One-pot microwave synthesized high-performance BiVO₄/InVO₄ heterojunction for photocatalytic reduction of Cr⁶⁺

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Graphical abstract
Abstract

A series of BiVO₄/InVO₄ composites were synthesized by one-pot microwave method based on the ratio regulation of Bi/In. Consequently, the as-fabricated BiVO₄/InVO₄ photocatalysts performed higher photocatalytic activities (100%) than pure InVO₄ and BiVO₄. The prepared photocatalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), UV–vis diffuse reflection spectroscopy (UV–vis DRS) and Fourier transform infrared spectra (FTIR). The results indicate the formation of BiVO₄/InVO₄ and it possesses enhanced solar light absorption. The enhanced reduction rate is ascribed to the efficient separation of photogenerated charge carriers due to the heterojunction formed between BiVO₄ and InVO₄. The possible photocatalytic mechanism of BiVO₄/InVO₄ composite was also discussed in detail.

Keywords: BiVO₄, InVO₄, heterojunction, Cr⁶⁺ reduction, photocatalytic activity.
1. Introduction

Chromium is the seventh most abundant element on the earth and is mainly mined in the form of chromite (FeCr$_2$O$_4$) ore (Cervantes and Campos-García, 2007; Sivaranjanee and Saravanan, 2018). Chromium plays an important role in industrial material and is widely used in electroplating, ferroalloy products, leather manufacturing, fuels and chemical products. Cr$^{6+}$ has been classified as a class A carcinogen by the U.S. Environmental Protection Agency (EPA), with high solubility and mobility in aqueous solutions, difficulty in biodegradation and enrichment in animal and human tissues through the food chain. According to pH and concentration, Cr$^{6+}$ mainly exists in the form of Cr$_2$O$_7^{2-}$, HCrO$_4^-$ and CrO$_4^{2-}$ (Miretzky and Cirelli, 2010; Sultana et al., 2014). Compared with Cr$^{6+}$, Cr$^{3+}$ is more stable, and Cr$^{3+}$ is an essential trace element for human body. Photocatalysis has been seen as a green route to convert Cr$^{6+}$ to Cr$^{3+}$ in aqueous media (Mao et al., 2016; Zhang et al., 2011; Zhao et al., 2021a). However, most photocatalysts still suffer from limited light absorption and especially the rapid recombination of photo-induced charge carriers (Cheng et al., 2021).

In recent years, Bi-based photocatalysts have been extensively studied (Yang et al., 2019), especially BiVO$_4$ due to the characteristics of wide range of component elements, good chemical properties and thermal stability in aqueous solution (Kim and Choi, 2014; Rao et al., 2014; Wang et al., 2020b). Hence, it has been reported to effectively use solar energy for pollutants removal (Wang et al., 2020a; Yang et al., 2020b). Chala (Chala et al., 2014) prepared pure BiVO$_4$ and 0.5 ~ 5.0mol% Fe loaded BiVO$_4$ samples by a hydrothermal method. The results clearly showed that Fe-loaded BiVO$_4$ sample exhibited remarkably higher activity than pure BiVO$_4$. Shi (Shi et al., 2017) showed that a novel bismuth vanadate-palygorskite (BiVO$_4$-Pal) photocatalyst exhibits photocatalytic activity for tetracycline hydrochloride removal under visible light. The pseudo-first-order degradation rate constant for BiVO$_4$-Pal composites was approximately 2.1 times higher than that of pure BiVO$_4$, and the photodegradation rate of the
BiVO<sub>4</sub>-Pal composite was 1.4 times greater than that of pure BiVO<sub>4</sub>. However, low surface adsorption capacity and rapid charge recombination were the two main reasons for limiting its application. In order to solve this problem, many methods such as metal ion deposition, non-metal doping have been adopted (Yang et al., 2020a). Noteworthy, two or more semiconductors are combined to form a heterojunction, which promotes the separation of photogenic carriers and provides additional active sites for photocatalytic reactions (Li et al., 2022; Sun et al., 2018; Zhao et al., 2021b). Many studies have shown that InVO<sub>4</sub> can enhance the photocatalytic degradation efficiency of organic pollutants under visible light irradiation (Lin et al., 2015).

