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Highly Promoted Photocatalytic Hydrogen Generation by Efficient Multiple Electron Transfer Pathways

Xiaojiao Yuan¹, Cong Wang¹, Diana Dragoe², Patricia Beaunier³, Christophe Colbeau-Justin¹,
Hynd Remita^{1,4*}

¹ Institut de Chimie Physique, UMR 8000 CNRS, Université Paris-Saclay, 91405 Orsay, France

² Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Saclay, 91405 Orsay, France

³ Sorbonne Université, CNRS, UMR 7197, Laboratoire de Réactivité de Surface, 75005 Paris, France

⁴ CNRS, Institut de Chimie Physique, UMR 8000, 91405 Orsay, France

E-mail : hynd.remita@universite-paris-saclay.fr

Abstract

A facile development of highly efficient photocatalytic nanostructures for solar fuel production via controlled cocatalyst deposition is described. 2 nm-Pt nanoparticles were selectively synthesized by radiolysis on polypyrrole (PPy), TiO₂ or on both PPy-TiO₂ (noted respectively (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂)). The PPy nanostructures not only act a photosensitizer, but also as a connection bridge between two light-harvesting semiconductors to form a p-n heterojunction, which absorbs UV and visible light efficiently. The designed heterojunction photocatalyst nanostructures (Pt-(PPy-TiO₂)) exhibit broadened absorption to the visible region, long life-time of charge carriers and high photocatalytic activity for hydrogen production. This activity is markedly enhanced compared with that of (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy, and is ascribed to more efficient multiple electron transfer pathways. Such designed structures provide promising ways for selected site deposition of

metal nanoparticles on heterojunction semiconductors in high efficiency conversion from solar energy to solar fuel application.

Keywords: Heterojunction photocatalyst, Hydrogen generation, Polypyrrole, TiO₂, Platinum cocatalyst.

1. Introduction

Hydrogen (H₂) is a considerable green and renewable energy. A lot of attention is presently paid to develop photo- or electro-catalysts to solve environmental issues and to produce solar hydrogen because of its high-energy capacity and environmental friendliness [1]. The photocatalytic hydrogen generation from water splitting with semiconductors under solar irradiation is a promising way to produce hydrogen, which has attracted many researchers to extensively investigate and develop appropriate semiconductor photocatalysts to increase their photocatalytic activity [2-7]. The enhancement of photocatalytic performance is generally owing to a fast transfer of photogenerated electrons from the semiconductor to metal leading to the longer lifetime of the excited charge carriers [8]. Besides, a suitable band gap (< 3.2 eV) and structure of the photocatalysts (heterojunction, p-n junction or phase junction), surface reactivity (doped cocatalysts), particle size and distribution of cocatalysts are also key factors for a photocatalytic reaction [9].

Recently, conjugated polymer nanostructures coupled with narrow band gap and unique π -conjugated electron systems as a new class of photocatalysts have received much attention in various photocatalysis application such as water treatment [10-13] and green H₂ production. [14, 15]. However, the photocatalytic efficiency of pristine conjugated polymers is very low due to their rapid charge carrier recombination and sluggish reaction kinetics. A promising way to increase the photocatalytic property of conjugated polymer-based photocatalysts is their combination with semiconductors such as poly(benzothiadiazole) (BBT) [16], poly(3-hexylthiophene) (P3HT) [17], or polypyrrole (PPy) [18]

modification with titania. Titania composites with conjugated polymers present in general high absorption efficiency in the visible region, less electron-hole recombination, high charge carrier mobility, good stability and excellent biocompatibility. In addition, introducing cocatalysts in conjugated-titania heterostructures can remarkably enhance the photocatalytic efficiency due to the prolonged life time of the charge carriers and increased active sites. Although some conjugated polymer-semiconductor-based ternary structure nanocomposites have successfully constructed such as Pt@TiO₂/g-C₃N₄ [19], CdS/Cu₇S₄/g-C₃N₄ [20], Au/TiO₂(P25)-gC₃N₄ [21], little attention has been paid to considering the multiple electron transfer pathways. Indeed, the multiple electron-transfer pathways are very important for the charge carrier separation and hot electron transfer and accumulation by manipulating deposition cocatalysts on different catalysts in a ternary system [22].

Based on the above considerations, here we successfully fabricated for the first time the ternary hybrid PPy-TiO₂ nanocomposites with small Pt nanoparticles (2 nm) induced by radiolysis, and we controlled the deposition site on PPy, TiO₂ or on both PPy-TiO₂ (noted respectively (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂)). The photocatalytic performance of the different Pt-modified PPy-TiO₂ composites for hydrogen production under both ultraviolet and visible light irradiation were investigated. The results indicate that Pt-(PPy-TiO₂) structures exhibit significantly enhanced photocatalytic hydrogen production due to more efficient electron separation and transfer compared with (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy. Our work provides a promising method for the design of ternary nanostructures of metal-semiconductor-conjugated polymer hybrids with high photocatalytic activity for production of solar fuels.

2. Experimental Section

2.1. Materials Preparation

PPy nanostructures were synthesized by chemical polymerization according to our previous work. In brief, hexagonal mesophases used as soft template were made of a mixture of NaCl (0.2 M), SDS

(sodium dodecyl sulfate, 0.8 g), cyclohexane as oil phase (6 mL) and surfactant (n-pentanol, 400 μ L). FeCl₃ used as oxidant (0.1 M) was added into the mixture, which was vortexed. PPy nanostructures were obtained by oxidation of Py by Fe³⁺ in the mesophases for 2 h. The mesophase was then destabilized by adding ethanol. Finally, the PPy nanostructures powder was collected by centrifugation, washing and drying [11].

TiO₂ P25 was purchased from Evonik Industries AG (surface area 50 m² g⁻¹). The PPy/TiO₂ composite was obtained by putting PPy and TiO₂ in contact under ultrasounds (30 min) in ethanol suspension. Different PPy/TiO₂ mass ratio were obtained. For the photocatalytic tests the optimized mass ratio between PPy and TiO₂ was found to be 1/4.

