Study on Degradation of Lignin by TiO$_2$-based Photocatalyst Doped with Carbon Dots

YU TAN, MINGYU HE, YING LI, MAMATJAN YIMIT*
Xinjiang University, College of Chemical Engineering, Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region, 666 Shengli Road, Tianshan District, Urumqi City, Xinjiang Province, China

Abstract: The carbon dots were prepared by the microwave method, and then the TiO$_2$ doped with carbon dots was successfully synthesized by the hydrothermal method. Its structure was investigated using TEM, XRD and XPS. The catalyst was applied to the degradation of lignin base solution (50 mg of lignin in 30 mL of sodium hydroxide solution pH = 12) under ultraviolet light. It was found that when the mass ratio of carbon point to TiO$_2$ was 1.5:1, the dosage of catalyst was 0.75 g/L, and the degradation time was 6 h, the degradation rate could reach more than 45%. The degradation rate of more than 40% could be maintained after seven cycles, indicating that the catalyst had good photocatalytic cycle stability. The degradation products were analyzed by GC-MS, and the main products were n-butyl acetate, butyl phthalate and alkanes with long carbon chains.

Keywords: carbon dots, lignin photocatalysis, TiO$_2$ catalyst, ultraviolet light

1. Introduction

Lignin is the only natural polymer material with aromatic structure in nature, which is composed of sinapyl alcohol group, coniferyl alcohol group and p-coumary alcohol group connected by 4-O-5, α-O-4, β-O-4, β-β, β-1, 5-5 and other bonds. Its typical structure is shown in Figure 1 [1-3]. However, the complex chemical structure of lignin makes it impossible to be used directly, it usually needs to be degraded before it is used. The lignin can be degraded to obtain products such as low molecular weight phenols and organic acids [4, 5]. These degradation products are not only important chemical raw materials but also can be converted into liquid fuels through hydrogenation and deoxygenation reactions.

![Figure 1. Structure diagram of lignin](image-url)

There are many degradation methods of lignin, such as enzymolysis, pyrolysis, hydrolysis and oxidative degradation. However, these methods all have some disadvantages, for example, enzymatic
hydrolysis reaction conditions for temperature, pressure requirements, difficulty to industrialization; Reunion of degradation products occurs; The degradation rate is not high and so on [6]. Photocatalysis has been considered as the optimal degradation method due to its advantages of cleanliness, high efficiency and low cost [7].

Gu et al. [8] used the La-modified SBA-15/H2O2 system as a catalyst to desorb lignin at the microwave power of 200 W and 150°C. After 10 min, monophenols with a mass yield of 2.7% were obtained. Wang et al. [9] prepared carbon-modified nickel catalyst by carbothermal reduction method, and studied the catalytic oxidation and hydrolysis of lignin sulfonate with it. The results showed that the three-dimensional electron distribution of nickel was changed by carbon modification, and it had a high selectivity for the hydrolysis of C-O bonds of lignin to generate aromatic hydrocarbons, with a yield of up to 22%.

At present, the most widely used photocatalyst is TiO2, which has the advantages of non-toxicity, stable chemical properties and low price [10, 11]. However, due to the low utilization of visible light and the electron-hole recombination [12-14], it is often necessary to modify it. The commonly used modification methods include ion doping, surface deposition of precious metals, surface photosensitization and so on [15-19].

It has been reported that carbon dots (CDs) can promote the photocatalytic activity of the materials [20]. It can convert longwave band light into short wave band light, to broaden the light absorption band of the material, and CDs also has a large electron storage capacity, which helps the transfer of photogenerated electrons in the material and inhibits the composite of electrons and holes [21-23]. Therefore, in theory, modification of TiO2 with CDs can effectively improve the two shortcomings of TiO2 as a photocatalyst.

Yiqing Deng et al. [24] used CDs/TiO2 to degrade methyl orange and found that the degradation rate could reach 70.56% under the irradiation of 600 nm light source. The results of fluorescence spectrum analysis and UV-Vis showed that the CDs could convert 600 nm visible light to 350 nm ultraviolet light. Zhang Bo et al. [25] used hydrothermal method to combine CDs and TiO2, and investigated the degradation effect of composite catalyst on pulping black liquor under visible light. The results showed that most of the organic matter in the pulping black liquor was degraded, and the CODCr removal rate was 81.2%.

