

imately 11 nm. The particle sizes of Pt and TiO₂ from the TEM analysis are in the region of 1–2 and 10–15 nm, respectively, as depicted by the TEM image in Fig. 3. The observed particle size of TiO₂ is in good accordance with the crystallite size calculated from the XRD result. In addition, homogeneously dispersed Pt nanoparticles on the TiO₂ surface are clearly seen from the TEM image.

The surface morphology of the synthesized photocatalyst was further investigated by using SEM. The acquired image is presented in Fig. 4. In the photocatalyst micrograph, particles with quite uniform size can be observed in aggregated clusters consisting of many nanoparticles. It can be seen that the photocatalyst was highly mesoporous, which is apparent by the SEM image. EDS analysis also provided useful information about the elemental distribution on the photocatalyst, as included in Fig. 4 by the elemental mapping of each component. The existence of dots in the elemental mapping images reveals the presence of all the investigated (Ti, O, and Pt) species. The EDS mappings reveal that all elements in the Pt-loaded TiO₂ were well distributed throughout the bulk photocatalyst, especially the investigated Pt species. This is another good verification of the high dispersion state of the deposited Pt nanoparticles. According to the N₂ adsorption–desorption, TEM, and SEM results, it is additionally worthwhile to emphasize that the mesoporous structure of the synthesized photocatalyst can be attributed to the pores formed between the nanocrystalline TiO₂ particles due to their aggregation, which is in the same line as the mesoporous TiO₂ reported in literature [38–43].

3.2. Photocatalytic H₂ evolution activity

3.2.1. Effect of sacrificial reagent type

In photocatalytic water splitting for H₂ evolution, the oxidation of water by holes is a much slower process than the reduction by electrons. In order to smooth the progress of the oxidation, sacrificial reagents or hole scavengers are often introduced, especially for the principal purpose of preventing the mutual electron–hole recombination process. Once the holes are scavenged from the photocatalyst surface, the longer decay time of surface electrons would certainly facilitate the reduction of

protons in the solution to form hydrogen on the Pt active sites [44–46]. It is also definitely important to first mention that no hydrogen evolution activity was experimentally observed for the blank tests (without photocatalyst or without sacrificial reagent).

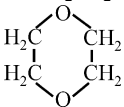
Initially, various types of sacrificial reagents were tested for the photocatalytic H₂ evolution to find which type of sacrificial reagent is the most effective in assisting the photocatalytic reaction. An aqueous solution containing the same amount of various sacrificial reagents was thus illuminated under identical reaction conditions. Table 1 shows the photocatalytic H₂ evolution activity of the synthesized nanocrystalline mesoporous Pt/TiO₂ photocatalyst using various sacrificial reagents, and Fig. 5 also shows the photocatalytic H₂ evolution profiles and activity using different sacrificial reagent types in an alcohol series. The results show that among the investigated sacrificial reagents, those in the alcohol series exhibited considerably higher photocatalytic activity than others. This might be attributable to the ease in donating lone-pair electrons to the valence band hole upon the photocatalyst excitation [47], as compared to other types of sacrificial reagents. Among the alcohol series itself, methanol was found to be the most effective and strongest sacrificial reagent to yield the highest photocatalytic H₂ evolution activity. It appears that compounds possessing very high polarity, such as acids and ketones, are unable to effectively suppress the electron–hole recombination, probably due to their stable electronic configuration. Apart from that, the carbon-to-carbon bond breaking also plays an important role in differentiating photocatalytic activity, since it directly involves the lone-pair electron donation. The extent of the carbon-to-carbon bond breaking decreases with the increase in chain elongation and complexity, as these factors contribute to enhance the steric hindrance in the molecule [47]. Since methanol was experimentally verified to be the most effective sacrificial reagent for the investigated system using the synthesized mesoporous Pt/TiO₂ photocatalyst, it was used as the main studied sacrificial reagent in further experiments.

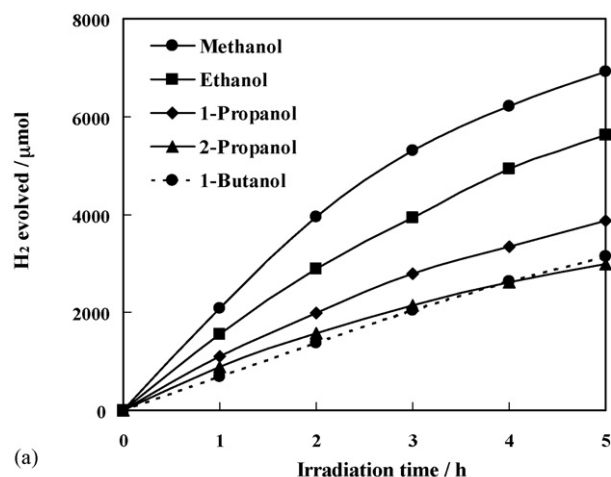
3.2.2. Effect of initial solution pH

One of the important parameters affecting the photocatalytic reactions taking place on the photocatalyst surfaces is the solution pH, since it primarily dictates the surface charge properties

