



## Visible Light-responsive Photocatalyst Synthesized by Incorporating CQDs into SiO<sub>2</sub>@TiO<sub>2</sub>

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### Abstract

In recent years, water pollution caused by population growth has become one of the most health-threatening problems. To solve this problem, photocatalytic degradation of organic pollutants using solar energy is expected. Among various photocatalysts, TiO<sub>2</sub> has been widely used and studied because of its non-toxicity, low cost, and high chemical stability. However, TiO<sub>2</sub> has a wide band gap of 3.2 eV, so only ultraviolet light is available. Since ultraviolet rays account for only about 3~5% of sunlight, research on the effective use of visible light, which accounts for about 45% of sunlight, has been active in recent years. Known major approaches include heterojunction coupling, doping, and dye sensitization. Among them, composites of carbon nanomaterials and TiO<sub>2</sub> have been shown to improve optical absorption in visible light. In recent years, carbon quantum dots (CQDs) have attracted attention as a new carbon nanomaterial because of their unique properties. CQDs are non-toxic, inexpensive, and easy to tune. Therefore, it has been applied as a composite material for TiO<sub>2</sub> and has been reported to have an optical absorption edge of 419 nm and a band gap of 2.96 eV. In this study, SiO<sub>2</sub>@TiO<sub>2</sub>/CQD heterojunction structures were fabricated, and their photocatalytic activity was evaluated using methylene blue. By adjusting the particle size of SiO<sub>2</sub>@TiO<sub>2</sub>, the optical wavelength to be reflected can be selected. Among them, SiO<sub>2</sub>@TiO<sub>2</sub> which can reflect optical wavelengths around 400 nm was adjusted to form a structure that allows more efficient optical utilization of TiO<sub>2</sub>/CQDs. SiO<sub>2</sub>@TiO<sub>2</sub>/CQD is a mixture of TiO<sub>2</sub> and CQDs coated on the surface of a SiO<sub>2</sub> porous structure prepared by the Stover method. This simple preparation method resulted in high surface area, efficient light utilization due to the heterostructure, and efficient charge mobility. As a result, the degradation performance against organic pollutants was shown to be improved.

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### Keywords

Mesoporous SiO<sub>2</sub>@TiO<sub>2</sub>; Photocatalytic; Methylene blue; CQD; Photocatalyst

### 1. Introduction

In recent years, water pollution caused by population growth has become one of the most health-threatening problems. (1) Among these, contamination by organic dyes is a serious problem. Organic dyes are a major pollutant of wastewater discharged in large quantities from the textile industry and other sources. These organic dyes cause significant damage to the land and the environment, and these residual dyes are toxic to humans and animals because

they are not decomposed by microorganisms. (2) Among these, contamination by organic dyes is a serious problem. Organic dyes are a major pollutant of wastewater discharged in large quantities from the textile industry and other sources. This organic dye is very damaging to the land and environment, and the residual dye is toxic to humans and animals because it is not decomposed by microorganisms. Physical and chemical treatment methods are gaining attention to solve these problems. However, conventional physical and chemical treatment methods have problems such as secondary contamination and long treatment cycles. Among these, the removal of organic dyes by photocatalysis is attracting attention. (3,4)

Photocatalysts have been widely used and studied because of their non-toxicity, low cost, and high chemical stability. The disadvantage of TiO<sub>2</sub>, a commonly used photocatalyst, is its wide band gap of 3.2 eV, which means that only UV light is available. (3,5) UV light is only about 5% of sunlight. For this reason, much research has been done over the past few decades to increase the number of usable wavelength bands. Among these methods, carbon and nitrogen loading, doping, and shape-changing are known as promising methods.

