

Photocatalytic removal of 2,4-dichlorophenoxyacetic acid herbicide on copper oxide/titanium dioxide prepared by co-precipitation method

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Abstract. In this work, suppression of the charge recombination on the titanium dioxide (TiO₂) was reported by the addition of copper oxide (CuO), which led to a higher activity of TiO₂ for removal of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide. A series of CuO/TiO₂ with CuO loadings of 0.1-1 wt% was prepared through a co-precipitation method. X-ray diffraction patterns revealed that the presence of CuO could not be detected as the low loading amount of CuO might have good dispersion on the surface of TiO₂. Diffuse reflectance UV-visible spectra suggested that low loading amount of CuO did not influence the optical property of TiO₂. Fluorescence spectroscopy revealed that TiO₂ possessed a dominant emission peak of 407 nm at an excitation wavelength of 218 nm. The increasing loading amount of CuO decreased the emission intensity of TiO₂, suggesting the successful reduction of charge recombination. After irradiation under UV light for 1 h, CuO(0.1 wt%)/TiO₂ gave the highest percentage removal of the herbicide among the samples. The optimum loading amount of CuO might improve the charge separation and reduce the electron-hole recombination on TiO₂ without blocking the active sites, thus leading to the improved photocatalytic activity. This work showed that CuO/TiO₂ is a potential photocatalyst for environmental remediation.

1. Introduction

Water contamination is a great concern that gains attentions due to the adverse effects it will bring to the ecosystem. The herbicide is one of the contaminants that can be detected from water source because of its wide usage for weeds control to increase production of crops [1, 2]. In order to have a clean water source, efficient water treatment approaches must be developed.

Photocatalysis has been considered as one green approach for environmental remediation since organic pollutants can be mineralized to non-harmful end products such as carbon dioxide, water and inorganic ions. Titanium dioxide (TiO₂) photocatalyst has been established for degradation of various organic pollutants due to several advantages such as low toxicity, low cost, good stability and good photocatalytic activity. Although TiO₂ possesses high photocatalytic activity as compared to many other photocatalysts, its photocatalytic efficiency is still limited by the high recombination rate of charge carriers. Various modifications have been done on TiO₂ in order to further improve its photocatalytic performance, such as using noble metals, metal oxides, non-metal ions and dyes [3, 4].



Recently, roles of cocatalyst in enhancing the photocatalytic efficiency of a semiconductor photocatalyst have been highlighted due to its capability in promoting charge separation and suppressing photo corrosion of a semiconductor photocatalyst [5-9]. Among types of cocatalyst, transition metal compounds are especially the topic of interest because they have advantages of earth abundance and low cost [5]. One of the most studied transition compounds is copper species. It has been reported that copper species-modified TiO₂ showed enhanced activity up to 3.4 and 1.6 times higher than the unmodified TiO₂ for photocatalytic degradation of organic pollutants such as 2-naphthol [6] and herbicides [7, 8], respectively.

In the present work, CuO modified TiO₂ photocatalysts prepared via a co-precipitation method was evaluated for removal of 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide, which is one of the commonly used herbicides. The effect of CuO cocatalyst on the properties and photocatalytic activity of TiO₂ was investigated.

2. Experimental

2.1. Preparation of samples

1 g of the commercial Hombikat UV100 TiO₂ (UV100, Sachtleben, Germany) without any treatments was weighed and transferred into a clean beaker. After addition of 20 mL double distilled water, the mixture was ultrasonicated for 5 minutes. The solution of copper(II) nitrate trihydrate (Sigma-Aldrich, 99-104%) with different weight percentages (wt%), which were 0.1, 0.25, 0.5, and 1.0 wt%, was added into the beaker while stirring, followed by the addition of ammonium hydroxide (Sigma-Aldrich, 28%) (dropwise) to adjust the pH to 9. After stirring for 1 hour, the mixture was dried at 55 °C until dried. The dried powder of TiO₂ was then calcined at a rate of 10 °C min⁻¹ to reach a temperature of 300 °C and was tempered for 4 hours. The prepared photocatalysts were denoted as CuO(x)/TiO₂, where x showed the loading of CuO (in wt%).

