Abstract

In this work, the carbon quantum dot (CQD)–decorated BiFeO$_3$ nanoparticle photocatalysts were prepared by a hydrothermal method. The TEM observation and XPS characterization indicate that the CQDs are well anchored on the surface of BiFeO$_3$ nanoparticles. Acid orange 7 (AO7) and hexavalent chromium (Cr(VI)) were chosen as the model pollutants to investigate the photocatalytic/photo-Fenton degradation and photocatalytic reduction performances of the as-prepared CQD/BiFeO$_3$ composites under visible and near-infrared (NIR) light irradiation. Compared with bare BiFeO$_3$ nanoparticles, the CQD/BiFeO$_3$ composites exhibit significantly improved photocatalytic and photo-Fenton catalytic activities. Moreover, the composites possess good catalytic stability. The efficient photogenerated charges separation in the composites was demonstrated by the photocurrent response and electrochemical impedance spectroscopy (EIS) measurements. The main active species involved in the catalytic degradation reaction were clarified by radicals trapping and detection experiments. The underlying photocatalytic and photo-Fenton mechanisms are systematically investigated and discussed.

Keywords: BiFeO$_3$ nanoparticles, Carbon quantum dots, CQD/BiFeO$_3$ composites, Photocatalysis

Background

In recent decades, wastewater containing heavy metal ions and organic compounds brings serious damages for environment and human beings. As one of common heavy metal ions, hexavalent chromium (Cr(VI)) derived from electroplating, leather tanning, and printing poses a serious threat for our health owing to its high toxicity [1]. On the other hand, most of organic pollutants (such as dyes) are also toxic and non-biodegradable, which destroy our living environment [2]. Up to now, many techniques have been developed to eliminate organic pollutants and reduce Cr(VI) to Cr(III) [3–5]. Among these methods, photocatalytic and photo-Fenton-like catalytic techniques are regarded to be the promising methods for efficient degradation of organic contaminants and Cr(VI) reduction in wastewater because of their inexpensive cost, non-selectivity, and simplicity of operation [6–9]. The basic steps involved in a photocatalytic degradation process can be described as follows: excitation of photocatalysts, separation and migration of the photogenerated charges, generation of active species on the surface of catalysts, and decomposition of organic compound as well as reduction of Cr(VI) caused by the redox reaction of active species and photo-induced charges [10, 11]. The photo-Fenton-like catalytic reaction is based on the synergistic effects of the Fenton reaction and photocatalytic process. The generation of active species during the Fenton reaction process can be promoted after the introduction of suitable light irradiation, which leads to improved catalytic activity [12, 13]. However, the wide application of photocatalytic and photo-Fenton-like catalytic techniques is limited due to the large bandgap of photocatalysts only responding to UV light (which accounts for ~ 5% of sunlight energy) and their low charge separation efficiency [14]. Generally, it is known that the visible light and near-infrared...
(NIR) light occupy ~ 45% and ~ 46% of solar energy, respectively, and their application has received a great deal of interest [15, 16]. As a result, the development of broad spectrum (UV-vis-NIR) active catalysts with efficient separation of photogenerated charges is very important for their practical applications [17–20]. Up to now, the iron-contained catalysts with narrow bandgap are considered as ideal candidates in the photocatalytic and photo-Fenton-like catalytic applications [21–25].

As one of typical iron-contained catalysts, BiFeO₃ with perovskite-type structure is known to be an interesting visible light-driven photocatalytic and photo-Fenton-like catalytic material for the degradation of dyes [26–34]. Nevertheless, its catalytic activity is not so strong to meet the application requirements owing to the high recombination rate of photogenerated charges. Moreover, the light response range of BiFeO₃ needs to be further extended to NIR light region for effective utilization of sunlight energy. Therefore, many strategies have been used to overcome these shortcomings [35–40].

Carbon quantum dots (CQDs), as an important class of zero-dimensional nanocarbon material, have attracted considerable attentions due to its distinct properties, such as large surface area, low toxicity, high biocompatibility, good water solubility, high chemical stability, good electrical conductivity, and excellent optical properties [41–44]. These prominent properties make it a promising candidate for the practical application in different fields [41–44]. More importantly, the photoexcited CQDs are demonstrated to be an excellent electron donors and acceptors to promote the separation of photogenerated charges in photocatalysts [45]. On the other hand, CQDs are found to be an unique up-converted photoluminescence material, which allows the generation of short-wavelength emission light (from 450 to 750 nm) by the excitation of long-wavelength light (NIR light, from 700 to 1000 nm) [42, 44]. The up-converted emission light can be employed as the excitation light for the production of photogenerated charges in the semiconductors, which extends their light response region [45]. As a result, incorporation of CQDs with photocatalysts is demonstrated to be a promising way to form excellent hybrid composite photocatalysts [46–52]. Chen et al. prepared CQD/BiFeO₃ nanocomposites and found their enhanced visible light photocatalytic activity for the dye degradation [53]. To the best of our knowledge, however, there is no work devoted to the photo-Fenton dye degradation and photocatalytic Cr(VI) reduction performances of CQD/BiFeO₃ composite photocatalysts under visible or NIR light irradiation.

In this work, the CQD/BiFeO₃ composite photocatalysts were prepared by a hydrothermal route. Their photocatalytic and photo-Fenton-like catalytic performance for acid orange 7 (AO7) degradation as well as photocatalytic Cr(VI) reduction activity under visible and NIR light irradiation were systematically investigated. The corresponding catalytic mechanism was proposed.

**Methods**

**Preparation of CQDs**

The CQDs were prepared by a hydrothermal method [54]. Glucose (1 g) was added into distilled water (80 ml) under magnetic stirring and ultrasonic treatment to obtain a homogeneous solution. Subsequently, this solution was transferred into a 100-mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h. After the reaction, the resultant solution was filtered by filter paper twice, and then, the reddish-brown CQDs suspension was obtained.

