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Electron beam irradiation treatment of Ag/Bi₂WO₆/CdWO₄ heterogeneous

material with enhanced photocatalytic activity

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An efficient ternary $Ag/Bi_2WO_6/CdWO_4$ heterostructure material was prepared through a facile hydrothermal route. The in-situ loading precisely regulated the distribution of silver nanoparticles on the heterojunction surface. Besides, electron beam irradiation was used for artificially creating interface defects to the material, so the specific surface area of the material was increased, the introduction of defects was conducive to the migration of catalytic active substances on the surface of the material. Under visible light irradiation, the degradation efficiency of the heterostructure material was improved obviously. Within 20 min, the removal efficiency of the treated material for carmine could reach about 100% (50 mL, 50 mg/L), while, that for hexavalent chromium (Cr⁶⁺) could reach about 100% (50 mL, 10 mg/L) within 90 min. In addition, the results showed that, 4% Ag load rate had the best improvement on the photocatalytic performance of the ternary

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heterostructure material before and after treatment, no matter in the degradation process of carmine, Cr6+ or rhodamin B (RhB). Proper amount of supported in-situ nano-silver induced the resonance of the plasma on the catalytic interface and synergized with Bi³⁺ to improve the catalytic efficiency. PL, DRS and XPS results proved that ternary heterostructure could effectively inhibit the rapid recombination of electron hole pairs of Ag/Bi₂WO₆/CdWO₄. As for the role of electron beam irradiation, it could improve the content of free hydroxyl groups on the material surface and enhance catalytic capacity of Ag/Bi₂WO₆/CdWO₄ heterogeneous material. A feasible reaction pathway and photocatalytic mechanism for the degradation of carmine was investigated by gas chromatography-tandem mass spectrometry (GC-MS), and the main role of •OH in the catalytic process was obtained by using different scavengers.

KEYWORDS: Ag/Bi₂WO₆/CdWO₄; Hierarchical heterostructure; In-situ silver loading; Electron beam irradiation; High efficient degradation

1. Introduction

With the development of the times, ecosystem contains a gradual accumulation of pollutants.^{1–5} As a nuisance to the world, water pollution has a huge impact on the ecosystem, mainly caused by organic pollutants and inorganic heavy metal pollutants in the water.⁶⁻⁹ Carmine, also known as scarlet and bright scarlet, is one of the most widely used azo dyes in China at present. Dyeing wastewater is very easy to carry carmine into the material flow of biological chain. It can accumulate in vivo, easily produce free radicals after oxidation, and produce a series of reactive oxygen species (ROS) with the metabolism of substances in vivo, which will lead to serious oxidative damage to DNA eventually.¹⁰⁻¹¹ At the same time, the production process of carmine will be contaminated by arsenic, lead, chloride and other substances, which will further aggravate the harm to organisms. As one of the heavy metal ions with the highest content in the wastewater of mining, metallurgy and machinery manufacturing industries, hexavalent chromium (Cr^{6+}) is carcinogenic and mutagenic to organisms, and extremely easy to damage human digestive and

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urinary systems. In contrast, trivalent chromium (Cr³⁺) is less toxic and less fluidity and water development of the port 10.1039/C9NJ02571E bioavailable. ^{12–16} In the natural environment, Cr⁶⁺ is hardly self-degradable and cannot be broken down by conventional water treatment methods. ^{17–18} Seeking an efficient conversion of chromium ions is particularly critical. Therefore, it is very important to find an environmentally friendly and efficient way to degrade pollutants in energy utilization.¹⁹

