



A Comparative Study of Pt Depositing Methods (Chemical Reduction vs Photo-Assisted Deposition) onto TiO₂ Nanoparticles for Hydrogen Photo-Production

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Highlights:

- The preparation method plays a major role in Pt deposition efficiency, Pt dispersion, and H₂ generation.
- Depositing Pt on TiO₂ inhibits the recombination and reduces the band gap.
- Pt-TiO₂-CR could enhance the H₂ production up to 1.65 times compared with Pt-TiO₂-PD.

Abstract. In this paper, we report a comparative study on two methods (chemical reduction and photo-assisted deposition) of incorporating Pt onto TiO₂ nanoparticles (TNP) for H₂ generation. The phase structure of the photocatalysts was scrutinized utilizing TEM and XRD. The degree of dispersion of Pt on the TNP was measured by a pulse chemisorption technique using TPDRO equipment. The results provided by TEM imagery, EDX spectra, elemental mapping, and AAS confirmed the successful deposition of Pt on TNP. XRD patterns confirmed an anatase and rutile crystallite structure, while UV-Vis spectra showed reduction of the bandgap from a typical value of 3.2 eV to ca. 2.9 eV. It was found that there is a correlation between the amount of Pt deposited on the TNP and Pt dispersion with H₂ generation. The chemical reduction method offered a higher degree of Pt deposition, resulting in a 2.75 times larger amount of deposited Pt compared to photodeposition. This feature is perceived to contribute a higher H₂ yield (3,283 μmol) at 1 w% of Pt loading.

Keywords: *chemical reduction; hydrogen; photodeposition; platinum; TNP.*

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1 Introduction

Energy and the environment have become crucial issues over the past few decades, mostly due to excessive exploitation of fossil-based fuels [1,2]. Hydrogen has attracted much attention in recent years, as it is a promising candidate for the replacement of fossil-based fuels, owing to its clean nature and the rapid development of fuel cells, for which hydrogen is the main fuel [3-8]. Tremendous efforts have been made on finding the most suitable technology to generate H₂. H₂ should be produced from renewable sources, e.g., water and biomass feedstock, via a benign pathway such as photocatalysis [3,5-7]. Utilizing solar energy for photocatalysis in producing hydrogen is perceived to be an ideal strategy as a conventional hydrogen route. Introducing organic and inorganic sacrificial agents in a cost-effective photocatalytic reaction system could enhance hydrogen generation from both kinetic and thermodynamic viewpoints [2,5,6,9].

Alcohols have been utilized as sacrificial agent due to their affinity towards photocatalytic reactions. The oxidation of alcohols such as glycerol suppresses the recombination of photogenerated electrons-holes [2,5,6,10-13]. To date, glycerol has been regarded as waste, however, it can be used as a renewable resource in H₂ production [5]. Thus, the production of H₂ and waste removal are expected to occur simultaneously [5,9]. It can serve as a reactant that undergoes hole-driven oxidation reactions, thus obstructing electron-hole recombination [9,14] and suppressing the O₂-H₂ back reaction to water [15,16]. The principle of water splitting, or photo-reforming of sacrificial agents is that when a semiconductor such as TiO₂ is contacted with H₂O that contains a sacrificial agent, an electron in the conduction band can reduce the water to produce H₂ if the level of the conduction band is more negative compared to the H⁺/H₂ reduction potential [9]. Liquids such as ethylene glycol, acetone, acetol, acetaldehyde, acetic acid, ethanol, and methanol, and gases such as methane, ethane, and CO are some intermediate products that evolve in the glycerol photo-reforming on Pt-TiO₂ as reported by previous studies [4,16].

TiO₂ is arguably the most promising and versatile material for photocatalytic systems owing to its cost-effectiveness, high photocatalytic activity, photostability, and non-toxicity [2,17,18]. However, it has high-rate recombination of photo-generated electron-hole pairs and can only absorb UV light (the bandgap of TiO₂ is 3.2 eV for anatase and 3.0 eV for rutile) are not ideal for solar application because only 3 to 5 % of UV light is present in solar energy [2,18-20]. Serious efforts have been conducted by loading noble metals such as Pt, Pd, Au, Rh, Ru, and Ag to hamper the rapid recombination of electron holes as well as to narrow the bandgap or activity under visible light illumination [6,10,11,21]. A noble metal with a larger work function and a lower Fermi level than TiO₂ would more easily trap electrons [21,22].

