Visible–Ultraviolet Upconversion Carbon Quantum Dots for Enhancement of the Photocatalytic Activity of Titanium Dioxide

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Abstract: Visible–ultraviolet upconversion carbon quantum dots (CQDs) are synthesized with a hydrothermal method using L-glutamic acid (L-Glu) and m-phenylenediamine (MPD) and then combined with commercial nano-TiO2 to prepare CQDs/TiO2 composites. The fluorescence spectra prove that the prepared CQDs can convert approximately 600 nm visible light into 350 nm ultraviolet light. In photocatalysis experiments, CT-1, a CQDs/TiO2 composite with 1:1 molar ratio of L-Glu to TiO2, has the best degradation efficiency for methyl orange (MO). Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) experiments confirm that CT-1 is composed of quasi-spherical nano-TiO2 and CQDs with a crystal plane of graphitic carbon. CT-1 can degrade 70.56% of MO (40 ppm) within 6 h under the irradiation of a 600 nm light source, which is close to its degradation rate of 78.75% under 365 nm ultraviolet light. The apparent rate constant of CT-1 degradation equation is 12.7 times that of TiO2. Free radical scavenging experiments and electron spin resonance (ESR) tests show that the degradation ability should be attributed to the existence of h+ and ·OH under visible light. Therefore, we provide a simple and low-cost solution with heavy-metal-free products to improve the photocatalytic performance of TiO2.

1. INTRODUCTION
Photocatalysis has received widespread attention due to its potential applications in environmental cleaning and energy conversion.1−5 The applications of TiO2, ZnO, CdS, CdIn2S4, WO3, and other semiconductor photocatalysts have been widely reported.6−9 Among these photocatalysts, nano-TiO2 is known as one of the most promising photocatalysts due to its various excellent properties, such as good chemical stability, photocatalytic activity, and environmentally friendly properties.10−12 However, the application of TiO2 is hampered by its wide-band-gap energy.13−15 This material is usually activated by ultraviolet light, which is only a small part of solar radiation falling on the earth.16

To improve the photocatalytic activity of TiO2, numerous research studies have been carried out on modifying TiO2 by chemical or physical methods, which include cationic/anionic doping, dye sensitization, coupling with other semiconductors, surface loading by various cocatalysts, etc.16−20 Among these strategies, loading a cocatalyst on the surface of TiO2 is an effective and facile way to improve the photocatalytic performance.21 Some noble metals acting as cocatalysts have been reported, such as Pt, Au, and Pd.22−24 But their high cost limits their commercial application. Therefore, it is necessary to develop low-cost cocatalysts with high efficiency.

Carbon quantum dots (CQDs), which have a suitable band gap, unique electron donor/acceptor properties, and excellent electron transfer characteristics, showcase great potential in enhancing the photocatalytic performance of TiO2.24−28 Some research studies on the combination of CQDs and TiO2 to improve the catalytic performance have been reported.14,29−31 Zhang et al.29 reported that N-doped CQDs were combined with rutile TiO2 to form hierarchical microspheres to improve the photodegradation of rhodamine B (RhB). Miao et al.30 embedded CQDs into mesoporous TiO2 materials. The CQDs/TiO2 material could remove up to 98% of methylene blue (MB) in 1 h under visible light irradiation, while commercial nano-TiO2 (P25) could remove only 10% of MB. In these reports, the goal is achieved by enhancing the band structure alignments, visible light absorption, or carrier separation in the system. There are few investigations on improving the photocatalytic performance of TiO2 from the perspective of visible–ultraviolet upconversion CQDs.

