Light Illuminated $\alpha-\text{Fe}_2\text{O}_3$/Pt Nanoparticles as Water Activation Agent for Photoelectrochemical Water Splitting

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The photoelectrochemical (PEC) water splitting is hampered by strong bonds of $\text{H}_2\text{O}$ molecules and low ionic conductivity of pure water. The photocatalysts dispersed in pure water can serve as a water activation agent, which provides an alternative pathway to overcome such limitations. Here we report that the light illuminated $\alpha-\text{Fe}_2\text{O}_3$/Pt nanoparticles may produce a reservoir of reactive intermediates including $\text{H}_2\text{O}_2$, $\cdot\text{OH}$, $\cdot\text{OH}_2$ and $\text{H}^+$ capable of promoting the pure water reduction/oxidation half–reactions at cathode and highly photocatalytically active TiO$_2$/In$_2$S$_3$/AgInS$_2$ photoanode, respectively. Remarkable photocurrent enhancement has been obtained with $\alpha-\text{Fe}_2\text{O}_3$/Pt as water activation agent. The use of $\alpha-\text{Fe}_2\text{O}_3$/Pt to promote the reactivity of pure water represents a new paradigm for reproducible hydrogen fuel provision by PEC water splitting, allowing efficient splitting of pure water without adding of corrosive chemicals or sacrificial agent.

The storage of solar energy in chemical bond of $\text{H}_2$ through water splitting under sun–light presents the most promising strategies to develop a solar–based energetic model in view of the abundant and renewable nature of solar and water resources$^{1-5}$. Since the pioneering studies of Fushijima and Honda in the early 1970s$^6$, which demonstrated oxidation of water on n-type TiO$_2$ single–crystal electrode by band–gap excitation, photoelectrochemical (PEC) water splitting is regarded as the simplest solar to hydrogen (STH) conversion scheme$^{7-10}$. In a typical PEC water splitting reaction, oxygen is produced on light–excited semiconductor electrode via water oxidation half–reaction $\text{2H}_2\text{O} + 4\text{h}^+ (\text{hole}) \rightarrow \text{O}_2 + 4\text{H}^+$, and hydrogen is generated on Pt counter electrode by water reduction half–reaction $\text{2H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$. Thus, sun light plus water gives us clean hydrogen plus oxygen. It sounds good, but it is not all that easy because the water splitting reaction is an uphill reaction in which the Gibbs free energy increases by 237 kJ mol$^{-1}$$^{11}$. Particularly, splitting of pure water is extremely difficult due to its prohibitively low ionic conductivity. A great deal of effort has been put to overcome the difficulty of splitting of the pure water. Electron donors (sacrificial reagents), including organic compounds (hydrocarbons)$^{12,13}$, weak acids$^{14,15}$, inorganic ions$^{16-19}$, etc., are widely used for photocatalytic hydrogen production as they enhances the photocatalytic electron/hole separation by scavenging the photo--generated valence band (VB) holes$^{20}$, resulting in higher quantum efficiency. However, since the electron donors are consumed in this photo--catalytic reaction, the product is only hydrogen and the reaction is not an overall splitting of water. Another way to increase the reactivity of the water splitting is to use the alkaline solutions, which enhance the forward photo--catalytic reaction and suppress backward reaction (recombination of hydrogen and oxygen into water) by scavenging of the photo-generated holes$^{20,21}$. It is demonstrated that both of the hydrogen and oxygen production can be increased. The limits of this strategy are low STH conversion efficiency and performance degradation due to the corrosive environment for the electrodes. Thus, it is highly desirable that the PEC water splitting technique which is aimed at providing a clean and renewable fuel can efficiently split water into hydrogen and oxygen without adding of corrosive chemicals or sacrificial agent.

It is generally accepted that the photo--illuminated photocatalysts provide extremely reactive intermediates in water, such as superoxide anion (O$_2^-$), hydroxyl radicals (·OH), and H$_2$O$_2$, which can reduce/oxidize the pollu-
reactive intermediates using the photo-illuminated reaction at photono- 
and cathode, respectively. However, the important and unique role of the light—illuminated photocatalysts in water and their consequent ability to serve as water activation agent by generating reactive intermediates for PEC water splitting has not been considered previously.