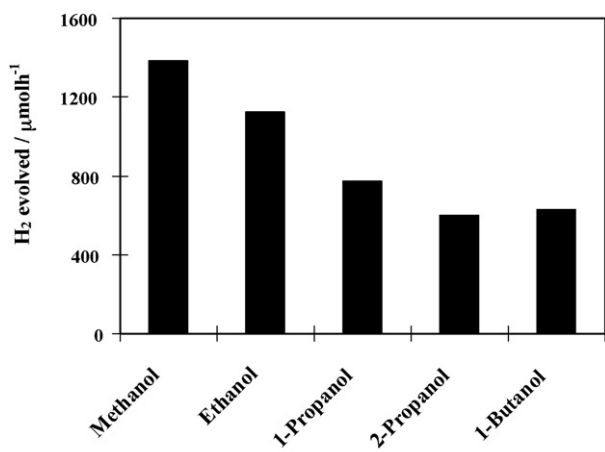
Table 1

Effect of various sacrificial reagent types on photocatalytic H₂ evolution activity of the synthesized mesoporous Pt/TiO₂ photocatalyst (reaction conditions: photocatalyst amount, 0.2 g; distilled water amount, 200 ml; sacrificial reagent amount, 20 ml; irradiation time, 5 h)

Type of sacrificial reagent	Molecular structure of sacrificial reagent	H ₂ evolution activity (μmol h ^{−1})
Methanol	CH ₃ OH	1385
Ethanol	CH ₃ CH ₂ OH	1123
1-Propanol	CH ₃ CH ₂ CH ₂ OH	775
2-Propanol	CH ₃ CH(OH)CH ₃	599
1-Butanol	CH ₃ CH ₂ CH ₂ CH ₂ OH	629
Acetic acid	CH ₃ COOH	78
Acetone	CH ₃ COCH ₃	22
Ethylene glycol	OHCH ₂ CH ₂ OH	451
Diethylene dioxide (1,4-dioxane)		292
Dimethyl formamide	HCON(CH ₃) ₂	87



(a)



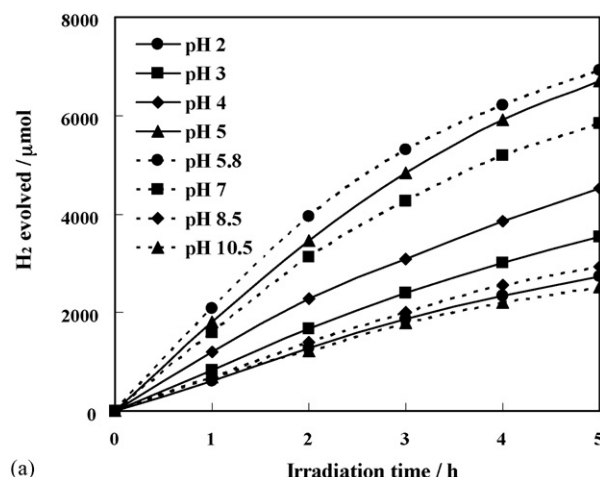
(b)

Sacrificial reagent type in alcohol series

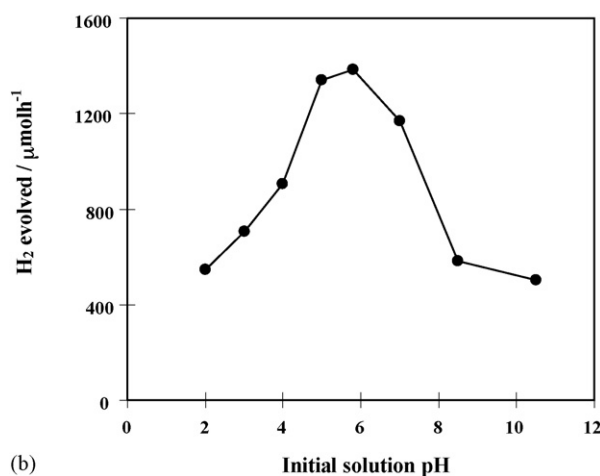
Fig. 5. Effect of sacrificial reagent type in alcohol series on (a) time course of H₂ evolved and (b) dependence of photocatalytic H₂ evolution activity of the synthesized mesoporous Pt/TiO₂ photocatalyst (reaction conditions: photocatalyst amount, 0.2 g; distilled water amount, 200 ml; sacrificial reagent amount, 20 ml; irradiation time, 5 h).

of the photocatalyst. In addition, the solution pH can affect the states of both reactant in solution and photocatalyst surface, which ultimately changes the electrostatic interaction between the reactant and the TiO₂ surface [48–50]. The role of initial solution pH on the photocatalytic H₂ evolution activity was studied over a broad pH range of 2–10.5 using methanol as a sacrificial reagent, noting that the initial pH of the original solution containing 200 ml distilled water and 20 ml methanol (2.25 M) is 5.8, and insignificant changes of solution pH were observed after the course of the photocatalytic reaction. The experimental results shown in Fig. 6 indicate that the efficiency of the H₂ evolution activity increases with an increase in solution pH from 2 to a range of 5–6, and a further increase in solution pH greater than 6 led to a drastic decrease in the H₂ evolution activity. The results imply that the H₂ evolution activity of the studied photocatalyst is favorable at mild acidic conditions, and the optimum initial solution pH is around 6.