In this work, we proposed a method to improve the catalytic ability of commercial TiO2 by converting visible light into ultraviolet light. After many attempts, visible–ultraviolet upconversion CQDs were synthesized with a hydrothermal method using L-glutamic acid (L-Glu) and m-phenylenedi-
amine (MPD), which were then combined with commercial TiO₂ to study the photocatalytic performance of TiO₂. The existence of CQDs helped in improving the photocatalytic performance of TiO₂ in the composites. Particularly, CT-1, a CQDs/TiO₂ nanocomposite with 1:1 molar ratio of L-Glu to TiO₂, had the best effect. The calculation results of the apparent rate constants showed that the constant of CT-1 (2.12 × 10⁻³ min⁻¹) was 12.7 times that of TiO₂ (1.67 × 10⁻⁴ min⁻¹) under 600 nm light source irradiation. The experimental results showed that the photocatalytic efficiencies of CT-1 were similar under 600 nm visible light and 365 nm ultraviolet light irradiation. Relative experiments confirmed that CQDs in the composites converted 600 nm visible light into 350 nm ultraviolet light, which then activated TiO₂ to generate electron–hole pairs. The excellent conversion performance of CQDs under monochromatic light will help in the study of the photocatalytic mechanism of composites and provide inspiration for the design of photocatalytic materials.

2. RESULTS AND DISCUSSION

The optical properties of CQDs were studied by UV–Vis and fluorescence spectral analyses. CQDs had a strong absorption of ultraviolet light, and the absorption band extended to the near-infrared light region (Figure 1A). The absorption band between 250 and 300 nm was attributed to the π–π* transition of the C≡C bond. The broad peak between 350 and 450 nm was due to the n–π* transition of the C≡O bond, which indicated that CQDs contained oxygenic groups such as carboxyl groups.

The photoluminescence (PL) spectra of CQDs with different excitation wavelengths are shown in Figure 1B,C. With the increase of excitation wavelength (290–530 nm), the position of maximum emission peaks shifted to a longer wavelength, and the PL intensity first increased and then decreased. The maximum emission peak at 510 nm was observed under excitation at 450 nm. The excitation-dependent fluorescence characteristic of CQDs was attributed...
to the abundance of groups on the surface and size distributions. Significantly, CQDs displayed obvious upconversion fluorescence characteristics. When the CQDs were excited by light from 560 to 760 nm, the upconversion PL spectra of CQDs appeared from 300 to 550 nm. The strongest emission peak located at 350 nm with an excitation wavelength of 600 nm. This characteristic could be attributed to the multiphoton active process, in which two or more photons were simultaneously absorbed and then shorter-wavelength fluorescence was emitted. Therefore, the combination of CQDs and ultraviolet semiconductor photocatalysts might increase the utilization of visible light and improve the photocatalytic ability.

TiO2/CQDs composites with different CQD contents were synthesized. The molar ratios of L-Glu to TiO2 in CT-100, CT-20, CT-10, CT-2, and CT-1 were 1:100, 1:20, 1:10, 1:2, and 1:1, respectively. We carried out Fourier-transform infrared spectroscopy (FTIR) analyses of CQDs, CT-100, CT-20, CT-10, CT-2, CT-1, and TiO2 (Figure 2A). Most characteristic peaks of CQDs could be found in the spectra of CQDs/TiO2 composites. With the increase of the CQD content, the absorption peaks of composites at 3400, 1720, 1233, and 714 cm⁻¹ were gradually strengthened. In the spectrum of CQDs, the broad peak in the 3200–3500 cm⁻¹ region was attributed to the stretching vibration of O−H and N−H groups, while an O−H bending from absorbed water molecules appeared at 1647 cm⁻¹. The sharp diffraction peaks around 23° and the weak peak at 42.6° corresponded to the (002) and (100) planes of CQDs. Hence, CQDs would not affect the crystal structure of TiO2 during the hydrothermal process.

Taking CT-1 as a representative, we studied the microstructure of composites by high-resolution transmission electron microscopy (HRTEM) (Figure 2C,D). CT-1 was composed of quasi-spherical nano-TiO2 (an average diameter of 25 nm) and CQDs. The lattice spacing of 0.35 nm was consistent with the crystallographic (101) spacing of TiO2. The lattice spacing of CQDs was 0.21 nm, which corresponded to the (002) crystal plane of graphitic carbon (sp² hybrid carbon). Selected area electron diffraction (SAED) patterns of CT-1 (Figure 2E,F) showed that CQDs and anatase TiO2 were combined, which would be beneficial to the charge separation and electron transfer of photocatalytic materials.

