**Materials Research Express**

**PAPER**

Preparation and photocatalytic activity of red light-emitting carbon dots/P25 heterojunction photocatalyst with ultra-wide absorption spectrum

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Keywords: carbon dots, P25, photocatalyst, degradation, rhodamine B

Abstract

Carbon dots have attracted growing research interest due to their unique properties, and are expected to be used in the field of photocatalysis to solve the visible absorption loss problem of TiO$_2$ (P25). In this paper, red light-emitting carbon dots (RCDs) with high fluorescence quantum yield (40%) and RCDs/P25 heterojunction photocatalysts were synthesized by a simple and green hydrothermal method. Characterization results indicated that RCDs were successfully coupled with P25, and RCDs could effectively broaden the visible absorption region of bare P25 from 410 nm to 800 nm. The photocatalytic activity of the as-synthesized RCDs/P25 on the degradation of rhodamine B (RhB) under visible light irradiation was greatly improved compared with that of bare P25. The degradation rate of RhB by 2%RCDs/P25 reached 98.4% in 150 min, the degradation efficiency was 7.4 times that of bare P25. The RCDs played an important role in improving the photocatalytic activity of RCDs/P25, which not only increased visible light absorption, but also promoted efficient separation of photogenerated electron-hole pairs. Furthermore, the possible degradation mechanism of RCDs/P25 heterojunction photocatalyst was given.

1. Introduction

With the growing environmental pollution and serious energy crisis, semiconductor photocatalysts for photodegradation of organic pollutants and photocatalytic hydrogen evolution from water have attracted worldwide attentions, such as ZnO, TiO$_2$, WO$_3$, Fe$_2$O$_3$, BiVO$_4$, etc. Among them, TiO$_2$ is one of the most promising photocatalysts due to its abundant storage, low cost, superior photo-stability, low toxicity and high intrinsic photocatalytic activity. However, its wide band gap (~3.0 eV for rutile TiO$_2$ and ~3.2 eV for anatase TiO$_2$) limit the visible light harvesting and the photogenerated electron-hole pairs recombination rapidly, which significantly limit the application of bare TiO$_2$ in photocatalysis. In order to solve these problems, plenty of methods have been adopted to improve photocatalytic efficiency of TiO$_2$, including element doping, construction of heterojunction, introduction of oxygen vacancy etc. The studies have found that constructing a heterojunction catalyst is one of the most efficient approaches to promote the separation efficiency of photogenerated electron-hole pairs and improve visible light harvesting.

Carbon dots (CDs) are a promising carbon-based nanomaterial, since they were first discovered by Xu et al in 2004, which have attracted growing research interest in recent years. Compared with traditional semiconductor quantum dot materials, CDs have many unique advantages, such as high quantum yield, excellent biocompatibility, low cytotoxicity, well water solubility, light-bleaching resistance, and low cost to preparation. The unique properties of CDs make them a promising candidate for traditional
semiconductor quantum dots, and have broad application prospects in the fields of photoelectric devices [27–30], heavy metal ion detection [31–33], photocatalysis [34–36], bioluminescence imaging [37, 38] and drug release [39]. In particular, carbon dots are an excellent electron donor and acceptor, and have proper band gap and good stability, constructing a heterojunction catalyst composed of CDs and TiO$_2$ to improve the photocatalytic activity of TiO$_2$ has attracted more and more researchers’ interests. For example, Zhang et al. [40] via a simple and efficient low-temperature process synthesized N-doped carbon quantum dots/TiO$_2$ (NCQDs/TiO$_2$) hybrid composites, NCQDs/TiO$_2$ exhibited obviously superior photocatalytic activity than TiO$_2$ in the experiment of degradation methylene blue under visible light irradiation. Sargin et al. [41] used a green method to synthesize CQDs as a sensitizer for TiO$_2$ photocatalytic hydrogen evolution, the results showed that in the absence and presence of Pt co-catalyst, photocatalytic hydrogen production activity of CQD/TiO$_2$ was found to be 472 mmol g$^{-1}$ h$^{-1}$ and 1458 mmol g$^{-1}$ h$^{-1}$ under visible light.

