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Novel heterojunction photocatalyst based on lanthanum titanate nanosheets and indium oxide nanoparticles with enhanced photocatalytic hydrogen production activity

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A lanthanum titanate (La$_2$Ti$_2$O$_7$) and indium oxide (In$_2$O$_3$) heterojunction nanocomposite is synthesized by a solvothermal method. The crystal phase, morphology, optical absorption activity and chemical composition of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction nanocomposites are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV-Vis diffuse reflectance spectra and X-ray photoelectron spectroscopy. The results reveal that In$_2$O$_3$ nanoparticles are uniformly dispersed on La$_2$Ti$_2$O$_7$ nanosheets surfaces with good adhesion. The In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite with a molar ratio of 1.5:1 exhibits the highest H$_2$ production rate when used in photocatalytic water splitting, as improved by 29.62 and 6.43 times relative to pure In$_2$O$_3$ and La$_2$Ti$_2$O$_7$, respectively. The enhanced photocatalytic H$_2$ production rate can be ascribed to the formation of the heterojunction structure that results from the homogeneous dispersion of In$_2$O$_3$ nanoparticles on La$_2$Ti$_2$O$_7$ nanosheets. The configuration of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction nanocomposite photocatalyst can promote the fast separation of photogenerated carriers in space and improve the rate of water-splitting to form H$_2$.

1. Introduction

With the depletion of fossil fuel reserves and the subsequent need for sustainable energy sources, hydrogen as a clean and renewable energy source has become a favored fuel for supplanting conventional fossil fuel-derived energy.\textsuperscript{1-5} Since Fujishima and Honda first reported the photoelectrochemical splitting of water into H$_2$ and O$_2$ on a TiO$_2$ semiconductor electrode, various photocatalytic water-splitting semiconductors for solar-driven H$_2$ production have been studied.\textsuperscript{6-10} Among these semiconductors, (110) layered-structure perovskites, such as M$_2$N$_2$O$_7$ (M = Ca, Sr, La; N = Nb, Ti), have received increasing attention because of their unique electronic configuration, high chemical resistance and interlayer spatial structure, enabling the use of different reaction sites for water oxidation and reduction.\textsuperscript{11,12} Among the perovskites, lanthanum titanate (La$_2$Ti$_2$O$_7$, LTO) has received major attention because of its efficiency in photocatalytic H$_2$ production from water splitting.\textsuperscript{13,14} The conventional preparation methods of La$_2$Ti$_2$O$_7$ are via solid-state reaction (SSR) and sol-gel methods. However, neither of these methods is convenient or economical. In addition, the particles obtained are large with undesirably low specific surface areas.\textsuperscript{13,14} These characteristics are not favourable to efficient and low-cost photocatalytic H$_2$ production activity.

Furthermore, the high recombination rate of photogenerated electron-hole pairs in La$_2$Ti$_2$O$_7$ restricts the enhancement of its photocatalytic H$_2$ production activity. Hence, the modulation of photogenerated charge carrier transformation in La$_2$Ti$_2$O$_7$ is crucial to enhancing the photoconversion efficiency of solar energy. One proposed and effective means of modulating carrier transformation is through the use of a heterojunction structure or coupling two semiconductor units with appropriate band alignment between the two units to allow interfacial charge transfer upon excitation and promote the separation efficiency of photogenerated electrons and holes.\textsuperscript{17-19} For example, Qian and coworkers found that novel Bi$_2$S$_3$/Bi$_2$O$_2$CO$_3$ heterojunction photocatalysts showed greatly improved photoactivity compared to that of pure Bi$_2$O$_2$CO$_3$.\textsuperscript{18} The enhancement was ascribed to the improved dispersion of Bi$_2$S$_3$ on the Bi$_2$O$_2$CO$_3$ nanoparticle surfaces and the more intimate Bi$_2$S$_3$/Bi$_2$O$_2$CO$_3$ heterojunction structure. Zhou et al. reported single n-ZnO/p-AlGaN heterojunction nanowires with excellent optoelectronic properties. The formation of a high-quality interfacial structure enhanced the excitation efficiency in the interfacial layer between ZnO and AlGaN.\textsuperscript{20}
In$_2$O$_3$ is a well-known semiconductor with an indirect bandgap of 2.8 eV. It has been demonstrated to be an efficient sensitizer for extending the absorption region from UV to the visible-light range. Because the conduction band (CB) and valence band (VB) positions of La$_2$Ti$_2$O$_7$ (-0.43 eV and 3.37 eV, respectively, vs. NHE) are both higher than those of In$_2$O$_3$ (-0.63 eV and 2.17 eV, respectively, vs. NHE), the use of an In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction would result in an improvement in the efficient separation of photogenerated charge carriers. In such an In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction structure, the coupling of La$_2$Ti$_2$O$_7$ with In$_2$O$_3$ creates an electrostatic field opposite to the built-in potential, which can improve the separation efficiency of photogenerated electron-hole pairs. To be specific, the accumulated photogenerated electrons of In$_2$O$_3$ are readily trapped by a co-catalyst, such as Pt, Ag or NiO, to reduce water to hydrogen. The accumulated photogenerated holes in La$_2$Ti$_2$O$_7$ are subsequently oxidized by a sacrifice reagent.

