Research Article

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Study on the photoelectrocatalytic activity of reduced TiO₂ nanotube films for removal of methyl orange

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Abstract: The reduced TiO₂ film on which a photoelectrocatalytic (PEC) process had occurred was created from TiO₂ nanotube film electrodes by the electrochemical reduction method. The obtained samples’ structure and morphology were characterized using UV-Vis diffuse reflectance spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy, photoluminescence, and X-ray diffraction. Cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy, chronoamperometry, UV-Vis absorbance spectroscopy, and Mott–Schottky plots were employed to examine the electrochemical and photoelectrocatalytic activities of the prepared electrodes. The results showed that the optimal conditions of cathodic polarization were a potential of −1.4 V for 60 min. The reduced TiO₂ nanotube film electrode had better photoelectrocatalytic activities than pristine TiO₂ under UV light due to the higher photocurrent density (13.7 mA·cm⁻²) at 1.5 V (vs Ag/AgCl, sat. KCl reference electrode) compared to pristine TiO₂ achieving 7.3 mA·cm⁻², indicating more effective charge separation and transport. The degradation of methyl orange (MO) on pristine TiO₂ and reduced TiO₂ electrodes was carried out in electrocatalytic (EC) and PEC conditions. The PEC process on the reduced TiO₂ electrode had the highest MO processing efficiency (98.4%), and the EC process for MO removal on reduced TiO₂ had higher efficiency (95.1%) than the PEC process on pristine TiO₂ (89.2%).

Keywords: reduced TiO₂, photoelectrocatalytic, electrocatalytic, cathodic polarization, MO treatment

1 Introduction

In recent years, TiO₂-based photoelectrochemical catalyst materials have been attracting the attention of many scientists all over the world because of their great potential in many fields such as solar cells, environmental treatment, solar water splitting, etc. [1–3]. TiO₂ is a wide band-gap semiconductor (3.0–3.2 eV) so it only works well in the UV domain that has less than 5% of the solar light [4]. Besides, the easy recombination of photogenerated charge carriers or photogenerated electron–hole (e⁻–h⁺) pairs has significantly reduced the photocatalytic activity of TiO₂. There are many methods to improve materials such as doping with transitional metal oxides like V₂O₅, SnO₂, ZnO, WO₃, SiO₂, etc. [5–7], transitional metals like V, Cu, Ni, and Zn, or precious metals like Rh, Ru, Ir, Pt, Au, etc. [8,9]. Many studies showed that nonmetal-doped TiO₂, such as N, P, S, C, and F [10–12], narrowed the band-gap energy of TiO₂ and enhanced photocatalytic activities in visible light. Similar to increasing solar harvesting, a number of TiO₂ composites were investigated like Sm₂O₃/TiO₂, Bi/CdS/TiO₂, ZnS/TiO₂, In₂S₃/TiO₂, Bi₂S₃/BiOBr/TiO₂, Bi₂WO₆/TiO₂, and TiO₂/Ti₃C₂ [13–19]. However, dopants create donor or acceptor states inside the TiO₂ band gap, leading to crystal instability and an increase in charge carrier trapping [20]. Reductive doping, often known as self-doping, is a recent approach to overcome these disadvantages. This reduction can be performed by two methods: (i) thermal hydrogenation and (ii) electrochemical reduction that changes the intrinsic defect concentration of TiO₂. In thermal hydrogenation, TiO₂ is heated in a hydrogen (H₂) atmosphere at high temperatures, and the reductive agent is a hydrogen atom. Also, they get inserted into the TiO₂ lattice as mobile donor sites. But,
this process takes place at high temperatures and requires complicated equipment [21]. In contrast, electrochemical reduction has a different mechanism. According to previous research [22], the reaction mechanism on the surface of TiO$_2$ in electrolyte solution occurs as shown in Eq. 1:

$$\text{Ti}^{4+} + e^- + \text{H}_2 \text{O} \leftrightarrow \text{Ti}^{3+}(\text{OH})$$  \hspace{1cm} (1)

where the electrons are transferred from the cathode, and the protons from the electrolyte are adsorbed and interleaved into the TiO$_2$ surface concurrently. The most important factor in the reduced process is the suitable voltage to avoid excessive hydrogen evolution, leading to interface fracturing [23]. The advantages of this method are that it does not require excessive heat treatment and the equipment is simple. This reductive doping causes the variation in the intrinsic defect concentrations in the semiconductor by creating oxygen vacancies and Ti$^{3+}$, which can significantly improve the photoelectrochemical characteristics [24]. As shallow donors, oxygen vacancies and Ti$^{3+}$ play an important role in the electronic properties of TiO$_2$, and the separation of charge carriers improves the charge transport behavior and light absorption. In fact, by reductive doping, the semiconductor behavior of TiO$_2$ could be converted to almost semimetallic behavior.

