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New Understanding on Photocatalytic Mechanism of Nitrogen-Doped Graphene Quantum Dots-Decorated BiVO₄ Nanojunction Photocatalysts

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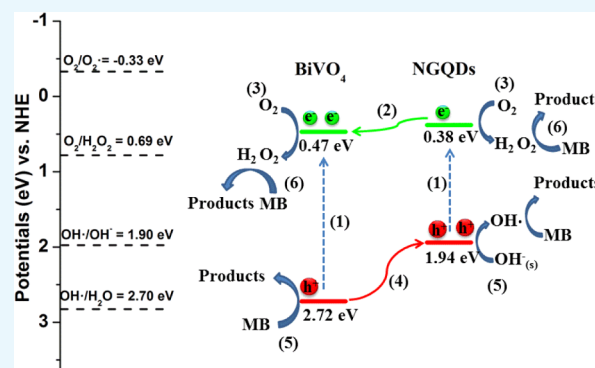
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Supporting Information

ABSTRACT: Bismuth vanadate (BiVO₄) is a promising candidate as a visible-light-driven photocatalyst in the aspect of practical applications. To investigate the origin of active species from BiVO₄ and understand the influence of the variations of the photocatalytic process, comparative studies on zero-dimensional nitrogen-doped graphene quantum dot (NGQD)-decorated BiVO₄ have been carried out for methylene blue photodegradation. It was found that the hydroxyl group-rich NGQD surface and the established heterojunction structure between NGQDs and BiVO₄ were greatly beneficial for the conversion of the [•]OH radical. With NGQD decoration, the dominant oxidant species for NGQDs/BiVO₄ were confirmed to be [•]OH and H₂O₂, rather than holes originating from the valence band of unmodified BiVO₄. The synergistic photocatalytic mechanism with respect to the interfacial charge transport and the conversion of active species was proposed. The achievement of the controllable active species significantly altering the activity may be applied for different photocatalytic reactions.



INTRODUCTION

Photocatalysis with semiconductor materials has attracted considerable interests in the past decades due to the potential applications in solar fuel production, environmental clean-up, water purification, etc.¹ Among various semiconductor materials, bismuth vanadate (BiVO₄) mixed transition-metal oxide with a bandgap of ~2.4 eV has been recognized as one of the excellent visible-light-response photocatalysts. The material can be capable of harvesting up to 11% of the solar spectrum but also possesses a strong oxidation property with chemical/photochemical stability. To date, it has been extensively used in various photocatalytic fields, such as elimination of organic pollutants^{2,3} and photoelectrochemical tandem cell.^{4–6} However, unmodified BiVO₄ usually shows low photocatalytic activity due to the high electron–hole recombination rate, poor charge transport, and slow surface reaction kinetics.^{7,8} To address the factors limiting the performance of BiVO₄, the modification approaches have been demonstrated to be necessary, such as decomposition of electrocatalysts (noble metals, carbon materials, cobalt phosphate, layered double hydroxide, etc.),^{9–11} metal or nonmetal doping (W, Mo, C, P,

etc.),^{12–15} and combination with other semiconductors (Si, WO₃, etc.).^{5,16} Yet, the surface chemistry of BiVO₄ has not been well described and the generation of the active species during photocatalytic processes is still in debate in the literature.^{17–19}

Inspired by recent significant advancements in the synthesis of zero-dimensional graphene quantum dots (GQDs) associated with the remarkable quantum-confinement and edge effects,^{20,21} GQDs have been used as a new type of electron-acceptor material for photocatalysis and solar cell applications.^{22–24} More interestingly, through atomic-scale tailoring, nitrogen-doped GQDs (NGQDs) could drastically alter their electronic characteristics and offer more active sites, thereby producing new phenomena and unusual properties.^{25,26} On the basis of the aforementioned argument on BiVO₄, it is highly desirable for the construction of the NGQD-decorated BiVO₄ to clarify the origin of active species on unmodified BiVO₄ and

