High Efficient Carbon Quantum Dots/BiOCl Nanocomposite for Photocatalytic Pollutant Degradation

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Abstract: To overcome the limitation of narrow photo-absorption range and high electron-hole recombination rate of pure BiOCl, a nanocomposite of carbon quantum dots (CQDs) and BiOCl with highly efficient photocatalytic activity was fabricated. The photocatalytic decomposition of rhodamine B (RhB) showed that the CQDs/BiOCl nanocomposite displayed superior photocatalytic performance to pure BiOCl, which was about 3.4 times higher than that of the latter. The optimal loading amount of CQDs was 7.1wt%, which could completely decolorize RhB within a short period of only 2 min, while the degradation rate of RhB was only 29.5% by pure BiOCl in the same period. UV-Vis diffuse reflectance spectra (UV-Vis DRS), photoelectrochemical measurement, and radicals trapping experiments were performed to elucidate the possible mechanism for the enhanced photocatalytic activity of the CQDs/BiOCl composite. The results show that CQD can expand the visible light absorption range of BiOCl, which is beneficial for light harvesting and generation of electron-hole pairs. Moreover, CQDs has unique up-converted photoluminescence behavior, as well as photo-induced electron transfer ability, which leads to enhanced photocatalytic performance of the CQDs/BiOCl composite.

Key words: photocatalysis; CQDs/BiOCl; nanocomposite; up-converted photoluminescence

As a new bismuth-based semiconductor material, BiOCl has recently become the focus of research in the field of photocatalysis and displays enhanced photocatalytic activity than TiO2 (P25, Degussa)\(^1\)-\(^4\). It possesses a unique layered structure, which can provide large enough space to polarize the related atoms and orbitals\(^5\). Then the induced dipole can promote the separation of the electron-hole pairs effectively, which accounts for its excellent photocatalytic performance. Nevertheless, BiOCl is a wide bandgap semiconductor (ca. 3.6 eV)\(^2\), which means that BiOCl cannot be excited by visible light and can only be excited by UV light. Due to this inherent limitation, the abundant solar energy cannot be utilized efficiently. To expand the excitation wavelength range of BiOCl, many strategies have been applied. For example, Lee, et al\(^6\) reported that the BiOCl/Bi2O3 heterojunction had high efficiency in organic compounds degradation. Zan, et al\(^6\) prepared black BiOCl by introducing oxygen vacancies, and found that its photocatalytic activity was 20 times higher than that of white BiOCl. Chen, et al\(^7\) reported a BiOCl/BiOI composite which showed superior photocatalytic performance on degrading Methyl Orange (MO) and RhB.

Another effective method for enhancing photocatalytic performance is to modify the semiconductor with CQDs, which are attracting intense attention due to their environmentally friendly nature, chemical inertness, simple synthetic routes, ease of functionalization, high aqueous solubility, low cost and so on\(^8\)-\(^10\). CQDs display strong up-conversion luminescence behavior, which can absorb two or more photons and emit light with wavelengths shorter than the excitation wavelength. Due to this unique photo-physical characteristics, CQDs have wide applications in such fields as light energy conversion, bioimaging, sensors, photovoltaic devices, electrocatalysis and photocatalysis, etc\(^11\)-\(^15\). In addition, CQDs have unique non-localized electron conjugated structure, which can function as an effective electron trap to promote the separation of photo-generated electron-hole pairs. Therefore, the excellent light capturing ability and photo-induced electron transfer capability make CQDs a promising candidate in the field of photocatalysis. Up to date, many CQDs/semiconductor composites with improved visible light photocatalytic performance have been reported, including CQDs/Fe2O3\(^16\), CQDs/Cu2O\(^17\), CQDs/ZnO\(^18\), CQDs/Ag3PO4\(^19\), CQDs/C3N4\(^20\), CQDs/
These studies indicate that CQDs are efficient components in the construction of composite photocatalysts.

