Novel 3DOM BiVO₄/TiO₂ nanocomposites for highly enhanced photocatalytic activity†

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Novel 3DOM BiVO₄/TiO₂ nanocomposites with intimate contact were for the first time synthesized by a hydrothermal method in order to elucidate their visible-light-driven photocatalytic performances. BiVO₄ nanoparticles and 3DOM TiO₂ inverse opal were fabricated respectively. These materials were characterized by XRD, XPS, SEM, TEM, N₂ adsorption–desorption and UV-vis diffuse (UV-vis) and photoluminescence spectroscopies. As references for comparison, a physical mixture of BiVO₄ nanoparticles and 3DOM TiO₂ inverse opal powder (0.08 : 1), and a BiVO₄/P25 TiO₂ (0.08 : 1) nanocomposite made also by the hydrothermal method were prepared. The photocatalytic performance of all the prepared materials was evaluated by the degradation of rhodamine B (RhB) as a model pollutant molecule under visible light irradiation. The highly ordered 3D macroporous inverse opal structure can provide more active surface areas and increased mass transfer because of its highly accessible 3D porosity. The results show that 3DOM BiVO₄/TiO₂ nanocomposites possess a highly prolonged lifetime and increased separation of visible light generated charges and extraordinarily high photocatalytic activity. Owing to the intimate contact between BiVO₄ and large surface area 3DOM TiO₂, the photogenerated high energy charges can be easily transferred from BiVO₄ to the 3DOM TiO₂ support. BiVO₄ nanoparticles in the 3DOM TiO₂ inverse opal structure act thus as a sensitizer to absorb visible light and to transfer efficiently high energy electrons to TiO₂ to ensure long lifetime of the photogenerated charges and keep them well separated, owing to the direct bandgap of BiVO₄ of 2.4 eV, favourably positioned band edges, very low recombination rate of electron–hole pairs and stability when coupled with photocatalysts, explaining the extraordinarily high photocatalytic performance of 3DOM BiVO₄/TiO₂ nanocomposites. It is found that larger the amount of BiVO₄ in the nanocomposite, longer the duration of photogenerated charge separation and higher the photocatalytic activity. This work can shed light on the development of novel visible light responsive nanomaterials for efficient solar energy utilisation by the intimate combination of an inorganic light sensitizing nanoparticle with an inverse opal structure with high diffusion efficiency and high accessible surface area.
efficiency. Coupling narrow-bandgap semiconductors such as CdS (ref. 7) and CuBi2O4 (ref. 8) with wide-bandgap semiconductors like TiO2, SnO2 (ref. 9) and WO3 (ref. 10) and forming composite photocatalysts such as Bi2WO6/TiO2, Bi2O3/TiO2, In2O3/TiO2, CuO/TiO2, WO3/TiO2, etc. have been extensively investigated.11–15 Ke et al.16 showed that WO3/TiO2 nanocomposites present much higher photocatalytic activity than pure TiO2 in the photodegradation reaction of rhodamine B (RhB) under UV light. Vinodgopal et al.17 studied a coupled SnO2/TiO2 semiconductor system which carried out a very rapid and complete decolorization of the textile azo dye under UV irradiation. Bessekhouad et al.18 reported that a Bi2O3/TiO2 heterojunction structure presented higher activity than pure Bi2O3 and TiO2:Fe25 for the photocatalytic degradation of Orange II under UV-vis irradiation.

The monoclinic BiVO4 structure was reported to show highly promising photocatalytic activity under visible light irradiation due to its relatively narrow bandgap energy of 2.4 eV, compared to its two tetragonal phases both with a bandgap energy of 3.1 eV.19–21 Due to its visible light photocatalytic activity, it has also been used for the degradation of organic pollutants and oxygen evolution in the water splitting reaction.22–23 The combination of a narrow bandgap semiconductor material such as BiVO4 with TiO2 to produce a BiVO4/TiO2 nanocomposite with an intimate heterojunction could be an efficient way to offer a visible light photocatalyst with high photocatalytic activity and attracts increasing attention.24–30 Cao et al.24 synthesized the porous peanut-like BiVO4/TiO2 composite nanostructures by a hydrothermal process and the photocatalytic activity of these BiVO4/TiO2 nanostructures was largely enhanced. Zhang et al.25 reported the synthesis of BiVO4/TiO2 by a one-step microwave hydrothermal method and found that the 20 wt% TiO2/BiVO4 nanocomposite exhibited better photocatalytic activity than pure monoclinic BiVO4 and other percentages of TiO2 in BiVO4 because of its high crystallinity, narrow bandgap, and most importantly, the hierarchical heterostructure which can effectively separate photoinduced electron–hole pairs on the surface of BiVO4/TiO2 photocatalysts. They claimed that BiVO4 played the role of a light sensitizer. The sensitizer effect of BiVO4 has also been pointed out by Tang et al.26 Colon et al.26,31 studied a ternary erbium doped BiVO4/TiO2 heterostructure made by a simple impregnation method which showed highly enhanced photocatalytic activity in the degradation of phenol29 and methylene blue.32 They attributed this high photocatalytic activity of erbium doped BiVO4/TiO2 to the occurrence of a luminescence process generated by erbium ions and the possibility to adjust the band position between Er3+ doped BiVO4 and TiO2, leading to the effective charge pair separation. Hu et al.28 prepared BiVO4/TiO2 with a mass ratio of 1:200 by hydrothermal treatment for the benzene degradation reaction and claimed that their material was 3–4 times more active than nitrogen doped TiO2 under visible light irradiation. A bilayer TiO2 photonic crystal (PC)/porous BiVO4 was constructed by using liquid-phase deposition and spin coating by Huo et al.33 The photocatalytic ability of porous BiVO4 was enhanced by combination with a TiO2 PC layer as the back reflector which intensified the light absorbance, showing another advantage of a TiO2 PC crystal in enhancing light absorption and the combination of BiVO4 and TiO2. In spite of these promising results, the role of BiVO4 in BiVO4/TiO2 heterostructures and the photoelectronic mechanism remain a point of debate. Moreover, the accessibility of reactants to these heterostructures is not favourable due to the low porosity, low surface area of TiO2 supports and poor adsorptive properties of BiVO4.21,25 Xie et al.29 in their recent paper showed very clearly the importance of the combination of TiO2 and BiVO4 to achieve long life visible light excited charge carriers which gave unexpectedly high photocatalytic activity for water splitting. Pure Mo doped BiVO4 inverse opal structures were prepared.34 Due to the specific structure, higher photocurrent density owing to effective charge collection was observed leading to an enhancement in photoelectrochemical water splitting and showing the importance of the macroporous inverse opal structure in charge collection.