Based on the narrow band gap of InVO<sub>4</sub> (E<sub>g</sub> = 1.9 eV) and BiVO<sub>4</sub> (E<sub>g</sub> = 2.4 eV), combining BiVO<sub>4</sub> and InVO<sub>4</sub> to form a type II staggered heterojunction is an effective route (Zhang et al., 2019). Besides, BiVO<sub>4</sub>/InVO<sub>4</sub> heterojunction allows photogenerated carriers to migrate from one semiconductor to another through the interface, thereby promoting photocatalytic property (Fang et al., 2022; Mu et al., 2022; Wang et al., 2021; Wang et al., 2022; Yang et al., 2020a).

In this work, BiVO<sub>4</sub>/InVO<sub>4</sub> heterojunction was obtained by one-pot microwave strategy. The suitable band structures between BiVO<sub>4</sub> and InVO<sub>4</sub> make it possible to form a heterojunction, allowing it to possess enhanced light absorption and charge transport, which was beneficial to the improvement of photocatalytic activity. The physical and chemical properties of the heterojunction were analyzed by XRD, SEM, FTIR, X- XPS and UV-vis spectroscopy. The photocatalytic performance of the samples was evaluated by the reduction of Cr<sup>6+</sup> under visible light irradiation. This study demonstrates that combining BiVO<sub>4</sub> and InVO<sub>4</sub> to form BiVO<sub>4</sub>/InVO<sub>4</sub> heterojunction is a feasible scheme for exploiting photocatalytic degradation of hexavalent chromium.
2 Materials and Methods

2.1 Materials and Reagents

The materials included analytical grade pure bismuth nitrate (Bi(NO$_3$)$_3$·5H$_2$O, Alfa Aesar), analytical grade pure sodium hydroxide powder (NaOH, SIGMA-ALDRICH), analytical grade pure bismuth nitrate (In(NO$_3$)$_3$·SIGMA-ALDRICH), ammonium metavanadate (NH$_4$VO$_3$, SIGMA-ALDRICH), nitric acid (HNO$_3$, SIGMA-ALDRICH), Potassium chromate (K$_2$CrO$_4$, SIGMA-ALDRICH), Sulfuric acid (H$_2$SO$_4$, SIGMA-ALDRICH), Methyl alcohol (C$_2$H$_6$O$_2$, Fisher Scientific), phosphoric acid (H$_3$PO$_4$, SIGMA-ALDRICH), citric acid (C$_6$H$_8$O$_7$, Fisher Scientific), which were purchased from Aladdin.

2.2 Synthesis of Photocatalysts

One-pot microwave strategy was used to prepare BiVO$_4$/InVO$_4$, as presented in Scheme 1. In detail, 2 mmol Bi(NO$_3$)$_3$·5H$_2$O and In(NO$_3$)$_3$·XH$_2$O with various molar ratio were dissolved in 4 mL of 4 mol/L HNO$_3$, followed by the addition of 50 mL of deionized water to form solution A. Similarly, 2 mmol NH$_4$VO$_3$ was dissolved in 4 mL of 4 mol/L NaOH to form solution B. Finally, solution B was mixed to solution A, and then transferred the mixed solution to a PTFE standard tank for the microwave reaction at 160°C (with a ramp of 25 min) for 40 min (power 120W). The mixed solution was allowed to cool to room temperature. The obtained precipitate was further rinsed until a pH of ~7, and then dried at 60°C for 24 h in vacuum. The obtained samples with expected Bi(NO$_3$)$_3$·5H$_2$O/In(NO$_3$)$_3$·XH$_2$O ratio of 0.75:0.25;0.5:0.5;0.25:0.75 were labeled as 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, BiVO$_4$, samples. As reference, normal InVO$_4$ and BiVO$_4$ were synthesized via the same strategy but without the introduction of NH$_4$VO$_3$ and In(NO$_3$)$_3$·XH$_2$O.
Scheme 1. schematic illustration for the preparation of InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, BiVO$_4$, samples.