However, in previous studies, most of the carbon dots that constructing heterojunction photocatalysts were blue light-emitting carbon dots (BCDs). The excitation and absorption of BCDs are in the range of 200–400 nm. It can be seen that most of the absorption of BCDs is in the ultraviolet region, and less absorption in the visible region. Therefore, the absorption and utilization of BCDs/TiO$_2$ photocatalysts in visible light region are still very low [17, 42]. Compared with BCDs, red light-emitting carbon dots (RCDs) have a wider absorption spectrum from 200 nm to 700 nm. Therefore, RCDs have higher absorption and utilization in the visible light region. Compared with BCDs/TiO$_2$, theoretically, RCDs/TiO$_2$ has more absorption and utilization of visible light, and RCDs/TiO$_2$ has stronger photocatalytic activity. As far as we know, there are few reports on the construction of RCDs/TiO$_2$ heterojunction photocatalysts.

Based on the above considerations, in this study, we synthesized RCDs with high quantum yield (40%) using citric acid and urea by a simple and green hydrothermal method. A series of composite RCDs/P25 heterojunction photocatalysts with different RCDs content were prepared. The prepared RCDs and RCDs/P25 were characterized by TEM, XRD, XPS, UV–vis, transient photocurrent response and cyclic voltammetry. RhB was used as a simulated pollutant for photocatalysis experiments. As expected, the absorption region of RCDs/P25 covers ultraviolet to near-infrared, the utilization of solar energy is substantially improved. The best photocatalytic degradation efficiency of RCDs/P25 with 2%RCDs content on RhB was 7.4 times that of bare P25. This work has potential application in the field of organic pollutants degradation and hydrogen evolution from water.

2. Experiment

2.1. Materials

Citric acid anhydrous (C$_6$H$_8$O$_7$, AR, 99.5%), urea (CH$_3$N$_2$O, AR, 99.0%) and ethanol (C$_2$H$_6$O, AR, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd N,N-Dimethylformamide (DMF, AR, 99.5%), nano TiO$_2$ (P25, 20 nm) and rhodamine B (AR) were purchased from Shanghai Macklin Biochemical Co., Ltd. All chemical reagents were analytical grade, and were used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of RCDs

Citric acid anhydrous and urea were used as reagents, and N,N-Dimethylformamide was used as solvent in the study. In a typical experimental procedure, 0.95 g citric acid and 2.4 g urea were added to 30 ml DMF solution, stirred until dissolved completely, and then transferred to a 50 ml polytetrafluoroethylene hydrothermal reactor, heated at 180 °C for 6 h. After the reaction completed, cooled to room temperature naturally. The obtained solution was centrifuged with the rate of 10,000 rpm for 10 min to remove precipitation, and then dialyzed via a 500 Da dialysis bag for 48 h. Finally, the solution was freeze-dried to obtain black carbon dots powder. The black powder can be redispersd and dissolved in the water or ethanol to obtain RCDs solution.

2.3. Preparation of RCDs/P25 heterojunction photocatalyst

In order to prepare RCDs/P25 heterojunction photocatalysts with different RCDs content, 2 mg, 4 mg, 6 mg or 8 mg RCDs powder and 0.2 g P25 powder were evenly dissolved in 30 ml deionized water respectively, the solution was magnetic stirred for 1 h at room temperature, then transferred to a 50 ml reactor and heated at 160 °C for 4 h. When the solution was cooled to room temperature, the solution was centrifuged at 10,000 rpm for 10 min. The precipitate was collected and washed with ethanol and deionized water for three times. Finally, the precipitate was collected and dried, the composite powders of 1%RCDs/P25, 2%RCDs/P25, 3%RCDs/P25 and 4%RCDs/P25 were obtained respectively. The schematic diagram of RCDs and RCDs/P25 preparation process is shown in figure 1.
2.4. Photocatalytic degradation experiment
The degradation of RhB was tested under visible light irradiation by a 300 W xenon lamp with a 400 nm cut-off filter. 100 ml RhB dyes aqueous solution (10 mg l\(^{-1}\)) and 50 mg RCDs/P25 photocatalyst were added into a 120 ml quartz glass reactor. First, the mixed solution was magnetically stirred for 60 min in a dark environment to ensure the establishment of adsorption–desorption equilibrium. Then, turned on the xenon lamp, the photocatalytic degradation of RhB started. 5 ml reaction solution was collected every 30 min to trace the concentration change of RhB. The concentration change of RhB was measured by the absorption spectrum of UV–vis spectrophotometer.

