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Introduction

The use of semiconductors in photocatalytic processes has many applications, due to the possibility of inducing reactions of great interest in a rapid and efficient way, such as: organic pollutants photodegradation and water-splitting.¹⁻⁴ Among various semiconductors, bismuth-containing materials such as bismuth subcarbonate (Bi₂O₂CO₃) have remarkable properties that make this a great candidate for photocatalytic applications.^{5,6} The origin of suitable properties of Bi₂O₂CO₃ is the internal layered structure of Aurivillius structure, which could guide the lower growth rate along the (001) axis compared to that along other axes, and thus form 2D morphologies like nanosheets.⁶⁻⁸ However, Bi₂O₂CO₃ exhibits two main drawbacks for photocatalytic applications: the rapid recombination of

Insights into the photocatalytic performance of $Bi_2O_2CO_3/BiVO_4$ heterostructures prepared by one-step hydrothermal method

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This paper describes the synthesis of $Bi_2O_2CO_3/BiVO_4$ heterostructures through a one-step method based on the difference in solubility between two semiconductors that possess a metal in common. The assynthesized Bi₂O₂CO₃/BiVO₄ heterostructures were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Raman spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ physisorption, X-ray photoelectron spectroscopy (XPS) and time resolved photoluminescence spectroscopy (TRPL). The role of the heterojunction formed was evaluated by methylene blue (MB) dye and amiloride photodegradation. The formation of the heterostructure was observed indirectly by the great increase in the thermal stability of the Bi₂O₂CO₃ phase when compared to its pure phase. The amount of heterojunctions formed between the Bi₂O₂CO₃ and BiVO₄ was tuned by vanadium precursor concentration. The proposed strategy was efficient for obtaining Bi₂O₂CO₃/BiVO₄ heterostructures with enhanced photocatalytic performance when compared to their isolated phases, MB and amiloride photodegradation occurred mainly by the action of 'OH radicals, i.e. by an indirect mechanism. Based on TRPL spectroscopy and VB-XPS results, an enhancement of photoactivity related to an increase in the spatial separation of photo-generated electron/hole pairs was observed due to the formation of a type-II heterostructure.

electron/hole pairs and the impossibility of activation under visible irradiation.⁷

Several strategies have been developed to minimize or overcome these undesirable effects.9 In particular, the association of semiconductors with metals or other semiconductors to form heterostructures is a promising approach.4,10 Previous studies have shown that heterostructure formation can extend spectral response range and efficiently separate charge carriers, provoking a synergistic effect between the semiconductors.9,11-14 In this sense, the formation of a heterostructure between Bi₂O₂CO₃ and BiVO₄ is an interesting approach to enhance photocatalytic properties due to their suitable electronic characteristics for a type-II heterostructure and also BiVO4 is active under visible irradiation.8 Different strategies have been studied to obtain heterostructures such as one-step methods (simultaneous crystallization)15-18 and the use of one and/or two preformed particles (heterojunctions formation by attachment).9,19-24 The growth of BiVO4 on Bi2O2CO3 surface (preformed) under hydrothermal conditions driven by their difference in solubility is a more interesting and efficient approach for the formation of this kind of heterostructure. This is because the formation of the heterojunction is unavoidable, since mandatorily BiVO₄ will grow using the bismuth present on the surface of Bi₂O₂CO₃.

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Therefore, we study this method to obtain $Bi_2O_2CO_3/BiVO_4$ heterostructure using preformed $Bi_2O_2CO_3$ particles based on hydrothermal treatment. The effect of the molar ratio between $Bi_2O_2CO_3$ and the vanadium precursor on the amount of $BiVO_4$ grown on $Bi_2O_2CO_3$ surface was evaluated. The role of heterojunction formation on photocatalytic performance was probed by methylene blue dye and amiloride photodegradation under visible and UV irradiation and by time resolved photoluminescence spectroscopy. The formation of a type-II heterostructure between $Bi_2O_2CO_3$ and $BiVO_4$ and its charge transfer mechanism for the increase in charge carrier lifetime was also proposed.