2.3 Characterization

The crystal structures of prepared samples were characterized using X-ray diffraction (XRD) under Mo Kα radiation with a Rigaku D/Max2500pc (Tokyo, Japan) diffractometer (scanning angle 2θ from 0° to 40°, and scanning rate of 4°/min). A high-voltage (10 kV) Tescan FEG-SEM microscope (TESCAN, MARI3, Brno, Czech Republic) was used to acquire scanning electron microscopy (SEM) images of the prepared samples. Transmission electron microscopic (TEM) images of the prepared samples were obtained by the JEM-2100F equipment (operating at 200kV). The chemical characteristics of sample surfaces were investigated using X-ray photoelectron spectra (XPS) acquired with a PHI5000 (ULVAC-PHI, INC, Kanagawa Prefecture, Japan) versa probe system under monochromatic Al K X-rays. The visible light source was a 300 W Xe lamp (with a <420 nm UV cutoff filter), and all experiments were carried out at room temperature. UV–vis absorbance spectra of the as-prepared samples were recorded with Solid Spec-3700/3700 DUV (Tokyo, Japan) in the range of 200–800 nm. Fourier transform infrared spectra (FTIR) of the samples were collected from IRAffinity-1S FTIR spectrometer in the range of 600–4000 cm$^{-1}$.

2.4 Evaluation of Photocatalytic Activity Based on Cr$^{6+}$ Reduction
The photocatalytic reduction of Cr$^{6+}$ was conducted as follows. 0.01g catalyst was added to 25ml of 10mg/L Cr$^{6+}$ solution (prepared with K$_2$CrO$_4$), the pH value of which was adjusted to 4.2 using the H$_2$SO$_4$ solution followed by introducing methanol as a hole scavenger. The mixed solution was stirred for 1h under dark to achieve adsorption equilibrium, which was seen as the initial concentration ($C_0$). A 300W Xe lamp with a <420nm cut-off filter was used for photocatalytic reduction, and the solution was measured at defined time intervals. In detail, 1mL of the reaction solution was diluted to 50 mL. Then 1:1 phosphoric acid and sulfuric acid solution were added to diphenyl carbazide (diphenyl carbazide, DPC), and then the final colored solution was measured at 540 nm by spectrophotometer (UV 3000).
3 Results and discussion

3.1 Morphological studies

Fig. 1a and b show SEM images of BiVO$_4$ sample, which presents a cluster structure consisted of several long rice grain particles accumulations with rough surface and an average diameter about 2 μm. The morphology of pure InVO$_4$ (Fig. 1c and d) demonstrates the bulb-like particles with an average diameter of 1 μm. Interestingly, the morphology and size of the BiVO$_4$/InVO$_4$ are totally different to the pristine, demonstrating a leaf-like nanostructure (Fig. 1e and f). This shows the formation of the hybrid BiVO$_4$/InVO$_4$. To further confirm the heterojunction structure between BiVO$_4$ and InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$ sample was studied by a high resolution transmission electron microscopy (HRTEM), as shown in Fig. 2. Fig. 2a clearly shows leaf-like nanostructure of BiVO$_4$/InVO$_4$. From the Fig. 2b, the resolved interplanar distances of BiVO$_4$ and InVO$_4$ are about 0.23 and 0.258 nm, corresponding to the (121) plane of BiVO$_4$ and the (022) plane of InVO$_4$, respectively. The observed interconnection demonstrates the formation of BiVO$_4$/InVO$_4$ heterojunction, which was further confirmed by the elemental mapping (Fig. 2e–i), where In, V, Bi, and O elements are uniformly dispersed in the obtained leaf-like nanostructure.
Fig. 1. SEM images of the as-synthesized samples: (a) and (b) BiVO₄, (c) and (d) InVO₄, (e) and (f) 0.75 BiVO₄/0.25 InVO₄.
Fig. 2. TEM image (a, c and d), HRTEM image (b), and the corresponding EDS elemental mapping images of 0.75 BiVO$_4$/0.25 InVO$_4$ (e–i).

3.2 Structural analysis

The purity and crystallinity of the samples was analyzed by the X-ray diffraction (XRD). Fig.3 shows the XRD patterns of InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, BiVO$_4$ samples. BiVO$_4$ exhibits peaks at 20 angles of 8.6°, 13°, 16°, 21.5°, 27°, which are consistent with the XRD standard card of the monoclinic system BiVO$_4$ (PDF#78-1534). InVO$_4$ presents the characteristic peaks at 8.5°, 15°, 15.9°, 21°, 27.2°, matching well with the XRD standard card of orthorhombic InVO$_4$ (PDF#71-1689). When introducing 0.25 BiVO$_4$ in InVO$_4$, the peaks of InVO$_4$ remain but exhibit slight shifts. Such the change of signals may be attributed to that InVO$_4$ may not crystallize well due to the adding of BiVO$_4$. With the increasing content of BiVO$_4$, the XRD pattern of BiVO$_4$/InVO$_4$ tends to be similar to the pristine BiVO$_4$ and InVO$_4$. XRD and morphology results indicate the formation of BiVO$_4$/InVO$_4$ heterojunction. The XRD patterns were analyzed by Rietveld refinement using the Maud 2.80 software. We can see from Fig.4 that the final calculation result of the mass percentage of BiVO$_4$ is 78.19% and InVO$_4$ is 21.81% (Cao et al., 2020; Lutterotti, 2010).
Fig. 3. XRD diffraction patterns of InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, and BiVO$_4$/0.75 InVO$_4$, BiVO$_4$ samples.

