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Novel visible-light-responding $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ ternary nanoheterostructure: Preparation and photocatalytic characteristics

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ABSTRACT

A novel visible-light-responding $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ ternary nanoheterostructure was designed on the basis of the strategy of energy gap engineering and prepared through ordinary wet chemistry methods. The as-prepared nanoheterostructure was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and diffuse reflectance ultraviolet-visible spectroscopy (UV-vis/DRS). The TEM and HRTEM images of 10% $\text{InVO}_4\text{-40%Cu}_2\text{O-50%TiO}_2$ confirm the formation of nanoheterostructures resulting from contact of the nanosized TiO_2 , Cu_2O and InVO_4 in the size of 5–20 nm in diameter. The $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ nanoheterostructure, when compared with TiO_2 , Cu_2O , InVO_4 , $\text{InVO}_4\text{-TiO}_2$ and $\text{Cu}_2\text{O-TiO}_2$, shows significant enhancement in the photocatalytic performance for the degradation of methyl orange (MO) under visible-light irradiation. With a 9 W energy-saving fluorescent lamp as the visible-light source, the MO degradation rate of 10% $\text{InVO}_4\text{-40%Cu}_2\text{O-50%TiO}_2$ reaches close to 90% during 5 h, and the photocatalytic efficiency is maintained at over 90% after six cycles. This may be mainly ascribed to the matched bandgap configurations of TiO_2 , Cu_2O and InVO_4 , and the formations of two p-n junctions by the p-type semiconductor Cu_2O with the n-type semiconductors TiO_2 and InVO_4 , all of which favor spatial photogenerated charge carrier separation. The X-ray photoelectron spectroscopy (XPS) characterization for the used 10% $\text{InVO}_4\text{-40%Cu}_2\text{O-50%TiO}_2$ reveals that only a small shakeup satellite peak appears for Cu(II) species, implying bearable photocorrosion of Cu_2O . This work could provide new insight into the design and preparation of novel visible-light-responding semiconductor composites.

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1. Introduction

The development of visible-light-responding photocatalysts has become one of the most challenging and urgent topics that needs addressing because of the increasingly grim environ-

mental and energy issues that confront mankind today [1–3]. Since Fujishima et al. [4] reported on water photolysis with titanium dioxide (TiO_2) as the anode in 1972, TiO_2 has been deemed as the most promising photocatalyst due to its outstanding performance, low cost, nontoxicity and stability.

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However, the shortcomings of a wide bandgap (3–3.2 eV) and fast photogenerated carriers recombination for TiO_2 hinder its extensive application in photocatalysis [5]. Therefore, improving its visible-light utilization and suppressing the photogenerated carriers recombination are significant foci in the field of photocatalysis.

The sensitization of TiO_2 by narrow bandgap semiconductors has proven to be an effective strategy to enhance its visible-light photocatalytic performance [3,6], resulting in the transfer of the photogenerated carriers from the narrow bandgap semiconductors to TiO_2 . In the past, cuprous oxide (Cu_2O), a fascinating p-type semiconductor with a 2.0 eV bandgap, has received significant research interest as a visible-light-responding photocatalyst [7–12]. However, the visible-light photocatalytic activity of bare Cu_2O is commonly comparatively low due to the rapid recombination of photogenerated carriers [13]. In the past few decades, increasing interest has been aroused on the combination of TiO_2 with Cu_2O to form a visible-light-responding heterostructure to be used as photocatalysts and photovoltaic cells because of their favorably matched band structures [14–25].

Indium orthovanadate (InVO_4), an n-type semiconductor with a bandgap of 2.0 eV, has also enjoyed considerable attention as a visible-light-responding photocatalyst for hydrogen evolution by water splitting [26–28] and organic pollutants degradation [29,30]. Similarly, InVO_4 commonly exhibits negligible photocatalytic activity because of its poor adsorption capability and facile photogenerated carrier recombination [31]. Therefore, much research effort has been directed towards the development of TiO_2 - InVO_4 composite photocatalyst [31–39].

