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A visible and near-infrared driven Yb³⁺/Tm^{3+OI: 10.1039/DDDT02318C} co-doped InVO₄ nanosheets for highly efficient photocatalytic applications

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Abstract: To enhance effectively the utilization of the cleanest sunlight energy 100/D0DT02318C harvesting a large percentage of near infrared (NIR) light is significant. One of the commonly used and much effective methods of modifying semiconductor is co-doping upconversion materials on semiconductor to heighten the photocatalytic efficiency. In this work, Yb^{3+}/Tm^{3+} co-doped InVO₄ nanosheets were synthesized by a facile hydrothermal path, and the crystal phases, morphologies, surface chemical compositions as well as optical properties were characterized. Yb³⁺/Tm³⁺ co-doped InVO₄ revealed a significant enhanced photoactivity towards chromium (VI) reduction and methyl orange oxidation under visible or NIR light irradiation. Furthermore, 5YT-IV presented the highest electrocatalytic performance and photocatalytic production of H₂O₂ under visible light irradiation, requiring lower overpotential and lower Tafel slope (390 mV dec⁻¹) for hydrogen evolution reaction than that of bare $InVO_4$ (731 mV dec⁻¹) as well as strengthening about 3.5 times in the yield of photocatalytic H₂O₂ production. This was primarily in ascription with the intensive light absorption resulted from the benign upconversion energy transfer of Yb³⁺/Tm³⁺ and the boosted charge separation caused by intermediate energy states. Moreover, the presences of h^+ and $\cdot O_2^-$ as the main oxidative species payed a significant attention during the photocatalytic oxidation process of methyl orange and electrons played a decisive role for Cr(VI) reduction. This study requires a promising platform for utilizing efficiently the visible-NIR energy of sunlight in the field of photocatalytic H₂O₂ production and alleviating environmental pollutions in the future.

1. Introduction

Over the past decades, the increasing energy shortage and enormous environmental pollution have presented much serious restrictions to rapid economic and society development.¹⁻⁴ For example, hexavalent chromium (Cr (VI)), as a king of environmental pollution, is applied in a wide field, such as electroplating, paint fabrication, metallurgical technology⁵⁻⁸ and so on. In addition, due to the serious shortage of H₂O₂, many methods are applied for abundant H₂O₂ production, such as anthraquinone autoxidation, oxidation of alcohols and electrochemical synthesis, 9-10 which require a large-scale of energy or organic solvents during the preparation process. Furthermore, it is easily inclined to be contaminated by organic impurities when they are extracted from these systems.¹¹ Fortunately, among the potential solutions, semiconductor photocatalysis as a promising and cost-effective technology in water or air purification has attracted significant attention for utilizing solar energy to convert into clean energy production and photo-degradation of pollutants.¹²⁻¹⁴ At the present period, the development of visible-near-infrared (Vis-NIR) light active photocatalysts is a significant matter for utilizing Vis-NIR light that accounts for 95% of the total solar spectrum.

So far, metal vanadate photocatalysts (MVO₄ where M = Ag, Bi, In, etc.) as the visible-light-driven objects have been in large-scale investigation and application for its excellent light absorption performance.¹⁵⁻¹⁶ Indium vanadate (InVO₄), as a significant visible-light responsive metal vanadate photocatalyst with narrow band-gap of 2.0 eV,¹⁷⁻¹⁹ has obtained extensive attention owning its better photocatalytic performance and higher chemical stability. Nevertheless, it is not considerable owning to the boosted difficulty on separating photoinduced free charge carriers. In a typical one-component system, the electrons and holes generated on the single photocatalyst can recombine so rapidly that it's too late to separate and migrate under the action of the electric field, which significantly inhibit the enhancement of photocatalytic activity. Moreover, it is still very challenging for harvesting and utilizing with high-efficiency in broad spectrum solar energy from ultraviolet (UV) to

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View Article Online near-infrared (NIR) light, in which 49% of total solar energy reaches the capth 30/DODT02318C surface with NIR light, whereas 46% is visible light as well as other 5% is UV light.²⁰⁻²² The broad-spectrum active photocatalysts have become a promising alternative for increasing efficiently solar energy conversion from UV to NIR region. There have made so much significant efforts to boost the utilization of UV and visible light but a little to concentrate upon the absorption efficiency of a larger fraction of NIR light.²³ A limited number of measures have been adopted to investigate the utilization of NIR light. In order to harvest rapidly NIR photons and boost NIR-induced photocatalytic performance, many scholars are encouraged to integrate carbon quantum dots (CQDs) owning the intense absorption of NIR light, or connect surface plasmon resonance (SPR) peaks of noble-metal plasmonic nanoparticles to respond to NIR light due to that it is capable of red-shifting to NIR region. ²⁴⁻²⁵ But they are beyond practical propositions owning the photocorrosion susceptibility and high cost during processing. Hence, it should be a strong priority to develop a UVvis-NIR full-solar-spectrum responsive photocatalyst by designing novel efficient photo-energy conversion materials.

To date, doping with transition metal ions on semiconductor's host lattice has been considered as one of most effective approaches to ameliorate the photocatalytic performance of broad light spectrum responsive photocatalysts,²⁶ which can harvest efficiently NIR light and then emit visible and UV light through upconversion luminescence process. The tight spaced energy levels presented in lanthanide ions are essential to accelerate the photon absorption in succession and energy transfer under the 980 nm NIR excitation. A bathochromic shift will be induced by transition metal ions, leading to a decrease in band gap and a new formation of intra-band gap state,²⁷ which is helpful for boosting efficiently the light absorption. Meanwhile, the doping enables the photo-excited free charge carriers to easily separate and transfer with the shortened transfer distance from the interior to the surface,²⁸ resulting in an enhancement in photocatalytic performance. Hence, high-volume investigations have devoted on modifying semiconductor materials with the application of lanthanide upconversion. Some related work have been done, such as YF₃:Yb³⁺, Er³⁺/ZnS,²⁹

Au/NaYF₄: Yb, Er/WO₃·0.33H₂O-W₁₈O₄₉,³⁰ NaYF₄:Yb³⁺, Er³⁺/Ag₂CrO₄ ³¹ and so on P/DODT02318C Numerous other photocatalysts, such as CdSe/TiO₂ /TiO₂:Yb³⁺, Er³⁺,³² Yb/Tm co– doped In₂S₃,²⁷ Nd/Er co–doped BiVO₄,³³ Yb/Tm co–doped BiPO₄/BiVO₄,³⁴ Yb/Er/Tm co–doped BiVO₄,³⁵ Er/Yb co–doped Bi₂MoO₆³⁶ and so on, have also presented excellent performance by designing with fluorescence resonance energy transfer. Yet, there are rare interests that have concentrated on doping directly lanthanides on InVO₄ semiconductor for enhancing the light absorption and the separation of photoinduced free charge carries.

