Communication

Enhanced Photocatalytic Hydrogen Production Activity by Constructing a Robust Organic-Inorganic Hybrid Material Based Fulvalene and TiO$_2$

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Abstract: A novel redox-active organic-inorganic hybrid material (denoted as $\text{H}_4\text{TFTFB}$-$\text{TiO}_2$) based on tetrathiafulvalene derivatives and titanium dioxide with a micro/mesoporous nanomaterial structure has been synthesized via a facile sol-gel method. In this study, tetrathiafulvalene-3,4,5,6-tetrakis(4-benzoic acid) ($\text{H}_4\text{TFTFB}$) is an ideal electron-rich organic material and has been introduced into TiO$_2$ for promoting photocatalytic H$_2$ production under visible light irradiation. Notably, the optimized composites demonstrate remarkably enhanced photocatalytic H$_2$ evolution performance with a maximum H$_2$ evolution rate of 1452 µmol g$^{-1}$ h$^{-1}$, which is much higher than the prototypical counterparts, the common dye-sensitized sample (denoted as $\text{H}_4\text{TFTFB}$-5.0/$\text{TiO}_2$) (390.8 µmol g$^{-1}$ h$^{-1}$) and pure TiO$_2$ (18.87 µmol g$^{-1}$ h$^{-1}$). Moreover, the composites perform with excellent stability even after being used for seven time cycles. A series of characterizations of the morphological structure, the photoelectric physics performance and the photocatalytic activity of the hybrid reveal that the donor-acceptor structural $\text{H}_4\text{TFTFB}$ and TiO$_2$ have been combined robustly by covalent titanium ester during the synthesis process, which improves the stability of the hybrid nanomaterials, extends visible-light adsorption range and stimulates the separation of photogenerated charges. This work provides new insight for regulating precisely the structure of the fulvalene-based composite at the molecule level and enhances our in-depth fundamental understanding of the photocatalytic mechanism.

Keywords: photocatalysis; titanium dioxide (TiO$_2$); tetrathiafulvalene derivatives; organic-inorganic hybrid nanomaterials; sol-gel method

1. Introduction

H$_2$, as a high calorific value and zero pollution, has attracted widespread attention [1–3]. Photocatalytic water splitting is considered to be one of the significant strategies for converting solar energy into chemical energy without pollution to the environment [4–9]. Using semiconductor photocatalysis to split water is an effective clean hydrogen production technology. Among many photocatalytic semiconductor materials, n-type TiO$_2$ has become one of the most promising photocatalysts due to its excellent photoelectrochemical performance, low cost, non-toxic and strong redox activity [10–13]. However, TiO$_2$ has a wide band gap and low visible-light absorption ability, and it can only absorb ultraviolet light (about 4% of solar energy) [14]. Simultaneously, photogenerated carriers are easy to recombine, and quantum efficiency is low, which seriously affects the development of TiO$_2$ in the field of photocatalytic hydrogen production. Adjusting the morphological structure and the energy band position on TiO$_2$, such as doping of metal and non-metal ions [15–17], dye sensitization [18–20] and semiconductor combination [14,21–23], has been carried out to enhance the photocatalytic activity of TiO$_2$. Especially, dye-sensitized composites have
been applied to utilize visible-light sections for photocatalytic conversion. However, dye-sensitized composites have poor stability and are easy to deactivate due to dyes detaching and degrading from the surface of the semiconductor under light irradiation [24,25]. To remedy the situation, we used the facile sol-gel method to design and synthesize a series of hybrid materials based on functional organic molecules (calixarene or pillararene derivative) and TiO$_2$ for photocatalytic H$_2$ production from splitting water under visible light irradiation [20,26,27]. Compared with the dye sensitization systems, these hybrid photocatalysts show outstanding photocatalytic stability due to high robust coordination linkage and efficient photogenerated charges separation and transfer from organic dyes to TiO$_2$. However, these calixarene or pillararene derivatives still have some disadvantages in the hybrid system, such as weak optical responsiveness ability (an absorption band edge <500 nm), which hinder its development in photocatalysis. Thus, it is essential to exploit functional organic molecules with their extended visible-light absorption wavelength range to achieve efficient solar-energy conversion.

Tetrathiafulvalene (TTF) and its derivatives own unique electron-rich and redox-active properties [28], which commonly work as functional building blocks to construct two-dimensional (2D) and three-dimensional (3D) framework materials (COF or MOF) and organic-inorganic hybrid materials, and have been intensively studied in the fields of photothermal conversion, photocatalysis [29–32], superconductors [33], sensors [34–36] and solar cell [37–39]. For example, Zhou et al. reported a composite (Ag@Dy-m-TTFTB) containing Ag nanoparticles and tetrathiafulvalene-based MOFs materials with a wide absorption wavelengths range (200–1000 nm) and efficient NIR photothermal conversion owing to the doping of the partially oxidized TTF ligands (TTF$^+$) and the plasmonic Ag nanoparticles [40]. Lan et al. designed and synthesized 2-dimensional COFs (TTCOF-Zn) based on porphyrin and tetrathiafulvalene, which worked as catalysts for the photocatalytic coupling reaction of CO$_2$ and H$_2$O, achieving high photocatalytic CO production with nearly 100% selectivity and accompanying with H$_2$O photooxidation to O$_2$ [41]. Dai et al. synthetized a self-condenses black organic-inorganic polymeric nanomaterials (B-1) assembled by a cyclic titanium-oxo cluster and organic TTF units, which owned multiporous nanostructure and generous electron density on TTF moiety for outstanding dye selection adsorption, and would even work as photocurrent-responsive electrode materials [42]. The studies above indicate that TTF derivatives have a huge potential application in the field of artificial photocatalysis and could greatly embellish the photophysics property of TiO$_2$ nanomaterials. However, the synthesis methods for TTF-based composites are still hard and complicated. Therefore, it is absolutely necessary to exploit TTF-based composites with a flexible, simple preparation processed to endow its wide optical spectrum responsiveness range to fully use solar energy and high optical quantum conversion efficiency for photocatalytic reaction.