Here, a new strategy of water activation by generation of various reactive intermediates using the photo-illuminated $\alpha-Fe_2O_3$ NPs has been demonstrated for PEC water splitting. $\alpha-Fe_2O_3$ was chosen in our experiment because it has a band-gap of 2.0 to 2.2 eV corresponding to the absorption of 564 to 620 nm light, allowing it a promising photocatalyst for harvesting solar energy for hydrogen production$^{27-29}$ or degradation of organic pollutants and toxics$^{29,30}$. Furthermore, because the conduction band (CB) bottom ($E_{CB}$) and VB top ($E_{VB}$) of $\alpha-Fe_2O_3$ is more positive than the hydrogen and oxygen evolution potential, respectively, only reactive intermediates can be generated into water, rather than evolution of hydrogen through photocatalytic water splitting. The application of $\alpha-Fe_2O_3$ as a potential photocatalysts is mainly limited by its short lifetime of photogenerated charge carriers (<10 ps) and short hole diffusion length (~2 to 4 nm)$^{27,31}$. To address these issues, Pt NPs were decorated on $\alpha-Fe_2O_3$ by a polyol reduction method, which can serve as cocatalysts to enhance the photocatalytic activity and increase the lifetime of the photogenerated charge carriers$^{32,35}$. Combined with the high photocatalytic active $TiO_2/In_2S_3/AgInS_2$ photoanode, remarkable photocurrent of $\sim 0.788 \text{ mA cm}^{-2}$ at 1.5 V vs. Ag/AgCl has been obtained with $\alpha-Fe_2O_3$/Pt as water activation agent, more than ten times as large as the values without $\alpha-Fe_2O_3$/Pt (0.075 mA cm$^{-2}$ at 1.5 V vs. Ag/AgCl).

**Results**

Figure 1a shows a schematic diagram of the reaction vessels, where $TiO_2/In_2S_3/AgInS_2$ photoanode pressed on the inner wall of the quartz vessel with conducting side facing the reaction solution serves as the working electrode, Pt foil as the counter electrode, and Ag/AgCl in saturated KCl as the reference electrode. The photoanode is the central to the PEC cell, whose material and structure both play critical roles in the device performance. An ideal photoanode requires fast water oxidation kinetics at the semiconductor/water interface, fast electron transport and suitable band gap large enough (>1.6 eV) to split water and small enough (<2.2 eV) to absorb a wide range of the solar spectrum. $TiO_2/In_2S_3/AgInS_2$ core–shell structure is one of the high—performance photoanodes that satisfy these requirements simultaneously, which is crucial to evaluate the ability of our strategy to promote the water splitting efficiency. Figure 1(b1) and (b2) shows the top and cross-sectional view of the $TiO_2/In_2S_3/AgInS_2$ photoanode, respectively. After growth of $In_2S_3$ and AgInS$_2$, the products inherit the morphology of the $TiO_2$ NW arrays, showing an average diameter of ~116 nm and a length of ~3.36 μm. A typical transmission electron microscopy (TEM) image of a single $TiO_2/In_2S_3/AgInS_2$ NW demonstrates that the surface of the $TiO_2$ NWs appears to be very coarse, and many NPs are coated over the surface of $TiO_2$ NWs, as illustrated in Figure 1(b3). Further insight into the structural information was obtained by high resolution TEM (HRTEM) taken from the $TiO_2/In_2S_3/AgInS_2$ interface, Figure 1(b4) and (b5). The $In_2S_3$ buffer layer and $TiO_2$ NW form a core–shell structure and the AgInS$_2$ NPs decorated on surface of $In_2S_3$. The resolved spacings between the two parallel neighboring fringes are 0.325 and 0.246 nm, corresponding to the [311] plane of cubic $In_2S_3$ and [122] plane of orthorhombic AgInS$_2$. The crystal phase of the three materials was further investigated by XRD spectrum; the diffraction peaks in Figure S1 are well indexed with the rutile $TiO_2$, cubic $In_2S_3$ and orthorhombic AgInS$_2$, respectively.