2.5. Characterization
The size and morphology of the prepared RCDs and RCDs/P25 were observed by transmission electron microscopy (TEM, JEM-2100F). The x-ray diffraction patterns of RCDs/P25 were recorded with an x-ray diffractometer (XRD, MiniFlex 600, Rigaku) at a scanning speed of 2° min\(^{-1}\). Fourier transform infrared (FTIR) spectra were measured with fourier infrared spectrometer (ISS, ThermoFisher). The high resolution XPS spectra were analyzed by x-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Scientific). The UV–vis absorption and fluorescence emission spectra of RCDs were measured using fluorescence spectrometer (Dual-FL, Horiba). Absolute photoluminescence quantum yield (PLQY) was measured using a FLS1000 fluorescence spectrometer. The UV–vis absorption spectra of RCDs/P25 were measured with an UV–vis-NIR double beam spectrophotometer (Lambda 1050, Perkin-Elmer). A 300 W xenon lamp (CEL-HXUV300, Beijing Ceaulight Technology Co. Ltd) was used as light source, which was equipped with an ultraviolet cut-off filter. Cyclic voltammetry and transient photocurrent curves were tested on a three-electrode electrochemical workstation (CHI 600E, Shanghai Instruments Co., Ltd) with RCDs/glassy carbon as the working electrode, Ag/AgCl as the reference electrode, platinum wire as the counter electrode. The electrolyte was 0.1 M Na\(_2\)SO\(_4\) aqueous solution.

3. Results and discussion
3.1. Characterization of the synthesized RCDs
The optical properties of the synthesized RCDs were studied by UV–vis absorption and photoluminescence. Figure 2(a) shows the UV–vis absorption spectrum of RCDs solution, which exhibits a very broad and strong absorption in the UV–vis region. The absorption peak at 240 nm is due to π–π\(^*\) transition of C=C/C=C in the RCDs carbon core, and the absorption peak at 567 nm is assigned to n–π\(^*\) transition of C=N in aromatic structures [43]. Figure 2(b) shows the fluorescence emission spectrum of the RCDs at different excitation wavelengths. With the gradually increasing of excitation wavelength from 510 nm to 600 nm, the corresponding fluorescence emission peaks shift from 632 nm to 646 nm. The red shift of emission peaks indicates that the synthesized RCDs have excitation wavelength dependence. Figure 2(c) is the three-dimensional fluorescence spectrum of RCDs, it can be seen that the fluorescence excitation and emission centers of RCDs are consistent with the measurement results of absorption and emission spectra. The center wavelength of the excitation spectra is 567 nm, and the peak wavelength of the emission spectrum is 640 nm when excitation with 567 nm, the absolute quantum yield is 40%. To determine the band gap of RCDs, the Tauc plot of RCDs is shown in figure 2(d). From figure 2(d), we can see that the band gap of RCDs is about 1.6 eV. The calculation formula of band gap is as follows:

\[ a\nu = A(\nu - E_g)^2 \]
Where $\alpha$ is the absorption coefficient, $h$ is the Planck’s constant, $\nu$ is the light frequency, $A$ is the proportionality constant, and $E_g$ is the band gap energy [13].

The size and morphology of the synthesized RCDs were examined by TEM. Figure 3 shows the TEM and HRTEM images. As shown in figure 3(a), the RCDs are approximately spherical, the size distribution range is from 3 to 9 nm, and the average size is 6.08 nm. The HRTEM image of the RCDs shown in figure 3(b) clearly indicates a lattice fringes with a spacing of 0.24 nm, which is consistent with the planar spacing of (1120) crystal planes of graphene [27].

3.2. Characterization of the prepared RCDs/P25
The following RhB degradation experiments showed that 2%RCDs/P25 had the best degradation efficiency, so the 2%RCDs/P25 was characterized as a typical composite photocatalyst. Figure 4(a) shows the XRD patterns of
RCDs, P25 and 2%RCDs/P25 respectively. From the XRD pattern of RCDs, we can observe a typical peak at around 27°, which corresponds to (002) plane of graphite (PDF # 89–8487). The appearance of the peak at 27° is attributed to the presence of sp² hybridized carbon in the basal plane of RCDs [44]. The diffraction peaks of the 2%RCDs/P25 have little change compared with the diffraction peaks of P25 because the content of RCDs in RCDs/P25 is too low [45].