Experimental

Synthesis of Bi₂O₂CO₃/BiVO₄ heterostructures

To obtain the Bi₂O₂CO₃/BiVO₄ heterostructures, 0.2 g of Bi₂O₂CO₃ (obtained by a typical synthesis²⁵ between Bi(NO₃)₃·5H₂O and Na₂CO₃) and suitable amounts of NH₄VO₃ (Vetec, 99%) were added to 35 mL of distilled water and the solution was hydrothermally treated at 150 °C for 12 h. The precipitate was washed with distilled water and centrifuged to remove impurities and was dried in an oven at 50 °C. Three different molar ratios of Bi : V were studied: 1 : 1, 1 : 0.7 and 1 : 0.3, which resulted in follow molar ratios of Bi₂O₂CO₃ : BiVO₄ after the synthesis: 0 : 1, 0.3 : 0.7 and 0.7 : 0.3, respectively. The samples were named as BiVO₄, Het-1:0.7, and Het-1:0.3, respectively. For comparative purposes, pure Bi₂O₂CO₃ was also hydrothermally treated at 150 °C for 12 h.

Characterization

X-ray diffraction (XRD) was conducted in a Shimadzu XRD6000 diffractometer operating with a nickel-filtered Cu Ka radiation generated at 30 kV and a filament current of 30 mA. The 2θ range from 10 to 60° was continuously scanned at speed of 1° min⁻¹ with a step width of 0.02°. Raman spectroscopy analyses were performed with a FT-Raman spectrometer (Bruker RAM II with a Ge detector), equipped with a Nd:YAG laser with a wavelength centered at 1064 nm generating a power of 100 mW at a resolution of 2 cm⁻¹. Thermogravimetric analysis (TGA) of the as-synthesized samples was performed in a TA Q500 thermogravimetric analyzer (TA Instruments) under the following conditions: weight 10.00 \pm 0.50 mg; synthetic air flow of 60 mL min⁻¹; heating rate 10 °C min⁻¹; and temperature range of 30-550 °C. UV-vis diffuse reflectance spectra (DRS) were recorded with a UV-2600 Shimadzu spectrophotometer coupled with an integrating sphere (ISR-2600Plus) from 250 to 800 nm to determine the band gap of the materials. The measurements were performed in the total reflection mode with BaSO₄ as a reference.

The morphology of the as-synthesized samples was verified by images obtained in a field emission gun scanning electron microscope (FE-SEM Jeol JSM 6701F) working at 5 kV. Semiquantitative atomic compositions were evaluated by energydispersive X-ray spectroscopy (EDS) using a Thermo Noran device coupled to a SEM (Jeol JEM 2010). High resolution transmission electron microscopy (HRTEM FEI – TECNAI) operating at 200 kV was employed to verify the formation of the heterostructures. The samples were prepared by wetting carbon-coated copper grids with a drop of colloidal alcoholic suspensions and drying in air.

Specific surface area (SSA) of the as-synthesized samples was estimated applying the BET model to N₂ adsorption data conducted at -196 °C with a Micrometrics ASAP 2000 equipment. Before the analysis, the samples were pre-treated (degassed) by heating at 80 °C under vacuum until reaching a degassing pressure lower than 20 µmHg. Chemical surface analysis was performed with a K-alpha XPS equipment (Thermo Fisher 1 Scientific, UK) using Al K α X-rays, vacuum >10⁻⁸ mbar and charge compensation during measurements. The survey and high-resolution spectra were recorded using a pass energy of 1.0 and 0.1 eV, respectively. The binding energy was referenced to the C 1s peak at 284.8 eV. The data analysis was performed using the CASA XPS software.

Photocatalytic measurements

The photoactivity of the as-synthesized samples was evaluated for the degradation of methylene blue (MB) dye under visible and ultraviolet (UV) irradiation, also the degradation of amiloride was evaluated. In typical procedure, 10 mg of a photocatalyst was placed in contact with 20 mL of aqueous solution of MB or amiloride (5 mg L^{-1}). All the experiments were carried out in a photoreactor equipped with six UVC (Philips TUV, 15 W, maximum intensity at 254 nm, and light intensity at 20 cm of 4.0 mW cm⁻²) or six fluorescent (Osram, 15 W, and maximum intensity at 440 nm) lamps, a magnetic stirrer, and a heat exchanger that maintained the temperature at 18 °C. The photodegradation of the MB dye or amiloride was monitored at regular intervals by their maximum absorbance at 654 or 286 nm, respectively, using a Shimadzu-UV-1601 PC spectrophotometer. Before the kinetic experiments, the suspensions were kept in the dark for 12 h to reach adsorption/desorption equilibrium.