For a photocatalyst to be efficient, a large specific surface area is desirable. To obtain such an area for the catalysts reported in this work, a hydrothermal method was used to prepare two-dimensional La$_2$Ti$_2$O$_7$ nanosheets because this morphology is more effective than zero-dimensional La$_2$Ti$_2$O$_7$ particles from the viewpoint of the mobility and recombination rate of charge carriers. Few studies have been conducted on La$_2$Ti$_2$O$_7$ nanosheet-based heterojunction photocatalysts. Here, we have used a solvothermal method to prepare In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction photocatalysts to investigate the synergistic effects of the In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ combination on the photocatalytic H$_2$ production activity. The as-prepared In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction nanocomposite with the optimal molar ratio of 1.5:1 shows much higher H$_2$ production activity and higher stability than the other materials tested under water-splitting conditions. The enhanced photocatalytic activity can be attributed not only to the large specific surface area of La$_2$Ti$_2$O$_7$ and the enhancement of visible light absorption by In$_2$O$_3$ but also can be ascribed to the more effective separation of photogenerated carriers that is driven by the electrostatic field in the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction structure.

2. Experimental

2.1 Materials

All chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification before use. High-purity deionized (DI) water was used throughout the experiments.

2.2 Preparation

La$_2$Ti$_2$O$_7$ nanosheets were prepared by a hydrothermal method. Specifically, 5 mmol Ti(OBu)$_4$ was mixed in 50 mmol CH$_3$COOH while stirring vigorously for 30 min and 5 mmol La(NO$_3$)$_3$·6H$_2$O was dissolved in 10 mL deionized water. This was added dropwise to the Ti(OBu)$_4$/CH$_3$COOH mixture, giving a clear aqueous solution. 30 mL 1.8 M NaOH solution was then added to this solution. The resulting solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heat-treated at 200 °C for 24 h. The product was collected after centrifugation, washed with water and ethanol repeatedly, and then dried at 80 °C for 12 h.

To form the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction, In$_2$O$_3$ nanocrystals were grown in situ on La$_2$Ti$_2$O$_7$ nanosheets. A mixture of 0.8 mmol In(NO$_3$)$_3$·5H$_2$O, 0.8 mmol La$_2$Ti$_2$O$_7$, 1 mL formamide and 2.4 mmol sodium dodecylbenzene sulfonate (SDBS) in 48 mL anhydrous ethanol was vigorously stirred magnetically for 1 h. The resulting precipitate was transferred into a 100 mL Teflon-lined stainless steel autoclave and heat-treated at 160 °C for 24 h. The precipitate was washed again and further annealed at 500 °C for 2 h to obtain an In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite photocatalyst. A series of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite photocatalysts with different molar ratios (2:1, 1.5:1, 1:1, 0.5:1 and 0.25:1) were synthesized in a similar fashion by adjusting the amount of In(NO$_3$)$_3$·5H$_2$O added. A pure In$_2$O$_3$ control catalyst was also synthesized following the same procedure in the absence of La$_2$Ti$_2$O$_7$.

Deposition of Pt (1.0 wt%) co-catalyst on a La$_2$Ti$_2$O$_7$ surface was achieved through typical in-situ photoreduction of H$_2$PtCl$_6$ with UV-light irradiation. One gram of the photocatalyst powder was suspended in 200 mL of aqueous solution containing 20 % (v/v) methanol as the sacrificial donor. 0.0265 g of H$_2$PtCl$_6$·6H$_2$O was added to the mixture. Following this, the suspension was stirred and purged with N$_2$ continually to ensure anaerobic conditions. After that, the suspension was illuminated with UV light for 4 h. The precipitate was collected by centrifugation and dried at 80 °C for 12 h.