Herein, we designed and synthesized binary organic-inorganic composite nanomaterials, which combine TTF derivatives with TiO$_2$ nanoparticles by a simple sol-gel method. Among them, TTF derivatives are tetrathiafulvalene-3,4,5,6-tetrakis(4-benzoic acid) (H$_4$TTFTB) structure, as superior electron donors/acceptors, enabling the formation of intermolecular $\pi$-$\pi$ stacking with relatively short S-S interactions, which could efficiently facilitate charges separation and transfer under illumination [40]. The organic-inorganic composite nanomaterials loaded with a co-catalyst are expected as an excellent photocatalyst owing to some advantages as below: (1) H$_4$TTFTB possesses donors-conjugation-acceptors (D-$\pi$-A) electric structure, achieving excellent photoresponse ability and promoting effective photogenerated charge separation from excited H$_4$TTFTB to TiO$_2$ nanoparticles; (2) high photostable and thermostable H$_4$TTFTB molecule has multiple -COOH functional groups that can integrate with Ti(OC$_4$H$_9$)$_4$ to come into being steady TiO$_2$-O-TTFTB bonds, improving the stability of the hybrid; (3) the composite nanomaterials have a large surface area due to a multiporous nanostructure, which endues the photocatalysts with ample light-response active sites, leading to effective light harvesting and utilizing in the pores and channels. In this work, we confirm the advantage of the composite based on H$_4$TTFTB.
and TiO$_2$ with Pt nanoparticles (Pt NPs) as a co-catalyst. We have optimized the activity of photocatalytic H$_2$ evolution from water for the hybrid materials with a mass percentage difference of H$_4$TTFTB and TiO$_2$. Remarkably, the hybrid materials with a 5.0% mass percentage of H$_4$TTFTB, denoted as H$_4$TTFTB-TiO$_2$-5.0, exhibit the best photocatalytic H$_2$ evolution activity with a rate of 1452 $\mu$mol g$^{-1}$ h$^{-1}$ (TON = 1101). Moreover, the photocatalytic mechanisms of the H$_4$TTFTB-TiO$_2$ composite have been explored. It testifies that the outstanding photocatalytic performance of H$_4$TTFTB-TiO$_2$ composite is attributed to a large surface area, suitable energy band position and multifunctional synergistic catalysis between H$_4$TTFTB and TiO$_2$.

2. Materials and Methods

2.1. Materials

The chemical reagents used in this work were of analytic grade and were used without further purification. Tetrabutyl titanate (Ti(OBu)$_4$, $\geq$99.0%), acetic acid (CH$_3$COOH, $\geq$99.5%), N,N-dimethylformamide (DMF, 99.9%), tetrahydrofuran (THF, 99.9%) and triethanolamine (TEOA, >99.0%) were purchased from Innochem company (Beijing, China). Tetrathiafulvalene-3,4,5,6-tetrakis(4-benzoic acid) (H$_4$TTFTB, 98%) was purchased from Chemextension company (Jilin, China).

2.2. Synthesis of Photocatalysts

2.2.1. Synthesis of H$_4$TTFTB-TiO$_2$ Materials

The structure of H$_4$TTFTB and H$_4$TTFTB-TiO$_2$ hybrid materials are shown in Figure S1a,b, respectively. To prepare H$_4$TTFTB-TiO$_2$-5.0, THF (2.0 mL), acetic acid (336 $\mu$L), distilled water (212 $\mu$L) and Tetrabutyl titanate (2 mL) were subsequently added to a 20 mL glass sample bottle, and then H$_4$TTFTB (24.0 mg) in DMF (2 mL) was added. The color of the mixture changed from light yellow to dark red and, when stirred, became transparent gelatum. The gelatum was heated at 75 $^\circ$C overnight to obtain a red solid. The residue was Soxhletted with distilled water at 100 $^\circ$C for 48 h and evaporated to dryness. The hybrid nanomaterials were calcined in a Muffle furnace at 250 $^\circ$C for 2 h to become yellow-brown powder. Similarly, the hybrid material was handled as the above process with different calcination temperatures (150 $^\circ$C, 250 $^\circ$C and 350 $^\circ$C) and then denoted as H$_4$TTFTB-TiO$_2$ (150 $^\circ$C), H$_4$TTFTB-TiO$_2$ (250 $^\circ$C) and H$_4$TTFTB-TiO$_2$ (350 $^\circ$C). In order to elaborate the formation process of the hybrid materials H$_4$TTFTB-TiO$_2$, the intermediate products at various reaction times were collected to characterize their crystalline states by checking their XRD patterns (Figure S2).