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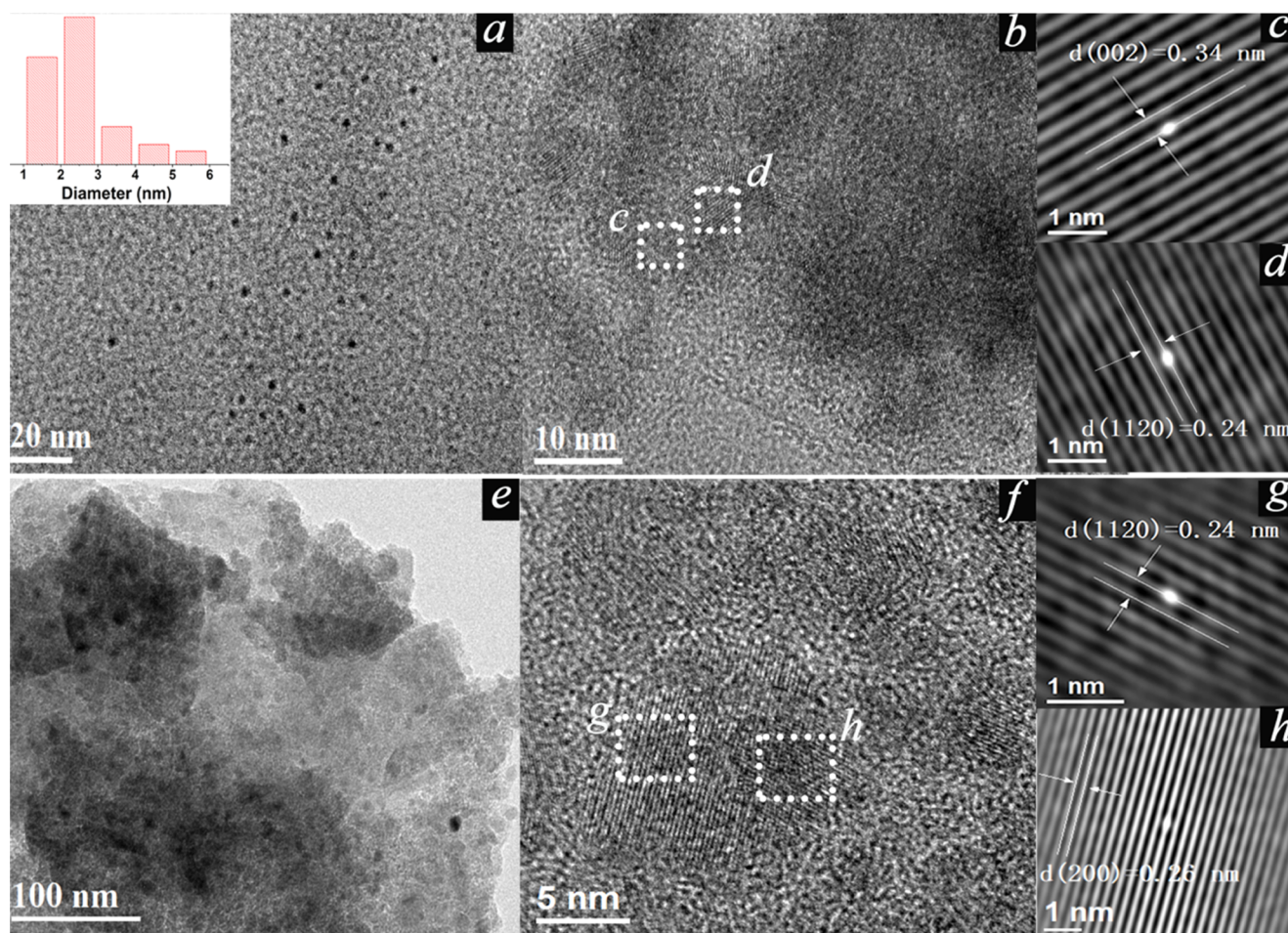


Figure 1. Representative TEM HRTEM and autocorrelated HRTEM lattice images of the pristine NGQDs (a–d) and 5 wt % NGQDs/BiVO₄ (e–h). The inset in (a) is the corresponding size distribution of the pristine NGQDs. The autocorrelated HRTEM lattice images of the pristine NGQDs (c, d) are recorded from the corresponding selected areas in the HRTEM image (b). Autocorrelated HRTEM lattice images of the NGQDs (g) and BiVO₄ (h) in the composite are marked in the corresponding selected areas of the HRTEM image (f).

the effects of NGQDs. In particular, the variation of the generated active species during the photocatalytic process is almost unknown so far.

Herein, we report, for the first time, the facile preparation of the NGQDs/BiVO₄ nanojunction photocatalysts by an ultrasonic-assisted method, which allows the successful deposition and uniform dispersion of NGQDs on the surface of BiVO₄ nanocrystals. Effects of NGQDs on the physicochemical property, optical property, electronic structure, and photocatalytic activity for the degradation of methylene blue (MB) were systematically studied. The surface effect of NGQDs, that is, the presence of plentiful hydroxyl groups, was found to be beneficial for the conversion of the $\cdot\text{OH}$ radical and the homogeneous dispersion on BiVO₄. The estimation of the band positions of both NGQDs and BiVO₄ revealed that the NGQDs acted as a junction component in the established heterojunction structure with BiVO₄. Furthermore, the formation of H₂O₂ and $\cdot\text{OH}$ active species was probed, and the synergistic photocatalytic mechanism of NGQDs/BiVO₄ related to the interfacial charge transport and variation of active species during the photocatalytic process was also discussed in detail.

RESULTS AND DISCUSSION

Figure 1 shows representative transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and autocorrelated HRTEM lattice images of the pristine NGQDs (Figure 1a–d) and 5 wt % NGQDs/BiVO₄ (Figure 1e–h). Note that the autocorrelated HRTEM lattice images were recorded from the corresponding selected areas in the HRTEM image (marked by a white rectangle). Figure 1a,b shows that the NGQDs have a uniform size ranging from 1.5 to 4 nm (inset of Figure 1a), with a small portion of aggregates of about 20 nm. The lattice fringes of 0.34 and 0.24 nm correspond to the (002) and (1120) plane of the graphite form, respectively (Figure 1c,d). The TEM image of 5 wt % NGQDs/BiVO₄ (Figure 1d) shows clear evidence for the deposition of NGQDs on the surface of BiVO₄ nanoparticles. The HRTEM (Figure 1e) and the autocorrelated HRTEM lattice images (Figure 1g–h) show the clear lattice fringes of 0.24 and 0.26 nm, corresponding to the (1120) plane of NGQDs and (200) plane of BiVO₄, respectively. The results unambiguously reveal the formation of an intimate contact between NGQDs and BiVO₄ components in the composite.