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

Among the noble metals, Pt has the largest work function (5.65 eV) and is a promising co-catalyst as electron trapper [6,17,22]. It also has low overpotential for solar harvesting fuel generation and is very stable [23]. Platinization of TiO₂ can be done with many methods, such as Pt ion-exchange, incipient wetness, chemical reduction, and photodeposition on TiO₂ nanotubes/TNT [21,24-26]. Wet/incipient impregnation, precipitation, photochemical deposition, impregnation, and sol-gel methods for decorating Pt on TiO₂ nanoparticles/TNP [21,26], modified photo irradiation-reduction, Pt photodeposition on TiO₂ nanotube arrays/TNTA have also been conducted. On the other hand, chemical reduction and photodeposition methods have been reported as effective and common techniques for depositing Pt on TNP [5,6,24]. The suspended photocatalytic system has benefits in terms of its inexpensiveness and easy operation. Our previous study used these two methods on TiO₂ nanotube arrays/TNTA [4] for H₂ generation.

It is urgent to study these two methods in detail and provide a comparison to find the most effective method for depositing Pt on TNP, due to its expensiveness, especially for hydrogen production from glycerol-water solution. Detailed studies comparing the two methods, evaluating the characteristics and their application to produce hydrogen with glycerol as a sacrificial agent have rarely been done. The previous studies that have been conducted on Pt-TNP/TNT as a photocatalyst for hydrogen production are presented in Table 1.

Table 1 Previous studies on Pt-TNP/TNT as a photocatalyst for hydrogen production.

Photocatalyst/Ref	Doping method	Sacrificial agent	H ₂ generation (4 hours)
Pt-TNP, 1 g/L	Photodeposition		1.988 mmol
Pt-TNP, 1 g/L (this study)	Chemical Reduction	Glycerol	3.283 mmol
Flourinated Pt-TNP, 1.5 g/L, [5]	Photodeposition	Glycerol	8.4 mmol
Pt-TNT, 1g/L [6]	Photodeposition	Butyric acid	2 mmol
Pt-TNP, 1g/L[11]	Photodeposition	Ethylene glycol	6 mmol
Pt-TNT [24]	Chemical Reduction	Ethanol	30 mmol/h/g cat
Pt-TNT [21]	Photodeposition/Chemical Reduction	Glycerol	173 mmol/h/g cat

Herein, we performed Pt deposition on the surface of TiO₂-P25 or TNP using chemical reduction with NaBH₄ as reduction agent (Pt-TNP-CR) and photodeposition with the electron as reductor (Pt-TNP-PD) to enhance the

photocatalytic performance in producing hydrogen from 10 v% glycerol solution as a model of biodiesel waste. Based on the above-mentioned data and the information in the previous paragraphs, we claim that the comparison of deposition methods is the academic novelty of this study. The photocatalysts were characterized with the use of TEM/FESEM-EDX, AAS, XRD, and UV-Vis DRS equipment. The Pt dispersion or chemisorption active surface area of the as-prepared samples was analyzed using TPDRO equipment. Based on the relevant characterization, the role of Pt depositing methods on TNP was investigated.

2 Material and Methods

2.1 Materials

TiO₂-P25 (TNP, Evonic Degussa Co), chloroplatinic acid (H₂PtCl₆·6H₂O, Sigma Aldrich), sodium borohydride (NaBH₄, Sigma Aldrich 99%), methanol (Merck, 99% and >99.9%), ethanol (Merck, 96% and >99.5%), and glycerol (Brataco, 98.8%) were purchased and used without further purification. All solutions were prepared using high-purity distilled water.

2.2 Platinized TiO₂ (Pt-TNP)

2.2.1 Chemical Reduction Method

To prepare Pt-TNP-CR, a suspension of 2 g TNP in 400 ml of aqueous solution with precursor H₂PtCl₆ (loading Pt = 1 wt%) was added with an excess of NaBH₄ under stirring for 1 h. After chemical reduction occurred, centrifugation of the solution for 20 min was performed and the filtrate was washed twice with distilled water and ethanol. The slurry was then evaporated by drying on a temperature-adjustable electric hot plate at 90 °C for about 3 h, heated at 130 °C for 1 h, and finally calcination was performed at 500 °C for 1 h in a furnace. The photocatalyst sample is denoted as Pt-TNP-CR.

2.2.2 Photodeposition

A suspension of 2 g TNP in 360 ml of aqueous solution with precursor H₂PtCl₆ (loading Pt = 1 w%) was added to 40 ml of a water-methanol mixture (10 v/v% methanol). Photodeposition of Pt on TNP was performed for 6 h in a Pyrex glass reactor that was placed inside a reflection box equipped with magnetic stirrer and six UV-A lamps (11 watts). After photodeposition, centrifugation of the solution was executed for 20 min and the filtrate was then washed with distilled water. Evaporation of the slurry was followed by calcination, similar to the chemical reduction method. The photocatalyst sample is denoted as Pt-TNP-PD.

