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Research Article

# Synthesis and Photocatalytic Activity for Toluene Removal of CDs/$TiO_2$ – Zeolite Y

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## Abstract

Hydrothermally synthesized carbon nanodots (CDs) were impregnated on $TiO_2$. The product (CDs/$TiO_2$) was mechanically mixed with zeolite Y for application in toluene photocatalytic oxidation reaction under UV radiation. Material properties of the samples were investigated by different methods. Toluene vapor was chosen as a typical volatile organic compound to investigate the performance of CDs/$TiO_2$ – zeolite Y photocatalyst when these technological parameters were changed: toluene concentration, gas flow rate, humidity and UV light intensity. In each reaction, only one parameter was changed and the remaining conditions were fixed. The toluene concentrations at the beginning and the end of each reaction were analyzed with the use of gas chromatography (GC). The results of different reaction conditions show the trends for toluene treatment of the CDs/$TiO_2$ – zeolite Y catalyst, thereby providing specific explanations for these trends. The experiments also show that toluene removal is highest when the toluene concentration in the inlet gas is 314 ppmv, the flow rate is 3 L/h, the humidity is 60%, and the catalyst (CDs/$TiO_2$ – zeolite Y composite with 70% zeolite in weight) is illuminated by 4 UV lamps.

***Keywords***: Zeolite; Photocatalyst; Toluene; Carbon nanodots; $TiO_2$

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## 1. Introduction

The industrialization and modernization revolution are promoting strong economic development, increasingly improving our material and spiritual life. However, they also cause a range of environmental and health problems. Currently, air pollution is one of the most pressing issues. In addition to PM 2.5, volatile organic compounds (VOCs) have also been a serious air hazard that is attracting worldwide attention. The majority of VOCs falls into these groups: halogens, alcohols, ketones, aldehydes, aromatic compounds as well as ethers [1]. Exposure to high levels of VOCs can result in irritability, nausea, dizziness, and headaches [2]. Some VOCs can even lead to certain types of cancer in humans and animals. Furthermore, VOCs are responsible for the formation of ozone and fine particles that cause smog [3], resulting in direct effects on humans and indirect effects on the economy. Therefore, the reduction of emissions and treatment of VOCs is an urgent issue that needs to be invested and focused on. In recent

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years, methods to decompose VOCs are constantly being researched and developed: oxidation method, biological filtration, membrane method, absorption, and adsorption. In general, all these methods are ineffective, only suitable for moderate and low levels of treatment, and recycling and reuse are often expensive. For these reasons, more efficient, economical and environmentally friendly ways for the treatment of VOCs are needed, and one method that meets these requirements are oxidation with the help of photocatalysts [4].

Many photocatalysts, such as ZnO, ZnS, CdS, $SrO_2$, and $WO_3$, have been applied for the removal of air pollutants, and it has been found that $TiO_2$ is the most suitable one [5]. In general, a photocatalytic reaction begins when an electron is excited by a photon with energy at least equal to the band gap of the catalyst, which is a semiconductor. This electron then jumps to the conduction band (CB), creating a hole in its original position in the valence band (VB). This can result in the formation of free radicals, such as OH•, with the ability to oxidize VOCs [6]. When $TiO_2$ is used as the photocatalyst, the reaction mechanism is as followed [7]:

$$TiO_2 + hv \rightarrow e^- + h^+ \quad (1)$$
$$h^+ + OH^- \rightarrow OH\bullet \quad (2)$$
$$h^+ + H_2O \rightarrow H^+ + OH\bullet \quad (3)$$
$$e^- + O_2 \rightarrow O_2^- \quad (4)$$
$$O_2^- + H^+ \rightarrow HO_2\bullet \quad (5)$$
$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$
$$H_2O_2 + O_2 \rightarrow OH^- + OH\bullet + O_2 \quad (7)$$
$$OH\bullet + VOCs + O_2 \rightarrow (CO_2, H_2O) \quad (8)$$

In order to overcome the disadvantages of $TiO_2$, such as a narrow absorption spectrum and fast combination of electron-hole pairs, various research has been conducted to modify the surface or structure of this material. In recent years, carbon nanodots (CDs) which are less than 10 nm in size have been considered as a potential photocatalytic material, especially when combined with $TiO_2$ [8]. However, CDs/$TiO_2$ photocatalysts still have some limitations, such as low values for surface area per unit of mass, low affinity for organic compounds and challenges in recovery and reuse (the tendency to agglomerate and scatter interferes with light reaching the active centers on the surface of the catalysts). In order to overcome these problems, a substance that has both good adsorption capacity and the ability to support the dispersion of the catalysts is required. With unique structural properties and chemical composition, Y zeolites can be considered as a promising candidate.

This study successfully synthesized carbon nanodots from citric acid monohydrate and urea through hydrothermal method. Commercial $TiO_2$ was then impregnated with the newly synthesized CDs, before being dispersed in zeolite Y with the help of ultrasound. The main focus of this study is the activity of the CDs/$TiO_2$ – zeolite Y photocatalyst for the treatment of toluene in different conditions of toluene concentration, humidity and UV intensity. As commercial $TiO_2$ struggles to maintain the stability of its photocatalytic performance in these conditions [9], the result of this study can be used to consider CDs/$TiO_2$ – zeolite Y photocatalyst as a surrogate of commercial $TiO_2$ in practical applications.