2.3 Characterization

X-ray diffraction (XRD) measurements were carried out using an X-ray diffractometer (XRD, XPert pro. PANalytical B.V) with Cu Kα radiation. Both scanning electron microscopy (FE-SEM, FEI, Sirion 200) and transmission electron microscopy (TEM, JEM-2100F) were used to characterize the morphologies of the samples. X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS165 X-ray photoelectron spectrometer. The UV-Vis diffuse reflectance spectra were recorded with a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. Photoluminescence (PL) spectra were measured using laser confocal Raman microscopy (LabRAM HR800, Horiba JobinYvon) with an excitation wavelength of 325 nm.

2.4 Photocatalytic activity

The photocatalytic H$_2$ production experiments were performed in a quartz reactor under solar light irradiation at ambient temperature and atmospheric pressure. A 500 W Xe lamp (100 mW cm$^{-2}$, CHF-XM 500, Beijing Trustech Co., Ltd.) was used as the simulated solar light source. In a typical photocatalytic experiment, 0.1 g photocatalyst powder was suspended in 150 mL aqueous solution containing 25 % (v/v) methanol. Before photocatalytic H$_2$ production experiments, the reaction vessel was evacuated for 30 min to remove dissolved oxygen and ensure anaerobic conditions. Throughout the experiment 1 mL of gas was sampled intermittently and hydrogen content was analyzed using a gas chromatograph (DongXi GC-A5000, with high purity Ar carrier gas) equipped with a thermal conductivity detector. The apparent quantum efficiency (AQE)
was measured under the same photocatalytic reaction conditions. The focused intensity and areas on the flask for Xe lamp was ca. 100 mW cm⁻² and 19 cm², respectively. The AQE can be calculated according to the following equation:

$$\text{AQE} \ [\%] = \left( \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \right) \times \left( \frac{\text{number of evolved } \text{H}_2 \text{molecules} \times 2}{\text{number of incident photons}} \times 100 \right)$$

2.5 Photo-electrochemical measurement

Photocurrents and Mott–Schottky plots were measured using an electrochemical analyzer (Zennium, Zahner) with a standard three-electrode system using the prepared samples as the working electrodes, a platinum plate as the counter electrode, and a Ag/AgCl (saturated KCl) electrode as the reference electrode in 1 M Na₂SO₄ aqueous solution. A 500 W Xe lamp (100 mW cm⁻², CHF-XM 500, Beijing Trusttech Co., Ltd.) was used as the light source. For the preparation of the working electrodes, 0.2 g of the photocatalyst was ground with 0.06 g polyethylene glycol (PEG, molecular weight: 20000 Da) and 0.5 mL water to make a slurry. The slurry was subsequently coated onto a 2 cm×1.5 cm FTO glass electrode by the doctor-blade method. The resulting electrodes were dried and calcined at 450 ºC for 30 min. All electrodes studied had a similar film thickness (10–11 μm). 28, 29

3. Results and Discussion

3.1. Crystal phase analysis

The XRD patterns of In₂O₃, La₂Ti₂O₇, and In₂O₃/La₂Ti₂O₇ nanocomposites with different molar ratios are shown in Fig. 1. It can be found that pure La₂Ti₂O₇ prepared by a hydrothermal method shows a monoclinic phase with a perovskite structure belonging to the P2₁ space group (JCPDS 81-1066). After forming a composite of La₂Ti₂O₇ with In₂O₃ by solvothermal treatment at 160 ºC for 24 h, additional diffraction peaks with 2θ = 30.48, 35.44, 45.71, 51.03, and 60.80º appear, which can be indexed to the (222), (400), (431), (440), and (622) crystal planes of the body-centered cubic In₂O₃ crystalline phase (JCPDS 71-2194). No characteristic peaks for any impurities, such as In, In(OH)₃ or InTiO₅, can be observed, suggesting that the composition of the photocatalyst is exclusively In₂O₃ and La₂Ti₂O₇.

