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Decomposition of methyl orange using C_{60} fullerene adsorbed on silica gel as a photocatalyst *via* visible-light induced electron transfer

Ryo Wakimoto[a], Tamako Kitamura[a],

Fuyu Ito[b], Hisanao Usami[c], Hiroshi Moriwaki[a]*

[a] *Shinshu University, Faculty of Textile Science and Technology, Division of Applied Biology, 3-15-1,*

Tokida, Ueda 386-8567, Japan, E-mail: moriwaki@shinshu-u.ac.jp

[b] *Satellite Venture Business Laboratory, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567,*

Japan

[c] *Shinshu University, Faculty of Textile Science and Technology, Division of Chemistry and Materials,*

3-15-1, Tokida, Ueda 386-8567, Japan

E-mail: moriwaki@shinshu-u.ac.jp

Tel: 81(0)268-21-5333

Fax: 81(0)268-21-5331

19   **Abstract**

20   **Visible-light induced electron transfer reactions of C_{60} fullerene adsorbed on silica gel**

21   **(C_{60}/SiO_2 powder) to methyl orange in water have been studied. The C_{60}/SiO_2 powder was**

22   **simply prepared by mixing a toluene solution of the C_{60} fullerene with silica gel followed by**

23   **evaporating the toluene. Irradiation by visible light (>420 nm) of the methyl orange aqueous**

24   **solution (25 μM) in the presence of the C_{60}/SiO_2 powder and ascorbic acid resulted in the**

25   **decomposition of the methyl orange. These results showed that the degradation conversion**

26   **reached 96% after a 25-min visible light irradiation. The reaction also occurred by the**

27   **irradiation   of   sunlight.   The   reductive   products   of   methyl   orange,**

28   ***N,N*-dimethyl-*p*-phenylenediamine and sulfanilic acid, were ascertained and monitored by**

29   **liquid chromatography/mass spectrometry (LC/MS). The reaction did not occur in the dark**

30   **and in the absence of C_{60}/SiO_2 or ascorbic acid. The possible mechanism of the reaction is**

31   **discussed. Furthermore, the C_{60}/SiO_2 powder was applied to a continuous flow system for the**

32   **photodecomposition of methyl orange. C_{60}/SiO_2 powder was packed in a glass tube. The methyl**

33   **orange solution was pumped into the glass tube, and the tube was irradiated by visible light or**

34   **sunlight. The continuous decomposition of methyl orange was achieved by this method.**

35   **Keywords: fullerene, C_{60} fullerene adsorbed on silica gel, photoinduced electron-transfer,**

36   **visible light, methyl orange**

1. Introduction

C_{60} fullerene has attracted special interest since its structure and properties are very unique [1,2]. In particular, the photoreactivity of C_{60} fullerene has received much attention because of its electron acceptability and broad absorbance in visible light region [3-5]. Intensive studies using C_{60} 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 C_{60}: 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 C_{60} derivatives by the irradiation of visible light [11]. However, there are very few examples of useful reactions for water clean-up using C_{60} as a photocatalyst to the best of our knowledge [12].

In this report, we describe a novel photoreaction of methyl orange using C_{60} fullerene adsorbed on silica gel (C_{60}/SiO_2) and ascorbic acid *via* visible-light induced electron transfer. The surface of fullerene is hydrophobic, and C_{60} powder cannot disperse in an aqueous solution without several treatments, such as the evaporation of the tetrahydrofuran (THF) /water solution of C_{60} and hydroxylation of the surface [13-14]. C_{60} adsorbed on silica gel powder could disperse using a stirrer in the aqueous solution.

55   It has been reported that C_{60} adsorbed onto silica gel acts as a photocatalyst for the oxidation of

56   olefins in acetonitrile [15-16]. However, to the best of our knowledge, there are no examples that C_{60}

57   adsorbed onto silica gel has been applied to a visible light-activated photocatalyst for the

58   decomposition of environmental pollutants in water. In addition, the photo-degradation of furfuryl

59   alcohol in water by C_{60} immobilized on silica gel by amine-fullerene covalent binding has been

60   reported [12]. It is well-known that the functional groups of fullerene affect the redox potential and

61   reactivity of fullerene [17], and the photoreactivity of fullerene without functional groups in water

62   has aroused considerable interest.

63   Methyl orange is one of the azo dyes, and it has been widely used as a model compound for the

64   research of photoreactions [18]. Many researchers have reported the decomposition of methyl orange

65   using TiO_2 as a photocatalyst under ultraviolet irradiation [19-21]. However, there are few examples

66   concerned with the decomposition of methyl orange by visible light irradiation [22]. In this study, we

67   discuss the utility and mechanism of the degradation of methyl orange using C_{60}/SiO_2 as a visible

68   light-activated photocatalyst. Furthermore, the C_{60}/SiO_2 powder was used in a continuous flow

69   system for the photodecomposition of methyl orange with the objective to apply the photoreaction to

70   water clean-up technology.

71

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 propham-$^{13}C_3$ 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 C_{60}/SiO_2 powder

The C_{60}/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 μg 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 C_{60}/SiO_2 powder was determined by the toluene extraction. The absorbance of the extract was

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90   measured at 330 nm (log $\varepsilon = 4.38$ at 330 nm) [23]. As a result, 1.7 mg of C_{60} was adsorbed onto 1.0

91   g of the SiO_2 powder. When the powder (100 mg) was stirred in distilled water (10 mL) for 1 hour,

92   C_{60} was not detected in the supernatant (<0.01 μg/mL). This result indicated that desorption of C_{60}

93   from the powder does not occur by mixing in aqueous solutions. The C_{60}/SiO_2 powder was

94   investigated using a transmission electron microscope (JEM-2100, JEOL, Tokyo, Japan) and Raman

95   microscope (inVia Reflex/StreamLine Plus 532/785, Renishaw, UK). The material was kept in the

96   dark at room temperature, and used within a month of its production.