The elemental compositions and the interaction between CQDs and TiO2 were investigated by X-ray photoelectron spectroscopy (XPS) (Figure 3). The CQD spectrum showed

Figure 3. XPS full spectrum of TiO2, CT-1, and CQDs (A). High-resolution Ti 2p spectra of CT-1 (B). High-resolution C 1s spectra of CT-1 (C). High-resolution O 1s spectra of CT-1 (D).
the peaks of C 1s (285.3 eV), N 1s (399.3 eV), and O 1s (531.3 eV), indicating that there were not only oxygen-containing groups but also amino groups.45 Besides above peaks, the CT-1 spectrum contained the peaks of Ti 2p3/2 (458.2 eV) and Ti 2p1/2 (463.9 eV) (Figure 3B). The splitting energy between them was 5.7 eV, which indicated that Ti4+ was the main state of Ti in CT-1.33 The high-resolution C 1s spectrum of CT-1 is shown in Figure 3C. This spectrum could be divided into four peaks, attributed to the C−C/C≡C bond (284.4 eV), C−N bond (285.8 eV), C−O bond (287.4 eV), and C−O−Ti bond (288.4 eV).45 In the high-resolution O 1s spectrum of CT-1 (Figure 3D), the peaks at 531.1 and 532.3 eV belonged to the C=O bond and C−O bond of CQDs, respectively. The peak at 530.0 eV belonged to the Ti−O bond in TiO2. And the peak at 531.9 eV revealed the existence of hydrogen bonds between CQDs and TiO2.46 Although the C−O−Ti bond was detected in the materials, its strength was weak. Therefore, composites were mainly formed by the electrostatic interaction and hydrogen bonding between the hydroxyl or amino groups of CQDs and TO2.

The photocatalytic properties of nanocomposites with different CQD contents were evaluated using methyl orange (MO) as the degradation target under UV light and simulated sunlight (Figure 4A,B). The concentration of MO was fixed in the photocatalytic experiments. CQDs had no photocatalytic ability for MO. All of the composites had photocatalytic degradation ability for MO, and CT-1 was the best one. After 480 min of UV light irradiation, the degradation rates of TiO2, CT-100, CT-20, CT-10, CT-2, CT-1, and CT-0.5 for MO were 46.85, 43.59, 54.18, 60.59, 35.78%, respectively. The results indicated that the contents of CQDs were nonlinearly related to the catalytic ability, and CT-1 had the highest catalytic ability. Moreover, compared with pure TiO2, the adsorption capacity of CQDs/TiO2 composites for MO had also been significantly improved during the process of adsorption equilibrium in the darkness. The adsorption of reactants usually depends on the structure or surface characteristics of the catalyst.43 Therefore, nitrogen adsorption−desorption isotherms and pore size distribution (PSD) of TiO2, CQDs, and CT-1 were further analyzed. As shown in Figure S1 and Table S1, the adsorption of MO was due to the microporous structure of nano-TiO2 and abundant surface functional groups introduced by CQDs.

The photodegradation rate of MO generally follows a pseudo-first-order kinetic process. The calculation results of the apparent rate constants are shown in Table 1. The rate constants of the catalysts generally increased with the increase of the CQD content. However, the rate constant decreased

**Table 1. First-Order Fitting Kinetic Data of Catalytic Degradation of MO under Ultraviolet Light and Simulated Sunlight**