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

2.3 Characterization of Pt-TNP

The surface morphology of the Pt-TNP was examined using a Transmission Electron Microscope (TEM, FEI BM-Eagle Microscope Tecnai 200 kV D2360 SuperTwin). To determine the elemental mapping in the photocatalyst, an energy dispersive X-ray analyzer (EDX) was attached to a FESEM (FEI-Inspect F50). The average size of the Pt nanoparticles was calculated by measuring the diameter of each Pt nanoparticle (using the Image J software) and then averaging was done according to the number of existing nanoparticles. Using the Origin software, we determined the Pt size distribution on the TNP. The real Pt deposited on the prepared Pt-TNP was measured using Atomic Absorption Spectroscopy (AAS Analyst 400 type, Perkin Elmer).

TPDRO equipment (Chemisorp 2750, USA Micrometric) was used to measure the chemisorbed surface area of the Pt-TNP by pulse chemisorption based on UOB Method 945-96. First, helium was introduced to the TPDRO quartz reactor containing the Pt-TNP sample, which was heated to 240 °C to remove any adsorbed gases and moisture. The temperature was then increased to 580 °C to remove other species, so that only pure Pt would be loaded on the surface of the TNP. Subsequently, the temperature was brought back to room temperature. Pulse chemisorption measurement was performed by introducing a known amount of pure hydrogen (UHP 99.999%) into the TPDRO quartz reactor, which contained a certain amount of the sample. The un-adsorbed residual hydrogen by Pt coming out after chemisorption was measured. Using this method, the chemisorption surface area was calculated from the amount of chemisorbed hydrogen mass of the sample and Pt loading. The ratio of H₂ chemisorbed by the photocatalyst with the amount of Pt in the photocatalyst (H₂/Pt) indicates the Pt dispersion in the photocatalyst. If this ratio is equal to 1, 100% of the Pt was dispersed completely.

The crystalline phases of the Pt-TNP were identified using an X-ray diffractometer (Shimadzu XRD 7000) with Cu K α ($\lambda = 0.154184$ nm) as the X-ray source, a scan rate of 2° min⁻¹ over a 2 θ range of 10-80°, operated at 40 kV and 30 mA. The crystallite sizes of the photocatalyst were estimated from FWHM (full-width at half-maximum) by the Scherrer equation. To study the effect of the Pt deposited on the TiO₂ on the energy bandgap of the photocatalyst samples, UV-Vis DRS analysis was employed using a spectrophotometer (Shimadzu 2450). The absorbance and reflectance of the samples were recorded under ambient condition in the wavelength range of 200 to 600 nm.

2.4 Photocatalytic H₂ Generation

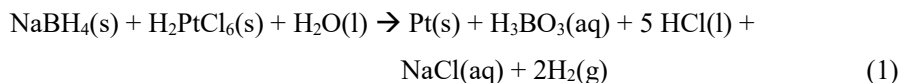
The photocatalytic H₂ production experiments were evaluated in a 500 ml Pyrex glass reactor that contained 200 ml of glycerol-water mixture with 10 v% glycerol

and was equipped with a mercury lamp (Philips HPL-N 250 W/542 E40 HG ISL, 83% visible and 17% UV light) as photon source and thermocouple. The lamp was positioned one cm away from the reactor as a photon source to trigger the reaction. The photoreactor system was placed inside a reflector box and the reactions were carried out under 4 h of irradiation. Before the commencement of the reaction, the Pt-TNP in the reactor flask was magnetically stirred for about 30 min. The reactor was then flushed with argon to remove air to avoid disturbance during H₂ generation. Any H₂ generated produces a peak and the amount of H₂ was estimated from the peak area every 30 min via online sampling using a Shimadzu Gas Chromatograph (GC 2014). For H₂ and CO₂ analysis, a molecular sieve (MS Hydrogen 5A, 80-100 mesh) column and CO₂ Porapak N packed column (L = 6 m, Di = 2.2 mm) were available in the GC that was interfaced to a personal computer. To record the signal/peak of H₂ and CO₂ generated, a Thermal Conductivity Detector (TCD) was employed. The data presented were processed repeatedly. This GC system could detect the area of H₂ and CO₂ peaks below 50 counts and was equipped with GC solution software. High-purity argon (99.99%) was used as carrier gas at 50 cm³/min.

3 Result and Discussion

3.1 Preparation of Pt Deposited on TNP

The reaction of Pt loading on TiO₂ (TNP) via chemical reduction with chloroplatinic acid as Pt precursor can be described as follows [4,24]:



NaBH₄ was added into an H₂PtCl₆ solution that had been pre-mixed with TiO₂, leading pH to increase from 5 to 9, as well as color alteration from white to black, indicating that ionic Pt was reduced to metallic Pt. The mixing of Pt with TiO₂ resulted in Pt deposition on the photocatalyst. The photo deposition method, on the other hand, involved the excitation of electrons from TiO₂ VB to CB, and hole scavenging by methanol. Electrons concomitantly reduce ionic Pt according to [4,21]:



In-situ reduction of ionic Pt on the TiO₂ surface allows the deposition of Pt on the TiO₂ surface, forming a Pt-TiO₂ composite.

