Contents lists available at ScienceDirect



Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

In-situ fabrication of 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction towards highefficiency degrading 2, 4-dichlorophenol and mechanism insight



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ARTICLE INFO

Keywords: 2, 4-DCP NiO/Bi₁₂O₁₇Cl₂ 0D/2D heterojunction Photocatalytic degradation Reaction mechanism

ABSTRACT

2, 4-dichlorophenol (2, 4-DCP) as a persistent pollutant is frequently detected in water environments, complete eradication of trace which in water is an important task. Hence, a 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction was achieved by in-situ fabrication of NiO nanodots on Bi₁₂O₁₇Cl₂ nanosheets, which obviously improved the physical, optical and photoelectrochemical properties. The photocatalytic degradation activity of 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction was boosted dramatically, which originated from the improved transfer and separation efficiency of charge carriers owing to the formation of Z-scheme heterostructure between NiO and Bi₁₂O₁₇Cl₂. The possible photocatalytic reaction mechanism including migration behaviors of charge carriers, generation of reactive species and degradation intermediate products were revealed in depth. This work provides the valuable experiences for designing and fabricating otherwise 0D/2D heterojunction photocatalysts in the application of environmental treating fields.

1. Introduction

Recently, the efficient development of industry brings convenience to human, but the environmental problems are increasingly prominent in the meanwhile [1-8]. 2, 4-dichlorophenol (2, 4-DCP) as one of the most important persistent pollutants has been widely released in industry, agriculture, medicine and planting. In recent years, 2, 4-DCP is frequently detected in a wide range of environmental samples, particularly in treated wastewater and even drinking water, which may cause some pathological symptoms and changes for human endocrine systems. Nevertheless, the complete elimination of trace 2, 4-DCP in water cannot be easily achieved by the natural environment itself or sewage treatment plants. As a result, it is urgent to explore an effective method to eliminate 2, 4-DCP in water environment. Recently, there are several methods to remove 2, 4-DCP in water, such as electrochemistry [17], precipitation [18], adsorption [19], photocatalysis [20], etc. Among them, photocatalysis has been proved to be a promising technology to completely degrade 2, 4-DCP owing to its high-efficiency, eco-friendly and using renewable solar energy, etc. advantages. [21-26]. However, it still is a significant and challenging work to explore high-efficiency photocatalysts.

Bismuth oxychloride (Bi₁₂O₁₇Cl₂), as an important semiconductor material, has been attracted broadly attention because of its unique open crystalline structure, appropriate band structure and high chemical stability [27–37]. Moreover, Bi₁₂O₁₇Cl₂ has a sillen-aurivilliusrelated oxide layered structure consists of [Bi₁₂O₁₇] layers between two slabs of [Cl] ions with an internal static electric field perpendicular to each layer, which is in favor of the transfer and separation of photogenerated charge carriers [34,38,39]. Meanwhile, the intrinsic polarizabilities induced by the synergy of Bi 6s² lone electron pairs with vacant Bi 6p orbits can facilitate the migration and mobility of photogenerated electrons. However, the rapid recombination of electron-hole pairs is still a significant restriction for photocatalytic performance of Bi₁₂O₁₇Cl₂, which needs to be improved via the rational martial design and fabrication strategies.

Nickel oxide (NiO) is one of the most widely used catalyst that have been caught the focus due to their excellent physical and chemical properties, which usually was investigated in some important application fields including catalysis, gas sensing, battery cathodes, magnetic materials, electrochromic films, chemical sensors, photovoltaic devices, etc. [40]. In consequence, if NiO combines with Bi₁₂O₁₇Cl₂ to construct the heterostructure, it may facilitate the separation and migration of

https://doi.org/10.1016/j.jphotochem.2019.112102

Received 15 August 2019; Received in revised form 12 September 2019; Accepted 21 September 2019 Available online 23 September 2019

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charge carriers, thus improving the photocatalytic performance.

In this work, therefore, a zero-dimensional/two-dimensional (0D/ 2D) NiO/Bi₁₂O₁₇Cl₂ heterojunction was obtained by in-situ fabrication of NiO nanodots on the surface of Bi₁₂O₁₇Cl₂ nanosheets in a facile hydrothermal process followed by simple calcination. The powerful interface interaction between NiO nanodots and Bi₁₂O₁₇Cl₂ nanosheets obviously improves the physical, optical and photoelectrochemical properties. The formed Z-scheme heterostructure distinctly enhances the transfer and separation efficiency of charge carriers, thus dramatically boosting the photocatalytic degradation performance for removing 2, 4-DCP in water. Moreover, the possible photocatalytic reaction mechanism is discussed in detail, including the separation and migration behaviors of charge carriers, generation of active species, intermediate products of degrading 2, 4-DCP and so on.