| photocatalyst | ultraviolet light | simulated sunlight |
|---------------|-------------------|---------------------|
|               | $k$ ($\times 10^3$ min$^{-1}$) | $R^2$ | $k$ ($\times 10^3$ min$^{-1}$) | $R^2$ |
| TiO2          | 1.05              | 0.964              | 0.265              | 0.992  |
| CT-100        | 0.844             | 0.942              | 0.378              | 0.967  |
| CT-20         | 0.776             | 0.971              | 0.869              | 0.985  |
| CT-10         | 0.806             | 0.933              | 0.893              | 0.989  |
| CT-2          | 1.21              | 0.945              | 1.54               | 0.990  |
| CT-1          | 3.27              | 0.975              | 1.38               | 0.989  |
| CT-0.5        | 0.764             | 0.998              | 0.369              | 0.978  |
when the molar ratio of L-Glu to TiO$_2$ in the material exceeded 1:1. This phenomenon could be attributed to the accumulation of excessive CQDs on the surface of TiO$_2$, which blocked the pore channels of TiO$_2$. A similar situation occurred under simulated sunlight irradiation, but the difference between the $k$ values of CT-1 and CT-2 was not obvious. Considering the photodegradation results of MO under two kinds of light exposure, we selected CT-1 for the catalytic study under 600 nm monochromatic light.

According to the PL of CQDs excited by different light sources, we selected two typical light sources for photocatalytic research, i.e., a purple light-emitting diode (LED) lamp (3 W, 420 nm) and an orange LED lamp (3 W, 600 nm). As shown in Figure 4C, the results indicated that CT-1 had good photocatalytic ability under the 600 nm light source (70.56%) but showed poor performance under the 420 nm light source (29.02%). The photocatalytic performance of CT-1 under 600 nm monochromatic visible light was close to that under UV light irradiation (78.56%). Tian et al.$^{47}$ reported that CQDs/TiO$_2$ could degrade 86% of MO (20 ppm) after being irradiated with a 350 W mercury lamp for 25 min. The S-GQDs/TiO$_2$ synthesized by Luo et al.$^{21}$ could degrade 70% of MO (20 ppm) after being irradiated with a 300 W mercury lamp for 8 min. Compared with these composite materials under similar degradation conditions, the photocatalyst prepared in our study had a higher catalytic efficiency (ppm·min$^{-1}$·W$^{-1}$).

We further investigated the photocatalytic performance of composites prepared by physical blending. The photocatalysis experiments were carried out under the irradiation of a 600 nm light source (Figure 4D). The calculation results of the apparent rate constants are shown in Table 2. Compared with CT-1p (physical blending) as a catalyst (about 40%), the degradation rate of the CT-1 catalyst to MO exceeded 70% after 360 min. This suggested that the improvement of catalytic performance by CQDs was affected by the degree of the combination of CQDs and nano-TiO$_2$. Due to the higher binding effect, TiO$_2$ combined with CQDs in the hydrothermal process showed better photocatalytic performance.

We explored the photocatalytic mechanism of CQDs/TiO$_2$ composites through a series of experiments. Potassium iodide (KI, 1 mmol), isopropanol (IPA, 1 mmol), and nitrotetrazolium blue chloride (NBT, 10 $\mu$mol) were added as scavengers to clear h$^+$, *OH, and *O$_2$* during the photocatalysis experiments, respectively.$^{33,35}$ The results of catalytic degradation experiments (Figure 5) showed that the degradation rate of MO decreased to 28.76% and 45.73% after adding KI and IPA, respectively. Furthermore, only 14.47% of MO degraded within 360 min when KI and IPA were added into the photocatalytic system at the same time. When NBT was added, the absorbance of the solution decreased significantly in the darkness, while the degradation rate of MO did not change much during the entire degradation process. This was not enough to prove that CT-1 produced *O$_2$* during the photocatalysis process. Therefore, we used p-benzoquinone (p-BQ, 10 $\mu$mol) as another *O$_2$* scavenger for experiments. Although C/C$_0$ of MO decreased from 70.56 to 46.08%, the reaction of p-BQ and CT-1 produced some byproducts, which gradually changed the color of the solution to black. It still cannot be concluded that CT-1 produced *O$_2$* in the photocatalytic process. The electron spin resonance (ESR) test was further used to verify the existence of free radicals generated from CT-1. As shown in Figure S3, the weak signal of *OH was detected by ESR technology under 600 nm light irradiation for 10 min, which were in agreement with the results of scavenger experiments. No signal of *O$_2$* was observed, indicating that CT-1 did not produce *O$_2$* during the photocatalysis process.

