Photodegradation of acetone vapor by carbon dots decorated TiO$_2$ catalyst: effects of experimental conditions

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Abstract. Being one of the most common volatile organic compounds (VOCs), acetone can be found in everyday products and high doses of acetone pose harmful effects on human health. Photocatalytic oxidation has captured the attention as an alternative feasible and cost-effective technology in treating VOCs. This study mainly focused on the photocatalytic performance of carbon dots (CDs) decorated TiO$_2$ prepared using the microwave-assisted method in degrading acetone in a continuous flow under UVA irradiation at room temperature with various experimental conditions (initial concentrations, water contents and flow rates). The presence of carbon dots on the surface of TiO$_2$ had improved the removal efficiency of the photocatalyst and maintained a good overall performance throughout the experiments. Significantly, the prepared CDs/TiO$_2$ exhibited sustainable performance under the change of water contents which usually significantly impacts the performance of photocatalysts in general.

1. Introduction
Photocatalytic oxidation (PCO) is one of the most common technologies used in treating harmful volatile organic compounds (VOCs) in the present day. Unlike biology-based or thermal oxidation methods which require significant investments in equipment and energy, PCO is feasible and cost-effective as it can utilize a free and abundant energy source which is sunlight to generate hydroxyl radicals to decompose organic matter [1]. Materials used in PCO must have appropriate band-gap energy to generate photoelectron-hole pairs under specific irradiation and TiO$_2$ is the most popular of them all [2, 3]. However, TiO$_2$ still exhibited many limitations which include low energy usage with only use 5% of sunlight in the form of UV radiation, short existing duration of the electron-hole pairs before being able to react with water molecules to form hydroxyl radicals and low affinity toward organic matters [4-6]. Thus, more studies have been carried out to improve the photocatalytic oxidation performance of TiO$_2$ such as doping of metal oxide, noble metal or non-metal element, adding adsorbent to enhance adsorption capacity [7-9].

Carbon dots (CDs), since its first literature report in 2004, have captured great attention due to their flexible physical, optical and chemical characterizations many of which can be implemented in photocatalyst [10, 11]. Several studies have reported the ability of carbon dots decorated semiconductors in the photodegradation of organic dye [12-14]. The improvement in photocatalytic activity of these composites was mainly attributed to the conjugated π structure of the carbon dots and
the strong chemical interaction between CDs and semiconductors which would promote adsorption of organic compounds and improve charge transfer on the catalyst surface [15]. Additionally, CDs prepared from different precursors such as ash, orange juice, coffee beans still exhibited similar properties [16-18].

In this paper, carbon dots decorated TiO$_2$ was prepared using citric acid, urea and commercial TiO$_2$ using a microwave-assisted method. Herein, the prepared material was used in the photocatalytic oxidation of acetone in comparison with commercial TiO$_2$ to illustrate the benefit of decorating carbon nanodots. This study focuses on the photocatalytic performance of CDs decorated TiO$_2$ in response to different conditions (continuous flow, moderate acetone initial concentration, different water vapor contents and flow rates) where it is challenging for commercial TiO$_2$ to maintain a stable efficiency. This result can reflect the potential of this material in practical use.

2. Experimental

2.1. Materials

3 g of citric acid monohydrate and 3 g of urea was dissolved in 10 mL of distilled water (DW). The colorless solution was heated using a domestic microwave (750W) for 5 min and changed into a dark brown solid. The solid was dispersed in 200 mL of DW and was centrifugated at 4000 rpm for 20 min to remove large particles. The dark brown solution was labeled CDs. 1 g of TiO$_2$ (P25-Degussa) and 500 µL of CDs solution were dispersed in 400 mL of DW and were ultrasonicated for 30 min. Afterward, the mixture was filtrated and washed with DW to obtain a light brown solid. The solid was dried overnight at 80 °C and was labeled CDs/TiO$_2$.

CDs solution was characterized by high-resolution transmitted electron microscope (HRTEM) using JEOL JEM-2100 and photoluminescence (PL) on Horiba Ihr550 Spectrometer instrument. CDs/TiO$_2$ was characterized using FT-IR spectra on Nicolet 7500 FTIR spectrometer - Thermo Fisher Scientific and Scanning electron microscopy/energy dispersive X-ray spectrometry (SEM-EDS) using EDX Horiba H-7593.