Fig. 4. Rietveld refinement of 0.75BiVO$_4$/0.25InVO$_4$.

The FT-IR spectra of the obtained samples are shown in Fig. 5, and the signals of pure BiVO$_4$ and InVO$_4$ match well with the earlier reports (Liu et al., 2016; Regmi et al., 2018; Shi et al., 2014). For BiVO$_4$, the peaks at 710 cm$^{-1}$ and 810 cm$^{-1}$ may be due to V-O symmetric and asymmetric stretching vibrations. The characteristic peak at 617 cm$^{-1}$ is ascribed to Bi-O vibration. For InVO$_4$, the characteristic peak at 956 cm$^{-1}$ may be due to V-O symmetric and asymmetric stretching vibrations. The peaks at 903 and 756 cm$^{-1}$ belong to the vibration modes...
of V–O–In. The characteristic peak at 717 cm\(^{-1}\) could be ascribed to VO\(_4^{3-}\) (Faisal et al., 2021).

For the 0.75 BiVO\(_4\)/0.25 InVO\(_4\) composites, the characteristic peaks at various positions are detected, where 898 cm\(^{-1}\) could be attributed to In-O vibration and 679 cm\(^{-1}\) may be ascribed to the vibration of V-O, suggesting that the formation of the hybrid BiVO\(_4\)/InVO\(_4\).

![Fig.5. FT-IR spectra of InVO\(_4\), 0.75 BiVO\(_4\)/0.25 InVO\(_4\), 0.5 BiVO\(_4\)/0.5 InVO\(_4\), 0.25 BiVO\(_4\)/0.75 InVO\(_4\), BiVO\(_4\) samples.](image)

The XPS was performed to study the surface elemental composition and electronic structure of the prepared samples. Fig.6a exhibits the XPS spectra of InVO\(_4\), 0.75 BiVO\(_4\)/0.25 InVO\(_4\), 0.5 BiVO\(_4\)/0.5 InVO\(_4\), 0.25 BiVO\(_4\)/0.75 InVO\(_4\), BiVO\(_4\), which manifests the existence of In, Bi, V and O elements of the hybrid samples. Given the carbon element in the air, C 1s characteristic peaks are observed (Lin et al., 2013). As presented in Fig.6b, In 3d is composed of two peaks situated at 445.2 eV and 452.6 eV in InVO\(_4\), 445.2 eV and 452.5 eV in 0.25 BiVO\(_4\)/0.75 InVO\(_4\), 445.2 eV and 452.5 eV in 0.5 BiVO\(_4\)/0.5 InVO\(_4\) and 445 eV and 452 eV in 0.75 BiVO\(_4\)/0.25 InVO\(_4\), which are due to In\(^{3+}\) (Min et al., 2012), in addition, Bi 4d peak located at 442.2 eV in 0.75 BiVO\(_4\)/0.25 InVO\(_4\), 442.6 eV in 0.5 BiVO\(_4\)/0.5 InVO\(_4\) and 442.5 eV in 0.25 BiVO\(_4\)/0.75 InVO\(_4\), which appears (Lakhera et al., 2019) It can be seen that the characteristic peaks of Bi 4f located at 158.7 eV and 164.5 eV in BiVO\(_4\), 159 eV and 164.7 eV in 0.25 BiVO\(_4\)/0.75 InVO\(_4\), 159.2 eV and 164.6 eV 0.5 BiVO\(_4\)/0.5 InVO\(_4\) and 158.7 eV and 164.5 eV in 0.75 BiVO\(_4\)/0.25 InVO\(_4\), are attributed to Bi\(^{3+}\) (Wu et al., 2013), from Fig.6c. Fig. 6d shows the XPS spectra of V 2p and O
1s orbital in InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, BiVO$_4$. The V 2p peaks are located at 517 eV and 524.9 eV in BiVO$_4$, 517.8 eV 525.2 eV in InVO$_4$, 517.4 eV and 524.9 eV in 0.25 BiVO$_4$/0.75 InVO$_4$, 517.4 eV and 524.9 eV in 0.5 BiVO$_4$/0.5 InVO$_4$ and 517 eV and 524.9 eV in 0.75 BiVO$_4$/0.25 InVO$_4$, which could be due to the surface V$^{5+}$ of BiVO$_4$ and InVO$_4$(Min et al., 2012). The O 1s peaks are situated at approximately 530 eV,530 eV and 532 eV in BiVO$_4$, InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, ascribable to the chemisorbed water, oxygen in metal oxide lattice and hydroxyl groups (Li et al., 2015; Li et al., 2008). Obviously, the XPS spectra of 0.5 BiVO$_4$/0.5 InVO$_4$ and 0.75 BiVO$_4$/0.25 InVO$_4$ composite film shifts to higher wavelength, indicating the combination of BiVO$_4$ and InVO$_4$ heterojunction was very successful.
Fig. 6. XPS spectra survey, (a), (b) and (e) of InVO₄, 0.75 BiVO₄/0.25 InVO₄, 0.5 BiVO₄/0.5 InVO₄, 0.25 BiVO₄/0.75 InVO₄, BiVO₄, samples.