One of the most widely used synthetic dyes is an azo dye, which has one or more azo bonds (–N=N–). Azo dyes typically cause significant pollution in wastewater released by the textile and dyeing industries, which not only potentially endanger humans and marine life but also seriously harm the biological environment [25]. Among azo dyes, owing to their complex structure and stability, it is difficult to remove and degrade MO because of high water solubility and low biodegradability [26]. To remove azo dyes from wastewater, a number of methods have been developed over the past few decades, including adsorption, biological treatment, photocatalysis, and electrocatalytic (EC) oxidation [27]. Among them, the EC oxidation method has many significant advantages due to its benefits of easy operation, affordability, environmental compatibility, high degradation efficiency, and no secondary pollution generation [28,29]. Recently, much attention has been paid to the EC degradation of MO with anodes based on TiO$_2$ [30,31]. The photoelectrocatalytic (PEC) method, in which an external potential bias combined with light irradiation effectively separates charge pairs into a cathode and an anode, is an ideal method for achieving various photochemical conversions such as the degradation of aqueous pollutants. By applying positive voltage bias to the photoanode, photoelectrocatalysis can further enhance the photocatalytic activity by preventing carrier charge recombination and extending the lifetime of photogenerated active holes [32,33]. A previous study has proved that mesoporous TiO$_2$ films and V-TiO$_2$ film electrodes can remove more than 90% MO in 2 h under UV light by the PEC method [34]. PEC degradation of MO on porous TiO$_2$ film electrodes was higher than that on smooth TiO$_2$ films. The removal efficiency of MO on porous TiO$_2$ films and smooth TiO$_2$ films could be achieved at 95.2% and 79.9% after 50 min, respectively. EC degradation of these two film electrodes almost had no effect on MO [35].

There have been a number of studies on modifying TiO$_2$ by electrochemical reduction [36,37], but there is still a lack of studies investigating PEC and EC degradation of MO on reduced TiO$_2$ nanotube electrodes. Hence, this research focuses on enhancing the electrochemical and photoelectrochemical activities by electrochemical cathodic polarization, and various methods such as UV-Vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), photoluminescence (PL) spectroscopy, and X-ray diffraction (XRD). Cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronocoulometry, UV-Vis absorbance spectroscopy, and Mott–Schottky plots were carried out to explain the characteristics of materials and the improvement of the photoelectrochemical properties. Moreover, activity tests toward MO degradation on pristine and reduced TiO$_2$ nanotube electrodes were determined by the PEC method under UV light irradiation and EC methods.

## 2 Materials and methods

All chemicals used in this work were purchased from Merck (Germany). Titanium foils from China (1 cm $\times$ 1 cm $\times$ 0.1 mm, 99.7% purity) were first degreased and then chemically polished in 20% HCl for 10 min. Finally, they were washed with deionized water and then dried at room temperature.

### 2.1 Synthesis of materials

TiO$_2$ nanotube arrays were prepared as described in our previous research by anodizing titanium foils in a solution consisting of 0.25% NH$_4$F, 5% H$_2$O, and 94.75% ethylene glycol at 40 V for 2 h [38]. After that, the electrode was annealed at 450°C for 1 h to form a pristine TiO$_2$ electrode.
After anodizing, the TiO₂ electrode was subjected to cathodic electrochemical polarization in a 1 M Na₂SO₄ solution at different potentials from −1.2 to −1.6 V and annealed at 450°C for 1 h to obtain a reduced TiO₂ electrode.

2.2 Characterization of materials

The diffuse reflectances of the samples were measured using a spectrophotometer (Model UV-2600, Shimadzu, Japan). The morphological structure and the microstructure of samples were observed with SEM images obtained on a FE-SEM Hitachi S-4800 (Japan) and HRTEM images obtained on a JEM-2100 (JEOL) respectively. The crystalline phase of samples was determined by XRD on a D8-ADVANCE (Germany).

The photoelectrochemical properties of TiO₂ before and after doping were carried out by CV, LSV, and EIS measurements on an electrochemical workstation system (Zahner Zennium Pro, Zahner-Elektrik, Germany) at ambient temperature. All experiments were carried out in a cell with the three-electrode system, including an Ag/AgCl electrode in saturated KCl solution as a reference electrode, a platinum rod as a counter electrode, and the prepared samples as a working electrode. The response photocurrent densities of the light on–off process with a pulse of 30 s at a voltage of 1.5 V (vs Ag/AgCl, sat. KCl reference electrode) were measured by the potentiostatic technique. All the working electrodes were irradiated with a lamp LS365-1 at a wavelength of 365 nm and an intensity of 100 W-m⁻².

The following equation (Eq. 2) was used to quantify the photoconversion efficiency (PCE) of light energy into chemical energy in the presence of an externally applied potential [39]:

\[ \eta = \frac{i_p[E_{\text{rev}}^0 - IE_{\text{app}}]}{I_0} \times 100\% \]  \hspace{1cm} (2)

where \( \eta \) is the PCE (%), \( i_p \) is the photocurrent density (mA·cm⁻²), \( E_{\text{rev}}^0 \) is the standard reversible potential (1.23 V vs RHE), \( IE_{\text{app}} \) is an externally applied potential (vs RHE) of the working electrode at which the photocurrent was measured under illumination, and \( I_0 \) is the power density of the incident light (mW·cm⁻²).