In a previous study, Xia, et al.[24] synthesized CQDs modified BiOCl ultrathin nanosheets via a solvothermal method, employing mannitol as solvent and PVP as surfactant. In this work, a modified solvothermal method was used to synthesize CQDs/BiOCl composites, using a more environment-friendly ethanol as the solvent. By adjusting the solvent and reaction parameters such as solvothermal temperature and time, high-performance BiOCl nanosheets were obtained. By further introducing CQDs as electron trap and light harvester, the photocatalytic performance of BiOCl is enhanced significantly. Furthermore, the mechanism for the improved photocatalytic performance was elucidated detailedly.

1 Experimental procedures

1.1 Preparation of CQDs/BiOCl nanocomposites

CQDs were prepared through a modified literature procedure[25]. By thermolyzing citric acid (100 g) in air at 180 °C for 40 h, an orange-brown liquid of CQDs capped by carboxylic acid was yielded. Then the high viscosity liquid was stirred with 100 mL of deionized water and 50 mL of NaOH aqueous solution (5 mol/L) to dissolve. Subsequently, approximately 25 mL of NaOH aqueous solution (5 mol/L) was added to neutralize the acidic CQDs, producing an orange-brown solution of sodium carboxylate capped CQDs. After isolating the product by freeze-drying, a yellow-orange powder was obtained.

In order to synthesize CQDs/BiOCl composites, 1 mmol of NaCl was dissolved into 17 mL of distilled water under stirring, then the solution was added into 17 mL of ethanol which contained 1 mmol of Bi(NO₃)₃·5H₂O. After that, 0.5, 1.0, and 1.5 mL of CQDs solution (20 mg/mL) were dropped into the above mixture, respectively. The samples with 0.5, 1.0, and 1.5 mL of CQDs were denoted as C_0.5/BiOCl, C_1.0/BiOCl, and C_1.5/BiOCl, respectively. Correspondingly, the mass percentages of CQDs were calculated to be 3.7wt%, 7.1wt% and 10.3wt% for C_0.5/BiOCl, C_1.0/BiOCl, and C_1.5/BiOCl, respectively. Then the resulting suspension was transferred into an autoclave and kept at 100 °C for 18 h. After cooling to room temperature, the product was separated by centrifugation and washed with distilled water for several times, and then dried in air. For comparison, pure BiOCl was synthesized without the addition of CQDs.

1.2 Characterization

X-ray diffraction (XRD) patterns of the products were recorded on an X-ray diffractometer (Rigaku Co. Ltd., Tokyo, Japan) with Cu Kα radiation and in the 2θ range from 20° to 80°. An FEI tecnaiG2F30 transmission electron microscope (TEM) was used to observe the microstructure of the samples. UV-Vis diffuse reflectance spectra (DRS) of the products were obtained from a PE Lambda 900 UV-Vis spectrophotometer using BaSO₄ as reference. The photocurrent measurements were conducted on a CHI 650 electrochemical workstation (Shanghai Chenhua, China) using a three-electrode system.

1.3 Photocatalytic test

Photocatalytic performances of the CQDs/BiOCl composites were tested by decomposition of RhB under a 500 W Xe lamp to simulate the solar light. During the experiment, 0.05 g of the photocatalyst was added to 50 mL of RhB (10⁻⁵ mol/L) solution to get a suspension, which was stirred magnetically in the dark for 1 h in order to establish an adsorption-desorption equilibrium between the pollutant molecules and the photocatalyst powders. 3 mL of suspension was collected at regular intervals, which was centrifuged to obtain a clarified solution for subsequent analysis. The concentration of RhB was analysed by recording the variations of the absorption band maximum (552 nm) on a UV-Vis spectrophotometer (754PC).

2 Results and discussion

2.1 Crystal structure

X-ray diffraction patterns of pure BiOCl and CQDs/BiOCl composites with different contents of CQDs are shown in Fig. 1. It can be seen that all the products are well crystallized, with all diffraction peaks consistent with the tetragonal BiOCl according to JCPDS 06-249. The introduction of CQDs has no obvious influence on the phase purity and crystallinity of the products.

![Fig. 1 XRD patterns of the products](image-url)
No diffraction peaks derived from CQDs can be observed, which is probably due to the low content and poor crystallinity of CQDs.