The hydroxyl radical ('OH) generated in the photocatalytic process under visible irradiation was indirectly detected by using a fluorescent probe, terephthalic acid (TA).^{26–29} TA readily reacts with 'OH to form 2-hydroxyterephthalic acid (HTA), a highly fluorescent product with emission at approximately 425 nm. The amount of HTA is directly proportional to the quantity of 'OH radicals produced by the irradiated photocatalyst. In a typical procedure, 10 mg of the photocatalyst was added to 20 mL of TA solution (5×10^{-4} mol L⁻¹) prepared from a dilute NaOH solution (2×10^{-3} mol L⁻¹), and the dispersions were maintained under visible irradiation for 2 h. After this period, an aliquot was analyzed in a Shimadzu RF-5301PC spectrofluorophotometer, and the fluorescence emission spectra were obtained with an excitation wavelength of 315 nm.

The lifetime of the charge carriers of the as-synthesized samples were determined by time resolved photoluminescence using time-correlated single photon counting (TCSPC). A pulsed diode laser head of 405 nm (LDH P-C-405, PicoQuant) with an approximate 50 ps pulse width and

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Results and discussion

X-ray diffraction (XRD) patterns of the as-synthesized samples were collected to verify the presence of BiVO₄ and Bi₂O₂CO₃ phases (Fig. 1). The pure Bi₂O₂CO₃ sample that was hydrothermally treated showed a typical XRD pattern assigned to tetragonal crystalline phase (JCPDS, no. - 041-1488) without any contaminant or spurious phase indicating crystallographic stability under the hydrothermal treatment. When Bi₂O₂CO₃ was hydrothermally treated in the presence of V precursor with molar ratio of Bi: V 1:0.3 (Het-1:0.3 sample), an intense diffraction peak at $2\theta \approx 28.8$ related to monoclinic BiVO₄ crystalline phase (JCPDS, no. - 083-1699) was observed. The decrease of Bi2O2CO3 content in the heterostructure is difficult to visualize by XRD patterns since the most intense diffraction peak, *i.e.* (103) plane, is overlapped by the diffraction peak of $BiVO_4$ referent to the (004) plane. However, the disappearance of Bi₂O₂CO₃ phase can be easily visualized by the decreasing intensity of the peak referent to the (110) plane. Further, it was observed that increasing the proportion of the V precursor (Het-1:0.7 sample) increased significantly the amount of BiVO₄ formed. With an increase in the molar ratio between Bi : V, i.e. 1 : 1, it was observed that $Bi_2O_2CO_3$ converted fully into $BiVO_4$, without any spurious phase. In this sense, the formation of BiVO₄ on Bi₂O₂CO₃ surface or the full transformation can occur according to the reactions below:30

> $Bi_2O_2CO_3 \rightarrow 2BiO^+ + CO_3^{2-}$ $NH_4VO_3 \rightarrow NH_4^+ + VO_3^{-}$



Fig. 1 XRD patterns of $Bi_2O_2CO_3$, $BiVO_4$ and $Bi_2O_2CO_3/BiVO_4$ samples in different molar ratios of Bi : V.

$$BiO^+ + VO_3^- \rightarrow BiVO_4\downarrow$$

These results are in agreement with previous studies,^{5,31} where the principle that compounds with high solubility can be converted into compounds with low solubility was utilized to obtain heterostructures of $Bi_2S_3/Bi_2O_2CO_3$ and $Bi_2S_3/BiVO_4$.^{5,31}

Fig. 2 shows the Raman scattering spectra of the assynthesized samples. The $Bi_2O_2CO_3$ sample showed a typical Raman spectrum, with characteristic bands at 1068, 367, 166 and 80 cm⁻¹. The band at 1068 cm⁻¹ was assigned to symmetric stretching of CO_3^{2-} , while the three bands below 400 cm⁻¹ were related to vibrational modes of Bi=O bond lattice.⁸ For the Het-1:0.7 and Het-1:0.3 samples, all the bands related to $Bi_2O_2CO_3$ disappeared, however the typical Raman spectrum of monoclinic BiVO₄ phase with characteristic bands at 826, 362, 330, 200, and 120 cm⁻¹ can be observed.³² This effect is most likely due to the coating of the $Bi_2O_2CO_3$ surface by BiVO₄, resulting in a higher Raman scattering intensity related to BiVO₄ rather than $Bi_2O_2CO_3$.