The photocatalytic behaviour of highly ordered three dimensional macroporous titanias with an inverse opal structure and good accessibility of reactants in dye molecule degradation has been investigated.35–40 Wu et al.35 studied the degradation of RhB with a 3DOM TiO2 inverse opal structure with different pore diameters. They have shown that the photocatalytic activity presents a variation with the pore diameter. In this framework, Zheng et al.36 demonstrated that the order of benzoic acid (BA), methyl orange (MO) and RhB photocatalytic degradation is related to the pore size of the TiO2 inverse opal structure (IOS). With the increasing pore size of the TiO2 IOS, mass transfer and light utilization efficiency are enhanced. The continuous pore voids facilitate the transfer of reactant molecules which is beneficial for dye sensitization.

On the other side, since 3DOM inverse opal structures as photonic crystals (PCs) have periodic dielectric contrast modulation in the length scale of the wavelength of light, coherent Bragg diffraction forbids light with certain energies to propagate through the material along a particular crystallographic direction. This gives rise to stop-band reflection, and the range of energies that is reflected back depends on the periodicity and dielectric contrast of the PC. At the wavelengths corresponding to the edges of these stop-bands, photons propagate with strongly reduced group velocity and hence are called ‘slow photons’. The slow photons can be used to enhance the light absorption of materials when the photon energy matches the absorbance of the material leading to the generation of a large number of electron–hole pairs and enhanced photocatalytic activity. Liu et al.37–40 investigated the slow photon effect on the photocatalytic activity of inverse opal ZnO by tuning the incident light angle.38–40 Compared with bulk ZnO, it was found that inverse opal ZnO exhibits much higher photocatalytic activity.

Chen et al.41 have also demonstrated that inverse opal WO3 photoanodes with different stop-bands showed enhanced photocurrent intensity. Photonic crystals, particularly titania, have been considered as components in dye-sensitized photoelectrochemical cells designed to increase the efficiency of the solar cells by enhancing photocurrent efficiencies due to the localization of heavy photons near the edges of photonic gaps.42–46 The slow photon effect on photovoltaic cells and the photochemical process was investigated by Nishimura et al.46 and Chen et al.47–49 as a means of promoting the optical
absorbance of the TiO$_2$ based composite system. In addition to this slow photon effect, the 3DOM structure has an open interconnected porous network, facilitating the diffusion of molecules and offering a larger surface area, both being quite favourable for photocatalysis.$^{50,51}$

In order to benefit from the advantages of both the composite system and the 3DOM structure, we have combined the 3DOM TiO$_2$ with the narrow bandgap semiconductor BiVO$_4$ as a light sensitizer leading to visible light absorbing materials with enhanced photocatalytic activity. To the best of our knowledge, we have for the first time prepared 3DOM BiVO$_4$/TiO$_2$ nanocomposites offering a heterojunction by their intimate contact. In this work, the synthesis, characterization, and photocatalytic activity of 3DOM BiVO$_4$/TiO$_2$ nanocomposites in the visible light degradation of a dye molecular model were studied. The mechanism of enhanced visible light photocatalytic activity of the as-synthesized nanocomposites is proposed and discussed. For comparison, TiO$_2$ inverse opal, BiVO$_4$ nanoparticles, a physical mixture of BiVO$_4$ nanoparticles and 3DOM TiO$_2$ powders, and the BiVO$_4$/P25 TiO$_2$ nanocomposite by a hydrothermal method were synthesized and used as references.

2. Experimental

2.1 Synthesis of 3DOM TiO$_2$, BiVO$_4$ and 3DOM TiO$_2$/BiVO$_4$ nanocomposites

Styrene, sodium hydroxide and potassium persulphate were purchased from Aldrich. Polystyrene (PS) spheres were synthesized by an emulsion polymerization method without the addition of a surfactant. Styrene (20 mL) was washed three times with a solution of NaOH (1 M) to remove the polymerization inhibitor, and then added to 160 mL of bidistilled water in a two-neck flask. This solution was stirred at 350 rpm under an inert atmosphere and heated to 70 °C. After 30 min and when the temperature was stabilised at 70 °C, 0.16 g of K$_2$S$_2$O$_8$ was added to initiate polymerization. After 30 min, the mixture became cloudy and after 6 hours the polymerization was stopped by cooling and centrifuging the flask. The white solution obtained was a dispersion of PS beads in water. The PS sphere size was around 350 nm.

To obtain an opal structured template, the PS beads dispersion was self-assembled by oven-drying at 40 °C for 5 days and characterised by scanning electron microscopy (SEM).

The fabrication of three dimensionally ordered macroporous (3DOM) titania was achieved via a templating strategy, as reported in the literature,$^{15,16,40,52,53}$ in which a thick layer of self-assembled polystyrene spheres (PS) was deposited onto a filter paper in a Buchner funnel under vacuum. The PS assembly was then infiltrated with the precursor solution. Titanium isopropoxide (Aldrich, 97%) was added dropwise to completely cover the PS spheres whilst under vacuum such that it occupied the voids inside the PS assembly. The precursor–template mixture was then air dried for 24 h and subsequently calcined at 550 °C for 12 h at a heating rate of 2 °C min$^{-1}$ to obtain TiO$_2$ photonic crystals (PCs) with an inverse opal structure (IOS). In order to incorporate BiVO$_4$ nanoparticles inside the voids of the 3DOM TiO$_2$, a hydrothermal method was used. In a typical process, stoichiometric amounts of Bi(NO$_3$)$_3$·5H$_2$O (Carl Roth, ≈98%, p.a. ACS) and NH$_4$VO$_3$ (Carl Roth, ≥98%, p.a.) were dissolved in a stoichiometric volume of an ethylene glycol–water mixture and stirred for about 10 min until a clear solution was formed. Then, different amounts of 3DOM TiO$_2$ were added into the solution and sonicated for 15 min. After 1 h stirring, the obtained yellow-coloured mixture was transferred into a Teflon-sealed autoclave which was maintained at 160 °C for 24 h. The solid powders were recovered by centrifugation and washed with distilled water and absolute ethanol three times. Finally, the obtained solid was vacuum-dried at 60 °C for 6 h and was then calcined at 300 °C for 1 h. Dumbbell-like BiVO$_4$ structures were synthesized under the same experimental conditions. Two other reference samples were prepared for comparison of photocatalysis. Firstly, BiVO$_4$ nanoparticles were introduced into P25 TiO$_2$ nanoparticles by the same method described above by hydrothermal synthesis. After washing, the sample recovered was labelled as the BiVO$_4$/P25-TiO$_2$ nanocomposite. Secondly, the obtained BiVO$_4$ dumbbell-like structure was mixed with 3DOM TiO$_2$ inverse opal powders, giving a physical mixture of BiVO$_4$ and 3DOM TiO$_2$, labelled as phy-mix BiVO$_4$/3DOM TiO$_2$.