Based on the strategy of energy gap engineering, compositing p-type Cu_2O and n-type InVO_4 semiconductors with n-type semiconductor TiO_2 to construct a novel ternary heterostructure can be expected to display improved visible-light photocatalytic performance because of coupling of their different energy levels and the unique properties of the formed heterostructures. Herein, we demonstrate a facile wet chemistry route to fabricate a novel InVO_4 - Cu_2O - TiO_2 ternary nanoheterostructure that shows enhanced photocatalytic performance compared with the InVO_4 - TiO_2 and Cu_2O - TiO_2 binary nanoheterostructures used for the degradation of methyl orange (MO) under visible-light irradiation. Furthermore, for the purpose of practical application, an ordinary 9 W energy-saving fluorescent lamp was used as the visible-light resource. To the best of our knowledge, no works have been documented on the fabrication of InVO_4 - Cu_2O - TiO_2 ternary nanoheterostructure for organic pollutant photodegradation.

2. Experimental

All chemical reagents used in the experiments were of analytical purity and employed without further purification.

2.1. Synthesis of InVO_4 nanoparticles

InVO_4 nanoparticles were prepared by a facile hydrothermal method similar to that reported by Ge et al [32]. In a typical

experiment, 0.001 mol InCl_3 was dissolved in 10 mL deionized water, and 20 mL of 0.05 mol/L NH_4VO_3 solution was then added dropwise under magnetic stirring. The pH value of the resulting mixture was adjusted to about 7 with 2 mol/L NaOH solution. After that, the mixture was kept stirring for 30 min and sonicating for 10 min before being transferred into a 60 mL Teflon-lined stainless steel autoclave. Hydrothermal reaction then proceeded at 120 °C for 8 h. Finally, the produced white slurry was centrifuged, washed with deionized water 3 times and dried at 60 °C for 12 h to give white InVO_4 nanoparticles.

2.2. Synthesis of 16.67% InVO_4 -83.33% TiO_2 nanoheterostructure

An InVO_4 - TiO_2 nanoheterostructure was synthesized by a sol-gel method. Typically, 0.0667 g of the as-prepared InVO_4 was dispersed in a mixture solvent of 5 mL deionized water and 5 mL ethanol, and 10 mL of 0.1% cetyltrimethylammonium bromide (CTAB) solution was then added and followed by sonicating for 10 min. A solution composed of 1.42 mL tetrabutyl titanate and 18.58 mL anhydrous alcohol was also added under magnetic stirring, and the resulting suspension was kept stirring for 30 min. Finally, the produced white slurry was centrifuged, washed with deionized water 3 times, dried at 60 °C for 12 h and calcined at 450 °C for 3 h to give the 16.67% InVO_4 -83.33% TiO_2 nanoheterostructure. In addition, TiO_2 , 5% InVO_4 -95% TiO_2 and 10% InVO_4 -90% TiO_2 were prepared via a similar route by changing the starting material ratios.

2.3. Synthesis of 50% Cu_2O -50% TiO_2 nanoheterostructure

A Cu_2O - TiO_2 composite was synthesized via an easy precipitation route similar to that reported by Huang et al. [15]. 0.4159 g $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ was dissolved in 50 mL anhydrous ethanol to obtain a deep green solution, and 0.15 g of the as-prepared TiO_2 was dispersed in the solution assisted by sonication for 10 min. 50 mL glucose solution (0.13 mol/L) as reducing agent and 60 mL NaOH solution (0.3 mol/L) in the mixed solvent of 35 mL anhydrous ethanol and 25 mL deionized water were added dropwise to the suspension in sequence under magnetic stirring, and then the resulting suspension was heated to 80 °C and kept stirring for 30 min. After the suspension was cooled to room temperature, the precipitates were collected by centrifugation, washed with anhydrous ethanol 2 times and deionized water 2 times, and then dried at 60 °C for 12 h in vacuum. Cu_2O , 30% Cu_2O -70% TiO_2 and 70% Cu_2O -30% TiO_2 were also prepared by a similar route through altering the starting material ratios.