2.2. Characterizations of samples

The TiO₂ and the prepared CuO/TiO₂ samples were characterized using various types of instruments. A Bruker D8 Advance diffractometer was used to record X-ray diffraction (XRD) patterns of the prepared samples, which was analysed at the 2θ range of 20-70° with a scan rate of 0.05° s⁻¹. A Shimadzu UV-2600 diffuse reflectance UV-Visible (DR UV-Vis) spectrophotometer was used to measure the absorption spectra of samples using barium sulfate (BaSO₄) as a reference. A JASCO FP-8500 spectrofluorometer was used to identify the emission sites of the samples, which the emission of TiO₂ was monitored at an excitation wavelength of 218 nm. For the determination of charge separation efficiency, electrochemical impedance spectra (EIS) were recorded on a Gamry Interface 1000 potentiostat/galvanostat/ZRA. For the preparation of working electrode for the measurements of EIS, 10 mg photocatalyst and 10 μL nafion (Aldrich, 5%) were dispersed in 1 mL water and sonicated for 10 min to form a homogeneous colloidal suspension. 20 μL photocatalyst colloid was deposited onto the working electrode of a screen printed electrodes (SPE, Dropsens DRP-110). The SPE was immersed in 6 mL electrolyte containing 0.1 M sodium sulfate (Fisher Chemical) and 2.5 mM potassium ferricyanide (Riedel-de Haën). The EIS was recorded at 10 mV over a frequency range of 1 MHz to 100 mHz.

2.3. Photocatalytic tests

The photocatalytic activities of the TiO₂ and the prepared CuO/TiO₂ samples were evaluated for the removal of 2,4-D herbicides under UV light irradiation. Typically, 0.5 mM 2,4-D was prepared by dissolving an appropriate amount of 2,4-D (Sigma, 98%) in double distilled water. 28 mL of 2,4-D solution was then transferred into a photocatalytic reactor containing 28 mg photocatalyst. The suspension was stirred under the dark condition for 1 hour to achieve adsorption-desorption equilibrium. After 1 hour, 3 mL of the suspension was taken and filtered for the measurement of absorbance monitored at 283 nm using a Shimadzu UV-2600 UV-Vis spectrophotometer, which the

value was taken as initial absorbance, A_0 . The 25 mL suspension in an open glass reactor was then irradiated by UV light from the top (200 W Hg-Xe lamp, the dominant wavelength of UV light at 365 nm with light intensity of 15 mW/cm²) for 1 hour at room temperature. After the reaction, the suspension was filtered and the absorbance of 2,4-D, A_t was measured.

Percentage of 2,4-D removal was calculated according to the equation (1).

$$\frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 showed the initial absorbance of 2,4-D after adsorption in dark condition, while A_t showed the 2,4-D absorbance after the reaction. A high-performance liquid chromatography (HPLC, Shimadzu Prominence LC-20A) equipped with a Hypersil GOLD PFP column was also used to analyse the intermediate of the photocatalytic reaction.

3. Results and Discussion

Figure 1 shows the XRD patterns of the TiO₂ and the prepared CuO/TiO₂ samples. The TiO₂ showed diffraction peaks at 2θ of 25.35° (101), 38.10° (004), 48.05° (200), 54.55° (105), and 62.60° (204) corresponding to the anatase phase [8, 10, 11], which are in good agreement with the standard values reported by International Centre for Diffraction Data (ICDD) number 211272. As for the CuO/TiO₂ series, the addition of CuO did not affect the diffraction patterns of TiO₂, in which the characteristic diffraction peaks of anatase phase of TiO₂ remained in all samples. On the other hand, there were no characteristic peaks of CuO found on the XRD patterns according to the ICDD number 801916, as has been reported on the CuO nanoparticles [12, 13]. The absence of CuO peaks on the CuO/TiO₂ series suggested that addition of 0.1 to 1.0 wt% could not be detected by XRD. This might be due to the low amount of CuO added to TiO₂ or the low amount of CuO added might be dispersed well on the surface of the TiO₂, which the result was in a good agreement with the ones reported elsewhere [7, 14].