The applied potentials versus Ag/AgCl were converted to the RHE scale using the Nernst equation (Eq. 3):

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^{\text{fl}} + 0.059pH \]  \hspace{1cm} (3)

where \( E_{\text{Ag/AgCl}}^{\text{fl}} = 0.1976 \text{ V at 25°C} \).

2.3 Removal of MO

The MO degradation tests were carried out on a three-electrode system, including the counter electrode (platinum plate), working electrode (pristine TiO₂ or reduced TiO₂ nanotube film electrodes), and reference electrode (Ag/AgCl, sat. KCl). The electrolyte solution contained 50 mg·L⁻¹ MO and 0.08 M Na₂SO₄ at pH values varying from 4 to 10. In the EC degradation of MO, the current density applied in each experiment was 3 mA·cm⁻² and the treatment time varied from 5 to 40 min. The volume of the MO solution was 15 mL, and the solution was stirred continuously during experiments. Photoelectrochemical degradation experiments were performed under the same conditions as in the case of electrochemical degradation but under UV light irradiation.

The concentration of MO before and after the degradation was determined using a UV-Vis spectrophotometer (the S80, England) at specific time intervals to confirm the change in the degradation over time. The MO removal efficiency (\( H \)) at various times was calculated according to the following equation:

\[ H = \frac{C_0 - C_t}{C_0} \times 100\% \]  \hspace{1cm} (4)

where \( C_0 \) is the initial MO concentration and \( C_t \) is the residual MO concentration after a time (\( t \)) of MO treatment.

3 Results and discussion

3.1 Structural and morphological characterization

Figure 1a shows the UV-Vis diffuse reflectance spectra of pristine TiO₂ and reduced TiO₂ nanotube electrodes in the range of 250–700 nm. Compared to pristine TiO₂, the absorption peak of the reduced TiO₂ shifted to a longer wavelength ranging from 385 to 405 nm. From the reflectance spectrum data, the band-gap energy can be calculated by the Tauc function (Eq. 5),

\[ (h\nu)^\frac{1}{n} = A(h\nu - E_g) \]  \hspace{1cm} (5)

where \( h \) is Planck’s constant, \( \nu \) is the frequency of vibration, \( \alpha \) is the absorption coefficient, \( E_g \) is the band gap, and \( A \) is the proportional constant.

The band-gap energy estimated from Tauc plots in Figure 1b was about 3.2 eV for pristine and 2.9 eV for reduced TiO₂. The results demonstrated that the reductive
The reductive doping process created oxygen vacancies and Ti$^{3+}$ and made the band gap narrow, thus, improving the light absorption of TiO$_2$ [36].

The XRD patterns of pristine, reduced TiO$_2$ nanotube electrodes, and reduced TiO$_2$ after six cycles of MO removal by the PEC method are shown in Figure 2. From the XRD patterns, the diffraction peaks located at 2$\theta$ of 40.26° and 53° derived from the Ti substrate, and peaks at 25.28°, 37.94°, 48.19°, 54.33°, 55.43°, and 63.18° were attributed to the tetragonal anatase TiO$_2$, indicating that the prepared TiO$_2$ nanotubes exist in the anatase phase [1,36]. Furthermore, there are no clear differences between the XRD patterns of all samples, so implying that the crystalline structure is not affected by the reductive doping process and the degradation process of MO by the PEC method.

Figure 3 shows the SEM images of pristine, reduced TiO$_2$ nanotube film electrodes, and the reduced TiO$_2$ after six cycles of MO degradation. Observing Figure 3, it is clear that there is no difference between the surface morphologies of all samples, and relatively uniform TiO$_2$ nanotubes were formed with a diameter ranging from about 140 to 150 nm and a wall thickness of about 20 nm. The reason is that all electrodes have the same conditions of anodizing and annealing processes. Moreover, the reductive doping process of TiO$_2$ modified the electronic and defect levels of
the material but did not change the surface morphology and the size of the TiO$_2$ nanotubes [37]. After six cycles of MO degradation by the PEC method, the surface morphology of reduced TiO$_2$ nanotubes had not changed significantly. Hence, reduced TiO$_2$ has remarkable stability for the PEC degradation of MO.

Figure 4 shows the microstructure characteristics of the reduced TiO$_2$ sample determined by TEM and HRTEM. The lattice stripes in different directions are observed in Figure 4b, and the lattice spacing, calculated to be $d = 0.358$ nm, corresponds to the (101) crystal plane of anatase TiO$_2$ [19]. Besides, the lattice spacing of 0.336 nm appears in a region due to the lattice distortion of atom layers at the surface of reduced TiO$_2$. Thus, reductive doping creates oxygen vacancies or Ti$^{3+}$, which may cause crystal distortion.