The effect of solution pH on the efficiency of the photocatalytic H₂ evolution process is quite complicated since it



(a)

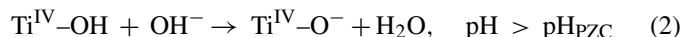
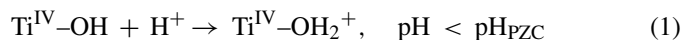


(b)

Initial solution pH

Fig. 6. Effect of initial solution pH on (a) time course of H₂ evolved and (b) dependence of photocatalytic H₂ evolution activity of the synthesized Pt/TiO₂ photocatalyst (reaction conditions: photocatalyst amount, 0.2 g; distilled water amount, 200 ml; sacrificial reagent type, methanol; sacrificial reagent amount, 20 ml; irradiation time, 5 h).

contributes to several roles. It is first related to the ionization state of the photocatalyst surface according to the following reactions:



As known, a pH change can influence the adsorption of these species onto the TiO₂ photocatalyst surfaces, an important step for the photocatalytic reactions to take place. The point of zero charge (PZC) of the TiO₂ is approximately at pH 5.8–6.0 [51–53]. Therefore, at a pH < pH_{PZC}, the TiO₂ surface is positively charged, whereas at a pH > pH_{PZC}, the TiO₂ surface is negatively charged. At acidic pHs (pH < 5), an electrostatic repulsion between the positively charged surface of the photocatalyst and the hydronium cations (H⁺) present in the solution retards the adsorption of the hydronium cations so as to accordingly be reduced to form hydrogen, resulting in a lower photocatalytic H₂ evolution activity. In the opposite manner, at alkaline pHs (pH > 7), an electrostatic repulsion between the negatively charged surface of the photocatalyst

and the molecules of the sacrificial reagent (lone-pair electron donor) also inhibits the adsorption of the sacrificial reagent as to scavenge the valence band holes for preventing electron–hole recombination. Besides, the photogenerated electrons cannot easily transfer to the photocatalyst surface, plausibly because of the negative charge repulsion, and subsequently transfer to outer system via the photocatalytic reduction reaction. Therefore, the electrons moving inside the bulk photocatalyst have high probability to recombine with holes at both bulk trap and defect sites. A higher rate of mutual recombination also consequently results in a lower photocatalytic H₂ evolution activity. These basically imply that complicated interactions between the species/molecules and the photocatalyst are taking place at acidic or alkaline conditions. When the photocatalyst contains no charge, the species/molecules are probably allowed to much more easily reach the photocatalyst surface and achieve higher photocatalytic reaction activity [54,55], thus experimentally obtaining the highest H₂ evolution activity at the initial solution pHs near the point of zero charge.

The TiO₂ particles, moreover, tend to agglomerate under acidic conditions [56]. This agglomeration can result in a lower surface area available for reactant adsorption and photon absorption, leading to a decrease in the photocatalytic activity; whereas another reason for the decrease in the photocatalytic activity under alkaline conditions can be attributed to the UV screening of the TiO₂ particles due to a higher concentration of OH[−] present in the solution [57]. Hence, the solution pH plays an important role both in the characteristics of reactant species-containing solutions and in the reaction mechanisms that can contribute to the H₂ evolution.

3.2.3. Effect of photocatalyst concentration

The effect of the concentration of the synthesized nanocrystalline mesoporous Pt/TiO₂ photocatalyst on the photocatalytic H₂ evolution was investigated in the range of 0–1.82 g l^{−1} by varying the amount of photocatalyst added to the reactor containing an original aqueous 2.25 M methanol solution (pH 5.8) without pH adjustment. Fig. 7 illustrates the photocatalytic H₂ evolution activity as a function of photocatalyst concentration. The H₂ evolution activity first increased and then decreased with an increase in the photocatalyst amount added to the reactor. A higher concentration of the photocatalyst is expected to correspond to a greater absorption of UV energy, leading to a higher photocatalytic H₂ evolution activity. However, the activity began to decline when the concentration of the photocatalyst exceeded 0.91 g l^{−1}, indicating that the addition of the photocatalyst has to be optimized. The obtained experimental results can be rationalized in terms of the availability of active sites on the TiO₂ surface and the light penetration of photoactivating light into the suspension. The availability of active sites increases with the increase in photocatalyst concentration in the suspension, but the light penetration and the consequent photoactivated volume of the suspension shrink [58]. The penetration of light is cloaked in the reactor by the large quantity of the photocatalyst in the aqueous solution. When the photocatalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes the further penetration of light in the reactor, indicating