Similar X-ray diffraction (XRD) patterns (Figure S1) were obtained for the pristine NGQDs, BiVO₄, and NGQD-decorated BiVO₄, indicating negligible change on the BiVO₄ crystal structure by the introduction of NGQDs. The diffraction

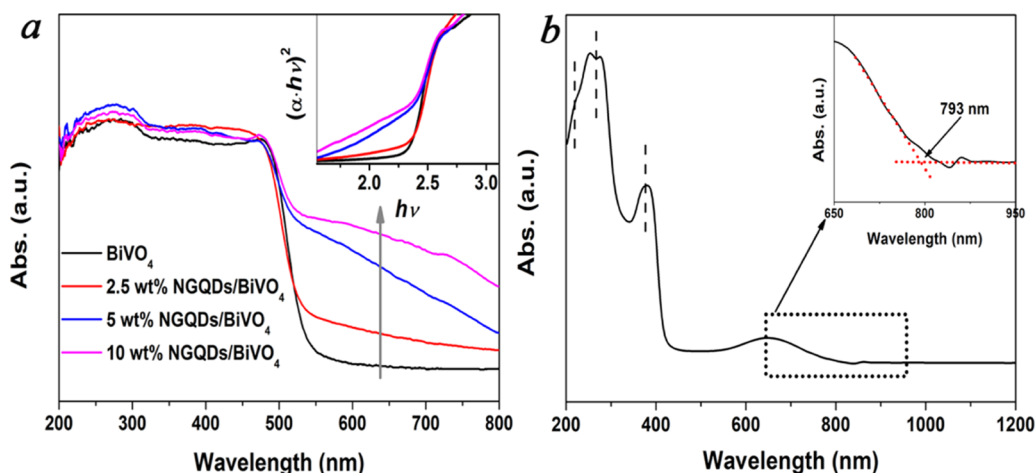


Figure 2. (a) Kubelka–Munk transformed UV–vis absorption spectra and Tauc plots (inset) of the as-synthesized samples. (b) UV–vis–NIR absorption spectrum of NGQDs (inset: the enlarged spectrum in the wavelength range of 650–950 nm).

peaks of all samples can be ascribed to the monoclinic BiVO₄ phase (JCPDS card 75-1867). As expected, no diffraction peaks of NGQDs were observed in the XRD patterns of NGQDs/BiVO₄ composites. This can be ascribed to the low loading and the high dispersion of NGQDs on the surface of BiVO₄.

The Fourier transform infrared (FTIR) spectra of the pristine NGQDs, BiVO₄, and 5 wt % NGQDs/BiVO₄ are shown in Figure S2. The spectrum of NGQDs shows that a broad absorption band at 3000–3500 cm⁻¹ can be assigned to the stretching vibrations of O–H and N–H, and the stretching vibration of C–H is displayed at ~2998 cm⁻¹.^{27,28} In the low-wavenumber region, two bands at 1667 and 1575 cm⁻¹ are attributed to the vibrational absorption band of C–O in COOH and CONH and the bending vibrations of C–C, respectively.²⁹ For the pristine BiVO₄, the strong absorption bands at ~548 and 735 cm⁻¹ are the characteristic bending vibration of the Bi–O bands^{30,31} and asymmetric stretching vibration of V–O bands.³² The results imply that there are plenty of hydroxyl and amino groups on the surface of NGQDs; in contrast, the hydroxyl groups are scarcely formed on BiVO₄. The hydroxyl groups play an important role in the formation of •OH during the photocatalytic process, as will be discussed in detail below. The FTIR spectrum of 5 wt % NGQDs/BiVO₄ is similar to that of pristine BiVO₄, and the characteristic peaks of NGQDs cannot be clearly observed, which is probably due to the overlap of the spectra.

The UV–vis absorption spectrum of the pristine BiVO₄ (Figure 2a) shows an absorption edge at around 550 nm, corresponding to the effective bandgap of 2.25 eV. Figure 2b shows the UV–vis–NIR absorption spectrum of NGQDs. Apparently in the UV region, there are three absorption peaks located at approximately 218 nm (5.68 eV), 269 nm (4.60 eV), and 378 nm (3.27 eV), corresponding to the π – π^* transitions from of C=C and C=N and n– π^* transition of the p– π orbit between the aromatic nitrogen and the conjugate structure, respectively. As shown in the enlarged resultant spectrum of NGQDs in the wavelength range from 650 to 950 nm (inset of Figure 2b), the absorption threshold of ~793 nm is clearly observed with a long tail absorption upon about 830 nm. It may be ascribed to the sub-bandgap transitions associated with the surface functional groups of NGQDs. The behavior is in good accordance with the results previously reported on surface-modified TiO₂.^{33,34} Therefore, the bandgap between the top of

the valence and bottom of the conduction band characteristic of the NGQDs can be determined to be ca. 1.56 eV. Consistently, the photograph shows a blue-green color of the NGQDs solution (Figure S3). For the NGQDs/BiVO₄ composites, an increased light-absorption capability and extended absorption onset are clearly observed in the visible region, along with the increase of the NGQD content (Figure 2a). With the benefits of the optical properties of NGQDs, the enhanced light absorption can refer to the higher production of electron–hole pairs under the same light irradiation condition.

