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PHOTOCATALYTIC HYDROGEN PRODUCTION FROM GLYCEROL-WATER OVER METAL LOADED AND NON-METAL DOPED TITANIUM OXIDE

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ABSTRACT

Modifications of the TiO_2 P25 photocatalyst with metals: Platinum (Pt), Copper (Cu) and non-metal: Nitrogen (N) doping to produce Hydrogen (H_2) from a glycerol-water mixture have been investigated. The metals (Cu and Pt) were loaded into Titanium Dioxide (TiO_2) surface by employing an impregnation and Photo-Assisted Deposition (PAD) method, respectively. As prepared the metal doped TiO_2 photocatalyst was then dispersed into an ammonia solution to obtain N-doped photocatalysts. The modified photocatalysts were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). XRD patterns indicated that the modified TiO_2 photocatalysts have a nano-size crystallite range of 16-23 nm, while the DRS analysis showed that the doping of both metal and non-metal into TiO_2 photocatalysts could effectively shift photon absorption to the visible light region. The optimum Cu loading of Cu-N-TiO_2 was found to be 5%, resulting in a 10 times higher H_2 production improvement level when compared to unloaded TiO_2, even though this is still considered to be inferior compared to that of a 1% Pt loading, which results in a 34 times higher level than an unmodified TiO_2 photocatalyst. The effect of glycerol concentrations on hydrogen production has also been studied. This method offers a promising technology to find renewable and clean energy by using cheap materials and a simple technology.

Keywords: Glycerol; Hydrogen production; Nanocomposite; Photocatalyst; TiO_2

1. INTRODUCTION

Hydrogen (H_2) is considered to be a promising alternative energy source, due to its high thermodynamic efficiency. Because it does not produce pollutant gases, such as mono-nitrogen oxides (NO and N_2) known generally as NO_x and Carbon Monoxide (CO_x) gases during combustion, H_2 is definitely a clean and green energy source (Iriondo et al., 2009; Daskalaki & Kondarides, 2009). However, about 95% of H_2 is still produced from fossil fuels (non-renewable resources) through pyrolysis (a thermodynamic or a reforming process), (Iriondo et al., 2009; Daskalaki & Kondarides, 2009), and only 5% of H_2 is produced from renewable resources through electrolysis of water. Moreover, these processes are still intermediate technologies, since they require a large amount of energy to produce H_2 (Luo et al., 2009).

One of the potential alternative methods to produce H_2 is the conversion from glycerol, $C_3H_8O_3$ which is cheap and sometimes found as waste. Such conversion has several advantages, including: (a) utilizing renewable energy resources as feedstock; (b) reducing the cost of

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glycerol handling and storage in the biodiesel industry, and (c) increasing the economic value of glycerol (Iriondo et al., 2009). Photocatalysis with a TiO_2 photocatalyst has been shown to be effective in the conversion from glycerol to H_2, and it is usually referred to as the photo-reforming of a glycerol-water mixture. In addition to being environmentally friendly, the photo-reforming process is considered to be an energy-efficient process, since the photons can be obtained from a UV lamp or sunlight. Once photons with suitable energy are exposed to a TiO_2 surface, electrons and holes are generated as photo-charges. The holes oxidize glycerol to produce protons in anode and electrons reduce protons into H_2 in the cathode (Lalitha et al., 2010).

Modification of TiO_2 to improve its performance in H_2 production has been widely studied in several aspects. Most of these aspects enhance photo-charge separation by loading metal as an electron trapper or modifying the band gap by non-metal doping, such as with Nitrogen (N) to improve the visible light response. Metals with a lower Fermi energy level than that of TiO_2 can trap and transfer the photo-excited electrons from the conduction band to reduce protons into H_2, while the holes remain in the valence band. Pt has also been widely used as co-catalyst for TiO_2-based H_2 production, due to its low Fermi energy level. However, Pt is an expensive material, so that it is not economically suitable for many applications. Therefore, other metals like Cu are promising candidates for the photocatalytic hydrogen production. Utilization of these metals gives an advantage not only in terms of electron-hole separation, but also synergisms in a ‘dark reaction’, since those metals, in and of themselves, are suitable for thermal reforming of hydrocarbons. On the other hand, incorporation of the N atoms in the TiO_2 lattice has been reported to effectively reduce the band gap by mixing the p states of N with the O-2p states, leading to the valence band rising, while the position of conduction band remain unchanged, (Zhang et al., 2010). Despite the advantage of this approach, which leads to a visible light active TiO_2, many obstacles then appear. These obstacles include the difficulty of synthesizing a composite catalyst with a high N content, low photocatalytic activity in the UV range, instability of N species in the catalyst system during photocatalytic process, the lack of oxidation power in the holes produced, and the high rate of recombination as a result of the band gap narrowing and the catalyst impurity factor (Zhang et al., 2010).