In this study, a series of novel Yb/Tm co–doped InVO₄ photocatalysts have been synthesized via simple hydrothermal method and evaluated the photocatalytic performance towards chromium (VI) reduction, methyl orange oxidation and photocatalytic H₂O₂ production under visible and NIR illumination, respectively. The results show that Yb/Tm co–doped InVO₄ photocatalyst presented superior photocatalytic performance. Furthermore, the NIR to visible upconversion mechanism has been discussed. First-principles calculations based on density functional theory (DFT)³⁷⁻⁴⁰ were performed to investigate the band structure and electronic properties of Yb/Tm doped InVO₄.

2. Experimental

All the chemicals used in the experiments were of analytical reagent grade without further purification. Ytterbium nitrate pentahydrate (purity 99.99%) and Thulium nitrate hexahydrate (purity 99.9%) were purchased from Aladdin Industrial Corporation. Ammonium metavanadate (purity 99.0%) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). As for indium (III) nitrate tetrahydrate (purity 99.9%), it was purchased from Shanghai Macklin Biochemistry Technology Co., Ltd.

2.1 Samples fabrication

The synthetic method of $InVO_4$: Yb^{3+} , Tm^{3+} was performed by the following hydrothermal process. In a typical synthesis, 4 mmol of $InCl_3 \cdot 4H_2O$ and the different mole ratio of $Yb(NO_3)_3 \cdot 5H_2O$ as well as $Tm(NO_3)_3 \cdot 5H_2O$ were dissolved in 30 mL

deionized water for stirring in 1h. After that, 4 mmol of ammonium vanadate/DoDT02318C (NH₄VO₃) was introduced in the above mixed solution to form a yellow turbid solution. After stirring for another 30 min, the pH value was adjusted gradually to be 2 by nitric acid. The obtained resultant transparent suspension was transferred into a 100 mL Teflon-lined autoclave for heating at 180 °C for 12 h. After the autoclave being cooled down to room temperature, the collected slurry was centrifuged and washed successively with deionized water and absolute ethanol for three times. Finally, the resulting production was dried in vacuum at 80 °C for 4 h. The synthetized productions with a different mole ratio of In³⁺:Yb³⁺:Tm³⁺ at 200:0:1, 200:4:1, 100:4:1, 50:4:1 and 25:4:1 were named as 0.5YT-IV, 2.5 YT-IV, 5 YT-IV, 10 YT-IV and 20 YT-IV, respectively. Meanwhile, the pure InVO₄ sample was synthesized with 4 mmol InCl₃·4H₂O and 4 mmol NH₄VO₃ in the absence of Yb³⁺ and Tm³⁺ for the comparison under the same condition, and it was denoted as IV.

2.2 Characterization

A Bruker AXS D8 Discover with Cu K α ($\lambda = 0.15418$ nm) was provided to test powder X-ray diffraction (XRD) patterns, performing with a scan rate of 0.05° s⁻¹ to characterize the crystal structures of as-prepared samples. Scanning electron microscopy (SEM) was evaluated on an FLA650F under an accelerating voltage of 15 kV, while high-resolution transmission electron microscopy (HRTEM) was conducted on JEM-2100F to record the morphology and structure of the obtained samples. X-ray photoelectron spectroscopy (XPS) was analyzed to reveal the chemical states of elements on a PHI Quantum 2000 XPS system, which was equipped with monochromatic Al Ka source as well as charge neutralizer. Fourier transform infrared (FT-IR) spectra were measured by Nicolet 5700 FT-IR spectrometer. UV-Vis diffuse reflectance spectra (DRS) were carried out from UV-Vis spectrophotometer (UV-2600, Shimadzu), calibrating with BaSO₄ reference standard. The upconversion photoluminescence (PL) spectra were conducted under 980 nm light excitation on an Edinburgh Instruments Model FLS980 spectrometer, coupled with a NIR laser, while the steady state photoluminescence spectra were obtained in fluorescence spectrometer (FL/FS920).

2.3 Photoelectrochemical performance

Photoelectrochemical measurements were carried out in 0.5 M Na₂SO₄ electrolyte on a CHI660E workstation, which the photocatalytic materials coating on FTO was used as the working electrode, as well as saturated Ag/AgCl and platinum electrode as the reference electrode and the counter electrode, respectively. The linear sweep voltammograms (LSV) were operated with a scan rate of 10 mV s⁻¹, irradiated by a Xe arc lamp (300 W) with $\lambda \ge 420$ nm wavelength. For the preparation of the working electrodes: the FTO glass was washed twice with ethanol and deionized water and dried at 80 °C. The slurry made by mixing 10 mg of sample with 0.5 mL ethanol was spread drop by drop onto FTO glass with 0.25 cm² in size. Before the experiment can be carried out, the adhesion of the working electrode could be improved by drying at 50 °C for 2 h. The non-working area of the FTO conductive surface was painted with nail polish.