2.4. Synthesis of 10% InVO_4 -40% Cu_2O -50% TiO_2 nanoheterostructure

The as-prepared InVO_4 - TiO_2 nanoheterostructure was coupled with Cu_2O by a simple precipitation route. In a typical experiment, 0.3328 g $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ was dissolved in 50 mL anhydrous ethanol, and 0.18 g of the as-prepared 16.67% InVO_4 -83.33% TiO_2 nanoheterostructure was dispersed in the solution

followed by sonication for 10 min. 50 mL glucose solution (0.1 mol/L) and 60 mL NaOH solution (0.3 mol/L) in the mixed solvent of 35 mL anhydrous ethanol and 25 mL deionized water were added dropwise to the suspension in sequence under magnetic stirring, and the resulting suspension was then heated to 80 °C and stirred constantly for 30 min. After the suspension was cooled to room temperature, the precipitates were collected by centrifugation, washed with anhydrous ethanol 2 times and deionized water 2 times, and dried at 60 °C for 12 h in vacuum. Additionally, 5%InVO₄-40%Cu₂O-55%TiO₂, 20%InVO₄-40%Cu₂O-40%TiO₂ and 30%InVO₄-40%Cu₂O-30%TiO₂ were fabricated via similar routes by changes to the starting material ratios.

2.5. Characterizations

Phase structures of the samples were determined by X-ray powder diffraction (XRD) taken on a Rigaku-D-Max rA 12 kW diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 300 mA. A JEM-2010 transmission electron microscope (TEM) and a JEOL-3010 high-resolution transmission electron microscope (HRTEM), operated at an acceleration voltage of 200 kV, were employed to observe the morphologies and sizes of the samples. X-ray photoelectron spectra (XPS) of the samples were collected on a K-Alpha 1063 XPS system with Al K α radiation. Diffuse reflectance ultraviolet-visible spectra (UV-vis/DRS) of the samples were recorded on a Beijing Purkinje TU-1901 UV-vis spectrophotometer equipped with a diffuse reflectance accessory with an IS19-1 integrating sphere and BaSO₄ powders as reference.

2.6. Photocatalytic tests

The visible-light photocatalytic activities of the samples were investigated in a self-assembly reactor using photocatalytic degradation of MO as the probe reaction and an ordinary 9 W energy-saving fluorescent lamp as the visible-light irradiation source. 0.15 g photocatalyst was put into 200 mL MO solution (20 mg/L). Prior to irradiating, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium, and then exposed to the lamp with a distance of 10 cm. Samples were taken from the reaction suspension at 60 min intervals. The upper, lucid liquid obtained after centrifugal separation was analyzed by a UV-vis spectrophotometer at the maximum absorption wavelength of MO of 464 nm. The total organic carbon (TOC) removal of MO solution was monitored on a Shimadzu TOC-V_{CPH} analyzer.

3. Results and discussion

The XRD patterns of the as-prepared InVO₄, Cu₂O, TiO₂, 70%Cu₂O-30%TiO₂, 10%InVO₄-90%TiO₂, 10%InVO₄-40%Cu₂O-50%TiO₂, together with the standard patterns of orthorhombic InVO₄ (PDF 48-0898), anatase TiO₂ (PDF 21-1272) and cubic Cu₂O (PDF 05-0667) are shown in Fig. 1. All the diffraction peaks of individual InVO₄, Cu₂O and TiO₂ in Fig. 1 match well with the standard patterns of orthorhombic InVO₄,

cubic Cu₂O and anatase TiO₂, respectively. These three phases can be readily found in the XRD patterns of their corresponding composites. However, it should be noted that only the strongest (001) crystal plane peak at *ca.* $2\theta = 32.9^\circ$ for the InVO₄ phase could be detected in 10%InVO₄-40%Cu₂O-50%TiO₂. This may be due to the lesser amount and high dispersion of InVO₄ in 10%InVO₄-40%Cu₂O-50%TiO₂ relative to the other systems studied. This agrees well with Min et al's report [37] in which no XRD diffraction peaks of InVO₄ appeared in an InVO₄-TiO₂ composite with a mass ratio of 1:10. In addition, no other clear peaks for impurities can be detected in Fig. 1, suggesting high purity in these compounds and composites.