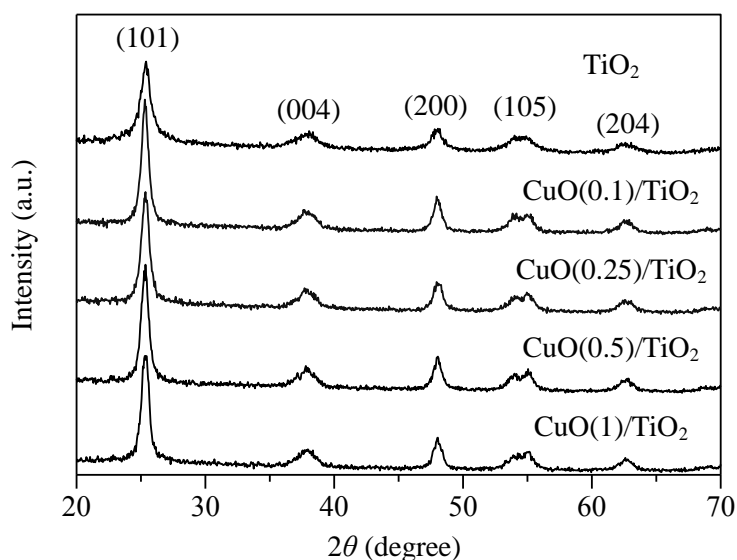


Figure 1. XRD patterns of the TiO₂ and the CuO/TiO₂.

In order to investigate the effect of CuO on the crystallite size of the TiO₂, the crystallite size of all the samples were calculated using Scherrer equation as shown in equation (2) based on peaks obtained from XRD patterns.

$$t = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where t is the average crystallite size in nm, while K is dimensionless shapes factor generally taken as 0.89, λ is the wavelength of the X-ray equals to 1.540, β is full width at half maximum (FWHM) at 2θ of 25.35° and θ is Bragg's angle. Table 1 shows the crystallite size of the TiO_2 and CuO/TiO_2 series. It was found that the crystallite size of the TiO_2 was 9.3 nm. Crystallinity of the TiO_2 was slightly improved after addition of CuO , which could be due to the thermal treatment during the synthesis process [3]. No significant changes of the crystallite size were obtained on the TiO_2 with the increase loading amount of CuO , in which the CuO/TiO_2 series have a crystallite size in the range of 11.3-12.1 nm.

Table 1. Crystallite size and bandgap energy of the TiO_2 and the CuO/TiO_2 series.

Sample	Crystallite size (nm) ^a	E_g (eV) ^b
TiO_2	9.3	3.30
$\text{CuO}(0.1)/\text{TiO}_2$	12.1	3.28
$\text{CuO}(0.25)/\text{TiO}_2$	12.1	3.29
$\text{CuO}(0.5)/\text{TiO}_2$	11.3	3.29
$\text{CuO}(1)/\text{TiO}_2$	11.3	3.28

^a Crystallite size was calculated using the Scherrer equation.

^b Bandgap energy (E_g) was determined from the Tauc plot.

Figure 2 shows the DR UV-Vis spectra of the TiO_2 and CuO modified- TiO_2 samples. The TiO_2 exhibited an absorption peak at around 300 nm, as also reported elsewhere [6, 10]. With the addition of CuO , the optical property of TiO_2 was not much altered. This might be due to the low amount of CuO added to TiO_2 .

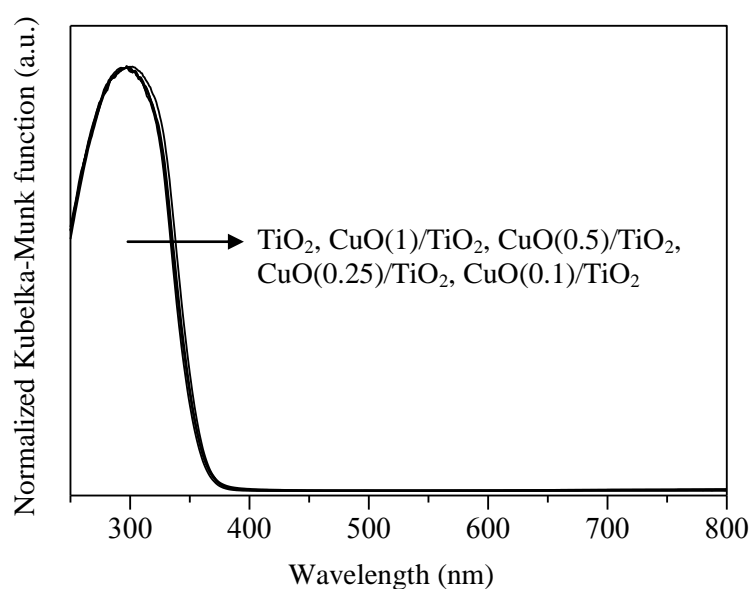


Figure 2. DR UV-Vis spectra of the TiO_2 and CuO/TiO_2 .