The optimization of NGQD loading was studied from 2.5 to 10 wt % for photocatalytic degradation of MB. Figure 3 displays the NGQD dose-dependent variation trend of the MB absorption capacity in the dark and the photodegradation rate constants under visible light irradiation ($\lambda > 420$ nm). The blank reaction without catalysts confirmed that the self-degradation of MB was negligible. A very high absorption ability was observed for the pristine NGQDs in the dark, owing to its unique properties, that is, size effect, plenty of surface sites, etc. Under irradiation, it was found to be photoactive, but a poor photocatalytic activity was observed. It may be ascribed to the intrinsic property for photogenerated charge separation or the deactivation caused by the possible agglomeration of NGQDs.³⁵ With increasing the loading content of NGQDs, the absorption capacities and degradation rates of the NGQDs/BiVO₄ composites were obviously increased and reached the optima at 5 wt % of NGQDs. Compared to that of the pristine BiVO₄ (0.51% min⁻¹), nearly twofold enhancement in the photodegradation rate constant was achieved for the 5 wt % NGQDs/BiVO₄ composite (1.14% min⁻¹). However, a large dose usage of NGQDs led to a significant decrease of the absorption capacity and photocatalytic performance in the 10 wt % NGQDs/BiVO₄ composite. The results indicated that the rational proportion of NGQDs/BiVO₄ had a crucial impact on the improvement of the absorption capacity and degradation rate. Otherwise, the reduction of synergistic efficacy between NGQDs and BiVO₄ and the deteriorative particle agglomeration occurred.³⁶ Besides, the light-screening effect of NGQDs can also be considered to be the possible reason, which partially blocked the visible-light absorption of BiVO₄.^{37,38} Furthermore, the addition of H₂O₂ (10 mg L⁻¹) in a parallel reaction enhanced the MB degradation rate of 5 wt % NGQDs/BiVO₄, suggesting the role of H₂O₂ as an effective active species in

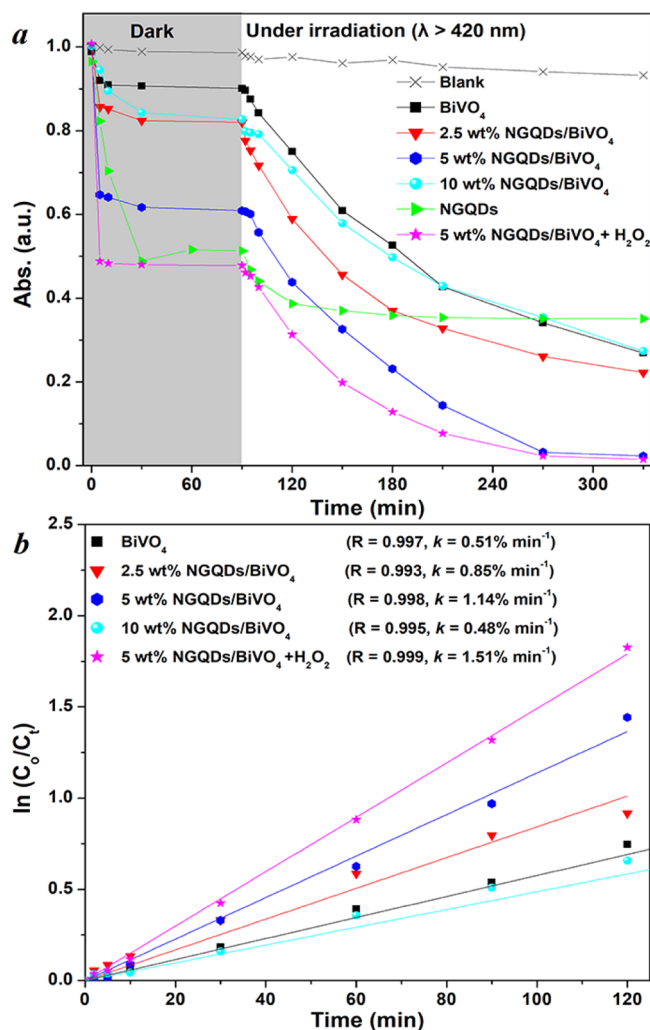


Figure 3. (a) MB absorption capacity in the dark and the photodegradation process under visible light irradiation ($\lambda > 420$ nm) over the as-synthesized samples. (b) Degradation rate constants of MB over the as-synthesized samples as fitted by using the first-order kinetics equation ($\ln(C_0/C_t) = kt$).

scavenging the photogenerated electrons and accelerating the photo-oxidation process.