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO_2 Nanoparticle for Hydrogen Photo-Production

3.2 FESEM/TEM and AAS Analysis

The EDX spectra and elemental mapping of Pt-TNP with 1 wt% Pt loading are presented in Figure 1. These results indicate the presence of Pt on the TNP. According to this data, the Pt was deposited on the TNP, both in case of chemical reduction and photodeposition.

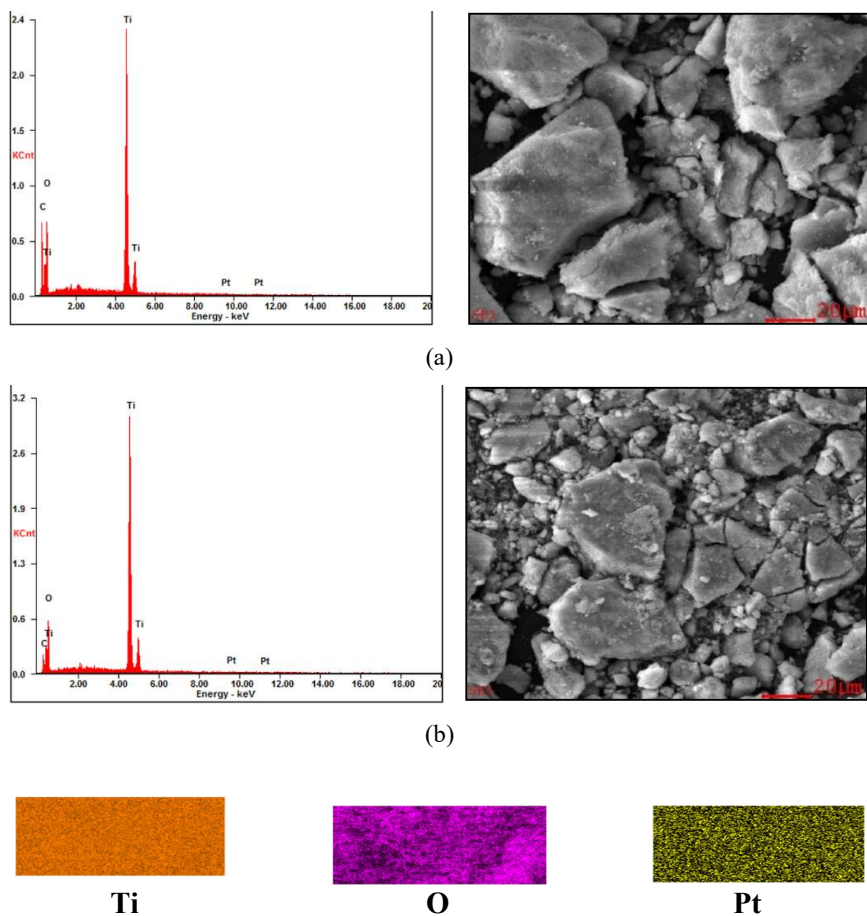


Figure 1 EDX spectra, SEM image and elemental mapping of synthesized catalyst: (a) Pt-TiO₂-CR and (b) Pt-TiO₂-PD.

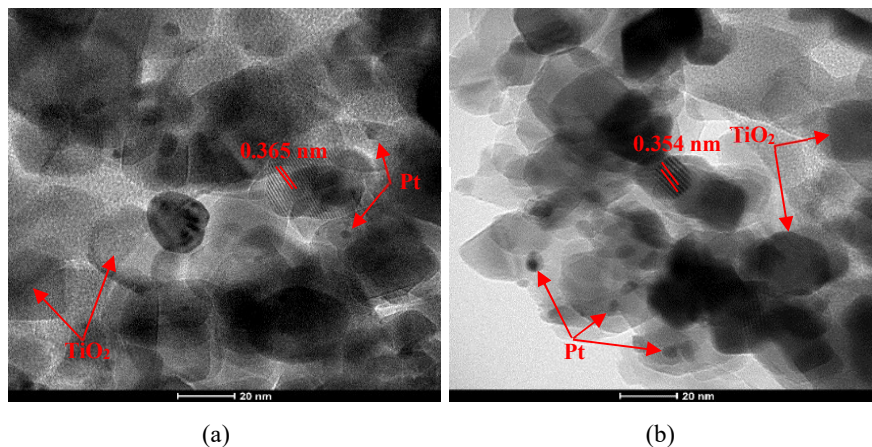


Figure 2 TEM images of: (a) Pt-TiO₂-PD, (b) Pt-TiO₂-CR with small dot nanoparticles showing decorated Pt on the surface of TiO₂ nanoparticles.