Besides UV absorption (Figure 2), the effect of CuO on the bandgap energy (E_g) of the CuO/TiO₂ series was also determined. The E_g can be estimated from Tauc plot by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ using equation (3).

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad (3),$$

where α is absorption coefficient, h is a Plank's constant, ν is the frequency of vibrant, A is a proportional constant, E_g is the bandgap energy and $n/2$ denotes the type of transition. It has been reported that anatase gives indirect transition [10]. Since the TiO₂ studied was consisted of anatase phase that prefers indirect transition, the n value should be 4. The E_g was determined from the value in x-intercept by taking the linear extrapolation in the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, as shown in Figure 3. The E_g of the samples is summarized in Table 1. The TiO₂ gave E_g of 3.30 eV. With the addition of CuO, the E_g of TiO₂ was not much affected, which the value of CuO/TiO₂ were in a range of 3.28-3.29 eV. Since the added amount of CuO was low, no clear correlation was observed between the crystallite size and the band gap energy.

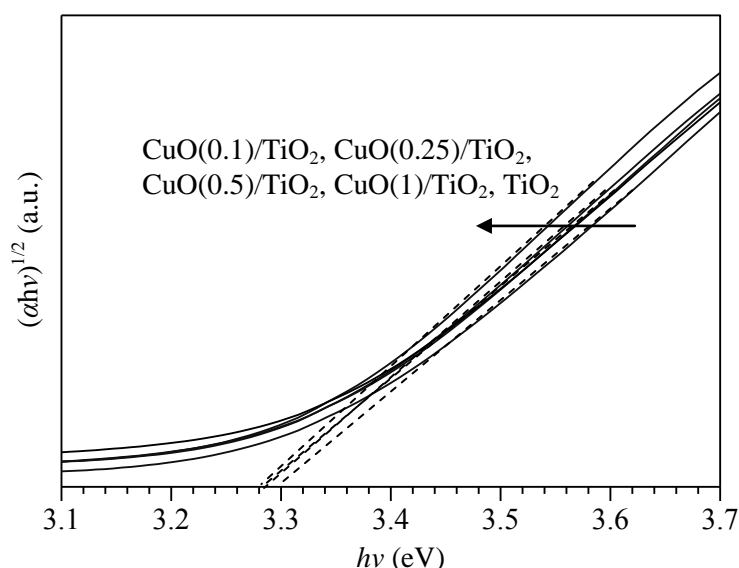


Figure 3. Tauc plots of the TiO₂ and CuO/TiO₂.

Figure 4 demonstrated the fluorescence spectra of the TiO₂ and CuO/TiO₂ series that were monitored at an excitation wavelength of 218 nm. There were three emission peaks obtained at 407, 466 and 562 nm, which the former one was the emission of the bandgap transition while the latter two were emission signals originating from the charge transfer transition of an oxygen vacancy trapped electron. The results were in good agreement with the reported TiO₂ [11]. As shown in Figure 4, the unmodified TiO₂ showed the highest emission intensity. It was found that addition of CuO reduced the emission intensity of the TiO₂, which the emission intensity of TiO₂ decreased gradually with the increasing of CuO loading amount, suggesting that CuO was loaded on the TiO₂.