Thermogravimetric analysis (TGA) of Bi₂O₂CO₃, BiVO₄ and Het-1:0.7 samples were performed to evaluate the thermal decomposition of $Bi_2O_2CO_3$ (*i.e.*, the formation of Bi_2O_3 by the loss of carbonate group) and the concentration of BiVO₄ in the heterostructured sample. As shown, in Fig. 3a the Bi₂O₂CO₃ sample lost \sim 9.0% of its initial mass, due to the total decomposition of the carbonate group. On the other hand, the BiVO₄ sample exhibited an insignificant weight loss (lower than 0.2 wt%), which confirms that the Bi2O2CO3 phase reacted completely to form BiVO4 when the Bi : V molar ratio of 1 : 1 was used. From these results, it is possible to observe that Bi₂O₂CO₃ reacts completely to form BiVO₄ in this condition. The Het-1:0.7 sample showed a weight loss of \sim 4.3%, meaning that the $Bi_2O_2CO_3$ content in this heterostructure is approximately 45 wt%, which is in close agreement with the theoretical amount, i.e. 40 wt% of Bi₂O₂CO₃. The analysis of the derivative thermogravimetry (DTG) curves in Fig. 3b showed that the decomposition temperature of Bi2O2CO3 occurs at 356 °C, while



Fig. 2 Raman scattering spectra of $Bi_2O_2CO_3,\ BiVO_4$ and $Bi_2O_2CO_3/$ $BiVO_4$ samples.



Fig. 3 (a) Thermogravimetric analysis (TGA) and (b) their respective derivative (DTG) for $Bi_2O_2CO_3$, $BiVO_4$ and Het-1:0.7 samples.

in the Het-1:0.7 sample this event occur at 460 °C. The increase in decomposition temperature of the carbonate group (>100 °C) for the Het-1:0.7 sample is due to the formation of a heterojunction with strong interaction between the phases. This result suggests that the heterojunction was not formed by the complete dissolution of the Bi₂O₂CO₃ phase followed by the subsequent crystallization of both phases in a segregated form, but rather the formation of BiVO₄ occurred directly on the surface of Bi₂O₂CO₃, which acts as a Bi provider.

The morphology of the as-synthesized samples was examined using scanning electron microscopy (SEM), and representative images are shown in Fig. 4. The $Bi_2O_2CO_3$ sample exhibited a typical morphology of this phase, *i.e.* micrometric sheets with nanometric thickness.^{6,8} Pure BiVO₄ showed dense micrometric particles with different shapes and sizes. The heterostructured $Bi_2O_2CO_3/BiVO_4$ samples exhibited characteristic morphology referent to both phases in the same region. However, it can be observed that in some regions, apparently the $Bi_2O_2CO_3$ phase was completely converted into $BiVO_4$, resulting in a heterogeneous morphology.

As shown in Fig. 5a, the Het-1:0.3 sample presented morphology very similar to pure $Bi_2O_2CO_3$, except for the nanoparticles on its surface. The HRTEM image of this sample (Fig. 5b) confirms that the particles on the $Bi_2O_2CO_3$ surface are



Fig. 4 (a) Representative FE-SEM images of (a) $Bi_2O_2CO_3$, (b) $BiVO_4$ (c) Het-1:0.3 and (d) Het-1:0.7 samples.



Fig. 5 (a) TEM and (b) HRTEM images of the Het-1:0.3 sample.

 $BiVO_4$ in the monoclinic phase, Fig. 5b. The presence of $BiVO_4$ over $Bi_2O_2CO_3$ was identified by its interlayer distance of 0.31 nm referent to the (121) plane. This result indicates the formation of heterojunctions between the $Bi_2O_2CO_3$ and $BiVO_4$ phases.

The absorbance spectra of the as-synthesized samples (Fig. 6a) showing that the intermediary samples present intermediate spectral features to the isolated phases. This indicates that the BiVO₄ formation acted by shifting the absorption spectra to the visible range, as initially proposed. However, it is clear that Het-1:0.7 sample is close to the expected BiVO₄ absorbance despite the attested presence of Bi2O2CO3. The band gap values of the as-synthesized samples were determined by applying the Tauc equation to UV-vis DRS data (Fig. 6b). The Bi₂O₂CO₃ and BiVO₄ samples exhibited band gap values of 3.40 and 2.40 eV, respectively, which are in agreement with those described in the literature for these phases.^{5,6,32} The Het-1:0.3 sample exhibited two band gap values of 2.35 and 2.75 eV, which are related to both phases that compose it. The Het-1:0.7 sample showed only a band gap value of 2.40 eV related to $BiVO_4$ phase, indicating that BiVO₄ covering the surface of Bi₂O₂CO₃, as observed by Raman analysis (Fig. 2).