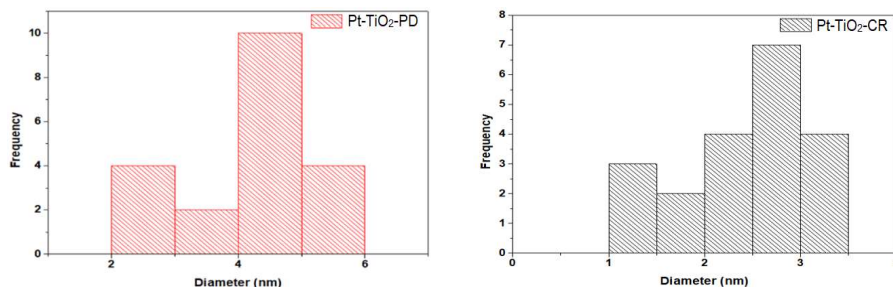


Figure 3 Pt deposit size distribution for Pt-TiO₂-PD and Pt-TiO₂-CR. The number of counts used to determine average Pt deposit size was 20 particles.

3.3 Pt Dispersion Analysis

The degree of dispersion (%) of the Pt on the TNP surface is the ratio between the amount of H₂ adsorbed (chemisorption) by the Pt and the total amount of Pt in the photocatalyst. Table 2 presents the chemisorption surface area and the degree of dispersion of the Pt-TNP. This characterization used the basic calculation of 1 wt% of Pt loading on the TNP.

From Table 2, it can be inferred that the chemical reduction method offered a higher degree of Pt dispersion (82.7%), i.e., 70% more than the photodeposition method (47.8%). As a result, this method presents a higher chemisorbed surface area. The higher the degree of dispersion, the better the photoactivity of the Pt-TNP since it has a larger surface area for reaction sites [6,24,28,29]. The lower Pt dispersion on Pt-TNP-PD could be caused by the lower amount of Pt deposited

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

on the TNP as shown in the AAS result. If 3.45 ppm of Pt deposited on Pt-TNP-PD gave 47.8% Pt dispersion, 9.48 ppm of Pt deposited on Pt-TNP-CR should give more than 82.7% Pt dispersion. This means that there is little agglomeration on Pt-TNP-CR. Since the Pt-TNP-CR photocatalyst has a smaller Pt particle diameter and this method can deposit a larger amount of Pt on TiO₂, chemical reduction is usually favored over other methods (e.g. evaporation or thermal decomposition). It has been reported that chemical reduction of Pt with precursor H₂PtCl₆ and NaBH₄ as reducing agents exhibited 95% dispersion for 1.25% wt of Pt-decorated TiO₂ nanotubes [24]. The chemisorption results (Table 2) were in accordance with the FESEM/TEM/AAS data and give evidence of Pt deposited on TNP. Highly dispersed Pt is better than agglomerated Pt in enhancing the photocatalytic performance on g-C₃N₄ [30].

Table 2 Chemisorption surface area and degree of dispersion of Pt on TNP.

Parameter	Pt-TNP-CR	Pt-TNP-PD	Unit
Degree of dispersion (%)	82.7	47.8	%
Chemisorbed surface area	2.04	1.18	m ² / g sample

3.4 XRD Analysis

XRD patterns of the photocatalyst samples are depicted in Figure 4. The observed peaks at 2θ of 25.3°, 37.8, 48.0°, 54.3°, 55.05° respectively, correspond to the Miller indices of (101), (004), (200), (105), (221), which conform to anatase phase (JCPDS No. 21-1272).

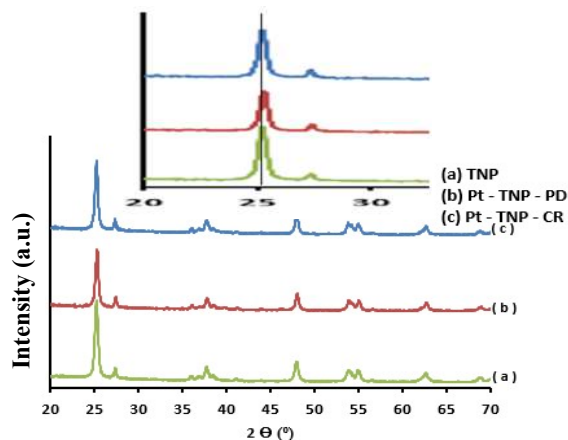


Figure 4 XRD patterns of TNP, Pt-TiO₂-PD, and Pt-TiO₂-CR.