Under the irradiation of ultraviolet light, the alkali-lignin was degraded to obtain n-butyl acetate, butyl phthalate and alkanes with longer carbon chains.

2. Materials and methods

2.1. Raw materials and instruments

Lignin, homemade [26], extracted from waste cotton stalks collected in the southern Xinjiang region of Xinjiang Uygur Autonomous Region, china; Nano TiO2 (particle size =100 nm, anatase, hydrophilic); Ethylenediamine (> 99.0%); Anhydrous ethanol (> 99.0%); Citric acid (analytically pure); Photochemical reactor, homemade (internal UV lamp is 1000 W, 300~400 nm); Microwave Reactor (700 W); Dialysis bag (MD44-1000); Ultrasonic cleaner (KQ-100VDB type); Hydrothermal reactor (containing 100 mL PTFE lining); Blast drying oven; Centrifuge.

2.2. The preparation of CDs/TiO2

The citric acid (1 g) was added into distilled water (10 mL) and stirred until completely dissolved. Ethylenediamine (500 mg) was added to it and stirred for 10 min. Then the mixed solution was placed in a microwave reactor and reacted for 5-7 min until a red-brown solid was generated. Once it has cooled to room temperature, distilled water (30 mL) was added to it and stirred until completely dissolved. In a centrifuge, it was centrifuged for 20 min at 3000 r/min. Then, 2/3 of the supernatant liquid was poured into a dialysis bag, and dialyze for 3 days. After dialysis, the solution was concentrated by a rotary evaporator and dried to obtain reddish-brown powder CDs.
A (125,250,375,500) mg CDs was added into a beaker containing anhydrous ethanol solution (20 mL), afterward, distilled water (40 mL) was added into it, and ultrasonic dispersion was carried out at room temperature for 1 h. After ultrasonic dispersion, 250 mg TiO\textsubscript{2} was added to the mixture and then ultrasonic dispersion was carried out for 1 h to obtain a uniformly dispersed mixture. The mixed solution was transferred to a hydrothermal reaction autoclave for reaction at 120°C for 5 h. After the reaction was completed, the kettle was allowed to cool naturally to room temperature, the mixed solution was taken out, centrifuged at 3000 r/min for 20 min, and collected the precipitate. Then the precipitate was washed three times with distilled water and dried at 60°C for 12 h to obtain CDs/TiO\textsubscript{2} doped with a mass ratio of 0.5:1, 1.0:1, 1.5:1, 2.0:1.

2.3. Characterization of CDs/TiO\textsubscript{2}

TEM: TiO\textsubscript{2} and CDs/TiO\textsubscript{2} were uniformly dispersed in ethanol solution and dropped on copper mesh. After drying, the surface morphology of TiO\textsubscript{2} and CDs/TiO\textsubscript{2} was observed by high-resolution transmission electron microscope (JEOL-JEM-2100F).

XRD: Cu-Ka (λ=0.154056 nm) was used to study the structure of TiO\textsubscript{2} and CDs/TiO\textsubscript{2} at 2θ=5°~80° by powder X-ray diffraction (Ultima IV) technique. Then, the grain diameter perpendicular to the (hkl) crystal plane was calculated by Debye - Scherrer’s equation:

\[ D_{hkl} = \frac{K\lambda}{\beta \cos \theta} \]  

\[ D_{hkl} \] is the grain diameter perpendicular to the (hkl) crystal plane, \( K \) is the Scherrer constant, \( \lambda \) is the incident wavelength, \( \beta \) is the half peak width (rad) of the diffraction peak, \( \theta \) is the Bragg’s diffraction Angle. Finally, the lattice parameters of tetragonal titanium dioxide (hkl) crystal plane can be calculated by the following formula

\[ \frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \]  

\( d \) is the spacing of crystal faces, \( a \) and \( c \) are lattice parameters.