The photocatalytic properties of the as-synthesized samples were evaluated by MB dye photodegradation under visible and





Fig. 6 (a) UV-vis absorption spectra and (b) Tauc equation applied to DRS UV-vis data to obtain the band gap values of the $Bi_2O_2CO_3$, $BiVO_4$, Het-1:0.7 and Het-1:0.3 samples.

UV irradiation (Fig. 7a and b). The experiments were conducted using two different radiation sources (visible and UV) because the Bi₂O₂CO₃ phase is only active under UV irradiation. The selfphotodegradation percentages of the MB dye (Fig. 7), i.e. direct photolysis, were approximately 6 and 14% under vis and UV irradiation, respectively. Further, before the photocatalytic tests, the as-synthesized samples were kept in contact with the MB dye solution for 120 min to reach adsorption/desorption equilibrium, and it was observed that all the samples presented insignificant MB adsorption, thus, the observed MB discoloration can be related to its oxidation. The MB photodegradation curves in Fig. 7a and b show that all samples were photoactive, since their curves are below the pure MB curve. The activity of the photocatalysts followed the same order under both radiation sources: Het-1:0.3 > Het-1:0.7 > BiVO₄ > Bi₂O₂CO₃, as observed in Table 1. In fact, from these results, it is clear that the heterostructured samples showed higher photoactivity than the pure Bi₂O₂CO₃ and BiVO₄ phases. This finding evidences interface creation between the Bi2O2CO3 and BiVO4 phases, resulting in the type-II heterostructure formation, and leading to an increase of charge carrier lifetime. It is worth pointing out that the heterostructure formation extended spectral response range since the heterostructure with the

Fig. 7 MB dye (5 mg L⁻¹) photodegradation curves catalyzed by the isolated phases and the Bi₂O₂CO₃/BiVO₄ heterostructures under (a) visible and (b) UV irradiation.

higher amount of $Bi_2O_2CO_3$ showed higher photocatalytic performance under visible irradiation.

Due to the nature of catalytic process, *i.e.* the process takes place on the catalyst's surface, the specific surface area (SSA) of the as-synthesized samples was determined (Table 1). The formation of $BiVO_4$ on $Bi_2O_2CO_3$ surface decreased the SSA compared to that of the $Bi_2O_2CO_3$ precursor, because of morphological transformation. As previously seen in the SEM images (Fig. 4), the size of the particles increased after the synthesis of $BiVO_4$. Therefore, this is an indication that any enhancement of the photocatalytic performance of the heterostructures cannot be related to their SSA.

Table 1 Kinetic constants for MB dye photodegradation under visible (k_{vis}) and UV (k_{UV}) irradiation, and specific surface area of the assynthesized samples

Samples	$k_{ m vis} imes 10^2/{ m h}^{-1}$	$k_{ m UV} imes 10^2/{ m h}^{-1}$	$SSA/m^2 g^{-1}$
MB	1.0	6.0	_
Bi ₂ O ₂ CO ₃	12.0	21.0	12.0
Het-1:0.3	33.0	89.0	7.70
Het-1:0.7	16.0	67.0	2.90
BiVO ₄	14.0	19.0	2.70



Fig. 8 Amiloride (5 mg L⁻¹) photodegradation curves catalyzed by the isolated phases and the Bi₂O₂CO₃/BiVO₄ heterostructures under visible irradiation.

In order to analyze the contribution of the sensitization mechanism in the degradation of organic pollutants catalyzed by as-synthesized samples, the photoactivity of samples (Fig. 8) was evaluated using a colorless organic pollutant, amiloride. Amiloride is a drug extensively used for the treatment of hypertension, belongs to a class of pharmaceutical compounds that are often found in wastewater and can adversely affect water quality. As shown in Fig. 8, the amiloride did not degrade significantly by direct photolysis even after 4.5 hours under visible irradiation. All samples were photoactive on degradation of amiloride, since their curves are below the pure amiloride curve. The activity of the photocatalysts followed the same order observed for MB degradation: Het-1:0.3 > Het-1:0.7 > Bi₂O₂CO₃ > BiVO₄. After 4.5 hours under visible irradiation, the amiloride degradation catalyzed by the heterostructured samples was up to 35%, whereas for Bi₂O₂CO₃ and BiVO₄ it was only 26 and 20%, respectively. In fact, from these results, it is clear that the heterostructured samples showed higher photoactivity than the

pure Bi₂O₂CO₃ and BiVO₄ phases. We can confirm that the degradation of organic pollutants not occurred only by photosensitization mechanism.

