Photoelectric catalytic degradation of methylene blue by C60-modified TiO2 nanotube array

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ABSTRACT

Fullerene (C60)-modified TiO2 nanotube array (TNA) was prepared by the electrophoresis deposition technique. The as-prepared samples showed the high efficiency for the photoelectric catalytic (PEC) degradation of nonbiodegradable azodyes methylene blue (MB). The highest PEC activity of C60-modified TNA (TNA/C60) was achieved at a lower bias potential (4.0 V), which was 2.3 times of the highest activity of TNA at 5.0 V. The high PEC activity came from the synergetic effect between C60 and TiO2, which promoted the charge separation, influenced the charge distribution of the electrical double layer and reduced the impedances of the Helmholtz and depletion layers. Moreover, the oxidation of MB was a quick process during the PEC degradation, and the process began with the oxidation of the dimethylamino group, which was different from the photocatalytic (PC) process began with the oxidation of S atom; MB was mineralized completely during PEC degradation.

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1. Introduction

Photocatalytic processes are a promising class of advanced oxidation technologies used for environmental remediation [1,2]. Among the photocatalysts, TiO2 has been intensively investigated for the complete degradation of recalcitrant organic pollutants [2–4], because it is easily available, nontoxic, low-cost and chemically stable. However, TiO2 has two typical shortcomings to render its wide application in practice: the difficult separation of TiO2 from aqueous phase and relatively low quantum yield due to the rapid recombination of charge carriers. Now, the separation of photocatalyst from the solution suspension can be fulfilled by the immobilization of TiO2 particles. Immobilization of TiO2 on the supporter, especially on the conducting substrate, not only can eliminate the need for separation of photocatalyst from the solution suspension, but also can provide more advantages, such as using electrochemical technique to study and cooperate with photocatalytic process expediently [5,6]. For the advanced oxidation application, TNA has been considered as the most suitable way to achieve larger enhancement of surface area without an increase in the geometric area [7]. Among the fabrication methods of TNA, the electrochemical synthesis method shows its advantages of good mechanical adhesion strength and electronic conductivity since it directly grows from the titanium metal substrate [8]. In addition, the thickness and morphology of such TiO2 film are easily controlled.

The high degree of recombination between photogenerated electrons and holes in semiconductor particles is a major limiting factor for photodegradation process [9]. Among the ways to enhance the separation of photogenerated charge carriers, the application of a low bias is an effective method. The bias drives the photogenerated electron to counter electrode in the PEC process, which could counteract the charge recombination process [10–12].

C60 have attracted extensive attentions for their various interesting properties due to their delocalized conjugated structures and electron-accepting ability. One of the most remarkable properties of C60 in electron-transfer processes is that it can efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination [13]. Thus, the combination of photocatalysts and C60 may provide an ideal system to achieve an enhanced charge separation by photoinduced electron transfer. Some of the fullerene-donor linked molecules on an electrode exhibited excellent photovoltaic effects upon photo-irradiation [14–16]. Our previous study showed that the photocatalytic activities of Bi2WO6 were improved remarkably after C60 modification [17], the combination of C60 and TNA may be an ideal system for the PEC degradation of organic pollutant.

In this work, the enhanced PEC activity of TNA/C60 was reported. A series of experiments aimed to investigate the relationship between the C60 modification and the PEC activity
were described. It showed that the enhanced activity was due to the synergistic effect of C60 and TNA. Moreover, the intermediates detected during the PEC process showed a different degradation path of MB from the PC process.

2. Experimental

2.1. Materials and preparation

All chemicals were analytical grade reagents and used without further treatment. Electrolyte was freshly prepared from deionized water. After chemical polishing, titanium foil (thickness about 250 μm, purity 99.4%, Beijing Cuibolin Non-Ferrous Technology Developing Co., Ltd.) was subjected to potentiostatic anodization in an electrochemical anodization cell with a platinum cathode in a 0.5 wt% HF + 1 M H3PO4 electrolyte at ambient temperature. The potential of 20 V was applied for 30 min. Then the samples were rinsed with deionized water and annealed at 450 °C for 4 h.