XPS: X-ray photoelectron spectroscopy (Thermo scientific K-Alpha) was used to analyze the surface chemical information of CDs/TiO\textsubscript{2}.

UV-vis DRS: The absorption range of CDs/TiO\textsubscript{2} was measured by ultraviolet/visible diffuse reflectance test (PE lambda 750), with BaSO\textsubscript{4} as reference, and the test wavelength was 200~800 nm. Then the band gap width of the material can be calculated from Kubelka-Munk equation:

\[ \alpha h \nu^n = B (h \nu - E_g) \]  

\( \alpha \) is the absorbance (absorbance); \( h \) is Planck’s constant; \( \nu \) is the frequency of light; \( B \) is a constant related to material; \( E_g \) is the band gap energy value; indirect band gap semiconductor \( n=1/2 \), direct band gap semiconductor \( n=2 \).

BET: According to N\textsubscript{2} adsorption-desorption isotherm at 77K, it was calculated by multi-point Brunauer-Emmett-Teller (BET: Mike-tristar ii3flex) method. The BET surface area was measured in a relative pressure range from 0.05 to 0.3. The average porosity is calculated by quenched density functional theory (QSDFT).

TGA: The thermal stability was analyzed on a thermogravimetric analyzer (TGA5500). It is tested in nitrogen at a heating rate of 10°C /min from room temperature to 800°C.

GC-MS: The product was dissolved in ethyl acetate and its components were analyzed by GC-MS (QP2010-SE).
2.4. Degradation of lignin by CDs/TiO$_2$ under ultraviolet light

Lignin (50 mg) was dissolved in NaOH solution (30 mL) with pH=12 and added a certain amount of CDs/TiO$_2$ to it. Then the mixture was placed on a magnetic stirrer and reacted for some time at room temperature under the irradiation of a 1000 W UV lamp. At the end of the reaction, the solid and liquid were separated at a speed of 3000 r/min in the centrifuge, and the solid was CDs/TiO$_2$. The liquid was extracted with ethyl acetate (15 mL). After extraction, the oil phase of the extract was analyzed by GC-MS and the aqueous phase was acidified to pH=3, then dried and weighed in a blast furnace. The degradation rate is calculated as the following formula:

$$\eta(\%) = \left(\frac{m_{\text{all}} - m_{\text{residual}}}{m_{\text{all}}}\right) \times 100\%$$ (4)

$\eta$ is degradation rate, $m_{\text{all}}$ is Initial quality of lignin, $m_{\text{residual}}$ is quality of residual lignin.

CDs/TiO$_2$ obtained by centrifugation was vacuum freeze-dried and recycled. The recovered CDs/TiO$_2$ was used as catalyst again in the degradation reaction of lignin. The degradation rate was calculated, and the lifetime of lignin was evaluated by the change value of degradation rate.

The effects of three factors were investigated including the doping mass ratio of CDs and TiO$_2$, the addition amount of catalyst, and the degradation time. Besides, considering the economic effect of the catalyst, we also experimented on the reutilization of the catalyst.

3. Result and discussions

3.1. Degradation results

![Figure 2](image_url)

**Figure 2.** (a) influence of doping amount of CDs on degradation rate (reaction condition: degradation time of 6 h, CDs/TiO$_2$ concentration of 0.75 g/L) (b) influence of CDs/TiO$_2$ concentration on degradation rate (reaction condition is the degradation time of 6 h, the doping mass ratio of CDs and TiO$_2$ is 1.5:10) (c) effect of reaction time on degradation rate (the reaction condition is that the doping mass ratio of CDs and TiO$_2$ is 1.5:10, and the CDs/TiO$_2$ concentration is 0.75 g/L) (d) CDs/TiO$_2$ recoverability test (reaction conditions: the doping mass ratio of CDs and TiO$_2$ is 1.5:10, CDs/TiO$_2$ concentration is 0.75 g/L, and the reaction time is 6 h)
According to Figure 2a, when the doping mass ratio of CDs and TiO₂ is 1.5:1, the degradation rate reaches the maximum of 48.45%. When the doping mass ratio of CDs to TiO₂ is less than 1.5:1, the degradation rate increases with the increase of the number of CDs. This is because within this range, the addition of CDs is beneficial to reduce the electron-hole recombination generated by TiO₂ itself, and at the same time, the band gap energy becomes low, which is conducive to the degradation reaction. When the doping mass ratio of CDs to TiO₂ is greater than 1.5:1, the degradation rate begins to decrease with the increase of the number of CDs. This is because the excessive addition of CDs accumulates on the surface and channels of TiO₂ and hinders light collection, so the degradation rate becomes low at the same degradation time.