Since the discovery of photocatalysis by Fujishima and Honda in 1967, the study of photodegradation has aroused a worldwide research upsurge. 20-23 In order to improve the photocatalytic properties of titanium dioxide-based photocatalysts, visible-light-driven photocatalysts have attracted much attention. ²⁴⁻²⁶ As the simplest oxidation Aurivillius, Bi₂WO₆ is found to have a narrow band gap and thus can respond to visible light. At the same time, it has unique structure and good stability, and has been widely studied in the degradation of organic pollutants.^{27–29} However, the simple Bi₂WO₆ has the problems of fast charge recombination and low light absorption efficiency, which will hinder the photocatalytic reaction. On the other hand, the morphology of Bi₂WO₆ obtained in the synthesis process is difficult to control.³⁰ CdWO₄ is also a type of tungstate that can be widely used as a variety of functional materials in different fields. It has the advantages of high refractive index, low radiation damage, large luminous intensity and excellent flicker performance, etc.³¹ Nevertheless, its wide band gap limits its practical application.³² It shows that the load of Bi₂WO₆ with CdWO₄ as the matrix may make up the power shortage of the two sheets to a certain extent. ^{33–34} Silver nanoparticles can be usually used as a bridge material to connect two materials or form an electronic sink,³⁵ such as Ag₃PO₄/Ag/BiVO₄,³⁶ Ag/Bi₂WO₆/GO³⁷ and Ag@AgI/CdWO₄.³² Some experimental data show that the introduction of silver can make the heterogeneous materials have better catalytic effect. In short, silver can induce plasma resonance of binary heterojunction materials, which can be used as an electronic medium to increase the electron transmittance and accelerate the separation efficiency of photogenerated carriers. Thus, ternary heterojunction will have better performance.^{38–39} As a new material treatment method, electron beam irradiation has been favored in food preservation, desulfurization and denitrification, and wastewater treatment. 40-43 Here, the electron beam irradiation was applied to the treatment of photocatalysts creatively. By modifying

the surface of materials with high-energy electron beam, the interface defects of materials werkew Article Online increased artificially. These defects will enhance the specific surface area of the material and improve the adsorption capacity to pollutants. ^{44–45} Meanwhile, the defects will expose more active oxygen vacancies, and make a better catalytic ability of the materials.⁴⁶ When the electron beam is processed, there is a probability of tunneling, which can modify the interior of the material to a certain extent and provide a new and feasible method for the material processing industry.⁴⁷

In this paper, a novel ternary heterostructure material based on Bi₂WO₆/CdWO₄ was synthesized by a simple hydrothermal method with in-situ loading silver, and then was modified by electron beam irradiation for artificially creating interface defects. By using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), Photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), UV-visible diffuse reflectance spectroscopy (UV-vis DRS), N₂ adsorption and desorption isotherm (BET), Electron spin resonance experiments (ESR), Electrochemical impedance spectroscopy (EIS), Photocurrent (PC) and other means, the chemical composition, morphology and optical properties of the material were explored. The catalytic ability of the material was evaluated by degradation of carmine, Cr⁶⁺, and rhodamin B (RhB) under visible light. The optimal Ag loading was explored and tested for cycle performance. Through the analysis of the experimental data, a viable catalytic pathway for the degradation of pollutants by materials was proposed. This study provided a newly high-performance catalyst for degrading both organic pollutants and inorganic heavy metal pollutants and proposed a new material interface treatment method for environmental green restoration.

2. Experimental

2.1 Chemical and regents

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), cadmium chloride (CdCl₂·2.5H₂O), sodium tungstate (Na₂WO₄·2H₂O), ethylene glycol(C₂H₆O₂), ethylenediamine (C₂H₈N₂), triaminopropyl triethoxysilane (KH550), glyoxalic acid (C₂H₂O₃), silver nitrate (AgNO₃), triethanolamine (TEOA), anhydrous ethanol (C₂H₅OH), carmine, rhodamine B (RhB), and potassium dichromate (K₂Cr₂O₇) were bought from National Medicine Group Chemical Reagent Co. LTD. Deionized water (DIW) was supplied through a Milli-Q water purification system and used in all experiments.

2.2 Catalyst synthesis

Figure 1 shows the following material synthesis steps.



Figure 1 Schematic diagram of ABC synthesis and electron beam irradiation treatment.

2.2.1 Synthesis of CdWO₄

When $CdWO_4$ was prepared, 4 mmol $CdCl_2 \cdot 2.5H_2O$ and 0.2 mL ethylenediamine were dissolved in 20mL deionized water. 20 mL of an aqueous solution containing 10 mmol of $Na_2WO_4 \cdot 2H_2O$

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2.2.2 Synthesis of Bi₂WO₆/CdWO₄

In this experiment, 0.4 mmol Bi(NO₃)₃·5H₂O and 0.2 mmol Na₂WO₄·2H₂O were added to 30 mL ethylene glycol and then were mixed into the reactor. 1 mmol CW was added to the forementioned solution. The mixture solution in the reaction kettle was hydrothermally treated at 160 °C for 24 h. The product was got for further usage, and was named as BCW.