2. Experimental section

2.1. Materials

BiCl₃ (\geq 98.0%, AR), C₆H₁₂O₆ (AR), NaOH (\geq 96.0%), CH₄N₂O (\geq 99.0%, AR), C₂H₆O (\geq 99.7%, AR)and NiCl₂•6H₂O (\geq 98.0%, AR) all were purchased from Sinopharm Chemical Reagents Co., LTD and used without any further purification.

2.2. Preparation process

4 mmol BiCl₃, 20 ml C₂H₅OH, 24 mmol NaOH and 20 ml deionized water were stirred to form a homogeneous solution, and then transferred into 50 mL Teflon autoclaves and heated in an oven at 120 °C for 6 h. The produced yellow precipitate was washed by distilled water and ethanol absolute for several times. After dried at 60 °C for 12 h, $Bi_{12}O_{17}Cl_2$ nanosheet was obtained.

NiO is prepared by a facile hydrothermal process followed by simple calcination. Typically, the mixed materials with 1 : 12 : 29 ratios of NiCl₂•6H₂O : CO(NH₂)₂ : C₆H₁₂O₆ were added in 70 ml deionized water, stirred for 30 min, transferred into 100 mL Teflon autoclaves, and heated in an oven at 160 °C for 20 h. The produced gray precipitate was washed by distilled water and ethanol absolute for several times, dried at 60 °C for 12 h. Furthermore, the NiO/Bi₁₂O₁₇Cl₂ samples were obtained by adding 0.3 g Bi₁₂O₁₇Cl₂ at the preparation process of NiO. The different mass ratios (1%, 3%, 5%, 7% and 9%) of NiO in NiO/Bi₁₂O₁₇Cl₂-2, NiO/Bi₁₂O₁₇Cl₂-3, NiO/Bi₁₂O₁₇Cl₂-4 and NiO/Bi₁₂O₁₇Cl₂-5, respectively.

2.3. Characterizations

The scanning electronic microscopy (SEM) was used to identify the morphology of as-prepared samples by JSM-7001 F. Raman spectra were performed on HORIBA HR 800 Laser Confocal Raman Microspectroscopy (Japan). The powder X-ray diffraction (XRD) patterns of samples were obtained on a D/MAX-2500 diffractometer (Rigaku, Japan) using a Cu K α radiation source ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the micromorphology and microstructure of samples by JEM-2100 (HR). The X-ray photoelectron spectroscopy (XPS) was obtained by Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al Ka radiations. The UV-vis diffuse reflectance spectra (DRS) were obtained by a UV-vis-NIR spectrophotometer (Cary 8454 Agilent, inc) with the scanning range of 200 nm -700 nm. Total organic carbon (TOC) was determined by multiple N/C 2100 TOC analyzer (Analytik Jena AG, Germany). The specific surface area and pore diameter distribution of the samples were measured on a nitrogen adsorption BET method (3H-2000PS1). The electron spinning resonance (ESR) analysis was carried out by the Bruker EPR JES-FA200 spectrometer. High performance liquid chromatography-mass spectrometry (HPLC-MS) system was used to test the structure of the intermediates.

2.4. Photocatalytic activity experiments

2, 4-DCP was used as the target molecules to evaluate the photocatalytic degradation activity of samples. 50 mg sample was dispersed in 100 mL 2, 4-DCP solution (20 mg L^{-1}) under the constant stirring. After ultrasonic treatment of 10 min, the solution was stirred for 30 min in the dark to make the adsorption-desorption equilibrium between 2, 4-DCP and sample [41]. Afterwards, a 250 W Xenon lamp covered with a UV filter ($\lambda > 420 \text{ nm}$) was used as light source. The specimen was pipetted from the suspension with 30 min intervals in the solution. The concentration of centrifugally separated supernatant was determined by an UV–vis spectrophotometer (Shimadzu, USA) at 286 nm which is the characteristic absorption wavelength of 2, 4-DCP.