The TNA/C60 samples were prepared using electrodeposition method as in Ref. [18]. The electrolytic suspension was prepared by adding C60 (purity 99.9%, Peking University, PR China) to a mixture of acetonitrile and toluene (3:1, v/v). The electrodeposition was carried out potentiostatically using a CHI660B electrochemical system (Shanghai, China), with the TNA film as working electrode, a platinum wire as counter electrode and a standard calomel system (Shanghai, China) as reference electrode, respectively. The coverage of C60 on the TNA film was estimated by the charge passed (after the correction for solvent blank) during the electrodeposition.

2.2. Characterization

The structures of the TNA and TNA/C60 samples were characterized by XRD (Rigaku D/MAX-2500 X-ray powder diffractometer), using graphite monochromatized Cu Kα radiation (λ = 0.154 nm). A 0.02 step in 2θ/count, beam voltage of 40 kV and beam current of 300 mA were used. The phase composition of the samples was determined by Microscopic Confocal Raman Spectrometer (Renishaw, RM2000) using 632.8 nm as the exciting light source. Spectra were collected in the range of 1000–200 cm⁻¹ with a resolution of 1 cm⁻¹. The morphologies and microstructures of the as-prepared samples were observed using a field emission scanning electron microscope (FE-SEM, LEO-1530) at 10 kV and a Tecnai TF20 high-resolution transmission electron microscope (HRTEM) operated at an accelerating voltage of 200 kV. Chemical characterization of the sample surface was recorded with scanning X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Quantera). The beam voltage was 3.0 kV, and the energy of Ar ion beam was 1.0 keV. The sputtering rate was approximately 9.5 nm/min for a thermally oxidized SiO2 thin film. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV.

2.3. Photoelectric properties and photoelectrocatalytic activities

All electrochemical and photoelectric studies were performed on a CHI660B electrochemical system (Shanghai, China) using a standard three-electrode cell with a working electrode (20 mm × 45 mm), a platinum wire counter electrode, and a SCE reference electrode. Photoelectrochemical properties were measured with an 18 W germicidal lamp (λ = 254 nm, Institute of Electric Light Source, Beijing). Unless otherwise stated, the intensity of light at the film electrode was 1.64 mW/cm² at the wavelength of 254 nm, and 0.1 M Na2SO4 electrolyte was used. The photocurrents were measured in the potential range of −0.3 to 1.0 V. The photoelectrochemical impedance spectroscopies (EIS) were carried out at the open circuit potential. A sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 0.05–10⁶ Hz. The EIS spectra were further fitted and interpreted by Zsimpwin software. The catalytic activities of the samples were all evaluated by the removal of MB dye (with an initial concentration of 10 mg/L). The changes of MB concentration were monitored by the variations in absorption intensity at 660 nm using a UV–vis spectrometer (Hitachi U-3010). The mineralization of the dye was followed by measuring the total organic carbon (TOC) concentration, utilizing a Shimadzu Corporation TOC-V wp Analyzer.

2.4. Analyses of MB intermediates

To analyze the PEC process of MB, the original concentration of MB was increased to 50 mg/L, and the neutral products were enriched by 140 times. Before the analysis, the samples were filtered through millipore discs of 0.45 μm to protect the chromatographic column. HPLC monitoring was carried out using an UV absorbance detector (K2501) operated at 280 nm coupled to a Venusil XBP-C18 (Agela Technologies Inc.) column. According to the literature [19], the reversed-phase eluent of pH 3 buffer and methanol (45:55, v/v) was used for aqueous solution, and water and methanol (40:60, v/v) was used for enriched neutral products. The neutral intermediates were finally identified by LC/MS (Thermo Fisher, LTQ).