Pt NPs were deposited on $\alpha-Fe_2O_3$ NPs by the polyol reduction method (see Experimental section and also Ref. 32). As illustrated in Figure 1(c1), the average size of the hybrid $\alpha-Fe_2O_3$/Pt NPs was ~38 nm. Pt NPs with average size of ~3 nm were decorated on $\alpha-Fe_2O_3$ NPs, as confirmed by the TEM image in Figure 1(c2) and (c3). The measured lattice spacing for Pt NPs was 0.226 nm, in agreement with the value for the [111] planes of Pt (JCPDS no. 04–0802). The presence of Pt on $\alpha-Fe_2O_3$ NPs can be further demonstrated by EDS mapping, where Fe, O and Pt elements are distributed uniformly in the hybrid $\alpha-Fe_2O_3$/Pt NPs (see supporting

![Figure 1](https://www.nature.com/scientificreports/) | Schematic diagram and morphology and structure characterization. (a) Schematic diagram of PEC cell. (b) FE-SEM (b1 and b2) and TEM (b3–b5) images of $TiO_2/In_2S_3/AgInS_2$ electrode. (c) FE-SEM (c1) and TEM (c2 and c3) images of $\alpha-Fe_2O_3$/Pt NPs.
PEC water splitting, we measured the current density versus applied voltage (J–V) curves of the TiO₂/In₅S₃/AgInS₂ working electrode in different electrolytes of 15 MΩ DI water, 15 MΩ DI water with α-Fe₂O₃/NPs and 15 MΩ DI water with α-Fe₂O₃/Pt NPs in the dark and under illumination. The photocurrent in DI water is only 0.075 mA cm⁻² at 1.5 V vs. Ag/AgCl, which increases sharply to 0.345 mA cm⁻² with α-Fe₂O₃ NPs added to DI water. When tested α-Fe₂O₃/Pt as a water activation agent, as expected, the J improvement is more pronounced for α-Fe₂O₃/Pt than for α-Fe₂O₃, to 0.788 mA cm⁻² at 1.5 V vs. Ag/AgCl, as shown in Figure 3a. What is more, the J value shows a α-Fe₂O₃/Pt concentration-dependent behavior, which increases with increasing of the concentration of α-Fe₂O₃/Pt, reaching a maximum value at 0.1 mg/mL, followed by decreasing with further increasing concentration, as shown in Figure 3b. Excessive α-Fe₂O₃/Pt in water decreases the light penetration depth, which reduces the rate of photo-catalyzed reaction of water and consequent generation of reactive intermediates by α-Fe₂O₃/Pt, resulting in the decrease of J. It is noteworthy that a minute amount of α-Fe₂O₃/Pt NPs remained in the photoelectrode (Figure S3) after PEC measurement, indicating that the α-Fe₂O₃/Pt NPs adsorbed on photoelectrode during the PEC measurement can be neglected.

To compare the effect of the addition of α-Fe₂O₃/Pt on the pure water splitting reaction rate to that of the addition of generally used chemicals, two control experiments were conducted by replacing the α-Fe₂O₃/Pt suspension with 1 M NaOH aqueous solution and 0.5 M K₂SO₄ aqueous solution containing H₂SO₄ (adjust the pH to 1.7). As shown in Figure S4, the J value is 1.07 mA cm⁻² at 0.9 V vs. Ag/AgCl for NaOH electrolyte and 0.981 mA cm⁻² at 1.5 V vs. Ag/AgCl for NaOH electrolyte and 0.981 mA cm⁻² at 1.5 V vs. Ag/AgCl for K₂SO₄ electrolyte.

**Figure 2** | UV–VIS optical absorption spectra of DI water, 0.1 mg/mL α-Fe₂O₃ in DI water and 0.1 mg/mL α-Fe₂O₃/Pt NPs in DI water.