2.2 Material characterisation

Powder X-ray diffraction was performed on a PANalytical X’pert Pro with Cu Kα radiation. Textural properties of the materials were evaluated via adsorption–desorption of nitrogen at −196 °C using a Micromeritics Tristar 3000 with prior outgassing. The morphological properties of the samples were observed by scanning electron microscopy (SEM) (FEI FEI Helios Nanolab 650). Furthermore, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and Energy Dispersive X-ray spectroscopy (EDX) were performed on a FEI Tecnai Osiris electron microscope fitted with Super-X windowless EDX detector system, operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-Alpha™ + X-ray photoelectron spectrometer (XPS). The binding energy for the C (1s) peak at 284.9 eV (relative to adventitious carbon from the XPS instrument itself) was used as a reference. The UV-vis absorbance spectra were obtained using a UV-vis spectrophotometer (Perkin Elmer Lambda 35 UV-visible spectrometer fitted with a Labsphere for analysis in diffuse reflectance mode) in the range of 200–750 nm. Photoluminescence properties of the samples were studied by Perkin Elmer LS45 luminescence spectrometry.

2.3 Photocatalytic testing

Photocatalytic testing was performed under visible light irradiation (400–800 nm) using 6 neon lamps of 18 W. The luminous power of each lamp was 1250 lm and the total luminous power was 7500 lm in the photocatalytic reactor. The emission spectrum of the neon light lamp is given in Fig. 1S.† It can be seen that the intensity of UV light emitted by the neon lamp was very low and can be neglected, and hence no UV filter was used to cut the UV light. The reaction temperature was maintained at room temperature. In each experiment 20 mg of the photocatalyst was placed in 50 mL of reactant solution with an initial
concentration of $10^{-3}$ M of RhB. The suspension was poured into a quartz tube, inserted into a reactor and stirred in the dark for 120 min to ensure adsorption/desorption equilibrium prior to irradiation. During irradiation, 2 mL of the suspension was removed at a given time interval for subsequent RhB concentration analysis.

3. Results and discussions

3.1 Phase composition

XRD patterns of the as-prepared 3DOM TiO$_2$ inverse opal, two BiVO$_4$/3DOM TiO$_2$ nanocomposites and BiVO$_4$ nanoparticles are shown in Fig. 1. The XRD pattern (Fig. 1a) of the TiO$_2$ inverse opal structure shows five peaks at $2\theta = 25.3^\circ$, $37.9^\circ$, $48.0^\circ$, $54.6^\circ$ and $62.8^\circ$ corresponding to the crystal planes of (101), (004), (200), (211), and (204), respectively (JCPDS card no. 14-0688), which indicates that the TiO$_2$ sample adopts an anatase phase after calcination at 550 $^\circ$C. The XRD peaks (Fig. 1d) of BiVO$_4$ nanoparticles correspond to the monoclinic scheelite phase (JCPDS 14-0688). The diffraction profiles reveal that both BiVO$_4$ and TiO$_2$ powder are highly crystalline. The diffraction patterns of BiVO$_4$/3DOM TiO$_2$ nanocomposites (Fig. 1b and c) showed the combination of the XRD profiles of both TiO$_2$ inverse opal and BiVO$_4$ nanoparticles. Weak XRD diffraction peaks of vanadate species at $2\theta = 18.8^\circ$, $28.8^\circ$, $30.5^\circ$, $35^\circ$, $39.9^\circ$ and $42.4^\circ$ corresponding to the crystal planes of (011), (121), (040), (002), (11,1,2) and (150), respectively, are observed as shown by (■) in Fig. 1b and c. This is presumably due to a combination of their low content and high dispersion.

The average crystallite sizes of pure BiVO$_4$ nanoparticles, pure TiO$_2$ inverse opal structure and TiO$_2$ nanoparticles in the 0.08BiVO$_4$/3DOM TiO$_2$ nanocomposite, calculated by the Scherrer equation, were found to be 30.0, 29.4 and 22.5 nm, respectively. In general, an increase of the crystallite size is observed in the high temperature treated samples. However, the TiO$_2$ crystallite size decreases in the BiVO$_4$/TiO$_2$ nanojunction composites compared to that in pure TiO$_2$ inverse opal, which is confirmed by the presence of broad peaks in the diffraction pattern of the 0.08BiVO$_4$/3DOM TiO$_2$ nanocomposite. This can be ascribed to the fact that the introduced BiVO$_4$ nanoparticles inhibit grain aggregation. With increasing content of BiVO$_4$ nanoparticles in BiVO$_4$/3DOM TiO$_2$, the nanoparticles of BiVO$_4$ grew from 30 nm to about 45.2 nm, indicating that the nanocrystals of BiVO$_4$ shifted to an agglomerated state as a result of densification, resulting in the growth of the crystal.

3.2 Morphology

Fig. 2 shows the SEM images of pure TiO$_2$ inverse opal (a and b), pure BiVO$_4$ nanoparticles (c and d) and the BiVO$_4$/3DOM TiO$_2$ nanocomposite (e and f) respectively.

The pure macroporous TiO$_2$ sample exhibits (Fig. 2a and b) a highly ordered three dimensional inverse opal structure with interconnected pores. The average pore size of the TiO$_2$ inverse opal is about 320 nm, being smaller than that of PS spheres used (350 nm) due to the contraction of the inverse opal structure after removing PS spheres upon calcination.

The pure BiVO$_4$ nanoparticles (Fig. 2c) exhibit dumbbell-like shapes, highlighting that the as-prepared BiVO$_4$ product is composed of countless dumbbell-like aggregates and nearly all of them adopt the same morphology. A single dumbbell aggregated from nanoparticles has a length ranging from 1 to 5 $\mu$m. Furthermore, we can notice that the surface of the obtained BiVO$_4$ sample is fairly rough as shown in Fig. 2c, which further indicates that every dumbbell is formed by an aggregation of
nanoparticles. Fig. 2d presents an enlarged SEM image of the top structure of the dumbbell (Fig. 2c). It confirms that the BiVO₄ is an aggregate of small sphere-like nanoparticles of 30–60 nm. Thus the dumbbell-like BiVO₄ is assembled by the oriented aggregation of nanoparticles. This morphology is quite similar to that previously reported.²¹

The SEM micrograph in Fig. 2e confirms that a BiVO₄/3DOM TiO₂ nanojunction was obtained. The TiO₂ inverse opal support has a highly ordered structure with few defects. In this image it can be seen that the morphology of BiVO₄ has changed and the particle size has greatly increased to around 45 nm (as highlighted by the arrows in Fig. 2f). This is due to the effect of the calcination temperature. This observation is in very good agreement with the XRD results.