Therefore, we proposed that when CT-1 was irradiated with visible light, CQDs absorbed photons and converted them into ultraviolet light (300–400 nm), which then excited TiO$_2$ to produce electron–hole pairs. The difference between photocatalytic results of composites prepared by physical blending and the hydrothermal method also supported this statement. The electron–hole pairs reacted with the surface-adsorbed

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c05182)

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Table 2. First-Order Fitting Kinetic Data of Catalytic Degradation of MO under 600 nm Light

| photocatalyst | $k$ ($\times 10^6$ min$^{-1}$) | $R^2$ |
|---------------|-----------------|------|
| TiO$_2$       | 1.67            | 0.940|
| CT-1p         | 7.47            | 0.919|
| CT-1          | 21.2            | 0.919|

*Figure 5. Effect of a free radical scavenger on the catalytic performance of CT-1 (A) and the photocatalyst mechanism (B) under 600 nm light irradiation ($n = 3$).*
H$_2$O/OH$^\cdot$ to produce *OH, which subsequently participated in the photocatalytic degradation reaction. Meanwhile, a part of h$^\cdot$ on the valence band could be directly transferred to oxidize methyl orange. Moreover, acting as remarkable electron collectors and transporters, CQDs could collect and store photogenerated electron from the conduction band of TiO$_2$, thereby hindering the recombination of electron–hole pairs and further promoting the photocatalytic activity.

3. CONCLUSIONS

In this work, visible–ultraviolet upconversion carbon quantum dots were successfully prepared by a one-step hydrothermal method, and they were applied to improve the visible light catalytic ability of TiO$_2$. The performance of the CQDs/TiO$_2$ nanocomposites for degrading MO was systematically evaluated. CQDs could effectively improve the catalyst’s ability to degrade MO, but excessive CQDs would lead to a decrease in degradability. Within 6 h, CT-1 could degrade 78.75 and 70.56% of MO (40 ppm) under 365 nm and 600 nm light irradiation, respectively. Furthermore, the better the combination of CQDs and TiO$_2$, the better the photocatalytic performance of the composite. Finally, a reasonable mechanism for enhancement of the photocatalytic ability of TiO$_2$ by CQDs under visible light was proposed. CQDs absorbed photons and converted them into ultraviolet light, which excited TiO$_2$ to generate h$^\cdot$ and *OH to degrade MO. Our work broadened the application of upconversion materials and improved the utilization efficiency of the light source.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals were of analytical grade and were used directly without any further purification. l-Glutamic acid (l-Glu), m-phenylenediamine (MPD), titanium dioxide (TiO$_2$, anatase, 10 nm), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were bought from Aladdin Industrial Co. Ltd. (Shanghai, China). Methyl orange (MO), potassium iodide (KI), isopropanol (IPA), and p-benzoquinone (p-BQ) were bought from Kelong Chemical Co. Ltd. (Chengdu, China).

4.2. Apparatus. High-resolution transmission electron microscopy (HRTEM) images were recorded with FEI Tecnai GF20S-TWIN equipment. X-ray photoelectron spectroscopy (XPS) results were obtained using XSAM 800 equipment (Kratos Analytical Ltd.; U.K.). X-ray diffraction (XRD) was performed using an Agilent Xcalibur E instrument. IR spectra were obtained using a Nicolet-6700 FT-IR spectrometer (Thermo Scientific). Fluorescence spectra were obtained using an F97-Pro fluorospectrophotometer (Lengguang Tech. Ltd.; China). UV–vis absorption spectra were recorded on a UV–vis spectrophotometer (Mapada Instruments Ltd.; China). The light sources used in photocatalytic experiments included an ultraviolet lamp (3 W, 365 nm, Shanghai Jiapeng Tech. Ltd.; China), a purple LED lamp (3 W, 420 nm, Epileds Tech. Ltd.; China), an orange LED lamp (3 W, 600 nm, Epileds Tech. Ltd.; China) and a xenon lamp (300 W, Beijing Zhongyiboteng Tech. Ltd.; China).