The weak signals at 2θ of 27.4° and 36° conform to rutile phase (JCPDS No. 21-1276) [14]. The amount of Pt loading on TNP (1 wt%) was not enough to induce

diffraction peaks, since Pt peaks would not be found at a low Pt concentration and a high Pt dispersion on TNP [10,21]. A Pt peak appears when Pt loading is 3 wt% at 2θ of 39.8, and 46.4° [23]. The crystallite size of the composites was calculated to be 24, 23, and 29 nm for bare TNP, Pt-TNP-PD and Pt-TNP-CR, respectively, based on applying the Scherrer formula on the broadening of the XRD peak at 25.3°.

The crystalline size is increased with the deposition of Pt on TNP and Pt deposited on TNP could influence the degree of crystallinity and the crystallite size. There was a small shift in the peak position on the Pt-TNP-PD and the Pt-TNP-CR (Figure 4 inset), meaning that Pt deposition alters the lattice parameters of TNP [30]. Meanwhile, the diffraction patterns of the photocatalyst samples were similar.

3.5 Bandgap Analysis

The bandgaps of various photocatalysts estimated by interpretation shown in Figures 5(a) and 5(b) present the UV-Vis absorption spectra of the photocatalyst samples. These results indicate that deposition of Pt on the TNP improved the response to visible light due to the lowered bandgap from 3.25 eV (TNP) to 2.96 eV (Pt-TNP-CR) and 2.98 eV (Pt-TNP-PD). The decrease in bandgap is most likely due to the deposition of Pt on TNP, as reported by several authors [6,10,16,25]. This phenomenon indicates that the loading of Pt affects the lattice of TNP, which is in line with the XRD results. A similar result, the bandgap of the original anatase TNTA (3.2 eV) was reduced to 2.93 eV after Pt was deposited on the TNTA as previously studied [4]. With a reduced bandgap of Pt-TNP, absorption of photon energy becomes lower for electron excitation, which is thermodynamically advantageous for hydrogen production and leads to high photocatalytic performance under visible light.

The bandgap energy of Pt-TNP-PD is bigger than that of Pt-TNP-CR because of the larger-size metal Pt particles on Pt-TNP-PD (4.4 Nm) compared to the Pt particles on Pt-TNP-CR (2.8 Nm) [25]. The lowering bandgap of Pt-TNP suggests that decoration of Pt on TNP can promote a redshift of photon absorption [6,10,25]. In addition, the ascension of visible-light absorption caused by the incident photon frequency resonates with the collective excitations of electrons of noble-metal nanoparticles on the conduction band. This phenomenon is called localized surface plasmon resonance (LSPR) [31].

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto Tio2 Nanoparticle for Hydrogen Photo-Production