In order to investigate the photocatalytic efficiency of the prepared photocatalysts, the TiO₂ and CuO/TiO₂ series were evaluated for photocatalytic removal of 2,4-D under UV light irradiation for one hour at room temperature. It was confirmed that the 2,4-D was stable and not degraded under UV light irradiation in the absence of photocatalyst. On the other hand, TiO₂ gave 2,4-D adsorption of about 30%, while the CuO/TiO₂ series gave 13-18% after one hour of the adsorption process. As shown in the equation (1), the photocatalytic activity was calculated by taking account of the remained 2,4-D after adsorption process as the initial concentration. Therefore, the obtained photocatalytic activities were solely caused by the photocatalytic reaction. As shown in Figure 5, the unmodified TiO₂ showed

21% of 2,4-D removal. An appropriate loading amount of CuO was found to improve the photocatalytic activity of the TiO₂ for removal of 2,4-D. It was obtained that addition of 0.1 wt% CuO enhanced the photocatalytic activity of the TiO₂ up to 38%, which the activity was 1.8 times higher than the unmodified TiO₂. Further addition of CuO from 0.25-1 wt% decreased the activity of the TiO₂, in which 1 wt% CuO showed activity similar to the one of the unmodified TiO₂. These results clearly suggested that small amount of CuO (0.1 wt%) was the optimum loading to achieve the improved activity of the TiO₂. The formation of the intermediate product, which was 2,4-dichlorophenol (2,4-DCP), was confirmed by HPLC on all photocatalysts. This is in good agreement with previously reported literature [15,16], suggesting that the 2,4-DCP was a crucial intermediate in the photocatalytic removal of 2,4-D.

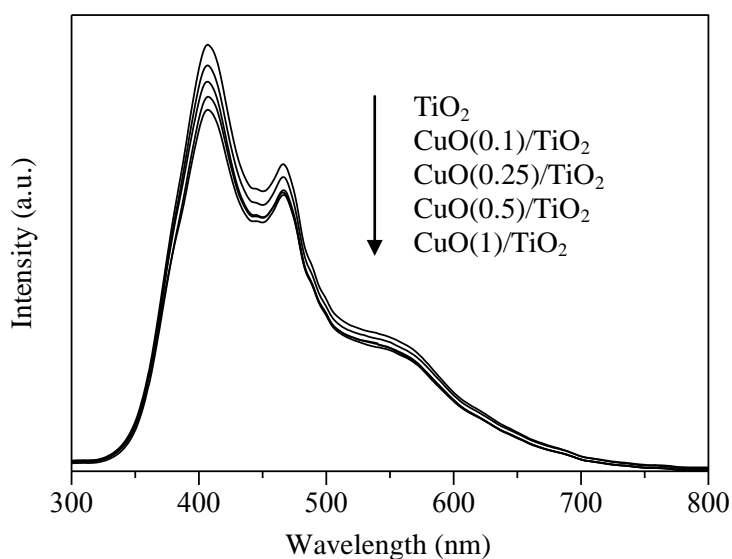


Figure 4. Fluorescence spectra of the TiO₂ and CuO/TiO₂ series monitored at an excitation wavelength of 218 nm.

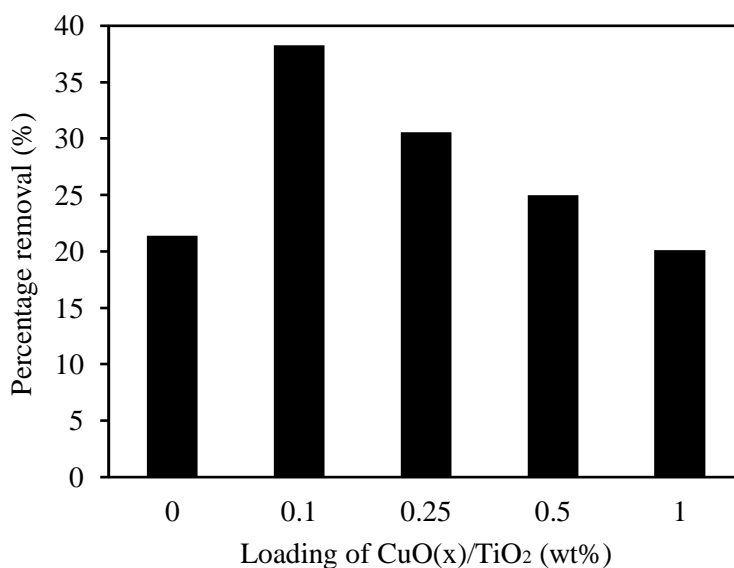


Figure 5. Photocatalytic removal of 2,4-D on the TiO₂ and CuO/TiO₂ series under UV light irradiation for 1 hour.