UV–vis spectroscopy was performed to study the electronic structure of semiconductors. The UV–vis diffuse reflectance spectra of the samples, displayed in Fig. 7a. The absorption edges of pure InVO₄ and BiVO₄ are at approximately 490 and 530 nm, respectively, in agreement with the published (Cheng et al., 2017; Meng et al., 2017). Comparatively, the adsorption edge of BiVO₄/InVO₄ heterojunction shows a significant red shift and enhanced the response of visible light. Particularly, 0.75 BiVO₄/0.25 InVO₄ shows the strongest absorbance in the visible light region, which might be helpful for the photocatalytic reaction. Further, the band gap energies of as-prepared samples were determined by Mott-Schottky plot. The absorption coefficient α and direct band gap Eg of InVO₄ and BiVO₄ are related to the following equation: $\alpha \nu = A_0 (\nu - E_g)^{n/2}$ (Hu et al., 2015), where $\alpha$, $A_0$, $E_g$ and $\nu$ demonstrate the absorption coefficient, the constant, the direct band gap energy and incident photon energy, respectively. Among these parameters, n is determined by the type of optical transition of a semiconductor (n=1 for a direct transition and n=4 for an indirect transition). For InVO₄ and BiVO₄, the value of n is 1 for the direct transition. The band gap energy of pure BiVO₄ and InVO₄ nanocomposite were depicted in Fig. 7b. According to the equation, the band gap energy of BiVO₄ nanocomposites is 2.20 eV, which is smaller than that of the pure InVO₄ particles (2.32 eV).
Fig. 7. (a) UV-Vis diffuse reflectance spectra of InVO$_4$, 0.75 BiVO$_4$/0.25 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, BiVO$_4$, samples. (b) plots of $(ahv)^2$ vs. photon energy $(hv)$ for the band gap energies of InVO$_4$ and BiVO$_4$.