3. Results and discussion

3.1. Photoelectric properties

The photoelectric properties of the TNA and TNA/C60 samples were evaluated by the photocurrent at bias 0 V and 1 V (Fig. 1). The amount of C60 on the TiO2 film was expressed by the charge passing during the electrodeposition. It can be seen that the photocurrent was enhanced with the deposition charge and reached the maximum at 0.123 mC. The further increase decreased the photocurrent and finally reached its balance even the deposition charge increased to 0.41 mC. The highest photocurrent of TNA/C60 was 30% higher at 0 V and 40% higher at 1 V than that of TNA, respectively.

To investigate the influence of C60 modification on the photoelectric property, the EIS technology was used to study the solid/electrolyte interfaces of the TNA and TNA/C60 samples. According to conventional double-layer theories, the electrical double layer at the solid electrode behaved as a frequency distribution impedance instead of a pure capacitance due to the surface heterogeneity. When the charge transfer reaction occurred,
the Nyquist plot was a semicircle; when semi-infinite diffusion was the rate-determining step, a linear with a slope of 45° appeared [20]. In our cases (Fig. 2a and b), only one semicircle on the EIS plane suggested charge transfer occurring, and the equivalent circuits were shown in Fig. 2c and d [21]: \( R_1 \), solution resistance; \( R_2 \), electric charge transfer resistance, corresponding to the Helmholtz layer; \( R_3 \), corresponding to the depleting layer; \( Q \), the constant phase elements (CPE) of the inner layer of the TNA/C\(_{60}\) sample. Using the equivalent circuit, the impedance fitting values were shown in Fig. 2e and f. The electric charge transfer resistance (\( R_2 \)) and the depleting layer resistance (\( R_3 \)) under dark field decreased significantly with C\(_{60}\) modification and reached the balance when deposition charge of C\(_{60}\) increased to 0.082 mC.

The C\(_{60}\) on the surface increased the process of charge separation, influenced the distribution of the electrical double layer, and promoted the electron transfer, so that the electric charge transfer resistance (\( R_2 \)) decreased. The charge distribution of electrical double layer also impacted the depleting layer, so that \( R_3 \) also decreased. With the increasing coverage of C\(_{60}\) on the surface of TNA film, the process of charge transfer reached the balance, and \( R_2 \) and \( R_3 \) were also invariable.

Under UV irradiation, the formation of photoinduced electron–hole pair reduced the resistance of depleting layer (\( R_3 \)) by one order. Different from dark field, the Helmholtz layer was mainly occupied by the photoinduced electron–hole pair, so \( R_2 \) was also reduced by one order. The electron-transfer characterization of C\(_{60}\)
increased the charge separation process of the Helmholtz layer and changed the charge distribution of depleting layer availability. The smaller arc radius on EIS Nyquist plot of TNA/C60 film under UV irradiation meant an effective separation of photogenerated electron–hole pairs and fast interfacial charge transfer occurred [17]. On the other hand, the C60 on the TNA surface reduced the UV absorption and the contacting area between the TiO2 and solution, which decreased the utilization efficiency of light. The enhanced charge separation process and reduced efficiency of light competed in our system, which caused the photoelectric properties increased initially then decreased to the balance, and the highest photoresponse was obtained at the deposition charge of 0.123 mC.

3.2. Photoelectrocatalytic activities

The PEC activities of TNA and TNA/C60 (deposition charge of 0.123 mC) were evaluated by the degradation of MB under UV irradiation. Only 1% of MB was adsorbed on the TNA/C60 film after 0.123 mC were evaluated by the degradation of MB under UV absorption and the contacting area between the TiO2 and solution, which decreased the utilization efficiency of light. The enhanced charge separation process and reduced efficiency of light competed in our system, which caused the photoelectric properties increased initially then decreased to the balance, and the highest photoresponse was obtained at the deposition charge of 0.123 mC.

Fig. 3. The catalytic activity of TNA and TNA/C60 samples. (a) The pseudo-first-order kinetic constants of the PEC degradation of MB with TNA and TNA/C60 samples; (b) the color removal of MB within 1.5 h under PEC, EC, UV reaction, respectively.