4.3. Preparation of Visible–Ultraviolet Upconversion Carbon Quantum Dots (CQDs). CQDs were prepared from l-glutamic acid (l-Glu) and m-phenylenediamine (MPD) by a one-step hydrothermal method. Typically, 3.6782 g of l-Glu (0.025 mol) and 0.2703 g of MPD (0.0025 mol) were added to 100 mL of ultrapure water. After 30 min of magnetic stirring, the mixture was transferred to a 250 mL Teflon reactor and allowed to react at 200 °C for 6 h. When the reactor was cooled to room temperature, a solution of CQDs was obtained. Then, the sample was lyophilized to obtain the powder.

4.4. Preparation of CQDs/TiO$_2$ Nanocomposites (CT). CQDs/TiO$_2$ nanocomposites were prepared by the hydrothermal method. In a typical hydrothermal process, 1.9975 g of TiO$_2$ (0.025 mol, anatase, 10–25 nm), 3.6782 g of l-Glu (0.025 mol), and 0.2703 g of MPD (0.0025 mol) were added to 100 mL of ultrapure water. After 30 min of magnetic stirring, the mixture was transferred to a 250 mL Teflon reactor and then allowed to react at 200 °C for 6 h. Then, the sample was cooled and freeze-dried to obtain CT-1 powder with 1:1 molar ratio of l-Glu to TiO$_2$. This compound was used to prepare nanocomposites with different CQD contents. The molar ratios of l-Glu to TiO$_2$ in CT-0.5, CT-2, CT-10, CT-20, and CT-100 were 2:1, 1:2, 1:10, 1:20, and 1:100, respectively. For comparison, TiO$_2$ (1.9975 g, 0.025 mol) was added into the pre-prepared CQD solution and was stirred magnetically in the darkness for 24 h. After that, the suspension was freeze-dried to obtain CT-1p powder prepared by physical blending.

4.5. Photodegradation Experiments. To determine the optimal content of CQDs in composites, the photocatalytic properties of nanocomposites with different CQD contents were evaluated by degradation of methyl orange (MO) under an ultraviolet lamp (3 W, 365 nm) and a xenon lamp (300 W). To study the photocatalytic performance of CQDs/TiO$_2$ under a monochromatic visible light source, we used CT-1 as a sample in photocatalytic experiments under a purple LED lamp (3 W, 420 nm) and an orange LED lamp (3 W, 600 nm). To study the influence of different preparation methods on the photocatalytic activity of nanocomposites, we compared CT-1 with CT-1p in photocatalytic experiments under 600 nm light irradiation. In a typical test, 0.2 g of CT-1 was added to 100 mL of MO solution (40 ppm). The mixture was stirred in the darkness for 30 min to reach adsorption equilibrium. Then, the solution was photodegraded under different light irradiation conditions. The concentration of MO was obtained by measuring the absorbance at 465 nm in specific illumination time intervals. All of the experiments were repeated three times.

4.6. Photocatalytic Mechanism. A hydroxyl radical (*OH), superoxide (*O$_2^-$), and a hole (h$^\cdot$) are generally the main reactive agents in photocatalysis. To evaluate the influence of these reactive species on photocatalysis, we carried out quenching experiments with isopropanol (IPA, a *OH radical scavenger), potassium iodide (KI, a hole scavenger), nitrotetrazolium blue chloride (NBT, an *O$_2^-$ radical scavenger), and p-benzoquinone (p-BQ, an *O$_2^-$ radical scavenger). In addition to these scavengers, CT-1 samples and a monochromatic orange light source (3 W, 600 nm) were used in the experiment. The subsequent experimental operations were the same as mentioned above.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05182.

Brunauer–Emmett–Teller data of TiO$_2$ CQDs, and CT-1; reusability of CT-1 under simulated sunlight irradiation; and DMPO spin-trapping ESR spectra of DMPO–*OH adduct and DMPO–*O$_2^-$ adduct over CT-1 (PDF)
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Notes
The authors declare no competing financial interest.

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