From the TEM images of the 10%InVO₄-40%Cu₂O-50%TiO₂ nanoheterostructure (Fig. 2(a) and (b)), it can be clearly observed that the obtained nanoparticles are in the size of 5–20 nm in diameter with agglomeration, which is exactly what is needed for the purpose of forming heterostructures resulting from contact of the nanosized TiO₂, Cu₂O and InVO₄. Furthermore, we can observe, from the corresponding HRTEM images, the formation of nanoheterostructures, as shown in Fig. 2(c) and (d). In addition, the fringe spacing values, measured to be 0.36, 0.24 and 0.27 nm, can be ascribed to the *d*-spacing values for (101) lattice planes of anatase TiO₂, (111) lattice planes of cubic Cu₂O and (112) lattice planes of orthorhombic InVO₄.

The photocatalytic activities of the as-prepared InVO₄, Cu₂O, TiO₂, InVO₄-TiO₂, Cu₂O-TiO₂ and InVO₄-Cu₂O-TiO₂ with different mass ratios for the MO degradations are illustrated in Fig. 3. From Fig. 3(a), it can be seen that bare TiO₂ and InVO₄ exhibit no discernable photocatalytic activities, and the highest MO degradation rate is only 8% for the 10%InVO₄-90%TiO₂ nanoheterostructure, obtained after illumination with the 9 W energy-saving fluorescent lamp for 5 h. As shown in Fig. 3(b), the bare Cu₂O also shows no photocatalytic activity. However, when coupling Cu₂O with TiO₂, the resulting nanoheterostruc-

Fig. 1. XRD patterns of the as-prepared InVO₄, Cu₂O, TiO₂, 70%Cu₂O-30%TiO₂, 10%InVO₄-90%TiO₂, 10%InVO₄-40%Cu₂O-50%TiO₂, together with the standard patterns of orthorhombic InVO₄ (PDF 48-0898), anatase TiO₂ (PDF 21-1272) and cubic Cu₂O (PDF 05-0667).

Fig. 2. TEM (a, b) and HRTEM (c, d) images of the as-prepared 10%InVO₄-40%Cu₂O-50%TiO₂.

tures reveal considerable activities. The MO degradation rate for the 70%Cu₂O-30%TiO₂ nanoheterostructure achieves 84% after illumination with the 9 W energy-saving fluorescent lamp for 5 h. Meanwhile, it can be also found that the MO degradation rate in the Cu₂O-TiO₂ nanoheterostructures increases upon an increase in the amount of Cu₂O. As for the TiO₂-Cu₂O-InVO₄ ternary nanoheterostructures, their initial photocatalytic activities are greater than those for the TiO₂-Cu₂O binary nanoheterostructures. For example, the MO degradation rate of 5%InVO₄-40%Cu₂O-55%TiO₂ reaches 62.9% after illumination for 2 h, as displayed in Fig. 3(c), while it is 46.7% for 70%Cu₂O-30%TiO₂. By prolonging the illumination time to 5 h, the MO degradation rate of 5%InVO₄-40%Cu₂O-55%TiO₂ is 86.3%, which is slightly higher than that for 70%Cu₂O-30%TiO₂. However, it should be pointed out that the as-mentioned MO degradation rates of 5%InVO₄-40%Cu₂O-55%TiO₂ were not the maxima in our experiments, as depicted

Fig. 4. TOC removal of MO under the visible-light irradiation for 10%InVO₄-40%Cu₂O-50%TiO₂.

in Fig. 3(c). After illumination for 2 h, the MO degradation rate of 30%InVO₄-40%Cu₂O-30%TiO₂ attains 65.4%, and the MO degradation rate of 10%InVO₄-40%Cu₂O-50%TiO₂ reaches 89.13% after illumination for 5 h, which are considerably greater than those of 70%Cu₂O-30%TiO₂.

The mineralization of MO (i.e. TOC removal) under visible-light irradiation for 10%InVO₄-40%Cu₂O-50%TiO₂ is presented in Fig. 4. 10%InVO₄-40%Cu₂O-50%TiO₂ affords only 32.17% TOC removal after illumination for 5 h, which is a common phenomenon for the MO photocatalytic degradation [40–42]. This may be due to the fact that MO degrades to stable intermediates such as aniline, phenol, benzene, benzene sulfonic acid, aliphatic acid or aldehyde [40,42], and therefore requires more time to achieve greater TOC removal.