Radiolysis is a powerful technique to synthesize metal nanoparticles (NPs) of controlled sizes and shapes [23]. Pt NPs were synthesized by radiolysis (using a panoramic ⁶⁰Co γ source) at a dose rate of 4 kGy h⁻¹. The metal salts or complexes (here Pt^{II}(acac)₂ purchased from Aldrich) are reduced by solvated electrons and alcohol radicals induced by solvent radiolysis [14].

In the following preparation of samples process, the samples are using theoretical loading rate of Pt (1wt%). The preparation route of (Pt-PPy)-TiO₂ is the following: Firstly, the PPy nanostructures (20 mg) were added to an ethanolic solution (25 mL) containing platinum acetylacetonate (5x10⁻⁵ M). The tube containing the dispersion was closed with a septum, degassed with N₂, and then irradiated with γ -rays (⁶⁰Co γ source). After 30 min irradiation at a dose rate of 4 kGy h⁻¹, the Pt-PPy powder was collected after centrifugation, it was then rinsed with water and ethanol and dried. In a second step, the Pt-PPy composite (20 mg) was mixed with TiO₂ (80 mg) in 25 mL of ethanol under sonication. Finally, the (Pt-PPy)-TiO₂ was dried in the oven at 60 °C for overnight (**Figure 1a**).

Synthesis of (Pt-TiO₂)-PPy. The synthesis procedure of (Pt-TiO₂)-PPy was summarized in **Figure 1b**. The preparation route is similar to that of (Pt-PPy)-TiO₂. The only difference is that, in the first step, TiO₂ (80 mg) was dispersed into 25 mL of an ethanol solution containing the Pt^{II} precursor (2x10⁻⁴ M). The dispersion was irradiated under N₂ atmosphere. The following steps were the same like the

above mentioned.

Synthesis of Pt-(PPy-TiO₂). PPy (20 mg) were mixed with TiO₂ (80 mg) in an ethanol solution (25 mL) containing platinum acetylacetonate (2.5×10^{-4} M). Then the mixture was sonicated for 10 min to disperse the aggregated nanoparticles and then degassed with N₂. The samples were exposed to γ -rays for 30 min (**Figure. 1c**).

Samples with different loading rates of Pt on PPy-TiO₂ were also synthesized labeled as x%Pt-(PPy-TiO₂).

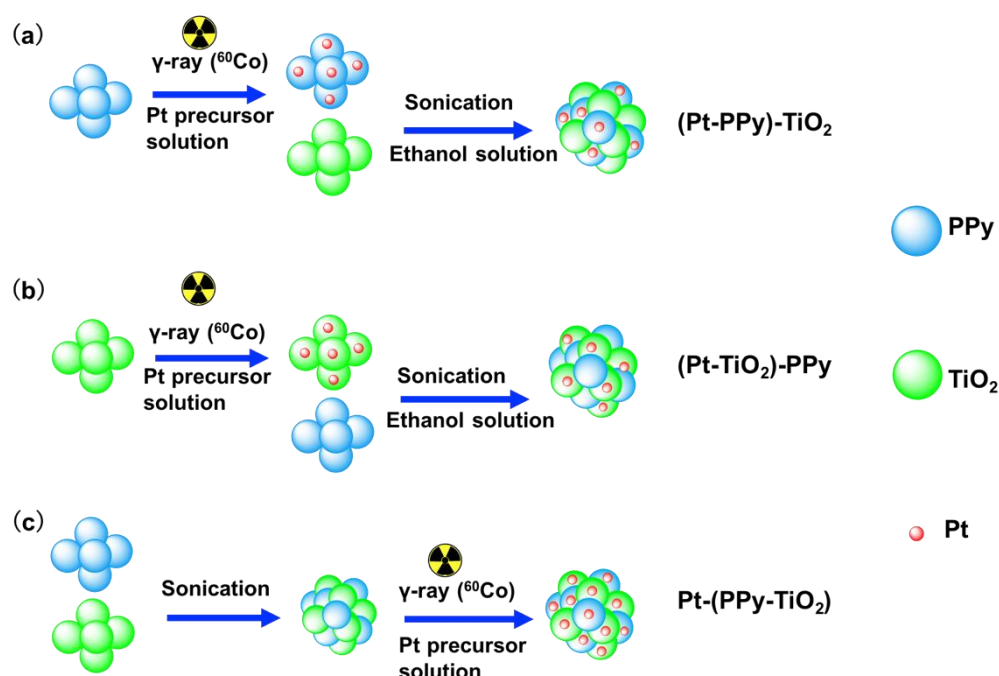


Figure 1. Schemes of modification of TiO₂-PPy with Pt cocatalyst deposited on different sites: on (a) PPy, (b) TiO₂, and (c) PPy-TiO₂.

2.2. Characterizations

Transmission electron microscopy (TEM) (JEOL JEM 2010 UHR operating at 200 kV) was used to observe the morphology and the structures of nanomaterials.

The UV-vis absorption spectra of the samples were recorded with a Cary 5000 Series, Agilent

Technologies.

Time-resolved microwave conductivity (TRMC) technique was applied to investigate the lifetime of charge carrier of photocatalysts under different excitation wavelengths. A pulsed light source (Nd: YAG laser) equipped with an optical parametric oscillator (OPO; EKSPLA, NT342B) was used to excite the samples and a Gunn diode (30 GHz) was used to generate microwaves. The principle of TRMC was described in supporting information [24-26].

X-ray photoelectron spectroscopy (XPS) studies were carried out on an Alpha X-ray Spectrometer with monochromatic Al/K α under ultrahigh vacuum. C 1s peak (284.6 eV) was used as reference.

The electrochemical measurements were performed in Origalys workstation with a three-electrode system (the prepared sample electrode, counter electrode of Pt foil and a Ag/AgCl electrode as the reference). The working electrodes were prepared by dispersing the samples (3 mg) in ethanol (3 mL) on fluorine doped tin oxide (FTO) substrate. The samples were then dried at room temperature. For photocurrent density with time (*i-t*) curve was recorded at a potential of -200 V. Electrochemical impedance spectra (EIS) were measured in 0.1 M Na₂SO₄ solution with an amplitude of 10 mV, Frequency: 0.1 Hz-1000 Hz at 0.2 V.