Figure 4 (a) XRD patterns of RCDs, 2%RCDs/P25 and P25; (b) FTIR spectra of RCDs, 2%RCDs/P25 and P25.

Figure 5. (a) TEM image of the 2%RCDs/P25; (b) HRTEM image of the 2%RCDs/P25.

The FTIR spectrum of P25 has two obvious absorption peaks, the absorption peak at 3410 cm⁻¹ could be assigned to the stretching vibration of the surface O–H groups, the absorption peak at 1636 cm⁻¹ could be assigned to the bending vibration of the surface O–H groups [46]. The FTIR spectrum of 2%RCDs/P25 has little changes compared with that of P25 due to the low content of RCDs.

Figure 5 (a) shows the TEM image of the 2%RCDs/P25. The size distribution range of RCDs/P25 is from 20 nm to 30 nm, similar to the size of bare P25. To confirm the coupling of the RCDs with P25, the HRTEM image of the 2%RCDs/P25 was examined as shown in figure 5(b). It can be seen that the lattice spacing are 0.24 nm, 0.33 nm and 0.35 nm, which correspond to the (1120) crystal plane of graphene, the (110) crystal plane of rutile TiO₂ and the (101) crystal plane of anatase TiO₂ respectively [35]. The HRTEM image reveals the presence of P25 and RCDs, which indicates that RCDs and P25 are successfully coupled.

To further investigate the interaction between RCDs and P25, the RCDs and 2%RCDs/P25 were examined by XPS. Figures 6(a)–(d) show the full-scale XPS spectrum, high-resolution XPS spectra of (b) C1s, (c) N1s and (d) O1s for the RCDs respectively. Peak fitting is performed on C1s, N1s and O1s spectra, as shown in figures 6(b)–(d). Figure 6(e) shows the full-scale XPS spectrum of the 2%RCDs/P25, which identifies the presence of C,N, Ti and O, and suggests the presence of the RCDs in 2%RCDs/P25. High-resolution XPS spectrum of C1s is composed of five peaks based on the peak fitting as shown in figure 6(f). The peaks at 284.6 eV, 285.5 eV, 286.5 eV, 287.9 eV and 288.7 eV are assigned to the C=C/C=C, C─N, C─O, C─N/C=O and
COOH bonds respectively [25, 27]. Figure 6(g) shows the high-resolution XPS spectrum of Ti2p, the peaks at 458.5 eV and 464.3 eV are Ti(2p$^{3/2}$) and Ti(2p$^{1/2}$), which are Ti$^{4+}$ sp peaks of TiO$_2$ [47]. Figure 6(h) shows the O1s spectrum of the 2%RCDs/P25, O1s spectrum is composed of four peaks based on the peak fitting, the peaks
Table 1. Binding energy and percentages of different bonds of RCDs and 2% RCDs/P25 according to the fitting results of the high resolution XPS spectra.

| Element | Bond | Binding energy (eV) | RCDs (%) | 2% RCDs/P25 (%) |
|---------|------|--------------------|----------|-----------------|
| C 1s    | C≡C/C/C | 284.6 | 36.54 | 51.34 |
|         | C=N   | 285.6 | 16.99 | 26.55 |
|         | C=O   | 286.5 | 10.46 | 7.50 |
|         | C≡N/C=O | 287.9 | 29.45 | 5.34 |
|         | COOH  | 290.1 | 6.56  | 9.07 |
|         |       |       |        | |
| N 1s    | pyridinic N | 399.5 | 49.26 | 30.8 |
|         | pyrrolic N  | 400.5 | 30.85 | 43.23 |
|         | graphitic N | 401.5 | 19.88 | 5.97 |
| O 1s    | Ti-O   | 529.8 | 0     | 91.33 |
|         | C=O   | 531.0 | 50.30 | 0.95 |
|         | O-H   | 531.5 | 0     | 5.08 |
|         | C-O   | 532.5 | 49.70 | 2.6 |
| Ti 2p   | Ti(2p\(^{3/2}\)) | 458.5 | 0     | 73.02 |
|         | Ti(2p\(^{1/2}\)) | 464.3 | 0     | 26.98 |