3.3 Photocatalytic activity

As shown in the Fig. 8a, the photocatalytic performance of the samples were tested by reduction of Cr$^{6+}$ within 60 min of dark adsorption and 40 min under visible light irradiation. The control experiment without adding any catalyst was carried out, and only the ignorable fluctuation of Cr$^{6+}$ concentration is observed. The dark adsorption efficiency of all samples is less than 10%. Under visible light irradiation, the Cr$^{6+}$ reduction efficiency of pure BiVO$_4$ and InVO$_4$ are improved to be 41% and 56.39% respectively within 40 min. The 0.75 BiVO$_4$/0.25 InVO$_4$ catalyst exhibits the highest photocatalytic activity, and the Cr$^{6+}$ reduced to Cr$^{3+}$ completely within 40 min. The efficiency of 0.5 BiVO$_4$/0.5 InVO$_4$ and 0.25 BiVO$_4$/0.75 InVO$_4$ are 71.6% and 46.81%, respectively after 40 min. From Fig. 8c, the absorption peak intensity of Cr$^{6+}$ were drastically decreased and finally disappear, suggesting complete reduction of toxic Cr$^{6+}$ to Cr$^{3+}$ within 40 min. In addition, as exhibited in the Fig. 8d, the color of the reaction solution becomes lighter with irradiation time increasing. The solution was completely transparent liquid after 60 min. The photocatalytic reduction kinetics could be depicted by pseudo-first-order kinetics equation (Xing et al., 2017): $-\ln(C/C_0) = kt$, where $k$ is the apparent rate constant, $C$ and $C_0$ are concentrations of Cr$^{6+}$, corresponding to time $t$ and $t_0$ respectively. As presented in Fig. 8b, it can be confirmed that the apparent rate constants of pure InVO$_4$ and BiVO$_4$ were 0.033 min$^{-1}$ and 0.011 min$^{-1}$, respectively. Nevertheless, the apparent rate constants of 0.75 BiVO$_4$/0.25 InVO$_4$, 0.25 BiVO$_4$/0.75 InVO$_4$, 0.5 BiVO$_4$/0.5 InVO$_4$, 0.75 InVO$_4$/0.25 BiVO$_4$ samples. (b) plots of $(ahv)^2$ vs. photon energy $(hv)$ for the band gap energies of InVO$_4$ and BiVO$_4$.
0.5 BiVO₄/0.5 InVO₄, 0.25 BiVO₄/0.75 InVO₄ were 0.089 min⁻¹, 0.015 min⁻¹ and 0.016 min⁻¹ respectively. It is obvious that the photocatalytic reduction performance for Cr⁶⁺ of 0.75 BiVO₄/0.25 InVO₄ is the best among these as-prepared samples.

**Fig.8.** (a) Photocatalytic reduction of Cr⁶⁺ with InVO₄, 0.75 BiVO₄/0.25 InVO₄, 0.5 BiVO₄/0.5 InVO₄, 0.25 BiVO₄/0.75 InVO₄, BiVO₄ samples. (b) Kinetics plots for photocatalytic reduction of Cr⁶⁺ with InVO₄, 0.75 BiVO₄/0.25 InVO₄, 0.5 BiVO₄/0.5 InVO₄, 0.25 BiVO₄/0.75 InVO₄, BiVO₄ samples. (c) Photocatalytic reduction of Cr⁶⁺ to Cr³⁺ in the presence of 0.75 BiVO₄/0.25 InVO₄ samples. (d) The color rendering of 0.75BiVO₄/0.25InVO₄, after reduction of Cr⁶⁺.

### 3.4 Proposed photocatalytic mechanism

To explore the mechanism of photocatalytic Cr⁶⁺ reduction via BiVO₄/InVO₄, the relative band positions of BiVO₄ and InVO₄ were studied. According to the equation (Ge et al., 2006; Jiang et al., 2009): $E_{VB} = X + 0.5E_g - E_0$, where the $E_{CB}$ is the potential of conduction band edge, $X$ is the electronegativity of the semiconductor, $E_0$ is the scale factor that correlates the redox level of the reference electrode with the absolute vacuum (for normal hydrogen electrode (NHE), $E_0 = 4.5$ eV), and $E_g$ is the band gap energy of the semiconductor. Combined with the following equation: $E_{VB} = E_g + E_{CB}$, the potential of conduction band edge (CB) and valence
band edge (VB) of BiVO$_4$ were calculated to be 0.4 eV and 2.8 eV, respectively, as well as the
CB and VB of InVO$_4$ were calculated to be -0.19 eV and 1.71 eV respectively. The electron
transfer mechanism is proposed in Fig.9. The CB of InVO$_4$ is more negative than that of the
BiVO$_4$, demonstrating that photoinduced electrons could shift from the CB of InVO$_4$ to the CB
of BiVO$_4$, which is beneficial to charge separation. According to the chromium concentration
and pH value, its primary existence form is HCrO$_4^-$ \((\text{CrO}_4^{2-} + 7\text{H}^+ + 3e^- \leftrightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O})\). The
theoretical potential of Cr$^{6+}$/Cr$^{3+}$ is 1.35eV, which is more positive than the CB of BiVO$_4$,
allowing the accelerated electrons in BiVO$_4$ thermodynamically reduce Cr$^{6+}$ to Cr$^{3+}$. Similarly,
given that the VB of InVO$_4$ is positive than that of BiVO$_4$, holes are transferred from the VB of
BiVO$_4$ to that of InVO$_4$, followed by the elimination of methanol.