## 2. Materials and Methods

### 2.1 Preparation of the photocatalysts

Carbon nanodots were prepared hydrothermally. Firstly, 3 g of citric acid monohydrate (Xilong Chemical Co., 99%) and 3 g of urea (Xilong Chemical Co., 99%) were mixed in 10 mL of pure water. Next, the solution was added to an autoclave with a volume of 20 mL. The whole mixture was then hydrothermally heated at 200 °C for 6 h, before being allowed to cool to room temperature. After that, the mixture underwent centrifugation at 4000 rpm for a quarter hour to remove the residue. The final product was a light brown solution of CDs.

CDs/$TiO_2$ photocatalyst was prepared by impregnation method. $TiO_2$ (Degussa, 99 %) (1 g) and the CDs solution (0.25 mL) were dissolved in 400 mL of deionized water. Next, ultrasound was used to treat the mixture during 30 minutes. After that, the mixture were filtered to collect the solid catalyst, which was then washed thoroughly with distilled water and dried overnight at 80 °C.

In order to synthesize CDs/$TiO_2$ – zeolite Y catalyst, the CDs/$TiO_2$ composite was mixed with zeolite Y at appropriate ratios. The samples with the mass percentage of zeolite being 20 %, 50 %, 70 %, and 80 % were named CDs/$TiO_2$ – zY20, CDs/$TiO_2$ – zY50, CDs/$TiO_2$ – zY70 and CDs/$TiO_2$ – zY80 respectively. Zeolite Y used in this study was synthesized according to the published procedure in the literature [7]. The mixtures were then dispersed individually in 10 mL of pure ethanol and treated with ultrasound for 5 min. Next, each mixture was coated layer by layer on the outer surface of a glass tube by the rotary spray coating method.

The glass tubes were placed horizontally and rotates about the shaft at 140 rpm. Finally, the catalysts underwent activation at 200 °C during an hour before the reactions started.

### 2.2 Characterization of the Materials

The CDs solution was characterized by high-resolution transmitted electron (HRTEM) with the help of JEOL JEM-2100, photoluminescence (PL) using Horiba Ihr550 Spectrometer instrument and FTIR spectra using spectrometer. $TiO_2$ and CDs/$TiO_2$ were characterized by FTIR spectra, $N_2$ physisorption analysis using NOVA 2200e Analyzer for the determination of surface area and thermogravimetric analysis (TGA) using analyzer. HRTEM and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM – EDX) by JSM – IT200 were also used for the characterization of CDs/$TiO_2$.

### 2.3 Photocatalyst Oxidation System

The photocatalyst oxidation system simulated the atmosphere to create the desired conditions for conducting the investigation. The two main gas sources, pure $N_2$ and $O_2$ (>99.99%), were mixed in a ratio of 4:1 which was similar to air. In particular, the source of $N_2$ was divided into three streams, including: (1) a stream purged through the toluene container to create streams with the required concentrations of toluene, (2) a stream blew through a container of distilled water to carry the water vapor (3) a stream of pure $N_2$ used to dilute the concentration of toluene in the gas mixture. These $N_2$ and $O_2$ gas flows were regulated with the help of flowmeters before entering a mixing vessel to stabilize the concentration and flow rate. After that, the mixture entered an annular reactor containing 0.2 g of photocatalyst (CDs/$TiO_2$ or CDs/$TiO_2$ – zeolite Y) for toluene treatment. The reactor had two telescopic tubes. The outer tube made of quartz. Its outside diameter was 35 mm and its thickness was 2 mm. The inner glass tube was also 2 mm thick, but its diameter was only 20 mm. The reactor used four Sankyo Denki F10T8BLBs lamps emitting UVA rays with a wavelength of 352 nm and an intensity of 1.5 W. The distance between the lamps and the photocatalysts was 2.5 cm. Under normal conditions, when all four lamps were turned on, the reaction temperature reached 39 °C, and this was maintained by a continuous flow of cool air through a fan located at the bottom of the reactor. The gas flow out of the reactor entered a gas chromatography analyzer (GC analyzer) with an FID probe through a six-way valve to measure the output concentration of toluene. The GC device used was the GC – FID Hewlett Packard 5890 plus. The gas stream was introduced into the chromatograph every 5 min. The gas sample was injected in and carried by pure $N_2$ (>99.99%) to the chromatographic column (stationary phase). The column used in this system was a Capillary VF-1ms column.

The toluene removal $\psi_i$ was calculated from the equation:

$$\Psi_i = \frac{P_k F}{R T_k} \times \frac{1}{m_{TiO_2}} \times \left(1 - \frac{A_i}{A_0}\right) \times 1000 \quad \left(\text{mmol.g}^{-1}.\text{h}^{-1}\right) \qquad (9)$$

where $P_k$ and $T_k$ stand for the saturation pressure (atm) and temperature (K) of toluene, $F$ is the inlet gas flow rate (L/h), $R$ is the gas constant (L.atm.K$^{-1}$.mol$^{-1}$), $m_{TiO2}$ stands for the mass of $TiO_2$ in the catalyst (g), $A_0$ and $A_i$ are the areas of the peaks obtained from the gas chromatograph at the beginning of the reaction and after *i* minutes, respectively.

## 3. Results and Discussion

### 3.1 Characterization of the Materials

The characterization results of CDs are shown in Figure 1. The first HRTEM image indicates that the CDs synthesized are mainly spherical in shape and quite uniform in size, at below 10 nm. The lattice structure of CDs can be observed through the second HRTEM image. The distance between the lattice fringes is about 0.265 nm, which is close to the distance between the (100) interfaces of graphene [10,11]. The FTIR spectrum of CDs shows the existence of many functional groups. The absorption band at about 3000 – 3600 cm$^{-1}$ represents the amino and hydroxyl groups. The peaks of 2091 cm$^{-1}$ and 1644 cm$^{-1}$ correspond to the triple bonds of carbon and the carbonyl functional group, respectively. The adsorption band from 1350 to 1460 cm$^{-1}$ indicates the vibrations of $CH_2$. The presence of hydroxyl and carbonyl groups on the surface of carbon nanodots results in solubility and stability in water, leading to the excellent applications of CDs. Figure 1 also shows that when CDs are excited at 355 nm, the PL spectrum of this material contains an emission peak at 426 nm (indigo region).