**Figure 3** | Photoelectrochemical properties. (a) J–V curves of TiO₂/In₅S₃/AgInS₂ in different electrolytes of 15 MΩ DI water, 15 MΩ DI water with α-Fe₂O₃/NPs and 15 MΩ DI water with α-Fe₂O₃/Pt NPs in the dark and under illumination. (b) α-Fe₂O₃/Pt concentration–dependent behavior of current density at Vₖ = 1.5 V vs. Ag/AgCl. (c) J–t curve of TiO₂/In₅S₃/AgInS₂ in DI water containing 0.1 mg/mL α-Fe₂O₃/Pt under chopped illumination at a bias of 1.5 V vs. Ag/AgCl. The inset in (c) shows the evolution of H₂ during the J–t curve measurement.
AgCl for K₂SO₄ electrolyte, which are slightly larger than that of ferring of photoelectrons from In₂S₃/AgInS₂ to current collector via of the In₂S₃/AgInS₂ heterostructure to the solution and rapid trans- and decay behavior implies the fast hole scavenging from the surface decays to the dark value of the current. This reproducible rapid rise constant until the light is turned off, where the current immediately on reaches the constant photocurrent density and remains can see that the instantaneous photocurrent density with turning the light on reaches the constant photocurrent density and remains.

Additionally, the photocurrent was conducted under the illumination of simulated solar light (AM 1.5 G, 100 mW cm⁻²) at 1.5 V vs. Ag/AgCl. Prior to the measurement, the newly synthesized TiO₂/In₂S₃/AgInS₂ were illuminated under simulated solar light for 200 s, allowing stabilization of the performance of TiO₂/In₂S₃/AgInS₂ electrode. From the result one can see that the instantaneous photocurrent density with turning the light on reaches the constant photocurrent density and remains constant until the light is turned off, where the current immediately decays to the dark value of the current. This reproducible rapid rise and decay behavior implies the fast hole scavenging from the surface of the In₂S₃/AgInS₂ heterostructure to the solution and rapid trans-fer of photoelectrons from In₂S₃/AgInS₂ to current collector via the interior TiO₂ NWs. Additionally, the photocurrent was steady for 1700 s, indicating stable photo-stability of both Fe₂O₃/ Pt and TiO₂/In₂S₃/AgInS₂ photoanode.

To reveal the differences in the interfacial charge-transfer characteristics of both half reactions in the PEC cell with and without α–Fe₂O₃/Pt, electrochemical impedance spectroscopy (EIS) mea- surements were carried out in a two electrode configuration PEC cell⁶⁷. The Nyquist plots of the obtained EIS data measured at open-circuit conditions under simulated solar-light illumination are shown in Figure 4. According to recent analysis on the EIS spectra of the PEC cell for water splitting⁶⁸, the first semicircle in the high-frequency region (>10⁶ Hz) represents the charge transfer (Rct) at the TiO₂/In₂S₃/AgInS₂/electrolyte interface; and the other arc in a frequency range of 100 mHz–10⁴ Hz corresponds to the reaction reaction (Rrx) at the Pt counter electrode. The fitting curves fitted by EIS Spectrum Analyser software using an equivalent circuit shown in the inset match well with the measured EIS data. The fitted Rct and Rrx values for the cells with DI water as electrolyte is as large as 112 kΩ and 527 kΩ, respectively; while Rct and Rrx for the cells with α–Fe₂O₃/Pt as water activation agent decreased to 0.985 kΩ and 2.5 kΩ, respectively. The EIS analysis revealed that the presence of α–Fe₂O₃/Pt in DI water can greatly promote the activity of water reduction/oxidation half-reactions at counter electrode and TiO₂/ In₂S₃/AgInS₂ photoanode, respectively.