According to Figure 2b, when the concentration of CDs/TiO₂ is 0.75 g/L, the degradation rate reaches a maximum of 48.23%. When the concentration of CDs /TiO₂ is less than 0.75 g/L, the degradation rate increases with the increase of the concentration of CDs/TiO₂. This is because the increase of CDs/TiO₂ amount represents the increase of active site of catalyst, which can produce more effective photons, which is conducive to the degradation reaction [27]. When the concentration of CDs/TiO₂ is greater than 0.75 g/L, the degradation rate begins to decrease with the increase of the concentration of CDs/TiO₂. This is because the concentration of the CDs/TiO₂ is equal to 0.75 g/L, per unit time of effective photon has reached saturation in solution, more CDs/TiO₂ is unable to produce a more effective photon. In addition, excessive CDs/TiO₂ will cause light scattering and cover each other, so that the generation rate of effective photons decreases. Therefore, the degradation rate becomes lower in the same degradation time [28].

According to Figure 2c, the degradation rate increases with the increase of reaction time. This is because the longer the reaction time is, the longer the illumination time is, the more light-energy TiO₂ gets, the more electron-hole pairs are generated, and the higher the degradation rate of lignin. However, after the reaction time reached 6 h, the increase in degradation rate was not significant (47.39% at 6 h, 49.61% at 8 h and 50.47% at 8 h). This is because the reaction time is too long, and the small molecules generated by degradation undergo micro-polymerization. On the whole, the optimal reaction time is 6 h and the degradation rate is 47.93%.

According to Figure 2d, the degradation rate decreases with the increase of the number of cycles. However, CDs/TiO₂ can still maintain a degradation rate of more than 40% after being used 7 times, which indicates that CDs/TiO₂ has good stability and can be recycled.

3.2. TEM of CDs /TiO₂

To observe the surface morphology of CDs/TiO₂, the TEM was performed. Figure 3 shows TEM images of TiO₂ and CDs/TiO₂. Through comparing the two figures, we can see that there are many small white spots on the surface of CDs/TiO₂. In addition, we did not find free CDs, indicating that CDs and TiO₂ are closely combined [29]. From Figure 3a and Figure 3b, it can be seen that the dispersion of nano-TiO₂ itself is not good, so the dispersion of CDs/TiO₂ is not good, and the agglomeration phenomenon appears. Moreover, CDs/TiO₂ is formed by the precipitation of CDs on the surface of TiO₂. From Figure 3c, we can see the characteristic lattice fringes of TiO₂ in the complex, and the spacing between crystal faces is 0.339 nm, which corresponds to the characteristic crystal faces (101) of anatase type TiO₂, indicating that the nanometer titanium dioxide we used is anatase type.
Figure 3. TEM images of (a) TiO$_2$ (b) CDs/TiO$_2$ (c) Typical lattice Fringe of Anatase Phase TiO$_2$

3.3. XRD of CDs/TiO$_2$

To understand the crystal structure of CDs/TiO$_2$, the XRD was done. Figure 4 shows the XRD patterns of TiO$_2$ and CDs/TiO$_2$. Firstly, the analysis of TiO$_2$ shows that the material has obvious diffraction peaks at 2θ = 25.2°, 37.7°, 47.8°, 53.6°, 54.8° and 62.5°, which correspond to (101), (004), (200), (105) and (211) crystal planes. This is the same as the crystal plane parameters of anatase TiO$_2$ [30], indicating that the purchased TiO$_2$ is anatase TiO$_2$. In addition, the diffraction peak in XRD is sharp and strong, which indicates that CDs/TiO$_2$ is single crystal structure and has good crystallinity.