2.2. Photocatalytic oxidation system

The bubbling method was used to generate a model gas of nitrogen and oxygen ($n_{N_2} : n_{O_2} = 4 : 1$) for the photocatalytic oxidation of acetone over the prepared material. The initial nitrogen stream (>99.99%) was split into three streams: an acetone feed stream, water vapor feed stream and a diluting stream. Three nitrogen streams and an oxygen stream (>99.99%) were collected into a mixing chamber and the outlet of the chamber was divided into two streams, a bypassing stream and a stream to the reactor. The reactor outlet was connected with gas chromatography (Hewlett Packard 5890plus) equipped with a Flame Ionization Detector (FID) via a 6-way valve for online injection and monitoring of acetone concentration. Each stream of nitrogen or oxygen was equipped with a set of a needle valve and a flow meter and thus, the concentration of acetone and water content could be controlled by simply changing the stream ratio. The photocatalytic oxidation of acetone was performed under a continuous stream using an annular reactor. The reactor consisted of two tubes: the inner tube coated with the prepared material via spin-spray coating method and a quartz outer tube connected with the feed stream and GC-PID. The light source was a set of four UV lamps (Sankyo Denki F10T8BLB, 1.5 W, UV-A, k = 315 - 400 nm) installed symmetrically with the annular reactor.

3. Results and discussion

3.1. Characterization of the prepared materials

Figure 1 and 2 illustrate the results for the characterization of the prepared material. CDs had spherical morphology with the size of 5-10 nm, as shown in Figure 1ab. The photoluminescence spectra (Figure 1c) exhibited an emission peak at 530 nm corresponding to green light.
Figure 1. (a, b) HRTEM images of CDs (scale bar of 20 nm and 10 nm), (c) PL spectra of CDs

Figure 2a illustrates FT-IR spectra of TiO$_2$ (red) and CDs/TiO$_2$ (black). Both materials exhibited peaks associated with stretching vibrations of hydrogen-bonded water molecules and hydroxyl groups, bending vibrations of the O-H group and Ti-O-Ti bridging stretching mode at wavenumbers of 3420, 1630, and 650 cm$^{-1}$, respectively [19]. The C=C, C-N and N-H stretching vibration could also be observed in FT-IR spectra of CDs/TiO$_2$ at 1630, 1385 and 3420 cm$^{-1}$. Furthermore, the absorption peak below 1000 cm$^{-1}$ became wider and shifted toward a higher wavenumber suggesting the presence of Ti-O-C bond [15]. As shown in Figure 2b, the calculated band-gap energy of CDs/TiO$_2$ and TiO$_2$ were 3.2 and 3.43 eV, respectively. This slight decrease is attributed to the bonding between TiO$_2$ – CDs and was discussed in previous studies [20, 21]. SEM-EDS images (Figure 2c-d) confirmed the presence of Ti, O and C-element on the prepared material and CDs (red dots) were distributed evenly on the TiO$_2$ surface (Figure 2d).
3.2. Effect of CDs the photocatalytic performance

Figure 3 shows the catalytic performance of TiO$_2$ and CDs/TiO$_2$ with an acetone concentration of 254 ppm, a water content of 18.20 mg L$^{-1}$ and a flow rate of 3 L h$^{-1}$. The removal efficiency of acetone in a continuous flow over TiO$_2$ increased gradually over the experiment duration, from 0.08 mmol g$^{-1}$ h$^{-1}$ after 5 min to 0.18 mmol g$^{-1}$ h$^{-1}$ after 50 min. Significantly, CDs/TiO$_2$ exhibited improved performance in terms of speed and sustainability. After 10 min, CDs/TiO$_2$ achieved the acetone removal efficiency of 0.21 mmol g$^{-1}$ h$^{-1}$, which was a 91% increase compared to that of TiO$_2$ at 10 min, and was able to maintain it until the end. Previous studies also confirmed the positive impact of CDs on photocatalyst but its mechanism is still vague until the present day. Two widely accepted assumptions included (i) the role of CDs as electron traps that hinder the recombination of photo-electrons and holes on the catalyst and (ii) the improvement of affinity toward organic compounds for a shorter route to react with hydroxyl radicals produced on the surface of photocatalyst [8, 12].