To further validate the synergistic effect of NGQDs, electrochemical impedance spectroscopy (EIS) and Mott–Schottky analysis measurements were conducted on the as-prepared NGQDs/F-doped SnO₂ (FTO) electrode, and the corresponding conduction band (E_{CB}) and valence band (E_{VB}) energy potentials can be estimated to be approximately +0.38 V versus reversible hydrogen electrode (RHE) and +1.94 V versus RHE, respectively (Figure 4). In contrast, according to the Butler and Ginley method (detailed calculations given in Supporting Information),³⁹ the positions of the E_{CB} and E_{VB} potentials of BiVO₄ can be calculated to be about +0.47 and +2.72 eV, respectively. The results reveal that the suitable band positions between NGQDs and BiVO₄ would be favorable for the establishment of the heterojunction structure. The photoactive NGQDs acted as a junction component, which is different from the well-known function of GQDs as a sole electron acceptor (as will also be discussed in detail later).⁴⁰

To gain more insight on the photocatalytic reaction process of the NGQD-decorated BiVO₄, schematic illustration of the proposed photocatalytic mechanism related to the interfacial

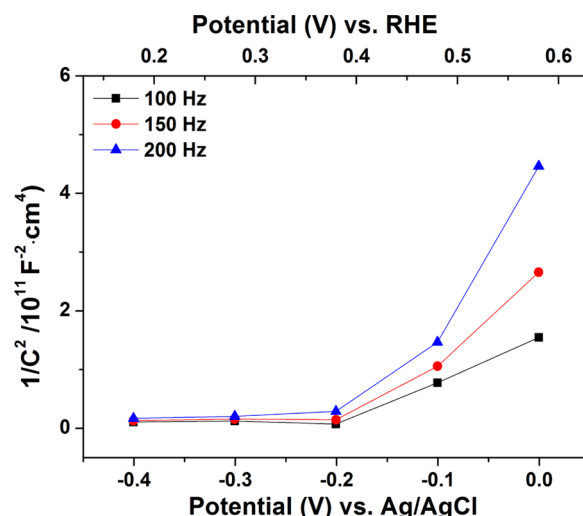


Figure 4. Mott–Schottky plots of NGQDs under dark conditions at various frequencies from 100 to 200 Hz with a three-electrode system in a 0.5 M Na₂SO₄ solution (pH 6.5).

charge transport and the generation of active species is shown in Figure 5a. The $\cdot\text{OH}$ trapping experiments by terephthalic acid (TA) photoluminescence (PL) probing were performed (Figure 5b,c). Under visible-light irradiation ($\lambda > 420$ nm), (1) both BiVO₄ and NGQDs can be excited and simultaneously the holes (h^+) and electrons (e^-) were produced. (2) The photogenerated electrons on NGQDs can smoothly transfer to BiVO₄ via the formed interfaces, due to the relatively low E_{CB} potential of BiVO₄. (3) Because the E_{CB} potentials of NGQDs and BiVO₄ are both located between the redox potential $\text{O}_2/\text{O}_2^{\cdot-}$ (-0.33 eV vs normal hydrogen electrode (NHE)) and $\text{O}_2/\text{H}_2\text{O}_2$ (+0.69 eV vs NHE), the consumption of the electrons involving molecular oxygen may proceed via the two-electron reaction for the formation of H₂O₂, instead of $\text{O}_2^{\cdot-}$ via a single-electron reaction. (4) Simultaneously, the holes on the surface of BiVO₄ can easily transfer to NGQDs via the interfaces, as the E_{VB} potential of NGQDs is much more negative than that of BiVO₄. As a result, the built-in type II junction structure was formed between NGQDs and BiVO₄. (5) In the case of BiVO₄, the surface photogenerated holes were directly trapped to react with adsorbed MB species on the condition they did not recombine with electrons because no obvious PL signal of $\cdot\text{OH}$ was observed (Figure 5b). This indicated that the generation of $\cdot\text{OH}$ was very scarce, which is in agreement with the reported results.¹⁸ The observation can be explained by two main reasons. First, the E_{VB} of BiVO₄ (+2.72 eV vs NHE) is located too closely to the redox couples $\cdot\text{OH}/\text{H}_2\text{O}$ (+2.7 eV vs NHE), and the generation of $\cdot\text{OH}$ via $\cdot\text{OH}/\text{H}_2\text{O}$ may be prohibited. Second, the lack of surface-adsorbed OH groups (OH_{ads}^-) on BiVO₄ as demonstrated by FTIR spectra would dramatically limit the generation of $\cdot\text{OH}$ via oxidation of OH_{ads}^- even though the E_{VB} of BiVO₄ is much more positive than the redox couples $\cdot\text{OH}/\text{OH}^-$ (1.9 eV vs NHE). In contrast, the holes accumulated in the E_{VB} of NGQDs (+1.94 V) can react with the surface-adsorbed OH groups (OH_{ads}^-) of NGQDs to generate a large amount of $\cdot\text{OH}$, showing a strong PL signal of $\cdot\text{OH}$ from the NGQDs/BiVO₄ (Figure 5c). We would like to note that the PL results also gave reliable evidence for the semiconducting characteristics of NGQDs with an opening bandgap,^{41,42} rather than an electron acceptor or even sensitizer. The induced interfacial