The specific surface areas of CDs/$TiO_2$ and $TiO_2$ are shown in Table 1. The figure for the CDs/$TiO_2$ composite is not significantly different from that of the commercial $TiO_2$ due to the relatively low carbon content impregnated with $TiO_2$. The HRTEM image of CDs/$TiO_2$ in Figure 2 indicates that $TiO_2$ has an irregular shape due to the difference in crystal structures of the anatase and rutile phases [12], whereas the CDs are dispersed quite uniformly throughout the surface of $TiO_2$. The SEM - EDX images (Figure 3) visually represent the distribution of the elements C, Ti, and O on the catalyst surface. The images show that the distribution density of carbon dots is quite dense and uniform on the $TiO_2$ surface. Additionally, the SEM-EDX images of the zeolite Y also reported in Figure 4 which indicated the morphology of the microporous crystalline aluminosilicate materials.

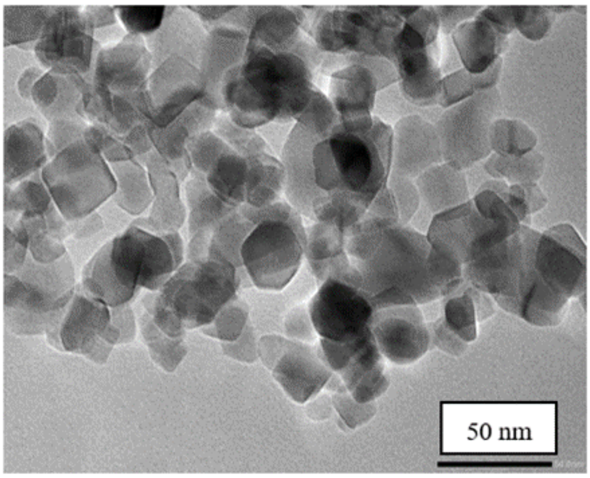

Figure 2. HRTEM image of $CDs/TiO_2$.

Figure 5 illustrates the FTIR and TGA spectra of $TiO_2$ and $CDs/TiO_2$. The FTIR spectrum of $CDs/TiO_2$ is similar to that of $TiO_2$, with the characteristic absorption band for the valence oscillation of Ti–O–Ti in the 400 – 900 $cm^{-1}$ region. There are also 2 peaks at 3421 $cm^{-1}$, which represents the valence vibrations of the hydrogen bonding between the water molecules, and at 1637 $cm^{-1}$, which corresponds to

Table 1. BET surface area analysis results.

| Sample | BET surface area ($m^2/g$) |
|---|---|
| $TiO_2$ | 50.9 |
| $CDs/TiO_2$ | 54 |