97   *2.3 Preparation of the aqueous suspension of the nanoparticles of C_{60}*

98   Deguchi et al. reported that the nanoparticles of C_{60} were obtained by hand-grinding the bulk solid of

99   C_{60} fullerene [24]. We prepared a suspension of the nanoparticles of C_{60} obtained by hand-grinding.

100   The hand-ground powder of C_{60} (20 mg) was mixed with distilled water (20 mL). The mixture was

101   then sonicated and filtered using a membrane filter with the pore size of 0.45 μm (Millipore

102   Corporation, Bedford, USA). The obtained suspension (C_{60} concentration, 5.6 μg mL^{-1}) was used as

103   a photocatalyst. The particle size distribution of C_{60} in the suspension was measured by a dynamic

104   light scattering method using Zetasizer Nano Series (Malvern Instruments Limited, Worcestershire,

105   UK).

106   *2.4 Photoreaction of methyl orange in the presence of the C_{60}/SiO_2 powder*

107   Irradiation of the methyl orange aqueous solution (25 μM, 10 mL) containing ascorbic acid (0.50

108   mM) and the C_{60}/SiO_2 powder (20 mg) was carried out under an air or nitrogen atmosphere (N_2

109   bubbling:10 min) with a xenon lamp (300 W cm^{-2}) through a filter (>420 nm, L42, Hoya, Tokyo,

110   Japan). The pH value of the solution was 4. The C_{60}/SiO_2 powder was dispersed in the reaction

111   liquid by a stirrer bar during the photoreaction.

112   To investigate the reusability of the C_{60}/SiO_2 powder, the photodecomposition of methyl orange

113   in water using the same C_{60}/SiO_2 powder was repeated. The suspension after the photoreaction was

114   centrifuged (3000 rpm, 3 min), and the supernatant was removed from the tube and analyzed. The

115   residue was mixed with the methyl orange aqueous solution in the presence of ascorbic acid, and

116   irradiated again.

117   The reaction liquid was centrifuged at 3000 rpm for 3 min, and the UV spectrum of the obtained

118   supernatant was analyzed by a UV absorption spectrometer (V-630, JASCO Corporation, Tokyo,

119   Japan). The methyl orange concentration was analyzed by measuring its absorbance at 500 nm. The

120   molar absorbance coefficient ε_m of the calibration curve was 3.1 x 10^4 L mol^{-1} cm^{-1} at pH 4. After the

121   filtration of the reaction liquid using filter paper (No. 5A, Advantec,Tokyo, Japan), the solution was

122   analyzed by electrospray ionization/ mass spectrometry (ESI/MS) in both the positive and negative

123   ion modes and liquid chromatography (LC)/MS for the detection and determination of its products.

124   The reactions using sunlight were studied in the laboratory (Ueda City, Nagano, Japan). The solar

125   radiation was monitored by 5 min by a photometer (TM-207, Tenmars Electronics, Taipei, Taiwan),

126 and the values of the solar radiation in this study were around 600 W m^{-2}.

127 *2.5 Photodecomposition of methyl orange by the continuous flow system*

128 The C_{60}/SiO_2 column was prepared by putting 300 mg of C_{60}/SiO_2 powder into a pipette glass (4mm

129 inner diameter）stuffed with cotton. The length of the column was 2.5 cm. A methyl orange aqueous

130 solution (25 μM) containing ascorbic acid (2.0 mM) was pumped through the C_{60}/SiO_2 column by a

131 microtube pump (EYELA, Tokyo, Japan) at 0.70 mL min^{-1}. The solution was held in the column for

132 35 sec. Irradiation of the column was carried out by a xenon lamp or sunlight. The eluent from the

133 column was sampled and analyzed by UV absorption, ESI/MS and LC/MS.

134 *2.6 ESI/MS analysis*

135 The filtered sample solutions were analyzed by ESI/MS in the positive and negative ion modes. An

136 LC/MS 2010A mass spectrometer (Shimadzu, Kyoto, Japan) was used for the ESI/MS measurement.

137 ESI/MS conditions were: scan range, *m/z* 50-500; heat block temperature, 200°C; interface voltage,

138 4.5 kV; CDL voltage, 20 V. The solutions (10 μL) were injected into the LC/MS system, and the

139 flow rate of the mobile phase (acetonitrile) was 0.20 mL min^{-1}.

140 *2.7 LC/MS analysis*

141 The filtered reaction solutions were analyzed using the LC/MS technique. The LC/MS 2010A was

142 also used for the LC/MS measurement. An L-column ODS (Chemicals Evaluation and Research

143 institute, Tokyo, Japan: 3 μm particle size, 2.1x150 mm i.d.) was used for the LC separation of the

144   substrate and its products. The HPLC separation was carried out at 40 °C using a gradient composed

145   of solution A (1.0 mM ammonium acetate solution) and solvent B (acetonitrile). The gradient

146   conditions were as follows: 0-5 min, hold at 2.5% B; 5-10 min, a linear increase from 2.5 to 5 % B;

147   10-15 min, a linear increase from 5 to 99 % B; 15-35 min, hold at 99% B. The flow rate was 0.20

148   mL min^{-1}. The ESI conditions were the same as described above. The sample solution (1.0 mL) was

149   mixed with the internal standard methanolic solution (propham-$^{13}C_3$, 100 μg ml^{-1}; sodium

150   dodecyl-d$_{25}$ sulfate, 100 μg ml^{-1}). The LC/MS acquisition was performed in the selected ion

151   monitoring (SIM) mode at *m/z* 137 for *N,N*-dimethyl-*p*-phenylenediamine, *m/z* 172 for sulfanilic

152   acid, *m/z* 187 for propham-$^{13}C_3$ and *m/z* 290 for sodium dodecyl-d$_{25}$ sulfate. The detection limits

153   (S/N 3) were 0.01 and 0.005 μM for *N,N*-dimethyl-*p*-phenylenediamine and sulfanilic acid,

154   respectively. The yields of the products were calculated based on the decomposed methyl orange.