Despite the interesting and promising photocatalytic performance of the Bi₂O₂CO₃/BiVO₄ heterostructures, it is necessary that the mechanism involved in the photocatalytic process is elucidated. For this purpose, the 'OH radicals were detected using the method proposed by Ishibashi et al.27,33 and also studied in great detail by our group.^{20,28} In this mechanism, the 'OH radical is trapped by TA producing the fluorescent 2-hydroxyterephthalic acid, as illustrated in Fig. 9. The photoactivity of the as-synthesized samples on 'OH radical formation followed the order: Het-1:0.3 > $BiVO_4$ > $Bi_2O_2CO_3$. Therefore, the observed trend in the photoactivity of the samples for MB dye degradation was the same as that observed for 'OH radical formation, which indicates that an indirect mechanism (i.e., by 'OH radical attack) plays an important role on the photoactivity of the as-synthesized heterostructure. The reduction potential of OH⁻ in solution to 'OH is approximately of 2.4 V,³⁴ however, some studies showed that when the OH groups are adsorbed on the catalyst surface the reduction potential is decreased for 1.5 V.³⁴⁻³⁶ In this sense, the formation of 'OH radical by the assynthesized samples can occur in two steps, *i.e.* the adsorption of OH group on catalyst surface and subsequently OH group oxidation by holes formed in the valence band of photocatalyst.

To confirm heterojunction formation and consequent increase in charge carrier lifetime the time resolved photoluminescence (TRPL) measurements of the BiVO₄ and Het-1:0.3 samples were performed to find the constant lifetime of the electron/hole pairs (t). Fig. 10 exhibits the decay of PL intensity monitored at 545 nm and excited by a laser source centered at 405 nm for both samples. The PL decays of all the samples were fitted with a first order exponential function to calculate the lifetime of the electron/hole pair. The PL lifetime of the bandband emission (*i.e.*, the electron/hole pair recombination) for



Fig. 9 PL spectra of 2-hydroxyterephthalic acid formation using pure $Bi_2O_2CO_3$, Het-1:0.3 and $BiVO_4$ photocatalysts after 2 h under visible irradiation.



Fig. 10 TRPL (lifetime decay) curves of the BiVO₄ and Het-1:0.3 samples. The powder was excited at 405 nm and photoluminescence was monitored at 545 nm. The lifetime decay curves observed (scatter) and calculated (red line).



Fig. 11 X-ray photoelectron spectra of the $BiVO_4$, $Bi_2O_2CO_3$ and Het-1:0.7 samples. (a) Survey spectra, (b) high-resolution spectra of Bi 4f, (c) C 1s, (d) V 2p, (e) O 1s and (f) valence band region.

Het-1:0.3 sample was 0.84 ns, while the BiVO₄ sample was approximately 0.69 ns, which presents an increase of approximately 18%. These results confirm that the lifetime of the electron/hole pair of heterostructure (Het-1:0.3 sample) is significantly higher than that of the pure BiVO₄ phase, proving that the heterojunction between $Bi_2O_2CO_3$ and $BiVO_4$ formed a suitable type-II heterostructure.

XPS analysis was performed to investigate the surface composition and chemical state of the elements of the BiVO₄, Bi₂O₂CO₃ and Het-1:0.7 samples, Fig. 11. From the survey spectra (Fig. 11a), the BiVO₄ sample showed the presence of Bi, V, O and C (this was used as an internal reference, 284.8 eV). The Bi₂O₂CO₃ and Het-1:0.7 samples showed only the presence of Bi, O and C. The high-resolution spectra of Bi 4f (Fig. 11b) exhibit two strong symmetrical characteristic spin-orbit splitting of Bi 4f peaks at about 158.9 and 164.4 eV, which are assigned to Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively.^{6,8,15} A shift in Bi 4f peaks was observed from BiVO4 to Bi2O2CO3 phase, indicating that Bi atoms are in different chemical environments, however with the same chemical state (Bi³⁺). The high-resolution spectra of C 1s for the as-synthesized samples (Fig. 11c) showed two peaks located at 284.8 and 288.8 eV, which are ascribed to the carbon reference from the XPS instrument and to the carbonate ion (O-C=O) related to the Bi₂O₂CO₃ phase.⁸ In this sense, although the XRD data (Fig. 1) showed a typical diffraction pattern of the pure BiVO₄ phase, the C 1s XPS results reveal the presence of a small amount of CO_3^{2-} group on the material's surface. The BiVO₄ and Het-1:0.3 samples exhibited two peaks of V 2p (Fig. 11d), which are related to the BiVO₄ phase, while