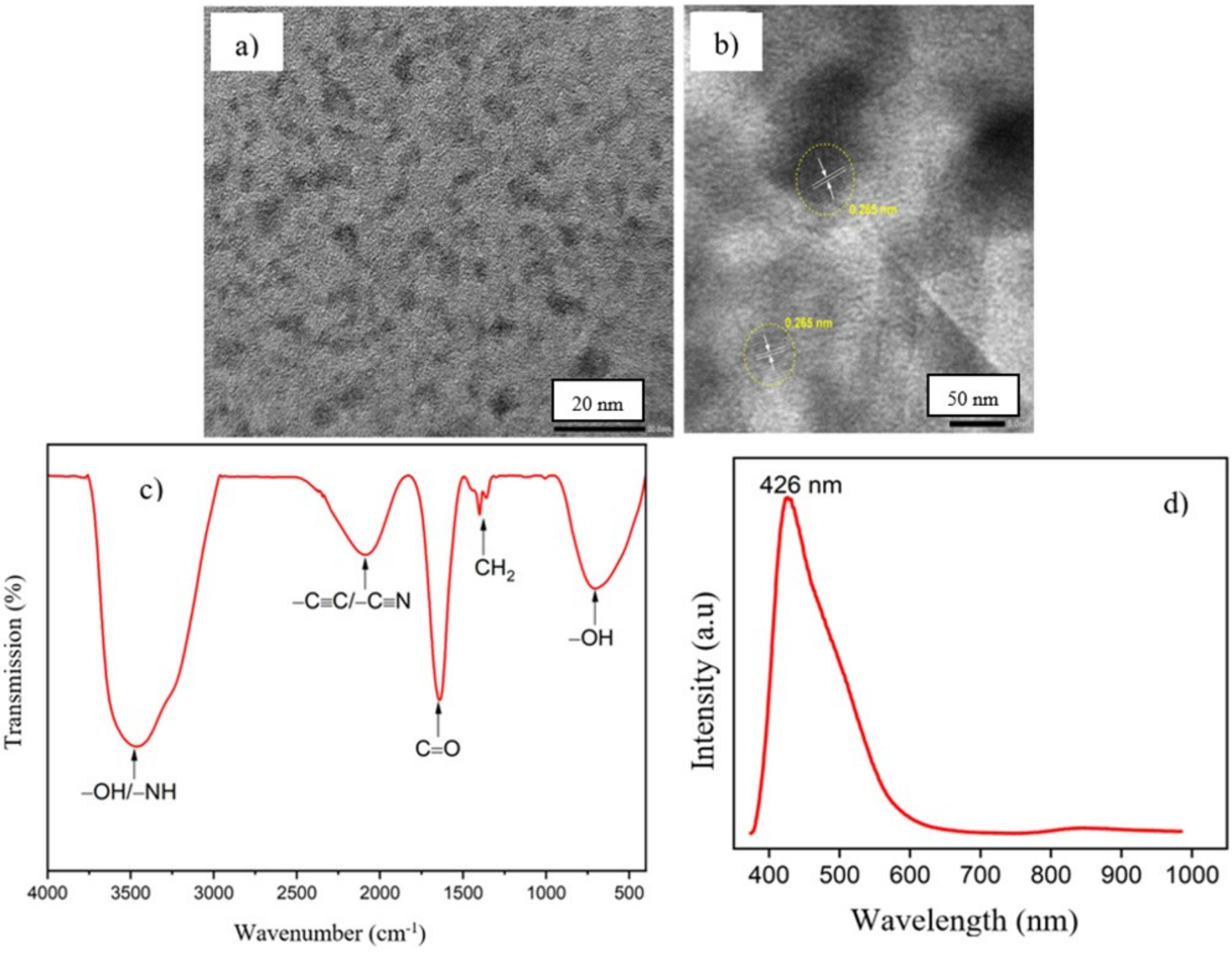

Figure 1. (a, b) HRTEM images, (c) FTIR spectrum, (d) PL spectrum of CDs.

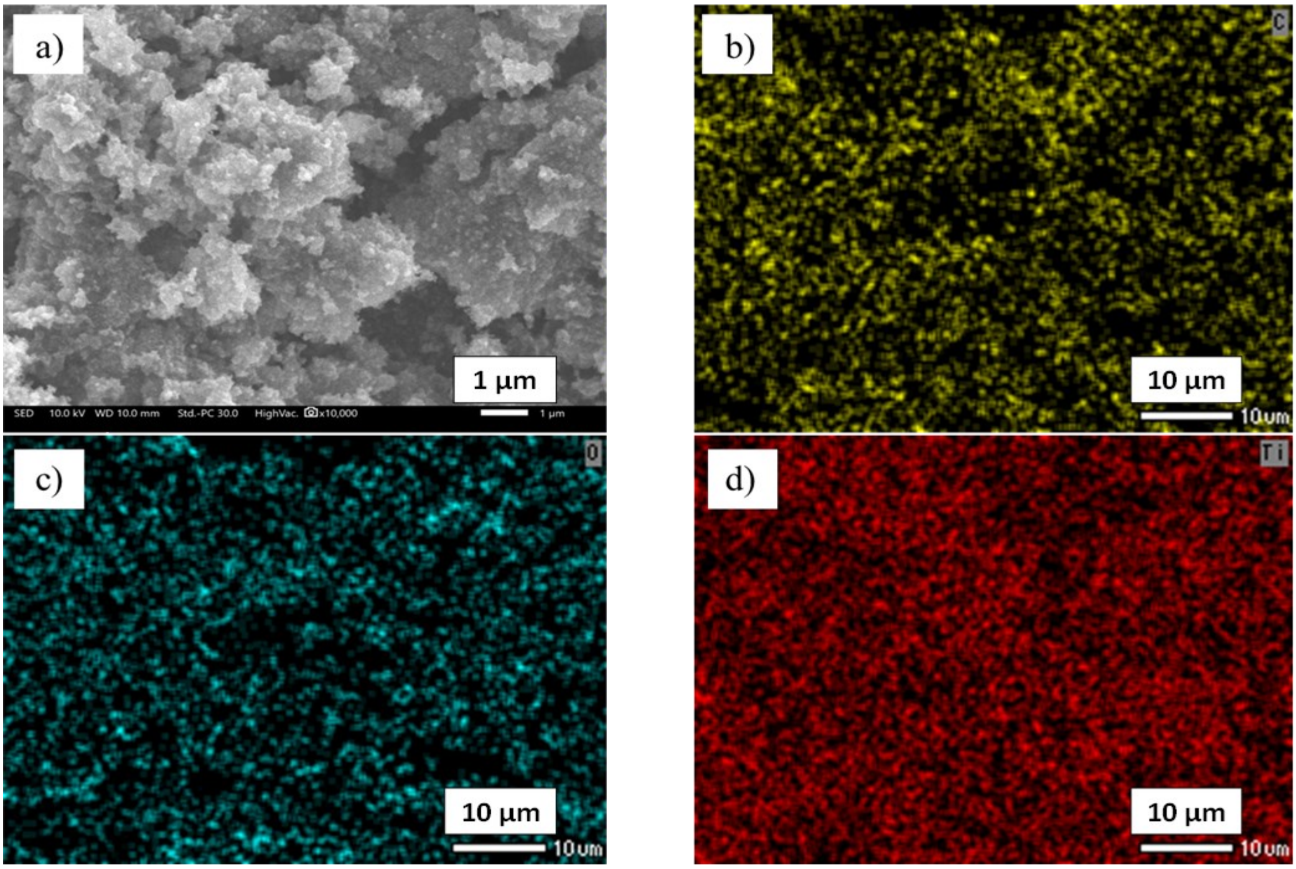

Figure 3. SEM – EDS of CDs/$TiO_2$: (a) SEM image, (b) C-element, (c) Ti-element and (d) O-element.