H$_4$TTFTB-TiO$_2$ materials with different H$_4$TTFTB mass contents (0, 1.7%, 3.4% and 6.5%) were prepared with the above method and denoted as $a$-TiO$_2$, H$_4$TTFTB-TiO$_2$-1.7, H$_4$TTFTB-TiO$_2$-3.4 and H$_4$TTFTB-TiO$_2$-6.5, respectively.

2.2.2. Synthesis of Dye-Sensitized Composites

The $a$-TiO$_2$ powder was dispersed in 0.7 mM DMF solution of H$_4$TTFTB at room temperature in the dark for 6 h and then centrifuged and washed with DMF and methanol until no color was observed from the eluent. The solid was dried under a vacuum oven at room temperature, denoted as H$_4$TTFTB-5.0/TiO$_2$.

2.2.3. Synthesis of Composites Materials Loaded with Pt NPs

The hybrid material above (20 mg) was dispersed in a photocatalytic reaction cell containing 4 mL H$_2$O and 10 mL methanol. K$_2$PtCl$_4$ aqueous solution (0.01 M) was added under stirring, and then the resulting mixture was stirred another 1 h under full-light irradiation by a 300 W xenon lamp. After illumination, the material was centrifugally washed with water and methanol and then dried in a vacuum. Pt NPs’ actual loading amounts tested by inductively coupled plasma atomic emission spectrometry (ICP-AES) were 0.39 wt%, 0.88 wt% and 1.0 wt% (Table S1).
2.3. Photocatalytic Hydrogen Production

The photocatalytic hydrogen evolution by water splitting was carried out in a glass reaction cell with a quartz cover connected to a closed gas circulation, which was swept by high-purity Ar before illumination. A total of 20 mg photocatalysts were dispersed in 20 mL of 10 vol% TEOA aqueous solution. Then the suspension was exposed to a 300 W Xe lamp equipped with an optical filter (λ > 400 nm) to cut off the light in the ultraviolet region. The reaction solution was stirred continuously and cooled to maintain a suitable temperature by the circulation of cooling water. The amount of hydrogen evolved was determined at an interval of 1 h with online gas chromatography.

2.4. Materials Characterization

The solid ultraviolet diffraction spectrum was measured using a Shimadzu UV-2600 spectrometer (Shimadzu, Kyoto, Japan), and fluorescence spectra were measured by a Fluorolog-3 spectrometer (HORIBA, Shanghai, China). The FT-IR spectra were monitored by a Nicolet iS50 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Powder X-ray diffraction (PXRD) was recorded on a Rigaku Smart Lab (Rigaku, Beijing, China) diffractometer (Bragg-Brentano geometry, Cu-Kα1 radiation, λ = 1.54056 Å). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) micrographs, selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDX) and elemental mapping were obtained by an FEI Talos F200X (FEI, Hillsboro, OR, USA) transmission electron microscope. Scanning electron microscope (SEM) micrographs were recorded on a SU8020 (HITACHI, Tokyo, Japan) ultrahigh resolution field emission scanning electron microscope. Gas adsorption measurements were performed using ultra-high purity N₂ on the Quantachrome Auto-sorb-iQ2-MP analyzer (Quantachrome, Beijing, China). X-ray photoelectron spectroscopy (XPS) (Thermo escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA) measurements were carried out using a monochromated Al Kα X-ray source (hν = 1486.6 eV) with a 400 μm spot size in an ultrahigh vacuum chamber. The pass energy was 30 eV. Thermogravimetric (TG) analysis was performed at a constant heating rate of 10 °C min⁻¹ from 30 to 600 °C in air, on a NETZSCH STA 449 F5/F3 Jupiter thermal analyzer (NETZSCH, Free State of Bavaria, Germany). The collection system of photocatalytic hydrogen production was Perfect Light Lab Solar-6A (PerfectLight, Beijing, China), and H₂ measurement was performed on FuLi GC9790II (FuLi, Taizhou, China). The amounts of Pt nanoparticles loaded on samples were detected by Agilent ICP-OES730 (Agilent, Palo Alto, CA, USA).

2.5. Photocell Electrochemical Methods

The Mott–Schottky curves were conducted on an Ivium-n-Stat electrochemical analyzer (Ivium Technologies B.V., Eindhoven, Netherlands) in a three-electrode cell. A platinum plate was used as a counter electrode, and an Ag/AgCl electrode (3 M KCl) was used as a reference electrode. The electrolyte was a 0.5 M Na₂SO₄ solution. In order to prepare the working electrolyte, 5 mg samples were added to a mixed solution of ethanol and Nafion. The photocurrent response and electrochemical impedance measurements were performed using a 0.5 M Na₂SO₄ solution electrolyte, using a 300 W xenon lamp with a 400 nm cut-off filter as the light source. Cyclic voltammograms (CVs) were recorded using an Ivium-n-Stat electrochemical analyzer with the platinum plate as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. CVs were measured using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte in DMF with a scan rate of 50 mV s⁻¹.