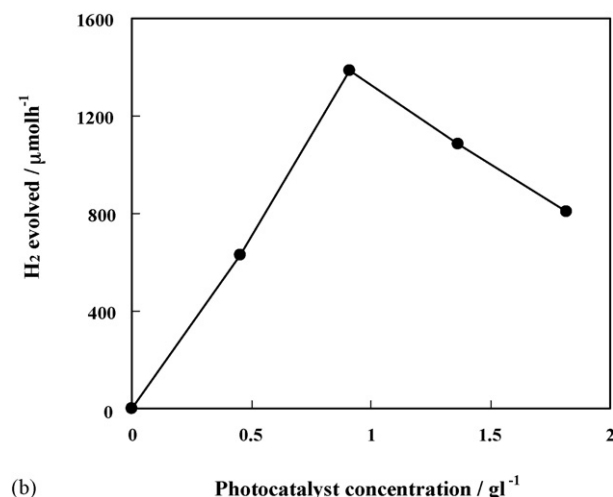
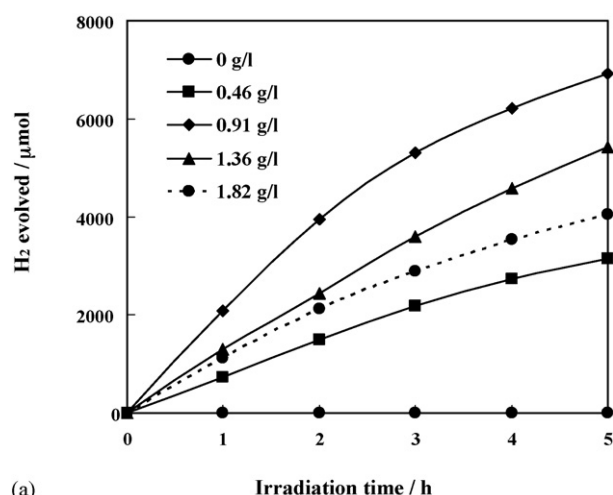
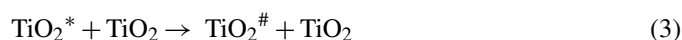


Fig. 7. Effect of photocatalyst concentration on (a) time course of H₂ evolved and (b) dependence of photocatalytic H₂ evolution activity of the synthesized mesoporous Pt/TiO₂ photocatalyst (reaction conditions: distilled water amount, 200 ml; sacrificial reagent type, methanol; sacrificial reagent amount, 20 ml; initial solution pH, 5.8; irradiation time, 5 h).

the block of the illuminating light. Although the light absorption of the outer photocatalyst increases, the capability of generating hydrogen from the inner photocatalyst decreases due to the lack of photoexcitation, signifying the screening effect of excess photocatalyst particles in the solution [49,59]. Consequently, the overall H₂ evolution activity decreases with a very high concentration of the photocatalyst. Moreover, the decrease in the photocatalytic activity at a higher photocatalyst concentration may be due to the deactivation of activated TiO₂ molecules by the collision with ground-state TiO₂ molecules (inactive TiO₂). The deactivation due to the shielding by TiO₂ can be explained according to the following reaction:



where TiO₂^{*} is the TiO₂ with active species adsorbed on its surface, and TiO₂[#] is the deactivated form of TiO₂ [60]. At a considerably high photocatalyst concentration, agglomeration and sedimentation of the photocatalyst particles have also been

reported. Under this condition, it leads to a reduction of the photocatalyst surface available for photon absorption and reactant adsorption, thus bringing lower stimulation to the photocatalytic reaction. An optimum photocatalyst concentration also greatly depends on the photoreactor geometry, the working conditions of the photoreactor, the degree of mixing, the UV lamp power, and the lamp geometry. The optimum amount of the photocatalyst has to be introduced into the system in order to avoid unnecessary excess photocatalyst and also to ensure total absorption of light photons for the efficient photocatalytic H_2 evolution reaction.