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The presence of C60 reduced the resistance of Helmholtz layer and depleting layer, so the direct electro-oxidation and indirect oxidation of MB occurred at a lower bias. The presence of C60 also improved the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity. In a word, the modification of C60 on the surface enhanced the separation of photoinduced electron–hole pairs and electron transfer, causing the increase of the photoelectrical activity.

3.3. Intermediates during the PEC degradation of MB

To investigate the PEC process of MB, the composition of MB intermediates were detected by HPLC (Fig. 4). There were only two peaks separated from the chromatogram spectra of the original reaction solution. The previous study [19] indicated that two forms of MB existed in the solution (Support Information Scheme S2), so the two peaks at 4.5 and 4.6 min assigned to compounds II and I, respectively. It was clear that the compound II was degraded more quickly than the compound I during the PEC process, which suggested the compound II was more easily oxidized. To examine the process in detail, the neutral intermediates enriched by 140 times were also detected by HPLC (Fig. 4b) and further identified by LC/MS. The suggested structures of the intermediates based on the LC/MS results were shown in Table 1.

The neutral intermediates separated at 11.2, 11.6 and 17.7 min accumulated during the PEC process (Fig. 4b). The fact that all the three intermediates had a cyclohexa-2, 5-diene structure suggested that the PEC process started with the oxidation of the dimethylamino group. Thus the compound II was considered as the initial reactant oxidized on the TiO2 surface, so that the concentration of the compound II decreased more quickly. The minor intermediates separated at 8.0 and 8.5 min showed the primal oxidation at S atom, which was also observed at the initial step of MB degradation during the EC process [23]. These two intermediates suggested that a part of MB was degraded via the EC route. For the concentrations of all the neutral intermediates were low and the small molecules at 3.7 min did not accumulated markedly, it made evident that the PEC degradation was a quick.
process. The mineralization of dye was also studied by measuring TOC removal. The samples corresponding to the HPLC results at 0 h and 12 h were used. After PEC process for 12 h, the TOC concentration decreased from 22.25 ppm to 4.37 ppm, namely 80% of TOC was removed by PEC oxidation. This result was consistent with the HPLC result. In a word, the photoelectrical oxidation of MB was a quick process and mainly began with the oxidation of the dimethylamino group; MB was mineralized by 80% during PEC degradation for 12 h.

3.4. Structure of TNA/C₆₀ film

The XRD results (Support Information Figure S3) demonstrated that TiO₂ nanotube held the anatase phase before and after C₆₀ modification. No diffraction peak of C₆₀ was detected and C₆₀ maybe existed in microcrystal or amorphous form. In addition, TiO₂ nanotube was oriented along [0 0 1] direction. The morphologies of the TNA and TNA/C₆₀ were obtained by FESEM (Fig. 5a and b). The TNA was estimated 400 nm long, and the internal diameter was in the range of 50–70 nm. The morphology of TNA/C₆₀ remained the same as that of TNA, and no aggregation of C₆₀ was observed on the surface of the TNA/C₆₀ sample. Further study by

### Table 1

Suggested structures for the intermediates based on LC–MS results.

<table>
<thead>
<tr>
<th>Retention time, t&lt;sub&gt;R&lt;/sub&gt; (min)</th>
<th>Structural formula</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>HO₃S</td>
<td>174</td>
</tr>
<tr>
<td>7.4</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;CCl&lt;sub&gt;2&lt;/sub&gt;O₂N</td>
<td>235</td>
</tr>
<tr>
<td>8.0</td>
<td>ClO₂N</td>
<td>202</td>
</tr>
<tr>
<td>8.5</td>
<td>ClO₂N</td>
<td>128</td>
</tr>
<tr>
<td>11.2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;SNO₂N</td>
<td>340</td>
</tr>
<tr>
<td>11.6</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;SNO₂N</td>
<td>369</td>
</tr>
<tr>
<td>14.2</td>
<td>NO₂S</td>
<td>337</td>
</tr>
<tr>
<td>14.6</td>
<td>NO₂S</td>
<td>256</td>
</tr>
<tr>
<td>17.7</td>
<td>NO₂S</td>
<td>274</td>
</tr>
</tbody>
</table>
HRTEM (Fig. 5c) showed the barrier layer (close-end) of TNA/C$_{60}$ was structurally uniform with a lattice spacing of 0.377 nm corresponded to the (1 0 1) plane of anatase TiO$_2$ and the [1 0 0] direction was vertical to the growth direction. At the open-end of the TNA/C$_{60}$ (Fig. 5d), some particles with amorphous form dispersed on the TiO$_2$ tube wall, and the average particle diameter was about 2 nm, which suggested that the C$_{60}$ on the TiO$_2$ tube wall existed in the cluster form.