3. Results and Discussions

Figure 1a,b display the XRD patterns of a-TiO₂ and H₄TTFTB-TiO₂(1.7/3.4/5.0/6.5) hybrid materials. The obtained diffraction peaks at 25.54°, 37.85°, 47.90°, 54.22° and 62.70° were consistent with the standard card of anatase TiO₂ (JCPDS 21–1272), which
demonstrated the formation of anatase TiO₂ (Figure 1a). Calcination at 250 °C can remove impurities and facilitate the separation and transfer of photogenerated carriers. Simultaneously, the XRD analysis of H₄TTFTB-TiO₂ hybrid materials calcined at 250 °C is shown in Figure 1b. As can be seen (Figure S3), no obvious diffraction peaks of H₄TTFTB can be found, and it shows little impact on the crystallinity due to low contents and high dispersion of H₄TTFTB in H₄TTFTB-TiO₂ hybrid nanomaterials.

Figure 1a,b display the XRD patterns of a-TiO₂ and H₄TTFTB-TiO₂-5.0 materials. The isotherms plots have a typical type IV pattern, which is evidently characteristic of mesoporous materials. The prepared a-TiO₂ and H₄TTFTB-TiO₂-5.0 possess high BET specific surface area, 184.1 m²/g and 212.7 m²/g, respectively. These results show that the introduction of H₄TTFTB could appropriately increase the specific surface area of the hybrid nanomaterials. Moreover, the pore size was simulated and calculated by the Barrett-Joyner-Halenda (BJH) method. From the pore size distribution diagram (Figure S4), it could be observed that the pore size distribution (3.630 nm) of H₄TTFTB-TiO₂-5.0 nanomaterial is smaller than that (4.411 nm) of a-TiO₂. The detailed data of the surface areas and the pore sizes are summarized in Table S2. In general, H₂ production involves surface adsorption and interface reaction of reaction substrates in the heterogeneous photocatalyst system, which could be significantly affected by the morphology and structure of the photocatalyst. Thus, H₄TTFTB-TiO₂ composite nanomaterials prepared through a sol-gel process endow mesoporous hierarchical structure and multifunctional synergistic effect, which results in broad visible-light response and more efficient photocatalytic performance.

Figure 2 shows the N₂ adsorption-desorption isotherms at 77K of a-TiO₂ and H₄TTFTB-TiO₂-5.0 materials. The isotherms plots have a typical type IV pattern, which is evidently characteristic of mesoporous materials. The prepared a-TiO₂ and H₄TTFTB-TiO₂-5.0 possess high BET specific surface area, 184.1 m²/g and 212.7 m²/g, respectively. These results show that the introduction of H₄TTFTB could appropriately increase the specific surface area of the hybrid nanomaterials. Moreover, the pore size was simulated and calculated by the Barrett-Joyner-Halenda (BJH) method. From the pore size distribution diagram (Figure S4), it could be observed that the pore size distribution (3.630 nm) of H₄TTFTB-TiO₂-5.0 nanomaterial is smaller than that (4.411 nm) of a-TiO₂. The detailed data of the surface areas and the pore sizes are summarized in Table S2. In general, H₂ production involves surface adsorption and interface reaction of reaction substrates in the heterogeneous photocatalyst system, which could be significantly affected by the morphology and structure of the photocatalyst. Thus, H₄TTFTB-TiO₂ composite nanomaterials prepared through a sol-gel process endow mesoporous hierarchical structure and multifunctional synergistic effect, which results in broad visible-light response and more efficient photocatalytic performance.

Figure 2. N₂ adsorption-desorption isotherms of H₄TTFTB-TiO₂ system measured under 77 K.
The morphology and structure of the hybrid were characterized by SEM, TEM, HRTEM and SAED, as well as the element mapping. The SEM image of H4TTFTB-TiO2-5.0 material is recorded in Figure S5, showing the size of ellipse nanoparticles as about 10–15 nm. To enhance the activity of photocatalytic H2 production, H4TTFTB-TiO2-5.0 was loaded with Pt NPs by the photodeposition method. TEM images of Pt@H4TTFTB-TiO2-5.0 show that platinum particles are uniformly distributed, and the size is about 2–5 nm (Figure 3a). The HRTEM image indicates that the distance of two adjacent lattice planes of Pt NPs is about 0.226 nm, consistent with the spacing of Pt NPs (111) planes (Figure 3b). The SAED result proves the crystallinity of H4TTFTB-TiO2-5.0 nanomaterials (Figure 3c). The HAADF-STEM mapping and EDX of Pt@H4TTFTB-TiO2-5.0 certify the existence of H4TTFTB, TiO2 and Pt NPs in the composite and C, O, Ti, S and Pt are uniformly dispersed throughout all of the composites (Figures S6 and 3d–i, Table S3). In addition, XPS measurements for a-TiO2, H4TTFTB-TiO2-5.0 and Pt@H4TTFTB-TiO2-5.0 were carried out (Figures S7–S9). Generally, pollution carbon C1s (284.8 eV) is used for charge calibration for all samples. In Figure S8, the survey spectrum displays that C, O, Ti and S exist in the H4TTFTB-TiO2-5.0. The binding energy of Ti 2p3/2 and Ti 2p1/2 is at 458.7 and 464.4 eV, respectively, and the binding energy of O 1s is at 529.9 eV, which could be attributed to the Ti-O bond of TiO2 for a-TiO2 and H4TTFTB-TiO2-5.0 (Figures S7 and S8). Moreover, the compositions of Ti and O for both a-TiO2 and H4TTFTB-TiO2-5.0 display the expected 1:2 ratio, indicating the existence of TiO2 in the hybrid. Compared to a-TiO2, the binding energy at 164.2 eV and 165.2 eV, 168.6 eV and 169.6 eV belongs to S 2p3/2 and S 2p1/2, respectively, demonstrating that H4TTFTB is successfully doped within TiO2. Furthermore, the two different types of peaks represent the existence of the neutral sulfur and oxidized sulfur of H4TTFTB in the composite (Figure S8d). However, the partially oxidized sulfur of H4TTFTB in the composite indicates that the electron-rich tetrathiafulvalene (TTF) could be oxidized easily to its stable radical oxidation states (TTF•+) during the synthesis process of the hybrid. Furthermore, when the composite H4TTFTB-TiO2-5.0 was loaded with the Pt NPs by the photoreduction with the aid of methanol, the proportion of neutral sulfur of H4TTFTB in the hybrid would increase owing to the reduction of the oxidized sulfur by methanol. In addition, the banding energy at 71.1 eV and 74.4 eV belongs to Pt 4f7/2 and Pt 4f5/2, respectively, which could be attributed to Pt (0), also the weak banding energy at 72.5 eV (Pt 4f7/2) and 75.6 eV (Pt 4f5/2), which could be attributed to a small amount of unreduced Pt2+ (Figure S9).