2.2.3 Synthesis of Ag/Bi₂WO₆/CdWO₄

Ag/Bi₂WO₆/CdWO₄ materials were prepared by in-situ formation. BCW was dispersed in deionized water, and heated under the temperature of 60 °C. Then, 10 mL of KH550 was added to the mixture solution in the condition of mechanical stirring. After 6 h of reaction, the product was washed by centrifugation for 3 times. BCW particles with amino groups on the surface were dispersed in 100 mL deionized water and 10 mL glycolic acid was added. The aforementioned solution was magnetically stirred at the temperature of 40 °C for 6 h. In this process, the amino group on the surface of the material reacted with glyoxylic acid to precisely control the distribution of the aldehyde group on the surface of the material. The product was centrifuged for 3 times with 100 mL deionized water as solvent. Silver ammonia solution prepared by AgNO₃ was added to a certain amount of the above product under mechanical stirring. Then the volume

 was fixed at 300 mL. The solution changed from colorless to black after 3 h of reaction in a 40¹⁰C^{9NJ02571E} water bath. The product was centrifuged for 10 min at a speed of 11000 rpm in a centrifuge, washed with deionized water for 3 times, and then dried overnight under natural conditions to obtain the catalyst. By controlling the mass ratio of AgNO₃ and BCW to adjust the load of Ag, the catalysts with a load of 2%, 4% and 6% of Ag were accurately prepared and named as ABC-2, ABC-4 and ABC-6, respectively.

2.2.4 Electron beam irradiation treatment

ABC-4 samples were uniformly dispersed on the glass sheet. And then, the materials were irradiated with electron beam. The total radiation dose was 100 kGy, and the radiation dose rate was 66.6 kGy/s. In this way, the material was processed into an electron beam irradiation material. Finally, the samples were collected and named as EABC.

2.3 Characterization method

The crystal structures of different photocatalysts were studied by XRD (Rigaku Rotaflex, Japan). The morphology and structure of the samples were determined by SEM (FEI QuANTA 200, USA) and TEM (Tecnai G2F20-TWIN, USA). The element composition and content of photocatalysts were determined by energy spectrometer (EDS). The surface element composition was determined by XPS (Thermo Fisher Scientific-k-alpha 1063, UK). Chemical bonds on the surface of the material were detected by FT-IR (Thermo Scientific Nicolet IS 50, USA). BET (SSA7300, China) was used to determine the specific surface area and void volume of the material. Through the PL (FS5–TCSPC, UK), the utilization efficiency of photogenerated carriers was tested. To investigate the optical properties of different catalysts, the UV-vis DRS for the 200-800 nm region was recorded on the UV-vis spectrophotometer detector (Cary 300, USA).

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The photodegradation ability of EABC was analyzed by carmine, rhodamine B (RhB) and Cr⁶⁺ degradation experiments under visible light. A 500 W xenon lamp was employed as the light source with a 420 nm cut filter (light intensity: 100 mW·cm²).⁴⁸ In the catalytic experiment of carmine, 10 mg photocatalyst was dispersed in carmine solution (50 mL, 50 mg/L). In Cr^{6+} catalytic experiment, 10 mg photocatalyst was dispersed in Cr^{6+} solution (50 mL, 10 mg/L). In RhB catalytic experiment, 10 mg photocatalyst was dispersed in RhB solution (50 mL, 10 mg/L). In the performance test, the mixture of catalyst and degradation product was stirred in darkness for 30 min to achieve the adsorption-desorption equilibrium between catalyst and degradation product. Samples were collected at regular intervals. Then, the samples were centrifuged on a 11000 rotary centrifuge for 10 min. The remaining particles were filtered by 0.45 µm filter. The corresponding concentration of catalytic substrates was determined by ultraviolet spectrophotometer. The maximum absorption wavelength of carmine, Cr⁶⁺ and RhB were 507 nm, 542 nm and 554 nm, respectively.