155

156   **3. Results and discussion**

157   *3.1 Characterization of C$_{60}$/SiO$_2$ powder*

158   The C$_{60}$/SiO$_2$ powder was tinged with yellow (Fig. 1a). The diffuse reflectance spectrum is shown in

159   Fig. 1b, and the result showed that the powder has an absorption band in the visible light region

160   (400-700 nm). The Raman spectrum of the C$_{60}$/SiO$_2$ powder was very similar to that of the

161   single-crystal C$_{60}$ (Figure S1) [25]. The strong line at 1468 cm^{-1} assigned to the A$_g$-pinch mode was

162   observed. This result indicated that C_{60} fullerene in the powder adsorbs onto the silica gel without

163   the formation of any covalent bonding.

164   Figure 2 shows a TEM image of C_{60}/SiO_2. Fullerene clusters around 500 nm were observed on

165   the SiO_2. When the electron diffraction pattern of the adhesive cluster was measured,

166   Debye-Scherrer rings were detected (Figure S2). This result suggests that the fullerene cluster on the

167   C_{60}/SiO_2 powder consists of many randomly-aligned micro-crystallites of C_{60}.

168   The average zeta potential of C_{60}/SiO_2 was -9.43 mV at pH 4. This result suggests that the

169   C_{60}/SiO_2 is distributed with a negative charge in water. On the other hand, the zeta potential of SiO_2

170   powder without treatment with C_{60} was -3.3 mV. Snow et al. (2012) reported that negatively-charged

171   C_{60} cluster in aqueous water did not exhibit significant $^1O_2$ production by visible-light irradiation

172   [26]. Therefore, it is expected that $^1O_2$ would not be produced by the C_{60}/SiO_2 powder under

173   visible-light irradiation.

174   *3.2 Photodecomposition of methyl orange in the presence of C_{60}/SiO_2 powder*

175   Methyl orange was not adsorbed by SiO_2 at pH 4. That makes easy to evaluate C_{60}/SiO_2 as a

176   photocatalyst. In addition, SiO_2 does not disrupt the visible light absorption of C_{60}, because SiO_2

177   does not have an absorption band in the visible light region. Therefore, we selected SiO_2 as a support.

178   The irradiation of a methyl orange solution containing the C_{60}/SiO_2 powder and ascorbic acid with a

179   xenon lamp through a filter (> 420 nm) resulted in the de-colorization of the solution due to the

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180   decomposition of methyl orange. Significant changes in the pH of the solution were not observed

181   before and after the photoreaction. Methyl orange was not decomposed by the visible light

182   irradiation without any additives. The photoreaction of methyl orange with C_{60}/SiO_2 in the absence

183   of ascorbic acid also did not occur. The results are summarized in Table 1. Methyl orange was

184   slightly decomposed in the presence of ascorbic acid without C_{60}/SiO_2 by the visible light irradiation

185   (Table 1, entry 2). Photolysis of methyl orange under direct excitation occurred in the presence of

186   ascorbic acid [27]. However, the efficiency of the reaction was significantly low compared to the

187   reaction in the presence of C_{60}/SiO_2 (Table 1, entries 2 and 7).The conversion of methyl orange

188   slightly decreased by the removal of oxygen (Table 1, entries 6 and 8 or entries 7 and 9). The

189   adsorptive removal of methyl orange by the C_{60}/SiO_2 powder was not observed, when 20 mg of the

190   C_{60}/SiO_2 powder was added to 10 mL of a methyl orange solution (25 μM, pH 4) in the presence of

191   ascorbic acid (0.50 mM), and mixed by a magnetic stirrer for 160 min in the dark. In addition,

192   methyl orange was slightly decomposed in the presence of ascorbic acid (2.0 mM) with the C_{60}

193   powder (the average particle diameter: 110 μm, 3.4 mg in 10 mL) by the visible light irradiation. The

194   decomposition of methyl orange was 7.2%. The decomposition (%) was lower than that using the

195   C_{60}/SiO_2 powder. The result is due to the differences of the dispersibility and surface area between

196   the C_{60}/SiO_2 powder and the C_{60} powder.

197   The effect of the ascorbic acid concentration on the decomposition of methyl orange was

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198   observed (Figure S3a). Methyl orange was completely decomposed by the photocatalyst in the

199   presence of ascorbic acid (>2.0 mM) under visible light irradiation for 15 min. The effects of the

200   quantity of the C_{60}/SiO_2 powder on the decomposition (%) of methyl orange was also investigated

201   (Figure S3b). Methyl orange was efficiently decomposed in the presence of the powder (>20 mg/10

202   mL). Based on these results, it was found that the optimum concentrations of ascorbic acid and the

203   C_{60}/SiO_2 powder were 2.0 mM and 20 mg/10mL, respectively.

204   Figure 3 shows the temporal absorption changes of the filtered solution by the photocatalytic

205   process. The plot of -ln C/C_0 versus time shows an approximate linearity, which indicated that the

206   photoreaction of methyl orange with C_{60}/SiO_2 in the presence of ascorbic acid (0.50 mM) fitted a

207   pseudo-first-order kinetic model (-ln C/C_0 =0.0837 t, R^2=0.9949; Fig. 3).