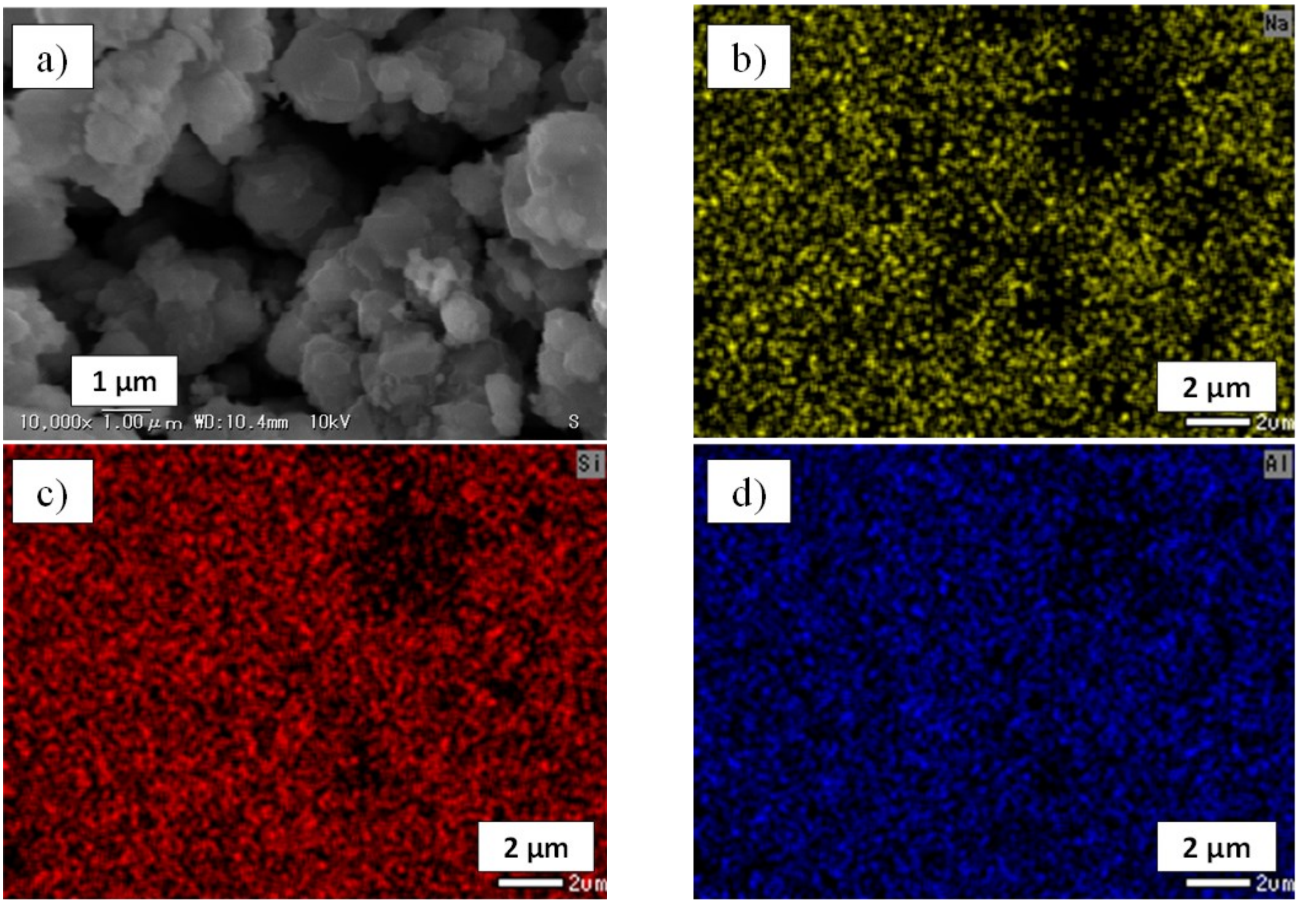

Figure 4. SEM – EDS of Zeolite Y: (a) SEM image, (b) Na-element, (c) Si-element and (d) Al-element.

the strain vibrations of the hydroxyl group. The absorption peaks below 1000 cm$^{-1}$ of CDs/$TiO_2$ are wider and have lower transmission compared to the peaks of $TiO_2$. This is due to the combination of $TiO_2$ and CDs in the composite.

The TGA results show that $TiO_2$ and CDs/$TiO_2$ (2) shared a common trend in the percentage of weight loss before 120 °C, corresponding to the removal of adsorbed water which was adsorbed by the materials. In the period from 120 °C to 300 °C, both of the catalyst samples continued to lose mass. The weight of the CDs/$TiO_2$ sample decreased by 0.841 %, and this can be explained by the hydroxylation of water and the hydroxyl groups on the surface [13,14]. Above 300 °C, only the CDs/$TiO_2$ sample lost mass because of the slow carbon combustion which resulted in the loss of the carbon nanodots. This means that the content of CDs impregnated on $TiO_2$ accounts for about 0.301 % of the mass. The amount of CDs lost is used to calculate the efficiency of the CDs impregnating process compared to the theoretical value of approximately 80 % [14].