3.2. Morphology and microstructure analysis

Typical SEM images of In₂O₃, La₂Ti₂O₇, and In₂O₃/La₂Ti₂O₇ nanocomposites with a molar ratio of 1.5:1 are shown in Fig. 2. As seen from Fig. 2A and 2B, In₂O₃ shows aggregated spherical nanoparticles with coarse surfaces that fall within the narrow size range of 40 to 60 nm (Fig. 2A), while pure La₂Ti₂O₇ shows irregularly dispersed thin nanosheets (Fig. 2B). The In₂O₃/La₂Ti₂O₇ nanocomposite with a molar ratio of 1.5:1 (Fig. 2C and 2D) exhibits a homogeneous dispersion of In₂O₃ spherical nanoparticles upon the La₂Ti₂O₇ nanosheets with good adhesion. No obvious aggregate formation is observed.
interplanar distances of 0.224 and 0.257 nm are in good agreement with the d-spacings of the (111) and (400) planes of Pt and In$_2$O$_3$, respectively.

**Fig. 3** Typical HRTEM images of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite with a molar ratio of 1.5:1 (A); In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite loaded with 1 wt% Pt (B) and (C).

### 3.3. XPS spectra analysis

To confirm the chemical composition and purity of the prepared nanocomposites, the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite with a molar ratio of 1.5:1 was further studied by XPS analysis. C 1s is used as a reference for correcting the spectra for charge In, La, O and C exist in In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite. The corresponding high-resolution XPS spectra of Ti 2p, In 3d, La In, La, O and C exist in In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite. The corresponding high-resolution XPS spectra of Ti 2p, In 3d, La accumulation. The full spectra (Fig. 4A) show that elements Ti, 3d and O 1s are shown in 4C-4F, respectively. In Fig. 4C, the peaks located at 464.1 eV and 458.7 eV correspond to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively. The splitting between Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ is 5.4 eV, indicating a normal state of Ti (IV) in the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite. For In 3d, shown in Fig. 4D, spin-orbital splitting causes the observed In 3d$_{5/2}$ and In 3d$_{3/2}$ peaks to have characteristic double peaks centered at binding energies of 444.4 eV and 451.9 eV, respectively, which agrees well with literature values recorded for In (III).

**Fig. 4** XPS spectra of an In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite with a molar ratio of 1.5:1. (A) Full spectra; (B) Partial enlarged spectra; (C) Ti 2p; (D) In 3d; (E) La 3d and (F) O 1s high-resolution XPS spectra.

### 3.4. UV-vis diffuse reflectance spectra

**Fig. 5** UV-vis diffuse reflectance spectra of In$_2$O$_3$, La$_2$Ti$_2$O$_7$ and In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites with different molar ratios.
3.4. UV-vis absorption

Fig. 5 shows the UV-vis diffuse reflectance spectra (DRS) of In$_2$O$_3$, La$_2$Ti$_2$O$_7$, and several In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites with different molar ratios. For pure La$_2$Ti$_2$O$_7$, the DRS spectrum presents a steep absorption edge at approximately 340 nm, which can be assigned to the intrinsic bandgap absorption of La$_2$Ti$_2$O$_7$ (3.8 eV). The DRS spectra of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites are composed of the absorption spectra of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$, and the absorption boundary red shifts with an increasing amount of In$_2$O$_3$ on the La$_2$Ti$_2$O$_7$ nanosheets. Meanwhile, the absorption edges do not change obviously, implying that the respective crystal structures of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ are retained after the heterojunction forms.

3.5. Photocatalytic water splitting for H$_2$ evolution activity

The photocatalytic activities of In$_2$O$_3$, La$_2$Ti$_2$O$_7$, and the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites with different molar ratios were evaluated by measuring H$_2$ production from water splitting under 500 W Xe lamp irradiation, as shown in Fig. 6. To improve photocatalytic H$_2$ production, 1 wt% Pt cocatalyst was loaded onto the photocatalyst surfaces to provide active sites for the reaction. The microstructure of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite loaded with 1 wt% Pt is shown in Fig. 3B. As seen from Fig. 6, the photocatalytic H$_2$ evolution rates over In$_2$O$_3$ and pristine La$_2$Ti$_2$O$_7$ are only 2.30 and 10.59 μmol h$^{-1}$ g$^{-1}$, respectively. The H$_2$ evolution rates are distinctly enhanced by increasing the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ molar ratio from 0.25:1 to 1.5:1 and subsequently decrease significantly upon further increasing the molar ratio to 2:1. A possible reason for the enhanced photocatalytic H$_2$ evolution rates when the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ is changed from 0.25:1 to 1.5:1 is the heterojunction effect existing between In$_2$O$_3$ and La$_2$Ti$_2$O$_7$. Despite the variation in their activities, all of the above nanocomposites are more active for photocatalytic water splitting than pure In$_2$O$_3$ and La$_2$Ti$_2$O$_7$, and even perform better than a mechanical mixture of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$. The In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite with molar ratio of 1:1.5 exhibits the maximum photocactivity (68.14 μmol h$^{-1}$ g$^{-1}$ with an apparent quantum efficiency (AQE) of 0.41%), which is 29.62 times higher than that of In$_2$O$_3$ and 6.43 times that of pure La$_2$Ti$_2$O$_7$.