3.2.4. Effect of initial methanol concentration

It is important, both from mechanistic and application points of view, to study the dependence of the photocatalytic H_2 evolution reaction on the concentration of methanol, the most effective sacrificial reagent. The influence of initial methanol concentration on the photocatalytic H_2 evolution activity over the synthesized photocatalyst is shown in Fig. 8. With an increase in the methanol concentration, the photocatalytic activity dra-

matically increased and reached a maximum at the methanol concentration of 2.25 M. Beyond this optimum methanol concentration, a further increase in methanol concentration led to a decrease in the photocatalytic activity. Under the studied conditions, the optimum methanol concentration was about 2.25 M. At relatively high concentrations of methanol beyond the optimum point, although the surface active sites remain constant for a fixed catalyst concentration, the number of adsorbed methanol molecules accommodated on the photocatalyst surface increases [50,61]. Because the generation of valence band holes on the surface of the photocatalyst required for reacting with methanol molecules does not increase as the intensity of light and amount of catalyst are unchanged, there was an observed decrease in the photocatalytic H_2 evolution activity, probably due to the blockage of the adsorption of hydronium cations at surface active sites, so as to be reduced to produce hydrogen. Besides, as the photocatalytic reaction is an ion and radical reaction, and methanol can also somewhat behave as a quenching agent of ions and radicals [62], more ions and radicals can be quenched with the increase in methanol concentration. These mentioned reasons consequently lead to the decrease of H_2 evolution activity, after methanol concentration is over the optimum level.

3.2.5. Effect of irradiation time

The time courses of the photocatalytic H_2 evolution over the synthesized mesoporous Pt/TiO₂ photocatalyst at various reaction conditions are given in part (a) of Figs. 5–8. It can be clearly seen that under light radiation, with increasing the time of irradiation up to 5 h, the amount of H_2 evolved increased almost proportionally to the irradiation time in the investigated period. This is because, with an increase in irradiation time, the photons absorbed on the surface of the photocatalyst become greater, which, in turn, helps in the photocatalytic process. However, a slight decrease in the H_2 evolution rate at a long irradiation time was observed. This can be explained that in a photocatalytic batch system, a long irradiation time regularly causes a progressive decline in the H_2 evolution rate due to the back reactions of products generated in the reaction system, as well as the pressure buildup in the gas phase [63]. Additionally, the active site deactivation due to the strong absorption of some molecular species might also be another cause of the decrease in the H_2 evolution activity after a long illumination time [58].

4. Conclusions

The use of SSSG-prepared 0.6 wt% Pt-loaded nanocrystalline mesoporous TiO₂ photocatalyst with high surface area and narrow monomodal pore size distribution for photocatalyzing H_2 evolution from water was studied under various reaction conditions. Several operational parameters were investigated in order to determine the optimum conditions exhibiting the maximum H_2 evolution activity. The experimental results showed that methanol was found to be the most efficient sacrificial reagent among several types of sacrificial reagents investigated. Mild acidic pH values in the range of 5–6 were favorable for the reaction. The optimum photocatalyst and initial methanol concentration were found to be 0.91 g l⁻¹ and 2.25 M, respectively.

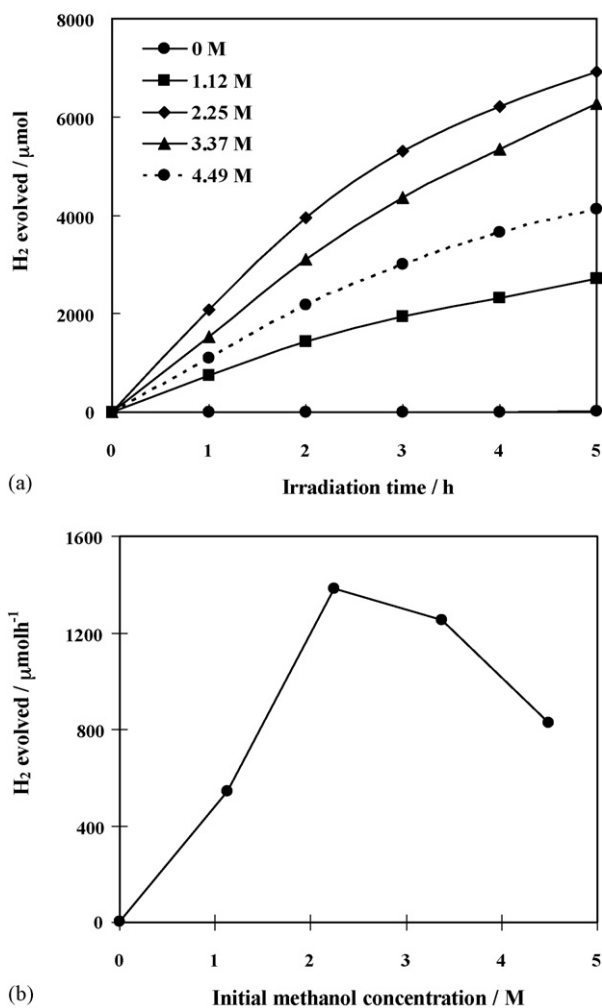


Fig. 8. Effect of initial methanol concentration on (a) time course of H_2 evolved and (b) dependence of photocatalytic H_2 evolution activity of the synthesized mesoporous Pt/TiO₂ photocatalyst (reaction conditions: photocatalyst amount, 0.2 g; solvent: distilled water; sacrificial reagent type, methanol; total solution volume, 220 ml; initial solution pH, 5.8; irradiation time, 5 h).