To investigate the stabilities of the 50%Cu₂O-50%TiO₂ and 10%InVO₄-40%Cu₂O-50%TiO₂ nanoheterostructures for the MO photocatalytic degradations under illumination with the 9 W energy-saving fluorescent lamp, we repeated the photocatalytic degradation experiments employing the same photocatalysts six times. The results are shown in Fig. 5. After six cycles, the MO degradation rate of 10%InVO₄-40%Cu₂O-50%TiO₂ maintains at ca. 80% and the degradation efficiency is maintained at over 90%, which is exactly the requirement needed

Fig. 3. Photocatalytic activities of the as-prepared InVO₄-TiO₂ (a), Cu₂O-TiO₂ (b) and InVO₄-Cu₂O-TiO₂ (c) with different mass ratios for the MO degradations under the visible-light irradiation.

Fig. 5. Cycling runs of 50%Cu₂O-50%TiO₂ (1) and 10%InVO₄-40%Cu₂O-50%TiO₂ (2) for MO degradations under visible-light irradiation.

for application to organic pollutant photocatalytic degradation. However, the MO degradation rate of 50%Cu₂O-50%TiO₂ is around 74%. We also find that the initial photocatalytic activity of 10%InVO₄-40%Cu₂O-50%TiO₂ in the first cycle is higher than that of 50%Cu₂O-50%TiO₂, which is in good agreement with the case described for Fig. 3.

Generally, Cu₂O is an efficient photocatalyst, but is not stable [43]. To examine the stability of Cu₂O, XPS characterization was performed for the used 10%InVO₄-40%Cu₂O-50%TiO₂, and the corresponding high-resolution XPS spectrum for the surface Cu 2p is displayed in Fig. 6. The peaks centered at binding energies of 932.5 and 952.6 eV can be attributed to the Cu 2p_{3/2} and Cu 2p_{1/2} peaks, respectively, confirming the existence of Cu(I) species [44]. Meanwhile, a shakeup satellite peak (denoted as Sat) can be found at 944.2 eV, suggesting the appearance of Cu(II) species [44]. Due to the fact that the contents of compositions are commonly proportional to the peak areas [45], the small peak area of the Sat peak for the Cu(II) species suggests that a small fraction of Cu₂O was oxidized to CuO during the use of 10%InVO₄-40%Cu₂O-50%TiO₂, thus implying bearable photo-corrosion of Cu₂O.

The UV-vis/DRS spectra of TiO₂, InVO₄, Cu₂O, 10%InVO₄-

Fig. 6. High-resolution XPS spectrum of Cu 2p for the used 10%InVO₄-40%Cu₂O-50%TiO₂.

90%TiO₂, 50%Cu₂O-50%TiO₂ and 10%InVO₄-40%Cu₂O-50%TiO₂ are presented in Fig. 7(a). The bare TiO₂ can only absorb UV light with a wavelength shorter than 400 nm. The bare InVO₄ has a weak absorbance in the wavelength range of 400–650 nm. Therefore, 10%InVO₄-90%TiO₂ also shows a weak absorbance in this wavelength range. Cu₂O exhibits the strongest absorbance with the wavelength extended to greater than 800 nm. 50%Cu₂O-50%TiO₂ and 10%InVO₄-40%Cu₂O-50%TiO₂ also display strong absorbances in the visible light region with the wavelength greater than 800 nm. Although Cu₂O and 50%Cu₂O-50%TiO₂ reveal wider and stronger visible light absorption than 10%InVO₄-40%Cu₂O-50%TiO₂, this does not mean that the photocatalytic activities of Cu₂O and Cu₂O-TiO₂ under visible light are greater than that of InVO₄-Cu₂O-TiO₂. This is because there exists an implicit conflict between wide-range visible light absorption and adequate redox capability, and a high quantum yield cannot be achieved simply by extending the absorption of visible light [3]. On the other hand, it is well known that the recombination rate of the photogenerated carriers for a photocatalyst plays a vital role in its photocatalytic activity.