As a carbon source, carbon quantum dots (CQDs) have recently attracted attention as a new carbon nanomaterial because of their unique properties. Muhammad Shafique et al. showed that the combination of TiO<sub>2</sub> and CQDs broadens the optical absorption edge and allows degradation under visible light. (6) In addition, SiO<sub>2</sub>@TiO<sub>2</sub> has been studied in various fields of particle shape change. One of the reasons why SiO<sub>2</sub>@TiO<sub>2</sub> is attracting attention is that the wavelength band that can be reflected is tuned by the particle size. To reflect visible light (about 380~780nm), a particle size of about 200nm~400nm is appropriate. (7)

Therefore, this study evaluated SiO<sub>2</sub>@TiO<sub>2</sub> supported by CQD for more efficient removal of organic contaminants. Previous studies of TiO<sub>2</sub>/CQDs have shown that visible light responsivity is improved by loading CQDs onto TiO<sub>2</sub>. To utilize visible light more efficiently, TiO<sub>2</sub> was changed to SiO<sub>2</sub>@TiO<sub>2</sub>. The SiO<sub>2</sub>@TiO<sub>2</sub> used was adjusted to a particle size of 200 nm to 350 nm for efficient reflection and utilization of visible light. The results showed that the photocatalytic activity of SiO<sub>2</sub>@TiO<sub>2</sub>/CQDs was enhanced, suggesting that SiO<sub>2</sub>@TiO<sub>2</sub>/CQDs can remove organic pollutants that cause water pollution more efficiently compared to SiO<sub>2</sub>@TiO<sub>2</sub>.

## 2. Methods

### 2.1. CQD fabrication

Put 0.720 g of urea (FUJIFILM Wako) in 20 ml of purified water and stir for 1 hour. Let this solution be Solution A. To this solution A, add 0.768 g of citric acid (FUJIFILM Wako) and stir for 1 hour. This solution is designated as Solution B. Solution B was transferred to a Teflon solution, and hydrothermal synthesis was performed at 200° for 6 hours. Impurities were then removed by filtration. The solution was stored in a refrigerator.

### 2.2. SiO<sub>2</sub>@TiO<sub>2</sub>/CQD

A two-step procedure was performed:

#### 2.2.1. SiO<sub>2</sub>

Here is a detailed explanation of how to make SiO<sub>2</sub> shown in Figure 1.

The detailed preparation of SiO<sub>2</sub> is shown in the upper part of Figure. 1 was carried out by adding 1.2 ml octadecyltrimethoxysilane (Tokyo Kasei Kogyo) and 4 ml TEOS (Fujifilm Wako) to 80 ml ethanol and stirring for 10 minutes. Next, 12 ml of ammonia was slowly added dropwise and stirred for 24 hours to form SiO<sub>2</sub>. The white precipitate was then washed several times with ethanol and dried.

#### 2.2.2. SiO<sub>2</sub>@TiO<sub>2</sub>/CQD

This section details the preparation of the SiO<sub>2</sub>@TiO<sub>2</sub>/CQD shown in Figure 1.

In the detailed preparation of SiO<sub>2</sub>@TiO<sub>2</sub>/CQD shown in the lower part of Figure 1, 800 μl of TBOT (Fujifilm Wako) and SiO<sub>2</sub> produced in step 1 were added to 80 ml of ethanol. The mixed solution was completely dispersed by ultrasound. In previous studies, 1.6 ml of purified water was slowly added dropwise. However, in this study, purified

water was replaced by CQD solution and 1 ml, 1.6 ml and 3.2 ml of CQD solution were slowly dropped into the mixed solution and stirred for 6 hours. The yellow precipitate was then washed several times with ethanol and dried. The dried powder was annealed at 900° for 2 hours.