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ภาคผนวก ข

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**Comparative Investigation of Mesoporous and Non-Mesoporous TiO₂
Nanocrystals for Photocatalytic H₂ Production over N-Doped TiO₂ under
Visible Light Irradiation**

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Abstract

In this paper, N-doped mesoporous TiO₂ and N-doped non-mesoporous commercial TiO₂ (Degussa P-25) nanocrystals were comparatively investigated for photocatalytic H₂ production from water splitting under visible light irradiation. The mesoporous TiO₂ photocatalyst with nanocrystalline and narrow monomodal pore size distribution characteristics was synthesized by a sol-gel process with the aid of structure-directing surfactant under mild conditions. The N-doping technique was directly performed by calcining the mixture of the TiO₂ photocatalysts and urea, as a N source, at different N contents and calcination temperatures. All prepared photocatalysts were systematically characterized by N₂ adsorption-desorption, Brunauer-Emmett-Teller (BET) surface area analysis, Barrett-Joyner-Halenda (BJH) pore size distribution analysis, UV-visible spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron microscopy (XPS). From the experimental results, it was found that N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C exhibited relatively high photocatalytic activity toward hydrogen production. For the N-doped commercial TiO₂, the preparation conditions of a molar ratio of 0.5:1 and a temperature of 250°C showed the best photocatalytic activity, but was still less photocatalytically active than N-doped mesoporous TiO₂ prepared at the optimum conditions. The results indicated the importance of the mesoporous characteristic of the photocatalyst in enhancing the photocatalytic activity by increasing the specific surface area and N-doping capability.

Keywords: N-doping; Mesoporosity; Titania; Visible light; Photocatalysis; Hydrogen production

1. Introduction

H₂ is considered to be a future fuel for replacing conventional energy resources, such as coal, natural gas, and fossil fuel, which are gradually depleting [1]. H₂ is a clean-burning fuel, unlike conventional ones, which unavoidably produce a large amount of CO₂, causing global warming upon their combustion. The combustion of H₂ can generate a huge amount of energy, and the only by-product is water or water vapor. Since it does not involve CO₂ emission, it introduces no pollutants to the environment. Moreover, it can be potentially used in several applications, such as for automobiles, airplanes, and furnaces. Although H₂ is a simple molecule, it can be found in very small quantities in the atmosphere. Because hydrogen atoms are mostly present in the associating forms of hydrocarbons and water, the production of H₂ has to be done by extracting it from these molecules.

Photocatalytic water splitting is a promising process for producing H₂ since water is used as a reactant, which is an abundantly available substance. Also, no pollutants are generated from the photocatalytic water splitting reaction because the reaction produces only H₂ and O₂. Moreover, solar energy, a renewable energy resource, is very appropriate to be used for the photocatalytic H₂ production from water, which occurs when a photocatalyst directly absorbs light with energy equal to or higher than its energy band gap, and the electrons are then excited from the valance band (VB) to the conduction band (CB) and reduce the protons to H₂ molecules [2]. After Fujishima and Honda [3] discovered the photochemical water splitting for H₂ generation using TiO₂ semiconductor electrodes in 1972, a multitude of research on water splitting and semiconductor development has been extensively done. TiO₂ has always been the most investigated semiconductor photocatalyst because it is chemically stable, non-corrosive, environmentally friendly, and cost-effective. Despite the positive attributes of TiO₂, there are two drawbacks associated with its use: (i) charge carrier (e⁻/h⁺) recombination

occurs easily due to its wide band gap and (ii) the light absorption ability of its band gap does not allow the utilization of visible light, which accounts for 42% of the solar energy exposed to the earth's surface, or in other words, only a small UV light fraction, 8%, can be absorbed and utilized [4].

In order to solve the aforementioned problem, the combination with other technologies, such as electron donor or hole scavenger addition, is necessary for preventing the mutual charge recombination. The addition of primarily oxygenated hydrocarbon electron donors in the photocatalytic H₂ production system, such as methanol and ethanol, has been found to greatly improve photocatalytic activity far more than the pure water system [5-7]. To improve the visible light absorption ability of TiO₂, anion doping, such as nitrogen-doped TiO₂ (N-doped TiO₂), is an effective method to enhance its visible light response. Subsequent to the report of Asahi et al. [8] for the preparation of N-doped TiO₂ in an atmosphere of N₂ or NH₃ with its improved light absorption ability into the visible light region, a number of attempts have focused on the synthesis and development of visible light-sensitive N-doped TiO₂ photocatalysts by using several techniques, which include thermal oxidation in N₂ and NH₃ atmospheres, thermal decomposition of N-containing compounds (such as urea, ammonia, ammonium hydroxide, ammonium carbonate, melamine, and guanidine), mechanochemical processes with thermal treatment, N₂-plasma treatment, sol-gel process with ammonia solution, solvothermal process, anodization, chemical vapor deposition, and supercritical NH₃/alcohol fluid process [9-26]. However, most of these techniques inevitably require a special apparatus, which are a major drawback. Since it is evident that the use of urea as a nitrogen source is more environmentally friendly than other N-containing compounds, especially NH₃ gas, due to safety and air pollution concerns, as well as the fact that the preparation of N-doped TiO₂ by thermal decomposition of urea is much more straightforward, this technique was used for

doping nitrogen onto TiO₂ photocatalysts in this study.