**Fabrication of CQD/BiFeO₃ Composites**

BiFeO₃ nanoparticles were prepared through a polyacrylamide gel route as reported in the literature [55]. The CQD/BiFeO₃ composites were fabricated as follows (Fig. 1): BiFeO₃ nanoparticles (0.1 g) were introduced into distilled water (70 ml), followed by ultrasonic treatment for 0.5 h to obtain uniform suspension. After that, a certain amount of CQD suspension was added drop by drop into the BiFeO₃ suspension under magnetic stirring. The mixture was
moved into the Teflon-lined stainless steel autoclave (100 ml) and heated at 130 °C for 4 h. Finally, the product was collected by centrifugation, washed with deionized water, and dried at 60 °C for 8 h. To explore the impact of the CQDs content on the catalytic actives of the composites, a series of CQD/BiFeO₃ composites with different mass contents of CQDs were prepared by adding different volumes of CQDs suspension (3, 6, 12, and 24 ml). These composites were correspondingly named as 3C/BFO, 6C/BFO, 12C/BFO, and 24C/BFO.

**Photo-Fenton Catalytic and Photocatalytic Degradation of Dye**

The photo-Fenton catalytic performance of the as-prepared CQD/BiFeO₃ composites was investigated toward the degradation of AO7 separately irradiated by visible light (300-W xenon lamp with a 420-nm cutoff filter) and NIR light (300-W xenon lamp with a 800-nm cutoff filter). In a typical experiment, the photocatalyst (0.1 g) was placed into AO7 solution (200 ml, 5 mg/L), and magnetically stirred in dark for 0.5 h to achieve a adsorption-desorption equilibrium between the photocatalyst and AO7 molecules. Subsequently, a certain amount of H₂O₂ solution was added into the suspension, and the xenon lamp was turned on to start the catalytic reaction. In the catalytic process, a small amount of the reaction solution (2 ml) was taken and centrifuged to eliminate the catalyst. The absorbance of the supernatant was measured by a UV-vis spectrophotometer at 484 nm to obtain the AO7 degradation. The initial concentration of Cr(VI) was 10 mg/l and the photocatalyst dosage was 0.2 g in 200 ml Cr(VI) solution (i.e., 1 g/l). The initial pH value of the Cr(VI) solution was adjusted to H₂SO₄ to 2~3. The residual concentration of Cr(VI) solution was detected by UV-vis spectrophotometry using the diphenylcarbazide (DPC) method.

**Hydroxyl Radical Detections**

Fluorimetry was employed to detect the ·OH radicals generated on the irradiated samples by using terephthalic acid (TA) as a probe molecule. Generally, the ·OH will react with TA to generate highly fluorescent compound, 2-hydroxyterephthalic acid (TAOH). The information of ·OH can be detected through measuring the photoluminescence (PL) intensity of TAOH with the excitation wavelength of ~ 315 nm. Typically, the TA was introduced into NaOH solution (1.0 mmol l⁻¹) to obtain TA solution (0.25 mmol l⁻¹). The catalyst (60 mg) was placed into TA solution (100 ml) under magnetically stirring for several minutes. After that, a certain amount of H₂O₂ was dissolved into above mixture, which was irradiated by visible light (300-W xenon lamp with a 420-nm cutoff filter) or NIR light (300-W xenon lamp with a 800-nm cutoff filter). At given intervals of irradiation, 3 ml of the reaction solution was sampled and centrifuged to remove the catalyst. The PL spectra of the supernatant were determined by fluorescence spectrophotometer. On the other hand, the generation of ·OH in the photocatalytic reaction was also measured under the same conditions without the addition of H₂O₂.

**Characterization**

The phase purity of the samples was examined by X-ray powder diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The morphology and microstructure of the samples were observed by field-emission transmission electron microscopy (TEM). The chemical states of the surface elements on the samples were detected by X-ray photoelectron spectroscopy (XPS). The ultraviolet-visible (UV-vis) diffuse reflectance spectra of the samples were recorded through a TU-1901 double beam UV-vis spectrophotometer. The PL spectra of the samples were determined by a fluorescence spectrophotometer. The transient photocurrent response and electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation with a three-electrode system. The working electrode fabrication and test procedures were similar to those previously reported. Particularly, the photocurrent response measurement was performed under visible light (300-W xenon lamp with a 420-nm cutoff filter) irradiation.
Results and Discussion

XRD Analysis

Figure 2 presents the XRD patterns of BiFeO$_3$, CQDs, and 24C/BFO. The BiFeO$_3$ and 24C/BFO sample show similar diffraction patterns, which can be readily indexed to the rhombohedral BiFeO$_3$ phase (JCPD file no: 74-2016). No trace of impurities, such as Fe$_2$O$_3$ and Bi$_2$O$_3$, is found. The results indicate that the high-purity BiFeO$_3$ is obtained and the introduction of CQDs and hydrothermal treatment do not obviously change the crystal structure of BiFeO$_3$. From the XRD pattern of CQDs, one can see that a broad diffraction peak is observed at ~ 23.5°, which is mainly attributed to the amorphous structure of CQDs. Notably, for the composite, no characteristic diffraction peaks of CQDs are detected owing to the low content of CQDs in the 24C/BFO sample. To confirm the existence of CQDs in the composite, the FTIR characterization is performed.

FTIR Analysis

Figure 3 shows the FTIR spectra of BiFeO$_3$, CQD, and 12C/BFO composites. In the case of bare BiFeO$_3$, the peaks at ~ 440 cm$^{-1}$ and ~ 560 cm$^{-1}$ are assigned to the stretching and bending vibrations of Fe–O, which is consistent with the reported result [55]. For the CQDs, the deformation vibration for C–H at ~ 638 cm$^{-1}$, the stretching vibration for C–C at ~ 1630 cm$^{-1}$, and C–OH stretching at ~ 1120 cm$^{-1}$ are found [58]. In addition, the characteristic peaks of BiFeO$_3$ and CQDs are detected in the spectrum of 12C/BFO composite. The results suggest the existence of CQDs and BiFeO$_3$ in the composite. Moreover, the peak located at ~ 1380 cm$^{-1}$ is attributed to the stretching vibration of O–H from the absorbed H$_2$O [59].