3.2 Optimal conditions of the cathodic polarization process

3.2.1 Effect of reduction potential

The anodized TiO$_2$ electrodes were prepared by cathodic polarization in 1 M Na$_2$SO$_4$ solution at potentials of $-1.2$, $-1.4$, and $-1.6$ V for 60 min. The reduction potentials particularly affected the electrochemical and photoelectrochemical properties of TiO$_2$ electrodes because the amount of charge passing through the reductive process from which the doping level can be estimated that affected the defect level in the crystal structure of samples. Figure 5 shows CV diagrams of the reduced TiO$_2$ electrode at different potentials without UV and with UV illumination. In the dark, the pristine TiO$_2$ electrode revealed a very low
current density (Figure 5a), so TiO$_2$ was almost non-conductive. Meanwhile, the CV curves of reduced TiO$_2$ electrodes have a rectangle shape, which indicates a modest dependence of the current density on the potential. The results improved the semi-metallic behavior of reduced TiO$_2$ electrodes, and the conductivity of reduced TiO$_2$ electrodes increased due to the reduction of Ti$^{4+}$ to Ti$^{3+}$ changing the stoichiometry or the intrinsic defect concentration of the semiconductor [37,40]. As seen from Figure 5a, the reduced TiO$_2$ synthesized at $-1.2$ V shows a lower current density and still slightly maintains semi-conducting features because of the low density of the Ti$^{3+}$ state. The sample synthesized at $-1.4$ V has the largest current density because of a higher concentration of the Ti$^{3+}$ state. This indicated that the sample with a high concentration of Ti$^{3+}$ states had more effective charge separation and transport. Additionally, increasing the cathodic voltage to $-1.6$ V caused more generation of H$_2$, so the current density was decreased [37]. Furthermore, under UV light (Figure 5b), the anode current density of all samples increased rapidly with anodic polarization. This illustrates that TiO$_2$, an n-type semiconductor, has photoelectrochemical activities. Besides, the photoelectrochemical properties of TiO$_2$ electrodes also depended on the reduction potential during the synthesis process. The results in Figure 5b and Table 1 indicate that the photoelectrochemical activity of the reduced TiO$_2$ samples at $-1.2$ and $-1.4$ V is higher than that of unreduced TiO$_2$. Among them, the highest photocurrent (12.3 mA·cm$^{-2}$) was obtained at $-1.4$ V; however, at higher reduced potential ($-1.6$ V), the photocurrent decreased. This means that at a too-high reducing voltage, the surface of the sample was fractured and dropped due to the strong generation of H$_2$ and the photocurrent.

**Figure 4:** TEM images (a) and HR-TEM images (b) of the reduced TiO$_2$ sample.

**Figure 5:** Influence of the reduction potential on the CV diagrams of reduced TiO$_2$ in 1 M Na$_2$SO$_4$ without UV (a) and with UV illumination (b) compared with pristine TiO$_2$.
density decreased noticeably [23]. Therefore, the optimal reduction potential at the TiO₂ electrode was −1.4 V and had the best photoelectrochemical properties.

### 3.2.2 Effect of the reduction time

The photoelectrochemical properties of TiO₂ electrodes depend not only on the reduction potential but also on the reduction time in the synthesis process of TiO₂ nanotubes. From the obtained results on the effect of the reduction potential on TiO₂ properties, the reduction potential was chosen as −1.4 V with a reduction time ranging from 20 to 80 min.

On the CV diagrams of Figure 6a, in the dark, the anode current density is low and fluctuates following the reduced time. However, when UV is irradiated, the photocurrent density increases significantly. Out of the four reducing times, the most favorable one is 60 min because the photocurrent density reached the highest peak at 12.3 mA·cm⁻² (Table 2). Thus, the optimum conditions for cathodic polarization are a potential of −1.4 V within 60 min.

### 3.3 Photoelectrochemical characterization

The LSV of pristine TiO₂ and reduced TiO₂ in the dark and under UV illumination are shown in Figure 7a and b. It can be observed from Figure 7a that the pristine sample shows negligible dark current density, demonstrating that there was no EC activity in the dark. However, the reduced TiO₂ shows higher current density with a peak at −0.024 V due to the oxidation process Ti³⁺ to Ti⁴⁺, which proved that the electrical conductivity of the material was enhanced after cathodic polarization. As shown in Figure 7b, the reduced TiO₂ had better photoelectrochemical activities under UV light, with a higher photocurrent density (13.7 mA·cm⁻²) at 1.5 V compared with that of pristine TiO₂ achieving 7.3 mA·cm⁻², indicating more effective charge separation and transport.