Fig. 7 displays the photostability of the Pt (1 wt%)-loaded In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1) photocatalyst, which was investigated in four runs performed over the accumulated course of 8 h. The average H$_2$ generation rate over Pt (1 wt%) loaded In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1) composite is approximately 56.41 μmol g$^{-1}$ h$^{-1}$ in the first run of 8 h photocatalytic reaction, and then slightly declines to 50.32 μmol g$^{-1}$ h$^{-1}$ in the fourth. The average H$_2$ generation rate decreases by approximately 10.8% when the reaction was performed over the nanocomposite for the fourth time, indicating that the photocatalyst has good stability.

3.6. Mechanism of enhanced photoactivity

On the basis of the above experimental results and discussion, we believe that the enhanced photocatalytic activities observed may be attributed to the formation of the heterojunction between In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ that facilitates interfacial transfer of photogenerated electrons and holes, as shown in Fig. 8. As reported, the CB potentials of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ are -0.63 eV and -0.43 eV, respectively. Because the CB potential of In$_2$O$_3$ is more negative than that of La$_2$Ti$_2$O$_7$, the interface band bendings are formed when In$_2$O$_3$ contacts with La$_2$Ti$_2$O$_7$, resulting in the formation of a built-in potential and a potential barrier of In$_2$O$_3$ (Fig. 8A). Under the influence of built-in potential, charges are redistributing for equilibrium, which will make the semiconductors, CH$_3$HO and H$_2$O having a same Fermi level. However, the thermodynamic equilibrium will be broken and quasi-Fermi levels are built for In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ when they are illuminated under solar illumination. Specifically, when the catalysts are under solar irradiation, only the photogenerated electrons in In$_2$O$_3$ which have enough energy to stride over the potential barrier can transport to La$_2$Ti$_2$O$_7$. The same principle can be applied to the transfer of photogenerated holes from La$_2$Ti$_2$O$_7$ to In$_2$O$_3$. Therefore, the photogenerated electrons in La$_2$Ti$_2$O$_7$ and the holes in In$_2$O$_3$ are more easily recombined with each other due to the role of built-in potential and the potential barrier. The accumulated holes in La$_2$Ti$_2$O$_7$ and electrons in In$_2$O$_3$ can form a photovoltage, resulting in the
anodic and cathodic shifts of the quasi-Fermi level of the La$_2$Ti$_2$O$_7$ and In$_2$O$_3$ heterojunction (Fig. 8B). In the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction structure, the accumulated holes in La$_2$Ti$_2$O$_7$ can be oxidized by sacrificial reagents and the accumulated electrons in In$_2$O$_3$ are subsequently transferred to the Pt co-catalyst to generate H$_2$. Therefore, increasing the amount of In$_2$O$_3$ is beneficial for promoting carrier separation in space and hindering charge recombination, leading to a higher rate of photocatalytic H$_2$ production. However, the decrease in photocatalytic H$_2$ production at excessive In$_2$O$_3$ levels in the composites is likely because the In$_2$O$_3$ particles shield the La$_2$Ti$_2$O$_7$ from exposure to incident light.