The FT-IR spectra of a-TiO2, H4TTFTB and H4TTFTB-TiO2-5.0 hybrid are displayed in Figure 4. Notably, 1621 cm−1 and 3417 cm−1 of absorption peaks are attributed to the bending and stretching vibrations of -OH groups from a-TiO2, which is pivotal for the combination with H4TTFTB molecules. The stretching vibrations of C=O groups and C-O groups from H4TTFTB are at 1696 cm−1 and 1103–1378 cm−1, respectively. Moreover, the characteristic vibration bands of the benzene skeleton are around 650–900 cm−1, which conforms to the structure feature of H4TTFTB. Compared with a-TiO2, the characteristic vibration bands of C=C from H4TTFTB and Ti-O from a-TiO2 appear at 1500 cm−1 and 500–700 cm−1, respectively, indicating the existence of H4TTFTB and TiO2 in the hybrid materials. Furthermore, the C=O stretching vibration of H4TTFTB at 1696 cm−1 disappears, and two new bands appear at 1407 cm−1 and 1621 cm−1 in H4TTFTB-TiO2-5.0, which could be attributed to the symmetric and anti-symmetric stretch of -COO-. Thus, H4TTFTB should be chemically combined with TiO2 through titanium ester bonds (O=C-O-Ti), which could also enhance the separation and transfer of photogenerated charges between H4TTFTB and Ti (3d) orbital manifold of a-TiO2 [43,44]. Further, thermogravimetric analysis (TGA) of H4TTFTB and of H4TTFTB-TiO2-5.0 were carried out to evaluate their thermostability, revealing that the organic molecular H4TTFTB and the hybrid materials could be stable up to 300 °C (Figure S10).
The UV-vis absorption spectrum and the emission spectra of $H_4TTFTB$ are shown in Figure 4. Notably, 1621 cm$^{-1}$ is a stretching vibration band of $C=C$ from $H_4TTFTB$ and Ti-O from TiO$_2$, indicating a robust combination between $H_4TTFTB$ and TiO$_2$ in the hybrid. The $\delta OH$ vibration bands of -OH groups from TiO$_2$ are at 1696 cm$^{-1}$, which conforms to the structure feature of $H_4TTFTB$. Compared with pure TiO$_2$, the stretching vibrations of $C=O$ groups and $C-O$ groups from $H_4TTFTB$ are at 1696 cm$^{-1}$ and 1103–1378 cm$^{-1}$, respectively, indicating the existence of $H_4TTFTB$ and TiO$_2$ in the hybrid. Furthermore, the $C=O$ stretching vibration of $H_4TTFTB$ at 1696 cm$^{-1}$ also enhances the separation and transfer of photogenerated charges between $H_4TTFTB$ and TiO$_2$.

The FT-IR spectra of $H_4TTFTB$, $H_4TTFTB$–TiO$_2$, and $H_4TTFTB$–TiO$_2$–5.0 were carried out to evaluate their thermostability. The FT-IR spectra of $H_4TTFTB$–TiO$_2$–5.0, $H_4TTFTB$, and TiO$_2$ are displayed in Figure 4. The characteristic $\pi^*$ transition of the phenyl-TTF moiety. The small bands at 1407 cm$^{-1}$ and 1500 cm$^{-1}$ in $H_4TTFTB$–TiO$_2$ are attributed to the $\delta OH$ and $\delta COO^-$ vibrations. The absorption peak at 650–800 nm, owing to the low contents of $H_4TTFTB$ doped. Compared with pure TiO$_2$, the absorption range at about 300–600 nm, along with a smaller shoulder adsorption peak at 650–800 nm, could be attributed to the partially oxidized TTF ligands.