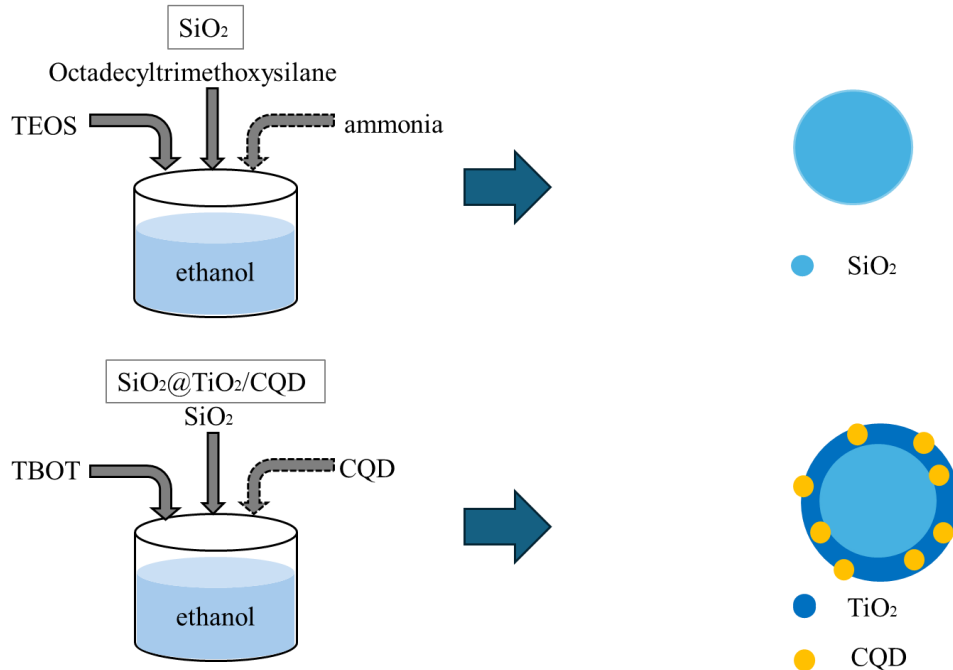


Figure 1: How to create an STC(source:by authors)

Translated with DeepL.com (free version). For  $\text{SiO}_2@TiO_2$ , the CQD solution was changed to purified water, and the same procedure was performed.

Table 1: Particle Name

Called name	Solution amount of CQD
ST	0ml
STC(1)	1ml
STC(2)	1.6ml
STC(3)	3.2ml

### 2.3. Photocatalytic evaluation methods

The photocatalytic activity was evaluated using model pollutants. Methylene blue (MB) (Fujifilm Wako) was used as the model contaminant. A 100 W LED floodlight was also used as the light source. UV-cut film (Azwan 2-9154-01 < 400 nm) was attached to the light source and used as a visible light source. The space from the light source to the decomposed material was fixed at 30 cm.

50 mg of the powder was mixed with 20 ml of MB solution, and the porcelain was stirred. The mixed solution was stirred for 1 hour in the dark to obtain sorption equilibrium. Then, they were irradiated with light. The mixed solution was sampled once every 30 minutes and centrifuged to remove the photocatalyst.

### 3. Experimental results

#### 3.1. XRD

Comparing Figures 2(a) and 2(b) shows that they are similar. This is thought to be due to the low amount of CQDs held, which is why CQDs are not detected. Analysis of the diffraction peaks from Figures 1(a) and 1(b) shows that both are TiO<sub>2</sub> in the anatase phase and that SiO<sub>2</sub> is also retained. These results indicate that incorporating CQD into the ST fabrication process does not change the crystal structure of the product.

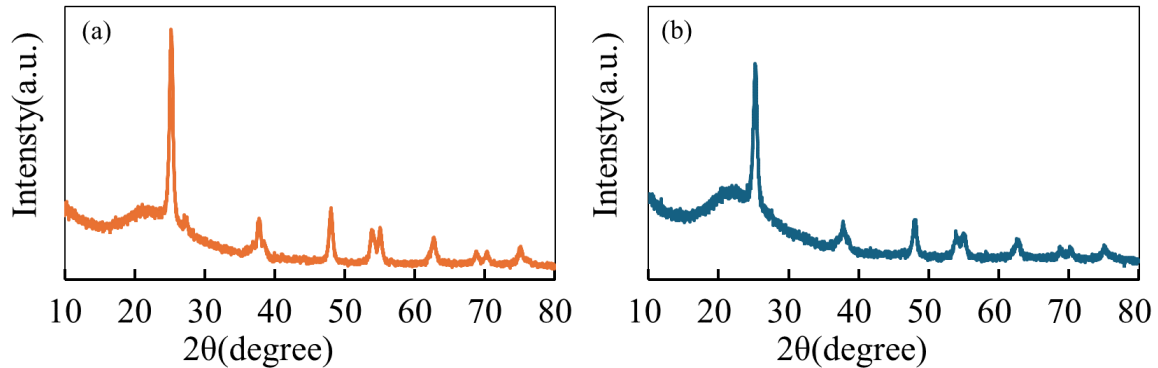


Figure 2: (a) The XRD data of ST and (b) the XRD data of STC. (source:by authors)

