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Submerged Photosynthesis of TiO$_2$-CuO Hetero-nanoparticles for the Solar Photo-electrolysis of Multiple Environmental Hazardous Substances

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Graphical Abstract

Abstract

Environmental challenges have become a matter of great concern, requiring immediate attention. Agricultural pollution, such as ammonia discharge, and industrial pollution, including the abuse
of organic dyes, present significant dilemmas for humanity. In response to these challenges, we propose an approach by synthesizing TiO$_2$-CuO hetero-nanoparticles capable of degrading multiple hazardous environmental substances. Submerged photosynthesis of crystallites (SPSC) can synthesize or assist in the synthesis of metal oxides due to its simplicity and environmentally friendly nature. TiO$_2$-CuO hetero-nanoparticles with varying Cu-Ti molar ratios were prepared, characterized, and evaluated for performance. The dispersion of CuO within TiO$_2$ was found to be relatively uniform. Increasing the amount of added Cu resulted in an increase in CuO content until reaching the upper limit. Despite minor variations, all hetero-nanoparticle samples exhibited excellent solar light absorption performance. The simultaneous utilization of solar light illumination and electrochemical techniques synergistically enhanced the degradation process of these hazardous substances. The hetero-nanoparticle with a Cu-Ti molar ratio of 0.17 demonstrated the optimal photo-electrochemical degradation performance, exhibiting a 150% increase in degradation efficiency under solar light illumination compared to dark condition. Furthermore, it exhibited superior efficiency in the electrochemical degradation of RhB under solar light, degrading 32% more than solar light alone, and 2% more than electrochemistry alone. The mechanisms behind the fabrication and degradation processes were also discussed, elucidating the underlying principles driving the observed performance. In conclusion, our research highlights the potential of TiO$_2$-CuO hetero-nanoparticles for solar light-assisted degradation of NH$_3$ and RhB, showcasing their environmental applications.

**Keywords:**
Submerged photosynthesis, titanium dioxide (TiO$_2$), heterojunction, oxygen vacancies, solar light, electrocatalysis
1. Introduction

To date, human beings have realized the serious consequences of uncontrolled pollution on the environment. In recent years, with the expansion of industrial production and population growth, the pollution problem has become more severe [1]. In agricultural production, the excessive use of nitrogen-containing fertilizers has led to a global issue of nitrogen pollution [2, 3]. Specifically, ammonia-polluted wastewater can cause eutrophication and contamination of water sources, posing a significant threat [4, 5]. On top of that, industrial wastewater is also a major source of pollution, with textile printing, dyeing, and treatment accounting for approximately 17-20% of industrial water pollution, as reported by the World Bank [6]. Fuel-related effluents contribute to non-aesthetic pollution and eutrophication, often undergoing chemical reactions and producing hazardous by-products [7-9]. Therefore, the degradation of these environmentally harmful substances has always been the goal of researchers.

Given the pressing environmental concerns, the adoption of clean energy has become imperative [10]. Solar light, as an inexhaustible huge energy source, supplies almost all the energy on earth [11, 12]. As a result, researchers have been working on the direct application of solar light and solar energy [13, 14], and of course, degradation. Solar light has been utilized for the degradation of various substances such as NH$_3$ [15], DBSNa [16], amoxicillin [17], and methylene blue [18]. Furthermore, electricity, as another clean energy, is also widely used in our daily lives and production processes [19]. The electrochemical method has also been applied to the degradation of pollutants, for example, nitrobenzene [20], tetracycline [21], and Orange G [22]. Additionally, solar light and electrochemical methods can be combined to degrade environmentally hazardous substances [23-25].
Metal oxides are widely recognized as the catalyst in these degradation processes, often involving heterogeneous oxidation reactions [26]. While individual metal oxides possess good catalytic degradation abilities under specific conditions, their applications are limited under other conditions [27]. To overcome this limitation, modification approaches have been explored [28], and heterojunctions have emerged as an effective strategy to expand the application range of specific metal oxides [29]. The submerged photosynthesis of crystallites (SPSC) method, first proposed by Jeem et al. [30], offers a novel route for the fabrication of metal oxide materials using UV light in aqueous solution (e.g., water, H₂O₂ solution). So far, SPSC has proven to be useful in synthesizing a wide variety of metal oxides [31-34]. Furthermore, the SPSC method can be employed to fabricate metal oxide doping or heterojunctions for various applications [35-37].