Although several research works have been done to synthesize N-doped TiO₂ photocatalysts and to examine their photocatalytic activity under visible light irradiation, most of them were carried out to use the N-doped TiO₂ photocatalysts for other probe photocatalytic reactions, such as photocatalytic degradation/decomposition of methylene blue [8-14], 2-propanol [15-17], nitrous oxide [18-21], phenol [22-24], azo dyes [25], and trichloroethylene [26], but not for the photocatalytic H₂ production from water. However, only a few investigations were conducted for photocatalytic H₂ production [27], no any study has ever reported the use of nanocrystalline mesoporous-structured TiO₂ for such the purpose.

Nanocrystalline TiO₂ generally possesses high photocatalytic efficiency because of the unique properties conferred by its very small physical dimensions. The large specific surface area and high volume fraction of atoms located both on the surface and at the grain boundaries result in an increased surface energy [28–30]. Therefore, nanocrystalline TiO₂ particles with a mesoporous structural network will be more promising because light absorption can be further improved owing to the enlarged surface area and multiple scattering. They can also facilitate better accessibility of reactants, leading to the enhancement of photocatalytic reactions [31]. Among various techniques, sol-gel is an effective route for the synthesis of mesoporous-structured materials under mild conditions with an excellent chemical homogeneity of the resulting products. Additionally, in conjunction with a structure-directing surfactant, the sol-gel process enables the formation of mesoporous-structured materials with successfully controlled porosity [32].

In this study, the N-doped mesoporous TiO₂ and N-doped non-mesoporous commercial TiO₂ (Degussa P-25) photocatalysts were directly prepared by calcining a mixture of TiO₂ photocatalysts and urea, and used for the photocatalytic H₂ production

from water under visible light irradiation. The mesoporous TiO_2 nanocrystal was synthesized via a sol-gel process with the aid of structure-directing surfactant, according to our previous work [32]. The main influences of the urea: TiO_2 molar ratio and the calcination conditions on the N-doping capability and consequent photocatalytic activity for both mesoporous- and non-mesoporous TiO_2 photocatalysts were also investigated.

2. Experimental

2.1 Materials

Tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, Merck) as a Ti precursor and acetylacetone (ACA, $\text{CH}_3\text{COCH}_2\text{COCH}_3$, Rasayan) as a modifying ligand were used for synthesizing a mesoporous TiO_2 photocatalyst. Laurylamine hydrochloride (LAHC, $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\cdot\text{HCl}$, Merck) was used as a structure-directing surfactant to control the mesoporosity of the synthesized TiO_2 photocatalyst. Urea (NH_2CONH_2 , Unilab) was used as a N source for doping on the TiO_2 photocatalyst. Methanol (CH_3OH , Lab-Scan Analytical Sciences) was used as a hole scavenger or electron donor for the photocatalytic H_2 production. All chemicals were analytical grade and were used as received without further purification. Commercial Degussa P-25 TiO_2 was selected for the comparative studies of the photocatalytic H_2 production.

2.2 Synthesis procedure of mesoporous TiO_2 and preparation of N-doped TiO_2

A nanocrystalline mesoporous TiO_2 photocatalyst was synthesized via a sol-gel process with the aid of structure-directing surfactant for a system of LAHC/TIPT modified with ACA [32]. In the typical synthesis, a specified amount of ACA was first introduced into TIPT with a molar ratio of unity. The mixed solution was then gently shaken until it was homogeneously mixed. Afterwards, a 0.1 M LAHC aqueous solution with a pH of 4.2 was added into the ACA-modified TIPT solution, in which the molar ratio of TIPT to LAHC in the mixed solution was tailored to 4:1. The mixture was

continuously stirred at room temperature for 1 h and was further aged at 40°C overnight to obtain a transparent yellow sol. Then, the condensation reaction-induced gelation was allowed to proceed by placing the sol-containing solution into an oven at 80°C for a week to ensure complete gelation. The gel was subsequently dried at 80°C overnight to eliminate the solvent, which was mainly the distilled water used in the preparation of the surfactant aqueous solution, and the dried gel was further calcined at 500°C for 4 h to remove the LAHC template and to consequently produce the nanocrystalline mesoporous TiO₂ photocatalyst. Afterwards, the synthesized mesoporous TiO₂ was thoroughly mixed with urea at various urea:TiO₂ molar ratios, and the mixture was ground by using an agate mortar. The resulting powder was finally calcined at different temperatures, between 200 and 300°C, for 2 h to acquire N-doped TiO₂ photocatalysts. The same procedure was also used to prepare N-doped commercial TiO₂ photocatalysts.