2.5. Photoelectrochemical measurements

The photocurrent and electrochemical impedance spectra were measured by using a standard three-electrode system. The as-prepared samples, saturated Ag/AgCl and Pt plate electrode are served as the working electrodes, reference electrode and counter electrode, respectively. The Na₂SO₄ and K₃Fe(CN)₆ aqueous solution (0.5 mol L⁻¹) as electrolytes can be applied to measure photocurrents and electrochemical impedance spectra (EIS), respectively. The working electrode was prepared by the following method: 0.05 g of the sample was dissolved in 1 mL mix solution consisted of 0.01 g PVP, 0.03 mL oleic acid and 3 ml ethanol. Afterwards, the dispersion mixture was spun onto 1.0×1.0 cm FTO substrates as working electrode. The light source was the same as the photocatalytic measurement experiments.

3. Results and discussion

The structure and phase composition of samples are analyzed by XRD. From XRD of Bi₁₂O₁₇Cl₂ sample in Fig. 1a, the characteristic peaks at 26.4°, 29.2°, 30.4°, 32.9°, 35.7°, 45.5°, 47.2°, 54.9° and 56.4° originate from (1 1 5), (1 1 7), (0 0 12), (2 0 0), (0 0 14), (2 0 12), (2 2 0), (3 1 5) and (3 1 7) lattice planes of monoclinic Bi12O17Cl2 (JCPDS No. 36-0760). In comparison, the relative diffraction intensity at 29.2° is significantly improved in XRD of NiO/Bi12O17Cl2-4 sample, which may result from the modification effect of NiO on the surface of Bi₁₂O₁₇Cl₂ nanosheets. No diffraction peaks of NiO phase are observed which probably due to its relative low contents in NiO/Bi₁₂O₁₇Cl₂-4 sample. Meanwhile, Raman spectrum of $\mathrm{Bi}_{12}\mathrm{O}_{17}\mathrm{Cl}_2$ in Fig. 1b show that the intense bands are centered at 96 cm^{-1} , 130 cm^{-1} , 165 cm^{-1} , $395\,\mathrm{cm^{-1}},~472\,\mathrm{cm^{-1}}$ and $600\,\mathrm{cm^{-1}}.$ Among them, the distinctive strong peaks at 96 cm⁻¹ and 130 cm⁻¹ are assigned to A_{1g} external Bi-Cl stretching mode; the band at 165 cm^{-1} is attributed to the E_g external Bi-Cl stretching mode; the intense band at 472 cm^{-1} is produced by the B_{1g} motion of oxygen atoms [32,42]. Although vibration mode of NiO is not detected owing to the relative contents, the signal peaks of Bi12O17Cl2 are distinctly increased, which may result from surface decoration effect of NiO on Bi12O17Cl2 nanosheets.

In order to further confirm the morphology and microstructure of samples, SEM, TEM and HRTEM characterizations were carried out. As shown in Fig. 2a–b, the SEM images of $Bi_{12}O_{17}Cl_2$ ample show a nanosheet structure with a clean and smooth surface. By contrast, the SEM image of NiO/Bi₁₂O₁₇Cl₂-4 sample in Fig. 2c shows the plenty of NiO nanodots are modified on $Bi_{12}O_{17}Cl_2$ nanosheets. In addition, the nanosheet structure with smooth surface is also observed in TEM image of $Bi_{12}O_{17}Cl_2$ sample (Fig. 2d). Similarly, the TEM image of NiO/ $Bi_{12}O_{17}Cl_2$ -4 sample further displays NiO nanodots are evenly distributed on $Bi_{12}O_{17}Cl_2$ nanosheets (Fig. 2e). Furthermore, the HRTEM image of NiO/ $Bi_{12}O_{17}Cl_2$ -1 sample is displayed in Fig. 2f, where the lattice spacing of 0.259 nm corresponds to the (220) lattice planes of



Fig. 1. XRD patterns (a) and Raman spectra (b) of Bi₁₂O₁₇Cl₂ and NiO/Bi₁₂O₁₇Cl₂-4 samples.

 $Bi_{12}O_{17}Cl_2$ phase and NiO nanodots are firmly anchored on the $Bi_{12}O_{17}Cl_2$ nanosheets. In addition, EDX elemental mappings of NiO/ $Bi_{12}O_{17}Cl_2$ -4 sample in Fig. 2g–k exhibit Bi, O, Cl and Ni elements are distributed throughout samples, implying the formation of NiO/ $Bi_{12}O_{17}Cl_2$ hybridization. The above results indicate that 0D/2D NiO/ $Bi_{12}O_{17}Cl_2$ heterojuction is fabricated.