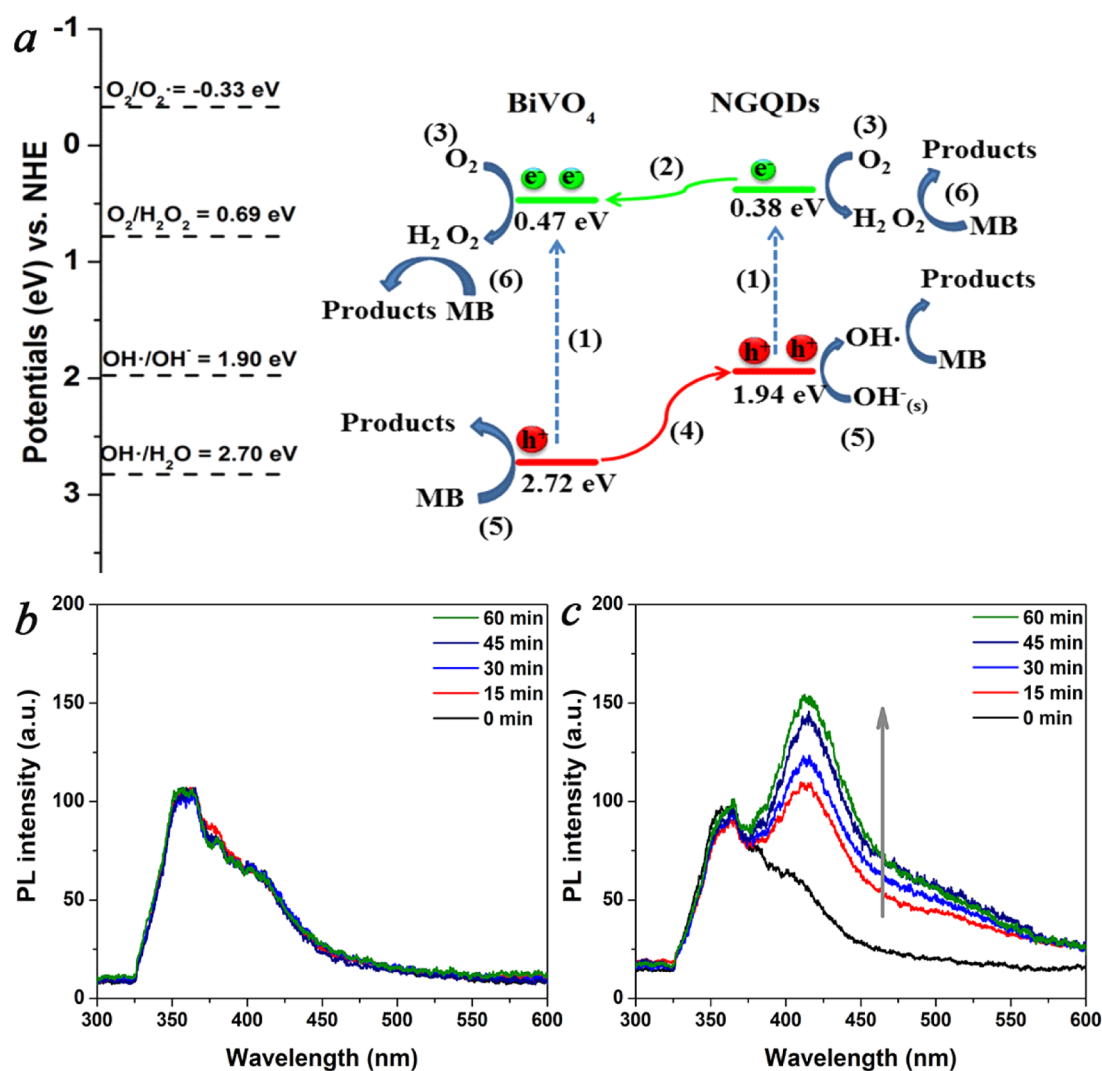


Figure 5. (a) Schematic illustration of the proposed photocatalytic mechanism and interfacial charge transport for the NGQDs/BiVO₄ nanojunction composite under visible-light irradiation ($\lambda > 420$ nm). [•]OH trapping PL spectra of (b) the pristine BiVO₄ and (c) 5 wt % NGQDs/BiVO₄ samples by TA hydroxylation. The observed PL peak at about 360 nm originated from the sampling capillary glass tube.⁴³