Fig. 12 Estimated band positions from XPS and DRS results for $Bi_2O_2CO_3$, $BiVO_4$ samples, (a) before and (b) after contact.^{38–41}

the Bi₂O₂CO₃ sample did not present any peaks related to the V atom. Fig. 11e shows that the high-resolution O 1s spectra of the Bi₂O₂CO₃, Het-1:0.3 and BiVO₄ samples exhibited three peaks (with different intensities) at 529.6, 530.8, and 531.8 eV, respectively. The shoulder peak at 529.6 eV is ascribed to the oxygen attached to the Bi–O bond, and the other two peaks at *ca*. 530.8 and 531.8 eV can be assigned to lattice oxygen and chemisorbed OH and C–O species in Bi₂O₂CO₃, respectively.⁶ The different intensities for the two peak related to O species are expected for the Het-1:0.3 samples due to the coexistence of both crystalline phases.

To determine the valence band (VB) edges of the assynthesized photocatalysts, the total densities of the VB states of the samples were measured by XPS valence band region (VB-XPS).³⁷ The conduction band (CB) bottom potentials of the three samples can be obtained using the equation $E_{\rm CB} = E_{\rm VB} - E_{\rm g}$. As shown in Fig. 11f, the VB top of Bi₂O₂CO₃, BiVO₄ and Het-1:0.3 were determined to be 1.8, 1.4, 1.5 eV, respectively. This result indicates that an interfacial structure was formed, and the local environment and electron density of the elements changed to some extent. Therefore, the comparison of the band structures of isolated Bi₂O₂CO₃ and BiVO₄ samples is shown in Fig. 12a (before contact). On the other hand, it is well know that when the two semiconductors are in contact Fig. 12b, their Fermi levels must be equal. Therefore, the CB and VB positions of Bi₂O₂CO₃ and BiVO₄ change to reach the equilibration of their Fermi levels $(E_{\rm f})^{.38-41}$ Therefore, heterojunction formation allows the diffusion of electrons from the CB of BiVO₄ to the CB of Bi₂O₂CO₃, while the holes transfer from the VB of $Bi_2O_2CO_3$ to the VB of $BiVO_4$, resulting in an accumulation of electrons in the CB of Bi₂O₂CO₃ and holes in the VB of BiVO₄. As a matter of fact, the Bi₂O₂CO₃/ BiVO₄ heterostructures could effectively separate the photogenerated electron/hole pairs and remarkably reduce the recombination of photogenerated charge carrier, as observed by the TRPL and photocatalytic results. Therefore, the Bi₂O₂CO₃/ BiVO₄ heterostructures exhibit the best photocatalytic activity for the degradation of MB dye under visible and UV irradiation.

Conclusions

In summary, the method proposed was efficient to obtain Bi2O2CO3/BiVO4 heterostructures with significant enhancement of photocatalytic performance. The formation of the heterostructure was observed indirectly by the great increase in thermal stability of Bi₂O₂CO₃ phase when compared to its pure phase. The heterojunctions formed between Bi2O2CO3 and BiVO₄ were indicated by HRTEM image. The Bi₂O₂CO₃/BiVO₄ heterostructures showed higher photoactivities than their isolated phases (i.e., Bi₂O₂CO₃ and BiVO₄) for MB degradation under both visible and UV irradiation. The photodegradation of MB dye is caused by the action of 'OH radicals, *i.e.* by an indirect mechanism. The TRPL spectroscopy and XPS results revealed that the formation of the heterostructure led to an effective spatial separation of charge carriers, with consequent increase in lifetime of heterostructure, which confirmed that Bi₂O₂CO₃/BiVO₄ is a type-II heterostructure.

Conflicts of interest

There are no conflicts of interest to declare.

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