl orange with the objective to apply the photoreaction to water clean-up technology.

2. Experimental

2.1. Materials

C_{60} fullerene was obtained from SES Research (TX, USA). Methyl orange, ascorbic acid, acetonitrile (HPLC grade), 2-propanol, *tert*-butyl alcohol, acetic acid, ammonium acetate, sulfanilic acid, SiO_2 for column chromatography (particle diameter: 20–40 μm), *N,N*-dimethyl-*p*-phenylenediamine, and prophan- $^{13}\text{C}_3$ were from Wako Pure Chemical Industries (Osaka, Japan). Toluene (HPLC grade) was obtained from Nacalai Tesque (Kyoto, Japan). Sodium dodecyl- d_{25} sulfate was obtained from CDN isotopes (Quebec, Canada). TiO_2 (JRC-TIO-4 (2)) was from AEROSIL (Tokyo, Japan).

Pure water was prepared using an automatic water distillation apparatus (MQ academic A10, Millipore, Billerica, MA, USA).

2.2. Preparation of the $\text{C}_{60}/\text{SiO}_2$ powder

The $\text{C}_{60}/\text{SiO}_2$ powder was prepared by a simple method using a rotary evaporator. The SiO_2 powder (1.0 g) was poured into the C_{60} toluene solution (30 mL, 133 $\mu\text{g mL}^{-1}$), and toluene was removed using a rotary evaporator. The obtained yellow powder was freeze-dried. In order to remove the fullerene, which is not steadily adsorbed on the silica gel, the powder was mixed with distilled water (40 mL) for 30 min followed by filtration, and freeze-dried again. The concentration of C_{60} adsorbed on the $\text{C}_{60}/\text{SiO}_2$ powder was determined by the toluene extraction. The absorbance of the extract was measured at 330 nm ($\log \epsilon = 4.38$ at 330 nm) [23]. As a result, 1.7 mg of C_{60} was adsorbed onto 1.0 g of the SiO_2 powder. When the powder (100 mg) was stirred in distilled water (10 mL) for 1 h, C_{60} was not detected in the supernatant ($<0.01 \mu\text{g/mL}$). This result indicated that desorption of C_{60} from the powder does not occur by mixing in aqueous solutions. The $\text{C}_{60}/\text{SiO}_2$ powder was investigated using a transmission electron microscope (JEM-2100, JEOL, Tokyo, Japan) and Raman microscope (inVia Reflex/StreamLine Plus 532/785, Renishaw, UK). The material was kept in the dark at room temperature, and used within a month of its production.

2.3. Preparation of the aqueous suspension of the nanoparticles of C_{60}

Deguchi et al. reported that the nanoparticles of C_{60} were obtained by hand-grinding the bulk solid of C_{60} fullerene [24]. We prepared a suspension of the nanoparticles of C_{60} obtained by hand-grinding. The hand-ground powder of C_{60} (20 mg) was mixed with distilled water (20 mL). The mixture was then sonicated and filtered using a membrane filter with the pore size of 0.45 μm (Millipore Corporation, Bedford, USA). The obtained suspension (C_{60} concentration, 5.6 $\mu\text{g mL}^{-1}$) was used as a photocatalyst. The particle size distribution of C_{60} in the suspension was measured by a dynamic light scattering method using Zetasizer Nano Series (Malvern Instruments Limited, Worcestershire, UK).

2.4. Photoreaction of methyl orange in the presence of the $\text{C}_{60}/\text{SiO}_2$ powder

Irradiation of the methyl orange aqueous solution (25 μM , 10 mL) containing ascorbic acid (0.50 mM) and the $\text{C}_{60}/\text{SiO}_2$ powder (20 mg) was carried out under an air or nitrogen atmosphere (N_2 bubbling: 10 min) with a xenon lamp (300 W cm^{-2}) through a filter ($>420 \text{ nm}$, L42, Hoya, Tokyo, Japan). The pH value of the solution was 4. The $\text{C}_{60}/\text{SiO}_2$ powder was dispersed in the reaction liquid by a stirrer bar during the photoreaction.

To investigate the reusability of the $\text{C}_{60}/\text{SiO}_2$ powder, the photodecomposition of methyl orange in water using the same $\text{C}_{60}/\text{SiO}_2$ powder was repeated. The suspension after the photoreaction was centrifuged (3000 rpm, 3 min), and the supernatant was removed from the tube and analyzed. The residue was mixed with the methyl orange aqueous solution in the presence of ascorbic acid, and irradiated again.

The reaction liquid was centrifuged at 3000 rpm for 3 min, and the UV spectrum of the obtained supernatant was analyzed by a UV absorption spectrometer (V-630, JASCO Corporation, Tokyo, Japan). The methyl orange concentration was analyzed by measuring its absorbance at 500 nm. The molar absorbance coefficient ϵ_{m} of the calibration curve was $3.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at pH 4. After the filtration of the reaction liquid using filter paper (No. 5A, Advantec, Tokyo, Japan), the solution was analyzed by electrospray ionization/mass spectrometry (ESI/MS) in both the positive and negative ion modes and liquid chromatography (LC)/MS for the detection and determination of its products. The reactions using sunlight were studied in the laboratory (Ueda City, Nagano, Japan). The solar radiation was monitored by 5 min by a photometer (TM-207, Tenmars Electronics, Taipei, Taiwan), and the values of the solar radiation in this study were around 600 W m^{-2} .

2.5. Photodecomposition of methyl orange by the continuous flow system

The $\text{C}_{60}/\text{SiO}_2$ column was prepared by putting 300 mg of $\text{C}_{60}/\text{SiO}_2$ powder into a pipette glass (4 mm inner diameter) stuffed with cotton. The length of the column was 2.5 cm. A methyl orange aqueous solution (25 μM) containing ascorbic acid (2.0 mM) was pumped through the $\text{C}_{60}/\text{SiO}_2$ column by a microtube pump (EYELA, Tokyo, Japan) at 0.70 mL min^{-1} . The solution was held in the column for 35 s. Irradiation of the column was carried out by a xenon lamp or sunlight. The eluent from the column was sampled and analyzed by UV absorption, ESI/MS and LC/MS.

2.6. ESI/MS analysis

The filtered sample solutions were analyzed by ESI/MS in the positive and negative ion modes. An LC/MS 2010 A mass spectrometer (Shimadzu, Kyoto, Japan) was used for the ESI/MS measurement. ESI/MS conditions were: scan range, m/z 50–500; heat block temperature, 200 °C; interface voltage, 4.5 kV; CDL voltage, 20 V. The solutions (10 μL) were injected into the LC/MS system, and the flow rate of the mobile phase (acetonitrile) was 0.20 mL min^{-1} .

2.7. LC/MS analysis

The filtered reaction solutions were analyzed using the LC/MS technique. The LC/MS 2010A was also used for the LC/MS measurement. An L-column ODS (Chemicals Evaluation and Research institute, Tokyo, Japan: 3 μm particle size, $2.1 \times 150 \text{ mm i.d.}$) was used for the LC separation of the substrate and its products. The HPLC separation was carried out at 40 °C using a gradient composed of solution A (1.0 mM ammonium acetate solution) and solvent B (acetonitrile). The gradient conditions were as follows:

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