This present study is intended to investigate the significant effect of metal and non metal doping on TiO_2 toward H_2 photo-production process from glycerol-water mixture. By those approaches, this study proposes an effective, environmentally friendly, and relatively low cheap process to produce H_2 from renewable resources.

2. EXPERIMENTAL PROCESS

2.1. Catalyst Preparation

M-N-TiO_2 photocatalysts were prepared in two stages: firstly, loading of the metal dopant M to TiO_2 and incorporating Nitrogen into M-TiO_2 photocatalyst. Preparations of M-TiO_2 were conducted by employing two distinct methods: (1) impregnation for Cu doping and (2) Photo-Assisted Deposition (PAD) method for Pt loading. Doping of N was performed by dispersing M-TiO_2 into the NH_3 solution (25% w).

Impregnation of Cu into TiO_2 was performed by the following steps: copper salt precursor ($Cu(NO_3)_2.3H_2O$, 99% purity, Merck) in desired amounts was dissolved into 100 mL of deionized (DI) water. TiO_2 was then dispersed into the solution, followed by stirring and sonication for 1 hour. The suspension was then heated to 90^oC for 1 hour. Solvent removal (drying) was performed in a furnace at a temperature of 130^oC for 1 hour. As for the (PAD) method, the desired amount of TiO_2 and $H_2PtCl_6.6H_2O$ was dispersed into 300 mL of DI water and methanol mixture (10% v/v of methanol). The PAD method was performed in a Pyrex photo-reactor using a 10W UV-A lamp (6 units). Furthermore, the solution was then separated by a centrifuge for 15 minutes and then dried in a furnace at 130^{o}C for 1 hour.

N atoms were doped into M-TiO_2 by dispersing M-TiO_2 into a 0.5 M NH_3 solution for 24 hours. The solution was separated by centrifugation for 15 minutes and then dried in a furnace at 130^{o}C for 1 hour. Finally, the M-N-TiO_2 powder was annealed at 500^{o}C for 1 h.

2.2. Catalyst Characterization

The M-N-TiO_2 photocatalysts were characterized by several analytical methods. Accordingly, Diffuse Reflectance Spectra (DRS) analysis was performed using a Shimadzu UV2450-type spectrophotometer. Reflectance spectra were measured at ambient conditions at wavelengths of 300-550 nm. XRD analysis was performed to identify the crystallite structure, size and preferred orientation of M-N-TiO_2. X-Ray Diffraction (XRD) analysis was performed using a XRD brand-type APD PHILIPS 1710 with a Cu anode tube (λ = 0.154184 nm). The XRD tube runs at a voltage of 40 kV and a current of 20 mA, with a scanning rate of 0.02 °/min and a scanning range of 2θ = 10–80^o. Crystallite size was obtained from the half maximum of the XRD peak width using the Scherrer equation. Scanning Electro-Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) analysis was conducted to investigate the surface morphology and determine the chemical composition of M-N-TiO_2 catalyst, using JEOL JSM 6510 LA, with 2000-50000× magnifications.

2.3. Photocatalytic Reaction

Photocatalytic reactions were performed in a Pyrex photo-reactor. The reactor was placed in a box equipped with several lamp fittings so that the source of photons could be replaced according to necessity. Prior to photocatalytic measurements, the reactor was purged by flowing 35 torr of Argon continuously in order to eliminate the influence of oxygen.

Photocatalytic H_2 productions were carried out for a 5-hour illumination of a Philips HPL-N 250 W/542 E40 HG 1SL lamp as a photon source (17.25% of UV and 82.75% of visible light). We note that the lamp comprises over 80% of light in the visible spectra (even more than that of solar light).

Photoactivity measurement using 500 mg of various photocatalysts was assessed in a 500 ml glycerol aqueous solution. Glycerol concentration was also varied in order to investigate the significance of such a sacrificial agent. The photo-reactor system was connected to an online Thermal Conductivity Detector Gas Chromatograph of the Shimadzu GC-8A type to periodically measure the amount of H_2 evolved.