The PCE of both samples with UV illumination, shown in Figure 7c, indicates that the PCE of the reduced

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**Table 1:** Photocurrent densities at a voltage of 1.5 V for the pristine TiO₂ electrode and reduced TiO₂ electrodes at different potentials (−1.2, −1.4, and −1.6 V)

<table>
<thead>
<tr>
<th>TiO₂ samples</th>
<th>Reduced potential (V)</th>
<th>i (mA·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO₂</td>
<td>−1.2</td>
<td>7.98</td>
</tr>
<tr>
<td>Reduced TiO₂</td>
<td>−1.4</td>
<td>9.75</td>
</tr>
<tr>
<td>Reduced TiO₂</td>
<td>−1.6</td>
<td>12.30</td>
</tr>
</tbody>
</table>

**Table 2:** Photocurrent densities at a voltage of 1.5 V for reduced TiO₂ electrodes at −1.4 V with different reduction times

<table>
<thead>
<tr>
<th>Reduction time (min)</th>
<th>i (mA·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8.9</td>
</tr>
<tr>
<td>40</td>
<td>10.9</td>
</tr>
<tr>
<td>60</td>
<td>12.3</td>
</tr>
<tr>
<td>80</td>
<td>11.8</td>
</tr>
</tbody>
</table>

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Figure 6: Influence of the reduction time on the CV diagrams of reduced TiO₂ in 1 M Na₂SO₄ without UV (a) and with UV illumination (b).
TiO₂ photoanode was higher than that of pristine TiO₂, achieving 41.3% at a potential of 0.417 V vs Ag/AgCl. The obtained efficiency was nearly 1.8 times higher than that of pure TiO₂ (23.5%). Moreover, Figure 7d shows the photoelectrochemical response current of the samples measured by the static potential method; the potential applied to the working electrode was 1.5 V. There was a noticeable increase or decrease in the response current for samples depending on whether UV illumination was used or not. The response currents were very small in the dark, but they increased considerably under UV light. The results proved that the reduced TiO₂ photoanode had a higher photocurrent response (16.1 mA·cm⁻²), showing higher photoelectrochemical activity.

To further study the charge separation and recombination of photogenerated electron–hole pairs, PL spectroscopy of samples was carried out. The PL spectra shown in Figure 8 indicate that pristine and reduced TiO₂ samples present an emission peak at 450 nm, which can be attributed to the electron trapped at shallowed level defects [41]. The reduced TiO₂ electrode exhibited a lower PL intensity, indicating a higher separation efficiency of photogenerated carriers. The PL result is consistent with the aforementioned results.

EIS diagrams in the Nyquist form have been used to study the electrode–electrolyte interfacial behavior and doping level of pristine TiO₂ and reduced TiO₂ samples. Figure 9a–c shows the Nyquist plots of pristine TiO₂ and reduced TiO₂ in the dark and under illumination in 1 M Na₂SO₄ solution. EIS diagrams were simulated by using Thales software following equivalent electrical circuits.
(EECs) from Figure 9d, and the values of elements in EECs are given in Table 3. The first EEC with four elements and the second one with six elements are presented for pristine TiO$_2$ and reduced TiO$_2$ electrodes, respectively. This result was the same as the one proposed in the previous literature [37].

As seen in Table 3, under UV illumination conditions, the charge transfer resistance ($R_{ct}$) values of pristine TiO$_2$ and reduced TiO$_2$ samples decreased about eight times in comparison with those in the dark. This proved that both samples show n-type semiconducting behavior because under UV light the charge carriers in the valence band get excited to the conduction band, which improves the electrical conductivity of samples. In addition, the $R_{ct}$ of pristine TiO$_2$ was around 300 times higher than that of reduced TiO$_2$ in dark or light conditions. This result was in agreement with the above LSV and chronoamperometry data because the reductive doping process creates more Ti$^{3+}$ states or forms oxygen vacancy states, which improved charge transfer properties and reduced charge transfer resistance ($R_{ct}$). A number of studies revealed that by lowering the resistance, electrons are more easily transported to the underlying TiO$_2$, resulting in increased electron injection and improved photoelectrochemical properties of the electrode [42].

The Mott–Schottky measurements were carried out at 1 kHz in 0.5 M Na$_2$SO$_4$ solution to study further their electronic properties. The Mott–Schottky plots of pristine TiO$_2$ and reduced TiO$_2$ electrodes in Figure 10 display a positive slope, demonstrating n-type semiconducting behavior. Obviously, the slope of pristine TiO$_2$ nanotubes is much higher than that of reduced TiO$_2$, which increases the charge carrier density for the reduced TiO$_2$ sample. The carrier density can be calculated by the Mott–Schottky plots using the following equation [43]:


Table 3: The values of ECC elements for the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition</th>
<th>( R_s ) (( \Omega ))</th>
<th>( C_d ) (( \mu F ))</th>
<th>( R_t ) (k( \Omega ))</th>
<th>( C_{CPE} ) (( \mu F ))</th>
<th>( n )</th>
<th>( R_{ct} ) (( \Omega ))</th>
<th>( W ) (k( \Omega ) s(^{-1/2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO(_2)</td>
<td>Dark</td>
<td>1.577</td>
<td>2.505</td>
<td>0.944</td>
<td>18.5</td>
<td>46.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>UV light</td>
<td>1.248</td>
<td>7.194</td>
<td>0.94</td>
<td>2.1</td>
<td>17.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reduced TiO(_2)</td>
<td>Dark</td>
<td>3.158</td>
<td>8.406</td>
<td>0.98</td>
<td>0.059</td>
<td>28.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>UV light</td>
<td>1.939</td>
<td>21.34</td>
<td>0.99</td>
<td>0.007</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: \( R_s \), electrolyte resistance; \( C_d \) and \( R_s \), capacitance and resistance of the material film, respectively. On the inside of nanotubes, CPE, constant phase element that has been used to replace the pure capacitor in non-ideality; \( R_{ct} \), charge transfer resistance; \( W \), Warburg diffusion element that relates to the mass transfer and ionic diffusion in nanotubes.

The EC and PEC activities of pristine TiO\(_2\) and reduced TiO\(_2\) electrodes for MO degradation were measured by the galvanostatic method with a current density of 3 mA cm\(^{-2}\), and the treatment time varied from 5 to 40 min. TiO\(_2\) is an n-type semiconductor and almost non-conductive; therefore, the EC activity on the pristine TiO\(_2\) electrode almost had no effect on MO. However, the reduced TiO\(_2\) nanotube film electrode had almost semimetallic behavior, so the electrical conductivity and charge carrier density of reduced TiO\(_2\) was much higher than those of pristine TiO\(_2\). As a result, the reduced TiO\(_2\) electrode can catalyze the EC degradation of MO. From the UV-Vis spectrum of the MO solution, the characteristic peaks of MO can be determined. Figure 11 shows the UV-Vis spectra of the MO solution that revealed two distinct absorption peaks: the peak of the aromatic ring at roughly 270 nm and the peak of the azo chromophores (\(-N\equiv-N\)–) at about 467 nm [30,45]. The intensity of the two peaks decreased gradually with increasing treatment time, demonstrating that the azo bond was broken and the aromatic rings were slowly destroyed. After 40 min of degradation, the two peaks were very faint, indicating that the majority of the MO and the intermediate organic compounds were degraded and eliminated [30].

Figure 10: The Mott–Schottky plots of pristine and reduced TiO\(_2\) electrodes.

\[
N_D = \frac{2}{ee\varepsilon_0} \left[ \frac{dE}{dC} \right]^{-1/2}
\]

where \( N_D \) is the carrier density, \( e \) is the electron charge (= 1.6 \times 10\(^{-19}\) C), \( \varepsilon \) is the dielectric constant (= 48 for TiO\(_2\) anatase), \( \varepsilon_0 \) is the permittivity of vacuum (= 8.86 \times 10\(^{-14}\) F cm\(^{-1}\)), \( C \) is the space charge capacitance, and \( E \) is the applied potential. Based on the Mott–Schottky plots and Eq. 6, the carrier densities of pristine TiO\(_2\) and reduced TiO\(_2\) were determined to be 1.25 \times 10\(^{20}\) and 1.7 \times 10\(^{25}\) cm\(^{-3}\), respectively. The carrier density of reduced TiO\(_2\) was significantly greater than that of pristine TiO\(_2\) nanotubes. The results demonstrated that the conductivity of TiO\(_2\) nanotubes remarkably increased via reductive doping. As seen in Figure 10, the capacitance of the pristine sample depends strongly on the applied voltage, which is typical for the space-charge layer-controlled capacity of an n-type semiconductor [44], and the flat-band potential of pristine TiO\(_2\) can be estimated as ~0.253 V. On the other hand, the reduced TiO\(_2\) sample showed little capacity dependence on the applied voltage, indicating semimetallic behavior. Because the capacitance of the metal was controlled by the Helmholtz layer at the solid–liquid interface, a flat-band potential of reduced TiO\(_2\) cannot be determined [37]. Thus, by the Mott–Schottky measurement, the reductive doping process significantly enhanced the donor density of TiO\(_2\), which tends to improve the electrochemical and photoelectrochemical characterization of the material.
According to previous studies \cite{29,30}, the EC degradation of MO on the reduced TiO$_2$ anode (r-TiO$_2$) occurs as follows. First, the hydroxyl radicals (\(\cdot\)OH) were created by direct oxidation of water following Eq. 7 and physically adsorbed on the anode surface. Consequently, it attacks the conjugated structure of the azo bond (\(-\text{N}==\text{N}\)-) and oxidizes MO to intermediates (Eq. 8). After that, the MO reduction intermediates will further oxidize to form aromatic metabolites, which ultimately mineralize into CO$_2$ and water as shown in Eq. 9:

\[
\text{r-TiO}_2 + \text{H}_2\text{O} \rightarrow \text{TiO}_2(\cdot\text{OH}) + \text{H}^+ + e^- \quad (7)
\]

\[
\text{r-TiO}_2(\cdot\text{OH}) + \text{MO} \rightarrow \text{TiO}_2 + \text{Intermediates} \quad (8)
\]

\[
\text{r-TiO}_2(\cdot\text{OH}) + \text{Intermediates} \rightarrow \text{TiO}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (9)
\]