#### 3.2. SEM

Figure (a) is an SEM image of ST. The SEM data in (a) shows that this is a mesoporous ST and spherical. The particle size is also found to be in the range of 250 nm to 400 nm. Figure (b) shows the SEM data of STC. The SEM data in (b) shows that it is also spherical. The size is also observed to be similar, ranging from 250 nm to 400 nm. However, when comparing (a) and (b), the surface of (b) is more uneven than that of (a), and it is thought that a higher surface area is acquired. This high surface area is believed to facilitate dye adsorption. In addition, the irregularity of the surface may cause incident light to enter the TiO<sub>2</sub> surface from different angles, scattering light in various directions.

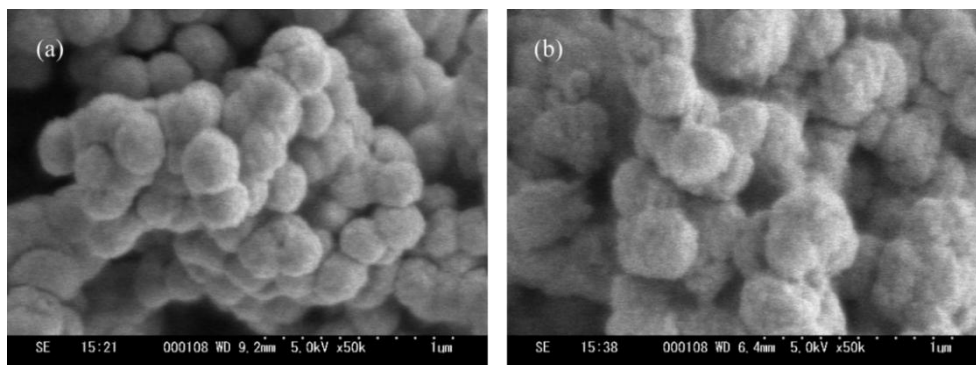


Figure 3: (a) is the Sem data of ST. (b) is SEM data of STC(source:by authors)

#### 3.3. Light Absorption Rate

Figure 4 shows the optical absorption coefficient. This shows that STC absorbs lighter than ST. Also, the difference in optical absorption between ST and STC increases from about 380 nm. These are thought to be influenced by CQD. The incorporation of CQD in the fabrication process improves the photo response in the ultraviolet region by increasing the surface area, and the visible light response is thought to be enhanced by the heterojunction of CQD and ST. It is also thought that making the surface uneven may lengthen the light path and allow more efficient use of light.

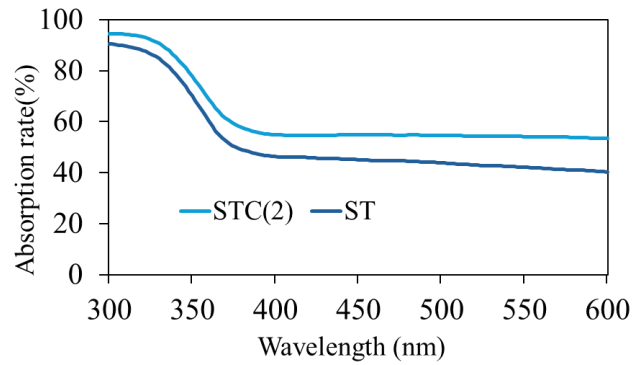


Figure 4: Light Absorption Rate(source:by authors)