### 2.2 Microstructure

The microstructure of CQDs and the CQDs/BiOCl composite (C\textsubscript{1.0}/BiOCl) were observed by the transmission electron microscope (TEM). Fig. 2(A) shows that the as-prepared CQDs are monodisperse with diameters of ca. 5 nm. Fig. 2(B, C) show that the CQDs/ BiOCl composite exhibits nanosheet structure of about 200 nm. HRTEM image is further used to investigate the fine structure of the CQDs/BiOCl composite (Fig. 2(D)). The lattice fringes at 0.335 nm in the HRTEM image agrees well with fringe spacing of (101) plane of BiOCl, and the lattice fringes at 0.321 nm coincide with (002) spacing of CQDs. These results further confirm that the CQDs/BiOCl nanocomposite has been successfully constructed with CQDs attached on the surface of BiOCl nanosheets.

### 2.3 UV-Vis diffuse reflectance spectra

UV-Visible diffuse absorption spectra (DRS) of pure BiOCl and CQDs/BiOCl composites are compared in Fig. 3. According to Fig. 3, no absorption in the visible region can be observed for pure BiOCl, and it only has photo-absorption at UV light region with absorption edge located at ca. 360 nm. However, when the BiOCl nanosheets are modified with CQDs, the absorption edge of CQDs/BiOCl composites are red-shifted to the visible range. Moreover, as the amount of CQDs increases, the absorption edge shifts monotonically to the longer wavelengths. This result indicates that CQDs play a crucial role in harvesting visible light, which implies that more efficient utilization of the sunlight can be realized.

### 2.4 Photocatalytic activity

The photocatalytic activities of the as-prepared products are evaluated by degrading RhB under simulated sunlight irradiation. Fig. 4(A) shows the photo-degradation rates of RhB by pure BiOCl, CQDs and CQDs/BiOCl composites. With the CQDs amount increasing, the photo-degradation rate of RhB increases initially and achieves a maximum at CQDs amount of 1 mL. Complete degradation of RhB is realized by sample C\textsubscript{1.0}/BiOCl within 2 min under simulated solar light irradiation, while the degradation rate of RhB is only 29.5% in the presence of pure BiOCl. However,
further increasing the amount of CQDs leads to a decreased photocatalytic activity, which implies that there is an optimal loading amount of CQDs. This can be ascribed to that excess amount of CQDs will compete with BiOCl for light harvest, which decreases the absorption of light for degradation of RhB. Moreover, control experiment by using CQDs only under identical conditions is performed, and the result shows that the decolorization of RhB is negligible in the presence of CQDs alone. This result indicates that the decolorization is due to the photocatalysis but not the adsorption of dye molecules on the surface of CQDs.

Moreover, the cycling stability of the CQDs/BiOCl composite is tested through circulating runs. As shown in Fig. 4(B), the photocatalytic activity of the CQDs/BiOCl composite remains basically unchanged after being reused for five runs, which indicates that the CQDs/BiOCl composite has good photocatalytic stability and recyclability.

2.5 Mechanism of the enhanced photo-activity

It has been reported that the upconversion emission of CQDs can enhance the photocatalytic activities of CQDs modified composite photocatalysts under visible light irradiation[26]. Upconversion emission has been frequently cited as an important feature in CQDs. For instance, Kang, et al.[27] reported that CQDs can be used as spectrum converters in photoelectro-chemical hydrogen generation systems due to their up-conversion luminescence property. In a previous report[28], we also found that the upconversion emission from CQDs can excite Bi2WO6 to produce photo-induced charge carriers, thus increasing the availability of sunlight. When CQDs are introduced into the composite system, a portion of visible light is transformed into ultraviolet light. Then the ultraviolet light excites BiOCl to produce photo-induced charge carriers, which leads to an enhanced photo-activity of the composite.

Another crucial factor that determines the photocatalytic performance is the separation rate of the photo-induced charge carriers, which can be reflected directly by the photocurrent produced by the photocatalyst[29]. The photocurrent generated by pure BiOCl and CQDs/BiOCl composite (C_1.0/BiOCl) are compared in Fig. 5. Obviously, the introduction of CQDs can significantly enhance the photocurrent of BiOCl. The photocurrent generated by CQDs/BiOCl composite is about 2.1 times higher than that of pure BiOCl electrode, indicating an improved separation rate of charge carriers of the CQDs/BiOCl composite. The enhancement of photocurrent can be attributed to the contribution of CQDs, which act as electron reservoirs. Electrons from the conduction band of BiOCl can be trapped by the CQDs electron reservoirs, thus suppressing the recombination of the photo-generated charge carriers.