3. RESULTS AND DISCUSSION

3.1. Characterization Results

Figure 1 depicts the Diffuse Reflectance Spectroscopy (DRS) spectra as prepared photocatalysts. The DRS spectra data were presented to evaluate the effect of N doping as well as metal loading in the optical response of the photocatalysts. The DRS spectra show that the doping of N into a TiO_2 lattice could shift the absorption edge to longer wavelengths and reduce the band gap from 3.28 to 2.91 eV, which in turn increase the photocatalyst activity under visible light illumination. This result is in agreement with that reported by Asahi et al. (2001), in which the mixing of the N- p state with the O-2p state can shift up the valence band in order to minimize the band gap of TiO_2, while the position of the conduction band remains the same. On the other hand, the presence of Pt and Cu along with N can drastically decrease the band gap of the M-N-TiO_2 catalyst to an even larger extent, i.e. from 2.91 to 2.36 and 2.47 eV, respectively. The increase of photon absorption in the visible region by simply loading metals to the surface of TiO_2 has also been observed by many other researchers (Yu et al., 2010 and Lalitha et al., 2010). This may be attributed to several reasons: (1) TiO_2 was coated by a partially oxidized co-catalyst metal (Bandara et al., 2005); (2) Co-catalyst ions may generate additional acceptor levels so that the band gap is subsequently reduced (Lalitha et al., 2010; Yoong, 2009); (3) Since the band gap is governed by the crystalline structure and TiO_2 network defects, co-catalyst loading may lead to a stoichiometric deficiency of Ti/O ratio (Slamet et al., 2005); and (4) Good contacts between TiO_2 and Cu grains (Tseng & Wu, 2004).

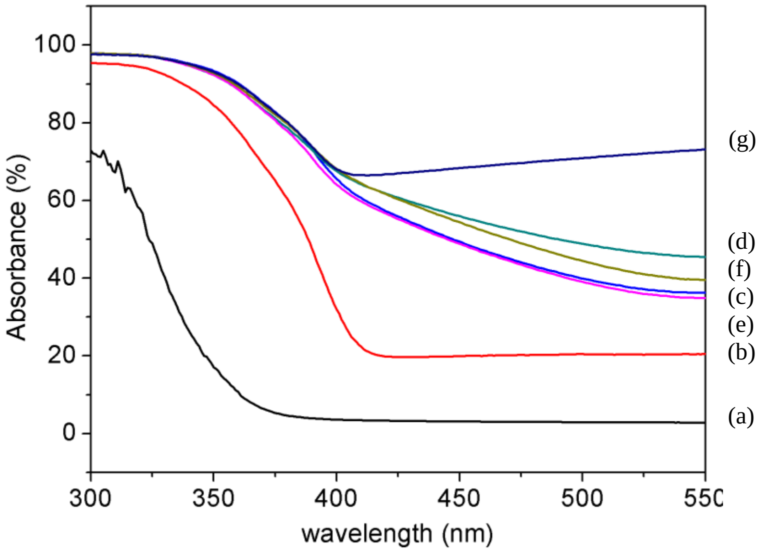

Figure 1 DRS spectra of: (a) TiO_2; (b) N-TiO_2; (c) Cu(1%)-N-TiO_2; (d) Cu(3%)-N-TiO_2; (e) Cu(5%)-N-TiO_2; (f) Cu(10%)-N-TiO_2; (g) Pt(1%)-N-TiO_2

Table 1 summarizes the band gap of M-N-TiO_2 with Pt and Cu and their different loading contents. It is noted that for the case of Cu-N-TiO_2, the change in loading content did not affect the band gap. So, it can be concluded that the band gap change of the photocatalyst by metal loading is controlled by the intrinsic properties of the metal, not by its loading content.

Table 1 Energy band gap of the modified TiO_2 catalysts

Sample	Absorbance Wavelength (nm)	Band Gap Energy (eV)
TiO_2P25	377	3.29
N-TiO_2	425	2.91
Pt(1%)-N-TiO_2	525	2.36
Cu(1%)-N-TiO_2	500	2.47
Cu(3%)-N-TiO_2	500	2.47
Cu(5%)-N-TiO_2	500	2.47
Cu(10%)-N-TiO_2	500	2.47

The XRD patterns of the as-prepared M-N-TiO_2 photocatalysts with Pt and Cu dopant and different Cu contents are shown in Figure 2; that of the unmodified TiO_2 is also depicted for comparison. All these photocatalysts showed quite similar XRD patterns. The dominant peaks at 2θ of about 25.2, 37.9, 47.8, 53.8, and 55.0°, respectively, which represent the indices of (101), (004), (200), (105), and (211) planes, respectively, confirming the crystalline structure of an anatase TiO_2 (according to JCPDS no.21-1272). On the other hand, the relatively small peak at 2θ of 27.4°, corresponding to the (110) plane of the rutile crystalline structure (JCPDS no. 21-1276) was also observed. Neither Pt nor Cu characteristic peaks were observed. This may be attributed to the low content of Pt and Cu, the small particle size, and a high dispersion of metals in the TiO_2 surface.