### 3.4. Evaluation of photocatalytic activity

Figure 5 (a) shows a methylene blue adsorption experiment. This shows that the adsorption force varies with the amount of CQD. STC(2) is about 70% adsorbed. Compared to the conventional ST, the adsorption volume has been improved by approximately 60%. This is the same result confirmed in Figure 3. This indicates that particles with enhanced surface area can be produced by incorporating CQDs into ST. It is generally believed that the larger the surface area, the more active sites and the higher the photocatalytic activity. (8)

Figure (b) shows a decomposition experiment. This degradation experiment was performed under visible light. Since  $\text{TiO}_2$  generally acts only at wavelengths in the ultraviolet region, the decomposition rate of ST is 0%. In comparison, STC(1), STC(2), and STC(3) all show progressive degradation. This indicates that the synthesis of ST and CQD could create visible light-responsive photocatalysts. STC(2) is degraded by about 50%. This indicates that, as in the adsorption experiment, the photocatalytic activity varies significantly with the amount of CQD. This is thought to be due to the fact that the larger the surface area, the more active sites and the higher the photocatalytic activity, as well as the effect of heterojunction.

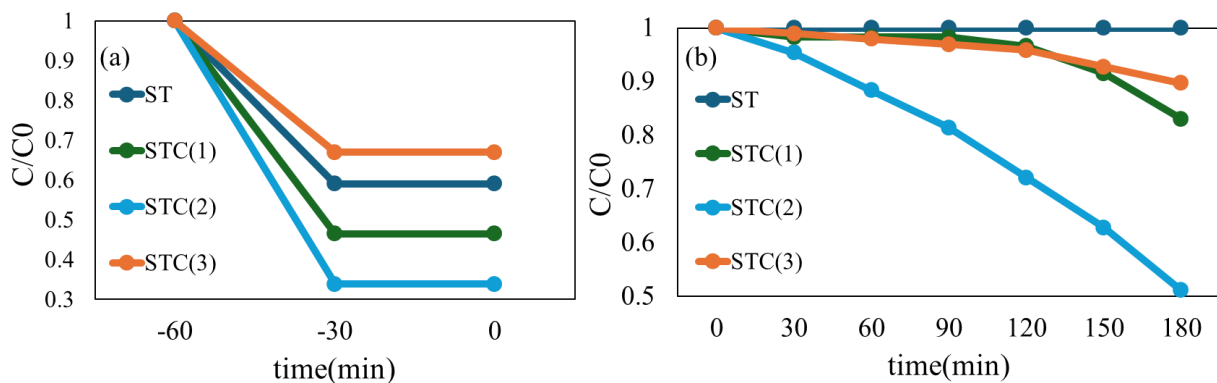


Figure 5: (a) Adsorption experiment. (b) The degradation of organic matter(source:by authors)

## 4. Discussion and conclusions

STC showed high adsorption to MB solution and high degradation under visible light. This would be attributed to the establishment of a hetero-bonded structure with the support of CQD and ST. (6) This has been shown to be useful in removing organic contaminants. In the degradation of organic matter from residual dyes, STC is expected to be a particle that combines the advantages of both the physical treatment method, which is a good adsorbent for the fast processing of organic matter, and the chemical treatment method, which is a high degradation power that prevents secondary damage. However, in terms of adsorption power, it is lower than that of smoked charcoal, etc. Therefore, it is essential to study photocatalysts with higher adsorption power.

## 5. Recommendation

This study has shown that the addition of CQD to the  $\text{SO}_2/\text{TiO}_2$  preparation process improves the surface area, which is a drawback of  $\text{SiO}_2/\text{TiO}_2$ , and amplifies the available wavelength range, which is a drawback of  $\text{TiO}_2$ . On

this basis, future research should study and optimise the light reflectance and absorptance of SiO<sub>2</sub>@TiO<sub>2</sub>/CQDs so far. This needs to be investigated for further applications, as SiO<sub>2</sub>@TiO<sub>2</sub> has so far been used as a scattering layer in solar cells.

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### **Ethics Approval**

Not applicable.

### **Conflict of Interest**

The authors declare there is no conflict.

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