In this study, we employed the SPSC method with H₂O₂ to fabricate TiO₂-CuO heterojunctions for the electrochemical degradation of environmentally hazardous substances (NH₃ and Rhodamine B) under simulated solar light. Heterojunctions with varying Cu contents were synthesized and characterized to compare their performance. Overall, the synthesized heterojunctions exhibited high solar light absorption and demonstrated effective electrochemical degradation, albeit with some variations. NH₃ and RhB were selected as target pollutants due to their distinct properties, and the heterojunctions successfully electrochemically degraded them under simulated solar light. The results highlighted the excellent photoelectrochemical properties of the synthesized heterojunctions for the successful degradation of NH₃ and RhB using electrochemical methods under simulated solar light. The optimal Cu addition was also determined. Furthermore, the potential mechanisms involved in the fabrication of heterojunctions, NH₃ degradation, and RhB degradation are also discussed.
2. Materials and Methods

2.1 Materials

In this study, copper powder (Cu, spheroidal, Aldrich Chemistry, 14 – 25 μm, 99%), titanium isopropoxide (TTIP, [(CH₃)₂CHO]₄Ti, Wako Pure Chemical Cooperation, 95%), and hydrogen peroxide (H₂O₂, Wako Pure Chemical Cooperation, 30%) were used as the raw materials for the synthesis of TiO₂-CuO heterojunction. Titanium dioxide (TiO₂, High Purity Chemicals, 2 μm, 99%) was used as the control group. Carbon black (Alfa Aesar, 99.9+%%) was used as the conductive agent for the electrode preparation, polyvinylidene difluoride (PVDF, -(C₂H₂F₂)ₙ-, Apollo Scientific) was used as the binder, and N-Methyl-2-pyrrolidone (NMP, C₅H₉NO, Wako Pure Chemical Cooperation, Wako special grade) was used as the solvent for active substances. 0.5 M sulfuric acid diluted from concentrated sulfuric acid (H₂SO₄, Wako Pure Chemical Cooperation, 95%) was used as the electrolyte for the electrochemical property test between TiO₂-CuO heterojunction and TiO₂. 0.25 M sulfuric acid (H₂SO₄, Thermo Scientific) was used as the electrolyte for the solar light electrochemical test. 0.1 M ammonia water was diluted from concentrated ammonia water (NH₃·H₂O, Wako Pure Chemical Cooperation, 25%), and worked as the main degradation target. Additionally, Rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, Wako Pure Chemical Cooperation) was formulated as a 10 mg/L solution as a secondary photo-electro degradation target, with 0.1 M sodium sulfate (Na₂SO₄, Kanto Chemical Co., Inc., 99.0%) solution as the electrolyte. All chemicals were used as received without further purification.

2.2 Synthesis Process of TiO₂-CuO Heterojunction

Cu powder of different mass (100 mg, 200 mg, 500 mg, 800 mg, 1000 mg) were used for the synthesis of TiO₂-CuO heterojunction. Cu powder was mixed with 10 mL of H₂O₂ solution and placed under UV lamp (~ 30 mW/cm², λ = 365 nm) illumination while stirring at 300 rpm.
Afterward, 1 mL of TTIP was added dropwise to the mixture and stirred for 2 hours until the solution changed color. The resulting precipitates were collected by centrifugation and washed three times with distilled water and ethanol to remove impurities. The washed precipitates were then dried in an oven at 50°C for 24 hours, resulting in bluish green particles.

The dried bluish green solid was further ground into powder and evenly placed in a crucible for calcination. The calcination temperature was 500°C. At first, the temperature was raised for 2 hours and kept for 12 hours, then the furnace was naturally cooled to ambient temperature. During this process, the sample underwent another color change. The product would be collected for further research.

2.3 Structural Characterization

All samples were observed by a field emission scanning electron microscope (FESEM, JEOL JSM-7001F) operated at 15 kV and a transmission electron microscope (TEM, JEOL JEM-2000FX) operated at 200 kV. High-resolution transmission electron microscopy (HRTEM) images were taken by a scanning transmission electron microscope (FEI Titan G3 60-300) operated at 300 kV. X-ray diffraction (XRD) measurements were conducted using an X-ray diffractometer (RIGAKU Miniflex 600) with the Cu Kα (λ = 1.5406 Å) radiation as the source. A photoelectron spectrometer with monochromatic Mg Kα radiation was used for X-ray photoelectron spectroscopy (XPS, JEOL JPS-9200). UV-vis absorption spectra were measured using a UV-vis spectrometer (JASCO V-770 spectrophotometer). The band gap information was obtained from Tauc’s plot calculated by the spectrometer.

2.4 Photo-electro Degradation Experiments

2.4.1 Electrode Preparation
TiO$_2$-CuO powder (electrode material), carbon black (conductive material), and PVDF (binder) were mixed in a mass ratio of 8:1:1. Then, a few drops of NMP were dropped into the solid mixture and stirred for 24 hours to ensure the thorough mixing of these materials. After this step, the mixed electrode material suspension was evenly spread on the cleaned carbon paper and dried under 50°C for another 24 hours. For comparison, TiO$_2$ powder was also used to prepare the electrode material as the control group.