The chemical compositions and elemental valence states of samples were investigated by XPS. Bi 4f XPS spectrum of $Bi_{12}O_{17}Cl_2$ sample in Fig. 3a shows the two characteristic peaks at 164.0 eV and 158.7 eV, which are assigned to Bi^{3+} $4f_{5/2}$ and Bi^{3+} $4f_{7/2}$ states, respectively [43]. Compared to $Bi_{12}O_{17}Cl_2$, these two binding energy peaks in XPS spectrum of NiO/Bi₁₂O₁₇Cl₂-4 sample shift 0.3 eV to high energy direction, respectively, which indicates the strong coupling effect between $Bi_{12}O_{17}Cl_2$ and NiO. In addition, O 2p XPS spectrum of $Bi_{12}O_{17}Cl_2$ in Fig. 3b presents two peaks at 530.9 eV and 529.3 eV,

which attributed to Bi-O bonds and surficial hydroxyl groups (Bi-O-H), respectively [44,45]. From Cl 2p XPS spectrum of Bi₁₂O₁₇Cl₂ in Fig. 3c, the binding energy peaks located at 199.5 eV and 197.9 eV are referred to Cl⁻¹ 2p_{1/2} and Cl⁻¹ 2p_{3/2} states [46]. It is worth noting that the similar shift phenomena are also observed in O 2 P and Cl 2 P XPS spectra of NiO/Bi₁₂O₁₇Cl₂-4 sample, further indicating the intense interaction existed inside NiO/Bi₁₂O₁₇Cl₂ heterojunction. In term of Ni 2p XPS spectrum of NiO/Bi₁₂O₁₇Cl₂-4 sample in Fig. 3d, there are two predominant peaks at 855.4 eV and 873.9 eV, corresponding to Ni 2p_{3/2} and Ni 2p_{1/2} states, while the peaks centered at 860.8 eV and 879.9 eV represented the shake-up satellite peak resulting from the presence of Ni²⁺ cations. [47,48].

The photocatalytic activity of samples was determined by degradation of 2, 4-DCP under the visible light irradiation. As shown in Fig. 4a, the NiO/Bi₁₂O₁₇Cl₂ samples exhibit the better degradation



Fig. 2. SEM images of $Bi_{12}O_{17}Cl_2$ (a, b) and $NiO/Bi_{12}O_{17}Cl_2-4$ (c) samples, TEM images of $Bi_{12}O_{17}Cl_2$ (d) and $NiO/Bi_{12}O_{17}Cl_2-4$ (e) samples, HRTEM image (f) and EDX elemental mappings (g-k) of $NiO/Bi_{12}O_{17}Cl_2-4$ sample.

0.0

Bi₁₂O₁₇Cl₂



Fig. 4. Dynamic curves (a) and plots of ln(C₀/C) versus time (b) of 2, 4-DCP over different samples, TOC removal rate of 2, 4-DCP over Bi₁₂O₁₇Cl₂ and NiO/ Bi₁₂O₁₇Cl₂-4 samples within 180 min (c) and absorbance variations of 2, 4-DCP solution within 180 min (d).

260

NiO/Bi,,O,,Cl,-4

280 300 32 Wavelengh (nm)

320

340

activity than Bi₁₂O₁₇Cl₂. The optimal degradation rate reaches to 89.3% over the NiO/Bi₁₂O₁₇Cl₂-4 sample. In addition, Fig. 4b shows that all degradation reactions are in great agreement with the quasi-first-order kinetic feature [49–51]. The rate constant of 2, 4-DCP degradation over NiO/Bi₁₂O₁₇Cl₂-4 sample (0.0116 min⁻¹) is about 3.2 and 3.7 times than that of NiO (0.0036 min⁻¹) and Bi₁₂O₁₇Cl₂ (0.0031 min⁻¹), respectively. Furthermore, Fig. 4c shows the TOC removal rates of 2, 4-DCP within 180 min over Bi₁₂O₁₇Cl₂ and NiO/Bi₁₂O₁₇Cl₂-4 samples. It is obvious that the mineralization rate of the latter (79.4%) is much higher than that of the former (39.1%). Moreover, the absorbance of 2, 4-DCP solution is distinctly decrease with prolonging reaction time, further suggesting that it may be decomposed into small molecules/ions, CO₂ and H₂O [52]. The results indicate that the fabrication of 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction enhances the photocatalytic degradation activity dramatically.