Under UV light, the conductivity of pristine TiO$_2$ and reduced TiO$_2$ significantly increased, and both electrodes had high photoelectrochemical properties due to the fact that the PEC degradation of MO occurred on both electrodes. A possible PEC mechanism for the MO degradation of both anodes is proposed in Figure 12. Similar to photocatalytic activity \cite{46}, when TiO$_2$ was exposed to UV light, a photogenerated electron (e\(^-\)) in the valence band is excited into the conduction band, leaving a positive hole (h\(^+\)) in the valence band. The holes oxidized water to generate hydroxyl radicals (\(\cdot\)OH) (Eq. 10) on the surface of photoanodes, which interacted with MO following Eqs. 8 and 9:

\[
h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \quad (10)
\]

Besides, a positive potential is applied to a photoanode under the PEC condition, which creates hydroxyl radicals (\(\cdot\)OH) on the surface of the anode (Eq. 7) similar to the EC condition and transfers the photogenerated electrons to the cathode. The transferred electrons reduce the absorbed oxygen (O\(_2\)) on the cathode to form superoxide anions (O\(_2^\cdot\)) (Eq. 11). The activated O\(_2\) further reacts with water to form hydroxyl radicals (\(\cdot\)OH) (Eq. 10) and release oxygen (O\(_2\)).

\[
\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\cdot\text{OH}
\]

**Figure 11:** UV-Vis spectra of MO solution after different treatment times.

**Figure 12:** The degradation mechanism of MO on pristine and reduced TiO$_2$ photoanodes by the PEC method.
with H\(^+\) and, after a series of reactions, produces hydroxyl radicals (\(\cdot\)OH) (Eqs. 12–14), which are responsible for the degradation of MO according to Eqs. 8 and 9. Thus, the important advantage of using the positive potential is the decrease in the charge–carrier recombination. Furthermore, as a result of the reduced recombination, oxidation rates may increase with UV intensity [47,48]:

\[
\begin{align*}
e^- + O_2 & \rightarrow \cdot O_2^- \quad (11) \\
\cdot O_2^- + H^+ & \rightarrow HO_2^- \quad (12) \\
2HO_2^- & \rightarrow O_2 + H_2O_2 \quad (13) \\
H_2O_2 + \cdot O_2^- & \rightarrow \cdot OH + OH^- + O_2 \quad (14)
\end{align*}
\]

To demonstrate that the degradation of MO was caused by hydroxyl radicals (\(\cdot\)OH), tert-butanol as a quenching agent was added to the MO solution before treatment by the PEC method. The results are shown in Figure 13, which indicate that the presence of tert-butanol in the MO solution enhanced the residual MO concentration and reduced the decolorization efficiency of the MO solution after different treatment times. The higher the tert-butanol, the lower the decolorization efficiency achieved. This can be explained as follows: the part of the newly produced \(\cdot\)OH radicals were quenched by tert-butanol following Eq. 15 [29,49]; consequently, the ability to oxidize MO was reduced:

\[
\cdot OH + (\text{CH}_3)_2\text{COH} \rightarrow H_2O + \text{CH}_3C(\text{CH}_3)_2\text{OH} \quad (15)
\]

The intermediates generated during the PEC process of the MO solution were studied by LC-MS analysis. LC-MS chromatograms of the MO solution before and after treatment for 5 and 40 min by the PEC method are shown in Figure 14. The results showed that MO was fragmented into intermediates (Table 4) before being decomposed into CO\(_2\) and H\(_2\)O.

MO has a quinoid structure with red color at a low pH value and an azo structure with yellow color at a high pH value [50]. Thus, the effect of solution pH on the degradation of MO was studied. Figure 15 shows that the residual MO concentration decreased, and the decolorization efficiency increased when the pH was increased from 4 to 6. After that, when the pH value increased from 7 to 10, the residual MO concentration increased and the decolorization efficiency decreased sharply. The removal efficiency was very high (95–99%) when the pH value was in the range of 5–7, and a pH of 6 was optimal for the MO treatment by the PEC method. This result was in agreement with previous studies [29,50].