Discussion

On the basis of the above experiments, it is reasonable to ascribe the significant improvement of the PEC water splitting efficiency to the generation of the reactive intermediates from the light illuminated α–Fe₂O₃/Pt NPs. Some potential reactions that could be initiated by photo electron–hole pairs generated in α–Fe₂O₃/Pt and the consequential process in relation to the water splitting can be depicted as in Figure 5. Under light illumination, the electrons in the VB of α–Fe₂O₃ are promoted to the CB of α–Fe₂O₃ by photo excitation (γ), and electron (e⁻) – hole (h⁻) pairs are generated. The E_CB of α–Fe₂O₃ (0.38 V vs. NHE) is more negative than the reduction potential to form OH⁻ (0.40 V vs. NHE) and H₂O₂ (0.70 V vs. NHE), allowing generation of OH⁻ and H₂O₂ through O₂ + 4H⁺ + 4e⁻ → 4OH⁻ and O₂ + 2H⁺ + 2e⁻ → H₂O₂, respectively. Previous study has predicted that H₂O₂ can also be produced via the oxidation of water in the absence of added electron donors via 2H₂O + 2h⁻ → H₂O₂ + 2H⁺. In a PEC cell, the H₂O₂ can be directly oxidized to O₂ by the photogenerated holes in photoanode through H₂O₂ + 2h⁺ → O₂ + 2H⁺ or reduced to ·OH and OH⁻ by the

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Figure 4 | Nyquist plots of TiO₂/In₂S₃/AgInS₂ in DI water and DI water containing 0.1 mg/mL α–Fe₂O₃/Pt measured at open-circuit conditions under simulated solar-light illumination.

Figure 5 | Energetics of operation of the PEC cell with light illuminated α–Fe₂O₃/Pt NPs as water activation agent. Potentials for the possible reactions that can be initiated by electron–hole pairs generated in α–Fe₂O₃/Pt NPs are standard E° values.
conduction band electron through H₂O₂ + e⁻ → OH⁻ + OH⁻ \(^{39,40}\); and the resultant \(\cdot\)OH may be further reduced to \(\cdot\)OH through \(\cdot\)OH + e⁻ → \(\cdot\)OH \(^{38}\). The resulting H₂O₂, \(\cdot\)OH and H⁺ in the above reactions are highly active for the water reduction/oxidation half-\(\rightarrow\)m reaction at the cathode and photoanode in a PEC cell. Thus, the \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) dispersed in pure water can serve as a water activation agent under light illumination, which could produce a reservoir of reactive intermediates (H₂O₂, \(\cdot\)OH, \(\cdot\)OH, H⁺) capable of promoting the water splitting reaction.

According to the above mentioned reaction mechanism, \(\cdot\)OH is a key intermediate relating to generation of substances (H₂O₂, \(\cdot\)OH⁻ and H⁺) that can directly promote the water splitting reaction at photoanode and counter electrode. It is widely accepted that the fluorescent probe method using terephthalic acid (TA) as the \(\cdot\)OH capture is a highly sensitive technique, in which the TA reacts with \(\cdot\)OH and generates luminescent 2-hydroxyterephthalic acid (TAOH) with a characteristic peak at \(\approx 426\) nm \(^{41–43}\). Figure 6 shows the fluorescence spectral changes observed during illumination of \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) suspension containing 0.5 mM terephthalic acid at various irradiation periods. Gradual increase in the fluorescence intensity at \(\approx 428\) nm with increasing illumination time implies that fluorescent TAOH was formed via the specific reaction between \(\cdot\)OH and TA during illumination of \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) suspension, which is a direct evidence of the presence of \(\cdot\)OH. In addition, H₂O₂ is another important intermediate, the existence of which can be verified by hydrogen peroxide indicator strip, as illustrated in Supporting Information, Figure S5. The observation of \(\cdot\)OH and H₂O₂ in the water splitting reaction provide a weighty evidence to the reaction mechanism.