In order to evaluate photostability and recyclability of 0D/2D NiO/ Bi₁₂O₁₇Cl₂ heterojunction, the recycling degradation experiments of 2, 4-DCP were performed. As shown in Fig. 8a, the degradation rates of 2, 4-DCP over NiO/Bi₁₂O₁₇Cl₂ sample have no obvious reduction after six successive photocatalytic reactions, which demonstrate the 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction possesses the outstanding stability and reusability. It is further confirmed by XRD of NiO/Bi₁₂O₁₇Cl₂-4 sample before and after photocatalytic reaction. XRD pattern of NiO/ Bi₁₂O₁₇Cl₂-4 sample in Fig. 5b displays that the characteristic diffraction peaks has almost no variation after six consecutive cycle reactions, which further proves that it has the superior stability.

The transfer and separation efficiency of photogenerated electronhole pairs of samples can be investigated by transient photocurrent responses. As displayed in Fig. 6a, the Bi12O17Cl2 and NiO/Bi12O17Cl2-4 samples both show the stable photocurrent responses under the visible light irradiation [53]. The photocurrent response of NiO/Bi12O17Cl2-4 sample is far higher than that of Bi₁₂O₁₇Cl₂, indicating that the modification effect of NiO nanodots on Bi12O17Cl2 nanosheets significantly promotes the transfer and separation efficiency of charge carriers. Furthermore, the electrochemical impedance spectroscopy (EIS) is an effective to reveal the interface transfer efficiency of charge carriers [54]. In Fig. 6b, the smaller arc radius is observed on NiO/Bi₁₂O₁₇Cl₂-4 sample, implying that it has the higher charge mobility and separation ability of charge cariers than Bi12O17Cl2. Therefore, the transfer and separation efficiency of photogenerated electron-holes are distinctly improved by the fabrication of 0D/2D NiO/Bi12O17Cl2 heterojunction, resulting in the enhanced photocatalytic activity for degrading 2, 4-DCP.

Fig. 7a displays the N₂ adsorption-desorption isotherms of $Bi_{12}O_{17}Cl_2$ and $NiO/Bi_{12}O_{17}Cl_2$ -4 sample, where they possess hysteresis loops at the range of 0.8–1.0 (P/P₀) in accordance with type H3 and the adsorbing capacity of NiO/Bi₁₂O₁₇Cl₂-4 sample is slightly decrease than

that of $Bi_{12}O_{17}Cl_2$. From Fig. 7b, the pore diameter distributions of $Bi_{12}O_{17}Cl_2$ and $NiO/Bi_{12}O_{17}Cl_2-4$ samples exhibit the mesoporous feature centered about 35 nm, which may result from the stacking of $Bi_{12}O_{17}Cl_2$ nanosheets. Meanwhile, the $NiO/Bi_{12}O_{17}Cl_2-4$ sample possesses a relatively low specific surface area ($8.49 \text{ m}^2 \text{ g}^{-1}$) compared with $Bi_{12}O_{17}Cl_2$ ($11.6 \text{ m}^2 \text{ g}^{-1}$), The results suggest that the boosted photocatalytic activity has little to do with specific surface area, pore diameter and absorptivity, and indirectly indicate that the improved transfer and separation efficiency of photogenerated charge carriers is main influence factor on the photocatalytic activity.

The capture tests are investigated in detail to detect the generated active species during the degradation reaction. As can be seen from Fig. 8 a–b, the degradation reactions of 2, 4-DCP are all obviously restrained when tetraacetic acid ethylenediamine disodium (EDTA-2Na), ascorbic acid (VC) and isopropyl (IPA) are used as trapping reagents to capture h^+ , $\bullet O_2^-$ and $\bullet OH$ in the photocatalytic reaction process, and the degradation rates of 2, 4-DCP are 10.6%, 5.0% and 82.2%, respectively, which indicate h^+ and $\cdot O_2^-$ are major active species and the influence of •OH is negligible. Moreover, $•O_2^-$ and •OH generated on NiO/Bi₁₂O₁₇Cl₂-4 sample are detected by ESR technology. From Fig. 8c, the intensity of DMPO- \cdot O₂⁻ produced over NiO/Bi₁₂O₁₇Cl₂-4 sample is far stronger than that over Bi12O17Cl2, which indicates that the formation of 0D/2D NiO/Bi $_{12}O_{17}Cl_2$ heterojunction immensely promotes the production of $\cdot O_2^{-}$ active species. Meanwhile, no detecting characteristic signals of DMPO-•OH over Bi12O17Cl2 and NiO/Bi12O17Cl2-4 sample (Fig. 8d), it suggests that •OH cannot be generated in the degradation process.