In order to get more information about the microstructure of the as-prepared products, further investigation was performed by TEM. The macrostructure of the pure TiO₂ inverse opal structure was examined by TEM, where the macropores can be clearly identified in Fig. 3a via a contrast in the image between voids and the material. As shown in Fig. 3b, TiO₂ is an aggregate of small nanoparticles. Fig. 3c shows a typical TEM image of dumbbell-like BiVO₄ nanoparticles. As can be seen in Fig. 3d, it confirms that BiVO₄ is an aggregate of small nanoparticles which is in good agreement with SEM observations. The TEM and STEM images and EDX mapping of the 0.08BiVO₄/3DOM TiO₂ nanocomposite are shown in Fig. 4. The 0.08BiVO₄/3DOM TiO₂ nanocomposite (Fig. 4a and b) has a dual morphology with small particles corresponding to BiVO₄ present on the 3DOM TiO₂ structure. The bismuth vanadate adopts a new morphology (Fig. 4b) with increased size after the formation of the nanocomposite (highlighted by arrows). The elemental compositions of the BiVO₄/3DOM TiO₂ heterojunctions were analyzed by energy dispersive X-ray spectroscopy (EDXS). As shown in Fig. 4c–e, the EDX mapping of 0.08BiVO₄/3DOM TiO₂ indicated the presence of Bi, V, Ti and O atoms in the sample. The red colour shows the Ti element and green represents bismuth vanadate nanoparticles which are homogeneously dispersed on the 3DOM TiO₂ IO structure. Fig. 4e shows the results for the combination of TiO₂ and BiVO₄. Fig. 4 evidences very clearly the intimate contact between the 3DOM TiO₂ IO structure and BiVO₄ nanoparticles.

### 3.3 Chemical states by X-ray photoelectron spectroscopy (XPS)

In order to elucidate the elemental composition, the oxidation states and the chemical environment of Bi, V and Ti elements in the BiVO₄/TiO₂ photocatalyst, XPS analysis was performed.

Fig. 5 shows the XPS spectra of the 0.08BiVO₄/3DOM TiO₂ nanocomposite (spectrum a), compared with the pure TiO₂ inverse opal structure (spectrum b) and pure BiVO₄ nanoparticles (spectrum c), in different spectral regions that correspond to different elements, revealing the binding energies for Bi 4f, Ti 2p, V 2p and O 1s of the as-prepared samples.

Fig. 5d–g show the high-resolution XPS spectra of the BiVO₄/TiO₂ sample. As shown in spectrum d, the binding energies of Bi 4f₇/₂ and Bi 4f₅/₂ are 159.0 and 164.3 eV, respectively, indicating that this element is present as Bi(III). The binding energy values are typical of bismuth in BiVO₄.²³ A shift of 0.3 eV to a higher binding energy in the peak positions of bismuth, as compared to pure BiVO₄ (158.7 eV and 164.0 eV), suggests that electron transfer from BiVO₄ to TiO₂ could occur, in accordance with the shift observed for bismuth. The high resolution V 2p spectrum reveals a doublet with peaks centred at 524 and 516.3 eV (spectrum e), which correspond to the V 2p₃/₂ orbit and V 2p₅/₂ orbit, respectively. These peaks also display binding energy
values typical of V(V) as reported in the literature.\textsuperscript{51–54} Thus, the analysis of the V 2p core lines of the as-prepared sample clearly indicates the presence of V\textsuperscript{5+} oxidation states. Compared with pure BiVO\textsubscript{4}, a slight shift of 0.3 eV is observed in the position peaks corresponding to V 2p (524.0 for the V 2p\textsubscript{1/2} orbit and 516.3 eV for V 2p\textsubscript{3/2}).

Spectrum f depicts two bands with binding energies of 458.2 eV and 463.9 eV that are assigned to Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2}, respectively, corresponding to Ti\textsuperscript{4+} in a tetragonal structure such as anatase titania.\textsuperscript{55} Compared to pure TiO\textsubscript{2}, a shift of 0.6 eV to a lower binding energy in the peak positions of TiO\textsubscript{2} (458.8 eV and 464.5 eV) is observed, confirming the possible charge transfer between BiVO\textsubscript{4} and TiO\textsubscript{2}. The high-resolution XPS spectrum of O 1s (spectrum g) shows a narrow peak at a binding energy of 529.6 eV. For pure BiVO\textsubscript{4} nanoparticles and the TiO\textsubscript{2} inverse opal structure, this peak was located at 529.4 and 530.0 eV, respectively. This asymmetric peak indicates that oxygen is present on the surface not only as lattice oxygen, but also as free oxygen.\textsuperscript{51,53–54} All of these results gave the insight that the composite was formed by TiO\textsubscript{2} and BiVO\textsubscript{4}. Moreover, the peaks for Bi 4f, V 2p, Ti 2p and O 1s in the BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} nanocomposite underwent a slight shift compared with those in pure BiVO\textsubscript{4} and TiO\textsubscript{2} resulting from the interaction between BiVO\textsubscript{4} and TiO\textsubscript{2} in the composite system.

3.4 Textural analysis

N\textsubscript{2} adsorption–desorption of the TiO\textsubscript{2} inverse opal, BiVO\textsubscript{4} and BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} nanocomposites revealed type II isotherms. For TiO\textsubscript{2} inverse opal, the pore size distribution plot calculated via the Barrett–Joyner–Halenda (BJH) method shows a narrow pore size distribution (inset Fig. 6a) centred at 2.3 nm, resulting from the aggregation of TiO\textsubscript{2} nanoparticles. The adsorbed nitrogen volume for TiO\textsubscript{2} inverse opal does not reach saturation at a high relative pressure $p/p_0 = 0.8–1.0$, which indicates the presence of large macropores. Thus, the N\textsubscript{2} isotherm obtained for TiO\textsubscript{2} inverse opal reveals macroporosity which arises from the inverse opal structure. BET specific surface areas of pure BiVO\textsubscript{4} nanoparticles, pure TiO\textsubscript{2} inverse opal structure and BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} heterojunction photocatalysts are shown in Table 1. BiVO\textsubscript{4} and TiO\textsubscript{2} inverse opal were found to have a surface area of 4 and 30 m\textsuperscript{2} g\textsuperscript{-1}, respectively. For BiVO\textsubscript{4} nanoparticles (inset of Fig. 6b), the pore size distribution is quite large. The N\textsubscript{2} adsorption–desorption isotherms exhibit hysteresis arising from the aggregation of large particles. In the case of the two BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} nanocomposites (Fig. 6c and d), other than macroporosity from inverse opal structures, two pore sizes centred at 2.4 and 8 nm for 0.04BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} and 2.5 and 7 nm for 0.08BiVO\textsubscript{4}/3DOM TiO\textsubscript{2} were observed, respectively. The pore size at 2.3–2.5 nm comes from the aggregation of BiVO\textsubscript{4} nanoparticles whilst the pores of 7–9 nm come from the aggregation of BiVO\textsubscript{4} nanoparticles. When the amount of BiVO\textsubscript{4}
nanoparticles is increased, the size of nanoparticles becomes bigger, larger pores can be formed, reducing the amount of pores of 7–9 nm. The XRD results confirmed the growth of nanoparticles with increasing BiVO₄ amount.