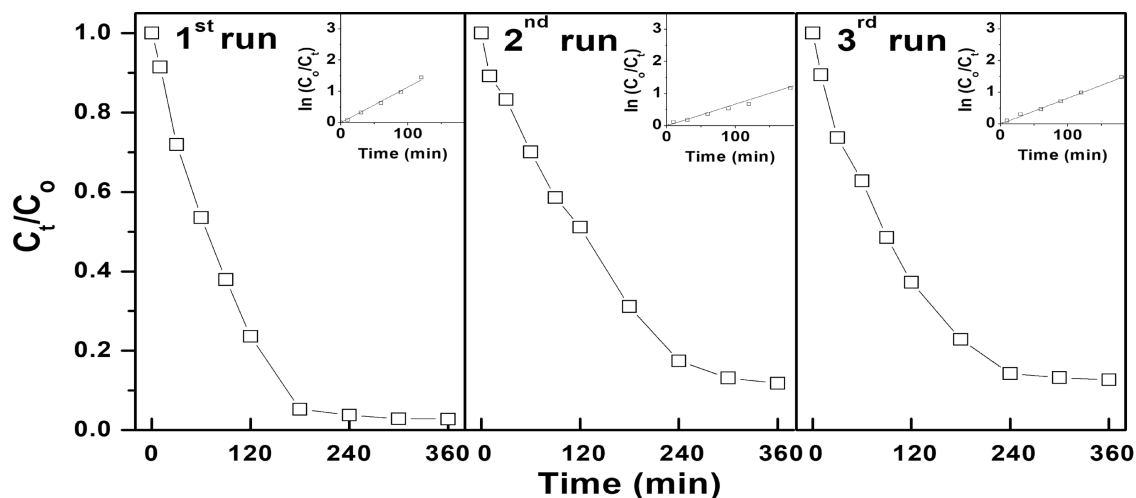


Figure 6. Recyclability of the 5 wt % NGQDs/BiVO₄ nanocomposite for photodegradation of MB. Insets: the corresponding first-order kinetic fitting curves.

hole transfer from BiVO₄ to NGQDs promoted the generation of [•]OH and greatly contributed to the enhancement of

photocatalytic degradation rate. (6) Presumably owing to the excessive consumption of electrons for the formation of H₂O₂

via the two-electron reaction, no superfluous electrons can further react with H_2O_2 to form $\cdot\text{OH}$. H_2O_2 as a characteristic of oxidative species would directly participate in the photocatalytic reaction. The decoration of a small amount of NGQDs not only increased the dye absorption capacity and visible-light-harvesting capacity but also facilitated the transfer and separation of photogenerated electron–hole pairs by aid of the built-in type II junction structure. Moreover, the results imply that the dominant oxidant species for NGQDs/ BiVO_4 were converted to H_2O_2 and the $\cdot\text{OH}$ radical rather than holes from the valence band of BiVO_4 . The formation of active species can be controlled during photocatalytic reactions, which may be useful for different photocatalytic applications.

The recyclability of the photocatalyst is an important parameter of the photocatalytic process for practical photocatalytic application. After each cycle, fresh MB solution was used for the next photocatalytic experiment, and taking into account the loss of the photocatalyst during the sampling process, the photocatalyst was collected from previous parallel experiments, followed by centrifugally washing and drying at $80\text{ }^\circ\text{C}$ overnight. Figure 6 shows the recycling test of 5 wt % NGQDs/ BiVO_4 and the corresponding first-order kinetic fitting curves (insets). A slight decrease in the degradation rate was observed after being used repetitively for three cycles. It unveiled that the NGQDs/ BiVO_4 nanocomposite was kept undamaged and the NGQDs remained tightly anchored on the surface of BiVO_4 . Therefore, the nanocomposite could be recognized as a stable photocatalyst, showing a good potential in the practical application for decomposing organic contaminant pollutants.

CONCLUSIONS

In summary, a novel NGQDs/ BiVO_4 nanojunction photocatalyst was prepared by a simple method. The positive influence of NGQDs on the physicochemical, optical, and electrical properties of NGQDs/ BiVO_4 has been demonstrated. The decoration of the optimum amount of 5 wt % NGQDs on BiVO_4 not only enhanced the absorption capacity and visible-light-harvesting capacity but also facilitated the interfacial charge transport by aid of the built-in type II junction structure. More interestingly, the conversion of the dominant active species during the photocatalytic process can be achieved after the decoration of NGQDs. This study on the new understanding of the photocatalytic mechanism will provide insights into the design of new photocatalytic materials with a required electronic property. Note that by exploitation of a new synthetic approach and control of technical parameters, the development of high-quality NGQDs will be one of the major concerns in the ongoing and future work for extending the great potential in the photocatalysis field.

EXPERIMENTAL SECTION

Preparation of Photocatalysts. All reagents used in this study were used without further purification. According to the literature,²³ the high-quality BiVO_4 nanoparticles were synthesized in an acidic environment,⁴⁴ where BiVO_4 photocatalysts have been proven to be more active than those prepared under higher pH conditions. Typically, 10 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (American Chemical Society (ACS) reagent, $\geq 98\%$; Alfa Aesar) and 5 mmol of V_2O_5 ($\geq 99.6\%$; Alfa Aesar) were mixed in 50 mL of 0.75 M HNO_3 solution. The resulting yellow product was collected by filtration and dried at $80\text{ }^\circ\text{C}$

overnight. The NGQDs were reproducibly prepared according to the one-pot hydrothermal method reported by Sun and coworkers:²⁹ 0.63 g of anhydrous citric acid (ACS reagent, $\geq 99.5\%$; Alfa Aesar) and 0.54 g of urea (ACS reagent, 99.0–100.5%; Alfa Aesar) were dissolved in 40 mL of water under stirring. The resulting solution was transferred into a 50 mL Teflon-lined stainless autoclave. The sealed autoclave was heated at $180\text{ }^\circ\text{C}$ for 6 h in an electric oven. The final product was centrifuged several times at 10 000 rpm for 10 min. The obtained NGQD supernatants were redispersed in 30 mL of water for further use, and the concentration of the NGQD solution was calculated to be about 43 mg mL^{-1} from balance measurements after drying at $80\text{ }^\circ\text{C}$ overnight. The ultrasonic-assisted method was used for the preparation of NGQDs/ BiVO_4 photocatalysts. Briefly, a desired weight ratio of NGQDs and BiVO_4 was added into ethanol. The bottle was placed in an ultrasonic bath for 2 h and then vigorously stirred for another 2 h. After drying at $80\text{ }^\circ\text{C}$ overnight, the resultant powders were directly heated at $180\text{ }^\circ\text{C}$ for 2 h in a tube oven under an argon atmosphere (quality 5.0).