Optical Absorption Property

It is well established that the optical absorption property of nanomaterials has an important effect on their performance [60, 61]. The optical absorption property of BiFeO$_3$, CQD, and CQDs/BiFeO$_3$ composites were investigated by UV-vis diffuse reflectance spectra, as shown in Fig. 4a. Compared with BiFeO$_3$, the CQD/BiFeO$_3$ composites exhibit obviously enhanced optical absorption capability in the entire UV-vis light region. It is worth noting that the optical absorption intensity of the composites gradually increases with increasing the content of CQDs. This phenomenon can be attributed to the strong light absorption of CQDs in the UV-vis light region. To obtain the light absorption edge of the samples, the first derivative curves of the UV-vis diffuse reflectance spectra are carried out (Fig. 4b), in which the peak wavelength is considered to be the absorption edge of the samples [62]. It is found that absorption edges of BiFeO$_3$ and CQD/BiFeO$_3$ composites are located at ~ 588 nm, suggesting that the decoration of CQDs does not change the bandgap energy of BiFeO$_3$.

XPS Analysis

The chemical states of elements in the 12C/BFO sample were monitored by XPS and the results are presented in Fig. 5. On the Bi 4f XPS spectrum (Fig. 5a), the observed two strong peaks at 164.1 (Bi 4f$_{5/2}$) and 158.8 eV (Bi 4f$_{7/2}$) demonstrate the existence of Bi$^{3+}$ in the composite [63]. In Fig. 5b, the Fe 2p XPS spectrum indicates two obvious peaks at 723.6 and 709.6 eV, which are attributed to Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$. Notably, the broad peak of Fe 2p$_{3/2}$ can be divided into two peaks at 712.0 and 709.6 eV, corresponding to Fe$^{3+}$ and Fe$^{2+}$, respectively [40]. In addition, it is seen that the satellite peak of Fe 2p$_{3/2}$ is found at 717.8 eV. As shown in the XPS...
spectrum of O 1s (Fig. 5c), the obvious peak located at 529.6 eV is attributed to the lattice oxygen and the shoulder peak at 531.3 eV belongs to the chemisorbed oxygen of surface vacancies [64]. For the XPS spectrum of C 1s (Fig. 5d), the signal of C 1s can be divided into two distinct peaks. The major peak at ~ 284.9 eV is ascribed to the C–C bond with sp² orbital, whereas the peak at 287.7 eV is caused by the oxygenated carbon. The results further demonstrate the coexistence of CQDs and BiFeO₃ in the composite [65].

Morphology Observation

The TEM and high-resolution TEM (HRTEM) images of BiFeO₃ nanoparticles are shown in Fig. 6a and b, respectively. It is seen that the bare BiFeO₃ possesses a sphere-like shape and smooth surface with an average diameter of ~ 120 nm. The lattice spacing of 0.288 nm belongs to the (110) spacing of BiFeO₃. The TEM image in Fig. 6c indicates that the CQDs are composed of spherical-like particles with an average particle size of ~ 15 nm. From the TEM image of the CQD/BiFeO₃ composites (Fig. 6d–g), one can see that the CQDs are decorated on the surface of BiFeO₃ nanoparticles. The HRTEM image of the 12C/BiFeO₃ sample (Fig. 6h) reveals the interplanar distance of 0.389 nm corresponding to the (012) plane of BiFeO₃. Alongside of BiFeO₃, the decorated CQDs exhibit amorphous characteristic. This result suggests the formation of hybrid composite structure between BiFeO₃ and CQDs.

The dark-field scanning TEM (DF-STEM) image and the corresponding elemental mappings of the 12C/BFO sample are shown in Fig. 7a–e, respectively. The results reveal that the sample presents not only uniform distribution of the Bi/Fe/O elements but also uniform distribution of the C element. This confirms that CQDs are uniformly assembled on the surface of BiFeO₃ nanoparticles.

Photo-Fenton Catalytic and Photocatalytic Performance

The photocatalytic performance of the samples was first assessed by the degradation of AO7 under visible light irradiation, and the result is shown in Fig. 8a. Prior to the photocatalytic reaction, the adsorption (in the dark) and blank (without catalyst) experiments were carried out. A small amount of AO7 (~ 5%) is degraded after 3-h irradiation without catalyst, indicating that the self-degradation of the dye can be neglected. In the photocatalytic reaction, the photodegradation ability of pure BiFeO₃ is weak and only ~ 33% of AO7 is observed to be decomposed after 3-h exposure. When BiFeO₃ nanoparticles are decorated by CQDs, the CQD/BiFeO₃ composites exhibit obviously enhanced photocatalytic activity. Moreover, it is found that the catalytic activities of the composites are highly related to the content of CQDs. Among these composites, the 12C/BiFeO₃ composite displays the optimal degradation percentage of ~ 73% after 3-h irradiation, which is 2.2 times higher than that of bare BiFeO₃. However, with further increase of the CQD content (e.g., 24C/BFO), excessive CQDs decorated on the surface of BiFeO₃ nanoparticles may shield BiFeO₃ from absorbing visible light, which leads to the decrease of the photocatalytic activity.