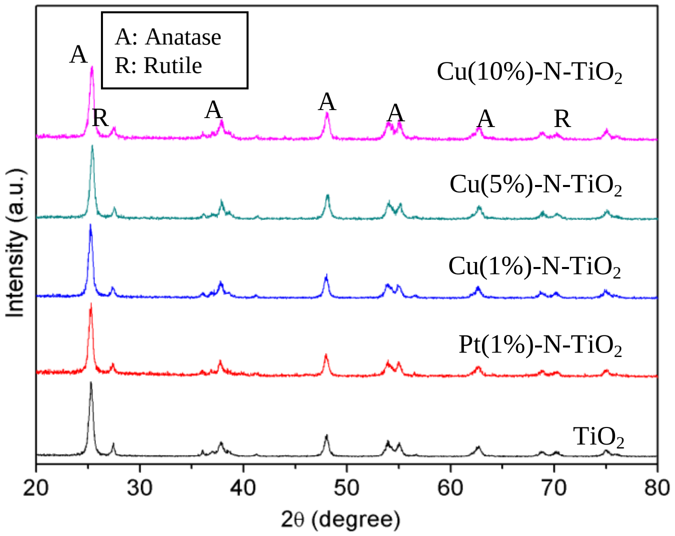

Figure 2 XRD diffraction patterns of TiO_2, Pt-N-TiO_2 and Cu-N-TiO_2

It can also be inferred from Figure 2 that the crystalline form of TiO_2 is not modified by either Pt or Cu loading, judging from the fact that the shapes and relative intensity of the characteristic TiO_2 peaks are relatively unchanged. The crystallite size of the synthesized samples estimated from the line broadening of the anatase (101) diffraction peak using the Scherrer equation (Cullity, 1978) is shown in Table 2. This implies that the loading of copper into TiO_2 does not result in significant changes in both the phase structure and the crystallite size of TiO_2 P25. This may be attributed to the good stability of TiO_2 P25 from the sintering effect and low temperature treatment (500°C) applied during this study. The phase transformation from anatase to rutile was reported to occur in much higher temperature levels (Cristallo et al., 2001).

Table 2 XRD characterization results of TiO_2 and modified TiO_2

Sample	Crystallite Size (nm)	Rutile Fraction	Anatase Fraction
TiO_2	17.61	0.19	0.81
Pt-N-TiO_2	16.51	0.20	0.80
Cu(1%)-N-TiO_2	18.43	0.18	0.82
Cu(5%)-N-TiO_2	17.61	0.18	0.82
Cu(10%)-N-TiO_2	22.64	0.19	0.81

The surface morphology of N doped TiO_2 photocatalysts resulted from the Scanning Electron Micrograph (SEM) procedure, as depicted in Figure 3. SEM photographs as- prepared for the N-TiO_2 photocatalyst showed a porous surface morphology, with relatively small and uniform grain size. Figure 4 represents the SEM photograph of Cu-N-TiO_2. As implied by Figure 4, the grain size of Cu (1%)-N-TiO_2 seems to be quite large and it is not uniformly distributed, while

Cu (3%)-N-TiO_2 shows smaller grain size with uniform distribution. As for Cu(5%)-N-TiO_2 and Cu(10%)-N-TiO_2, which look quite similar, the grain size is even smaller and the morphology also seems to be more porous than in the other two samples.

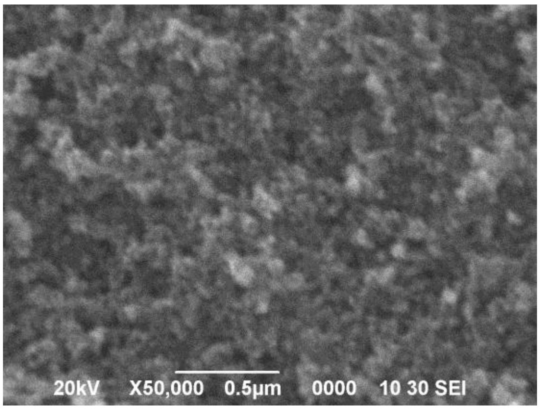

Figure 3 SEM topography of Pt(1%)-N-TiO_2

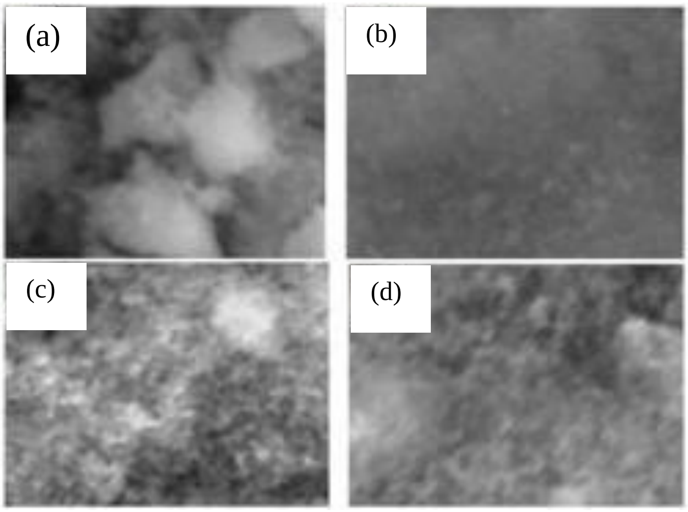

Figure 4 Scanning Electron Micrograph of: (a) Cu(1%)-N-TiO_2; (b) Cu(3%)-N-TiO_2; (c) Cu(5%)-N-TiO_2; (d) Cu(10%)-N-TiO_2