### 3.2 Effect of CDs/$TiO_2$ – Zeolite Y Ratio on the Catalytic Performance

The influence of the CDs/$TiO_2$ – zeolite Y ratio was investigated by changing the mass ratio of CDs/$TiO_2$ and zeolite Y in 0.2 g of the catalyst sample for each experiment. Other reaction conditions were kept constant. The results shown in Figure 6 indicate that the CDs/$TiO_2$ - zeolite Y catalyst samples with different mass ratios all showed high toluene treatment efficiency initially, and then the activity slowly de-

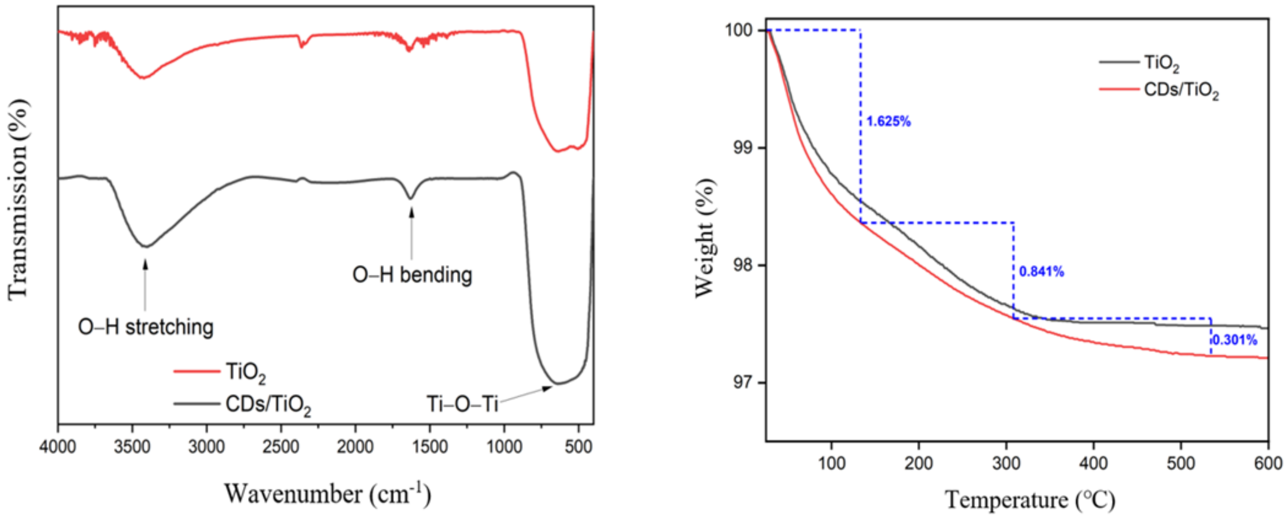

Figure 5. (a) FTIR spectra and (b) TGA spectra of $TiO_2$ and CDs/$TiO_2$.

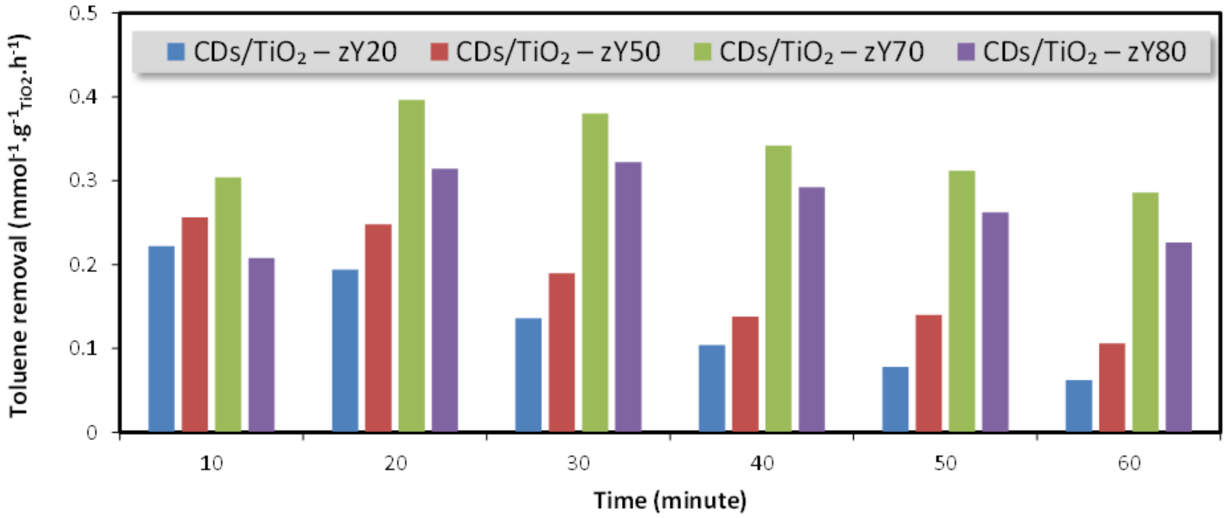

Figure 6. Toluene removal over CDs/$TiO_2$ – zeolite Y samples with different ratios (concentration 314 ppmv, flow rate 3 L/h, humidity 60%, 4 UV lamps).

creased with time. Overall, the catalytic activity increased gradually when increasing the amount of zeolite Y, in which the sample CDs/$TiO_2$ – zY70 reached the highest conversion rate of 0.396 mmol.g$^{-1}$.h$^{-1}$ after 20 min then decreased slightly to 0.286 mmol.g$^{-1}$.h$^{-1}$ at the 60th minute. However, the CDs/$TiO_2$ – zY80 sample has lower conversions than the CDs/$TiO_2$ – zY70 sample, and this can be explained that when the Y zeolite occupies a high volume, CDs/$TiO_2$ content becomes too low, leading to a lack of catalyst sites for completely removing toluene.