In order to further elucidate the photocatalytic mechanism, the main oxidative species are determined by radicals trapping experiments, using benzoquinone as superoxide radical (•O2−) scavenger, EDTA-2Na as holes scavenger and tert-butanol (t-BuOH) as hydroxyl radical (•OH) scavenger, respectively[30-31]. As shown in Fig. 6, the additions of EDTA-2Na and benzoquinone cause a severe depression of the photocatalytic activity, which indicates that both holes and •O2− are the main oxidative species and play crucial roles in the photocatalytic process. On the contrary, the addition of t-BuOH has a negligible influence on the photocatalytic activity, implying that •OH is not the main oxidative species.

Based on the above experimental results, a mechanism is proposed to explain the enhanced photo-activity of the CQDs/BiOCl composite, as illustrated in Fig. 7. Under the irradiation of visible light, CQDs with upconversion luminescence behavior can convert the visible light into ultraviolet light, which can be absorbed by BiOCl to generate electron-hole pairs. On the other hand, CQDs as an excellent electron reservoir can trap electrons from the conduction band of BiOCl, and then transfer the electrons quickly to the surface of the photocatalyst. In this way, the charge recombination is restricted effectively, while the migration of the charge carriers is promoted significantly. The transferred electrons as good reducing
agents can react with the adsorbed O$_2$ on the surface of CQDs to yield superoxide radicals ($\cdot$O$_2$$^-$), which are highly oxidative agents and can oxidize the pollutant molecules. Moreover, the long-lived holes on the valence band of BiOCl with strong oxidability can react with the RhB molecules directly, as confirmed by the radicals trapping experiments. Above all, due to the efficient harvest of sunlight, as well as the fast separation and migration of the photo-induced electron-hole pairs, the CQDs/BiOCl composite exhibits excellent photocatalytic performance, which can decolorize RhB in a short period of only 2 min.

3 Conclusions

In summary, a highly efficient CQDs/BiOCl composite photocatalyst has been successfully prepared through a modified solvothermal process. Due to upconversion luminescence effect and photo-induced electron transfer ability of CQDs, the photo-absorption range of BiOCl is extended, while the recombination of photo-generated charge carriers is effectively suppressed. Consequently, the as-synthesized CQDs/BiOCl composite shows excellent photocatalytic performance under simulated solar light irradiation, which can decolorize RhB within only 2 min. This study demonstrates that introducing CQDs is an effective way to enhance the photocatalytic activity of the semiconductors.

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高效碳量子点/BiOCl 纳米复合材料用于光催化污染物降解

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摘 要：为了克服单纯 BiOCl 光谱吸收范围窄和载流子复合几率高的缺点，本研究制备了一种具有高效光催化活性的碳量子点(CQDs)/BiOCl 纳米复合材料。光催化降解罗丹明 B 染料实验表明 CQDs/BiOCl 纳米复合材料的光催化性能远优于单纯的 BiOCl，其光催化性能约为后者的 3.4 倍。当 CQDs 的复合量为 7.1wt%时，样品的光催化性能最佳，能够在 2 min 之内将罗丹明 B 完全脱色，而单纯的 BiOCl 在相同时间内对罗丹明 B 的降解率仅为 29.5%。通过紫外-可见漫反射谱、光电化学测试以及自由基捕获实验揭示了 CQDs/BiOCl 纳米复合材料的光催化性能提升机理。结果表明 CQDs 可以拓展 BiOCl 的可见光吸收范围，这有利于增强其光捕获能力以及促进电子-空穴对的产生。除此之外，CQDs 独特的上转换发光行为，以及光诱导的电子转移能力提升了 CQDs/BiOCl 纳米复合材料光催化性能。

关 键 词：光催化; CQDs/BiOCl; 纳米复合材料; 上转换发光

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