2.3. Photocatalytic tests

The photocatalytic activity of the different samples for hydrogen generation under UV and visible light was evaluated. 20 mg of the photocatalyst were dispersed in water-methanol mixture solution (20 mL, $V_{\text{methanol}}/V_{\text{water}}$ is 1/4) under stirring. The suspension was bubbled with N₂ to remove oxygen and then illuminated under 300 W xenon lamp. For the experiments under visible irradiation, a filter cutting at 420 nm was used. Every 10 min (for UV light) or 1 h (for visible light), 0.2 mL of the gas was taken and injected in the gas chromatograph (GC, Shimadzu GC-14B) instrument to analyze the amount of H₂.

3. Results and Discussion

3.1 Characterizations of photocatalysts

Figure 2 presents the TEM images of Pt-(PPy-TiO₂), (Pt-TiO₂)-PPy, (Pt-PPy)-TiO₂ nanocomposite materials. When the Pt precursor is irradiated in the presence of the PPy-TiO₂ composite, Pt NPs are formed on both TiO₂, on the polymer and at the interface, with a preferential deposition on PPy. The TEM images of Pt-(PPy-TiO₂) present small and monodisperse Pt nanoparticles (black dots, ~2.2 nm, **Figure S1**) on the surface of the PPy-TiO₂ composite (**Figure 2a-b**). The yellow circled parts show preferential deposition of Pt NPs on PPy nanostructures (NSs).

Figure 2c-d shows TEM images of the samples with Pt NPs synthesized on TiO₂ previous to the heterojunction with PPy: 2 nm Pt NPs uniformly dispersed on the TiO₂ were observed. In addition, Pt NPs were found to deposit at the edges of TiO₂ by radiolytic reduction [27] and Pt NPs were not observed on PPy. **Figure 2e-f** present TEM images of the samples with Pt NPs synthesis on PPy NSs previous to the heterojunction with TiO₂: Pt NPs of homogeneous size were well dispersed on PPy, and no Pt NPs were observed on TiO₂.

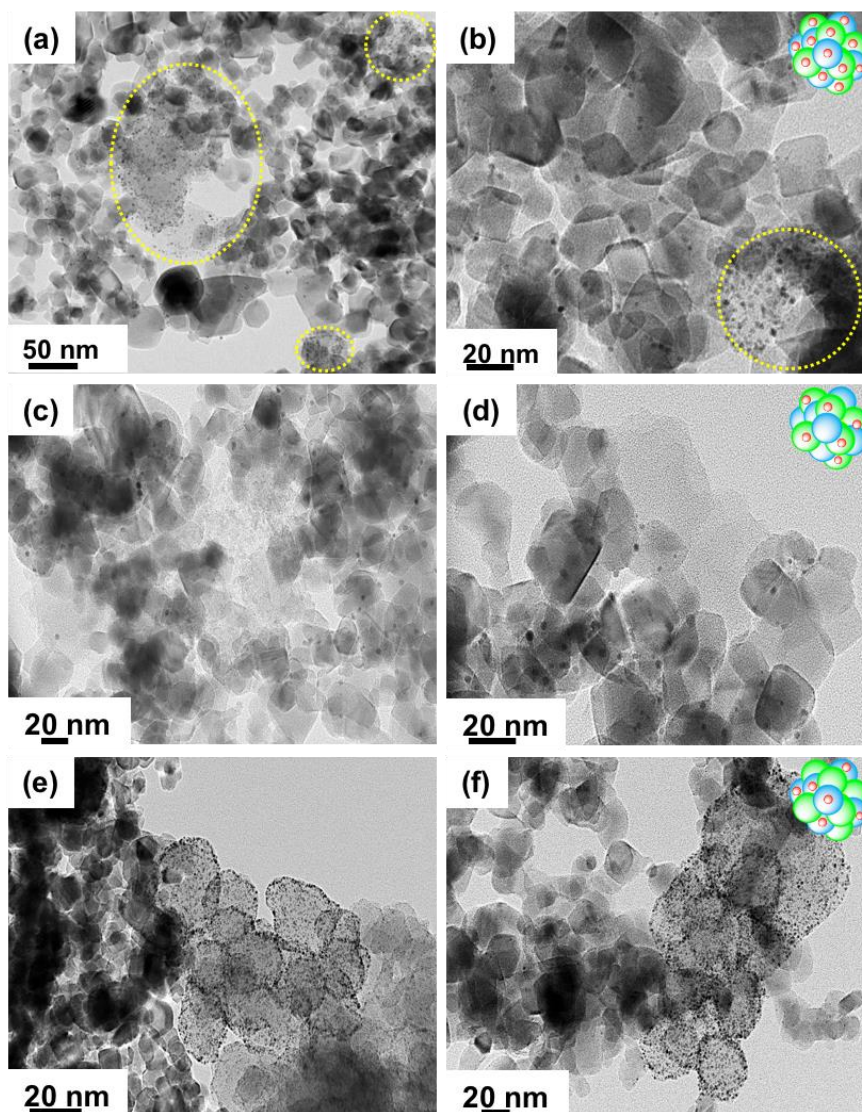


Figure 2. TEM images of (a-b) Pt-(PPy-TiO₂), (c-d) (Pt-TiO₂)-PPy, (e-f) (Pt-PPy)-TiO₂. The mass ratio between PPy and TiO₂ was 1:4 for all the samples.

The UV-vis diffuse reflectance spectra (DRS) of the photocatalysts are shown in **Figure 3a**. The absorption bands from 200 nm to 400 nm are observed owing to the electrons promotion of TiO₂ from valence band (VB) to the conduction band (CB) [28]. Compared with bare TiO₂, Pt-TiO₂ show higher absorption under visible light and red shift (to some extent), which characterize the optical properties of Pt NPs on TiO₂ [29]. Thanks to the strong absorption of PPy in the visible light region, Pt-(PPy-TiO₂) shows high absorption intensity from 400~800 nm, indicating a significantly improved

activation under visible light. Moreover, based on the Kubelka-Munk method, the estimated band gap for TiO₂, Pt-TiO₂ and Pt-(PPy-TiO₂) are 3.20 eV, 3.06 eV and 2.83 eV, respectively (**Figure 3b**). The narrower band gap of Pt-(PPy-TiO₂) is mainly attributed to the heterojunction of titania with PPy nanostructures, which can adsorb more photons to provide more photogenerated charge carriers and improve the photocatalytic property of the photocatalyst. **Figure S2** shows the UV-Vis absorption spectra of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(TiO₂-PPy) samples. All these three samples present high absorption in the visible region and the spectra are quite similar. A small difference was observed probably due to the shield of PPy by TiO₂ during the synthesis.