The in situ by sol-gel method to obtain composite $H_4TTFTB$–TiO$_2$. The composite has a broad gap of 2.8 eV (Figure 5a), attributed to the symmetric and anti-symmetric stretch of -COO-. Thus, $H_4TTFTB$ should be chemically combined with TiO$_2$ through titanium ester bonds (O=C-O-Ti), which could also enhance the separation and transfer of photogenerated charges between $H_4TTFTB$ and TiO$_2$.

The UV-vis diffraction spectra of $H_4TTFTB$, $H_4TTFTB$–TiO$_2$, and $H_4TTFTB$–TiO$_2$–5.0 are shown in Figure 5. $H_4TTFTB$ exhibits a strong UV absorption peak with a 400 nm absorption edge, which matches the verified band gap (about 3.2 eV) (Figure 5b) [12]. $H_4TTFTB$ is reacted with tetrabutyl titanate to form a band gap of 2.8 eV (Figure 5b) attributed to the symmetric and anti-symmetric stretch of -COO-. The maximum emission wavelength of $H_4TTFTB$ is located at 650 nm; thus, its transition energies ($E_{0-0}$) are calculated to be 2.34 eV. However, the calculated gap of $H_4TTFTB$ in the composite is lower than the $E_{0-0}$ value of 2.34 eV in pure $H_4TTFTB$, revealing that the organic molecular $H_4TTFTB$ and the hybrid materials could be stable up to 300 °C (Figure S10).

Figure 3. (a) TEM, (b) HRTEM, (c) SAED of $H_4TTFTB$–TiO$_2$, $H_4TTFTB$, and $\alpha$-TiO$_2$ [43,44]. Further, thermogravimetric analysis (TGA) was performed to evaluate the thermostability of $H_4TTFTB$–TiO$_2$ and $H_4TTFTB$–TiO$_2$–5.0. The positive slopes of the M-S plots match with an n-type semiconductor. The flat band positions ($V_{fb}$) of a-TiO$_2$ are calculated to be -0.7 V (vs. Ag/AgCl). As well known, the conduction band (CB) of n-type TiO$_2$ is also enhanced up to 300 °C (Figure S10).

Figure 4. The FT-IR spectra of $H_4TTFTB$–TiO$_2$–5.0, $H_4TTFTB$, $\alpha$-TiO$_2$, and $H_4TTFTB$–TiO$_2$.
The UV-vis diffraction spectra of H$_4$TTFTB, H$_4$TTFTB-TiO$_2$-5.0 and a-TiO$_2$ are displayed in Figure 5a. As we can see, H$_4$TTFTB shows a strong absorption range of about 300–650 nm, ascribing to n-π* or π-π* transition of the phenyl-TTF moiety. The small shoulder at around 650–800 nm could be attributed to the partially oxidized TTF ligands (TTF$^{\bullet\bullet\bullet}$) [40]. The UV-vis absorption spectrum and the emission spectra of H$_4$TTFTB are exhibited in Figure S11. The maximum emission wavelength of H$_4$TTFTB is located at 650 nm; thus, its transition energies (E$_{0-0}$) are calculated to be 2.34 eV. However, a-TiO$_2$ only has a strong UV absorption peak with a 400 nm absorption edge, which matches the verified band gap (about 3.2 eV) (Figure 5b) [12]. H$_4$TTFTB is reacted with tetrabutyl titanate in situ by sol-gel method to obtain composite H$_4$TTFTB-TiO$_2$. The composite has a broad absorption range at about 300–600 nm, along with a smaller shoulder adsorption peak at around 650–800 nm, owing to the low contents of H$_4$TTFTB doped. Compared with pure TiO$_2$, the H$_4$TTFTB-TiO$_2$-5.0 composite has two band gaps: a wide band gap of 2.8 eV and a narrow band gap of 2.0 eV (Figure 5b), attributed to a-TiO$_2$ and H$_4$TTFTB, respectively. The band gap of H$_4$TTFTB in the composite is lower than the E$_{0-0}$ value of 2.34 eV in pure H$_4$TTFTB, indicating that a robust combination exists between H$_4$TTFTB and TiO$_2$ in the hybrid.

![Figure 5](image_url)

In order to elucidate the photocatalytic mechanism of H$_4$TTFTB-TiO$_2$ under visible light irradiation, Mott-Schottky (M-S) measurements of a-TiO$_2$ were carried out at different frequencies of 500 Hz, 1000 Hz and 1500 Hz (Figure S12). The positive slopes of the M-S plots match with an n-type semiconductor. The flat band positions ($V_{fb}$) of a-TiO$_2$ are calculated to be $-0.7$ V (vs. Ag/AgCl). As well known, the conduction band (CB) of n-type semiconductors is approximately the same as the value of $V_{fb}$ [25]. Consequently, the CB of a-TiO$_2$ is about $-0.7$ eV (vs. Ag/AgCl), being more negative than the redox potential of H$^+$/H$_2$; thus, favoring the photoreduction of the proton from water to produce H$_2$. The valence band (VB) of a-TiO$_2$ is counted to be 2.5 eV (vs. Ag/AgCl). Moreover, the first oxidation potential of H$_4$TTFTB was detected by CVs characterization to acquire the highest occupied molecular orbital (HOMO) value (Figure S13). The redox potential of excited H$_4$TTFTB$^*$ is about $-1.64$ eV (vs. Ag/AgCl); namely, the bottom of the lowest unoccupied molecular orbital (LUMO) is counted from the HOMO and the E$_{0-0}$ value of H$_4$TTFTB, which is more negative than the CB of a-TiO$_2$. Thus, it is thermodynamically favorable for the transfer to be directly from the H$_4$TTFTB$^*$ to CB of a-TiO$_2$.