To confirm the existing form of C$_{60}$ on the TiO$_2$ surface, the pristine C$_{60}$, TNA/C$_{60}$ and fresh TNA samples were further characterized by Laser Raman spectroscopy (Fig. 6). The peaks of the TNA and TNA/C$_{60}$ samples at 144, 397, 517 and 633 cm$^{-1}$ belonged to the vibration mode of anatase phase, which confirmed the TiO$_2$ nanotube array held the anatase phase during the C$_{60}$ modification. The two peaks of the pristine C$_{60}$ at 1468 cm$^{-1}$ and 1571 cm$^{-1}$ were observed, which was corresponded to the Ag (2) and Hg (8) mode of C$_{60}$ single crystal [24]. With Gaussian fitting, the wide peak of TNA/C$_{60}$ around 1600 cm$^{-1}$ was fitted to three peaks at 1561, 1580 and 1623 cm$^{-1}$, which connected with Hg (8) modes of C$_{60}$, the first-order G band and the disorder-induced D$'$ band of quasi-graphite structure, respectively [25]. Compared with the pristine C$_{60}$, the peaks of Ag (2) and Hg (8) modes in the TNA/C$_{60}$ sample downshifted to 1460 and 1561 cm$^{-1}$, and the line widths increased observably. The downshift and increased line widths
widths of Ag pentagonal pinch mode indicated the electron transfer from TNA to C60 [26]. The appearance of G band and D band was supposed due to the partly ordered arrangement of C60 on the surface of TiO2. The ordered arrangement of C60 increased the charge transfer and fluorescence by conjugation effect, so that Raman spectrum of the TNA/C60 sample displayed observable fluorescence background.

Based on the XPS results of TNA/C60 sample (Support Information Figure S4), the existence of the peak at 282.3 eV in C 1s spectrum and the peak at 457.6 eV in Ti 2p spectrum confirmed that C and Ti had a weak chemical interaction, which was consistent with the Raman results. Based on the results above, the coverage of the C60 on the TNA/C60 sample with the deposition charge of 0.123 mC was estimated in Supporting Information Figure S5. In the TNA/C60 sample of the best photoresponse (the deposition charge was 0.123 mC), nearly 88% of the TiO2 tube wall was covered the C60 clusters.

4. Conclusions

In summary, TiO2 nanotube array modified with C60 was formed by the electrodeposited method, and the synergetic effect between C60 and TNA enhanced charge separation process remarkably. C60 modification on the TNA surface with 88% coverage optimized the competition of enhanced charge separation process and reduced efficiency of light, and the sample obtained the highest photoelectric response. The enhanced charge separation process induced the TNA/C60 sample reached the highest PEC activity at a lower bias. Furthermore, the photoelectrical oxidation of MB was a quick process and began with the oxidation of the dimethylamino group on the TiO2 surface; 80% of MB was mineralized during PEC degradation for 12 h.

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Appendix A. Supplementary data


References


Fig. 6. Raman spectra for (a) TNA, (b) pristine C60 and (c) TNA/C60 samples. The inset was the comparison spectra of (b) and (c) in the range of 1400–1680 cm⁻¹ after background correction.