2.4.2 Electrochemical Degradation of NH$_3$

Both the TiO$_2$-CuO electrode and TiO$_2$ electrode underwent the electrochemical test using a three-electrode system (Metrohm Multi Autolab M101) as illustrated in Supplementary Fig. S1. The surface area of the working electrode (WE) was 1 cm$^2$. A platinum foil with an area of 1 cm$^2$ served as the counter electrode (CE), while a silver chloride electrode (Ag/AgCl/KCl) functioned as the reference electrode (RE). 40 mL of 0.5M H$_2$SO$_4$ was used as the electrolyte, and 10 mL of 0.1 M NH$_3$·H$_2$O was added into the electrolyte for the electrochemical test. The linear sweep voltammetry (LSV) method was used to find the differences in electro degradation efficiency between TiO$_2$/CuO electrode and the TiO$_2$ electrode. In this experiment, the current data were recorded under different scan rates (25, 50, 75, 100, 150, 200, unit: mV/s) within the voltage range of −0.1 V to 0.7 V for further analysis.

2.4.3 Photo-Electro Degradation of NH$_3$

In the photo-electro degradation test, the three-electrode system remained the same as the previous test, with the exception that the electrolyte was replaced with 0.25 M H$_2$SO$_4$. A solar light simulator (Asahi Spectra HAL-320W, AM 1.5G, ~ 200 mW/cm$^2$) was used as the solar light source in this test. The LSV method was used again under both solar light illumination and dark condition. Similarly, the current data was recorded under different scan rates (10, 25, 50, 75, 100, 150, 200,
unit: mV/s) from the same potential range for analysis. In addition, the potentiostatic light-dark cross experiment and light-dark contrast test were also taken to prove the electrochemical catalytic effect of the heterojunction under solar light. The whole light-dark cross experiment would last for 30 mins, switching the solar light simulator on and off per 30 s. 0.5 V potential was applied for the system, while 0.5 M H₂SO₄ worked as the electrolyte. In the light-dark contrast experiment, the whole process would also last for 30 mins with continuous solar light illumination and dark condition, respectively. All conditions, except for the light conditions, remained the same as the light-dark cross experiment.

2.4.4 Photo-Electro Degradation of RhB

The ability of the TiO₂-CuO electrode to degrade RhB under solar light was tested using the constant current method. A total of 50 mL of Na₂SO₄ (0.1 M) and RhB (10 mg/L) mixture was used as the electrolyte and degradation target. The experiment was conducted for 1 hour under three different conditions: solar light only, constant 0.03 A current only, solar light and 0.03 A current simultaneously. Then, the absorbance of the solution at the beginning and end were recorded to determine the solar light electro degradation efficiency.

3. Results and discussion

3.1 Characterizations of TCO Samples

Table 1. Naming principles of different TiO₂-CuO heterojunctions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Mass of Cu powder added per 1 mL TTIP</th>
<th>Cu-Ti molar ratio of precursor</th>
<th>Cu-Ti molar ratio in TCO heterojunctions</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCO 100</td>
<td>100 mg</td>
<td>0.47</td>
<td>0.11</td>
</tr>
<tr>
<td>TCO 200</td>
<td>200 mg</td>
<td>0.94</td>
<td>0.17</td>
</tr>
<tr>
<td>TCO 500</td>
<td>500 mg</td>
<td>2.34</td>
<td>0.38</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>TCO 800</td>
<td>800 mg</td>
<td>3.75</td>
<td>0.49</td>
</tr>
<tr>
<td>TCO 1000</td>
<td>1000 mg</td>
<td>4.68</td>
<td>0.52</td>
</tr>
</tbody>
</table>

The naming principle of different TCO (TiO$_2$-CuO) heterostructures fabricated by the SPSC methods is shown in Table 1, based on the Cu powder addition during the synthesis. The Cu-Ti addition ratios are calculated by a TTIP density of 0.955 g/cm$^3$ according to the data provided by the manufacturer. Fig. 1(a) shows the transmission electron microscopy (TEM) observation of the TCO 200 heterojunction, displaying particles with an average size of approximately 20 nm. The particle size distribution is uniform, indicating good homogeneity of the products by the SPSC method. In addition, according to the TEM observation, the particles are relatively perfect. Other TCO samples, shown in supplementary Fig. S2, also exhibit a similar particle size, indicating that different Cu addition would not significantly affect the particle size of TCO samples. Supplementary Fig. S3 also shows the absence of pores, indicating the excellent quality of the TCO particles.