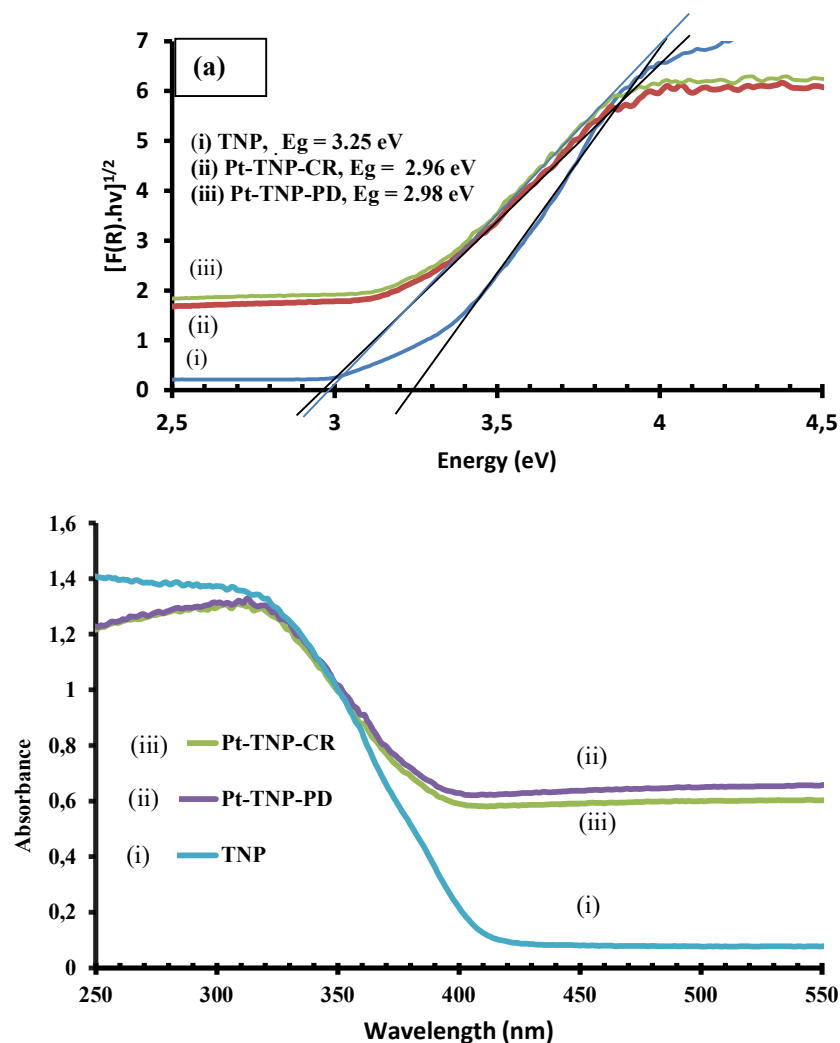


Figure 5 (a) Tauc plot of transformed Kubelka-Munk function vs energy ($h\nu$) and (b) UV-Vis absorption spectra for TNP, Pt-TiO₂-PD, and Pt-TiO₂-CR.

3.6 Photocatalytic Test for H₂ Generation

Figure 6 presents the accumulative H₂ production (μmol) from the glycerol solution as a function of irradiation time (240 min) for different photocatalyst samples. From this figure, the rate of hydrogen generation was 97.5, 4104 and

2485 $\mu\text{mol}/(\text{h.g catalyst})$ for the TNP, the Pt-TNP-CR, and the Pt-TNP-PD, respectively. The temperature of the photoreactor was measured using a thermocouple along the process; it was constant at about 80 °C after 75 min of irradiation. To maintain this condition, an exhaust fan was set up. The 10% glycerol concentration in this study represents its concentration in biodiesel waste, which is sufficient to give a substantial improvement to photocatalytic H_2 generation by Pt-N-TNT [4,16].

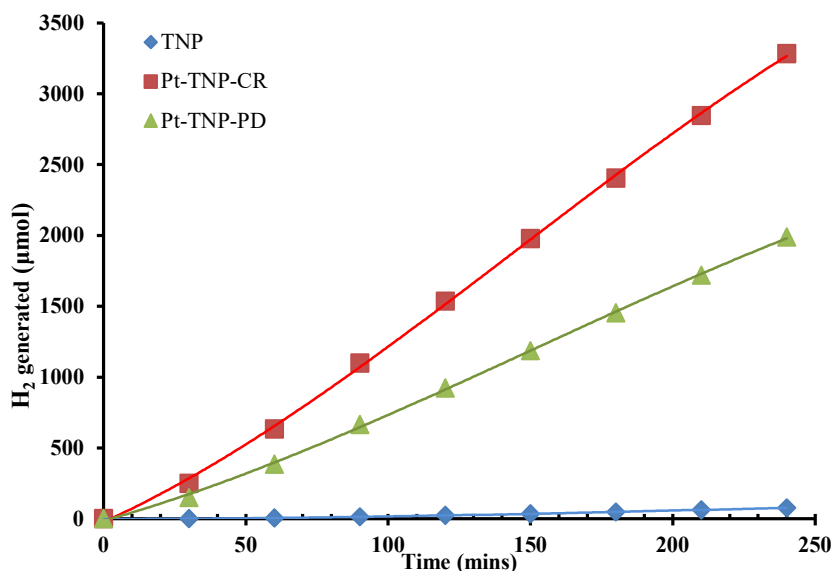


Figure 6 Accumulative H_2 production on the TNP, the Pt-TNP-CR and the Pt-TNP-PD as a function of irradiation time. Suspension volume = 200 ml; catalyst loading = 1 g/L.

The Pt-TNP-CR produced 3283 μmol of H_2 , i.e., 1.65 times higher compared to the Pt-TNP-PAD (1988 μmol). These results are significantly higher than those obtained by unmodified TNP (78 μmol). The small H_2 production by pure TiO_2 compared to platinumized TiO_2 has also been reported by Xing *et al.* [5,11,21,32]. The enhancement in H_2 production over deposition of Pt on TNP is attributed to the fact that Pt acts as an electron trapper that inhibits electron-hole recombination, thus increasing the photocatalytic activity [6,10]. It is well-documented that electron-hole recombination occurs in the order of ns, while charge conduction occurs in the order of μs or even ms. Therefore, without an electron anchor, photogenerated electron-hole pairs typically undergo unrestricted recombination [24]. The superiority of Pt-TNP-CR over Pt-TNP-PD

A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

in photocatalytically producing H₂ can be ascribed to its higher Pt depositing amount and smaller Pt size, which may lead to better interaction between Pt and CB electrons, as well as with H⁺ as a reduction target on the CB. Electron anchoring by Pt requires an abundance of holes available for oxidation in VB, hence improving the reaction rate of glycerol oxidation. As a result, recombination could be suppressed, since more electrons react with H⁺, producing H₂, and more holes oxidize glycerol, producing CO₂ and H₂. However, the Pt nanoparticle size in the range of 1-4 nm is not a major determining factor in the photocatalytic production of H₂, as reported by previous researchers [32].