The photocatalytic activities of H$_4$TTFTB-TiO$_2$-5.0 catalysts with different amounts of H$_4$TTFTB-doping and with different contents (0.5/1.0/1.5 wt%) of Pt NPs loading have been optimized under visible light irradiation. A series of experiment data are presented in Figure 6a. The results demonstrate that H$_4$TTFTB-TiO$_2$-5.0 with 1.0 wt% Pt NPs has the optimized photocatalytic activity (Figure S14). Moreover, the photoactivity increases with the addition of H$_4$TTFTB-doped amount (1.7 wt%, 3.4 wt% and 5.0 wt%), reaching a maximum for H$_4$TTFTB-TiO$_2$-5.0. However, further increasing the percentage of H$_4$TTFTB to 6.5 wt% with a decrease in photoactivity indicates that the photoactivity of H$_4$TTFTB-TiO$_2$ nanomaterials could not correlate only to H$_4$TTFTB amounts. Reasonable
speculation is that excessive H₄TTFTB in the composite could block porous channels and impede electron migrating and transporting. The photocatalytic activity of the composites nanomaterials is influenced by many factors, such as temperature, pH, solvents, additives, etc. Among them, the calcination temperature is pivotal in building up the structural morphology of composites and enhancing the photocatalytic activity. Thus, the calcination temperature of H₄TTFTB-TiO₂-5.0 was optimized. In addition, H₄TTFTB-TiO₂-5.0 with 250 °C calcination exhibits the best photocatalytic rates of H₂ production, which is greatly superior to higher or lower calcination temperature (150 °C or 350 °C) (Figure S15). It is believed that appropriate calcination temperature not only could eliminate the impurity but also improve the crystallinity of the hybrid materials. However, a lower temperature (150 °C) could not meet the requirements for the synthesis of the hybrid, and a higher calcination temperature (350 °C) could destroy the organic component H₄TTFTB.

In contrast, the rate of photocatalytic H₂ production of α-TiO₂ and sensitization H₄TTFTB-5.0/TiO₂ with only 1.0 wt% Pt (0) loading are 18.87 and 390.8 μmol g⁻¹ h⁻¹ which are both less than the rates of H₄TTFTB-TiO₂-5.0. It demonstrates that the composites have excellent photocatalytic activity than the dye sensitization TiO₂ system owing to the more efficient migration of photogenerated electrons from H₄TTFTB⁺ to TiO₂ through the robust linkages between H₄TTFTB and TiO₂. Moreover, to assess the stability of H₄TTFTB-TiO₂ nanomaterial, we conducted photocatalytic H₂ evolution experiments at intervals of 5 h. The H₄TTFTB-TiO₂ composite was reused by centrifugation, washed with water and methanol and then vacuum dried. As shown in Figure 6b, the photocatalytic activity

Figure 6. (a) Effect of the amount of H₄TTFTB doped into the TiO₂ on the performance of photocatalytic hydrogen production, (b) Photocatalytic H₂ production over the recyclability of H₄TTFTB-TiO₂-5.0 in 20 mL H₂O/TEOA (9:1 v/v) with 1.0 wt% Pt loading under visible light irradiation (λ > 400 nm), (c) Transient photocurrent responses and (d) EIS Nyquist plots.
of H4TTFTB-TiO2 shows no significant decrease, revealing high photocatalytic stability in photocatalytic reducing H2 with seven recycles. The TONH2 is calculated as the mole numbers of H2 over the mole numbers of Pt NPs, giving significant results of 1101 after 35 h of photoreactions. In general, compared with other reported photocatalysts (Table S4), the photocatalytic activity of the H4TTFTB-TiO2-5.0 system is moderate. However, the simple and flexible synthesis approach has been proposed in this study to obtain the robust fulvalene-based composite, which is significant to shed light on the rational design of photocatalysts and understand the photocatalytic inherent nature. Thus, our next work will focus on regulating precisely the structure of the fulvalene-based composite at a molecule level, which would enhance our in-depth fundamental understanding of the photocatalytic mechanism.

The photocurrent-time (i-t) curves and the electrochemical impedance spectroscopy (EIS) of α-TiO2, H4TTFTB-5.0/TiO2 and H4TTFTB-TiO2-5.0 have been monitored under visible light illumination to further verify the influence of enhanced photosresponse on the photocatalytic process (Figure 6c,d). It is clear that the photocurrent of H4TTFTB-TiO2-5.0 is higher than H4TTFTB-5.0/TiO2, indicating that effective interfacial electrons migration and transfer between H4TTFTB and TiO2 in H4TTFTB-TiO2-5.0 (Figure 6c). Figure 6d displays the EIS Nyquist plots for samples. Compared with α-TiO2 and H4TTFTB-5.0/TiO2, H4TTFTB-TiO2-5.0 exhibits a smaller semicircular diameter in Nyquist plots, suggesting that the smaller resistance of photogenerated charge migration and transfers on the electrode surface. Thus, the result demonstrates that the hybrid materials possess a smaller interfacial charge-transfer resistance, which could significantly enhance the photoactivity for H2 generation, hinting that more effective interfacial photogenerated electrons migrate and transfer between H4TTFTB and TiO2 in H4TTFTB-TiO2 composites.