Because the \(E_{\text{CB}}\) of \(\alpha–\text{Fe}_2\text{O}_3\) (0.38 V vs. NHE) is less negative than the hydrogen evolution potential (0.00 V vs. NHE), it is not able to reduce the H⁺ to give H₂ directly by \(\alpha–\text{Fe}_2\text{O}_3\). Therefore, in the PEC cell with \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) activated pure water as reaction solution, the reduction of H⁺ takes place only on Pt cathode, which requires efficient oxidation of the water or reactive intermediates including H₂O₂, \(\cdot\)OH⁻ by the photoanode. Thus the water oxidation ability of the photoanode plays a key role for water splitting in this PEC cell. In this work, we investigated three TiO₂ NW based electrodes including TiO₂ NW, TiO₂ NW/ Çalış and TiO₂/In₂S₃/AgInS₂. Identical behavior has been observed for the three photoanodes, as illustrated in Figure 3, Figure S6 and S7. Due to the excellent light harvesting (see Supporting Information, Figure S8) and photocatalytic activity property \(^{44}\), the TiO₂/In₂S₃/AgInS₂ working electrode shows the highest photocurrent value. To double check the reasonability of this conclusion and the reaction mechanism described in Figure 5, we compare the \(J–V\) curves of a PEC cell with a Pt–foil as working electrode, another Pt–foil as counter electrode and \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) NPs dispersed in DI water as electrolyte in dark and under light illumination. As shown in Figure 7, identical behavior has been observed for \(J–V\) curves with and without light illumination. Furthermore, no instantaneous photocurrent was observed on the chopped—light current density versus time (\(J–t\)) curve of the cell. These results indicate that oxidation of water at the working electrode (Figure 5) plays a key role for water splitting in our PEC cell.

In conclusion, an alternative pathway to activate the pure water for PEC water splitting by introducing photocatalysts into water has been developed. The light illuminated \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) NPs may produce a reservoir of reactive intermediates including H₂O₂, \(\cdot\)OH⁻, \(\cdot\)OH and H⁺ capable of promoting the water reduction/oxidation half-\(\rightarrow\)m reactions at cathode and TiO₂/In₂S₃/AgInS₂ photoanode, respectively. Remarkable photocurrents of \(\approx 0.788\) mA cm⁻² at 1.5 V vs. Ag/AgCl has been obtained with \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) as water activation agent, more than ten time as large as the values without \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) (0.075 mA cm⁻² at 1.5 V vs. Ag/AgCl). The present results provide a fertile base for further investigation. The strategy of using photocatalysts to generate reactive intermediates in pure water for PEC water splitting demonstrated by \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) NPs can be leveraged to other, more promising semiconducting materials with novel nanostructures to greatly improve their efficiencies and application areas. The approach could also be extended to other energy and artificial photosynthesis applications.

**Methods**

**Preparation of \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) NPs.** \(\alpha–\text{Fe}_2\text{O}_3\) NPs with diameter \(\approx 30\) nm were purchased from Aladdin Industrial Inc. (Shanghai, China). Deposition of Pt onto \(\alpha–\text{Fe}_2\text{O}_3\) NPs followed procedures outlined previously \(^{25}\). Typically, \(\alpha–\text{Fe}_2\text{O}_3\) powder (0.5 g) was dispersed in a mixed solution (40 mL) containing H₂PtCl₆ aqueous solution (1 wt.%) and ethanol under ultrasonication for 30 min. Then the slurry was dried at 60°C. Ethylene glycol (40 mL) was added to the dry powder followed by stirring and ultrasonication to form a homogenous suspension. The suspension was kept at 100°C in dark for 6 h. At last the \(\alpha–\text{Fe}_2\text{O}_3/\text{Pt}\) powder was collected by centrifugation, washed with distilled water for several times, dried at 60°C and sintered at 400°C for 20 min.

**Preparation of \(\text{TiO}_2/\text{In}_2\text{S}_3/\text{AgInS}_2\) core–shell electrodes.** At first, a TiO₂ polymeric sol was prepared by the sol gel process according to the previous reports \(^{37}\). Then the TiO₂ sol was spin–coated on the fluorine–doped SnO₂ (FTO) substrates followed by annealing at 450°C for 2 h. The TiO₂ NW arrays were grown directly on seeded FTO substrates by using the hydrothermal method reported previously \(^{37}\). In a typical synthesis process, titanium (IV) butoxide (0.5 g) was added into an aqueous HCl solution (25 mL of deionized water and 25 mL of concentrated HCl (38%)) under
magnetic stirring. The solution was stirred for another 10 min and then poured into a Teflon-lined stainless steel autoclave (100 mL capacity). Six pieces of the seeded— FTO (0.8 cm x 2 cm, with seeded area of 0.8 cm²)— were placed at an angle against the wall of the Teflon—liner with the conducting side facing down. The autoclave was sealed, heated to 170°C and held at the temperature for 6 h. After cooling down to room temperature, the obtained products were washed successively by DI water and finally annealed at 110°C for 2 h.