2.4 Photocatalytic performance

2.4.1 Photocatalytic production of H₂O₂

According to the previous method, the experiment of photocatalytic H₂O₂ production was operated under a 300W Xenon lamp with 420 nm cutoff filter.³¹ 20 mg of sample was dispersed in the mixed solution with 18 mL of deionized water and 2 mL of absolute ethanol, afterwards transferred fleetly into the lining of high-pressure reactor. Oxygen was injected subsequently for 10 min in order to exhaust air. After irradiated for 2 h under 0.2 Pa pressure oxygen atmosphere, 3~4 mL of solution was collected and filtered by syringe with 0.45 µm of filter membrane. 500 µL of supernatant was added into the mixture consisted of 2 mL of KI solution (0.1 M) and 50 µL ammonium paramolybdate (H₂₄Mo₇N₆O₂₄•4H₂O, 0.01 M). Following, it was probed to estimate the concentration of H₂O₂ production after dispersing ultrasonically about 10 min. The absorption wavelength could be at about 352 nm measured by ultraviolet–visible spectrophotometry.

2.4.2 Photocatalytic degradations of pollutants

The performances on resolving contaminants over the synthesized materials were conducted in a photochemical reactor, in which the photocatalytic system can be

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maintained at room temperature by circulating cooled water. In theotypical PDODT02318C photocatalytic experiment, the suspension mixed with 30 mg of photocatalyst for Cr (VI) reduction (or 15 mg photocatalysts for MO oxidation) and 50 mL of pollutant solution (10 ppm chromium (VI), 10 ppm methyl orange) was magnetically stirred in the dark for 40 min for achieving the dynamic equilibrium of adsorption and desorption. Then, 400 W metal halide lamp (light intensity: 148.36 mW cm⁻²) with a < 420 nm UV filter and another > 760 nm IR filter was applied to simulating visible light, and the NIR photocatalytic experiments were conducted by a 980 nm diode laser with a beam expander (VA-I-DC-980, VIASHO). After a given time interval, 4 mL of the mixed suspension was extracted for the further centrifugation during the photocatalytic process, and then analyzed by using a UV-vis spectrophotometer (UV-6300 Double Beam Spectrophotometer, Mapada Instruments). Moreover, the Cr (VI) concentration in the supernatant was measured by 1, 5-diphenylcarbazide colorimetric method, and the degradation or reduction efficiency (η) could be calculated as follows:

$$\eta = (1 - C_t / C_0) \times 100\%$$

where C_0 is the initial concentration of pollutants, and C_t is temporal concentration.

2.5 Computational models and methodology

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First-principles calculations based on density functional theory (DFT) were performed to investigate the band structure and electronic properties of Yb/Tm doped InVO₄. All calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector augment wave (PAW) method. The exchange and correlation potentials were described with the Perdew–Burke–Ernzerhof(PBE) of the generalized gradient approximation (GGA). The kinetic energy cutoff (420 eV) of the plane wave basis was used throughout, and was well within the convergence of a total-energy calculation. The Brillouin zone was sampled with special *k*-points of a $2\times2\times3$ grid for relaxation process, whereas 20 k-points along high symmetry lines was used for electronic structure calculations. The forces on each ion converged to less than 0.01 eVÅ⁻¹, and the stress was less than 0.02 GPa. All the atoms of the structures were fully relaxed to their equilibrium positions with an energy

convergence of 1×10^{-5} eV, and the atomic displacement was less than 5×10^{-4} : Å¹(as)/DOT02318C well as the self-consistent field (SCF) tolerance was 5×10^{-7} eV. The pseudopotentials used for the adopted models were constructed by the electron configurations as V-3d³4s², In-5s²5p¹, O-2s²2p⁴, Yb-4f¹⁴6s² and Tm-4f¹³6s² for the ground-state electronic structure calculations. The convergences with respect to the cutoff energy and the k-points mesh were tested, and the results showed that the cutoff energy and the k-points mesh used in this work were enough for the system.

3. Results and discussion

Fig.1 shows the XRD patterns of as-prepared photocatalysts synthetized by hydrothermal synthesis. For pure InVO₄, every diffraction peaks can be clearly indexed to the orthorhombic InVO₄ corresponding to the standard data (JCPDS No. 48-0898),^{41, 42} which matched well with every diffraction peaks of as-synthesized products. Specifically, the diffraction peaks presented at $2\theta = 18.59$, 20.84, 23.02, 24.89, 31.07, 33.05, 35.21, and 47.04 are distinctly indexed to the (110), (020), (111), (021), (200), (112), (130), and (222) crystal planes, respectively. The samples show the high degree of crystallinity and no peaks concerning to other impurities are observed about 0.5YT-IV, 2.5 YT-IV and 5 YT-IV samples, which indicates that doping Yb^{3+/} Tm³⁺ cannot change the crystalline phase of orthorhombic InVO₄ due to the low contents of Tm³⁺ and Yb³⁺. Importantly, two diffraction peaks at 25.5 and 34 correspond to the YbVO₄ (JCPDS No. 01-072-0271) or TmVO₄ (JCPDS No. 01-072-0272) over 10 YT-IV and 20 YT-IV samples, because of the increasing concentration of Yb3+ and Tm3+ ions. A detailed comparison based on the corresponding enlarged patterns of undoped and doped InVO₄ samples presents the shifts of diffraction peak position to lower 2θ angles, indicating the presence of the obvious change in the unit cell volume due to that In³⁺ could be substituted by Tm³⁺ and Yb^{3+} . It is well known that θ can be in variation with the different d according to the Bragg equation $2dsin\theta = n\lambda$. Therefore, the peak at 25.5 shifts as the different ions radius (R_{In}=0.94Å, R_{Tm}=1.02Å and R_{Yb}=1.008Å). This result reveals that the crystal lattice of InVO₄ can be incorporated and substituted by Tm³⁺ and Yb³⁺ ions. In addition, it can be obviously observed that for the effect of doping content on the popto2318C crystalline phase, the increased doping content of Tm³⁺ and Yb³⁺ ions weakens gradually the intensity of diffraction peak at 33, suggesting that the sample prefers orientation growth along with the addition of Tm³⁺ and Yb³⁺ ions dopants. Moreover, the phase structure did not change for other phases over YT-IV sample, indicating the well crystallization and the successful preparation of Yb³⁺/Tm³⁺ co-doped InVO₄ samples.