The XRD peaks of the samples correspond to typical anatase and rutile TiO₂ patterns, which match with the PDF card number of 99-0008 (anatase) and 99-0090 (rutile) [31] (**Figure S3**). Because of the small size of Pt NPs, almost no XRD signal of Pt was observed.

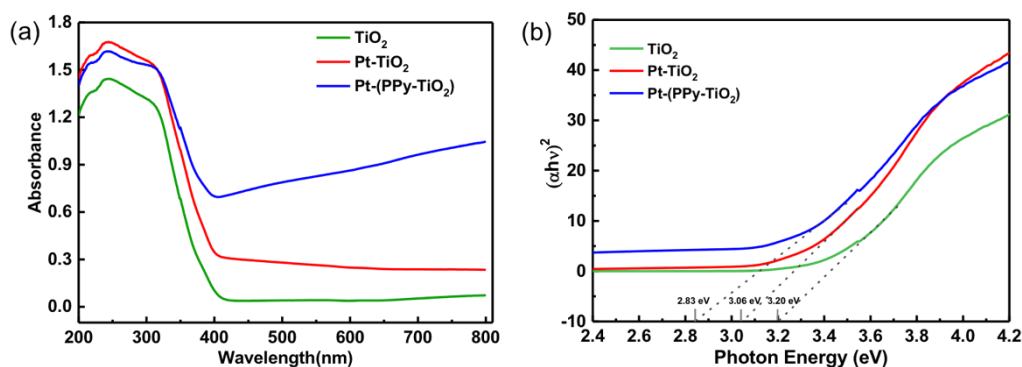


Figure 3. UV-vis absorption spectra (a) and Mott-Schottky plot of the as-prepared samples, (b) (The mass ratio PPy/TiO₂ was 1:4 for all the samples).

The TRMC technique was used to evaluate the dynamics of charge-carriers in TiO₂-based composites at different wavelengths. **Figure 4a** presents the TRMC signals at 360 nm excitation for pure TiO₂, and its platinized form. Pt NPs accelerate the decay at short time range, and does not modify it at long time range [30]. Pt NPs are known to be a sink for electrons, and a sharp fast decay of the signal for the Pt-modified samples is obtained: Pt NPs deposited on TiO₂ act as electron scavengers

decreasing the recombination of charge-carriers, which is beneficial for the photocatalytic activity [20]. Nevertheless, in our previous work, after introducing PPy in TiO₂, the lower signal decay in PPy-TiO₂ than pristine TiO₂ was obtained, which may be due to PPy shield effect, fast recombination effect, or fast electron trapping [31]. Interestingly, **Figure 4a** evidences that the TRMC signal of Pt-(PPy-TiO₂) is not an addition of separate effects of Pt and PPy. A synergetic influence seems to occur. Indeed, the observed signal is quite flat, with a very slow decay. It indicates a real low amount of fast recombination and free e⁻ with high lifetime resulting from good charge-carrier separations. Those effects should be favorable to the activity.

Under visible illumination (at 420 and 450 nm), as expected, the TRMC signal is reduced. Pt-(PPy-TiO₂) shows faster decay at very short range time compared to that of Pt-TiO₂ and TiO₂, which indicates more efficient electron trapping and transfer. Moreover, Pt-(PPy-TiO₂) presents a slightly longer lifetime of electrons from the trend of long-rang decay than that of Pt-TiO₂ and TiO₂ (**Figure 4b-c**).

The TRMC signals of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) under UV, at 360 nm, are shown in **Figure 4d**: Unlike Pt-(PPy-TiO₂), the composites (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy present a fast-global decay, leading to a really low number of charge-carriers after 0.2 μs. It means that the synergetic effect is only observed on Pt-(PPy-TiO₂), which leads to the most efficient electron transfer and the longest life time of electrons. In (Pt-TiO₂)-PPy and (Pt-PPy)-TiO₂ the fast decay is probably be due to high level of recombination.