3.3. Effect of initial condition on the photocatalytic performance of CDs/TiO$_2$

3.3.1. Total flow rate

The experiment to study the effect of flow rate on the photocatalytic performance of CDs was conducted at an acetone concentration of 254 ppm, a water content of 18.20 mg L$^{-1}$ and a flow rate of 3 to 12 L h$^{-1}$. In general, at each flow rate, the prepared CDs/TiO$_2$ exhibited a stable performance after 10-15 minutes and that trend was kept until the end of the experiment, as shown in Figure 4. It is worth noticing that a higher acetone removal efficiency per mass of catalyst was observed at a higher flow rate. The highest removal efficiency at 3 L h$^{-1}$, 6 L h$^{-1}$ and 12 L h$^{-1}$ were 0.21 mmol g$^{-1}$ h$^{-1}$, 0.41 mmol g$^{-1}$ h$^{-1}$ and 0.71 mmol g$^{-1}$ h$^{-1}$, respectively. It seems that the current reaction conditions are still in the mass flow control regime which means increasing the flow rate will increase the total removal efficiency [22].
3.3.2. Acetone initial concentration

The experiment to study the impact of initial acetone concentration on the performance of the prepared material was conducted at a water content of 18.20 mg L\(^{-1}\), a flow rate of 12 L h\(^{-1}\) and acetone concentrations of 254, 631 and 1444 ppm (Figure 5). When the concentration increased from 254 ppm to 631 ppm, the total removal per mass of CDs/TiO\(_2\) doubled. However, when it reached 1444 ppm, the efficiency only increased by about 20% and ended at 1.87 mmol g\(^{-1}\) h\(^{-1}\). In the first phase, the increase in efficiency was maybe because there were still available active sites for acetone to react. However, in the second phase, as the concentration became higher, all active sites of the photocatalyst were occupied; thus, the photocatalytic efficiency could not increase any further [23].

![Figure 4](image_url)

**Figure 4.** Effect of flow rate on the acetone removal over CDs/TiO\(_2\)

\((C_{acetone} = 254 \text{ ppm}, \ C_w = 18.20 \text{ mg/L}, \ m_{cat} = 0.2 \text{ g, } T = 39 \, ^\circ\text{C})\)

![Figure 5](image_url)

**Figure 5.** Effect of acetone concentration on the photocatalytic performance of CDs/TiO\(_2\)

\((C_w = 18.20 \text{ mg/L, } F = 12 \text{ L h}^{-1}, \ m_{cat} = 0.2 \text{ g, } T = 39 \, ^\circ\text{C})\)
3.3.3. Water content
The impact of water content on the removal of acetone over CDs/TiO$_2$ was investigated at an acetone concentration of 254 ppm, a flow rate of 3 L h$^{-1}$ and the water content of 6.07, 12.13 and 18.20 mg L$^{-1}$. In general, CDs/TiO$_2$ still exhibited a stable catalytic activity throughout the experiments, as shown in Figure 6. Higher water content had higher start-up efficiency (after 5 min) but there was a light decrease with the increase of water content as the experiment carried on. Water molecules are essential in photocatalytic oxidation as they react with photoelectron-hole pairs on the catalyst’s surface to form hydroxyl radicals, the primary oxidizing agent to degrade organic compounds, resulting in higher start-up efficiency at the water content of 18.20 mg L$^{-1}$. However, because of the polarization of the photocatalyst surface under UV irradiation which can interact with water molecules, more water molecules per unit volume will obstruct the adsorption of VOCs onto the catalyst and may hinder the photocatalytic efficiency [8]. This phenomenon was still observed in this study but the difference was reduced to less than 10% when the water content tripled and it supports the assumption of improving the affinity of the prepared material toward organic matter mentioned in section 3.2.

![Figure 6. Effect of humidity on acetone removal over CDs/TiO$_2$](image)

$C_{acetone} = 254$ ppm, $F = 3$ L h$^{-1}$, $m_{cat} = 0.2$ g, $T = 39$ °C

4. Conclusion
The presence of CDs on the surface of TiO$_2$ had improved the overall acetone removal efficiency in continuous flow under UVA irradiation compared to TiO$_2$ under the same condition with higher removal efficiency and stability. At the acetone concentration of 254 ppm, the water content of 18.20 mg L$^{-1}$ and the flow rate of 3 L/h, the removal efficiency was 0.21 mmol g$^{-1}$ h$^{-1}$. In the scope of this study, different initial conditions had different impacts on the photocatalytic performance of CDs/TiO$_2$. The water content in the model gas had a minor effect on the acetone removal as the differences were limited to under 10% at three different contents. There is room for improvement and optimization of the catalyst as the acetone removal per mass of catalyst still increased with the increase of total flow rate and VOC initial concentration. Nevertheless, the catalyst exhibited sustainable catalytic activity at the most extreme condition in this paper. For future study, the mechanism for the photocatalytic oxidation of CDs/TiO$_2$ need to be investigated to determine the role of CDs.
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