In this work, the photocatalytic ability of the samples for the reduction of Cr(VI) under visible light irradiation was also studied, as shown in Fig. 8b. The blank experiment indicates that the reduction of Cr(VI) after 3-h illumination in the absence of catalysts is negligible. It is seen that the CQD/BiFeO₃ composites exhibit obviously enhanced photocatalytic activity. Moreover, it is found that the catalytic activities of the composites are highly related to the content of CQDs. Among these composites, the 12C/BiFeO₃ composite displays the optimal degradation percentage of ~ 73% after 3-h irradiation, which is 2.2 times higher than that of bare BiFeO₃. However, with further increase of the CQD content (e.g., 24C/BFO), excessive CQDs decorated on the surface of BiFeO₃ nanoparticles may shield BiFeO₃ from absorbing visible light, which leads to the decrease of the photocatalytic activity.

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Besides the photocatalytic activity, it is demonstrated that BiFeO₃ also displays promising photo-Fenton-like
catalysis ability. Figure 8c shows the photo-Fenton degradation of AO7 over the samples under visible light irradiation with the addition of H2O2, from which one can see that the degradation percentage of AO7 in the photo-Fenton-like catalytic process is much higher than that in bare photocatalytic reaction. For example, about 96% of AO7 is photo-Fenton catalytically degraded over 12C/BFO sample under 3-h irradiation, which has a ~23% enhancement compared with the photocatalytic degradation of AO7 (~73%). In addition, it is found that the photo-Fenton catalytic activities between the samples have an order same to the photocatalytic activities between the samples. This suggests that the CQD/BiFeO3 composites can be used as effective photo-Fenton catalysts for the degradation of dyes.

Generally, the reusability of catalysts is regarded as an important parameter for their practical application. According to above catalytic results, the 12C/BFO sample was chosen as the catalyst for the investigation of photocatalytic and photo-Fenton catalytic stabilities. Figure 8d presents the catalytic activities of the 12C/BFO sample during three successive visible light-driven photocatalytic and photo-Fenton catalytic processes. After three consecutive cycles, the catalytic activities of the 12C/BFO sample do not undergo obvious decrease. This indicates that the CQD/BiFeO3 composite exhibits good catalytic reusability under visible light irradiation.

In this work, the NIR light-driven photocatalytic and photo-Fenton catalytic activities of BiFeO3 and 12C/BFO were investigated. Figure 9a–c display the time-dependent photocatalytic degradation of AO7, photocatalytic reduction of Cr(VI), and photo-Fenton catalytic degradation of AO7 over BiFeO3 and 12C/BiFeO3 under NIR light irradiation, respectively. It can be seen that bare BiFeO3 exhibits almost no NIR light photocatalytic activity because it cannot respond to NIR light, while about 22% of AO7 is degraded by BiFeO3 during the photo-Fenton catalytic reaction. In contrast, the 12C/BFO sample displays obvious NIR light-driven catalytic activities. After 3-h NIR light irradiation, the photocatalytic degradation of AO7, photocatalytic reduction of Cr(VI), and photo-Fenton degradation of AO7 over the 12C/BFO sample reach ~35%, ~63%, and ~49%, respectively. The result indicates that the introduction of CQDs onto the surface of BiFeO3 plays an important role in the enhancement of its NIR light-driven catalytic activity. The NIR light catalytic stabilities of the 12C/BFO sample were also studied by recycling catalytic experiments, as shown in Fig. 9d. It is found that the CQD/BiFeO3 composite also has steady NIR light-driven catalytic activity.

Active Species Trapping
To explore the effect of active species on the catalytic degradation reaction, reactive species trapping experiments...
were carried out. Figure 10a and b show the photocatalytic and photo-Fenton catalytic degradation of AO7 using the 12C/BFO sample with the addition of quenchers under visible light illumination, respectively. From Fig. 10a, the introduction of ethanol and AO leads to relatively small inhibition on the AO7 degradation. In contrast, the photocatalytic degradation of AO7 is dramatically suppressed with N₂ purging. This suggests that the ·O₂⁻ is the primary reactive
species, whereas -OH and h+ are the secondary reactive species responsible for the dye degradation. As shown in Fig. 10b, the degradation percentage of AO7 decreases from 96% (without scavengers) separately to ~ 60% (N2 purging), ~ 71% (adding AO), and ~ 45% (adding ethanol). This reveals that O2−, h+, and -OH participate in the visible light-driven photo-Fenton catalytic reaction, and -OH plays a relatively large role in this process. Figure 10c and d present the photocatalytic and photo-Fenton catalytic degradation of AO7 over the 12C/BFO sample in the presence of scavengers with the irradiation of NIR light, respectively. It can be seen that in the both catalytic processes, the dye degradation depends on O2−, h+, and -OH. Particularly, O2− is demonstrated to be the main active species in the NIR light-driven
photocatalytic process, whereas ·OH exhibits a key duty in the NIR light photo-Fenton catalytic reaction.

Figure 11 displays the time-dependent PL spectra of the TPA solution using the 12C/BFO sample as the catalyst in the photocatalytic and photo-Fenton catalytic reaction under visible and NIR light illumination. It is seen that, in all cases of the catalytic processes, the PL emission peak located at ~ 429 nm becomes intense gradually with the increase of the illumination time, indicating the generation of ·OH radicals. Based on the PL signal intensity, it is concluded that more ·OH radicals are generated in the photo-Fenton process than in the photocatalytic process, and the visible light irradiation leads to the increased generation of ·OH radicals when compared with the NIR light irradiation.

Photogenerated Charges Performance

Photoelectrochemical measurement is very useful for the investigation of the migration and recombination performance of photogenerated charges. The transient photoresponse currents of BiFeO$_3$ and 12C/BFO under visible light irradiation with several on/off cycles are shown in Fig. 12a. One can see that the photocurrent density of 12C/BFO is much higher than that of bare BiFeO$_3$, indicating the effective separation of photogenerated charges in the CQDs/BiFeO$_3$ composite. Figure 12b displays the EIS curves of BiFeO$_3$ and 12C/BFO. It is well known that the semicircle in the Nyquist plot at the high-frequency region reflects the interfacial charge-transfer process and a smaller diameter of semicircle means a lower charge-transfer resistance [66]. The 12C/BFO sample exhibits a smaller semicircle diameter compared with bare BiFeO$_3$, suggesting that the migration of photogenerated charges can be promoted in the CQD/BiFeO$_3$ composites.