3.2. Photocatalytic Performance

3.2.1. Effect of N doping

Figure 5 represents photocatalytic H_2 production from a glycerol-water mixture as a function of irradiation time. The activity of N doped TiO_2 to pristine TiO_2P25 is also shown for comparison purposes. From Figure 5, one can see that N-TiO_2 has shown better photocatalytic performance than the unmodified P25. N-TiO_2 photocatalyst. This effect has been proven to facilitate the photocatalytic reaction to produce 42 μmol of H_2 in 4 h, or 4 times higher than TiO_2P25, which can only produce 10 μmol during the same irradiation time. This observation supports the idea of photocatalytic activity improvement by N doping into the lattice of TiO_2.

During preparation of N-TiO_2, NH_4^+ ions are adsorbed in the surface of TiO_2 and react afterward to form an ammonium titanate complex. The calcination process at 500°C transforms the crystal structure from amorphous to TiO_2 anatase and decomposes the existing bond in the NH_4^+ ion so that N atoms can be separated from the compound. The released N atoms enter into the crystal structure of TiO_2 and take a lattice position in the O atom and then bond with Ti to form covalent bonds (Nosaka et al., 2005).

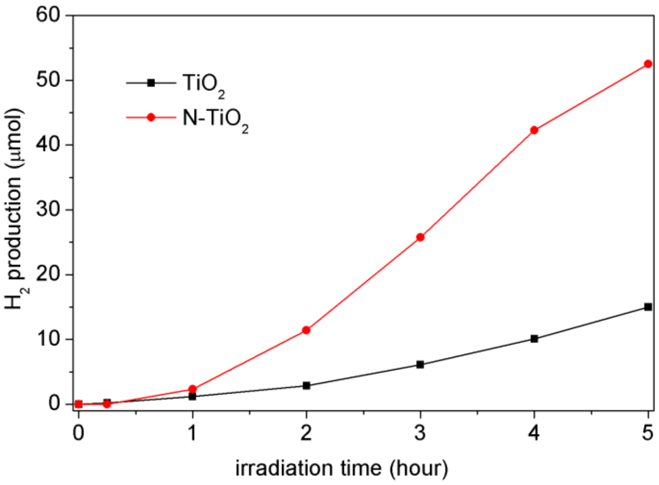

Figure 5 Effect of nitrogen addition on the hydrogen production from glycerol and water (10 % v/v glycerol) with various irradiation time

Therefore, the conduction band of the photocatalyst is no longer in the orbital of the O atom, rather it is that of the N atom. Consequently, the valence band position shifts to a value that is negative, while the conduction band remains unchanged. This shift leads to the band gap decreasing, which in turn results in lowering the photonic activation energy of the photocatalyst and increasing the absorption efficiency. This result may be the main reason for the enhanced photocatalytic performance of N-TiO_2.

The modified N-TiO_2 possesses remarkable photocatalytic activity improvement compared to the unmodified N doped TiO_2 (Zhang et al., 2010). In this particular study, the presence of the metal co-catalyst may enhance the N doped photocatalyst activity, due to the cooperation effect between N and metallic particles (Zhang et al., 2010).

The doping of N atoms into TiO_2 crystal matrix led to a higher negative valence band energy level. Consequently, less hole generation took place. Meanwhile the conduction band remains constant along with the doping. However, in the case of H_2 photoproduction with sacrificial agents (hole scavengers), the cathodic proton reduction in the conduction band is the determining factor. The hole anodic reaction does not significantly affect the overall process, since the anodic resistance has been overcome by introducing sacrificial agents. This indicates that the doping of N atoms into the TiO_2 lattice leads to a better H_2 photoproduction under visible light without losing any proton reduction ability.

3.2.2. Effect of M (Pt, Cu) loading

Figure 6 represents photocatalytic H_2 production from the glycerol-water mixture as a function of irradiation time, when comparing the activity of Cu-N-TiO_2 with the various Cu loading content. It should be noted that under experimental conditions, production of H_2 is enhanced by depositing Cu in TiO_2 photocatalyst support. Deposition of 1wt% Cu on TiO_2 results in a generated H_2 level of almost 12 times and 3 times compared to pristine TiO_2 (10 µmol) and unloaded N-TiO_2 (42 µmol), respectively. From 0% to 5% copper loading, the H_2 evolution rate increased monotonously. Furthermore, dispersion of higher amounts of Cu in TiO_2 surface results in a decrease in the reaction rate. It was observed that optimal photocatalytic performance for photocatalytic H_2 production from the glycerol water mixture was obtained in the case of Cu(5%)-N-TiO_2.