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Fig. 1 XRD patterns of InVO₄ and Yb³⁺/Tm³⁺ co-doped InVO₄ samples (a) and the corresponding enlarged patterns (b).

The morphologies of as-obtained samples were in investigation by SEM, TEM and EDX mapping images. As illustrated in Fig. 2a, the typical SEM image diffuses that the obtained IV products consist mainly of high-yield sheet-like nanostructures with floccule surface, without the presence of adhesive particles. After doping Yb³⁺/Tm³⁺ (Fig. 2b), it still preserves the nanosheets structure. In addition, similar morphological structure can be found from the SEM images of 0.5YT-IV, 2.5 YT-IV and 10 YT-IV samples (Fig. S1), but excess Yb³⁺/Tm³⁺ doping (20 YT-IV) has a great of structural effect on the host InVO₄, changing from sheet-like nanostructures to block aggregates. This can be attributed to the formation of REVO₄ (RE= Yb³⁺, Tm³⁺), which is consistent with the conclusion from the XRD patterns. Fig. 2c and d confirm extremely the presence of thin nanostructures over IV and 5YT-IV sheets, as can be seen in TEM images. The HRTEM image of 5YT-IV (Fig. 2e) signifies a lattice spacing of ~0.389 nm consistent with the (111) plane of IV, revealing the high

Dalton Transactions

crystallinity of 5YT-IV sample. Importantly, the EDX spectra (f), TEM imag@@g)oan@/DODTO2318C corresponding EDX mapping images (h-l) of 5YT-IV nanosheets testify the presences of the In, V, O, Yb and Tm elements, indicating the successful preparation of Yb³⁺/Tm³⁺ co-doped InVO₄.



Fig. 2 The SEM images of IV (a) and 5YT-IV nanosheets (b); TEM image of IV (c) and 5YT-IV (d); HRTEM images (e) and EDX spectra (f) of 5YT-IV; TEM image of 5YT-IV (g) and the corresponding EDX mapping images of In (h), V (i), O (j), Yb (k) and Tm (l).

The elemental compositions of as-prepared samples were probed by X-ray photoelectron spectra (XPS). As presented in Fig.3a, there are in the presence of In3d, V2p, O1s, Yb4d and Tm4d for 5YT-IV sample in the XPS survey spectra. The binding energies at 18.7 and 42.07 eV are belonged to O2s and Yb5p, respectively. The peaks corresponding to the V3s and V2s are distributed in 69.8 and 632.98 eV, and the peaks at 120.7, 665.45, 704.93 and 827.79 eV are attributed to the presence of In4s, In3p3, In3p1 and In3s, respectively. In detail, the two individual peaks in the high-resolution In3d spectrum (Fig. 3b) at 444.3 eV and 451.9 eV correspond to the In3d_{5/2} and In3d_{3/2},

respectively.^{43, 44} Moreover, the peaks located at 516.4 eV and 523.7 eV in the $W_2^{Verv Article Online}$ spectrum are related to the V2p_{3/2} and V2p_{1/2} contributing to V⁵⁺ (Fig. 3c).⁴⁵ The characteristic peak of lattice oxygen in the InVO₄ locates dominantly at 529.1 eV.^{46, 47} and the shoulder peaks at 530 and 531.9 eV in Fig. 3d are dominantly assigned to the weakly bonded O⁻ and OH⁻ in the substance,⁴³ respectively, which can further boost the trapping of photo-induced electrons and holes, resulting in enhancing the photocatalytic process. The symmetrical peaks of Yb4d (Fig. 3e) centered at binding energies of 197.5 eV and 199.1 eV correspond to the Yb 4d_{3/2} and Yb 4d_{5/2} in consistence with the previous reports.^{48, 49} The Tm4d peak is positioned at 175.5 eV (Fig. 3f). In addition, a presentable shift in the direction of low binding energies about In3d, V2p and O1s can be observed for 5YT-IV sample (Fig.3 and Fig. S2), suggesting that there are in the presence of strong interaction between Yb³⁺/Tm³⁺ and InVO₄. Based on the above detailed analysis, the XPS analysis further implies that Yb³⁺ and Tm³⁺ were successfully doped into the InVO₄ materials.



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Fig. 3 XPS spectra of 5YT-IV nanosheets: (a) survey, (b) In 3d, (c) V 2p, (d) O 1s, (e) Yb 4d and (f) Tm4d.

To understand furtherly the surface chemical structure of as-prepared IV and YT-IV samples, the infrared spectra were applied and showed in Fig.4. FT-IR spectrum of pure InVO₄ exhibits strong bands in the region of 1000-500 cm⁻¹: one hand, the band positioned detailedly at 531 cm⁻¹ is ascribed to the V-O-V vibration; on the other hand, the bands centered at 1052~634 cm⁻¹ are assigned to the V-O-In stretching.^{48, 50} The peak at 773 cm⁻¹ presents a significant change from broad peak of IV sample to sharp peak for doped InVO₄ samples, which may be caused by Yb³⁺/Tm³⁺ doping. It's worth noting that there exists a strengthened variation of peak at around 946 cm⁻¹ after doping Yb³⁺/Tm³⁺, it is attributed to the different dipole moment, corresponding to the characteristic stretchings of V-O-RE (RE= Yb, Tm) on YbVO₄ and TmVO₄.⁵¹ Additionally, the bands located at 3155~3500 cm⁻¹ are corresponded to the stretching vibrations of the surface hydroxyl groups. Furthermore, the band at 1622 cm⁻¹ is attributed to the presence of residual hydroxyl groups. In the case of the YT-IV samples, Yb³⁺/Tm³⁺ doping does not change the characteristic peaks based on the comparison of that of pure InVO₄ sample.

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Fig. 4 FT-IR spectra of IV and YT-IV samples.