Catalytic Mechanism

A possible visible light-driven photocatalytic mechanism of CQDs/BiFeO$_3$ for the dye degradation and Cr(VI) reduction is proposed, as shown in Fig. 13a. When the CQD/BiFeO$_3$ composite is irradiated by visible light, the BiFeO$_3$ nanoparticles will be excited to generate photogenerated electrons and holes. On the other hand, the electrons in the CQDs can be also excited from their $\pi$ orbital or $\sigma$ orbital to the lowest unoccupied molecular orbital (LUMO) to obtain photoexcited electrons. It has been demonstrated that the excited CQDs can act as excellent electron donors and electron acceptors.
Therefore, the photogenerated electrons in the conduction band (CB) of BiFeO₃ nanoparticles will easily migrate to the $\pi$ orbital or $\sigma$ orbital of CQDs, while the photoexcited electrons of CQDs will transfer to the CB of BiFeO₃. During the above converse electron migration process, the separation of photogenerated charges in BiFeO₃ can be promoted, as revealed by photoelectrochemical measurement (see Fig. 12a). Thus, more photogenerated charges are available for participating in the photocatalytic reaction, leading to the improvement of photocatalytic activity.

More importantly, the up-converted PL property of CQDs also plays an important role in the enhancement of photocatalytic activity. Figure 13b presents the up-converted PL spectra of CQDs with the excitation wavelength from 810 to 890 nm, from which one can see that the up-converted emission peaks are centered at shorter wavelengths in the range of 400–680 nm. Because the light absorption edge of the as-prepared BiFeO₃ nanoparticles is located at ~ 588 nm (see Fig. 4), the up-converted emission light (400–588 nm) of CQDs can be used to excite BiFeO₃ nanoparticles to produce photogenerated electrons and holes, which provides additional photogenerated charges for the photocatalytic reaction. This also contributes to the enhancement of photocatalytic activity for BiFeO₃ nanoparticles.

Besides the yield of photogenerated charges, the redox ability of photogenerated charges is considered to be another important factor for understanding the catalytic mechanism of catalysts. In our previous work, the CB and VB potentials of prepared BiFeO₃ nanoparticles are calculated to be + 0.4 and + 2.47 V vs. NHE, respectively [55]. From a thermodynamic point of view, the generation of ·OH will be smoothly achieved because the VB potential of BiFeO₃ is more positive than the redox potential of OH$^-$/·OH (+ 1.99 V vs. NHE) [67]. Compared with the redox potential of Cr(VI)/Cr(III) (+ 0.51 V vs. NHE) [57], the photogenerated electrons in the CB of BiFeO₃ is negative enough to reduce Cr(VI) to Cr(III). Another active species ·O₂$^-$ can be obtained from the reaction between the photoexcited electrons of CQDs and O₂ [68].

Figure 13c presents the visible light-driven photo-Fenton catalytic degradation mechanism of the dye over the CQD/BiFeO₃ composites. In this case, the photocatalytic and Fenton reactions will simultaneously happen. When H₂O₂ is introduced into visible light-driven photocatalytic system, the H₂O₂ can react with Fe²⁺ on
the surface of BiFeO$_3$ to obtain additional ·OH along
with the generation of Fe$^{3+}$. Simultaneously, the Fe$^{3+}$ will
be reduced to Fe$^{2+}$ by the photogenerated electrons of
BiFeO$_3$ and CQDs [69]. During this cycle reaction, more
·OH is produced, which is beneficial for the enhance-
ment of catalytic efficiency.

Figure 13d and e display the photocatalytic and
photo-Fenton catalytic mechanism of the CQDs/
BiFeO$_3$ composite under NIR light irradiation. It is
known that the BiFeO$_3$ do not response to NIR light (>800 nm). As a result, only CQDs can be excited under
NIR light irradiation in the two catalytic processes. The photogenerated charges migration and up-converted excitation of CQDs are similar to those as
depicted in Fig. 13a and b. Because the BiFeO$_3$ cannot
be directly excited by NIR light, NIR light-excited
CQD/BiFeO$_3$ composite has a relatively lower yield of
photogenerated charges compared with the visible
light-excited composite. This is why photocatalytic and
photo-Fenton catalytic activities of the CQD/BiFeO$_3$
composites under NIR light irradiation are weaker
than those under visible light irradiation.
Conclusions
The CQDs were successfully decorated on the surface of BiFeO₃ nanoparticles through a hydrothermal route to obtain CQD/BiFeO₃ composites. Under visible and NIR light irradiation, these composites manifest remarkably enhanced photocatalytic degradation of AO7, photocatalytic reduction of Cr(VI), and photo-Fenton catalytic degradation of AO7 compared with bare BiFeO₃ nanoparticles. They can be reused without obvious decrease of catalytic activities. It is found that the introduction of CQDs leads to the efficient separation of photogenerated charges in the composites. The improved catalytic activities of CQD/BiFeO₃ composites can be ascribed to the two factors: the excellent up-converted photoluminescence property and photogenerated electron transfer ability of CQDs.

Abbreviations
AO: Ammonium oxalate; AO7: Acid orange 7; CB: Conduction band; CQDs: Carbon quantum dots; Cr(VI): Hexavalent chromium; DF-STEM: Dark-field scanning transmission electron microscope; DPC: Diphenylcarbazide method; DRS: UV-vis diffuse reflectance spectra; \( E_g \): Bandgap energy; EIS: Electrochemical impedance spectroscopy; FTIR: Fourier-transform infrared spectroscopy; \( h^+ \): Photogenerated holes; HRTEM: High-resolution transmission electron microscope; LUMO: Lowest unoccupied molecular orbital; NIR: Near-infrared light; \( O_2^- \): Superoxide radical; OH: Hydroxyl radical; PL: Photoluminescence; TA: Terephthalic acid; TAOH: 2-Hydroxyterephthalic acid; TEM: Transmission electron microscope; VB: Valence band; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffractometer

Acknowledgements
The authors appreciate the National Natural Science Foundation of China (Grant No. 51602170), the Natural Science Foundation of Qinghai Normal University (Grant No. 2019qz003).