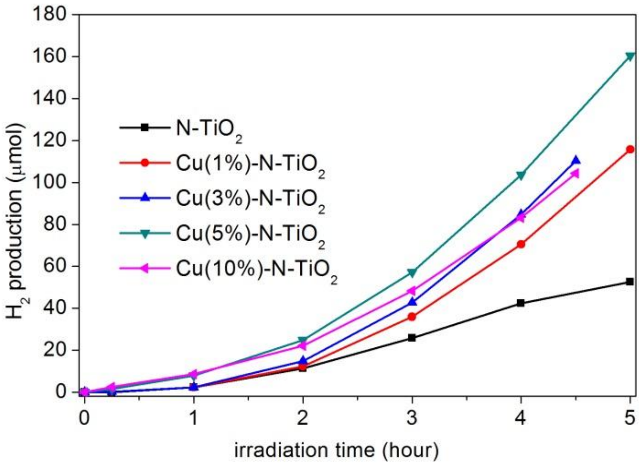

Figure 6 Effect of Cu dopant on the performance of TiO_2 in producing hydrogen from glycerol and water (10 %v/v glycerol) over various irradiation time intervals

The presence of an optimum loading value above which metal deposition will decrease the activity is often observed in photocatalytic reactions. For Cu supported on TiO_2, this value is usually higher than 1 wt%, as in this case study, it is in agreement with the results of other research groups (Wu et al., 2004; Slamet et al., 2009; Bandara et al., 2005; Xu & Sun, 2009; Lalitha et al., 2010). Higher Cu loadings above the optimum loading generally result in reduced photocatalytic efficiency, due to UV-shielding of the TiO_2 particles by the metal deposits. Another explanation is that, at higher metal loadings the deposited metal particles may act as recombination centers for photo-generated electrons and holes (Millard & Bowker, 2002). It is also possible that the observed dependence of the rate on the Cu loading is due to a variation in the number of active sites located at the metal/support interface (Daskalaki & Kondarides, 2009; Bahruji et al., 2010). Higher metal loading may lead to agglomeration, hence decreasing the photocatalyst-metal interface area.

3.2.3. Effect of Pt loading

Figure 7 depicts photocatalytic H_2 production from glycerol-water mixture as a function of irradiation time under visible light illumination; when comparing the activity of Pt(1%)-N-TiO_2 to Cu(5%)-N-TiO_2 and TiO_2 P25. Significant improvement of photocatalytic H_2 production over Cu(5%)-N-TiO_2 and Pt(1%)-N-TiO_2 was observed. Figure 7 clearly shows that, after 5 h illumination, Pt(1%)-N-TiO_2 and Cu(5%)-N-TiO_2 can produce 337.5 and 160 μmol, respectively, while N-TiO_2 and TiO_2 can only produce 42 and 10 μmol, respectively. It is noted that the doping of N can increase the hydrogen production up to 4 times higher when compared to P25. Moreover, the N doping along with Pt or Cu loading into TiO_2 can improve the production of hydrogen to even a greater extent, i.e. 34 or 16 times, respectively compared to P25. In addition, Table 1 implies that Pt(1%)-N-TiO_2 has the smallest band gap compared to other photocatalysts and its absorbance band is also high along the spectrum of visible light, so that the energy absorption in this region is very effective, hence it can improve the photocatalytic performance. From these results, we infer that the improvement of the H_2 photoproduction rate may be attributed to these two reasons. Firstly, the band gap narrowing of the photocatalyst is considered to influence its light-harvesting ability, since the lamp used in this study is rated at a high level in the visible spectrum. Secondly, the ability of Pt to trap electrons plays a major role and has a considerable effect on inhibiting the photocharge recombination and enhancing electron separation (Lin, 2009).