In5s2O3/Ag/Ni2S2 were deposited on TiO2 NWs by sequential chemical bath deposition (S-CBD) method according to a previous report but with a modified recipe4. Typically, the TiO2 NWs on FTO substrate were successively dipped into InCl3 solution (3 mM) for 4 min, ethanol for 1 min, Na2S·9H2O water–methanol solution (3 mM) (1:1 volume ratio) for 4 min and water–methanol (1:1 volume ratio) mixture for 1 min at 25°C. The desired deposition of In5s2O3 was achieved after 12 cycles, where the white/pale yellow mixture was gradually changed to the TiO2/In5s2O3 film on the Ag/AgCl electrode films in an AgNO3 solution (2 mM) at 25°C for 2 min. The resultant brown TiO2/In5s2O3/Ag/Ni2S2 films were washed with ethanol and sintered at 400°C for 30 min in N2 atmosphere.

Photoelectrochemical measurements. All the PEC measurements were performed in a quartz reaction vessel containing DI water (20 mL, 15.0 MQ, Elix Advantage 10, Merck Millipore) and \( \Delta \text{Fe} \text{O}_3/\text{Pt} \) NPs. The PEC measurements were performed in a three-electrode configuration with TiO2/In5s2O3/Ag/Ni2S2 as the working electrode, Pt—foil (surface area of 1.0 cm²) as the counter electrode, and Ag/AgCl in saturated KCl as the reference electrode. To prevent suspended \( \Delta \text{Fe} \text{O}_3/\text{Pt} \) NPs from screening the photo—absorption of the photoelectrode, the TiO2/In5s2O3/Ag/Ni2S2 electrodes were pressed against the inner wall of the quartz vessel with conducting side facing the reaction solution. The TiO2/In5s2O3/Ag/Ni2S2 electrode was connected to the measuring instrument by pressing a Pt foil on the FTO layer of the TiO2/In5s2O3/Ag/Ni2S2 electrode. The PEC performances were measured using an Electrochemical Workstation (Bio–Logic SAS, VSP–300). Illumination was from a solar simulator (Omni-pR-PL, Beijing Zolix Instruments CO., LTD) with an excitation at 420 nm. Irradiation periods were centrifuged at 10 000 rpm for 2 min. Fluorescence spectra of the TiO2/In5s2O3/Ag/Ni2S2 after irradiation was measured by the EIS Spectrum Analyser software. Hydrogen peroxide indicator strips were used for in situ infrared spectroscopy.

Characterizations. The morphology and microstructure of the TiO2/In5s2O3/Ag/Ni2S2 electrode and \( \Delta \text{Fe} \text{O}_3/\text{Pt} \) NPs were characterized by a field emission scanning electron microscopy (FE—SEM, Hitachi S–4800) and transmission electron microscopy (TEM, FEI Tecnai F30). Elemental analysis was performed on an energy—dispersive x—ray (EDX) spectroscopy attached to the FE—SEM. X—Ray diffraction spectra (XRD) was collected on a Bruker D8 Advance X—ray diffractometer using a Cu Kα source (\( \lambda = 0.154056 \) nm). The optical absorbance spectra were acquired using a UV—visible spectrophotometer (TU—1901). Electrochemical impedance spectroscopy (EIS) was measured using the Electrochemical Workstation in a two electrode configuration within a frequency range of 0.1 Hz to 800 kHz at open—circuit voltage with a potential pulse of 100 mV in amplitude under simulated solar—light illumination (AM 1.5 G, 100 mW cm⁻²). Prior to the recording of EIS data, the PEC cell was illuminated for 10 min at an applied bias of 1.5 V to establish equilibrium of the system. The EIS data were fitted by EIS Spectrum Analyser software. Hydrogen peroxide indicator strips (Quantox Peroxide 25, MACHEDER—NAGEL, Germany) were used to test the existence of \( \text{H}_2\text{O}_2 \).