Authors’ contributions
TX and LD conceived the idea of experiments. LD, XS, HL and YZ performed the experiments. TX and LD discussed and analyzed the experimental results. TX and LD drafted the manuscript. HY revised the manuscript. All authors read and approved the final manuscript.

Funding
This work was supported by the National Natural Science Foundation of China (Grant No. 51602170), the Natural Science Foundation of Qinghai, China (Grant No. 2016-ZJ-954Q), and the Youth Science Foundation of Qinghai Normal University (Grant No. 2019yq003).

Availability of data and materials
All data analyzed during this investigation are presented in this article.

Competing interests
The authors declare that they have no competing interests and the mentioned received funding in our manuscript does not lead to any conflict of interests regarding the publication of this work.

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Received: 29 August 2019 Accepted: 8 November 2019
Published online: 30 December 2019

References
1. Richard FC, Bourg A (1991) Aqueous geochemistry of chromium: a review. Water Res 25:807–816
2. Brown MA, De Vito SC (1993) Predicting azo dye toxicity. Citt Rev Environ Sci Technol 23:249–324
3. Li H, Li Z, Liu T, Xiao X, Peng Z, Deng L (2008) A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads. Biosens Res Technol 99:6271–6279

4. Teh CY, Budiman PM, Shok KPY, Wu TY (2016) Recent advancement of coagulation-flocculation and its application in wastewater treatment. Ind Eng Chem Res 55:4363–4389

5. Yi Z, Li Z, Wu H, Chen XF, Yang H, Tang YI, Yi YG, Wang JQ, Wu PH (2019) Fabrication of ZnOQgAgPCQ core-shell nanocomposite arrays as photoanodes and their photovoltaic properties. Nanomaterials 9:1254

6. Wang SY, Yang H, Yi Z, Wang XX (2019) Enhanced photocatalytic performance by hybridization of Bi2WO6 nanoparticles with honeycomb-like porous carbon skeleton. J Environ Manage 248:109941

7. Yan YX, Yang H, Yi Z, Xian T (2019) NaBH4-reduction induced evolution of Bi nanoparticles from BiOCl nanoparticles and construction of promising Bi@BiOCl hybrid photocatalysts. Catalysts 9:795

8. Li MR, Song C, Wu Y, Wang M, Pan ZP, Sun Y, Meng L, Han SG, Xu LJ, Gan L (2019) Novel Z-scheme visible-light photocatalyst based on CoFe2O4/BiOBr/A. Graphene composites for organic dye degradation and Cd2+ removal. Appl Surf Sci 478:744–753

9. Palas B, Eröz G, Atalay S (2017) Photo-Fenton-like oxidation of tartrazine under visible and UV light irradiation in the presence of La2CuO4 perovskite catalyst. Process Saf Environ Prot 111:270–282

10. Yamashita H, Morii K, Kuwahara Y, Kamegawa T, Wen MC, Verma P, Che M (2018) Single-site and nano-confined photocatalysts designed in porous materials for environmental uses and solar fuels. Chem Soc Rev 47:8072–8096

11. Fujishima A, Zhang X, Tryk DA (2007) Heterogeneous photocatalysis: from basic principles to advanced applications. J Photochem Photobiol C 8:1–19

12. Shiraz AD, Takdastan A, Borghei SM (2018) Photo-Fenton like degradation of Orange II in water. Appl Catal B Environ 202:130–137

13. Wang SY, Yang H, Yi Z, Wang XX (2019) Enhanced photocatalytic performance by hybridization of Bi2WO6 nanoparticles with honeycomb-like porous carbon skeleton. J Environ Manage 248:109941

14. Yi Z, Zeng Y, Wu H, Chen XF, Fan YX, Yang H, Tang YI, Yi YG, Wang JQ, Wu PH (2018) Synthesis, surface properties, crystal structure and dye-sensitized solar cell performance of TiO2 nanotubes anodized under different parameters. Results Phys 15:102609

15. Yu PQ, Chen XF, Yi Z, Tang YJ, Yang H, Zhou ZG, Duan T, Cheng SB, Zhang JG, Yi YG (2019) A numerical research of wideband solar absorber based on refractory metal from visible to near infrared. Opt Mater 97:109400

16. Liang CP, Yi Z, Chen XF, Tang YI, Yi Y, Zhou ZG, Wu XG, Huang Z, Yi YG, Zhang GF (2019) Dual-band infrared perfect absorber based on a Ag-dielectric-Ag multilayer films with nanogrooves array. Plasmonics. https://doi.org/10.1007/s11468-019-01018-4

17. Tian J, Leng YH, Zhao ZH, Xia Y, Yang SY, Hao P, Zhan J, Li MC, Liu H (2019) Carbon quantum dots/hydrogenated TiO2 nanobelt heterostructures and their broad spectrum photocatalytic properties under UV, visible, and near-infrared irradiation. Nano Energy 57:1149–1151

18. Wei N, Cui HZ, Song Q, Zhang LQ, Song XJ, Wang K, Zhang YF, Li J, Wen J (2019) Synthesis, surface properties, crystal structure and dye-sensitized solar cell performance of TiO2 nanotube arrays anodized under different parameters. Results Phys 15:102609

19. Dai C, Zhang ZY, Liu J, Shan N, Zhang H, Dionysiou DD (2016) Visible light-assisted heterogeneous Fenton with ZnFe2O4 for the degradation of Orange II in water. Appl Catal B Environ 182:456–468