The UV-vis DRS is used to analyze the light absorption property of samples. As presented in Fig. 9a, the Bi₁₂O₁₇Cl₂ and NiO/Bi₁₂O₁₇Cl₂-4 sample displays the superior visible light absorption ability. Meanwhile, according to the Tauc formula $(ahv) = A(hv - E_g)^{n/2}$, the plots of $(ahv)^2$ versus hv (n = 1) is executed based on the direct band gap characteristic of Bi₁₂O₁₇Cl₂ and NiO [35,47]. As shown in the Fig. 9b, the band gap values (E_g) of Bi₁₂O₁₇Cl₂ and NiO are estimated to be 2.87 eV and 3.29 eV, respectively. It is noteworthy that Bi12O17Cl2 and NiO samples all form midgap levels of 2.62 eV and 2.30 eV due to the defects created in the preparation process possibly [55], which avails the visible light response. Additionally, the bandgap and midgap of Bi₁₂O₁₇Cl₂ have no changes after modification of a spot of NiO. Moreover, to further identify the energy band position, the flat band potentials of Bi₁₂O₁₇Cl₂ and NiO samples were carried out. The positive slopes of Mott-Schottky curves (Fig. 9c-d) imply the Bi₁₂O₁₇Cl₂ and NiO samples are n-type semiconductors, and their flat band potentials are -0.73 V and 0.25 V (vs. Ag/AgCl), respectively. So, the conduction band (CB) potentials of Bi₁₂O₁₇Cl₂ and NiO sample are approximately -0.53 eV and 0.45 eV; the valence band (VB) potential are calculated to be 2.34 eV and 3.74 eV; as well as the intermediate levels are -0.28 eV and 1.44 eV (vs. NHE),



Fig. 5. Cycle degradation dynamic curves of 2, 4-DCP over NiO/Bi₁₂O₁₇Cl₂-4 sample (a), XRD patterns of NiO/Bi₁₂O₁₇Cl₂-4 sample before and after six cycle reactions.



Fig. 6. Transient photocurrent responses (a) and EIS Nyquist plots (b) of Bi₁₂O₁₇Cl₂ and NiO/Bi₁₂O₁₇Cl₂-4 samples.

respectively [55-60].

Moreover, HPLC-MS technology was used to analyze the intermediates in the degradation of 2, 4-DCP over NiO/Bi₁₂O₁₇Cl₂-4 sample [61]. According to the detected specific charge in mass spectra (Fig. 10), the possible reasonable degradation pathway of 2, 4-DCP is proposed (Fig. 11). We know that the ortho- or para- Cl of 2, 4-DCP are easily replaced by \cdot O₂⁻ through addition reaction. Therefore, \cdot O₂⁻ firstly attacks and removals ortho-Cl is considered to produce parachlorophenol superoxide radicals (*m*/*z* = 159, B) and transform into 4chloro-catechol (*m*/*z* = 143.5, C) [62]. With prolonging to reaction time, 4-chloro-catechol is further oxidized to 2-hydroxyphenol (*m*/ *z* = 109, D). Finally, accompanied by ring-opening reaction of 2-hydroxyphenol, maleic acid (*m*/*z* = 115, E) and oxalic acid (*m*/*z* = 89, F) are produced, which are mineralized into CO₂ and H₂O with the reaction going on.