The light absorption performance is known to be one of critical parameters that can determine the performance of the photocatalyst. UV-Vis DRS of all samples were conducted to further characterize the light absorbance properties. As depicted in Fig. 5a, the bare InVO₄ exhibits apparent fundamental adsorption in the UV-Vis region, and performed an absorption edge at about 560 nm, indicating the boosted adsorption towards visible light. Meanwhile, the light absorption intensity presents an apparent enhancement after doping Yb³⁺ and Tm³⁺ into InVO₄ crystal, indicating the possession of stronger visible light response for YT-IV composites, which may be attributed to the decrease of band gap and the boosted adsorption of photon energy from the upconversion process of Yb³⁺/Tm³⁺ in YT-IV. Furthermore, a distinct red shift exists in the YT-IV samples, which can be ascribed to optical transition of the intermediate energy states within energy gap of IV,^{27, 50} in favor of utilizing largely solar energy and boosting photocatalytic performance. Generally, the band gap energies of as-prepared photocatalysts are determined and listed in Table S1. A obvious change in band gap energies can be obtained from the doped InVO₄ samples. Codoping Yb³⁺ and Tm³⁺ can lower the band gap for 5YT-IV samples (1.95 eV) on the comparison of bare InVO₄ sample (2.07 eV), indicating again the formation of intermediate energy states and a promoted light absorption (Fig. 5b).

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Fig. 5 (a) DRS and (b) Plots of $(ahv)^2$ versus photon energy (hv) for samples.

As is known to all, the charge separation efficiency and transfer resistance are fatal for enhancing photocatalytic activity. It can be revealed directly by the transient photocurrent response and electrochemical impedance spectroscopy (EIS) on the electrode, for which the photoelectrochemical experiments were accepted to investigate the transmission and separation efficiency of photogenerated charge carriers under 300 W Xe lamp irradiation with 420 nm cutoff tablets. As presented in Fig. 6a, based on the comparison of IV sample, the transient photocurrent density on YT-IV photocatalyst is remarkably higher in favor of enhancing photocatalytic efficiency, implying the more excellent light harvesting capability. The fast and steady photocurrent responses profit from Yb³⁺/Tm³⁺ doping that can boost the photo-induced generation and separation of free charge carriers.

In general, the radius of EIS arc over photocatalyst can also directly uncover the resistance in photo-induced charge transfer, for which the small EIS arc radius reflects the low transfer and separation resistance in this system. Obviously, YT-IV photocatalyst exhibits lower EIS arc radius compared with pure IV sample (Fig. 6b), especially 5YT-IV sample presents the smallest one, further indicating the more efficient photoinduced charge transfer capability and the enhanced separation efficiency. Combined with the above analysis, it can be obtained that doping Yb³⁺/Tm³⁺ in IV sample could be anticipated to boost photocatalytic performance.

The interfacial charge transfer kinetics was used to get a better insight with an equivalent circuit model (the inset of Fig. 6b), consisting of Warburg element (Zw),

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constant phase element (CPE), electrolyte resistance (Rs) and charge Dtransfer/DODTO231BC resistance at the electrolyte–electrode interface (Rct). The values of Rcts are 17.66, 17.3, 16.25, 15.09, 16.41 and 17 Ω cm² for IV, 0.5YT-IV, 2.5 YT-IV, 5 YT-IV, 10 YT-IV and 20YT-IV, respectively, and the smaller Rct value implies a much smaller interfacial resistance between the electrolyte and electrode. Therefore, doping Yb³⁺/Tm³⁺ on IV sample can enhance the photocatalytic performance due to the much smaller interfacial charge transfer resistance. Moreover, it is well known that the Fermi level (E_F) is closer to the flat band potential from Mott–Schottky relationship of n-type semiconductor. Therefore, the energy-level structure of undpoed IV and 5YT-IV samples can be gained by Mott-Schottky analysis, in which there exists a significant negative shift from the -0.98 V (vs. Ag/AgCl) for IV to -1.07 V (vs. Ag/AgCl) for 5YT-IV, respectively (Fig. S3). The conduction band edge potentials of undpoed IV and 5YT-IV are 0.358 eV and 0.448 eV, respectively.



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Fig. 6 Photoelectrochemical measurement over pure IV and YT-IV samples: (a) photocurrent measurements; (b) electrochemical impedance spectra (Inset: the equivalent circuit mode).

Upconversion luminescence spectra of the obtained YT-IV samples can be observed under the excitation of 980 nm NIR light. The result as demonstrated in Fig. 7a makes clear that the emission peaks at 474 nm (blue light), 621 nm (red light) and 800 nm could be matched well with ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$, ${}^{1}G_{4} \rightarrow {}^{3}F_{6}$ and ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transitions of Tm³⁺,^{27, 35, 52, 53} respectively. Yb³⁺ can be excited efficiently by 980 nm wavelength, where it possesses a large absorption, and then transfers successively the energy to Tm³⁺, signifying the formation of upconversion process. And also, 5YT-IV doesn't present the most obvious transformation in the visible light region, which may be because that the energy from Yb³⁺ to Tm³⁺ further transfers to InVO₄ semiconductor

Dalton Transactions

under 980 nm NIR irradiation.⁵⁴ Therefore, doping Yb^{3+}/Tm^{3+} can extend on the /Dod T02318C semiconductor's absorption to NIR light and harvest effectively NIR photons by InVO₄.

Inspired by NIR photons, Yb³⁺/Tm³⁺ co-doping InVO₄ semiconductor could adsorb the lower energy photons, and follow to convert into the emitted photons with higher energy via upconversion. The mechanism of upconversion processes can be illustrated by the Yb³⁺/Tm³⁺ energy level structures and presented in Fig. 7b. Upon NIR irradiation, Yb³⁺ ions can be excited by 980 nm pump photons from ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$, and then the energy can be transferred to Tm³⁺ ions by phonon assisted energy transfer, resulting in populating the higher energy levels of ${}^{3}\text{H}_{5}$, ${}^{3}\text{F}_{3}$ and ${}^{1}\text{G}_{4}$ over Tm³⁺ through successive energy transfers. Nonradiative relaxation of ${}^{3}H_{5} \rightarrow {}^{3}F_{4}$ and ${}^{3}F_{3} \rightarrow {}^{3}H_{4}$ populates ³F₄ and ³H₄ level of Tm³⁺ ions.⁵⁵ The next energy transfer to the Tm³⁺ ion finally populates ¹G₄. Tm³⁺ ions of ¹G₄ energy levels are more inclined to relax non-radiatively to ³H₄ owning the multiphonon relaxation rather than decaying radiatively to the ${}^{3}H_{6}$. Thence, radiative transition from ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ and ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ deliver weak blue and red emission positioned at 474 nm and 621 nm. Fig. 7c shows the color coordinates of the fluorescence based on the CIE chromaticity diagram, upconversion spectra of all samples are distributed in the white light region, corresponding to this result presented in Fig. 7a. Therefore, InVO₄ semiconductor can further absorb and utilize these fluorescent excitation energies, resulting in the enhanced light adsorption and the boosted the photocatalytic performance on the photocatalytic Cr (VI) reduction, MO oxidation and production of H_2O_2 through irradiative energy transfer as well as non-irradiative energy transfer process.⁵⁶⁻⁵⁸