The mechanism of electron trapping and H₂ production on the Pt-TNP is shown in Figure 7. In the context of Pt as an electron trapper, thermodynamic requirements entail that the work function of Pt must be higher than that of TNP [15,26], and the Fermi level of the TNP should be higher than that of the Pt. When Pt particles are coupled with TNP, electron transfer takes place from the CB of the TNP to the Pt until their Fermi levels are aligned or reach the same level [6,33]. As a result, a space charge region is formed on the side of the TNP, which causes an upward bending of the energy band. When the Pt-TNP absorbs photons, electrons are excited from the TNP VB to the CB and are subsequently transferred to the Pt, allowing a further upward bending of the energy band over the TNP. Thus, the photogenerated electrons cannot backflow due to the Schottky barrier. As a result, electron-hole pair recombination is reduced since the Pt-TNP composite facilitates their separation, which results in boosted photocatalytic activity [34]. Furthermore, the smaller the metal particle size, the greater the shift in Fermi level to the CB, which results in greater photocatalytic reduction efficiency [24,33]. Dispersed Pt on the TNP could also improve the reaction rate of water splitting by reducing the overpotential of proton reduction [15]. Electron transfer from Pt-TNP to H⁺ adsorbed species can only occur when the Fermi level of the composite is more negative than the H⁺/H₂ reduction potential [24]. In this case, the Pt acts as a co-catalyst for hydrogen production as well as for glycerol photo-oxidation.

The existence of CO₂ was detected by the GC probe, but it was not measured. It gave evidence that photo-reforming of glycerol occurs since it is oxidized by the hole, ·OH and/or oxygen produced by the splitting of water to produce several intermediate compounds, followed by H₂ and CO₂ generation as the end product [4, 9,15,16]. Thus, the availability of glycerol in the reactant could enhance the photoactivity of TNP, since it is involved in the hole-participated oxidation reaction, which results in reducing electron-hole recombination, avoiding backward reaction regenerating water molecules [4, 9,15,16].

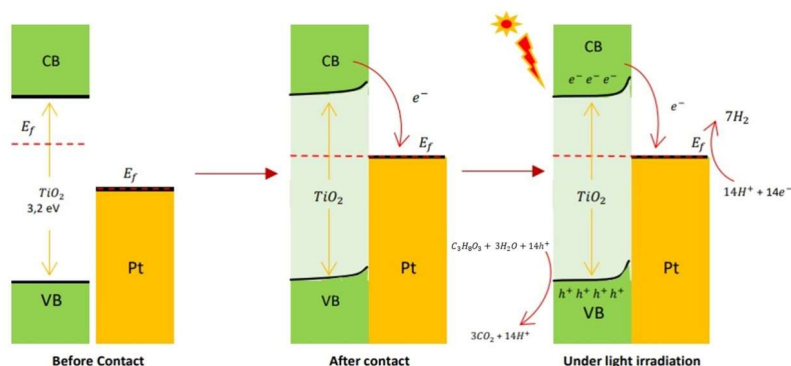


Figure 7 The mechanism of electron trapping and H₂ production on the Pt-TNP before and after coupling under light irradiation, and the redox reaction in the photo-reformation of glycerol.

4 Conclusion

Deposition of Pt on TiO₂-P25/TNP via chemical reduction and photodeposition methods was successfully achieved. The characterization results confirmed that the chemical reduction method offers more efficient Pt deposition and better nano-sized features. Ultimately, Pt-TNP obtained by chemical reduction offers more prominent photocatalytic H₂ production than its counterparts (unmodified TNP and Pt-TNP obtained via photodeposition). While depositing Pt on TNP did not affect the structure and overall morphology of the TNP, the data indicated that the band gap was lowered.

Loading 1 wt% of Pt on TNP is necessary since it can reduce recombination and promote photocatalytic activity and therefore can enhance hydrogen generation from a glycerol-water mixture under UV and visible light as compared to unmodified TNP. Thus, we conclude that the preparation method by which photocatalysts are synthesized plays a major role in the deposition efficiency and the dispersion of Pt particles, which eventually determine H₂ generation activity.

Acknowledgments

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A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

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A Comparative Study of Pt Depositing Methods (Chemical Reduction Vs Photo-Assisted Deposition) Onto TiO₂ Nanoparticle for Hydrogen Photo-Production

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