3. Result and discussion

3.1 Characterization

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3.1.1 XRD analysis

XRD reflects a series of information about the crystalline properties of prepared samples, as shown in the Figure 2. It could be noticed that pure CdWO₄ powder was in good agreement with the body-centered monoclinic phase of CdWO₄ (JCPDS NO. 14-0676). The XRD spectrum of $Bi_2WO_6/CdWO_4$ was obviously different from that of single CdWO₄. The clear characteristic peaks of Bi_2WO_6 were easy to see at 20 of 28.3°, 32.7° and 56.0°, corresponding to (131), (060)

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and (133) crystal planes of cubic Bi₂WO₆ (JCPDS No. 39-0256).⁴⁹ Owing to the small dosage (C9NJ02571E amount of Ag in the materials, the characteristic peaks of Ag species were weak. The peaks of the Ag phase (JCPDS NO. 04-0783) could be found in Ag/Bi₂WO₆/CdWO₄ before and after electron beam irradiation. There was no difference in peak strength between them. Notably, no additional crystalline phases were found in all images and no sharp diffraction peaks were observed, which meant that few impurities were produced during the manufacturing process. The intensity of the peaks did not differ significantly before and after electron beam irradiation, indicating that the technique could not cause damage to the crystal form of the material interface.



Figure 2 XRD pattern of original CW, BCW, ABC and EABC (a), and the amplified images from 26 to 39 degree (b).

3.1.2 SEM analysis

In order to accurately grasp the shape and detailed structure of the material, SEM was detected with the results depicted in Figure 3. It can be seen from Figure 3a that the morphology of pure CdWO₄ sample was rod-like structure and the crystal surface was smooth. Figure 3b reflected that the lamellar Bi₂WO₆ was loaded on pure CdWO₄. This lamellar structure provided the material with larger specific surface area and more active sites. The in-situ silver-carrying materials were

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shown in Figure 3c. Through in-situ regulation, $-NH_2$ and -CHO successively coated on the surface of the material, so that silver nanoparticles could be uniformly loaded on the material. Nano-sliver could provide a high specific surface area for the material and reduce the hole-electron recombination in the catalytic process by bridging. The structure of the sample treated by electron beam irradiation (Figure 3d) was similar to that of the sample before treatment. This technology did not cause damage to the material matrix. For different Ag loadings, SEM visually reflected the distribution of nano-silver (Figure 4). As the amount of AgNO3 increased, it could be clearly seen that, nano-silver particles on the surface of the material increased. Satisfactorily, the samples in the synthesis process and the finished product stage havd smaller particle size, about 1 µm in diameter and about 5 µm in length. Their morphologies were more regular and uniform, showing rod-like structure.





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Figure 4 SEM of ABC-2 (Ag/BCW mass ratio of 2%) (a), ABC-6 (Ag/BCW mass ratio of 6%)(b), ABC-4 (Ag/BCW mass ratio of 4%) (c) and EABC (ABC-4 irradiated by electron beam) (d).

3.1.3. TEM, EDS analysis

TEM technology further confirmed the successful synthesis of Ag/Bi₂WO₆/CdWO₄ nanorods with regular morphology and clear structure. CdWO₄, Bi₂WO₆ and Ag corresponded to (331), (111) and (111), respectively. The clear matrix-load boundary could be clearly observed (see Figure 5a) before irradiation, while the boundary disappeared after electron beam irradiation (see Figure 5b). The reason might be that high-energy electrons made the load looser and more densely covered, or Ag oxidation was caused in the process of treatment, resulting in the newly forming Ag₂O without definite form. The absence of the clear lattice in the enlarged image also provided evidence for this conclusion. TEM results were in good agreement with the SEM micrograph. The high-resolution image showed that the crystal form of the sample was complete. The

corresponding lattice parameters directly reflected the related properties of the material. EDS wakew Article Online used to analyze the elements in Ag/Bi₂WO₆/CdWO₄ nanocomposite, and the results were shown in Figure 5c. Ag, Bi, Cd, W and O elements coexisted in the materials, proving the formation of corresponding substances. What we could see was that the Ag load was about 3.66%, which was lower than the theoretical value of 4%. The possible reason was that the silver ammonia ions bound to the aldehyde group rapidly during the formation of in situ silver, which resulted in partial aldehyde group occlusion. The SEM, TEM and EDS results had the good coherence with the analysis of XRD.



Figure 5 TEM of ABC-4 (a), EABC (b) and the SEM EDS of ABC-4(c).