208   The mass spectrum of the filtered solution after the irradiation (15 min) is shown in Figure 4.

209   The product of the photoreaction was assigned to N,N-dimethyl-p-phenylenediamine (**1**) based on

210   ESI/MS and LC/MS measurements. The retention time of the product in the LC/MS measurement in

211   the selected ion monitoring mode (m/z 137) was in agreement with that of the standard sample **1**,

212   therefore, it was concluded that one of the products of this reaction was

213   N,N-dimethyl-p-phenylenediamine. The ion peak at m/z 172 by ESI/MS in the negative ion mode

214   also corresponded to the product of the photoreaction. The peak was assigned to sulfanilic acid

215   (molecular weight: 173). The retention time of the product in the LC/MS measurement in the

216   selected ion monitoring mode (*m/z* 172) was in agreement with that of the standard sulfanilic acid (**2**),

217   and it was concluded that one of the products of this reaction was sulfanilic acid. The yields of **1** and

218   **2** were 88% and 55%, and the conversion of methyl orange was 96% (Table 1, entry **7**). The yield of

219   **2** was low compared to the yield of **1** and the conversion of methyl orange. The result indicates that

220   the product **2** underwent further reactions, and there are several products, which were not detected

221   by ESI/MS. We also measured the filtered reaction solution by ion chromatography. As a result, the

222   formations of NO_2^-, NO_3^-, and SO_4^{2-} were not observed. It is probable that the oxidation of ascorbic

223   acid in the photoreaction results in the formation of dehydroascorbic acid as a similar photoreaction

224   using ascorbic acid as an electron donor [28]. However, when the filtered solution after the

225   photoreaction was injected into ESI source in the positive or negative ion modes, no ions assignable

226   to dehydroascorbic acid were observed (Fig. 4 for the positive ion mode). It is possible that further

227   reactions of dehydroascorbic acid occur and result in the formation of products that are not detected

228   by ESI/MS.

229   The decomposition of methyl orange using the C_{60}/SiO_2 powder as a photocatalyst also occurred

230   by the sunlight irradiation. The decomposition (%) of methyl orange was 97% by the sunlight

231   irradiation for 25 min (Table 1, entry 15).

232   The photodecomposition of methyl orange in water using the same C_{60}/SiO_2 powder was

233   repeated five times to observe the reusability of the C_{60}/SiO_2 powder (Figure S4). The

13

234   decompositions (%) of methyl orange were over 95% and did not significantly decrease throughout

235   the photoreaction cycles (1-5 times). Therefore, the C_{60}/SiO_2 powder can be repeatedly used as a

236   photocatalyst to decompose methyl orange in water. This result suggests the possibility that the

237   powder can be continuously use for a long period as a photocatalyst.

238   *3.3 Photodecomposition of methyl orange in the presence of the C_{60} nanoparticles*

239   We prepared a suspension of the C_{60} fullerene nanoparticles, and studied the potential of the particles

240   as a photocatalyst for the decomposition of methyl orange by visible light irradiation. The adsorption

241   spectrum of the suspension of C_{60} was measured, and the suspension revealed absorption bands in

242   the visible light region (400-700 nm) similar to those of the C_{60}/SiO_2 powder. The size distribution

243   of the C_{60} particle in the suspension was 100-500 nm, and the average diameter was 192 nm. In the

244   case of the visible light irradiation (2 hours) of a methyl orange aqueous solution (4.2 mL)

245   containing the C_{60} nanoparticles (16.8 μg) and ascorbic acid (2.0 mM), the decomposition of the

246   methyl orange was observed. The decomposition (%) of methyl orange was 75%, which was lower

247   than that using the C_{60}/SiO_2 powder as a photocatalyst. This result would be due to the quantity of

248   C_{60} in the reaction system. Product **1** and **2** were also detected in the solution after irradiation, and

249   the yields of **1** and **2** were 100 and 56%, respectively. Based on these results, it is suggested that the

250   photocatalytic reaction using C_{60} nanoparticles is similar to that by the C_{60}/SiO_2 powder, and the

251   efficiency of the photoreaction by C_{60}/SiO_2 is higher than that of C_{60} nanoparticles.

252   *3.4 Mechanism of photodecomposition of methyl orange by the C_{60}/SiO_2 powder*

253   The color of the methyl orange solution turned from orange to red by the addition of ascorbic acid,

254   because methyl orange is protonated by the addition of ascorbic acid and forms the quinoid structure.

255   The protonated methyl orange shows a stronger electron-acceptability compared to the neutral form

256   of methyl orange. Recently, it was reported that methyl orange was decomposed into products

257   containing *N,N*-dimethyl-*p*-phenylenediamine by visible light-irradiated natural sphalerite

258   (conduction band: -1.4 V vs SCE; E_g: 2.95 eV) in the presence of ascorbic acid (the oxidative

259   potential: 0.127 V vs NHE) [28]. The mechanism of the reaction was proposed as follows: methyl

260   orange (the reduction potential: -(0.058 pH) V vs. SCE) was reduced by the excited-state natural

261   sphalerite, and destruction of the azo bond resulted in the formation of **1**.

262   Based on the photoreaction using natural sphalerite and the results from the present

263   photoreaction of the C_{60}/SiO_2 powder, we have proposed a possible mechanism for the photoreaction

264   of methyl orange as shown in Figure 5. The first step is the photoexcitation of the C_{60} fullerene on

265   the surface of the C_{60}/SiO_2 powder. It has been reported that the triplet state of C_{60} fullerene is

266   formed with a quantum yield of 1.0 [29], and it is probable that the excited C_{60} fullerene on the

267   surface of the C_{60}/SiO_2 powder undergoes an intersystem crossing from the singlet to triplet state. In

268   addition, it was reported that $E_{red}(C_{60})$ was -0.42 V (vs SCE, solvent benzonitrile) and $E_S(^1C_{60})$= 1.9

269   eV [29, 30]. The next step is the electron transfer from the excited C_{60} to the protonated methyl

270   orange (quinoid structure) and from ascorbic acid to the excited C_{60}. The radical species of methyl

271   orange undergo bond cleavage to generate the product **1**. The efficiencies of the reaction at pH 6-10

272   were significantly low compared to the reaction at pH 4 (decomposition (%) of methyl orange at pH

273   6 was 4.8%). These results support the proposed mechanism.