at 529.8 eV, 531.0 eV, 531.5 eV and 532.5 eV are assigned to Ti–O, C≡O, O–H and C–O bonds respectively. Compared with the O 1s spectra of RCDs (figure 6 (d)), two new peaks of Ti–O and O–H appear in figure 6 (h) due to the presence of P25. Carboxyl (COOH) of RCDs could react with the hydroxyl (TiO\(_2\)–OH) which located at the surface of TiO\(_2\) and formed C–O–Ti bonds [42]. Therefore, the RCDs and P25 may be coupled by C–O–Ti chemical bond. Comparing the Cls spectra of 2%RCDs/P25 (figure 6 (f)) and RCDs (figure 6 (b)), the binding energy of carbonyl group (O=C–OH) has a 1.4 eV blue shift, which also confirmed the presence of C–O–Ti bonds [42].

In order to show the changes of XPS spectra before and after RCDs coupling with P25 more clearly, the binding energy and percentage of different bonds are calculated according to the peak fitting results of RCDs and 2%RCDs/P25, and the results are listed in table 1. From table 1, we can see the changes in the percentage of different bonds, which indicates the change of the chemical environment after RCDs coupling with P25 [48]. For example, comparing the Cls of RCDs and that of 2%RCDs/P25, it can be seen that the percentage of C≡N bond dropped from 29.45% to 5.54%, and the percentage of C–N bond increased from 16.99% to 26.55%. This can be attributed to the change of the chemical environment during the coupling of RCDs and P25, which resulted in the conversion of C≡N bond to C–N bond.

Light absorption is an important factor affecting the performance of the photocatalyst. Figure 7 shows the UV–vis diffuse reflection absorption spectra of P25 and RCDs/P25 photocatalysts. Compared with bare P25, the absorption intensity of RCDs/P25 in the visible region is significantly increased. With the increase of RCDs content, the absorption intensity of the RCDs/P25 also increases, which indicates that the construction of heterojunction photocatalyst successfully improves the absorption of P25 in the visible region. It is worth noting that the absorption peak of RCDs/P25 is at 500 nm in the visible region, it is derived from n–π\(^*\) transition of sp\(^2\) aromatic system C≡O [27], which is different from the n–π transition of C≡N at 567 nm in RCDs. This is because that C≡N bond was destroyed and converted to C–N bond during the coupling process of RCDs with P25, and the result is consistent with the XPS analysis results. Moreover, compared with previous studies [45, 48], the absorption range of the RCDs/P25 heterojunction photocatalysts we prepared extends from ultraviolet to near-infrared (over 780 nm), which greatly increases the utilization of solar energy and could obtain high photocatalytic activity of the RCDs/P25.

### 3.3. Photocatalytic activity of RCDs/P25

In order to evaluate the photocatalytic activity of P25 and RCDs/P25 composites, RhB was selected as the target degradation pollutant. Figure 8 shows the degradation curves of RhB by P25 and RCDs/P25 with different RCDs content. From figure 8, it can be seen that RhB itself shows no obvious self-degradation under visible light irradiation. Compared with bare P25, the photocatalytic degradation efficiency of RCDs/P25 on RhB is greatly improved. The photocatalytic degradation efficiency of RCDs/P25 with 1%, 2%, 3% and 4% RCDs content on RhB reached 92.2%, 98.4%, 86.9% and 78.6% in 150 min, respectively, while the photocatalytic degradation efficiency of bare P25 is only 46.9% in 150 min.

| Table 1. Binding energy and percentages of different bonds of RCDs and 2% RCDs/P25 according to the fitting results of the high resolution XPS spectra. | Binding energy (eV) | RCDs (%) | 2% RCDs/P25 (%) |
|---------------------------------|-----------------|----------|-----------------|
| C 1s                            | C≡C/C/C         | 284.6    | 36.54           | 51.34 |
|                                 | C=N             | 285.6    | 16.99           | 26.55 |
|                                 | C=O             | 286.5    | 10.46           | 7.50 |
|                                 | C≡N/C=O         | 287.9    | 29.45           | 5.34 |
|                                 | COOH            | 290.1    | 6.56            | 9.07 |
|                                 |                 |          |                 |     |
| N 1s                            | pyridinic N     | 399.5    | 49.26           | 30.8 |
|                                 | pyrrolic N      | 400.5    | 30.85           | 43.23 |
|                                 | graphitic N     | 401.5    | 19.88           | 5.97 |
| O 1s                            | Ti-O            | 529.8    | 0               | 91.33 |
|                                 | C=O             | 531.0    | 50.30           | 0.95 |
|                                 | O-H             | 531.5    | 0               | 5.08 |
|                                 | C-O             | 532.5    | 49.70           | 2.6  |
| Ti 2p                           | Ti(2p\(^{3/2}\)) | 458.5    | 0               | 73.02 |
|                                 | Ti(2p\(^{1/2}\)) | 464.3    | 0               | 26.98 |
To further investigate the difference in photocatalytic efficiency of different photocatalysts and estimate the apparent degradation rate constant of RhB. The kinetic linear fit for three repeated degradation reactions is shown in figure 9(a), the equation is as follows