**Fig. 1** (a) TEM observation of TCO 200; (b) SAED of TCO 200; (c) the relationship between addition Cu-Ti molar ratio and TCO Cu-Ti molar ratio

The selected area electron diffraction (SAED) result of TCO 200 is shown in Fig. 1(b). Ring-shaped diffraction spots can be clearly observed in these diffraction patterns, which proves that all
TCO samples have polycrystalline structures. Anatase (101), rutile (110), and tenorite (111) phase were recognized in TCO particles. The SAED patterns of other TCO samples are also shown in supplementary Fig. S2, showing the same results as TCO 200. These findings confirm the successful combination of CuO and TiO$_2$ through the SPSC method.

Moreover, the Cu-Ti molar ratio results of TCO heterojunction samples, determined by electron dispersive spectroscopy (EDS), are provided in Table 1. With the increment of Cu powder addition, the Cu-Ti molar ratio gradually rises. The relationship between TCO Cu-Ti molar ratio and addition Cu-Ti molar ratio is shown in Fig. 1(c). For TCO 100, TCO 200 and TCO 500, the TCO Cu-Ti molar ratio is related to the addition Cu-Ti molar ratio as the following linear equation (1):

$$r = k \times r_o$$  \hspace{1cm} (1)

where $r$ is the Cu-Ti molar ratio of TCO samples, and $r_o$ is the Cu-Ti addition molar ratio. In equation (1), $k$ is introduced and defined as the hetero constant in this study, as a dimensionless unit. In the SPSC method, the $k$ is found as 0.167. However, while the amount of Cu powder addition was higher than 500 mg (Cu-Ti addition molar ratio higher than 2.341), the increase in the Cu-Ti molar ratio of TCO started to slow down, which is manifested by the exponential fitting curve, shown in Fig. 1(c). At this time, the relationship between the addition Cu-Ti molar ratio and the TCO Cu-Ti molar ratio can be expressed by the following equation:

$$r = 0.640 - 0.640 \times 0.689^{r_o}$$  \hspace{1cm} (2)

The calculation shows the maximum Cu-Ti molar ratio of TCO for 1 mL TTIP addition is 0.640.

XRD patterns of different TCO samples are displayed in Fig. 2(a). Different phases are represented by different symbols. The red diamonds represent the anatase (TiO$_2$) phase, whose peaks locate at around 25°, 48°, 70°, and 75°. The blue hearts represent the rutile (TiO$_2$) phase, which exhibit peaks at 27° and 41°. The black dots represent the tenorite (CuO) phase, which locate at 32°, 35°,
39°, 49°, 53°, 58°, 62°, 66°, and 68°. These results confirm that TCO consists of their own structures of TiO$_2$ and CuO. According to the XRD patterns, with the increase of Cu powder addition, the ratio of the peak intensity of CuO and TiO$_2$ also increases to varying degrees, which is consistent with the EDS results. When the Cu powder addition is low, increasing Cu addition would significantly enhance the peak intensity of CuO (TCO 100 and TCO 200). However, when the Cu powder addition is high, increasing Cu addition does not result in a significant increase in the peak intensity of CuO (TCO 800 and TCO 1000). Furthermore, the tiny peak located at 45° may indicate the presence of trace unoxidized Cu in the samples.

Fig. 2(b) shows the UV-vis-NIR spectra of TCO samples, along with P25 and CuO as control groups. All TCO samples have high absorption in the UV range (300 – 380 nm), visible light range (380 – 750 nm), and NIR range (750 – 800 nm). The UV-vis-NIR spectrum of P25 (represented by the black dashed line) does not show significant absorption in the visible light and NIR regions, while CuO (represented by the red dashed line) lacks substantial UV absorption. Considering that solar light predominantly falls within the wavelength range of 250 – 1000 nm [38, 39], compared to P25 and CuO, TCO would have higher solar light absorbance. Furthermore, different TCO samples exhibit varying levels of absorbance. According to the UV-vis-NIR spectra, TCO 100 shows the highest absorption of visible light across all wavelengths, including red light and orange light (~ 600 nm to 750 nm). With the increase of Cu content, the absorption of red light and orange light by TCO decreases slightly. Despite the slight differences in absorbance, all these heterojunction samples appear black, as shown in Fig. 2(c). This result suggests that these samples have differences in the absorption of solar light.
The XPS spectra of different TCO samples are shown in supplementary Fig. S4. In general, for TCO samples with different Cu content, there is no significant difference in the peak position. The similar peaks in the Ti 2p range (458 eV and 464 eV, representing the peak of TiO$_2$ Ti 2p3/2 and TiO$_2$ Ti 2p1/2, respectively [40, 41]), Cu 2p range (932 eV as CuO Cu 2p3/2 peak [42]), and O 1s range (529 eV as O 1s peak [43]) indicate that the surface element conditions of these TCO samples are largely consistent. However, despite the identical peak position, there are differences in the O 1s peak, as shown in Fig. 3. The O 1s peak of all TCO samples can be split into two different peaks. The main peak, located at around 529 eV, corresponds to the lattice O 1s peak. The smaller peak at 531 eV is attributed to oxygen vacancies in CuO [44, 45]. These results indicate that there are
oxygen vacancies on the surfaces of all TCO hetero particles. Furthermore, as shown in Table 2, TCO 200 has the highest peak intensity (~ 367 counts), indicating a possibility of more promising applications for this particular composition. The small bumps around 525 eV are considered as noise without discussion.