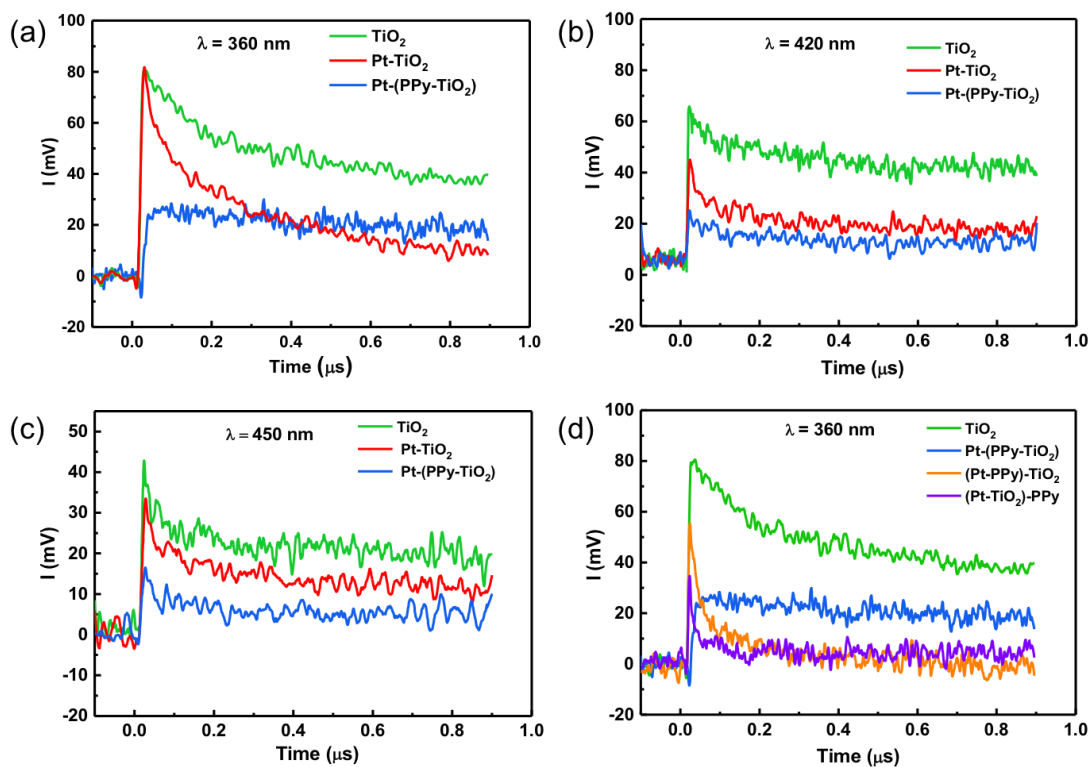


Figure 4. TRMC measurements of Pt-(PPy-TiO₂), Pt-TiO₂ and TiO₂ at 360 nm (a), 420 nm (b), 450 nm (c), respectively. The laser energy of these wavelengths was 1.1, 2.3, 2.3 mJ·cm⁻². TRMC measurements of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy, Pt-(PPy-TiO₂) and TiO₂ at 360 nm (d). The mass ratio between PPy and TiO₂ was 1:4 for all the samples and the Pt loading is 1%.

The surface composition and chemical states of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) were studied by XPS spectroscopy (**Figure 5a-d**). The full spectrum of Pt-(PPy-TiO₂) contains the signals of C, N, O, and Pt (**Figure S4**). Pt 4f spectrum of Pt-(PPy-TiO₂) shows that part of Pt in the composite is oxidized. The doublet at 70.78 eV (Pt 4f_{7/2}) and 73.98 eV (Pt 4f_{5/2}) corresponds to metallic Pt which are lower than pure metallic Pt (Pt 4f_{7/2} = 71.2 eV) due to the electron transfer happens from TiO₂ and PPy to Pt nanoparticles with higher work function [32]. The binding energy at 74.95 eV (Pt 4f_{7/2}) and 76.41 eV (Pt 4f_{5/2}) are corresponding to PtO₂, (**Figure 5a**) [33]. Different valence states of Pt nanoparticles can provide higher active sites and more oxygen defects, which is beneficial for surface chemical adsorption and catalysis [19]. The characteristic peaks of Ti 2p_{3/2} (458.9 eV) and Ti

$2p_{1/2}$ (464.6 eV) spectrum of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) show a slight shift (0.4 eV) toward higher binding energies compared to pure TiO₂ (458.5 eV, Ti $2p_{3/2}$) (**Figure 5b**). With reference to previous reports on TiO₂ [34, 35], such higher energy shifts suggest the formation of heterojunction and interactions of the ternary compounds [36]. The C 1s signal for the PPy is located at a binding energy of 284.9 eV (C-C), 286.2 eV (C-O) and 289.0 eV (O-C=O), respectively (**Figure 5c**). The N 1s high resolution spectra in **Figure 5d** can be fitted into two peaks, which can be attributed to N-C (399.9 eV) and N-C=O (409.1 eV) [37].

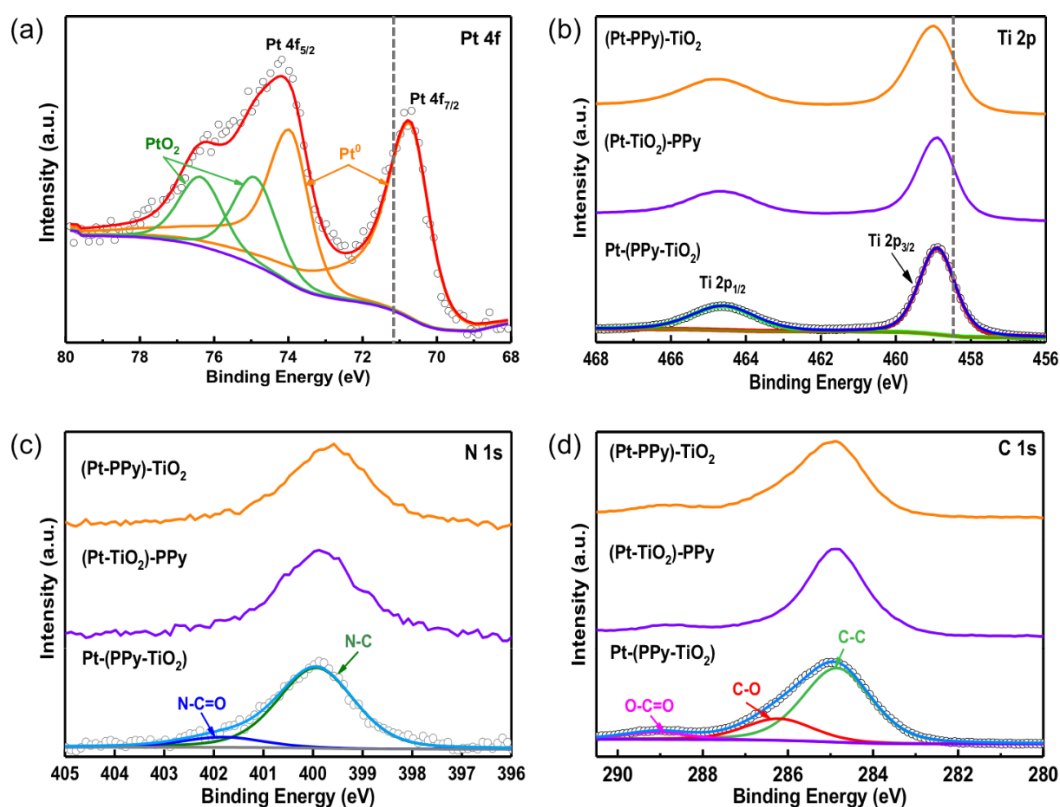


Figure 5 Pt 4f XPS spectra of the Pt-(PPy)-TiO₂ (a); Ti 2p (b), C 1s (c) and N 1s (d) of the (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂), respectively. The mass ratio between PPy and TiO₂ was 1:4 for all the samples and the Pt loading is 1%.