Figure 7 compares the converted toluene amount of $TiO_2$, CDs/$TiO_2$ and CDs/$TiO_2$ – zY70 catalyst samples. It can be seen that the addition of CDs slightly increases the activity of $TiO_2$ due to the upconversion photoluminescence property and the fact that the dopant can act like an electron reservoir [15]. However, the overall efficiency of the toluene removal process is better maintained and rises significantly when zeolite Y is added to the CDs/$TiO_2$ catalyst. With the use of zeolite Y as a supporter, the surface area of CDs can be improved through better dispersion and the aggregation of these dots are prevented [16]. Besides providing high surface area and good absorbent capacity [16], zeolite also assists the transfer of excited electrons from CDs to its framework, thereby lengthening the lifetime of electrons and holes [17]. All of these factors contribute to the significant rise in toluene treatment efficiency.

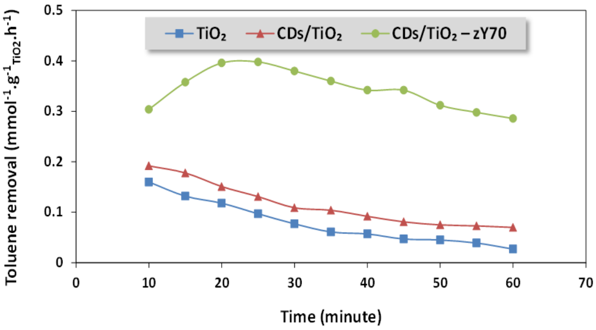

Figure 7. Toluene removal over $TiO_2$, CDs/$TiO_2$ and CDs/$TiO_2$ – zY70 samples (concentration 314 ppmv, flow rate 3 L/h, humidity 60%, 4 UV lamps).

### 3.3 Effect of Toluene Concentration on the Catalytic Performance of CDs/$TiO_2$ – Zeolite Y

The influence of toluene concentration on the performance of CDs/$TiO_2$ – zeolite Y was studied when all reaction conditions were fixed and the toluene concentration changed by 341 ppmv, 832 ppmv and 1768 ppmv. The results are shown in Figure 8. The conversion of toluene generally increased in the early stages and dropped with increasing reaction time. The input flow with 832 ppmv of toluene showed better conversion during the first 20 minutes compared to the flow with 314 ppmv of toluene, and this may be due to the increase in reaction rate caused by the higher concentration of the reactant. From the 20th minute, the toluene removal of the 314 ppmv flow was higher than that of the 832 ppmv flow, and this can be explained by the higher amount of by-products generated from the latter flow. The formation of by-products, which inhibit the adsorption and processing of toluene [18], may also be the culprit of the low photocatalytic performance of the 1768 ppmv flow.

### 3.4 Effect of Flow Rate on the Catalytic Performance of CDs/$TiO_2$ – Zeolite Y

The influence of gas flow rate on toluene treatment through CDs/$TiO_2$ – zeolite Y photocatalysts was investigated when other reaction conditions were fixed and the gas flow rate changed from 3 L/h to 9 L/h. The results are shown in Figure 9. At the beginning of the reaction, all of the three flows showed the same conversion, at about 0.2 mmol.g$^{-1}$.h$^{-1}$. During

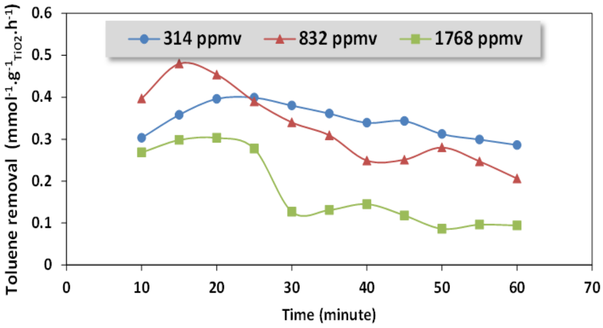

Figure 8. Effect of concentration on toluene treatment over CDs/$TiO_2$ – zY70 (flow rate 3 L/h, humidity 60 %, 4 UV lamps).

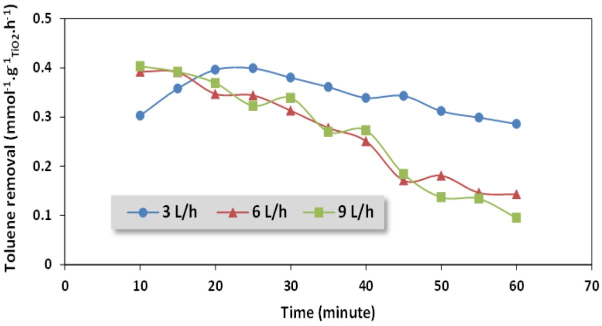

Figure 9. Effect of total gas flow rate on toluene treatment over CDs/$TiO_2$ – zY70 (concentration 314 ppmv, humidity 60 %, 4 UV lamps).

the first 15 min, the flows of 6 L/h and 9 L/h had better toluene removal than the 3 L/h flow, and the reason for this may be the increase in mass transfer rates achieved at higher flow rate. However, increasing flow rate leads to too many toluene molecules adsorbed while the intermediate products are not degraded fast enough [19], thus reducing the overall efficiency of the process for the flows of 6 L.h$^{-1}$ and 9 L.h$^{-1}$ over time.