According to the XRD analysis of CDs/TiO$_2$, we can see that both the diffraction peak position and the intensity of the diffraction peak correspond well with the spectrogram of TiO$_2$, which shows that TiO$_2$ has good stability and that doping CDs into TiO$_2$ has no effect on the crystal form and crystal structure of TiO$_2$, and TiO$_2$ in the synthesized CDs/TiO$_2$ completely retains its original structure.
According to eq.1, the grain diameter of anatase TiO$_2$ used by us along the direction perpendicular to the (101) crystal plane is 21.831 nm.

As can be seen from Figure 3c, the interplanar spacing of the titanium dioxide (101) crystal plane in the complex is $d = 0.339$ nm, and $h = 1$, $k = 0$, $l = 1$ of (101) crystal plane. According to eq. 2, we can calculate $a = 3.7781$ Å, $c = 9.4737$ Å. The deviation between the lattice constant of TiO$_2$ and the tetragonal anatase cell ($a = 3.7821$ Å, $c = 9.5022$ Å) may be related to the doping of CDs.

3.4. XPS of CDs/TiO$_2$

![Figure 5. XPS diagram of CDs/TiO$_2$ (a) Survey (b) O 1s (c) Ti 2p (d) C 1s](image)

To understand the chemical element information on the surface of CDs/TiO$_2$, the XPS was performed. Figure 5 shows the XPS spectra of CDs/TiO$_2$. In the full spectrum of Figure 5a CDs/TiO$_2$, we can see the absorption peaks of O1s, Ti2p, N1s and C1s, this indicates that the composite material is composed of O, Ti, N and C elements (the appearance of N element is due to the presence of ethylenediamine in the raw materials used to prepare CDs). And the proportion between them is Ti 2p =20.86%, O 1s=49.5%, C 1s=23.65%, N 1s=5.98%. In Figure 5b O 1s spectra, we can see the absorption peaks at 529.8 eV and 531.8 eV, corresponding to R=O and R-O-R bonds respectively. The appearance of these two bonds is related to TiO$_2$ and CDs. In Figure 5c Ti 2p spectrum, we can see that there are absorption peaks at 458.7 eV and 464.5 eV, which correspond to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ respectively. This indicates that the valence state of Ti in CDs/TiO$_2$ is Ti$^{4+}$ [31]. In Figure 5d C 1s spectrogram, we can see that absorption peaks appear at 284.5 eV and 278.8 eV, corresponding to C-R and C=O bonds respectively. This is the same as the bond of CDs reported in the literature [32].

Through the above XPS analysis, we can confirm that CDs has successfully compounded on the surface of TiO$_2$, and Ti-O-C bond is formed between the two, which makes the two bond closely, which is corresponding to the analysis in TEM.

Moreover, the electron binding energy of Ti in CDs/TiO$_2$ indicates that TiO$_2$ is high-purity anatase type TiO$_2$, which is corresponding to the analysis in XRD.
3.5. UV-DRS of CDs/TiO$_2$

![UV-DRS diagram of TiO$_2$ and CDs/TiO$_2$](image)

![Band gap width diagram of CDs/TiO$_2$ fitted by Kubelka-Munk equation](image)

Figure 6. (a) UV-DRS diagram of TiO$_2$ and CDs/TiO$_2$ (b) The band gap width diagram of CDs/TiO$_2$ fitted by Kubelka-Munk equation

To study the optical properties of CDs/TiO$_2$, the UV-Vis DRS was performed. Figure 6 shows the UV-DRS diagram of TiO$_2$ and CDs/TiO$_2$ and the band gap width diagram of CDs/TiO$_2$ fitted by the Kubelka-Munk equation. According to Figure 6a, the absorption range of anatase TiO$_2$ is mainly concentrated in the ultraviolet region, while the absorption range of TiO$_2$ doped with CDs is from the ultraviolet region to the visible region, but it is mainly concentrated in the ultraviolet region. This shows that the absorption range of CDs/TiO$_2$ prepared by us has been expanded, which is attributed to the interaction of Ti-O-C bond between CDs and TiO$_2$ [33]. This interaction can effectively change the interface transmission rate of the carrier, which is beneficial to the catalytic action of TiO$_2$ in the visible light range.