274   It has been reported that the irradiation of C_{60} fullerene forms reactive oxygen species in the

275   presence of oxygen [31, 32]. This pathway leads to the electron transfer from donors to the

276   excited-state C_{60}, forming the C_{60} radical anion [29]. Next, the superoxide anion radical ($O_2^{\cdot -}$) can

277   form via O_2 receiving the electron from $C_{60}^{\cdot -}$.

278   The decomposition (%) of methyl orange slightly decreased by the removal of oxygen (Table 1,

279   entries 6 and 8 or entries 7 and 9). This result would be caused by the reaction of methyl orange with

280   the superoxide anion radical formed by electron transfer between the C_{60} radical anion and oxygen.

281   The addition of 2-propanol slightly decreased the decomposition (%) of methyl orange (Table 1,

282   entries 6, 7, 10 and 11). Furthermore, for the addition of *tert*-butylalcohol, the decomposition (%) of

283   methyl orange also decreased (Table 1, entries 6, 7, 12 and 13). These results also indicated that the

284   formation of the superoxide anion radical affects the photodecomposition of methyl orange [33].

285   Recent study has suggested that the photoinduced electron transfer from a photoexcited dye to

286   TiO_2 by the irradiation of visible light lead to the decomposition of the dye [34]. Methyl orange was

287   not decomposed by the visible light irradiation (15 min) of a methyl orange aqueous solution (pH 4)

288   containing C_{60}/SiO_2 in the absence of ascorbic acid. The pH value of the aqueous solution was

289   adjusted by HCl. This result indicates that the photodecomposition of methyl orange is not occurred

290   by only effect of pH change, and the reaction does not proceed without ascorbic acid. Furthermore,

291   methyl orange was not decomposed by the visible light irradiation of a methyl orange solution (pH

292   4) containing TiO_2 in the absence of ascorbic acid. In the case of the irradiation of sunlight (15 min),

293   methyl orange was decomposed by using TiO_2 as a photocatalyst in the absence of ascorbic acid (pH

294   4, decomposition (%): 28.6%). The photodecomposition of methyl orange would be induced by the

295   ultraviolet radiation of sunlight. In addition, an earlier study has shown that mixing TiO_2 with

296   ascorbic acid resulted in the formation of charge-transfer bidenate complex [35].

297   *3.5 Continuous flow system of photodecomposition of methyl orange using C_{60}/SiO_2 packed column*

298   With a aim to apply the C_{60}/SiO_2 powder as the photocatalyst for water clean-up, a continuous flow

299   system for the photoreaction of methyl orange with the C_{60}/SiO_2 powder was studied. Figure 6 is a

300   schematic of the continuous flow system for the photodecomposition of methyl orange by the

301   C_{60}/SiO_2 powder. The conditions for the system, such as the flow rate of the sample solution, and

302   continuous reaction time, were changed, and the changes in the decomposition (%) of methyl orange

303   were investigated.

304   The continuous decolorization of the sample solution was achieved by the visible light

305   irradiation. When the initial concentration of ascorbic acid in the solution was 2.0 mM, the

306   decomposition (%) of methyl orange was around 90% at the flow rate 0.70 mL min^{-1} by the

307   photoreaction for 1 hour. Products **1** and **2** were detected in the solution under the continuous flow

308   condition. The decomposition of methyl orange through the column did not occur in the dark. The

309   mobile phase passed through the column in 35 sec at this flow rate. The continuous decomposition

310   of methyl orange was achieved, because the reaction of methyl orange by photoinduced electron

311   transfer with the C_{60}/SiO_2 powder is very rapid. When the flow rates were 1.1 or 1.4 mL min^{-1}, the

312   decompositions (%) of methyl orange were 88 and 74%, respectively. The decrease in the

313   decomposition (%) of methyl orange compared to the flow rate at 0.70 mL min^{-1} would be due to the

314   insufficient holding time of methyl orange in the column.

315   A similar reaction occurred by the sunlight irradiation (the decomposition (%) of methyl orange:

316   89% at the flow rate 0.80 mL min^{-1}). This result indicated that the present method is useful as a

317   novel water clean-up technology without using fossil energy.

318   **4. Conclusion**

319   The irradiation of visible-light led to the decomposition of methyl orange using C_{60}/SiO_2 powder

320   in the presence of ascorbic acid. The reaction also occurred by the irradiation of sunlight, therefore,

321   indicating that the C_{60}/SiO_2 powder could be used as a novel sunlight-sensitized photocatalyst for the

322   decomposition of pollutants.

323   No additional reactions of the products (**1** and **2**) were observed under the condition described

324 above. The development of the method to mineralize the products is needed together with the

325 establishment of the presented method.