$$\ln \left( \frac{C_0}{C_t} \right) = kt$$

where $C_0$ is the concentration of RhB at 0 min, $C_t$ is the concentration of RhB at different degradation time, and $k$ is the apparent degradation rate constant of RhB [48]. The fitted curve basically conforms to the first-order dynamic model ($R^2 > 0.94$), and the degradation rate constant ($k$) of RhB can be obtained from the slope of the fitted line. The average apparent degradation rate constants ($k$) of different photocatalysts for three repeated degradation reactions are shown in figure 9(b). The values of $k$ for photocatalytic degradation of RhB by bare P25 and RCDs/P25 with 1%, 2%, 3%, 4% RCDs content are 0.00412, 0.01684, 0.03032, 0.01311, 0.01164 min$^{-1}$, and the $k$ of RCDs/P25 with different RCDs content is 4.1, 7.4, 3.2, 2.8 times that of bare P25, respectively. From figure 9(b), we can see that when the loading of RCDs exceeds 2%, the photocatalytic degradation efficiency of RCDs/P25 begins to decrease. This may be attributed to excessive RCDs cover the surface of P25, occupying the active sites of P25 and reducing the catalytic performance of RCDs/P25. Moreover, excessive RCDs compete with P25 for photons, reducing the generation of photogenerated electron-hole pairs [45].

In order to test the photocatalytic stability and recyclability of the RCDs/P25 photocatalyst, photocatalytic degradation of RhB by 2%RCDs/P25 was recycled three times under the same experimental conditions. The photocatalyst was filtered and washed with deionized water, then dried at 80°C after each degradation experiment. The reproducibility results of 2%RCDs/P25 photocatalyst for the RhB degradation is shown in figure 10(a). It can be seen that the degradation efficiency of 2% RCD/P25 on RhB decreases as the increase of
the number of cycles in the same irradiation time, but it is still greater than 90% after three cycles, which indicates that the RCDs/P25 photocatalyst has good photocatalytic stability and recyclability.

The FTIR spectra and XRD patterns of 2%RCDs/P25 photocatalyst before and after degradation reaction are shown in figures 10(b) and (c). It can be seen that the FTIR spectra and XRD patterns of 2%RCDs/P25 photocatalyst after three cycles have no obvious changes in structure compared with fresh 2%RCDs/P25, indicating that RCDs/P25 can stably exist in the photocatalytic degradation process of RhB. Furthermore, the photoluminescence analysis of P25 and 2%RCDs/P25 under 330 nm excitation light, which indicate that the recombination of photogenerated electron-hole pairs of 2%RCDs/P25 is obviously inhibited [48, 49].

**Figure 9.** (a) Plots of ln(C0/Ct) versus irradiation time and (b) average degradation rate constant for the photodegradation of RhB by P25 and RCDs/P25 with different RCDs content.

**Figure 10.** (a) Recycling test of 2%RCDs/P25 photocatalyst for the RhB degradation; (b) FTIR spectra of 2%RCDs/P25 before and after degradation reaction; (c) XRD patterns of 2%RCDs/P25 before and after degradation reaction; (d) PL spectra of P25 and 2%RCDs/P25 under 330 nm excitation light.
3.4. Electrochemical properties