3.1.4. XPS analysis

Elemental states of the composites before and after electron beam irradiation were studied by

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XPS. Full spectrum (0–1300 eV) showed that carbon, bismuth, cadmium, tungsten, $shVe1^{0}hMd^{2/C9N302571E}$ oxygen existed in the materials before and after irradiation, as shown in Figure 6a. The peak value of carbon belonged to the XPS instrument itself. In order to accurately analyze the elemental states, the amplified spectrum of the Ag 3d, Bi 4f and O 1s were employed. Two main peaks of Bi 4f at 164.90 eV and 159.60 eV belonged to Bi $4f_{5/2}$ and Bi $4f_{7/2}$, corresponding to Bi³⁺ in Ag/Bi₂WO₆/CdWO₄ crystalline structure. The specific binding energy decreased after irradiation, possibly due to the change of crystal form of Bi³⁺ (Figure 6b). As for Ag 3d (Figure 6c), the characteristic peaks 373.90 eV and 367.90 eV represented the electron orbitals of Ag $3d_{3/2}$ and Ag $3d_{5/2}$, respectively. After electron beam irradiation, the specific binding energy of Ag has changed. Both the Ag $3d_{3/2}$ and Ag $3d_{5/2}$ electron orbits have increased, so was the O 1s at 529.80 eV. It could be speculated that Ag⁺ was produced after electron beam irradiation and combined with O to form Ag₂O.



Figure 6 XPS result of ABC and EABC: Survey scan (a), Bi 4f (b), Ag 3d (c), and O 1s (d).

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3.1.5 FT-IR, BET analysis

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In order to evaluate the chemical structure of photocatalyst, Figure 7a showed the FT-IR spectral information of recorded ABC and EABC. Obviously, compared with the material without electron beam irradiation, the peak intensity of 3411 cm⁻¹ was greatly improved after irradiation. And the peak corresponded to the free hydroxyl (•OH). Therefore, after the processing of electron beam irradiation, the number of free hydroxyl groups on the surface of the material could be increased, thus enabling material interface on the catalytic degradation rate of ascension. The peak intensity at 1626 cm⁻¹ has also increased. It might be that the high-energy electron beam exposed KH550 as an azo agent. The corresponding C=O characteristic peak was also in good agreement with the KH550 azo group. Through BET analysis (Figure 7b), the Ag/Bi₂WO₆/CdWO₄ that irradiated by electron beam displayed a higher surface area (25.61 m²/g), pore size (3.04 nm) and total pore volume (0.013 cm³/g), compared to the material without treatment (surface area = 23.29 m²/g, pore size = 2.15 nm, total pore volume = 0.010 cm³/g), suggesting that the electron beam irradiation could introduce interface defects into the material and improve the specific surface area of the material, ⁴⁸which was in good accordance with the adsorption results in darkness.



Figure 7 FT-IR spectra of ABC and EABC(a) and data of BET (b).

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3.1.6 PL analysis

To further confirm the influence of the change of material interface on the catalytic capacity of materials, photoluminescence spectra (PL) of various catalysts was determined. The higher PL intensity meant the less photoexcited carriers joining in catalytic reaction. It can be seen from Figure 8a that the emission intensity of the samples decreased in the following order: EABC < ABC-4 < ABC-6 < ABC-2 <BCW < CW, indicating that the charge recombination was inhibited by the introduction of in-situ silver, and the catalytic performance of the material was improved best when the Ag loading was 4%. Simultaneously, electron beam irradiation caused interface defects on the surface of the material, which exposed more active sites and further improved the catalytic ability of the material.

3.1.7 DRS analysis

For photocatalysts, the optical absorption property might be one of the most important factors in determining their photocatalytic performance. Therefore, the UV–vis diffuse reflection spectra (UV–Vis DRS) of CW, BCW, ABC-2, ABC-4, ABC-6 and EABC were conducted, and the abrupt change of spectra showed that the absorption of light was not caused by the transition of impurity level, but by the transition of energy level. According to Kubelka-Munk equation, the energy gaps of various photocatalysts could be obtained. The band gaps of CW, BCW, ABC-2, ABC-4, ABC-6 and EABC were 3.40 eV, 2.85 eV, 3.00 eV, 3.04 eV, 3.20 eV and 2.39 eV, respectively (Figure 8b). The results showed that the band gap of the material increased after the loading of Ag, but its catalytic capacity did not decrease. The introduction of Ag increased the utilization efficiency of the material on photogenic carriers, so the influence of band gap promotion could be ignored. After electron beam irradiation, the composite of electron hole pair was inhibited, the

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band gap was reduced. The electron transmission distance was shortened, resulting in that the photocatalytic ability of the material was improved.