According to the literature, for the anatase phase of TiO$_2$, being an indirect band gap semiconductor, the value of $n$ is 0.5, and $E_g$ is 3.20 eV [20]. From Figure 6b, we can find that the band gap energy of CDs/TiO$_2$ is 2.649 eV, and the CDs/TiO$_2$'s band gap energy is reduced by 0.551 eV. This shows that CDs/TiO$_2$ has better photocatalytic performance than ordinary TiO$_2$ [34]. As mentioned above, CDs can improve the catalytic effect of the catalyst by absorbing two or more photons with longer wavelengths, converting low-energy photons to high-energy photons. Therefore, we can speculate that CDs can act as electron mediators, photosensitizers and spectral converters in the process of photocatalysis.

3.6. BET of CDs/TiO$_2$

![BET diagram of CDs/TiO$_2$](image)

Figure 7. (a) N$_2$ adsorption and desorption curve of CDs/TiO$_2$ (b) pore size distribution of CDs/TiO$_2$

To study the pore structure of CDs/TiO$_2$, the BET was done. The specific surface area of solid catalysts plays an important role in the catalytic performance of photocatalysts. Catalysts with large specific surface areas have better photocatalytic performance because they provide a large number of
active sites and can effectively adsorb reactants. The specific surface area, pore size and pore volume of CDs/TiO$_2$ were studied by BET method. Figure 7 shows the N$_2$ adsorption and desorption curve of CDs/TiO$_2$ and the pore size distribution of CDs/TiO$_2$. According to the BET test, the specific surface area of CDs/TiO$_2$ is 89.2411 m$^2$/g, the average pore diameter is 72.059 Å, and the pore volume is 0.1915 cm$^3$/g. According to Figure 7a, the adsorption isotherm of CDs/TiO$_2$ follows the type IV isotherm of mesoporous nanomaterials. In addition, it can be seen that there is an H3 type hysteresis loop in the adsorption and desorption curve, which is mainly since the composite material is a mesoporous structure, and the capillary condensation phenomenon occurred during the test. It can be seen from the hysteresis loop of the H3 type that the hole in the composite material is wedge-shaped structure and does not show adsorption saturation in the region of high relative pressure. and according to Figure 7b, the pore size distribution is 34.9 Å. The larger specific surface area of CDs/TiO$_2$ ensures that lignin molecules can be fully adsorbed, which is conducive to the photodegradation of lignin molecules. Moreover, the narrower pore size distribution enables the composites to have more active sites.

### 3.7. Thermal gravimetric analysis of CDs/TiO$_2$

To study the thermal properties of CDs/TiO$_2$, the TG was done. Figure 8 shows the TGA and DTG curves of CDs/TiO$_2$ from room temperature to 790°C in N$_2$ atmosphere. It can be found that the decline of the curve can be divided into two stages. The first stage is from room temperature to 135.18°C, and the second stage is from 135.18°C to 790°C. In the first stage, because the catalyst was not dried thoroughly, water was adsorbed on the surface and heated water was evaporated, the mass loss in this stage was 1.463%, and the fastest water loss temperature was 58.25°C. The second stage corresponds to the decomposition of CDs/TiO$_2$, and the initial decomposition temperature of CDs/TiO$_2$ is 135.18°C. The weight loss at this stage is mainly related to the bond breaking of oxygen-containing groups (such as epoxy group, carbonyl group, carboxyl group, etc.) on the surface of CDs and TiO$_2$ by covalent bonds [34], and the fastest decomposition temperature is 415.76°C. In the whole thermal analysis process, the mass loss of CDs/TiO$_2$ is 8.681%, indicating that it has a higher thermal stability property.

### 3.8. The degradation mechanism

When the light irradiates TiO$_2$, the electrons in the valence band of TiO$_2$ will be excited and transition to the conduction band. However, TiO$_2$ has a wide band gap (3.20 eV), and the excited electrons tend to return to the valence band and recombine with the holes generated when excited. When CDs modified TiO$_2$, the band gap decreased to 2.649 eV, and the excited electrons were more likely to reach the conduction band, and the electrons would migrate to CDs.