![XPS spectra](image)

**Fig. 3** XPS spectra O 1s peak splitting of (a) TCO 100, (b) TCO 200, (c) TCO 500, (d) TCO 800, and (e) TCO 1000

<table>
<thead>
<tr>
<th>Samples</th>
<th>TCO 100</th>
<th>TCO 200</th>
<th>TCO 500</th>
<th>TCO 800</th>
<th>TCO 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity</td>
<td>138</td>
<td>367</td>
<td>262</td>
<td>250</td>
<td>266</td>
</tr>
</tbody>
</table>

Table 2. XPS counts of oxygen vacancy peaks for different TCO samples (unit: counts).

The detailed structural analysis of TCO samples was carried out using a scanning transmission electron microscope. Fig. 4 shows the high-resolution TEM (HRTEM) images of TCO 200 and 800 as examples, while additional images are displayed in supplementary Fig. S5. Anatase (1 0 1) plain (3.51 Å and 3.63 Å) is recognized in TCO 200 and TCO 800, respectively. Rutile (1 1 0)
plain (3.32 Å) is found in TCO 200, while rutile (2 0 0) plain (2.26 Å) is found in TCO 800. These results suggest the existence of two different TiO$_2$ phases in TCO heterojunction. Also, tenorite is found to exist in TCO. Tenorite (1 1 1) plain exists in TCO 200, and (−1 1 1) plain exists in TCO 800. Besides the results just discussed, other TCO samples also have three phases simultaneously. Additionally, the HRTEM analysis reveals that different phases can coexist within the same particle, providing strong evidence for the heterojunction structure of TCO.

The high-angle annular dark field and energy-dispersive X-ray spectroscopy (HAADF-EDS) mapping results from TCO 200 and TCO 800 are present in Fig. 4, with others shown in supplementary Fig. S5. The EDS mapping includes Ti and Cu elements. HAADF imaging is highly sensitive to the change of atomic number within the sample, with brighter positions (circled by red dotted lines) indicating higher atomic numbers, where exhibit a higher content of Cu in TCO samples. The corresponding EDS results in the same area circled by red dotted lines also show a high density of Cu, confirming the consistency between HAADF and EDS results. Based on these findings, it can be concluded that in the TCO heterojunction, TiO$_2$ forms the main component with CuO uniformly distributed within the heterojunction. When the Cu addition is low, the area of Cu in the EDS mapping is small. When the addition of Cu amount increases, the area of Cu in EDS would also increase, eventually reaching the limitation calculated beforehand. Moreover, the thickness of TCO 200 at position 1 in supplementary Fig. S6 is estimated is 20.34 nm, which meets the TEM stats [46]. This result provides evidence for the absence of pores within the TCO samples together with supplementary Fig. S3.
Fig. 4 HRTEM and HAADF images, and EDS mapping of (a) TCO 200 and (b) TCO 800

3.2 Fabrication Mechanism of TCO Heterojunction

The fabrication mechanism of TCO heterojunctions is depicted in Fig. 5. Based on our previous research, it was observed that Cu does not react with H$_2$O$_2$. When TTIP was dropped into the mixed solution of Cu and H$_2$O$_2$, a rapid formation of a yellow solid occurred (Supplementary Fig. S7). This can be represented by the following equation:
\[ \text{TTIP} + 2\text{H}_2\text{O}_2 \rightarrow \text{Ti}(\text{O}_2)_2 + 4\text{IPA} \quad (3) \]

The product formed in this step, \( \text{Ti}(\text{O}_2)_2 \), is an unstable yellow intermediate \([47, 48]\). After a short period, the liquid started to boil, accompanied by the release of a significant amount of heat, then the liquid began to change color from yellow to bluish green, suggesting the oxidation of Cu powder, and the bluish green product obtained in this step may be \( \text{Cu}_2(\text{OH})_2\text{CO}_3 \), as represented by the equation below \([49]\):

\[
2\text{Cu} + \text{Ti}(\text{O}_2)_2 + \text{H}_2\text{O} + \text{CO}_2 \xrightarrow{\text{UV}} \text{TiO}_2 + \text{Cu}_2(\text{OH})_2\text{CO}_3 \quad (4)
\]

Control group experiments revealed that UV illumination played a crucial role in step 2. When applying UV illumination, the time required for the solution to boil and change color was approximately 90 s after dropping TTIP. However, under dark conditions, this time was extended to about 120 s. The presence of UV significantly reduced the reaction time by 25%.