Based on the aforementioned experimental results, the photocatalytic reaction mechanism of 2, 4-DCP over 0D/2D NiO/Bi12O17Cl2 heterojunction is proposed (Fig. 12). UV-vis DRS reveals that the midgaps are created within the band gap of NiO and Bi₁₂O₁₇Cl₂, which are 1.44 eV and -0.28 eV, respectively, suggesting that electrons on VB preferentially transfer to the intermediate levels under the visible light irradiation. The electrons on the intermediate level of Bi12O17Cl2 can oxidize the O2 molecules in the solution to generate •O2⁻ instead of NiO due to the standard redox potential of O2/+O2- with -0.046 eV [63]. The VB potential of NiO and Bi12O17Cl2 are 3.74 eV and 2.34 eV, respectively, which implies that the holes on the VB of NiO rather than Bi₁₂O₁₇Cl₂ can oxidize H₂O to form •OH owning to the standard redox potential of H₂O/•OH with 2.7 eV [23]. As a result, after NiO nanodots decorate on Bi12O17Cl2 nanosheets, Z-scheme heterojunction should be constructed between them. Therefore, when 0D/2D NiO/Bi12O17Cl2 heterojunction is exposed to the visible light, the electrons on VB of NiO and Bi₁₂O₁₇Cl₂ preferentially migrate to the intermediate levels along with holes generation on their VB, respectively. Then, photogenerated electrons on CB of NiO and holes on VB of Bi₁₂O₁₇Cl₂ recombine rapidly at their interfaces, which can tremendously improve the transfer and separation efficiency of charge carriers. Afterwards, the plenty of photogenerated electrons accumulated on Bi₁₂O₁₇Cl₂ react with the O₂ molecules dissolved in water to produce •O₂-. Finally, the holes remained on NiO and •O₂- will directly oxidize 2, 4-DCP to small molecules/ions, CO₂ and H₂O.

4. Conclusions

In conclusion, a 0D/2D NiO/Bi12O17Cl2 heterojunction was synthesized in a facile hydrothermal process followed by simple calcination. The in-situ decoration of NiO nanodots on Bi12O17Cl2 nanosheets implies the formation of compact heterostructure, which is in favor of transfer and separation of charge carriers. The photocatalytic degradation performance of 2, 4-DCP over 0D/2D NiO/Bi12O17Cl2 heterojunction was significantly higher than those of single NiO and Bi12O17Cl2 under the visible light irradiation. The optimal NiO/ Bi12O17Cl2-4 sample shows the highest degradation rate of 2.4-DCP reaching up to 89.29% within 180 min, and the corresponding reaction rate constant (0.0116 min $^{-1}$) was 3.2 and 3.7 times higher than that of single NiO (0.0036 min⁻¹) and $Bi_{12}O_{17}Cl_2$ sample (0.0031 min⁻¹). The photocatalytic reaction mechanism reveals the •O₂- and holes are main active species and the possible degradation process of 2, 4-DCP is also discussed. The enhanced photocatalytic performance derives from the formation of Z-scheme heterostructure between NiO and Bi₁₂O₁₇Cl₂.



Fig. 7. N₂ adsorption-desorption isotherms (a) and pore diameter distributions (b) of Bi₁₂O₁₇Cl₂ and NiO/Bi₁₂O₁₇Cl₂-4 sample.



Fig. 8. Degradation dynamic curves (a) and degradation rates (b) of 2, 4-DCP over NiO/Bi₁₂O₁₇Cl₂-4 sample when adding different trapping reagents, ESR spectra of DMPO- \cdot O₂⁻ (c) and DMPO- \cdot OH (d) over NiO/Bi₁₂O₁₇Cl₂-4 sample.



Fig. 9. Normalized UV-vis DRS (a) and plots of $(ahw)^{1/2}$ versus (hw) (b) of Bi₁₂O₁₇Cl₂ and NiO samples, Mott-Schottky plots of Bi₁₂O₁₇Cl₂ (c) and NiO (d) samples.



Fig. 10. Mass spectra of 2, 4-DCP over NiO/Bi₁₂O₁₇Cl₂-4 sample at 0 min (a), 90 min (b) and 180 min (c), respectively.

Declaration of Competing Interest

Acknowledgments

None.

This work was supported by the NSFC-Shanxi Coal Based Low Carbon Joint Fund (U1810117), National Natural Science Foundation of China (21606114, 21546006, 21878131), Postdoctoral Science Foundation of China (2017M611712, 2017M611717), Jilin province



Fig. 11. Possible intermediate products at the degradation process of 2, 4-DCP over NiO/Bi12O17Cl2-4 sample.



Fig. 12. Possible photocatalytic degradation mechanism of 2, 4-DCP over 0D/2D NiO/Bi₁₂O₁₇Cl₂ heterojunction.

science and technology innovation center construction project (20180623042TC) and Scientific Research Foundation for Senior Talent of Jiangsu University (17JDG020).

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