Fig. 7 The upconversion emission spectra upon 980 nm excitation (a); schematic diagram based on the energy-level structures and upconversion processes of Yb³⁺ and Tm³⁺ ions(b); the CIE coordinates of all samples(c).

Water electrolysis is usually used to obtain pure hydrogen provided by a convenient and clean way, and a high current density at low overpotential can achieve over an efficient hydrogen evolution reaction (HER) catalyst.^{59, 60} Meanwhile, to make a better comprehension of the enhancement of interfacial charge transfer, HER performances were carried out to investigate the changes of the active sites and interfacial charge transfer by Yb³⁺/Tm³⁺ doping. The electrocatalytic HER performances over bare IV and 5YT-IV samples were estimated in acidic solution (0.5 M H₂SO₄) in a three-electrodes configuration. As expected in Fig. 8a, 5YT-IV sample reveals excellent HER performance and while pure IV presents no HER activity, for which 5YT-IV sample requires lower overpotential for electrocatalytic HER under the same current density than that of pure IV. The HER kinetics was tested by the corresponding Tafel plots, as show in Fig. 8b. 5YT-IV presents a lower Tafel slope (390 mV dec⁻¹) than that of pure IV (731 mV dec⁻¹), revealing that 5YT-IV delivered

performance for HER. Double-layer capacitance (C_{dl}) was carried out to assess the effective electrochemical active area. Obviously, as shown in Fig. 9, the C_{dl} of 5YT-IV (30.67 μ F cm⁻²) is much larger than that of bare IV (7.77 μ F cm⁻²), suggesting that Yb³⁺/Tm³⁺ doping could induce an enhancement in active area and is helpful to HER performances for providing more exposed sites.







Fig. 9 Cyclic voltammetry curves of IV (a) and 5YT-IV (b) with the different scanning rates; Plots

of the capacitive current measured at -0.35 V vs RHE as a function of scan rate (c) View Article Online Vi

The activity of photocatalytic H_2O_2 production was evaluated under the xenon lamp illumination with a < 420 nm UV filter. As described in Fig. 10, H_2O_2 could be generated over IV and 5YT-IV systems, and while no H_2O_2 production can be found without the presence of photocatalyst and light source, meaning unambiguously that the program in generating H_2O_2 production was operated by photocatalysis. Interestingly, the yield of H_2O_2 production over YT-IV suspension increases slowly and then decreases with the incremental doping amount of Yb^{3+}/Tm^{3+} , and they show a stronger photocatalytic activity of H_2O_2 production compared with pure IV, indicating more positive action for photoreducing O_2 to H_2O_2 . The enhanced photocatalytic activity for H_2O_2 production maybe because of the boosted visible light absorption from DRS result, and the improved efficiency towards the photoinduced interfacial charge transfer and separation.



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Fig. 10 Photocatalytic H₂O₂ production over these different photocatalysts.

The photocatalytic activities of chromium (VI) reduction and methyl orange oxidation (MO) were carried out under visible light or NIR light irradiation as introduced in Fig. 11 and 12 over as-synthesized YT-IV and pure IV photocatalysts. As shown in Fig. 11, the reduction efficiencies of Cr(VI) over different YT-IV photocatalysts exhibited excellent photocatalytic performance in comparison to pure IV under visible or NIR light irradiation, suggesting that doping Yb³⁺ and Tm³⁺ in InVO₄ is essential for enhancing photocatalytic performance. As shown in Fig. 11a, it is worth noting that no signal can be traced in the removal of Cr(VI) in the absence of photocatalyst, indicating that it is stable that it cannot be directly reduced by light. In

addition, it could be clearly concluded that co-doping Yb^{3+}/Tm^{3+} remarkably/DODT02318C enhances the photocatalytic performance, following the order of 5YT-IV > 2.5 YT-IV > 10 YT-IV> 20 YT-IV > 0.5 YT-IV > IV. Meanwhile, 5YT-IV exhibits the optimum photocatalytic performance on the removal of Cr(VI). The same result with the enhanced photocatalytic performance in the presence of YT-IV can also be concluded under NIR light irradiation (Fig. 11b). As presented in Fig. 11c, the comparisons of the photocatalytic performance of Cr(VI) reduction under visible or NIR irradiation prove brightly the contribution of doping Yb³⁺/Tm³⁺, in which their optimum photocatalytic performances are 21.03% and 37.45% over 5YT-IV photocatalyst (only 3.38% and 6.22% for IV nanosheets) under NIR and visible irradiation, respectively. The rate constants are shown in Fig. S5, which were estimated to be 0.00298 min^{-1} under visible light irradiation and 0.00156 min⁻¹ under NIR irradiation, respectively. They are higher than that of bare IV sample $(0.00042 \text{ min}^{-1} \text{ and } 0.00024 \text{ min}^{-1})$. In addition, 5YT-IV photocatalyst presents also the boosted photocatalytic performance for 5 ppm Cr(VI) reduction under visible light irradiation (Fig. S4a), reducing 42% of Cr(VI) for 150 min. But the degradation efficiency is only 16% for undoped InVO₄ samples. 5YT-IV photocatalyst can almost reduce 99.3 % Cr(VI) (10 ppm) under 500 min irradiation, and while only 25% for bare IV sample (Fig. S4c). It is ascribed to Yb³⁺/Tm³⁺ for converting long wavelength light (such as NIR, visible) into short wavelength light (visible, UV), which can again stimulate InVO₄ to produce photoexcited charge carriers.