The final step in the fabrication process involved calcination at 500°C, leading to the decomposition of \( \text{Cu}_2(\text{OH})_2\text{CO}_3 \). This can be represented by the following equation:

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3 \xrightarrow{500^\circ\text{C}} 2\text{CuO} + \text{H}_2\text{O} + \text{CO}_2 \quad (5)
\]

Recrystallization occurred in this process with the color changed from bluish green to black. Fig. 5 shows the overall fabrication mechanism of the TCO heterojunctions.
3.3 Photo-electro Properties of TCO Samples

3.3.1 Electrochemical Performance of TCO Samples

The electrochemical performance of TCO samples was evaluated, and TCO 200 was chosen as the representative electrochemical catalyst sample for comparison with TiO$_2$, as shown in Fig. 6. The potential sweep range was set from $-0.1$ V to $1.5$ V (vs. Ag/AgCl), and the scan rate was varied as 25, 50, 75, 100, 150, and 200 mV/s. Fig. 6(a) shows the linear sweep voltammetry (LSV) of the TCO 200 electrode in the dark. Within the scanning range, only a single oxidation peak appeared at around $0.2$ V, which is attributed to the oxidation of NH$_3$ [50]. As the potential exceeded $1.0$ V, the current density increases again. This rise is generally associated with the oxidation of H$_2$O and the generation of O$_2$. As the scan rate increases, both the current density and the peak current rise. Additionally, the polarization effect occurs, causing a shift in the peak potential towards the positive direction. Electrochemical polarization and concentration polarization appear with the
increase in scan rate, confirming the irreversible nature of NH$_3$ oxidation process. On the other hand, the TiO$_2$ electrode (Fig. 6b) did not exhibit any current peak at 0.2 V, regardless of the scan rate, indicating that TCO can be used as the electrode for the NH$_3$ degradation, whereas TiO$_2$ cannot fulfill this function. Furthermore, TCO has also been proven to work better than CuO under the same condition [50].

![Image of LSV curves](image)

**Fig. 6** The LSV curves for the degradation of 0.1 M NH$_3$ in 0.5 M H$_2$SO$_4$ using (a) the TCO 200 electrode and (b) the TiO$_2$ electrode

3.3.2 Solar-Electro Degradation Performance of TCO Samples

Solar-electro degradation performance is discussed in this section since TCO samples have been proven to have a high absorption of solar light (section 3.1) and good electrochemical degradation performance of NH$_3$ (section 3.3.1). All the TCO samples were prepared as electrodes and subjected to various scan rates ranging from 10 to 200 mV/s. The results are shown in Fig. 7 and supplementary Fig. S8. Despite the drop in electrolyte concentration, all TCO samples still exhibit NH$_3$ degradability, which is displayed by the peaks around 0.2 V. These results indicate that all TCO samples can degrade NH$_3$ by electrochemistry under solar light. Same as the data in section 3.3.1, the current density would generally increase as the scan rate increases, and the electrode
polarization still exists in all kinds of TCO, proving that for all TCOs, the electrochemical degradation of NH₃ under solar light is still an irreversible reaction. In addition, under solar light, the degradation peak of NH₃ in LSV is generally higher than those of the same TCO sample under dark conditions. In electrochemistry, the current density has a positive linear correlation with the electrochemical reaction rate:

\[
i = \frac{I}{A} = nF \times v
\]

where \( i \) is reaction current density (A·cm⁻²), \( A \) is electrode area (cm⁻²), \( I \) is the reaction current (A), \( n \) is the number of electrons transferred, \( F \) is Faraday constant (96500 A·s·mol⁻¹), and \( v \) is the rate of reaction (mol·s⁻¹·cm⁻²). In this reaction, the greater the current density of the reaction under the same conditions, the faster the degradation rate.
Then, according to the formula above, a comparison has been taken among all TCO samples. Under solar light illumination, there are differences in the performance of electrodes with different Cu contents. The current peak of TCO 200 is the highest at different scan rates. The highest peak current density is 5 mA/cm$^2$ under 200 mV/s scan rate. This result means that the degradation rate of TCO 200 for NH$_3$ can be as high as $1.73 \times 10^{-8}$ mol·s$^{-1}$·cm$^{-2}$, estimated by equation (6). In dark condition, the highest peak current density is 2 mA/cm$^2$ under 200 mV/s scan rate, at which time the degradation rate is $6.91 \times 10^{-8}$ mol·s$^{-1}$·cm$^{-2}$. Compared to the dark condition, solar light can increase the rate of electrochemical degradation by 150%. Below which is the TCO 100, whose
current density can reach 3.5 mA/cm² at 200 mV/s. The degradation rate is calculated as $1.21 \times 10^{-8}$ mol·s⁻¹·cm⁻², which is 30% lower than that of TCO 200. Compared Fig. 7 and supplementary Fig. S8, TCO 200 is the best solar light electrochemical catalyst, followed by TCO 100. The degradation efficiency of TCO 500, TCO 800, and TCO 1000 are lower.