### 3.5 Optical properties

In order to understand the photocatalytic characteristics of the synthesized BiVO₄/TiO₂ nanocomposites, it is important to compare some of their typical properties such as reflectance and photoluminescence with those of pure BiVO₄ and TiO₂. The ordinary photographs and the UV-visible absorbance spectra of TiO₂ inverse opal, BiVO₄ nanoparticles and two BiVO₄/TiO₂ nanocomposites are shown in Fig. 7A and B, respectively. From Fig. 7A it can be seen that titania inverse opal (a) has a white color. On adding bismuth vanadate (d), which has a strong yellow color, the tone of the white color changes in two different manners. In the sample with 0.04BiVO₄/3DOM TiO₂ (b), the color turns to a light yellow tone. On increasing the amount of BiVO₄ to 0.08 (c), the yellow colour becomes more intense. It can be clearly seen that with an increasing amount of BiVO₄, the absorption edge of the BiVO₄/3DOM TiO₂ nanocomposite is red shifted to longer wavelengths within the visible-light range (spectra b and c of Fig. 6B), with the spectral response range of TiO₂ being extended. The BiVO₄ nanoparticle sample (spectrum d of Fig. 7B) showed an absorption edge around 527 nm, which could be responsible for any potential visible-light induced photocatalytic activity.

The steep absorption edge in the visible range indicates that the absorption of visible light is not due to the transition from impurity levels but due to the bandgap transition, originating from the charge transfer response of monoclinic BiVO₄ from the valence band populated by the hybridization of the O 2p orbital and Bi 6s orbital to the conduction band formed by the V 3d orbital. As can be seen, the absorbance of the BiVO₄/3DOM TiO₂ nanocomposites in the visible light region increases with increasing the amount of bismuth vanadate (spectra b–d of Fig. 6B). The change in light absorption can be inferred even from the colours of the various compounds.

The bandgap energies of the as-prepared samples could thus be estimated from a plot of \((ahv)\) versus photon energy \((h\nu)\) via the Kubelka–Munk method:\(^{35–56}\) 
\[
\frac{ahv}{E_g} = \frac{A}{(h\nu - E_g)^{1/2}},
\]
where \(a, h, \nu, E_g\), and \(A\) are the absorption coefficient, Planck’s constant, light frequency, bandgap energy, and a constant, respectively.

The intercept of the tangents to the \(x\)-axis gives a good approximation of the bandgap energy for the materials. As shown in Fig. 7C, the estimated bandgaps of the BiVO₄ nanoparticles, TiO₂ inverse opal, 0.04BiVO₄/3DOM TiO₂ and 0.08BiVO₄/3DOM TiO₂ photocatalysts were about 2.37, 3.15, 2.45 and 2.4 eV, respectively. From these results it can be confirmed that the BiVO₄ semiconductor acts as a visible light absorber for TiO₂, leading to effective separation of photoinduced electron–hole pairs, thus reducing the likelihood of recombination. In order to investigate whether this could be possible, photoluminescence (PL) measurements were carried out.

Fig. 8 shows the photoluminescence (PL) emission spectra of pure BiVO₄ nanoparticles, pure TiO₂ inverse opal and BiVO₄/3DOM TiO₂ nanoheterostructured photocatalysts, which have been used to provide information on the efficiency of charge carrier trapping, migration and transfer.

It is very helpful to understand the fate of the electron–hole pairs in semiconductors as PL emission stems from the recombination of free carriers. The PL intensity depends on the recombination of excited electrons and holes. The lower the PL emission intensity is, the lower is the recombination property of the sample. As can be seen, BiVO₄ (spectrum a) exhibits a weak emission at 525 nm which is caused by electron–hole recombination at surface traps. The overall PL emission intensity of BiVO₄ is the lowest, indicating the very low recombination rate of electron–hole pairs in this material. It can also be observed that the bare TiO₂ (spectrum d) exhibits a strong PL signal in the range of 400 to 450 nm, and has four obvious PL peaks at about 442, 460, 493 and 525 nm, respectively, possibly the former mainly resulting from band edge free excitons and the latter mainly from binding excitons.\(^{39–60}\) The overall PL emission intensity of TiO₂ is the highest, showing its highest recombination rate of electron–hole pairs, being unfavourable for photocatalysis. However, the characteristic emission of TiO₂ is...
significantly affected after the introduction of BiVO₄ nanoparticles and the intensity is progressively reduced with increasing BiVO₄ amount in the 3DOM TiO₂ IO structure. This behaviour shows that efficient charge or energy transfer occurs at the BiVO₄/TiO₂ heterojunction interface. The observation of PL bands depends on the excitation wavelengths. For example, no PL bands when the excitation wavelength is 320 nm for BiVO₄ nanoparticles while some PL bands, in spite of low intensity, are indeed observed with an excitation wavelength of 515 nm (Fig. 2S†). These are due to different electron–hole generation and recombination rates between different bands (Fig. 3S†).

The positions of the CB and VB of TiO₂ and those of the BiVO₄ and XPS results also suggest that interactions between BiVO₄ and TiO₂ involve charge transfer of photoexcited electrons from the conductive band of the donor BiVO₄ to the empty electronic states of the acceptor TiO₂ and a better charge separation in space in BiVO₄/3DOM TiO₂ nanocomposites. These observations are in good agreement with those observed by the XPS study. More details will be given in the following sections.