3.1.8 PC and EIS analysis

The photocurrent response test verified that EABC has higher current response capability than ABC under the same conditions. The defects in electron beam irradiation fabricated at the material catalytic interface were favorable for charge separation, which means better catalytic performance. What's more, electrochemical impedance spectroscopy (EIS) testing can be an effective method for detecting the separation and transfer of electron/hole pairs. The data was processed to obtain Figure 8d. The smaller radius of the arc in the figure meant the higher the charge transfer efficiency of the material.⁵⁰ So, the results clearly showed that EABC has better photoelectric performance than ABC.



Figure 8 PL spectra of CW, BCW, ABC-2, ABC-4, ABC-6 and EABC (a) and energy gaps of the

pure CW, BCW, ABC-2, ABC-4, ABC-6 and EABC determined by Tauc plot (b), Photocurrent

(PC) responses of ABC-4 and EABC (c) and Electrochemical impedance spectroscopy (EIS)

3.2 Photocatalytic results analysis

3.2.1 Photocatalytic behavior of different materials

The degradation of carmine, Cr⁶⁺ and RhB by CW, BCW, ABC-2, ABC-4, ABC-6 and EABC were studied. The light utilization ability and stability of the prepared samples were evaluated in combination with practical applications. As shown in Figure 9a, the degradation of carmine by different samples was a function of light time. The carmine was first stirred under dark conditions for 30 min to reach the adsorption-desorption equilibrium with the catalysts. The concentration of carmine decreased with the increase of light time. Within 60 min of visible light irradiation, the removal rate of pure CdWO₄ was only 21.9%, and Bi₂WO₆/CdWO₄ was about 70%. The removal rate of Ag loaded with 4% content could reach 100% within 30 min after illumination. The degradation capacity of the material was further improved after electron beam irradiation. In addition, the ternary heterostructure improved the utilization rate of electron-hole pairs.⁵¹ The above results showed that Ag/Bi₂WO₆/CdWO₄ with 4% Ag content after electron beam irradiation had the best visible light utilization ability. There were two aspects to the improvement of the catalytic ability. One was that the surface area of the material was increased after electron beam irradiation, which could be visually observed from the BET result. Electron beam irradiation improved the adsorption capacity obviously, so that the surface contact area between the degradation product and the catalyst was larger. Thus, active catalytic materials could be used more efficiently. The other one was electron beam irradiation increased the amount of free

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hydroxyl group and reactive oxygen vacancy on the material interface, and the active substances^{10,10,1039/C9NJ02571E} involved in the catalytic process were enhanced.

Photostability is a crucial parameter to assess a sample practical application. The cycling experiment for carmine degradation by ABC-4 was performed to evaluate its stability. The result revealed the photocatalytic performance of ABC-4 almost did not display any palpable reduction for carmine removal after five recycling runs for carmine removal. It confirmed that the ABC-4 heterojunction was not easily photocorroded during the reaction process, which further suggested that the ABC-4 was considerably stable. Meanwhile, the light stability of EABC to carmine was analyzed, and also conducted for five cycles (Figure 9d). According to the results, the defect of EABC on the interface did not affect the light stability of the material itself. Such a new treatment technology which could improve the catalytic properties of materials was bound to have a broad application prospect in the future.



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Figure 9 The degradation of carmine (a), Cr⁶⁺ (b) and RhB (c) by CW, BCW, ABC-2, ABC-2, ABC-4, ABC-4, ABC-6 and EABC, cycling experiments for carmine degradation (d) by ABC and EABC (conducting in the same experiments condition).