Based on the above analysis, the possible photocatalytic mechanism of BiVO$_4$/InVO$_4$
heterojunction catalyst was proposed. First, BiVO$_4$ and InVO$_4$ semiconductors are excited under
visible light to produce photogenerated electron-hole pairs. The h$^+$ of BiVO$_4$ is migrated to
InVO$_4$, while the e$^-$ of InVO$_4$ is migrated to BiVO$_4$. Importantly, the addition of methanol
eliminated the holes and inhibited the recombination of electron hole pairs. Finally, e$^-$ participate
in the reduction-oxidation reaction. The detailed reaction process is as follows:

\begin{align}
\text{BiVO}_4 + \text{hv} & \rightarrow \text{e}^- + \text{h}^+ \quad (1) \\
\text{InVO}_4 + \text{hv} & \rightarrow \text{e}^- + \text{h}^+ \quad (2) \\
\text{Cr}^{6+} + \text{e}^- & \rightarrow \text{Cr}^{3+} \quad (3)
\end{align}

The main reasons of the excellent performance of BiVO$_4$/InVO$_4$ heterojunction are following.
Firstly, the enhanced light absorption of the hybrid is observed compared with two
semiconductors, which helps to capture more photons for the photocatalytic reaction. What’s
more, the formed heterojunction facilitates the charge separation and transport, allowing the
photo-generated electrons to be accelerated for Cr$^{6+}$ reduction.
Fig. 9. Schematic illustration for the possible photocatalytic mechanism of the 0.75 BiVO₄/0.25 InVO₄ composite for Cr⁶⁺ reduction under visible light irradiation.

3.5 Stability and recyclability properties

To investigate the stability and recyclability of 0.75 BiVO₄/0.25 InVO₄, we have conducted Cr⁶⁺ reduction efficiency recycling test by 5 times. Figure 10 shows the before and after recycling XRD diffraction patterns of 0.75 BiVO₄/0.25 InVO₄. The results show that the reduction efficiency of Cr⁶⁺ tends to be nearly constant over five cycles. In the repeated tests, the reduction efficiency after each cycle is maintained at 100%. In addition, the phase structures of the sample remain unchanged, which verifies that the components of the 0.75 BiVO₄/0.25 InVO₄ are difficult to be photo-decomposed and its structure is stable during the photocatalytic process. This feature is very important for its practical application and modification.
Fig. 10 Before and after recycling XRD diffraction patterns of 0.75 BiVO$_4$/0.25 InVO$_4$ and Cr$^{6+}$ reduction efficiency as inset.
4 Conclusions

In summary, a green conversion from Cr$^{6+}$ to Cr$^{3+}$ has been presented using BiVO$_4$/InVO$_4$ heterojunction that was obtained using a one-pot microwave strategy. The optimized sample exhibited the degradation rate of almost 100% in 40min, which was 2 times higher than that of BiVO$_4$ and InVO$_4$. The high photocatalytic performance could be ascribed to the thin leaf-like structure of BiVO$_4$/InVO$_4$ heterojunction, strong visible light absorption and more importantly hinders the recombination of photo-generated charge carries.

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Deqiang Zhao (Corresponding Author): Conceptualization, Methodology, Software, Investigation, Formal Analysis;
Ling Yu (First Author): Data Curation, Writing - Original Draft;
Hui Wang: Conceptualization, Funding Acquisition, Resources, Supervision, Writing - Review & Editing;
Qi Huang: Visualization, Investigation;
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Qingkong Chen: Software, Validation;
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References


Li, J., Zhao, W., Guo, Y., Wei, Z., Han, M., He, H., Yang, S., Sun, C., 2015. Facile synthesis and high activity of novel BiVO₄/FeVO₄ heterojunction photocatalyst for degradation of metronidazole. Applied Surface Science 351, 270-279.


Miretzky, P., Cirelli, A.F., 2010. Cr (VI) and Cr (III) removal from aqueous solution by raw and modified
Scheme heterojunction into gold decorated carbon nitride/cuprous oxide catalyst for photocatalysis. Journal of Cleaner Production 360, 131948.