326   In this study, the detachment of C_{60} from the C_{60}/SiO_2 powder was not confirmed. However,

327 there is the possibility that the fullerene cluster is desorbed using the powder for a long time. The

328 toxic effects of fullerene on aquatic organisms have been extensively studied in order to understand

329 its environmental risk when used. For example, Oberdörster reported the toxicity of C_{60} cluster

330 dispersed in water for fish [36]. However, in most of these studies, there is the possibility that the

331 test solution contains a trace amount of THF, which was used for the preparation of the particle, and

332 the residual THF is related to the toxic effects of the C_{60} cluster. In fact, Deguchi et al. reported that

333 C_{60} nanoparticles prepared without THF or other organic solvents revealed no toxic effects on the

334 growth of *E. coli* (the concentration of C_{60} in a nutrient-poor minimal Davis medium: 5 μg mL^{-1} of

335 C_{60} nanoparticle) [24].

336   In order to evaluate the utility of the C_{60}/SiO_2 powder, it is important to study the decomposition

337 of other environmental pollutants by the C_{60}/SiO_2 powder as a photocatalyst. We have already

338 confirmed that methyl red was decomposed by C_{60}/SiO_2 powder under the same condition described

339 above. In addition, further studies on the influences of various environmental matrices on the

340 reaction using the C_{60}/SiO_2 powder are needed. We observed the photodecomposition of methyl

341 orange in seawater using the C_{60}/SiO_2 powder. The sunlight irradiation to a methyl orange seawater

19

342   solution (25 μM) in the presence of the C_{60}/SiO_2 powder (20 mg) and ascorbic acid (5.0 mM)

343   resulted in the decomposition of methyl orange. The decomposition (%) of methyl orange was 93%

344   by the irradiation of sunlight for 10 min.

345   Furthermore, the necessity of ascorbic acid for the reaction is questionable from the viewpoint of

346   water purification because of cost-effectivity and the load of ascorbic acid to environment. The next

347   step in this study is to develop the photoreaction system of the C_{60}/SiO_2 powder using other

348   compounds instead of ascorbic acid as an electron donor.

352

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403

404   <u>Figure captions</u>

405   **Fig.1** a) Photograph and b) diffuse reflectance spectrum of C_{60}/SiO_2 powder.

406   **Fig.2** TEM image of the C_{60}/SiO_2 powder.

407   **Fig.3** UV spectral changes in the degradation of methyl orange by the photocatalytic process. Inset:

408   Pseudo-first order plots of degradation of methyl orange vs. irradiation time. The initial

409   concentrations of methyl orange and ascorbic acid were 25 μM and 0.50 mM, respectively. The

410   sample volume was 10 mL, and the additive amount of the C_{60}/SiO_2 powder was 20 mg.

411   **Fig.4** Mass spectrum of the filtered solution after the photoreaction of methyl orange with C_{60}/SiO_2

412   powder for 15 min (ESI in the positive ion mode). The initial concentrations of methyl orange and

413   ascorbic acid were 25 μM and 0.50 mM, respectively. The sample volume was 10 mL, and the

414   amount of C_{60}/SiO_2 powder was 20 mg.

415   **Fig.5** A possible mechanism for the photodecomposition of methyl orange in the presence of

416   aqueous C_{60} cluster.

417   **Fig.6** An outline of the continuous flow system for the photo-decomposition of methyl orange by the

418   C_{60}/SiO_2 powder.

419

420   **Fig. S1** a) Raman spectrum of the C_{60}/SiO_2 powder. b) Raman spectrum of the C_{60} powder.

421   **Fig. S2** The electron diffraction pattern of the adhesive cluster on the C_{60}/SiO_2 powder.

422   **Fig. S3** a) Effects of ascorbic acid concentration on the decomposition (%) of methyl orange using

423   the C_{60}/SiO_2 powder as a catalyst. The irradiation time was 15 min. The initial concentration of

424   methyl orange was 25 μM. The sample volume was 10 mL, and the additive amount of the C_{60}/SiO_2

425   powder was 20 mg. b) Effects of the quantity of the C_{60}/SiO_2 powder on the photodecomposition of

426   methyl orange. The irradiation time was 15 min. The initial concentrations of methyl orange and

427   ascorbic acid were 25 μM and 0.50 mM, respectively. The sample volume was 10 mL.

428   **Fig. S4** Photodecomposition (%) of methyl orange in water using the same C_{60}/SiO_2 powder (1-5

429   cycles). The initial concentrations of methyl orange and ascorbic acid were 25 μM and 0.50 mM,

430   respectively. The sample volume was 10 mL, and the initial amount of C_{60}/SiO_2 powder was 20 mg.

431

432

433   b)
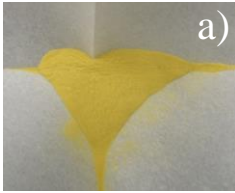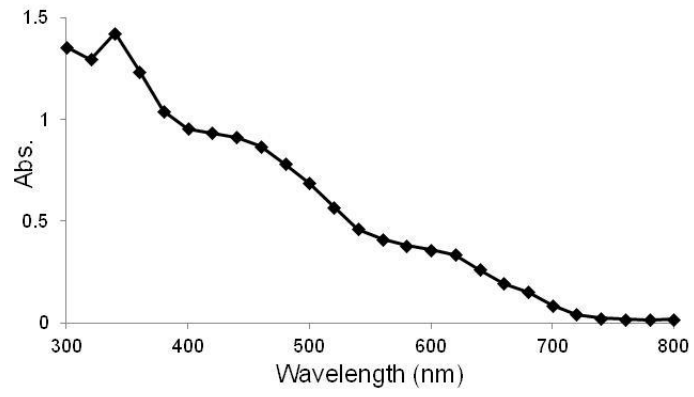
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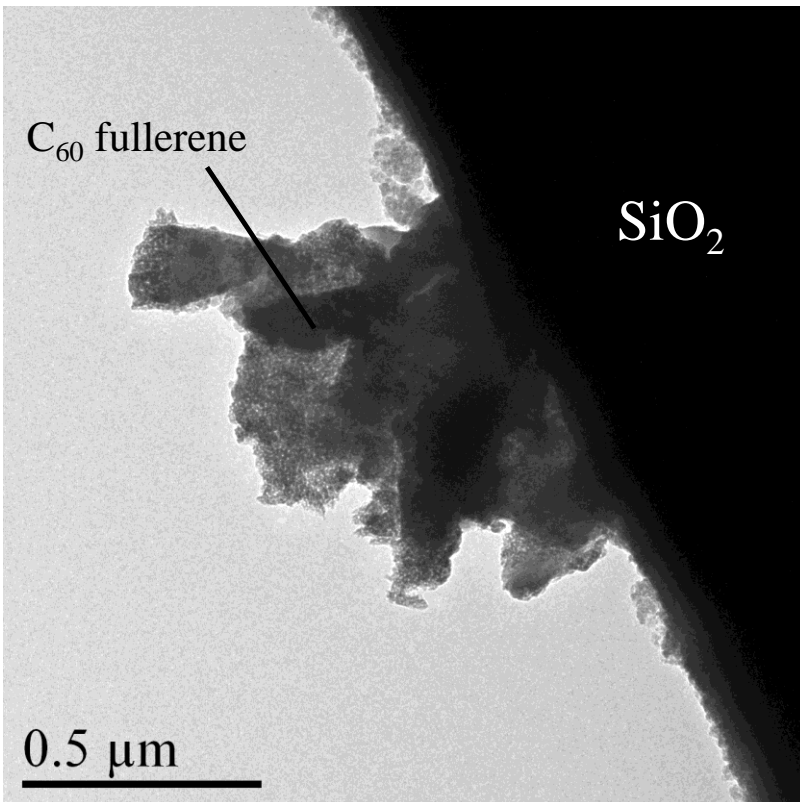439   Fig. 1