Apart from the LSV experiment, the potentiostatic light-dark cross experiment and light-dark contrast test are also taken to find out the improvement of electrochemical degradation properties under solar light illumination. TCO 200 was chosen as the electrode active material because of its superior performance, and 0.5 M H₂SO₄ was used as the electrolyte. Fig. 8(a) shows the solar-dark cross current curve of NH₃. The reaction current rises when applying solar light, indicating the increase in reaction rate. After running 900 s, the current rises by about 2 μA, which is a 33% increase compared to the case without solar light. Additionally, Fig. 8(b) shows the current curve of NH₃ electrochemical degradation by TCO under solar light and in the dark, separately. Compared to the electrochemical reactions in the dark, the current of reaction under solar light increases at different periods of the process, about twice the current in dark conditions. In summary, together with the LSV results, solar light illumination can effectively promote the electrolysis of NH₃ through the TCO electrode.
Fig. 8 (a) Light/dark cross experiment and (b) potentiostatic light-dark contrast test of TCO 200 electrode

3.3.3 Solar-Electro Degradation Performance of TCO Samples for Other Environmentally Hazardous Materials

Except for NH$_3$, RhB, which is one kind of organic dye, was also considered as the target material for electrochemical degradation under solar light. Table 3 shows the results of RhB electrochemical degradation after 1 h under three different conditions: solar light only, constant current only, and both solar light and constant current. In this experiment, TCO 200 was chosen as the active material of the electrode. When applying solar light and current, TCO has the highest photodegradation efficiency. After 1 h, 67.06% of the RhB remained in the solution. If there is only one condition, then the degradation ability will decrease. If only applied solar light, there would be 99.37% of RhB remained in the solution. Meanwhile, 69.46% of RhB would remain in the solution if only applied 30 mA DC. Overall, the degradation of the ability of TCO for RhB is not high. This may be due to the limited reaction area (1 cm$^2$), or the inconvenient stirring of the three-electrode system, which limited the reaction rate. From the results of the control group, it can be deduced that applying current is the main reason causing the degradation of RhB, and the solar light plays an auxiliary role. Supplementary Fig. S9 proves that carbon paper cannot be used for the electrochemical degradation of RhB. Therefore, TCO is critical for the solar light electrochemical degradation of RhB.

Table 3. Results of RhB solar light electrochemical degradation by TCO 200.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Light source</th>
<th>Galvanostatic</th>
<th>RhB content after 1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-electro</td>
<td>Solar light</td>
<td>30 mA DC</td>
<td>67.06%</td>
</tr>
<tr>
<td>Solar</td>
<td>Solar light</td>
<td>None</td>
<td>99.37%</td>
</tr>
</tbody>
</table>
3.4 The Mechanisms of Degradation

3.4.1 NH$_3$ Solar-Electro Degradation Mechanism

The degradation mechanism of TCO for NH$_3$ can be inferred from Fig. 6 and Fig. 7. Taking scan rate 25 mV/s as an example. After scanning pass 0.1 V, the current density rises rapidly. This may be due to the adsorption of NH$_3$ on the electrode surface being hindered by hydroxyl ions [50]. Under solar light, TiO$_2$-CuO worked as a photosensitizer. TiO$_2$ can absorb light, excite photogenerated electrons, and transfer electrons to the conduction band (CB) of TiO$_2$ [51].

\[
\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + h^+ + e^- \quad (7)
\]

Meanwhile, as a p-type semiconductor, the oxygen vacancies in the CuO can absorb the O$_2$. When the p-type semiconductor (CuO) and n-type semiconductor (TiO$_2$) form a PN junction, the photogenerated electrons would flow from TiO$_2$ to CuO, combining with the absorbed O$_2$, to form the superoxide anion radical ·O$_2^-$ [51].

\[
\text{O}_2 + e^- \rightarrow \cdot \text{O}_2^- \quad (8)
\]