The photocatalytic activities obtained on the CuO/TiO₂ revealed the importance of CuO cocatalyst loading amount to improve the photocatalytic performance of TiO₂. A suitable amount of cocatalyst loaded on a semiconductor could trap photogenerated electrons efficiently to suppress electron-hole recombination, which improves the photocatalytic efficiency of a semiconductor. Since photoluminescence study has been used to investigate and associate recombination of electron-hole pairs of semiconductors [11], the high photocatalytic activity obtained on the CuO(0.1)/TiO₂ could be related to the suppressed electron-hole recombination, as supported by the fluorescence results (Figure 4). The reduced emission intensity of the TiO₂ with the increased loading of CuO suggested that lower amount of CuO (0.1 wt%) acted to trap electrons and suppress the electron-hole recombination, leading to high photocatalytic activity. However, further reduced emission intensity with the increasing loading of CuO (above 0.1 wt%) might be due to the covering of TiO₂ emission sites by the loaded CuO, as can be suggested from the decreased photocatalytic activity of TiO₂ with CuO loading of higher than 0.1 wt% (Figure 5).

In order to support the good charge separation of the CuO(0.1)/TiO₂ that lead to the high photocatalytic activity, EIS of TiO₂ and CuO/TiO₂ with CuO loading amount of 0.1 and 1 wt% were recorded as shown in Figure 6. Impedance arc radius of the CuO(0.1)/TiO₂ was much smaller than the unmodified TiO₂, which indicated that conductivity of the sample was enhanced when 0.1 wt% CuO was loaded, revealing the better charge separation. When 1 wt% CuO was loaded, the impedance arc radius was similar to the one of the unmodified TiO₂. It is therefore suggested that only suitable loading of CuO would show good charge separation on the TiO₂ that would improve the photocatalytic activity.

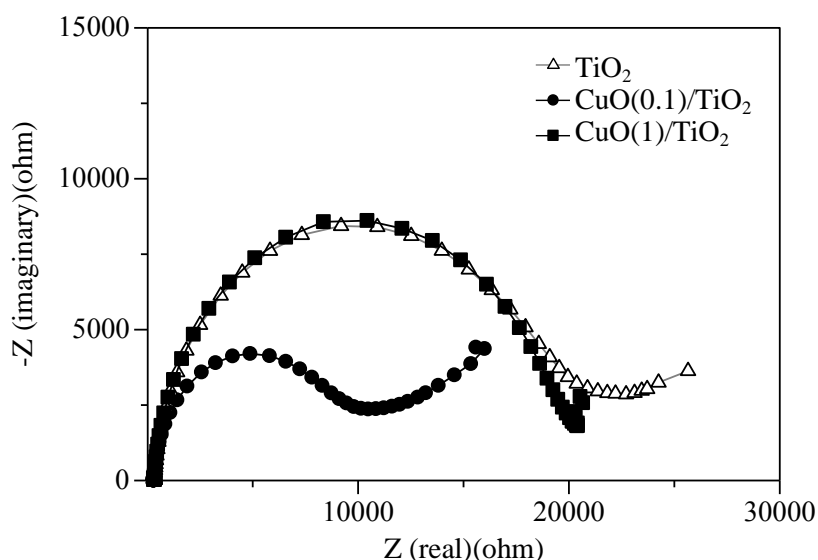


Figure 6. EIS measurements of the TiO₂ and CuO/TiO₂ with CuO loading amount of 0.1 and 1 wt%.

4. Conclusions

A series of CuO/TiO₂ with various CuO loading of 0.1-1 wt% was prepared through a co-precipitation method. All samples were UV light-active and possessed E_g of about 3.3 eV. The CuO with 0.1 wt% was the optimum loading amount for the modification on the TiO₂, which showed 1.8 times higher photocatalytic activity than the unmodified TiO₂ for the removal of 2,4-D under 1 hour of UV light irradiation. The high photocatalytic activity obtained on the CuO(0.1 wt%)/TiO₂ could be due to the

good dispersion of CuO on the surface of the TiO₂ as well as efficient charge separation and suppressed electron-hole recombination on the TiO₂ without blocking the active sites.

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