440

441

442 C$_{60}$ fullerene

443   SiO$_2$

444

445

446

447

448 0.5 μm

449   Fig. 2

25

450

451

452

453

Abs

454

455

456

457

458

$-\ln (C/C_0) = 0.0837\ t$
$R^2 = 0.9949$

$-\ln (C/C_0)$

Irradiation time (min)

0 min

5 min

10 min
15 min

25 min

30 min

Wave length (nm)

Fig. 3

459

460

461

462

463

464

Peak intensity

137.05

N,N-dimethyl-p-phenylenediamine

methyl orange

63.95 79.95   104.95 122.00   178.05   194.95 221.05   262.00   306.05 316.60   347.05 365.15 385.15   418.90   454.30   485.50

m/z

465

466

Fig. 4

467

468

methyl orange

469

H_3C—N—⟨ ⟩—N=N—⟨ ⟩—SO_3^-

470   ascorbic acid C_{60}/SiO_2

$h\nu$

471 H_3C—$\overset{+}{N}$=⟨ ⟩=N—$\overset{H}{N}$—⟨ ⟩—SO_3^- + C_{60}/SiO_2^*

quinoid structure   electron
transfer

472

methyl orange$^-$· + C_{60}/SiO_2^{+}·

473

Further reactions ← NaO_3S—⟨ ⟩—NH_2 H_2N—⟨ ⟩—N$\overset{CH_3}{\underset{CH_3}{}}$

474   2   1

sulfanilic acid   N,N-dimethyl-p-phenylenediamine

475

P.E.

Visible light

Donor
(ascorbic acid)

C_{60}/SiO_2^*

methyl orange
(quinoid structure)

Fig. 5

476

Visible light
(Sunlight)

477

478

479   C_{60}/SiO_2 powder

Pump

Photo-induced
decomposition
of methyl orange

480

481   Decoloration

Methyl orange
+ ascorbic acid

482

Fig. 6

483

484

485

27

486

487

488

489

490

491

492

493

494

Fig. S1

495

496

497

498

499

500

501

502

Fig. S2

503

a) b)