The transient photocurrent response curves of P25 and 2%RCDs/P25 were measured to study the photogenerated electron transfer efficiency. As shown in figure 11(a), it can be seen that the photocurrent density of P25 is very low during the cyclic irradiation of the visible light on/off for several intermittent cycles, while 2%RCDs/P25 exhibit a very fast and higher transient photocurrent response. The transient photocurrent density of 2%RCDs/P25 is about 14 times that of P25, and the photocurrent of 2%RCDs/P25 is more stable than that of P25. The results indicate that the RCDs/P25 composite photocatalyst has higher separation and transfer efficiency of photogenerated electron-hole pairs than P25. In order to investigate the bandgap structure of RCDs/P25 composite photocatalyst, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy level of RCDs were tested and calculated by electrochemical cyclic voltammetry. As shown in figure 11(b), the initial oxidation peak potential of RCDs is 0.41 V versus Ag/AgCl. According to the following formulas [50]:

\[
E_{\text{HOMO}} = -e(E_{\text{Ox, Versus NHE}} + 4.75) \text{ (eV)}
\]

\[
E_{\text{LUMO}} = E_{\text{HOMO}} + E_g
\]

\[
E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197
\]

The calculated value of the HOMO energy level of RCDs is −5.36 eV versus vacuum (0.61 V versus NHE). From figure 2(d), it can be seen that the \(E_g\) of RCDs is 1.6 eV. Therefore, the LUMO energy level of RCDs is −3.76 eV versus vacuum (−0.99 V versus NHE). The potentials of the conduction band and valence band of P25 are −0.24 V versus NHE and 2.88 V versus NHE according to the reference [51].

3.5. Degradation mechanism of RCDs/P25 heterojunction photocatalyst on RhB

Based on the above research, the possible band gap structure and degradation mechanism of RCDs/P25 heterojunction photocatalyst is given, as shown in figure 12. Since the conduction band potential of P25 is more positive than the potential of \(E(O_2^-/O_2)\) (−0.24 V > −0.33 V) [52, 53], the electrons on the conduction band of P25 cannot react with \(O_2\) to generate \(O_2^-\). The electrons on the conduction band of P25 will migrate to the valence band of RCDs, and recombination with the holes on the valence band of RCDs. Therefore, RCDs/P25 as a Z-scheme heterojunction can effectively improve the separation of photogenerated electron-hole pairs. Photogenerated holes and photogenerated electrons accumulate on the valence band of P25 and the conduction band of RCDs, respectively. The potential of the conduction band of RCDs is more negative than the potential of \(E(O_2^-/O_2)\) (−0.99 V < −0.33 V), the accumulated electrons are capable of produce \(O_2^-\) radicals. The potential of the valence band of the P25 is more positive than the potential of \(E(OH^-/\cdot OH)\) (2.88 V > 2.40 V) [52], the photogenerated holes on the surface of P25 have a strong oxidizing ability and can directly oxidize \(H_2O\) or \(OH^-\) to \(\cdot OH\). RhB adsorbed on the surface of RCDs/P25 photocatalyst can be oxidized into \(CO_2\) and \(H_2O\) by \(h^+\), \(\cdot OH\) and \(O_2^-\).

4. Conclusions

Red light-emitting carbon dots (RCDs) were successfully synthesized using citric acid and urea by simple hydrothermal method. TEM showed that the average size of RCDs was 6.08 nm, and the PLQY of RCDs was as
high as 40%. A series of RCDs/P25 heterojunction photocatalysts with different RCDs content were synthesized. TEM and XPS results indicated that the RCDs were successfully coupled with P25, and connected by C–O–Ti bond. The results of diffuse reflection absorption spectrum and photocatalytic degradation on RhB under visible light showed that RCDs can significantly improve the visible light absorption capacity of P25, and the degradation rate constant of 2%RCDs/P25 was 7.4 times that of bare P25. The energy band structure of RCDs/P25 was determined by electrochemical cyclic voltammetry tests. The high photocatalytic efficiency of RCDs/P25 came from RCDs, which improved the visible light absorption and the effective separation and transfer of photogenerated electron-hole pairs, and the possible degradation mechanism of RCDs/P25 heterojunction photocatalyst was given. This work is expected to be used in the field of photodegradation of organic pollutants and hydrogen evolution from water under visible light.

Acknowledgments

This work was sponsored by the Shanghai Foundation for Science and Technology Innovation Action Plan (17142202700, 1714220060), the National Natural Science Foundation of China (61775140, 61775141) and Shanghai Pujiang Program (18PJ1408800).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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