1. Walter, M. G. et al. Solar Water Splitting Cells. Chem. Rev. 110, 6446–6473 (2010).
2. Ding, Q. et al. Efficient Photoelectrochemical Hydrogen Generation Using Heterostructures of Si and Chemically Exfoliated Metallic MoS2. J. Am. Chem. Soc. 136, 8504–8507 (2014).
3. Voig, D. et al. Conducting MoS2 Nanosheets as Catalysts for Hydrogen Evolution Reaction. Nano Lett. 13, 4222–4227 (2013).
4. Zhu, T. et al. Formation of 1D Hierarchical Structures Composed of Ni3S2 Nanosheets on CNTs Backbone for Supercapacitors and Photocatalytic H2 Production. Adv. Energy Mater. 2, 1497–1502 (2012).
5. Yan, L., Yu, L. & Ren, Z. Mini review on photovoltaic of titanium dioxide nanotubes and related applications. J. Alloys Compd. 559, 260–276 (2013).
6. Fujishima, A. & Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 238, 37–38 (1972).
7. Cheng, C. et al. Quantum-Dot-Sensitized TiO2 Inverse Opals for Photoelectrochemical Hydrogen Generation. Small 8, 37–42 (2012).
8. Yin, Z. et al. Full-Process-Solution-Processed Synthesis of All Metal Oxide-Based Tree-like Heterostructures on Fluorine-Doped Tin Oxide for Water Splitting. Adv. Mater. 24, 5374–5378 (2012).
9. Alotaibi, B. et al. Highly Stable Photoelectrochemical Water Splitting and Hydrogen Generation Using a Double-Band InGaN/GaN Core/Shell Nanowire Photocathode. Nano Lett. 13, 4356–4361 (2013).
10. Huang, Z. et al. Enhanced photoelectrochemical hydrogen production using single nanowires@MoS2. Nano Energy 2, 1337–1346 (2013).
11. Hisatomi, T., Kubota, J. & Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. Chem. Soc. Rev. 43, 7520–7535 (2014).
12. Gurunathan, K., Maruthamuthu, P. & Sasri, M. V. C. Photocatalytic hydrogen production by dye-sensitized TiO2 and Pt/TiO2. J. Photochem. Photobiol. A 89, 177–189 (1995).
13. Li, X., Lu, G. & Li, S. Photocatalytic production of hydrogen and oxide component and mixture systems of electron donors and monitoring adsorption of donors by in situ infrared spectroscopy. Chemosphere 52, 843–853 (2003).
14. Nada, A. A. et al. Studies on the photocatalytic hydrogen production using suspended modified photocatalysts. Int. J. Hydrogen Energy 30, 687–691 (2005).
15. Koca, A. & Sahin, M. Photocatalytic hydrogen production by direct light from solar simulator. Int. J. Hydrogen Energy 27, 363–367 (2002).
16. Bamwenda, G. R., Tsubota, S., Nakamura, T. & Haruta, M. Photoassisted hydrogen production from a water-ethanol solution: a competition of Au/TiO2 and Pt/TiO2. J. Photochem. Photobiol. A 89, 177–189 (1995).
17. Li, X., Lu, G. & Li, S. Photocatalytic production of hydrogen.
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Author contributions

X.L. and B.W. designed the experiment, analyzed data and wrote the paper. Z.W. prepared TiO$_2$/In$_2$S$_3$/AgInS$_2$ photoanode. Z.Z. prepared Fe$_3$O$_4$/Pt NPs, conducted hydroxyl radical detection using TA fluorescence probe method. L.C. conducted the TEM measurements. Z.W. and Z.Z. performed PEC measurements. J.C. and W. Ni performed optical property measurements and analyzed part of the data. E.X. discussed the PEC results and provided part of the financial support. All authors reviewed the manuscript.

Additional information

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