Fig. S3

98.8   97.6   97.6   96.8   96.4

Fig. S4

29
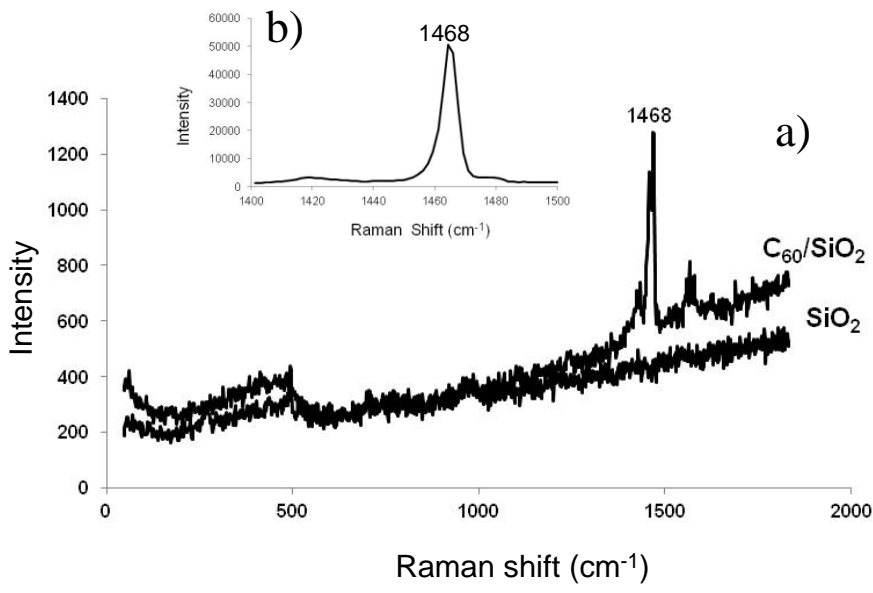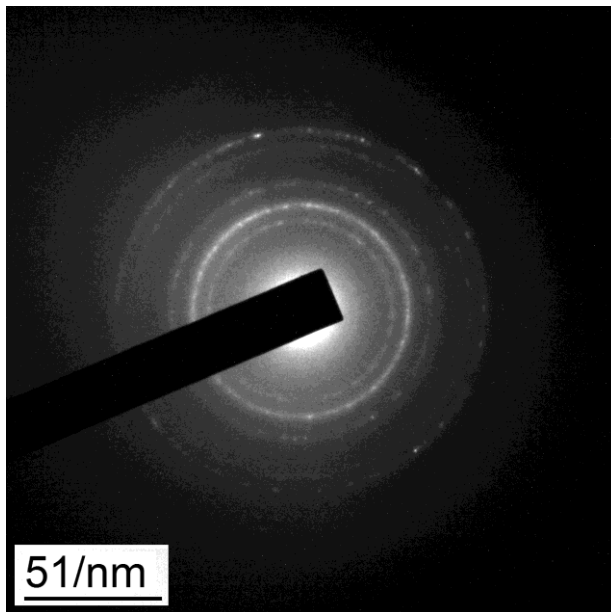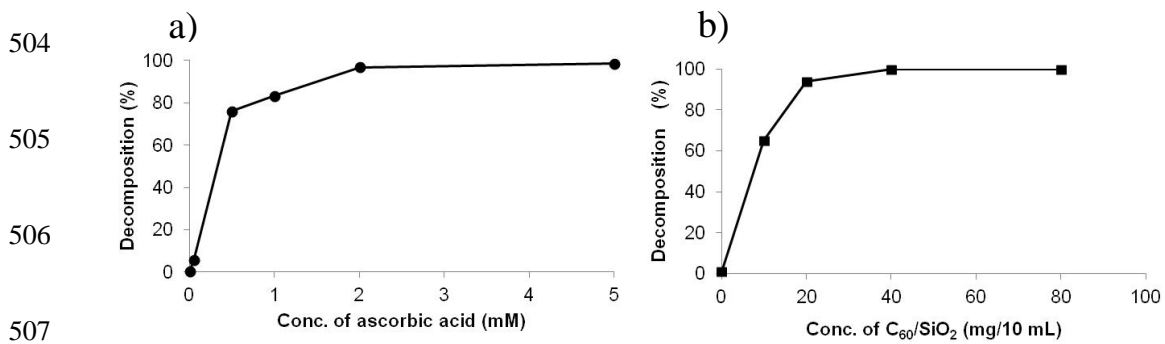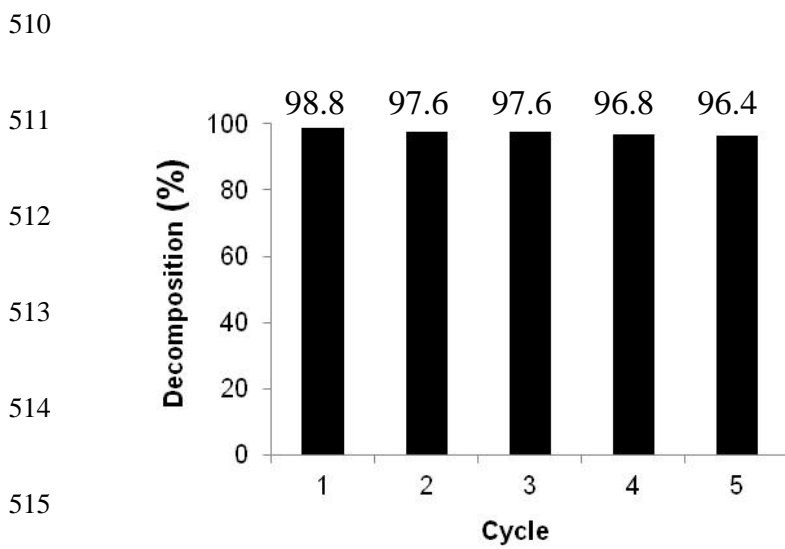
Table 1 Photodecomposition (%) of methyl orange with C_{60}/SiO_2 [a]

Entry	Additives	Atmosphere	Light	Irradiation time (min)	Decomposition (%)
1	C_{60}/SiO_2	Air	Visible Light (>420 nm)	25	0.80
2	Ascorbic acid (AA)	Air	Visible Light (>420 nm)	25	4.0
3	None	Air	Visible Light (>420 nm)	25	0.0
4	C_{60}/SiO_2	Air	Dark	25	0.40
5	C_{60}/SiO_2+AA	Air	Dark	25	5.2
6	C_{60}/SiO_2+AA	Air	Visible Light (>420 nm)	15	85
7	C_{60}/SiO_2+AA	Air	Visible Light (>420 nm)	25	96
8	C_{60}/SiO_2+AA	N_2	Visible Light (>420 nm)	15	70
9	C_{60}/SiO_2+AA	N_2	Visible Light (>420 nm)	25	95
10	C_{60}/SiO_2+AA+2-propanol[b]	Air	Visible Light (>420 nm)	15	73
11	C_{60}/SiO_2+AA+2-propanol[b]	Air	Visible Light (>420 nm)	25	95
12	C_{60}/SiO_2+AA+tert-butyl alcohol[c]	Air	Visible Light (>420 nm)	15	68
13	C_{60}/SiO_2+AA+tert-butyl alcohol[c]	Air	Visible Light (>420 nm)	25	84
14	C_{60}/SiO_2+AA	Air	Sunlight	15	86
15	C_{60}/SiO_2+AA	Air	Sunlight	25	97
16	C_{60}/SiO_2+AA	N_2	Sunlight	15	85
17	C_{60}/SiO_2+AA	N_2	Sunlight	25	95
18	SiO_2+AA	Air	Visible Light (>420 nm)	25	4.0

[a] Initial concetrations of methyl orange and ascorbic acid were 25 μM and 0.50 mM, and the amount of C_{60}/SiO_2 powder was 20 mg/10 mL.

[b] The concentration of 2-propanol was 0.1 M. 2-propanol was used as a radical scavenger.

522 [c] The concentration of *tert*-butyl alcohol was 0.1 M. *Tert*-butyl alcohol was used as a radical scavenger.