Figure 16 shows the residual MO concentrations and the decolorization efficiencies of MO solution after different treatment times by different degradation processes, in which the EC process on the reduced TiO\(_2\) electrode and the PEC process on both pristine and reduced TiO\(_2\) electrodes. As seen in Figure 16, the residual MO concentration significantly decreases and the MO removal efficiency considerably increases with the increase in the treatment time. However, after 30 min of the processing time, the removal efficiency of MO of all samples increase slightly: from 98.4% to 99.5% for PEC on reduced TiO\(_2\), from 95.1% to 97.4% for EC on reduced TiO\(_2\), and from 89.2% to 91.8% for EC on pristine TiO\(_2\). The PEC process for the degradation of MO on the reduced TiO\(_2\) electrode had the highest efficiency, and the EC process for MO removal on reduced TiO\(_2\) had higher efficiency than the PC process on pristine TiO\(_2\). This can be explained by the synergetic effect of EC and photocatalytic oxidations, and the PEC condition decreasing the charge–carrier recombination. This result is consistent with the results of the above study that, under UV illumination, the reduced TiO\(_2\) had the best photoelectrochemical properties.

There is a linear relationship between \(\ln(C_0/C)\) and the treatment time \(t\), as shown in Figure 17, which indicates the EC and PEC processes on reduced TiO\(_2\), and the

**Figure 13:** Influence of the tert-butanol concentration on the residual MO concentration (a) and (b) the decolorization efficiency of MO by the PEC method on the reduced TiO\(_2\) photoanode.
PEC process on pure TiO\textsubscript{2} following the pseudo-first-order kinetic reaction [29] described in the following equation:

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

where \(C_0\) (in mg\textperiodcentered L\textsuperscript{-1}) is the initial MO concentration, \(C_t\) (in mg\textperiodcentered L\textsuperscript{-1}) is the MO concentration after processing at time \(t\) (in min), and \(k\) (in min\textsuperscript{-1}) is the first-order rate constant.

The rate constant \(k\) can be determined from the plot \(\ln(C_0/C_t)\) vs \(t\); they are 0.1358 min\textsuperscript{-1} (\(R^2 = 0.997\)), 0.0934 min\textsuperscript{-1} (\(R^2 = 0.990\)), and 0.0688 min\textsuperscript{-1} (\(R^2 = 0.976\)) for PEC and EC processes on reduced TiO\textsubscript{2} and the PEC process on pure TiO\textsubscript{2}, respectively. This result demonstrated that the degradation of MO on reduced TiO\textsubscript{2} by the PEC process was faster than the EC process and almost two times faster than that on pristine TiO\textsubscript{2}.

Table 4: Intermediates of the degradation of MO by the PEC method

<table>
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<th>Structure</th>
<th>Molecular weight</th>
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<td><img src="image7" alt="Structure" /></td>
<td>94</td>
<td><img src="image8" alt="Structure" /></td>
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</tbody>
</table>
The comparison of pristine and reduced TiO$_2$ samples with other systems of TiO$_2$ for MO treatment is listed in Table 5. The reduced TiO$_2$ showed outstanding PEC performances and prospective potential in the treatment of MO.

In order to examine the stability of the reduced TiO$_2$ sample, six cycles of the degradation of MO by the PEC method were carried out. The applied current density was 3.0 mA·cm$^{-2}$ and the treatment time of one cycle was 40 min. As seen in Figure 18, after 40 min treatment, the removal efficiency of MO varied slightly from 99.5% to 96.8% in six cycling runs, indicating the remarkable stability of reduced TiO$_2$ nanotubes. Moreover, the results of SEM and X-ray of reduced TiO$_2$ after six cycles revealed that the crystal phase and surface morphology of the TiO$_2$ nanotubes had not changed significantly. Therefore, reduced TiO$_2$ possesses excellent stability for PEC degradation of MO.

4 Conclusions

Reduced TiO$_2$ nanotube film electrodes have been synthesized successfully by cathodic polarization under optimal conditions of $-1.4$ V potential and 60 min. The obtained samples were characterized by using DRS, SEM, XRD, and a variety of electrochemical methods such as CV, LSV, EIS, chronoaanperometry, and Mott–Schottky plots. The main results of this study are as follows: (i) the photoelectrochemical properties of reduced TiO$_2$ are higher than those of pristine TiO$_2$ materials due to the creation of more Ti$^{3+}$ states or oxygen vacancy states, which significantly increased the donor density (from $1.25 \times 10^{20}$ to $1.7 \times 10^{25}$ cm$^{-3}$) and photocurrent density (from 7.3 to 13.7 mA·cm$^{-2}$ at 1.5 V vs Ag/AgCl) and (ii) the degradation of MO on pristine TiO$_2$ and reduced TiO$_2$ electrodes was carried out by EC and PEC processes, in which the PEC process on the reduced TiO$_2$ electrode after 30 min had...
the highest efficiency (98.4%) and the EC process for MO removal on reduced TiO₂ had higher efficiency (95.1%) than the PEC process on pristine TiO₂ (89.2%). This can be explained by the synergetic effect of EC and photocatalytic oxidations as well as the PEC process decreasing the charge–carrier recombination.

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Data availability statement: All data generated or analyzed during this study are included in this published article.

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