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Fig. 11 The photocatalytic reduction performance of Cr(VI) over as-synthesized YT-IV photocatalysts under visible (a) and NIR (b) irradiation; the comparison of reduction performance (c).

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The photodegradation of MO in aqueous solution was also implemented to prove the contribution of Yb^{3+}/Tm^{3+} doping to the photocatalytic activity of InVO₄ under visible or NIR illumination. As introduced in Fig. 12, there is no photocatalytic activity in the absent of photocatalyst, implying that no photolysis is presented but the photocatalysis stays a key significant role in MO degradation. Comparatively, YT-IV nanosheets present far superior photocatalytic ability towards MO degradation than that of pure IV, as shown in Fig. 12a and b. 5YT-IV photocatalyst shows the degradation rates of 23.1% and 37.7% (low photocatalytic efficiency of 1.4% and 2.9% for pure IV) under NIR and visible irradiation, respectively (Fig. 12c). The rate constants were calculated to be 0.00307 min⁻¹ under visible irradiation and 0.00172 min⁻¹ under NIR irradiation, while it was only 0.00018 min⁻¹ and 0.00011 min⁻¹ for undoped InVO₄ sample (Fig. S6), respectively. In addition, 5YT-IV photocatalyst can degrade 56% MO (5ppm) under visible irradiation (Fig. S4b), while it is only 15% for undoped InVO₄ Moreover, as it can be seen from Fig. S4d, the time required by the best sample to degrade MO to at least >95% is ca. 350 min. In addition, the total organic carbon (TOC) of MO over 5YT-IV sample has been tested (Fig. S4e), it can be found that the TOC amount decreases as the illumination time, suggesting that MO is decomposed rather than decolorized. With an increasing ratio of doping Yb³⁺/Tm³⁺ on InVO₄, the photocatalytic efficiency of YT-IV presents variable tendency on enhancing first and then reducing, which can attribute to the light decay caused by the Yb³⁺ loadings.⁶¹ Inspired comprehensively by above investigations, the boosted photocatalytic efficiency maybe due to the boosted NIR absorption, the improved

electrons/holes pair separation generated by intermediate energy states in YT-IV. In addition, an overall view of the comparison in NIR photoactivities toward dye degradation over other Yb³⁺/Tm³⁺ upconverting photocatalysts is displayed in Table S2, the Yb³⁺/Tm³⁺ codoped InVO₄ delivers a relatively high photodegradation activity under NIR light irradiation, indicating that Yb³⁺/Tm³⁺ codoped InVO₄ photocatalyst presents a better promising application as NIR-activated photocatalyst.





Moreover, the stability of the better photocatalyst of 5YT-IV was carried by the recycled test during MO degradation. As shown in Fig. S7, with an overall view of the MO degradation performance, a slight change for the degradation activity is presented after three successive cycles. It indicates that YT-IV photocatalysts present good stability as well as better promising application. In addition, XRD pattern of 5YT-IV

photocatalyst after three cycles for the photocatalytic MO degradation presents 100/DODT02318C evident variation of crystalline structure (Fig. S8), testifying further the chemical stability of doping Yb³⁺/Tm³⁺ on InVO₄.

To further investigate the recombination capability of the photogenerated charge carriers, the steady-state photoluminescence (PL) spectra were performed over as-synthesized samples under the 380 nm wavelength excitation (Fig. 13). The stronger PL intensity suggests the higher recombination capability of the photoexcited charge carriers,⁶² which will inhibit the enhancement of photocatalytic performance. It can be clearly observed that 5YT-IV sample exhibits dramatically lower PL spectra than that of IV photocatalyst, implying that it presents the impeded recombination and the promoted separation efficiency of charge carriers over 5YT-IV sample, in consistent with the results of transient photocurrent response and EIS.



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Fig. 13 The steady-state PL spectra with the 380 nm excitation wavelength.

In order to identify the enhanced photocatalytic mechanism in depth, the primary reactive species were recorded with trapping experiment of MO degradation and Cr(VI) reduction over 5YT-IV under visible light irradiation. During the photocatalytic reaction process, 1 mM tertbutyl alcohol (t-BuOH), 1 mM p-benzoquinone (p-BZQ) and 1 mM EDTA-2Na as the scavengers were mainly selected to capture hydroxyl radical (•OH), superoxide radical (•O₂⁻) and hole (h⁺), respectively. In addition, 1 mM of KBrO₃ was used to capture the electrons during the Cr(VI) reduction. As introduced in Fig. 14a, the MO degradation efficacy in the presence of 5YT-IV photocatalyst weakens dramatically from 37.7% to 14.8% and 13.2% with the respective addition of EDTA-2Na and p-BZQ, implying that the

presences of h^+ and $\bullet O_2^-$ as the main oxidative species payed a significant attention (0) DODT02318C the degradation. On the contrary, the addition of t-BuOH has slightly negative effect on the degradation, denoting that •OH did not participate in the reaction as the predominant active species. As displayed in Fig. 14b, the photocatalytic effect of the Cr(VI) reduction is inhibited with the addition of KBrO₃ as electrons scavenger, and while that is promoted with the addition of EDTA-2Na as electrons donor, suggesting that electrons played a decisive role in Cr(VI) reduction.



Fig. 14 Trapping experiment towards the active species in MO degradation (a) and Cr(VI) reduction (b) under visible light irradiation.

To understand the boosted photocatalysis over 5YT-IV sample, as shown in Fig. 15, the supercells with $4 \times 2 \times 3$ unit cells containing 576 atoms were constructed for the Yb/Tm doped InVO₄. In the supercell, four In atoms were replaced by Yb dopant and one In atom was replaced by Tm in the doping case, yielding a dopant concentration of 4.2% and 1.0% for Yb and Tm, respectively. As tabulated in Table 1, the fully-relaxed lattice parameters of InVO₄ and Yb/Tm doped InVO₄ crystals are listed. It can be seen that the calculated lattice parameter is $5.844 \times 8.677 \times 6.754$ after the geometric optimization of InVO₄, which is very similar to the literature value of 5.769×8.546×6.565.63 It shows that the model structure is consistent with the reality and the calculation process is reasonable.