To estimate the bandgap energies of the above photocata-

Fig. 7. UV-vis/DRS spectra (a) and bandgap energy estimations from the plots of $(ah\nu)^{1/2}$ versus $h\nu$ (b) for TiO₂, InVO₄, Cu₂O, 50%Cu₂O-50%TiO₂, 10%InVO₄-90%TiO₂ and 10%InVO₄-40%Cu₂O-50%TiO₂.

lysts, plots of $(ah\nu)^{1/2}$ versus $h\nu$ are presented in Fig. 7(b), where a and $h\nu$ are the absorption coefficient and discrete photon energy, respectively. The bandgap energies of photocatalysts can be obtained from the extrapolated values of the tangents to the X-axis. Therefore, the bandgap energies of bare TiO_2 , InVO_4 and Cu_2O are estimated to be 3.13, 2.11 and 2.02 eV, respectively, which are very close to the reported values [15,39]. The bandgap energies of 10% InVO_4 -90% TiO_2 , 50% Cu_2O -50% TiO_2 and 10% InVO_4 -40% Cu_2O -50% TiO_2 are estimated as 3.17, 2.58 and 2.78 eV, respectively, suggesting that the introduction of Cu_2O can efficaciously decrease the bandgap energies of composites. The high bandgap energy for 10% InVO_4 -90% TiO_2 may account for its extremely low visible-light photocatalytic activity, as shown in Fig. 3(a).

Fig. 8 illustrates the bandgap configurations of Cu_2O , InVO_4 and TiO_2 [15,39] and the charge separation and transfer behaviors between them under visible-light irradiation. As indicated in Fig. 8, both Cu_2O and InVO_4 can be excited under visible-light irradiation to generate electron-hole pairs due to their narrow bandgaps. The conduction and valence band edge potentials of Cu_2O (−1.6 and +0.4 eV vs. SHE, respectively) and InVO_4 (−0.5 and +1.5 eV vs. SHE, respectively) are more negative than those of TiO_2 (−0.23 and +2.97 eV vs. SHE, respectively). As a result, the photogenerated electrons on the Cu_2O and InVO_4 conduction bands can transfer to the TiO_2 conduction band. On the other hand, the conduction and valence band edge potentials of Cu_2O are also more negative than those of InVO_4 , leading to the photogenerated electron injection from the Cu_2O conduction band to the InVO_4 conduction band and the photogenerated hole migration from the InVO_4 valence band to the Cu_2O valence band. Therefore, the spatial separation of photogenerated electron-hole pairs can effectively promote the visible-light photocatalytic performance of the TiO_2 - Cu_2O - InVO_4 ternary nanoheterostructure. Moreover, two p-n semiconductor heterojunctions can be formed by p-type Cu_2O with respective n-type TiO_2 and InVO_4 upon their close contact, as observed in Fig. 2(c) and (d). The resulting inner electric fields with orientations from TiO_2 and InVO_4 to Cu_2O can further boost the migration of photogenerated electron-hole pairs mo-

tivated by the potential energy difference.

4. Conclusions

A novel visible-light-responding TiO_2 - Cu_2O - InVO_4 ternary nanoheterostructure with excellent photocatalytic performance relative to TiO_2 , Cu_2O , InVO_4 , Cu_2O - TiO_2 and InVO_4 - TiO_2 has been successfully fabricated by facile wet chemistry methods. With 10% InVO_4 -40% Cu_2O -50% TiO_2 as the photocatalyst, the MO degradation rate achieves close to 90% under illumination by a 9 W energy-saving fluorescent lamp for 5 h, and the degradation efficiency is maintained at over 90% after six cycles. This can be ascribed to the band configuration optimization of TiO_2 , Cu_2O and InVO_4 in the composite and the formation of two p-n semiconductor heterojunctions by p-type Cu_2O with n-type TiO_2 and InVO_4 . The excellent performance of TiO_2 - Cu_2O - InVO_4 fits the requirements needed for its application to photocatalytic degradation of organic pollutants.

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Fig. 8. Bandgap configurations of Cu_2O , InVO_4 and TiO_2 and the charge separation and transfer behaviors between them under visible-light irradiation.

Graphical Abstract

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Novel visible-light-responding $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ ternary nanoheterostructure: Preparation and photocatalytic characteristics

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A novel visible-light-responding $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ ternary nanoheterostructure was designed based on the strategy of energy gap engineering and prepared through wet chemistry methods. The system exhibits excellent visible-light photocatalytic performance for methyl orange degradation.