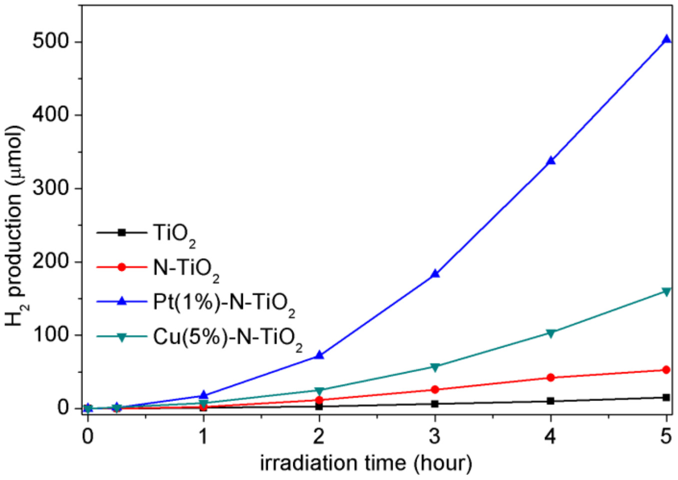

Figure 7 Effect of N, Pt and Cu dopant on the performance of TiO_2 in hydrogen production from glycerol and water (10% v/v glycerol) over various irradiation time intervals

The photocatalytic improvement effect of Pt and Cu deposition into TiO_2 is attributed to its ability to trap electrons, thus inhibiting the hole-electron recombination and extending the lifetime of the charge carriers. On the other hand, the contact between metals and TiO_2 may form a Schottky barrier, i.e. rectifying the potential electronic barrier generated by the metal-semiconductor junction, which may lead to better electron transfer. In addition, metal can also reduce H_2 over-potential in the system, since the reduction of protons takes place in the metal site, instead of in TiO_2 (Wu et al., 2008; Daskalaki & Kondarides, 2009). Moreover, any metals, in and of themselves, may take a role in the ‘dark reaction’ of converting glycerol-water mixture into H_2, since the metal based catalyst has been known as and has been proven to be an excellent catalyst for glycerol steam reforming.

From the thermodynamics point of view, a metal can be utilized as an electron trapper for the TiO_2-based photocatalyst, only if it has a higher electron work function (Φ) than TiO_2 (Φ = 4.6 eV). The electron work function is the minimum energy required to extract an electron from the surface of a solid (Lide & Haynes, 2010). The greater the difference between the metal work function and that of the TiO_2 leads to the higher Schottky barrier, which consequently increases the efficiency of electron trapping and transfer (Chiarello et al., 2010). From this concept, Figure 7 is not a surprising finding, since the work function of Pt (Φ = 5.93 eV) is much higher than that of Cu (Φ = 4.94 eV). In fact, the work function of Pt has the highest reading, when compared to any other metals such as Ni, Ag, Au, Pd, or Ir (Lide & Haynes, 2010).

The work function approach can also be applied to explain kinetic reasons for Pt superiority as a co-catalyst in a photocatalytic H_2 production system, particularly in terms of overcoming hydrogen over-potential (also known as an energy barrier for proton reduction to produce H_2). In general, the experiment indicates that the higher the work function result, the lower the hydrogen over-potential, (Strataki et al., 2007). So, the TiO_2-contained high energy barrier facilitates proton reduction in its surface due to its low work function. Once metal is loaded onto the surface of TiO_2, proton reduction (hydrogen evolution) no longer takes place in the TiO_2 conduction band, rather it takes place in the metal site. Therefore, loading metal in TiO_2 can enhance H_2 generation efficiency by lowering H_2 over-potential.

3.2.4. Effect of Glycerol concentration

Figure 8 shows the rate of H_2 evolution as a function of irradiation time of various glycerol concentrations. It is noted from Figure 8 that 10% glycerol is sufficient to give a substantial improvement to the photocatalytic hydrogen production, while the absence of glycerol in the solution did not produce any detectable H_2. This undetected hydrogen phenomenon may happen due to the high rate of electron-hole recombination and H_2-O_2 backward reaction to reproduce water molecules.

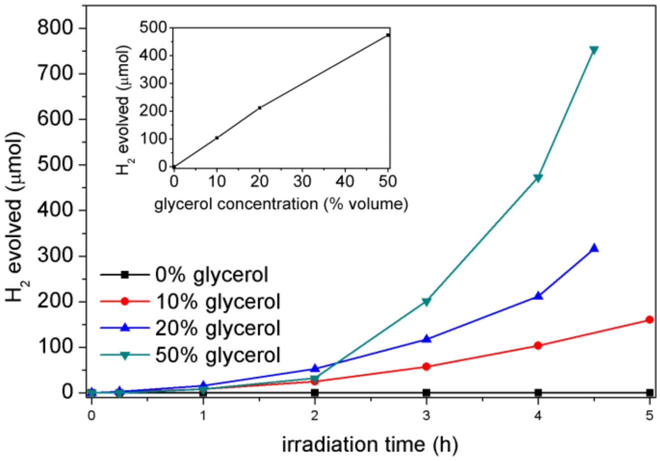

Figure 8 Effect of glycerol concentration on hydrogen production (photocatalyst: 500 mg of Cu(5%)-N-TiO_2) over various irradiation time intervals