The transient photocurrent response curves of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) are shown in **Figure 6a**. As expected from the TRMC results, the photocurrent intensity of Pt-(PPy-

TiO₂) is 2.7 times higher than that of (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy under AM1.5G, which suggests enhanced efficiency of charge transfer and separation of electron-hole pairs in this sample. Additionally, EIS Nyquist plots were used to explore the interface charge transfer resistances of the electrode materials. The smallest semicircle in EIS for Pt-(PPy-TiO₂) further demonstrated the highest efficient and fastest interfacial charge transfer ability than (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy (**Figure 6b**). These results are consistent with TRMC results and strongly support the excellent photocatalytic activity of Pt-(PPy-TiO₂) shown by the following photocatalytic tests.

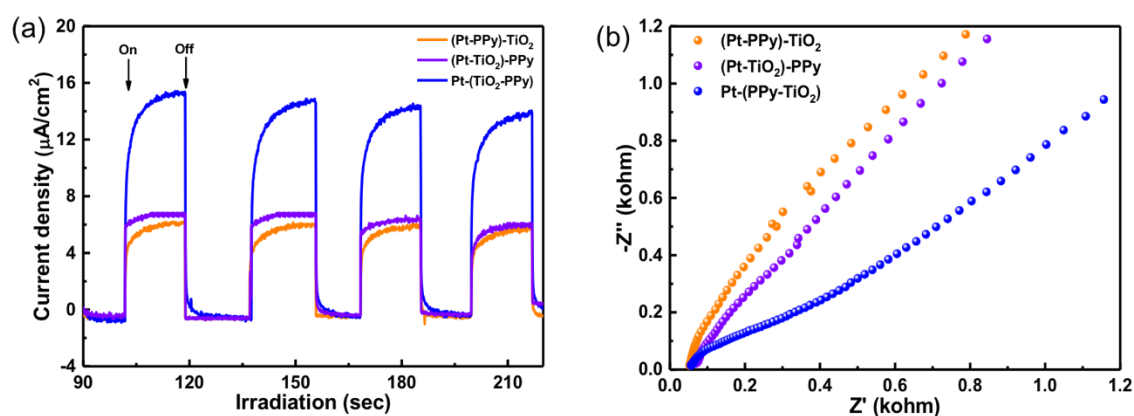


Figure 6. Photocurrent transient (a) and Nyquist plots of EIS (b) for (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) FTO electrodes under UV-vis light irradiation. The mass ratio between PPy and TiO₂ was 1:4 for all the samples and the Pt loading 1%.

3.2 Photocatalytic activity for hydrogen generation

In order to achieve a good photocatalytic activity for hydrogen production, different volume ratios of methanol-water mixture (**Figure S5**), sacrificial electron donors (**Figure S6**), and mass ratios of PPy and TiO₂ were investigated (**Figure 7a**). As shown in **Figure S5**, hydrogen production with 1%Pt-(PPy-TiO₂) increased with increasing methanol content until reached to 25%. The photocatalytic activity decreased when the $V_{\text{methanol}}/V_{\text{water}}$ was more than 25%, and the very low conversion rate was obtained for the case of 100% water or pure methanol. F. Besenbacher et al. revealed a proton-transfer

mechanism that proceeds via an H_3O^+ -like transition state, which can explain why the methanol-water mixture presents higher photocatalytic activity compared with pure methanol [38]. The effect of different sacrificial reagents (with the same concentration: 0.2 M) for photocatalytic hydrogen generation was studied (**Figure S6**). We have found that the highest yield of hydrogen was obtained by the use of methanol owing to the partial production of hydrogen through the methanol conversion ($\text{MeOH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$, $\Delta G^0 = 16.1 \text{ kJ/mol}$) [39]. Furthermore, it is clearly observed that the weight ratio (PPy/TiO₂) has a great influence on hydrogen production (**Figure 7a**). Modification of TiO₂ with a small amount of PPy (maximum 25% in mass) induced an increase in its photoactivity. The photocatalytic activity of 1%Pt-(PPy-TiO₂) is maximum for the PPy/TiO₂ mass ratio 2:8 and decreases drastically with higher ratios. The presence of a large amount of PPy may cover the surface of TiO₂ hindering the light absorption and the injection of excited electrons from the LUMO of PPy to the CB of TiO₂ [40].

Photocatalytic hydrogen evolution experiments were conducted in aqueous solution containing 25% methanol as a hole scavenger. The photocatalyst (1%Pt-(PPy-TiO₂)) is very active for hydrogen production in pure water under UV and visible light. The yield of H₂ production reaches 850.0 μmol and 27.0 μmol after 5 h under UV and visible light irradiation, respectively (**Figure 7b**). As shown in **Figure 7c-d**, 1%Pt-(PPy-TiO₂) exhibits the highest activity for hydrogen production with 125.1 $\text{mmol h}^{-1} \text{ g}^{-1}$ under UV light and 3.2 $\text{mmol h}^{-1} \text{ g}^{-1}$ under visible light irradiation compared with other loading rates of Pt NPs. The hydrogen evolution rate of 1%Pt-(PPy-TiO₂) was greatly enhanced with composite materials with appropriate proportion.