According to the results and discussions above, a possible photocatalytic mechanism for the H4TTFTB-TiO2 catalytic system is proposed, as shown in Figure 7. H4TTFTB owns excellent light absorbance ability to act as a light harvester under visible light irradiation. The excited electrons jump from HOMO into LUMO of H4TTFTB and inject into the CB band of TiO2. The electrons separated successfully could reduce proton to H2 production with the aid of Pt (0) NPs. Herein, Pt (0) NPs are loaded on the surface of H4TTFTB-TiO2 by the in-situ photodeposition and commonly work as co-catalysts to provide reactive sites, owing to the formation of the Schottky barrier at the interface of Pt NPs and the hybrid, which could be beneficial to promote the separation and transfer of photogenerated charges and enhance the photocatalytic activity. The electrons on the CB of α-TiO2 could be captured by the co-catalysts and then efficiently photoreduce H+ to H2. The holes retained in the VB of H4TTFTB are neutralized by sacrificial reagent triethanolamine (TEOA). Furthermore, the oxidative H4TTFTB+ could also be reduced by TEOA to obtain relative H4TTFTB.

![Figure 7. Proposed mechanism of photocatalytic H2 production over Pt@H4TTFTB-TiO2.](image-url)
4. Conclusions

In summary, we have in situ synthesized organic-inorganic H$_4$TTFTB-TiO$_2$ composite containing organic light-harvesting unit H$_4$TTFTB and inorganic semiconductor TiO$_2$ by the sol-gel method. H$_4$TTFTB-TiO$_2$-5.0 material exhibits high photocatalytic efficiency under visible light irradiation. A series of characterizations on structural morphology and photoelectric physical and chemical properties suggest that H$_4$TTFTB is successfully doped into H$_4$TTFTB-TiO$_2$, which is attributed to the formation of stable titanium ester bond linkage between H$_4$TTFTB and TiO$_2$. The absorption ability of H$_4$TTFTB extended to visible light range could fully use the solar energy. The multifunctional synergistic effect of organic and inorganic components of H$_4$TTFTB-TiO$_2$ composite could promote efficient electron migration and transfer in the interface. This work sheds light on the relationship of structure, photocatalytic activity and reaction pathway of TTF-based composite nanomaterials for splitting water to H$_2$ production under visible light irradiation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/10.3390/nano12111918/s1. Figure S1. (a) The structure of H$_4$TTFTB, (b) illustration of the fabrication of the H$_4$TTFTB-TiO$_2$. Figure S2: The XRD patterns of the intermediate products at different reaction times. Figure S3: The XRD patterns of the a-TiO$_2$, H$_4$TTFTB and H$_4$TTFTB-TiO$_2$-5.0. Figure S4: The pore size distributions of (a) a-TiO$_2$, (b) H$_4$TTFTB-TiO$_2$-5.0. Figure S5: The SEM of H$_4$TTFTB-TiO$_2$-5.0. Figure S6: EDX of the Pt@ H$_4$TTFTB-TiO$_2$-5.0. Figure S7: X-ray photoelectron spectra for Ti and O of a-TiO$_2$. Atomic ratio of Ti:O = 35%-65% ≈ 1:2. Figure S8. X-ray photoelectron spectra for C, O, Ti and S of H$_4$TTFTB-TiO$_2$-5.0. Atomic ratio of Ti:O:C:S = 27%-51%-21%-11.8%. Figure S9: X-ray photoelectron spectra of C, O, Ti, S, Pt of Pt@ H$_4$TTFTB-TiO$_2$-5.0. Figure S10: Thermal gravity analysis of (a) H$_4$TTFTB compound and (b) H$_4$TTFTB-TiO$_2$-5.0. Figure S11: UV-vis absorption spectra and photoluminescence spectra of H4TTFTB in DMF (E0–0 = 1240/λint). Figure S12: Mott-Schottky plot of a-TiO$_2$ in 0.5 M Na$_2$SO$_4$ aqueous solution. Figure S13: Cyclic voltammogram of H$_4$TTFTB in 0.1 M TBAPF$_6$ of DMF solutions measured with a scan rate of 50 mV s$^{-1}$. Figure S14: Comparison of photocatalytic H$_2$ evolution of 5 h of H$_4$TTFTB-TiO$_2$-5.0 hybrid material under different loads of Pt. Figure S15: Comparison of photocatalytic H$_2$ evolution of H$_4$TTFTB-TiO$_2$-5.0 hybrid material under different calcined temperature loaded with 1.0 wt% Pt. Table S1. The amount of Pt NPs of Pt@H$_4$TTFTB-TiO$_2$. Table S2: BET surface area, pore volume and pore width of a-TiO$_2$, H$_4$TTFTB-TiO$_2$-5.0 derived from 77 K N$_2$ sorption isother. Table S3: Atmico Fraction of Pt@H$_4$TTFTB-TiO$_2$-5.0. Table S4: Comparison of H$_2$ evolution activity of TTF and TiO$_2$ photocatalytic systems. References [45-56] are cited in the supplementary materials.

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