20. Liang C, Liu YH, Li K, Wen J, Xing GT, Ma ZC, Wu YS (2017) Heterogeneous photo-Fenton degradation of organic pollutants with amorphous Fe-Zn-oxide/ hydroxyl under visible light irradiation. Sep Purif Technol 188:105–111

21. Gao F, Chen XY, Yin KB, Dong S, Ren ZF, Yuan F, Yu T, Zou ZG, Liu JM (2007) Visible-light photocatalytic properties of weak magnetic BiFeO3 nanoparticles. Adv Mater 19:2889–2892

22. Rabbani M, Rahimi R, Ghadi HF (2018) Photocatalytic application of BiFeO3 synthesized via a facile microwave-assisted solution combustion method. J Sol-Gel Sci Technol 87:346–349

23. Bosthi MA, Yesmin N, Hossain R (2018) Low temperature synthesis of BiFeO3 nanoparticles with enhanced magnetization and promising photocatalytic performance in dye degradation and hydrogen evolution. RSC Adv 8: 29613–29627

24. Lam SM, Sin JC, Mohamed AR (2017) A newly emerging visible light-responsive BiFeO3 perovskite for photocatalytic applications: a mini review. Mater Res Bull 90:15–30

25. Bai X, Wei J, Tian BB, Liu Y, Reiss T, Guiblin N, Gemeiner P, Dkhil B, Infante IC (2016) Size effect on optical and photocatalytic properties in BiFeO3 thin films. J Phys Chem C 120:3595–3601

26. J W, Yao K, Lim YF, Yang YC, Xuward A (2013) Epitaxial ferroelectric BiFeO3 thin films for unassisted photocatalytic water splitting. Appl Phys Lett 103: 062901

27. Bhardwaj Kumar S, Sakar M, Vinod PK, Balakumar S (2015) Versatility of electrospraying in the fabrication of fibrous mat and mesh nanostructures of bismuth ferrite (BiFeO3) and their magnetic and photocatalytic activities. Phys Chem Chem Phys 17:17745–17754

28. Zou L, Chen JG, Yi YG (2019) A numerical research of wideband solar absorber based on refractory metal from visible to near infrared. Opt Mater 97:109400

29. Tang JH, Wang RX, Liu MY, Zhang ZH, Song YT, Xue S, Zhao ZG, Dionysiou DD (2018) Construction of novel Z-scheme Ag/FeTiO3/Ag/BiFeO3 photocatalyst with enhanced visible-light-responsive and photo-Fenton catalytic activity for degradation of bisphenol A under visible light. Chem Eng J 337:788–791

30. Soltani T, Lee BK (2017) Enhanced formation of sulfate radicals by metal-doped BiFeO3 under visible light for improving photo-Fenton catalytic degradation of 2-chlorophenol. Chem Eng J 313:1258–1268

31. Vanga PR, Mangalaraj RV, Ashok M (2016) Effect of co-doping on the optical, magnetic and photocatalytic properties of the Gd modified BiFeO3 thin films for unassisted photocatalytic water splitting. Appl Phys Lett 103: 062901

32. Tooskolytna NA, Latoye GS (2017) Plasmonic enhanced photocatalytic activity of Ag nanoparticles decorated BiFeO3 nanoparticles. Catal Today 147:1640–1645

33. Ji YF, Wu CJ, Kim DH, Lee BW, Rhee SJ, Park YC, Kim CS, Wang QJ, Liu CL (2018) Nitrogen doped BiFeO3 with enhanced magnetic properties and photo-Fenton catalytic activity for degradation of bisphenol A under visible light. Chem Eng J 337:788–791

34. Di LJ, Yang H, Xian T, Chen XJ (2018) Facile synthesis and enhanced visible-light photocatalytic activity of novel p-Ag/Ag3PO4/BiFeO3 heterojunction composites for dye degradation. Adv Mater Res 209:591–599

35. Wang XF, Mao WW, Zhang J, Han YM, Quan CY, Zhang QX, Yang T, Yang JP, Li XA, Huang W (2015) Facile fabrication of highly efficient g-C3N4/BiFeO3 nanocomposites with enhanced visible light photocatalytic activities. J Alloys Comp 630:289–296

36. Li XF, Quan X, Chen S, Yu HT (2017) Ferroelectric-enhanced Z-schematic nanohybrids for efficient photocatalytic hydrogen evolution. J Mater Chem A 5:29613–29627

37. Liu WJ, Li C, Ren YJ, Sun XB, Pan W, Li YH, Wang JF, Wang WJ (2016) Carbon dots: surface engineering and applications. J Mater Chem B 4: 5772–5788

38. Li HT, Kang ZH, Liu Y, Lee ST (2012) Carbon nanodots: synthesis, properties and applications. J Mater Chem 22:24392–2453

39. De B, Karak N (2017) Recent progress in carbon dot-metal based nanohybrids for photochemical and electrochemical applications. J Mater Chem A 5:1826–1859

40. Lim SY, Shen W, Gao ZZ (2015) Carbon quantum dots and their applications. Chem Soc Rev 44:362–381

41. Wang R, Lu KQ, Tang ZR, Xu YJ (2017) Recent progress in carbon quantum dots: synthesis, properties and applications in photocatalysis. J Mater Chem A 5:3717–3734