Table1	Comparison	of lattice	parameters(Å)
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	-		
System	Lattice parameters(Å)		
System	а	b	с
InVO ₄ calculation value	5.844	8.677	6.754
InVO ₄ literature value [64]	5.769	8.546	6.565
Yb/Tm doped InVO ₄ 4×2×3	23.378	17.355	20.263
super cell			

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Fig. 15 Models of pure InVO₄ and Yb/Tm doped InVO₄: (a) pure InVO₄ unit cell; (b) Yb/Tm doped InVO₄ super cell.

The introduction of impurity Yb and Tm atoms causes the lattice to be distorted, the volume is slightly greater than that of pure $InVO_4 4 \times 2 \times 3$ super cell. The reason for this phenomenon is mainly due to that the ion radius of In^{3+} is 0.94 Å, which is close to that of $Tm^{3+}(1.02 \text{ Å})$ and $Yb^{3+}(1.008 \text{ Å})$.

To evaluate the thermodynamic stability of Yb and Tm dopants in the InVO₄, the formation energies (E_f) were calculated via the following formula:

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$$E_f = E_{\text{doped}} - E_{\text{InVO}_4} - E_{\text{Yb}} - E_{\text{Tm}} + E_{\text{In}}$$
(1)

where E_{doped} and E_{InVO_4} correspond to the total energies of the pure and Yb/Tm-doped InVO₄, respectively. E_{Yb} , E_{Tm} and E_{In} are the chemical potentials of Yb, Tm and In metals, respectively. According to this definition, the nanomaterials with a negative E_f is energetically favorable and can be fabricated easily with more intimate interface binding. The obtained result of -5.02 eV of E_f for the Yb/Tm doped InVO₄ indicates the stable structure.

To have an insight about the electronic distribution properties of Yb/Tm-doped InVO₄, the electron density differences around Tm and Yb atoms can be seen from Fig. 16. Herein, the red regions indicate the electrons accumulation, and the blue regions indicate the electrons depletion. Obviously, there is a considerable charge accumulation close to V and O atoms, indicating the electron transfer from Yb or Tm atoms to O or V atoms. The distribution of the charge density is nearly spherical around O atoms, and a small overlap in the charge density exists between Tm(Yb) and O atoms, presenting an ionic feature. And meanwhile, In atoms have small charge



Fig.16 Charge density difference map of Yb/Tm doped InVO₄.

The change of band gap about doping Yb/Tm can be demonstrated by density of states (DOS). It shows clearly that the InVO₄ has a direct energy gap of 2.923 eV (Fig. 17). The calculated band gap is different from the value of experiments due to the difference between ideal crystal cell and actual crystal. But it can respond our results of the corresponding electronic band structures. The energy gap of Yb/Tm doped InVO₄ is 2.292 eV, which significantly decreases compared with that of pure InVO₄. The decease of band gap leads to a much wider visible-light absorption range. This is consisting with the results of experiments from DRS result.



Fig. 17 The projected band structures of IV (a) and 5YT-IV (b).

Inspired by the above investigations, as schemed in Scheme.1, a possible enhanced mechanism is proposed over Yb^{3+}/Tm^{3+} co-doped InVO₄ photocatalyst. In detail, under the irradiation of NIR light, the electrons over Yb^{3+} ions could be

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transited from the ${}^{2}F_{7/2}$ level (ground state) to ${}^{2}F_{5/2}$ level (the excited state), which //DODTO23IBC then will be introduced into the higher energy levels (${}^{3}H_{5}$, ${}^{3}F_{3}$ and ${}^{1}G_{4}$) of Tm³⁺ ions through energy transfer process. After absorbing the energy transferred from upconversion luminescent, InVO₄ semiconductor can photoinduce the formation of free charge carries over the CB and VB, and the photogenerated electrons could be separated immediately in the presence of intermediate energy states, leading to the lower recombination and high efficient separation rate. The Cr(VI) could be reduced to form Cr(III) owning the more negative CB edge potential of YT-IV than the Cr(VI)/Cr (III) potential of +0.51 V vs NHE. Furthermore, O₂ of the reaction system can contact easily with the photoexcited electrons owning that the CB edge potential of YT-IV (-0.448 eV vs NHE) is far higher than the standard redox potential E_{θ} (O₂/•O₂⁻) of -0.33 eV vs NHE, resulting in the generation of ${}^{\circ}O_{2}^{-}$ radicals for H₂O₂ production or MO oxidation.



Scheme. 1 The schematic illustration of the photocatalytic process under Vis-NIR light irradiation.

4. Conclusions

In summary, the boosted photoactive Yb^{3+}/Tm^{3+} co-doped InVO₄ was successfully synthesized via hydrothermal process. The upconversion process induced by Yb^{3+}/Tm^{3+} offered a certain amount of suitable energy in this system of activation and subsequent photocatalysis under NIR irradiation. The excellent photocatalytic performance for photocatalytic H₂O₂ production, Cr(VI) reduction as well as MO oxidation and electrocatalytic HER performance were beneficial from the shortened

transfer distance of free charge carriers owning the generation of intermediate energy/Dodt02318C states induced by doping Yb^{3+}/Tm^{3+} , the enhanced light absorption and the reduced recombination chance towards free charge carriers in the body. Thence, it highlights a path for the enhancement of solar-energy utilization and photocatalytic performance.

Conflicts of interest

There are no conflicts to declare.

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A possible enhanced process was proposed about the excellent photocatalytic H_2O_2 production, Cr(VI) reduction as well as MO oxidation. The upconversion process induced by Yb³⁺/Tm³⁺ offered a certain amount of suitable energy in this system of activation and subsequent photocatalysis under NIR irradiation.