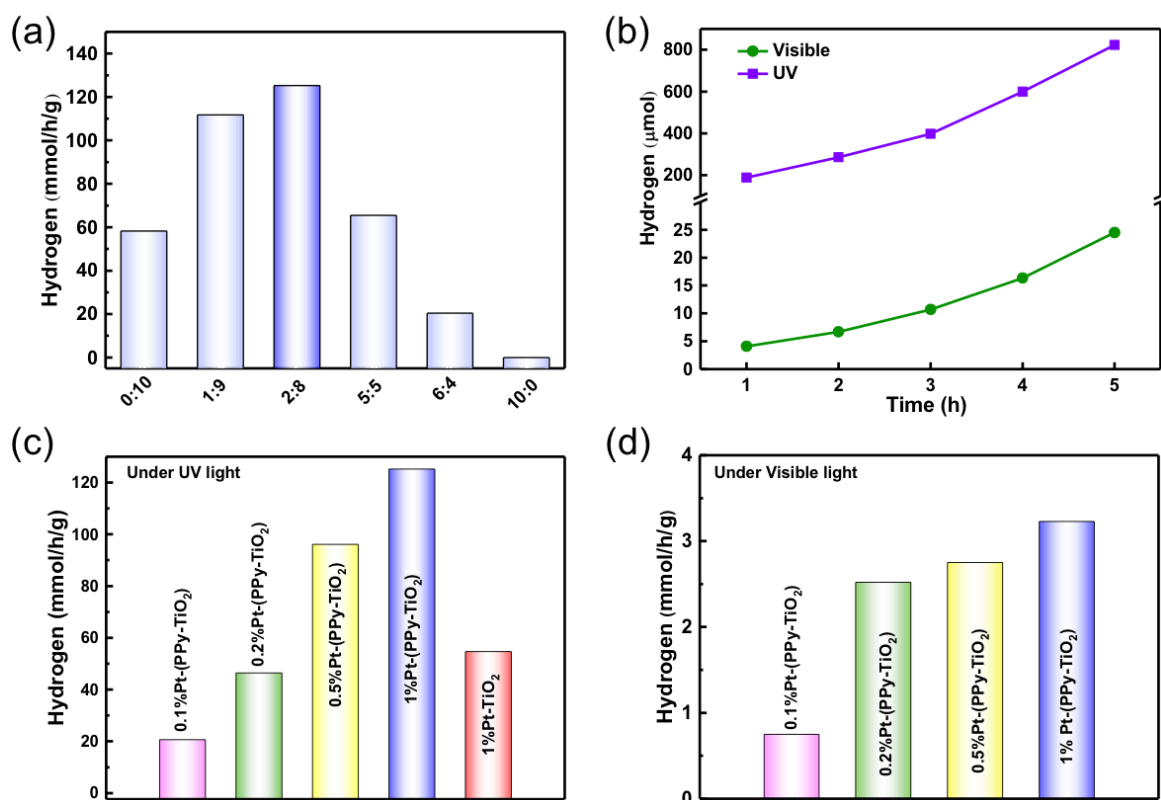


Figure 7. Different mass ratio between PPy and TiO₂ for photocatalytic hydrogen generation (a), Hydrogen production with 1%Pt-(PPy-TiO₂) in pure water under UV and visible light (b), hydrogen production with different loading rate of Pt NPs on PPy-TiO₂ (with the fixed mass PPy/TiO₂ ratio 20:80) in methanol-water mixture solution (25% methanol) under both UV light (c), and visible light (d).

1%Pt-(PPy-TiO₂) photocatalyst shows a significantly enhanced photocatalytic activity for hydrogen generation ($125.1 \text{ mmol h}^{-1} \text{ g}^{-1}$ and $3200 \text{ } \mu\text{mol h}^{-1} \text{ g}^{-1}$ under UV and visible light irradiation, respectively) compared with the same loading rate of Pt NPs deposited on PPy ($11.8 \text{ mmol h}^{-1} \text{ g}^{-1}$ under UV light and $70.9 \text{ } \mu\text{mol h}^{-1} \text{ g}^{-1}$ under visible light, respectively) and TiO₂ ($24.2 \text{ mmol h}^{-1} \text{ g}^{-1}$ under UV and $454.2 \text{ } \mu\text{mol h}^{-1} \text{ g}^{-1}$ under visible light irradiation), respectively (**Figure 8a**). The higher photocatalytic activity of Pt NPs deposited on PPy-TiO₂ can be ascribed to the routes of effective electron transfer ($e^-_{\text{PPy(LUMO)}} \rightarrow \text{Pt}$ and $e^-_{\text{PPy(LUMO)}} \rightarrow \text{TiO}_2(\text{CB}) \rightarrow \text{Pt}$) compared with (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy. Other photocatalysts for hydrogen production have been compared in **Table S1**. Our

photocatalyst Pt-(PPy-TiO₂) is very active for hydrogen production under both UV and visible light, and its performance equal or even surpass the literature reports for photocatalysts based on TiO₂ or PPy (Table S1)

For practical applications, it is important to check the stability of the photocatalyst. Figure 8b shows that the photocatalyst Pt-(PPy-TiO₂) is stable with cycling.

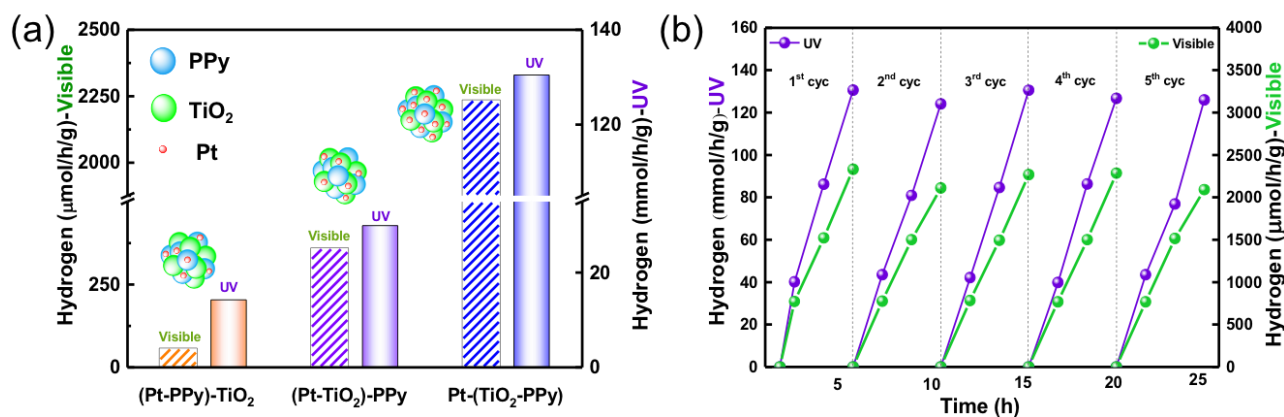


Figure 8. Hydrogen production with (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂) in methanol-water mixture solution under UV light and visible irradiation (a); The photocatalytic hydrogen production of Pt-(PPy-TiO₂) with cycling in methanol-water mixture solution (25% methanol) (b).