Increasing the scan rate will increase the current density, which is because that NH$_3$ interacts with the ·O$_2^-$ on the surface of the TCO electrode, making the electrons back to the conduction band of CuO, thus increasing the resistance of the TCO electrode [52], causing the polarization. The current peak represents the highest reaction rate. After that, the current gradually decreases, which may be due to the formation of adsorbed nitrogen atoms (N$_{\text{ads}}$) [53, 54]. N$_{\text{ads}}$ have been proven to be dehydrogenated from NH$_3$ on the Cu site of the TCO electrode [55]. The reactive oxygen species ·O$_2^-$ can lead to the dehydrogenation of NH$_3$ and form N$_{\text{ads}}$. In this step, solar light can induce more oxygen vacancies in the TCO electrode [56] to increase the degradation efficiency.
N_{ads} can also be adsorbed by the electrode, clogging the surface of the electrode, and making the decrease of current density. Fig. 9 shows the degradation mechanism of NH$_3$ by TCO electrode under solar light. The whole process is written as the following equations (9 – 12):

Anode: $\text{NH}_3 \rightarrow \text{N}_{ads} + 3\text{H}^+ + 3\text{e}^-$ \hspace{1cm} (9)

Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ \hspace{1cm} (10)

$\text{N}_2$ formation: $2\text{N}_{ads} \rightarrow \text{N}_2$ \hspace{1cm} (11)

Overall: $4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$ \hspace{1cm} (12)

3.4.2 RhB Degradation Mechanism

According to the results of 3.3.3, TCO can also degrade RhB under solar light. After the end of the electrochemical degradation, brown impurities appear on the Pt counter electrode. These impurities could be washed by excess dilute HCl solution, and the platinum electrode returned to its original color. From the above, it is considered that Cu$_2$O is generated from the working electrode to the counter electrode. Furthermore, in the experiments, gas generation was observed on the surface of the platinum counter electrode. It is inferred that in the electrochemistry device, the current flows from WE to CE. At this time, H$_2$ was generated on the surface of the CE. The cathode half reaction is as the following equation (13):

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(g)$$ \hspace{1cm} (13)

During this process, the active material on the WE were damaged, and it can be judged that part of the copper oxide is hydrolyzed, which explains the reduction reaction of copper on the cathode:

$$2\text{CuO} + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{Cu}_2\text{O(s)} + \text{H}_2\text{O}$$ \hspace{1cm} (14)

Meanwhile, RhB was oxidized in the photo-electro process as the anode reaction with the assistance of solar light.

$$\text{RhB} \stackrel{hv}{\rightarrow} \text{RhBO} + 2\text{H}^+ + 2\text{e}^-$$ \hspace{1cm} (15)
In equation (15), RhBO refers to the oxidation product of RhB. During the degradation process, the color of the RhB solution did not change (supplementary Fig. S10), indicating a cleavage of RhB chromophore by the oxidant during the electrochemical degradation under solar light [57, 58]. The mechanism of the RhB process is shown in Fig. 9.

**Fig. 9** Electrochemical degradation mechanism of NH₃ and RhB under solar light
4. Conclusion.

In conclusion, we have successfully fabricated TiO₂-CuO (TCO) heterojunctions with different Cu-Ti molar ratios using the SPSC method with H₂O₂ for solar light electrochemical applications. The SPSC method, utilizing only UV light and H₂O₂, offers an environmentally friendly approach without the need for high temperature and pressure. These as-synthesized TCO samples consist of anatase TiO₂, rutile TiO₂, and tenorite CuO phases. The CuO content in the samples increases with the addition of Cu with an upper limit, which is lower than that of TiO₂. The particle size of these samples ranges from 20 to 25 nm, and they exhibit a dark color due to the presence of oxygen vacancies, resulting in high solar light absorption. Furthermore, compared to the commercially available TiO₂, TCO samples exhibit electrochemical catalytic effects on various environmentally hazardous substances, such as NH₃ and RhB. Through experimental investigation, TCO 200 sample (200 mg Cu powder addition) exhibited the highest catalytic efficiency. The combined effect of solar light illumination and electrochemical methods synergistically promote the degradation process of these hazardous substances. Solar light increased the rate of electrochemical degradation of NH₃ by 150%. Meanwhile, through experimental observations and data analysis, we elucidated the reaction mechanism behind the TCO heterojunction fabrication and the degradation of hazardous substances. The current work significantly simplifies the synthesis steps of high-performance TiO₂-CuO heterojunctions, which can effectively degrade different environmental pollutants using a single catalyst, holding great practical significance for future applications.

CRediT authorship contribution statement
Zhehan Yu: Conceived the idea, Carried out the structure fabrication, Structure/material characterization, Data curation, Writing - original draft. Shilei Zhu: 3D structure modeling, Assisted figure drawing. Lihua Zhang: Formal analysis, Writing-review & editing. Seiichi Watanabe: Supervision, Conceptualization, Methodology.

Data availability statement
The original data in this work is available from the corresponding authors upon reasonable requests.

Declaration of Competing Interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


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