3.6 Photocatalytic activity

The degradation of rhodamine B (RhB) under visible light irradiation was conducted, as a test reaction, in the presence of each material. The absorption spectrum in the range of 500–600 nm for different time intervals for the 0.08BiVO₄/3DOM TiO₂ nanocomposite photocatalyst is shown in Fig. 9A as an example. It has been shown that the major absorption peaks of RhB, located at around 554 nm, diminished gradually under visible light irradiation in the presence of the BiVO₄/3DOM TiO₂ nanocomposite. The photocatalytic efficiencies (C/C₀) of pure BiVO₄ nanoparticles, pure 3DOM TiO₂ inverse opal, two reference samples (phy-mix 0.08BiVO₄/3DOM TiO₂ IO and 0.08BiVO₄/P25-TiO₂ nanoparticles) and two BiVO₄/TiO₂ nanocomposites are illustrated in Fig. 9B. The blank experiment of RhB degradation without the presence of a photocatalyst is shown in curve (a) of Fig. 9B. A very low degradation rate of RhB, similar to that reported in the literature, was observed and can be neglected. It can clearly be observed that for all samples the degradation of RhB increases gradually with increasing irradiation time. BiVO₄ nanoparticles exhibit very poor photocatalytic activity, with only 22% of RhB being degraded in 50 min, despite its strong absorption in the visible region. Under the same illumination conditions 28% of the RhB solution was degraded by 3DOM anatase TiO₂ inverse opal. However due to its wide bandgap energy in the UV range, TiO₂ could not absorb in the visible range. Thus theoretically, no possible degradation of dye molecules by TiO₂ can be expected. Nevertheless, good degradation rate can be expected for the 3DOM IO structure. We will explain this observation in the following paragraph. The photocatalytic performance of TiO₂ can be improved by coupling catalysts with sensitizers leading to the BiVO₄/TiO₂ nanocomposite proposed herein with a narrow bandgap and thus higher photocatalytic activity. The increase in performance was demonstrated by a superior photodegradation of RhB, with the destruction of 80% and 95% RhB over a 120 min period in the presence of 0.04BiVO₄/3DOM TiO₂ and 0.08BiVO₄/3DOM TiO₂, respectively.
It has been reported that the photocatalytic degradation process of RhB follows first-order kinetics. The kinetics of RhB degradation with the different samples is illustrated in Fig. 10. The rate constants for the pure BiVO₄ nanoparticles, pure TiO₂ inverse opal, phy-mix 0.08BiVO₄/3DOM TiO₂, 0.08BiVO₄/P₂5-TiO₂, 0.04BiVO₄/3DOM TiO₂ and 0.08BiVO₄/3DOM TiO₂ photocatalysts are calculated to be 0.0062, 0.0078, 0.0079, 0.0084, 0.0152 and 0.0256 min⁻¹ respectively. From the rate constants (k) in Fig. 10, it can be inferred that the order for the photodegradation rates is: 0.08BiVO₄/3DOM TiO₂ > 0.04BiVO₄/3DOM TiO₂ > 0.08BiVO₄/P₂5-TiO₂ > phy-mix 0.08BiVO₄/3DOM TiO₂ ≥ 3DOM TiO₂ > BiVO₄. The nanocomposite of 0.08BiVO₄/3DOM TiO₂ has photocatalytic activity 4 times and 3 times higher than pure BiVO₄ and 3DOM TiO₂ respectively, showing the high impact of the BiVO₄/3DOM TiO₂ heterojunction on the photocatalytic performance. The reference sample prepared by the physical mixing of BiVO₄ and 3DOM TiO₂ IO has similar photocatalytic activity to that of pure 3DOM TiO₂ IO, indicating that the introduction of a low amount of BiVO₄ into 3DOM TiO₂ IO by physical mixing does not induce an effect on the photocatalytic activity and hence the importance of the intimate contact between BiVO₄ and the 3DOM TiO₂ IO structure. Another reference sample 0.08BiVO₄/P₂5-TiO₂ prepared by the same hydrothermal method as BiVO₄/3DOM TiO₂ showed higher photocatalytic activity than pure 3DOM TiO₂, the physical mixing sample and pure BiVO₄ nanoparticles, but it was much lower than that of BiVO₄/3DOM TiO₂ nanocomposites, confirming again the enhancement of photocatalytic activity by the intimate contact between BiVO₄ and TiO₂ and the importance of the 3DOM inverse opal structure.

It is clear that the photocatalytic activity of BiVO₄/TiO₂ nanocomposite photocatalysts is strongly dependent on the amount of BiVO₄. The photodegradation activity of (x) BiVO₄ : TiO₂ increases remarkably with an increasing amount of BiVO₄ up to x = 0.08. The enhanced photocatalytic activity may originate from the interfacial transfer of electrons and holes as observed by PL and XPS studies. The lifetime of the charge carriers is increased and thus the recombination of electron–hole pairs can be inhibited, which resulted in an elevation of the photocatalytic efficiency of TiO₂ under visible-light irradiation. As a comparison, Cao et al. studied the photocatalytic activity of the BiVO₄/TiO₂ composite under simulated sun-light irradiation. The photocatalytic activities of the BiVO₄/TiO₂ composites with different ratios were evaluated by the degradation of RhB at room temperature. They found that 20 wt% TiO₂/BiVO₄ shows higher activity with a constant rate equal to 0.04 min⁻¹.

### 3.7 Photocatalysis mechanism

The coupling of different semiconductor oxides seems to be useful in order to absorb a wide range of solar radiation and to achieve more efficient electron–hole pair separation when under irradiation and, consequently, higher photocatalytic activity. A schematic representation of our BiVO₄/3DOM TiO₂ nanocomposites with bismuth vanadate nanoparticles incorporated in the 3DOM inverse opal TiO₂ matrix is presented in Fig. 11A. The combination of BiVO₄ and TiO₂ has attracted much attention recently in photocatalysis. However, the photocatalysis promoting mechanism remains unclear and diverging. Hu et al. proposed a band configuration where the CB and VB of BiVO₄ were positioned at locations higher than the CB and VB of pure TiO₂ respectively. Under visible light irradiation, the electrons of the VB of BiVO₄ are promoted to its CB, leaving holes behind. Electrons in the CB of BiVO₄ can now be transferred to the CB of TiO₂. Electrons in the CB of TiO₂ are
good reductants which can capture the adsorbed O$_2$ and reduce it to O$_2^-$ to oxidize dye molecules. The holes at the VB of BiVO$_4$ can react with OH$^-$ to give rise to OH$^-$ which can also be used for the degradation of dye molecules. The authors claimed that BiVO$_4$ played the role of a light sensitizer. The photodegradation of organic molecules occurred at the surface of BiVO$_4$. However, our present results show that pure BiVO$_4$ gave very low photocatalytic activity. A different electronic mechanism should thus be involved. Zhang et al.$^{25}$ proposed one such different electronic mechanism. On the basis of their calculations, they placed the CB and VB of BiVO$_4$ between the CB and VB of TiO$_2$. They suggested that under both UV and visible light irradiation the photogenerated electrons from RhB dye molecules are transferred to the CB of TiO$_2$ which are in turn transferred to the CB of BiVO$_4$, leaving the holes in the VB of TiO$_2$. They proposed that the reduction of RhB occurs in the CB of BiVO$_4$ and the oxidation of RhB can take place in the VB of both TiO$_2$ and BiVO$_4$. Colon et al.$^{31}$ postulated a similar electronic mechanism with similar positions of the CB and VB of TiO$_2$ and those of BiVO$_4$. However, this proposition concerning the positions of the CB and VB of TiO$_2$ and those of BiVO$_4$ remains to be confirmed. In some very recent papers, the positions of the CB and VB of TiO$_2$ and BiVO$_4$ were revisited. A generally accepted point is that under visible light irradiation, electrons of the VB of BiVO$_4$ will be firstly excited to the CB of BiVO$_4$, leaving holes behind and these photogenerated electrons will be transferred to the CB of TiO$_2$. Tang et al.$^{30}$ pointed out that electron transfer from BiVO$_4$ to TiO$_2$ is feasible since $E_{cb}$ of TiO$_2$ is considered to be located just under the conduction band of BiVO$_4$. Fu et al.$^{29}$ in their excellent recent paper confirmed this suggestion that electrons are transferred from BiVO$_4$ to TiO$_2$. BiVO$_4$ can be considered as a light sensitizer for TiO$_2$.