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新型可见光响应的 $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ 三元纳米异质结: 制备及其光催化性能

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摘要: 由于日益严重的环境和能源危机, 可见光催化剂的开发已成为当今最具挑战和紧迫的任务之一. 将 TiO_2 和其它窄禁带半导体复合, 已被证明是一种有效的可提高其可见光光催化性能的策略. Cu_2O 是一种禁带宽度为 2.0 eV 的 p 型窄禁带半导体, InVO_4 则是一种禁带宽度为 2.0 eV 的 n 型半导体, 因它们可用于可见光光解水产氢和有机污染物的可见光降解而在过去的数年中引起了人们广泛的关注. 但是纯的 Cu_2O 和 InVO_4 由于光生电子空穴对在其内部快速地复合, 光催化活性通常都比较低. 基于能带工程的策略本文设计了一种新型的可见光响应的 $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ 三元纳米异质结, 并通过普通的湿化学法进行制备: 先通过水热法制备 InVO_4 , 再通过溶胶-凝胶法制备 $\text{InVO}_4\text{-TiO}_2$ 二元复合物, 最后通过沉淀和还原过程制备得到 $\text{InVO}_4\text{-Cu}_2\text{O-TiO}_2$ 三元纳米异质结.

在 10% InVO_4 -40% Cu_2O -50% TiO_2 三元纳米异质结的 X-射线衍射谱中没有观察到明显的杂质峰; 通过透射电子显微

技术和高分辨透射电子显微技术观察到了它们之间异质结的形成, 纳米颗粒的尺寸范围在 5–20 nm; 经紫外可见漫反射光谱估算得到 10%InVO₄-40%Cu₂O-50%TiO₂ 的禁带宽度为 2.78 eV, 在可见光区域具有较强的吸收. 以普通的 9 W 节能灯作为可见光光源光照甲基橙 5 h 后, 纯的 InVO₄, TiO₂ 和 Cu₂O 几乎没有光催化活性; 10%InVO₄-90%TiO₂ 的光催化活性也很低, 甲基橙降解率为 8%; 70%Cu₂O-30%TiO₂ 对甲基橙降解率达 84%, 但初始活性较低; 10%InVO₄-40%Cu₂O-50%TiO₂ 对甲基橙降解率接近 90%, 并且循环使用 6 次后, 其光催化活性的保持率还维持在 90% 以上, 而 50%Cu₂O-50%TiO₂ 光催化活性的保持率只有 74%.

经对使用过的 10%InVO₄-40%Cu₂O-50%TiO₂ 进行 X 射线光电子能谱表征发现, 存在一弱小的 Cu(II) 震动卫星峰, 表明在 InVO₄-Cu₂O-TiO₂ 的光催化过程中 Cu₂O 的光蚀并不严重. 从能带工程的角度分析, InVO₄-Cu₂O-TiO₂ 三元纳米异质结具有优异的可见光催化性能的主要原因为: InVO₄ 的导带电极电位约为 -0.5 eV (vs. SHE, 下同), 价带电位约为 +1.5 eV, Cu₂O 的分别约为 -1.6 和 +0.4 eV, 与 TiO₂ (导带和价带电极电位分别约为 -0.23 和 +2.97 eV) 相比, 它们的导带位置更负, 将它们组装成三元复合结构, 可见光激发的导带电子就可能从 InVO₄ 和 Cu₂O 的导带迁移到 TiO₂ 的导带上去. 同时, n 型的 TiO₂ 和 InVO₄ 都与 p 型的 Cu₂O 形成 p-n 异质结, n 型的 TiO₂ 和 InVO₄ 之间形成 n-n 异质结, 由于 p-n 异质结中内电场的存在以及不同能级相互耦合, 可进一步促进可见光激发的导带电子从 InVO₄ 和 Cu₂O 的导带迁移到 TiO₂ 的导带上去, 以及可见光激发的价带空穴从 InVO₄ 的价带迁移到 Cu₂O 的价带上去, 从而实现光生载流子空间上的有效分离. 本文有望为新型可见光响应的半导体复合催化剂的设计和制备提供新的思路.

关键词: 钒酸铜; 氧化亚铜; 二氧化钛; 纳米异质结; 可见光; 光催化降解; 甲基橙

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