3.2.2 The exploration of main active substances in photocatalytic process

The addition of Ag in Ag/Bi₂WO₆/CdWO₄ ternary heterojunction could effectively inhibit the electron-hole pair recombination, which might lead to more kinds of free radicals. In order to find the major active substances that have catalytic degradation ability in the reaction process, isopropanol (IPA), ethylenediamintetraacetic acid disodium (EDTA-2Na) and 1,4 -benzoquinone (BQ) were used as quencher for hydroxyl radical (•OH), hole (h^+) and superoxide radical (•O₂⁻), respectively.^{36, 52} The catalytic degradation of carmine was carried out as a reference, as shown in Figure 10a. The addition of 1 mmol IPA in the photocatalytic process greatly reduced the catalytic efficiency of the material. It could be known that •OH was the main active material in the degradation process. However, after the addition of 1 mmol BQ, the degradation efficiency of the material was still 88.21%, indicating that less $\bullet O_2^-$ was involved in the degradation process of pollutants. The addition of 1 mmol EDTA-2Na also reduced the degradation efficiency of the material to 55.92%. It can be concluded that h⁺ was also an important active material involved in the catalytic process. The overall results show that due to the complex ternary heterojunction, there are many kinds of catalytic active substances produced in the catalytic process, among which the active groups play the role in the catalytic process in the order of $\cdot OH > h + > \cdot O_2^-$. Based on the above data, we further carried out electron spin resonance experiments (ESR). The results showed that the materials irradiated by electron beam were used for higher signals, which meant that more catalytic active substances participated in the catalytic reaction and the number of



Figure 10 Comparison of the degradation capacity of materials under different scavengers under visible light irradiation (a), the maximum absorption wavelength of carmine changes with the degradation process (b), possible pathways of carmine degradation (c), ESR spectrum of ABC and EABC under visible light (d), (e).

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3.3 Photocatalytic mechanism

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The image (Figure 10b) showed the change of the maximum absorption wavelength of the carmine with the degradation process. It was obvious that the maximum peak had a slightly blue-shifts. The blue-shift was attributed to the intermediates generated by the degradation of carmine. By GC-MS, it could be speculated that the degradation of carmine first removed $-SO_3^-$, followed by the degradation of its benzene ring structure into small molecular compounds, through a series of reactions, and finally into CO_2 and H_2O (Figure 10c). The degradation process of RhB was similar to that of carmine, in which the removed group was ethyl. As for the Cr^{6+} , the material generated electrons under illumination, which converted Cr^{6+} into $Cr^{3+}.^{53}$

4. Conclusions

In this paper, a kind of ternary Ag/Bi₂WO₆/CdWO₄ heterostructure material was prepared by a simple solvothermal method. And, electron beam irradiation was used for artificially creating interface defects in the synthesis of catalytic materials. In the Ag/Bi₂WO₆/CdWO₄ composite, the CdWO₄ nanorods were used as the matrix and modified by Bi₂WO₆. The content and distribution of nano-silver on the surface of the material were precisely controlled by the in-situ technology. The introduction of appropriate Ag could induce the separation of photogenic electron hole pairs in the catalytic process of materials and enhance the utilization efficiency of carriers. Based on the experimental data and characterization results, the catalytic activity of the material reached its maximum catalytic ability when Ag content was 4%. On this basis, electron beam irradiation could make it achieve the second improvement of catalytic performance on the original basis.⁵⁴ The optimum photocatalytic performance of EABC was attributed to the effectively photoinduced carrier separation and large amount of reactive oxygen vacancies. Here, the catalytic degradation

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of carmine, Cr^{6+} , RhB and other substrates were investigated. Through experiments, $fr^{6}Card^{1}Be^{9/CONJO2571E}$ speculated that hydroxyl radical, as the main active catalytic material, played a role in degradation of pollutants in the reaction process. The possible degradation pathways of carmine and RhB were proposed, in which the branched chains on the benzene ring were first degraded, then the benzene ring was degraded to small molecular compounds, and finally the benzene ring was further degraded to H₂O, CO₂ and other substances. For Cr^{6+} , the material generated electrons under illumination with converting Cr^{6+} into $Cr^{3+},^{55}$ The degradation rate of carmine could reach 100% within 20 minutes. After 5 cyclic experiments on the degradation of carmine, the photocatalytic activity of the material was still about 93% of its initial use. From PL data, we can know that the utilization efficiency of photogenerated carriers was increased, and the number of active catalytic substances on the catalytic interface was improved. The material can effectively utilize visible light with wide applicability for effective degradation of pollutants, and provide a simple method for repairing the actual environment.

Conflicts of interest

The authors declare no competing financial interest.

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Graphic Abstract

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 $Ag/Bi_2WO_6/CdWO_4$ ternary heterostructure materials treated by electron beam irradiation are used for highly efficient degradation of inorganic and organic pollutants.