### 3.5 Effect of Humidity on the Catalytic Performance of CDs/$TiO_2$ – Zeolite Y

The influence of humidity on the activity of CDs/$TiO_2$ – zY70 was studied when all reaction conditions were fixed and the humidity was changed (0%, 30% and 60%). Based on Figure 10, it can be seen that the performance gradually increased with increasing humidity. Compared with the non-humidity condition, the toluene removal increased significantly at 30% humidity. The highest and lowest values at this humidity were 0.321 mmol.g$^{-1}$.h$^{-1}$ and 0.105 mmol.g$^{-1}$.h$^{-1}$, respectively. Increasing the humidity for the system up to 60%, the conversion continued to increase to 0.399 mmol.g$^{-1}$.h$^{-1}$ and 0.202 mmol.g$^{-1}$.h$^{-1}$ at the highest and lowest values. The improvement in toluene removal when the humidity is increased can be explained by the importance of water vapor for the generation of hydroxyl radicals to oxidize organic molecules [9] as well as the support of water in the elimination of benzaldehyde - a by-product- which was adsorbed on the catalyst surface [20].

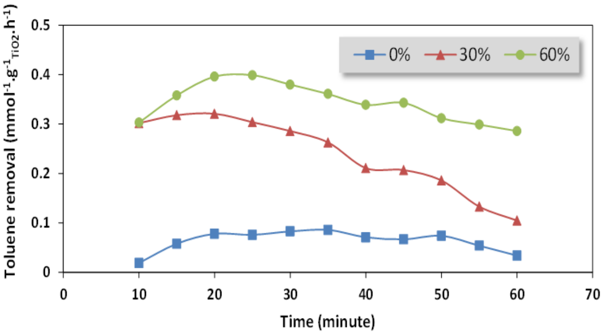

Figure 10. Effect of relative humidity on toluene treatment over CDs/$TiO_2$ – zY70 (concentration: 314 ppmv, flow rate: 3 L/h, 4 UV lamps).

### 3.6 Effect of UV Intensity on the Catalytic Performance of CDs/$TiO_2$ – Zeolite Y

The effect of UV intensity was studied while fixing all reaction conditions and varying the light intensity using 2 UV lamps and 4 UV lamps. Figure 11 shows that the light intensity significantly affected the toluene treatment efficiency of CDs/$TiO_2$ – zY70. When using 2 UV lamps, the toluene removal varied around 0.19 mmol.g$^{-1}$.h$^{-1}$. When 4 UV lamps were used, the toluene removal increased significantly, peaking at 0.399 mmol.g$^{-1}$.h$^{-1}$ after about 25 min of reaction and then slightly decreasing to about 0.3 mmol.g$^{-1}$.h$^{-1}$ at the 60th minute. This can be explained by an increase in the number of photons when more UV lamps were used, generating more free radicals for the decomposition of toluene. The UV lamps used in this study were Sankyo Denki F10T8BLBs lamps emitting UVA rays with a wavelength of 352 nm and an intensity of 1.5W. When 4 lamps were turned on, total UV capacity was quite low, only 6.0 W. Therefore, it is possible that there is still room for improving the photocatalytic activity of the CDs/$TiO_2$-Zeolite Y by increasing the UV capacity of the lamps.

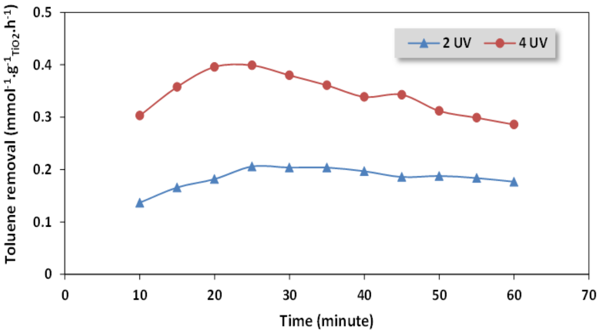

Figure 11. Effect of UV intensity on toluene treatment over CDs/$TiO_2$ – zY70 (concentration: 314 ppmv, flow rate: 3 L/h, humidity 60%).

## 4. Conclusions

The study has successfully synthesized carbon nanodots from citric acid and urea by the hydrothermal method at 200 °C for 6 h. Microstructural studies show that the carbon nanodots are spherical in shape with a uniform size below 10 nm. The photocatalysts CDs/$TiO_2$ and CDs/$TiO_2$ – zeolite Y were also successfully synthesized and the efficiency of toluene treatment was investigated under different conditions in terms of initial toluene concentration, inlet gas flow rate, humidity and light intensity. The results indicate that CDs/$TiO_2$ – zeolite Y, of which zeolite accounts for 70 % by mass, has better catalytic activity than CDs/$TiO_2$. The toluene removal obtained on CDs/$TiO_2$ – zeolite Y was used was above 0.3 mmol.g$^{-1}{}_{TiO2}$.h$^{-1}$ while that of the commercial $TiO_2$ (P25) was less than 0.15 mmol.g$^{-1}{}_{TiO2}$.h$^{-1}$

at similar testing condition. Our study also shows that increasing the relative humidity from 0 to 60 % can enhance toluene removal on the CDs/$TiO_2$ – zeolite Y from nearly 0.1 $mmol.g^{-1}{}_{TiO2}.h^{-1}$ to above 0.3 $mmol.g^{-1}{}_{TiO2}.h^{-1}$. Further research work on catalyst development should be conducted for improvement of the photocatalyst stability.

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## CRediT Author Statement

Author Contributions: Le K. Anh: Formal analysis, Methodology, Writing - Original Draft; Nguyen T. K. Oanh: Methodology, Investigation; Tran L. M. Hieu: Methodology, Investigation; Nguyen T. T. Phuong: Methodology, Validation, Formal analysis; Ngo T. H. Duong: Conceptualization, Methodology, Writing - Review & Editing ; Nguyen V. Dung: Conceptualization, Methodology, Writing - Review & Editing ; Nguyen Q. Long: Conceptualization, Methodology, Supervision, Formal analysis, Writing - Review & Editing.

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