Introducing glycerol into the system led to significant improvement of hydrogen production. This may be attributed to the function of glycerol in the system, which not only enhances electron-hole separation by the scavenging hole that in turn reduces the photo-anodic resistance and frequency of recombination, but also additionally acts as hydrogen source for the overall hydrogen production process (Li et al., 2006; Daskalaki, 2008). In other words, water reduction producing H_2 water and glycerol oxidation producing H_2 and CO_2 take place simultaneously. The combination of those two processes can then be referred to as glycerol steam reforming, described as the following reaction (Daskalaki, 2008).

$$C_3H_8O_3 + 3H_2O \rightarrow 7H_2 + 3CO_2 \quad (1)$$

From the stoichiometric point of view, the photocatalytic reaction between glycerol and water can produce more H_2 than using water only. As implied by the above reaction formula, one mole of glycerol could produce seven moles of H_2, while only one mole of hydrogen can be produced from a pure water splitting reaction. It was also observed from Figure 8 that along with irradiation time, the rate of hydrogen production increased at a certain extent for each glycerol concentration up to a 50% volume. It was also observed that the gradient of H_2 evolved-irradiation time plotting increased at an increasing rate of glycerol concentration. The inset in Figure 8 shows the effect of glycerol content on the amount of H_2 produced after 4 h from 0–50 % volume of glycerol concentration. In Figure 8 for the case of 0% glycerol in the solution, no H_2 was detected, while for the respective cases of 10, 20 and 50% of glycerol concentration in the solution, H_2 can be produced (after a 4 h illumination) of 57, 212, and 473 μmol, respectively. The effect of glycerol concentration on photocatalytic H_2 production represents nearly a linear relationship.

Another interesting aspect of these results can be seen in the 'delay' of the H_2 produced. For all cases of glycerol concentration, a significant amount of H_2 was detected only after 2 h of illumination. This, in fact, coincides with temperature profile of the system, which is depicted in Figure 9. It is clearly shown that after only 2 hours, the temperature remains constant, which indicates that the reactor has approached its isothermal condition at a relatively high photoreaction temperature (almost 50°C). Within the first 2 hours (below the isothermal condition of reactor), H_2 production was observed, although it is not yet as high. It indicates that H_2 photoproduction is a temperature-dependent process. However, in the present configuration, it is difficult for our photoreactor to be operated at an elevated temperature, since the relative position of the lamp was far above the reactor and there was no heater jacket installed. Therefore, an improvement in terms of photoreactor arrangement would be subject to a further study.

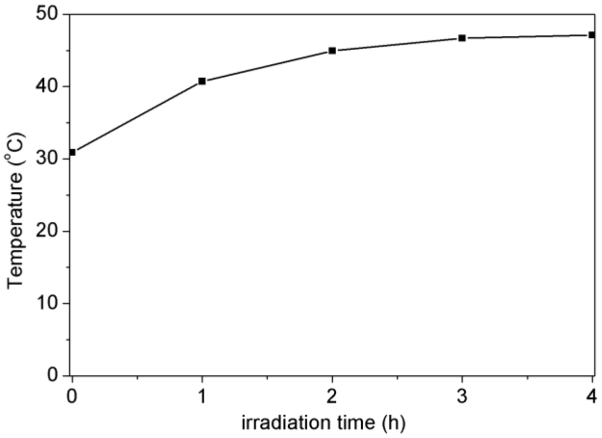

Figure 9 Effect of irradiation time to the temperature profile of the reaction system

4. CONCLUSION

Modification of the TiO_2 photocatalyst to produce H_2 from a glycerol-water mixture has been investigated in this present study. Both non-metal (N) doping and metal (Pt, Cu) loading are effective ways to improve photocatalytic hydrogen production activity. N-TiO_2 could enhance hydrogen production 4 times higher than that of undoped TiO_2. This improvement may be due to band gap narrowing and an increase in the absorption efficiency because of N doping into the lattice TiO_2 which substitutes the O position in the valence band. On the other hand, Pt-N-TiO_2 had a better H_2 production performance up to 34 times higher than TiO_2, while Cu-N-TiO_2 could enhance the activity up to 10 times higher than TiO_2. Photocatalytic activity improvement by metal loading may be attributed to its ability to trap electrons, thus improving the electron-hole separation and inhibiting recombination and then lowering the H_2 over-potential and its capacity to facilitate the ‘dark reaction’. Despite its inferior characteristics in comparison with Pt, Cu may be more advantageous for widespread application, since it is abundantly available and at a lower price than Pt. H_2 production was proportionally enhanced by increasing glycerol concentration up to 50 % v/v (percentage volume for volume). By introducing glycerol into the system, this improvement in activity may be attributed to glycerol’s ability to be oxidized by hole to produce H_2 and CO_2, to reduce photo-anodic resistance, and to provide more hydrogen atoms.

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