On the basis of the above analysis, our XPS results, photocatalytic performance of a series of materials studied herein and the fact that pure BiVO$_4$ gives an unexpectedly low photocatalytic activity in the degradation of RhB dye molecules, a new energy band diagram of the BiVO$_4$/TiO$_2$ heterojunction photocatalysts is proposed and presented in Fig. 11B. It should be taken into account that the work function for RhB is $-5.45$ eV and $-3.08$ eV for excited RhB.$^{41}$ For BiVO$_4$, a valence band (VB) edge potential of 1.90 V (NHE scale) was reported by Su et al.$^{32}$ while the VB of TiO$_2$ was reported to be 2.82 V (NHE scale) by Hagfeldt et al.$^{42}$ and Sayama et al.$^{43}$ The measured bandgap energies of TiO$_2$ and BiVO$_4$ by the present study were around 3.15 and 2.37 eV, respectively. The position of a conduction band (CB) edge is determined by $E_{cb} = E_{vb} - E_F$. Thus, the calculated CB energies of BiVO$_4$ and TiO$_2$ were $-0.47$ and $-0.27$ eV, respectively. The difference in the conduction band energies between BiVO$_4$ and TiO$_2$ allows the transfer of electrons from the conduction band of BiVO$_4$ to that of TiO$_2$ since the position of the CB of TiO$_2$ is just under that of BiVO$_4$.

When the system is irradiated with visible light, BiVO$_4$ is activated to generate electron–hole pairs. An electron (e$^-$) is promoted from the valence band, VB, into the conduction band, CB, of BiVO$_4$, leaving a hole (h$^+$) behind. The excited-state electrons produced by BiVO$_4$ can be injected into the conduction band of the coupled TiO$_2$ due to the intimate matching of the electric fields between the two materials and because the position of the CB of TiO$_2$ is just under the CB of BiVO$_4$ as indicated by Tang et al.$^{30}$ The electron transfer is now feasible. The electron and holes are physically separated in space, reducing the opportunity of their recombination. The conduction electrons at the TiO$_2$ side are good reductants which can be scavenged by molecular oxygen, O$_2$, to yield the superoxide radical anion O$_2^-$.$^{26}$ The holes at the VB of BiVO$_4$ will interact with hydroxyl groups to form OH$^-$ radicals. It is well known that the OH$^-$ radical is a powerful oxidizing agent capable of degrading most pollutants. In the present case, RhB dye model molecules will be degraded by O$_2^-$ and OH$^-$ radicals. Anatase TiO$_2$ inverse opal has a very large gap so that no electrons can be promoted from the VB to CB, thus no electron–hole pairs can be formed under visible light irradiation.

Concerning pure BiVO$_4$ nanoparticles, the bandgap is around 2.4 eV and located in the visible light zone. However, an unexpected low photocatalytic activity towards RhB dye molecules, even lower than that of the anatase TiO$_2$ inverse opal structure, has been observed. The same phenomenon that the photocatalytic activity of monoclinic BiVO$_4$ in the degradation of phenol is lower than that of pure anatase TiO$_2$ in the visible light range has been previously reported by Colon et al.$^{26}$ The low photocatalytic activity of the single phase of BiVO$_4$ photocatalysts was also pointed out by Fresno et al.$^{27}$ Li et al.$^{28}$ and Jiang et al.$^{33}$ The lower photocatalytic activity of pure monoclinic BiVO$_4$ compared to 3DOM TiO$_2$ observed in the present study can be due to two different reasons. Firstly, although our PL study showed that pure monoclinic BiVO$_4$ has a very low recombination rate of electrons–holes, due to its intrinsic characteristics such as the very poor adsorptive performance towards organic dye molecules and the inefficient migration of photogenerated electron–hole pairs to the surface for photocatalytic reactions, the pure monoclinic BiVO$_4$ presented an unexpectedly low photocatalytic activity in the visible light degradation of organic dye pollutants.$^{31,33}$ The combination with TiO$_2$ can largely improve the adsorption properties and migration rate of electron–hole pairs towards the surface of BiVO$_4$/3DOM TiO$_2$ facilitating electron transfer from the CB of BiVO$_4$ to the CB of TiO$_2$. Secondly, as RhB molecules can absorb visible light, it is possible that some electrons can be promoted from the HOMO ($-5.45$ eV) to LUMO ($-3.08$ eV) and these electrons of RhB can migrate to the CB of anatase TiO$_2$ to generate reactive O$_2^-$ to degrade RhB dye molecules. This is why the degradation of RhB can be observed on anatase TiO$_2$ inverse opal in the visible light range although TiO$_2$ absorbs only UV light and the activity is even higher than that of BiVO$_4$ nanoparticles.