42. Zhang HC, Huang H, Ming L, Li HT, Zhang LL, Liu Y, Kang ZH (2012) Carbon quantum dots/Ag3PO4 complex photocatalysts with enhanced...
photocatalytic activity and stability under visible light. J Mater Chem 22: 10501–10506
47. Wang S, Li LP, Zhu ZH, Zhao ML, Zhang LM, Zhang NN, Wu QN, Wang XY, Li GS (2019) Remarkable improvement in photocatalytic performance for tannery wastewater treatment using CQDs-based ZnO/Au nanocomposites. J Colloid Interface Sci 533:227–237
48. Huang WY, Wang SH, Zhou Q, Liu X, Chen XR, Yang K, Yu CL, Li D (2017) Constructing novel ternary composites of carbon quantum dots/Bi4MoO12/graphitic nanofibers with tunable band structure and boosted photocatalytic activity. Sep Purif Technol 217:195–205
49. Sharma S, Mehta SK, Ibhadon AO, Kansal SK (2019) Fabrication of novel carbon quantum dots modified with N-doped carbon quantum dots: synthesis, characterization, and 4-nitrophenol-aided Cr(VI) photo-reduction. Small 2019:1804515
50. Zhang YF, Park M, Kim HY, Ding B, Park SJ (2017) A facile ultrasonic-assisted fabrication of nitrogen-doped carbon dots/BiOBr up-conversion nanocomposites for visible light photocatalytic enhancements. Scientific Reports 7:45086
51. Zhang HC, Ming H, Lian SY, Huang H, Li HT, Zhang LL, Liu Y, Kang ZH, Lee ST (2011) Fe2O3/carbon quantum dots complex photocatalysts and their enhanced photocatalytic activity under visible light. Dalton Trans 40:10822–10825
52. Di J, Xia JX, Ji MX, Wang B, Yin S, Zhang Q, Chen ZG, Li HW (2015) Carbon quantum dots modified BiOCl ultrathin nanosheets with enhanced molecular oxygen activation ability for broad spectrum photocatalytic properties and mechanism insight. ACS Appl Mater Interfaces 7:20111–20123
53. Chen CC, Fan T (2017) Study on carbon quantum dots/BiFeO3 heterostructures and their enhanced photocatalytic activities under visible light irradiation. J Mater Sci Mater Electron 28:10019–10027
54. Gao HJ, Zheng CX, Yang H, Niu XW, Wang SF (2019) Construction of a CQDs/Au3PO4/BiPO4 heterojunction photocatalyst with enhanced photocatalytic degradation of rhodamine B under simulated solar irradiation. Micromachines 10:557
55. Xian T, Yang H, Dai JF, Wei ZQ, Ma JY, Feng WJ (2011) Photocatalytic properties of BiFeO3 nanoparticles with different sizes. Mater Lett 65:1573–1575
56. Zheng CX, Yang H, Cui ZM, Zhang HM, Wang XJ (2017) A novel Bi4Ti3O12/Au3PO4 heterojunction photocatalyst with enhanced photocatalytic performance. Nanoscale Res Lett 12: 608
57. Huang W, Liu N, Zhang XD, Wu MH, Tang L (2017) Metal organic framework g-C3N4/MIL-53(Fe) heterojunctions with enhanced photocatalytic activity for Cr(VI) reduction under visible light. Appl Surf Sci 425: 107–116
58. Xie RY, Zhang LP, Liu HC, Xu H, Zhong Y, Sui XF, Mao ZP (2017) Construction of CQDs-Bi20TiO32/PAN electrospun fiber membranes and their photocatalytic activity for isoproturon degradation under visible light. Mater Res Bull 94: 7–14
59. Yan YY, Yang H, Li Y, Xian T, Li RS, Wang XX (2019) Construction of Ag2S@CaTiO3 heterojunction photocatalysts for enhanced photocatalytic degradation of dyes. Desalin Water Treat (https://doi.org/10.1007/s11356-019-06085-y)
60. Wang YY, Qin F, Yi Z, Chen XF, Zhou ZG, Yang H, Liao X, Tang YJ, Yao WT, Yi YG (2019) Effect of slit width on surface plasmon resonance. Results Phys 15:102635
61. Liang CP, Zhang YB, Yi Z, Chen XF, Zhou ZG, Yang H, Yi Y, Tang YJ, Yao WT, Yi YG (2019) A broadband and polarization-independent metamaterial perfect absorber with monolayer Cr and Ti ellipsoidal disks array. Results Phys 15:102635
62. Yan YX, Yang H, Yi Z, Wang XX, Li RS, Xian T (2019) Evolution of Bi nanowires from BiOBr nanorods through a NaBH₄ reduction method with enhanced photodegradation performance. Environ Eng Sci (https://doi.org/10.1089/ees.2019.0284)
63. Wang SY, Yang H, Wang XX, Feng WJ (2017) Surface disorder engineering of flake-like Bi2WO6 crystals for enhanced photocatalytic activity. J Electron Mater 48: 2067-2076
64. Poojadi M, Shokrollahi H, Lavasani SANN, Yang H (2019) Investigation of the structural, magnetic and dielectric properties of Mn-doped Bi5FeO12 produced by reverse chemical co-precipitation. Mater Chem Phys 229: 39-48
65. Zhang XY, Liu JK, Wang JD, Yang XY (2015) Mass Production, Enhanced Visible Light Photocatalytic Efficiency, and Application of Modified ZnO Nanocrystals by Carbon Dots. Ind Eng Chem Res 54: 1766-1772
66. Yan YX, Yang H, Yi Z, Xian T, Wang XX Direct Z-scheme CaTiO3@BiOBr composite photocatalysts with enhanced photodegradation of dyes. Environ Sci Pollut R (https://doi.org/10.1007/s11356-019-06685-y).
67. Zhao XX, Yang H, Cui ZM, Yi Z, Yu H (2019) Synergistically enhanced photocatalytic performance of Bi4Ti3O12 nanosheets by Au and Ag nanoparticles. J Mater Sci Mater Electron 30: 13785-13796
68. Ren HT, Ge L, Guo Q, Li L, Hu GK, Li JG (2018) The enhancement of photocatalytic performance of SrTiO3 nanoparticles via combining with carbon quantum dots. RSC Adv 8: 20157-20165
69. Ye YC, Yang H, Zhang HM, Jiang JL A promising (2019) Ag3CrO4/ LaFeO3 heterojunction photocatalyst applied to photo-Fenton degradation of RhB. Environ Technol (https://doi.org/10.1080/09593330.2018.1538261)

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