Fabrication of NGQD Electrodes. The NGQDs/FTO electrodes were fabricated by the modified electrophoretic deposition (EPD) method.⁴⁵ Typically, 10 mL of NGQDs suspension (40 mg mL^{-1}) was prepared in 100 mL of isopropyl alcohol by sonication for 6 h, followed by adding 0.005 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98\%$; Alfa Aesar) into the suspension with an ultrasonic dispersion for 1 h. A clean FTO (as cathode) facing the stainless steel anode was immersed into this suspension. The distance between the two electrodes was fixed at about 5 cm. The Mg^{2+} -absorbed NGQD suspension was loaded in a quartz vessel as the electrolyte, and the electrophoresis process was performed at 50 V for 120 s. After the EPD process, the prepared NGQDs/FTO electrodes were washed by ethanol and deionized water several times and dried in an argon stream at room temperature.

Characterization. The XRD patterns of all samples were recorded with a PANalytical MPD diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541\text{ nm}$), and the data were recorded from 10 to 70° (2θ). Powder samples were examined by scanning electron microscopes using a LEO (Zeiss) 1530 Gemini field-emission. TEM images were recorded by a Philips/FEI Tecnai F20 S-TWIN TEM instrument operating at 200 kV. The UV–vis absorption spectra of the as-synthesized powdered samples were measured using BaSO_4 as a reference on a Shimadzu UV-2450 spectrophotometer. Bandgap energies were calculated by the analysis of the Tauc plots resulting from Kubelka–Munk transformation of the absorption spectra. The absorption spectrum of the NGQD solution was recorded by UV–vis–NIR spectroscopy (PerkinElmer LAMBDA 750) at room temperature. FTIR spectroscopy was performed on a PerkinElmer Spectrum 100 spectrometer using the typical potassium bromide (KBr) pellet technique. The PL spectra were recorded at room temperature by using a HORIBA LabRam HR spectrometer with the 325 nm line of the He–Cd laser as the excitation source.

Evaluation of Photocatalytic Activity. MB (Aladdin Chemical Reagent Corporation, Shanghai, China) was adopted as a hazardous organic pollutant. The evaluation of photocatalytic activity of the samples was performed on a home-built multizone photocatalytic reaction system, which consists of eight parallel windows and a 500 W midpressure Hg lamp (Hg Arc lamp source; Shanghai Bilon Instrument Co., Ltd., Shanghai, P. R. China) equipped with a water filter and a

420 nm cutoff filter as a visible-light irradiation source. In a typical run, 10 mg of catalysts was added into 50 mL of a 10.0 mg L⁻¹ MB solution. Before irradiation, the suspension was magnetically stirred in the dark to ensure the adsorption–desorption equilibrium of MB on the surface of the photocatalyst. Approximately 2 mL of the suspension was collected at certain time intervals and then centrifuged at 10 000 rpm for 10 min. The concentration change of the MB solution was determined using a UV/vis spectrophotometer by monitoring its characteristic absorption peak at 665 nm.

Detection of Hydroxyl Radicals (•OH). Generation of •OH during the photocatalytic process was detected by the PL technique using TA as the probe molecule. TA can react with highly reactive •OH to form highly fluorescent 2-hydroxyterephthalic acid, which can be used to decompose, for example, organic pollutants. Experimental procedures were similar to the measurement of photodegradation, except that the MB solution was replaced by a freshly prepared mixed solution (0.05 mM TA and 0.2 mM NaOH). Typically, the powder samples (20 mg) were dispersed in the TA solution (20 mL) and when irradiated under visible light for a certain time interval, a negligible amount of the reaction solution was sampled by a capillary glass tube and measured on a HORIBA LabRam HR spectrometer with an excitation wavelength of 325 nm.

Mott–Schottky Analysis. The EIS were measured by a potentiostat (Interface 1000 potentiostat; Gamry Instruments) with a three-electrode system in a 0.5 M Na₂SO₄ solution (pH 6.5). The potential was measured against an Ag/AgCl reference and converted to NHE potentials by using $E(\text{NHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V}$. In the case of the Mott–Schottky analysis, it can be estimated from the intersection of a plot of $1/C^2$ against E by the following equation

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 N} \left(E - E_{\text{fb}} - \frac{kT}{e} \right) \quad (1)$$

where C is the space charge capacitance (F cm⁻²), e is the elementary charge (1.62×10^{-19} C), ϵ the relative dielectric constant of the semiconductor, ϵ_0 is the permittivity of vacuum (8.85×10^{-12} N⁻¹ C² m⁻²), N is an acceptor density, E is the applied potential (V), k is the Boltzmann constant (1.38×10^{-23} J K⁻¹), and T is the absolute temperature (K).

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00603.

Powder XRD patterns; FTIR spectra; photograph of NGQD solution; detailed calculation of band positions (PDF)

■ AUTHOR INFORMATION

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Author Contributions

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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