The O$_2$ attached to the surface of the catalyst will react with the excited electron on the CDs to get the superoxide radical. H$_2$O reacts with the superoxide radical to get the hydroxyl radical. At the same time, the holes in the valence band of TiO$_2$ will convert water into hydroxyl radical. The hydroxyl radical can degrade lignin [35].
Compared with TiO$_2$, CDs/TiO$_2$, due to the existence of CDs, the band gap energy becomes narrower, which means that the responsiveness to visible light is enhanced, more excited electrons can reach the conduction band, and more holes exist above the valence band so that the oxidation capacity is stronger [0].

Based on GC-MS analysis, we know that the products are n-butyl acetate, butyl phthalate and longer carbon chain alkanes (5,6-dimethyl-undecane and 2,6,10-trimethyl-dodecane). As can be seen from Figure 1, lignin does not have such a long carbon chain in its molecular structure, so there is no doubt that benzene ring opening and C-C bond breaking occurred in the degradation process. The presence of butyl phthalate indicates the presence of phthalic acid in the reaction, which may be due to the oxidation of the methoxy groups of the two side chains of the methoxy group to formic groups, the breaking of the remaining bonds, and then the reaction with the ring opening of the benzene ring and the breaking of the C-C bond to the butanol.

The presence of butyl acetate indicates the presence of acetic acid in the reaction, which may be derived from the cleavage of $\alpha$-O-4 and $\beta$-O-4 and the oxidation of the alcohol derived from the cleavage of the C-C bond attached to the benzene ring, followed by reaction with butanol derived from the ring opening of the benzene ring and the cleavage of the C-C bond.

4. Conclusions

CDs was prepared by microwave method and then doped onto TiO$_2$ by simple hydrothermal synthesis. The surface morphology of CDs/TiO$_2$ was observed by TEM, and the results show that CDs has been successfully compounded to the surface of TiO$_2$. The crystal structure of CDs/TiO$_2$ was investigated by XRD, and the results showed that the addition of CDs did not affect the crystal form of TiO$_2$, and both TEM and XRD indicated that the TiO$_2$ used was anatase type TiO$_2$. XPS proves that the composite contains three elements, Ti, C and O, which proves that the catalyst is successfully synthesized, and the Ti-O-C bond is formed between CDs and TiO$_2$.

It was found by UV-Vis DRS technology that the edge of the absorption region of CDs/TiO$_2$ moved to the visible light region compared with that of pure TiO$_2$. Then, the band gap width of CDs/TiO$_2$ was calculated by the Kubelka-Munk equation, and it was found that the band gap width of CDs/TiO$_2$ decreased from 3.20 eV of pure TiO$_2$ to 2.649 eV. This indicates that CDs/TiO$_2$ has better photocatalytic performance. BET test shows that the adsorption isotherm of CDs/TiO$_2$ is IV isotherm, and its specific surface area is 89.241 m$^2$/g, with many active sites. In TGA, it can be seen that the weight loss rate of CDs/TiO$_2$ is divided into two sections. The first section is room temperature to 135.18°C, with a weight loss rate of 1.463% and the fastest weight loss temperature of 58.25°C. The second section is 135.18°C to 790°C, with a weight loss rate of 7.218% and the fastest weight loss temperature of 415.76°C. In the whole process, the weight loss rate of CDs/TiO$_2$ is 8.681%, which indicates that it has good thermal stability. The prepared CDs/TiO$_2$ catalyzed the degradation of lignin alkali solution under ultraviolet light, and the degradation rate reached more than 45%. The degradation products were mainly n-butyl acetate, butyl phthalate and alkanes with long carbon chains (5, 6-dimethyl-undecane, 2,6, 10-trimethyl-dodecane). All these indicate that lignin is expected to be degraded to produce raw materials for applications.
traditional petrochemical products. In the end, a reasonable explanation of the mechanism of CDs/TiO$_2$ photocatalysis is proposed.

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