3.3 Electron transfer mechanism of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-(PPy-TiO₂)

The migration of electrons under visible-light in the ternary photocatalysts can be explained by the proposed mechanism in Figure 9. Firstly, photocatalytic hydrogen generation involves three main steps: (i) light absorption, (ii) charge carriers generation and charge transfer to the surface of photocatalysts, and (iii) surface redox reactions [41]. Here, PPy as a photosensitizer was used to absorb the incident light to generate e⁻ and h⁺. Pt NPs used as a cocatalysts not only serve as sinks for electrons, but also provide proton reductive sites, and centers for H[•] radical recombination leading to H₂ formation [14]. In addition, thanks to the suitable CB and VB potential positions of PPy and TiO₂, we could design this very active composite photocatalyst. The energy band structures are described in SI.

As shown in Figure 9a, for the (Pt-PPy)-TiO₂ system, the photogenerated electrons in the LUMO

of PPy transfer to Pt NPs of PPy surface and also to TiO₂ CB. Although for (Pt-PPy)-TiO₂ two electron transfer pathways are proposed, its photocatalytic activity is much lower than Pt-(PPy-TiO₂) because the protons can be reduced into H[•] on the surface of Pt much more efficiently than on bare TiO₂. Pt NPs help also to form H-H bond to lead to H₂. In addition, TRMC signals and photocatalytic tests for H₂ generation indicate that the electron could transfer from PPy to TiO₂, the LUMO of PPy being situated at higher energy position than the CB of TiO₂ [31]. The oxidation of an electron donor (such as methanol) with h⁺ happened on the HOMO of PPy (MeOH → 3H₂ + CO₂).

In (Pt-TiO₂)-PPy ternary system, PPy is introduced to create electrons from the HOMO to LUMO under visible light illumination (**Figure 9b**). The photo-induced electrons migration from PPy to the TiO₂ CB due to the position of the PPy LUMO is much more negative than that of TiO₂, and are eventually injected into the low Fermi level of Pt. As a result, rapid charge separation and slow charge recombination occurred, which results in a good photocatalytic performance. This electron transfer scheme is also illustrated in other ternary systems such as PPy-Ag-TiO₂ [40], TiO₂/CuO/Cu [42], In₂O₃-TiO₂-Pt [43].

More interestingly, the Pt-(PPy-TiO₂) composite shows the best photocatalytic activity compared with (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy, because the active Pt sites coexist in both PPy and TiO₂ (as seen in Figure 2a-b). **Figure 9c** illustrates two efficient routes of electron transfer. The excited electrons from PPy LUMO migrate to the surface of PPy and TiO₂, and then are trapped by Pt deposited on PPy and TiO₂ leading to very efficient separation of charge carriers. The most efficient charge carrier separation and transfer in Pt-(PPy-TiO₂) compared with (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy were demonstrated by TRMC technique, photoelectrochemical tests and photocatalytic activity. Furthermore, Pt NPs act as a cocatalysts for H⁺ reduction and as a site for H[•] recombination. The synergistic effect of the two electron transfer routes and formation of PPy-TiO₂ heterojunction facilitate the photocatalytic reaction process.

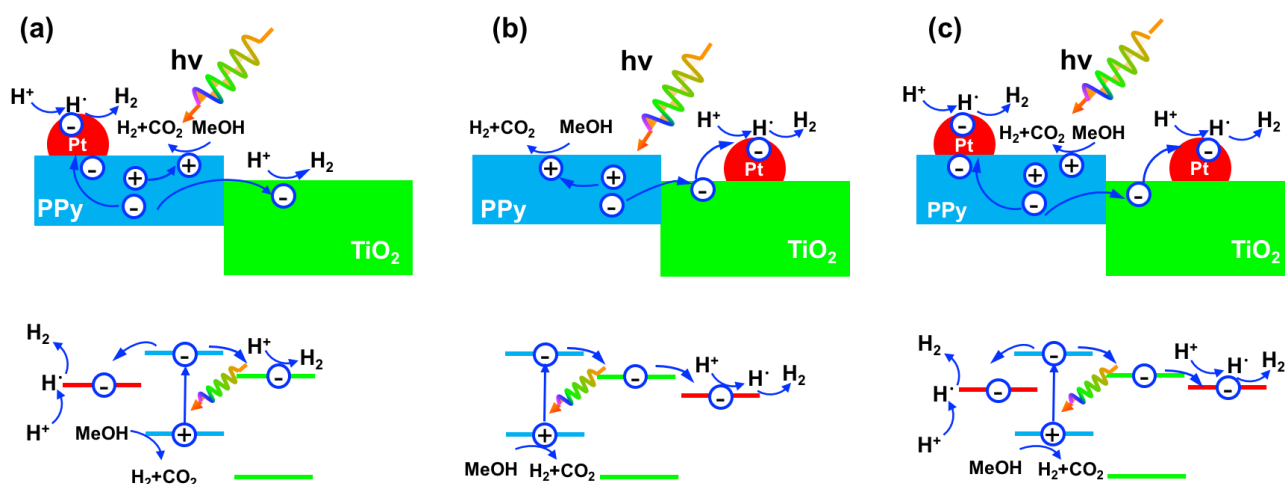


Figure 9. Scheme representation of the electron transfer, migration and hydrogen production mechanism in the hybrid photocatalysts: **(a)** (1%Pt-PPy)-TiO₂; **(b)** (1%Pt-TiO₂)-PPy; **(c)** 1%Pt-(PPy-TiO₂)

4. Conclusions

In summary, different ternary nanostructures based on PPy-TiO₂ composites with controlled site modification with Pt nanoparticles were designed. The photocatalytic activity of Pt-(PPy-TiO₂) for hydrogen generation under UV and visible light is very high and drastically surpasses those of (Pt-PPy)-TiO₂, (Pt-TiO₂)-PPy and Pt-TiO₂. With modification of both PPy and TiO₂ surface with Pt NPs, an efficient electron transfer from PPy to Pt NPs and through TiO₂ to Pt were achieved, which leads to higher charge carriers' separation and accumulation of electrons for the Pt-(PPy-TiO₂) compared with (Pt-PPy)-TiO₂ and (Pt-TiO₂)-PPy. More electrons are driven by and to the Pt nanoparticles, which also act as cocatalysts for H⁺ reduction and H-H bond formation. The Pt-(TiO₂-PPy) photocatalyst is stable with cycling. This composite may find promising applications in solar fuels generation. This study will open perspectives in the rational design of ternary composites to facilitate charge transfer for high efficient conversion of solar to chemical energy.

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