As known, the position of CB and CB edges strongly depends on the preparation methods and experimental condition. Therefore, we measured Mott-Schottky plots for better understanding the intrinsic electronic properties of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction, as shown in Fig. 9. All of La$_2$Ti$_2$O$_7$, In$_2$O$_3$ and In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction show the characteristic behaviors of n-type semiconductors because of the positive slopes of the linear plots. In addition, the flat-band potentials of La$_2$Ti$_2$O$_7$, In$_2$O$_3$ and In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction that measured from Mott-Schottky plots are ca. -0.39, -0.54 and -0.46 eV vs. NHE at pH=7. Because of the different experiment condition, these values have distance with the reported. For n-type semiconductors, donor states and flat band potentials are located just below the bottom of the CB and close to the Fermi level. Therefore, we confirmed La$_2$Ti$_2$O$_7$ and In$_2$O$_3$ are suitable for water splitting. The location of VB edges can be obtained by DRS and the results are given in Table 1. From the experiment results, we confirmed the CB and VB positions of In$_2$O$_3$ are both higher than those of La$_2$Ti$_2$O$_7$, the use of an In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction would result in an improvement in the efficient separation of photogenerated charge carriers. To further prove that the enhanced photocatalytic H$_2$ production is due to the formation of the heterojunction rather than simple or random surface contact between the In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ species, we performed photocatalytic H$_2$ production and photoluminescence (PL) spectroscopy measurements on In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1), a homogenous, mechanically mixed blend of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ with a molar proportion of 1.5:1. The results are shown in Fig. 6 (S8) and Fig. 10. The rate of H$_2$ production on In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1) (Fig. 6 (S8)) is between La$_2$Ti$_2$O$_7$ (Fig. 6 (S6)) and In$_2$O$_3$ (Fig. 6 (S7)) and far lower than In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1) (Fig. 6 (S4)). Additionally, the PL spectrum of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1) catalyst exhibits a fluorescence increase when compared with In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1), indicating that photogenerated carrier recombination and/or non-radiative recombination is higher than in In$_2$O$_3$/La$_2$Ti$_2$O$_7$ (1.5:1). Comparison with the mechanical mixture of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ indicates that the intimate connection arising from the heterojunction structure and the synergistic effects of the various components promote the spatial separation of the photogenerated carriers and result in the improvement in catalyst photoactivity for H$_2$ evolution.
observed that all of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites possess that end is found to be 1.5:1, and the corresponding H$_2$ evolution activity over the 2:1. This changing trend of photocurrent magnitude to 1.5:1 and later decrease on further increase in the molar ratio In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ that significantly enhances photogenerated heterojunction, which can result in a synergistic combination of This combination structure is be neficial for the formation of a heterogeneous H$_2$ production. The optimal molar ratio of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ to grown on and attached to the La$_2$Ti$_2$O$_7$ nanosheets surfaces.

To better understand the influence of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ molar ratio on the photogenerated carrier separation probability of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites, the photocurrent response (J-t) experiments shown in Fig. 11 were performed. It can be observed that all of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites possess a relatively stable photocurrent response. The photocurrent values of the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites are enhanced with an increase in the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ molar ratio from 0.25:1 to 1:5:1 and later decrease on further increase in the molar ratio to 2:1. This changing trend of photocurrent magnitude correlates with the trend in H$_2$ evolution activity over the nanocomposites. These results indicate that the formed In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction is the key to the efficient separation of photogenerated carrier.

4. Conclusions

In$_2$O$_3$/La$_2$Ti$_2$O$_7$ heterojunction nanocomposites were successfully prepared by a solvothermal method. The investigation of their photocatalytic H$_2$ production abilities shows that the In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposites possess a higher photoactivity for H$_2$ production than In$_2$O$_3$ and pristine La$_2$Ti$_2$O$_7$. SEM and TEM reveal that In$_2$O$_3$ nanoparticles are grown on and attached to the La$_2$Ti$_2$O$_7$ nanosheets surfaces. This combination structure is beneficial for the formation of a heterojunction, which can result in a synergistic combination of In$_2$O$_3$ and La$_2$Ti$_2$O$_7$ that significantly enhances photogenerated carrier separation and thus improves the rate of photocatalytic H$_2$ production. The optimal molar ratio of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ to that end is found to be 1.5:1, and the corresponding H$_2$ production rate is 68.14 μmol h$^{-1}$ g$^{-1}$ with an apparent quantum efficiency (AQE) of 0.41 %, which is 29.62 times higher than that on pure In$_2$O$_3$ and 6.43 times higher than on La$_2$Ti$_2$O$_7$. The possible enhancement route and mechanism have also been analyzed. In sum, it has been demonstrated that manipulating the configuration of In$_2$O$_3$/La$_2$Ti$_2$O$_7$ nanocomposite heterostructures is a quite efficient way to improve photocatalytic H$_2$ production activity.

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Notes and references

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