It is worth noting that our 3DOM TiO$_2$ presented very interesting photodegradation activity in the visible zone. It is well-known that TiO$_2$ has a large electronic bandgap and cannot absorb visible light and should not exhibit photodegradation activity of dye molecules in the visible zone. The dye molecule degradation rate of pure TiO$_2$ inverse opal has been reported by Lee et al.$^{43}$ Their TiO$_2$ IO sample gave a degradation rate of 5% after 120 minutes much lower than the photocatalytic activity observed for our pure TiO$_2$ inverse opal. The difference is
because of the following reasons. (1) Different preparation conditions: their TiO₂ IO sample was calcined at 850 °C and contained mainly the rutile phase, while our sample was calcined at 550 °C and contained only the anatase phase. It is well known that the rutile phase is less active than the anatase phase. (2) Different photocatalytic conditions: in their case they used methylene blue while in our case we used RhB as the reactant. (3) Different characteristics of samples: their sample had a macropore size of 500 nm while our sample had a macropore size of 250 nm. Their sample was in the shape of a film while our sample was in a powder form. Our sample had a higher surface area, i.e. higher contact area. Due to the above reasons, their sample presented different activity compared to our 3DOM TiO₂ powder. However, one point is important to underline that our bare 3DOM TiO₂ IO sample gave an unexpectedly high degradation rate of 28%. The reason is quite probably related to the 3DOM TiO₂ IO structure which could generate the slow photon effect so that the photocatalytic activity was enhanced. Ozin’s group and our group have reported this effect for TiO₂ IO in the form of films for visible light and UV light in gas phase⁴⁷–⁴⁹ and liquid phase⁴⁹,⁵⁰–⁵⁸ photocatalytic degradation of dye molecules, respectively. Our present sample could have exhibited this slow photon effect that facilitated enhancement in photocatalytic activity even in the visible light zone, in good agreement with the observation made by Ozin et al. with a similar pore size of TiO₂ IO.⁴⁷–⁴⁹ That is why we observed a degradation activity of 28% which is not observed for P25 in the visible light zone. We are working on this effect to better investigate the slow photon effect in the visible light zone to enhance the photocatalytic activity. However, due to the powder form of the sample, the investigation is much more difficult than that of film shaped samples. Another point is that the 3DOM TiO₂ can provide a more active surface area, more contact area and increased mass transfer because of its highly accessible 3D porosity. We prepared a reference sample by the deposition of BiVO₄ nanoparticles on P25-TiO₂ nanoparticles using the same hydrothermal preparation method. The photocatalytic activity of 3DOM BiVO₄/TiO₂ nanocomposites is much higher than that of the BiVO₄/TiO₂-P25 nanocomposite, showing very clearly the effect of the 3DOM TiO₂ inverse opal structure.

We also performed a control experiment for the photodegradation of RhB using a physical mixture (e.g., grinding) of BiVO₄ dumbbell nanoparticles and 3DOM TiO₂ powder and compared its photocatalytic activity with that of the BiVO₄/3DOM TiO₂ nanocomposite. It is evidenced that the photocatalytic activity of the physical mixture (e.g., grinding) of BiVO₄ dumbbell and 3DOM TiO₂ is very similar to that of the pure 3DOM TiO₂ inverse opal structure and slightly higher than that of pure BiVO₄ dumbbell, but much lower than that of BiVO₄/3DOM TiO₂ IO nanocomposites prepared by careful deposition of BiVO₄ nanoparticles on the 3DOM TiO₂ IO structure to have an intimate contact between the two phases, illustrating the advantage of the intimate contact between BiVO₄ nanoparticles and the 3DOM inverse opal structure.

When the narrow bandgap sensitiser BiVO₄ and the large bandgap photocatalyst TiO₂ are in intimate contact in 3DOM BiVO₄/TiO₂ nanocomposites, drawbacks such as the rapid e⁻–h⁺ recombination that occurs in TiO₂, the poor adsorption properties and low migration rate of electrons–holes of pure BiVO₄ towards its surface and the absence of excitation of TiO₂ in the visible light range can all be avoided. Under visible light irradiation, the electrons in the CB excited from the VB of BiVO₄ can migrate to the CB of the TiO₂ photocatalyst to generate very reactive O₂⁻ species. The h⁺ generated in the VB of BiVO₄ can react with hydroxyl groups to form the oxidizing agent OH⁻. Both O₂⁻ and OH⁻ at the surface of the BiVO₄/3DOM TiO₂ nanocomposite will degrade RhB dye pollutants adsorbed by TiO₂. BiVO₄ in our BiVO₄/3DOM TiO₂ nanocomposites plays the role of a light sensitizer, accelerating the photodegradation rate of RhB by 3DOM TiO₂. Larger the amount of BiVO₄, greater is the sensitizing effect, i.e. better light absorption (suggested by diffuse reflectance) and better charge separation effect (suggested by PL). These two effects make the 0.08BiVO₄/3DOM TiO₂ sample a better photocatalyst. However, there exists an optimal amount of BiVO₄. We are working to determine this optimal amount. Larger the amount of BiVO₄ in TiO₂ inverse opal, greater the number of electrons–holes generated in the BiVO₄/3DOM TiO₂ nanocomposite, and higher is the photocatalytic activity. It is clear that the 3DOM BiVO₄/TiO₂ nanocomposite with intimate contact can provide an efficient way to design long-lived visible light excited charge carriers for photocatalysis.

4. Conclusions

Novel 3DOM BiVO₄/TiO₂ nanocomposites have been successfully synthesized. According to the UV-vis DRS results, the absorption of BiVO₄/TiO₂ nanocomposites increased in the visible region. Moreover, the low bandgap energy of BiVO₄/TiO₂ nanocomposites also influenced dye degradation and showed significant promise for these nanocomposites to be employed as effective visible light photocatalysts for dye wastewater treatment, photocatalytic water splitting, CO₂ reduction and other solar applications. In fact, by coupling different bandgap semiconductors such as TiO₂ and BiVO₄, the resultant nanocomposites facilitate the separation of the photogenerated carriers under the internal field induced by the different electronic band structures of the semiconductors. Thus the photocatalytic activity of TiO₂ inverse opals was efficiently improved. It can be concluded that adding narrow bandgap energy materials as light sensitizers to TiO₂ is a very promising method to render 3DOM TiO₂ inverse opals more efficient in the photodegradation of organic pollutants and in the water splitting reaction under visible light. Thus, compared to 3DOM TiO₂ the 3DOM BiVO₄/TiO₂ nanocomposites presented herein exhibit higher photocatalytic activities and can be considered as more efficient as they promote visible-light-driven photocatalysis. Increasing the BiVO₄ amount in nanocomposites can increase the photogenerated charge separation time and in consequence improve the photocatalytic performance again. In the present work, the benefits of 3D porosity and high surface area of the TiO₂ inverse opal structure were essential for the accessibility of dye molecules to photocatalysts and for better dispersion of BiVO₄ nanoparticles. However, the benefit of the slow photon
effect of the 3DOM TiO₂ inverse opal photonic crystal structure has not been studied. The future work will focus on the optimisation of the amount of BiVO₄ in nanocomposites, the study of other large bandgap photocatalysts such as ZnO and taking equal attention to the possible slow photon effect of the 3DOM TiO₂ inverse opal.

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Notes and references