2.3 Photocatalyst characterizations

A nitrogen sorption system (Quantachrome, Autosorb 1) was employed to measure the adsorption–desorption isotherms at a liquid nitrogen temperature of -196°C. The photocatalyst sample was degassed at 150°C for 2 h to remove the physisorbed gases prior to measurement. The Brunauer–Emmett–Teller (BET) approach using adsorption data over the relative pressure ranging from 0.05 to 0.35 was utilized to determine the specific surface areas of all studied photocatalysts. The Barrett–Joyner–Halenda (BJH) approach was used for the calculation of the mean pore sizes and pore size distributions of the photocatalyst samples. X-ray diffraction (XRD) was used to identify the crystalline structure and composition of the photocatalysts. A Rigaku RINT-2100 rotating anode XRD system generating monochromated CuK α radiation with continuous scanning mode at a rate of 2°/min and operating at 40 kV and 40 mA was used to obtain the XRD patterns of all the photocatalysts. A Shimadzu UV-2550 UV-visible spectrophotometer was used to record the diffuse reflectance spectra of the

photocatalyst samples at room temperature with BaSO₄ as the reference. The oxidation state and surface composition were analyzed by an X-ray photoelectron spectroscope (XPS). A MgK α source emitting an X-ray energy of 1,253.6 eV was used as the X-ray source. The relative surface charging of the samples was removed by referencing all the energies to the C1s level as an internal standard at 285 eV.

2.4 Photocatalytic H₂ production experiments

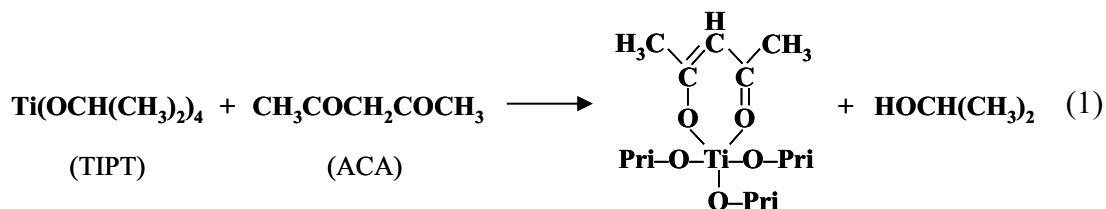
Photocatalytic H₂ production experiments were performed in a closed-gas system. In a typical run, a specified amount of all prepared photocatalysts (0.2 g), namely N-doped synthesized TiO₂ and N-doped commercial TiO₂, was suspended in an aqueous methanol solution (CH₃OH 50 ml and distilled water 150 ml) by using a magnetic stirrer within a reactor made of Pyrex glass. The mixture was initially deaerated by purging with Ar gas for 45 min in a dark environment. The photocatalytic reaction was then started by exposing the mixture with visible light irradiation from a 300 W Xe arc lamp (Wacom Electric, KXL-300F) emitting light with a wavelength longer than 400 nm using a UV cut-off glass filter (ATG, B-48S). The gaseous samples from the headspace of the reactor were periodically collected and analyzed for hydrogen by a gas chromatograph (Perkin Elmer/Arnel, HayeSep D, Ar gas) equipped with a thermal conductivity detector (TCD).

3. Results and discussion

3.1 Mesoporous TiO₂ photocatalyst synthesis results

In this study, the nanocrystalline mesoporous TiO₂ photocatalyst was synthesized via the sol-gel process with the aid of structure-directing surfactant by using TIPT as the Ti precursor modified with an ACA agent and LAHC as the structure-directing surfactant. Firstly, TIPT was mixed with ACA, resulting in a change of the coordination number of the Ti atoms from 4 to 5 [33], as shown in Eq. (1). This also

causes the change of solution color from colorless to yellow. The obtained ACA-modified TIPT is comparatively less active to the moisture in air than the TIPT itself, and is more suitable for the sol-gel synthesis.



Ti coordination number: 4

Ti coordination number: 5

In order to control the mesoporous structure of the TiO_2 , the LAHC aqueous solution was added into the TIPT/ACA solution. The precipitation of a yellow solution occurred immediately after the aqueous solution addition, owing to the partial hydrolysis of the modified TIPT molecules. Then, the solution was continuously stirred at 40°C to dissolve the precipitates. Consequently, a transparent yellow sol was obtained, which resulted from the interaction between the hydrolyzed TIPT molecules and the hydrophilic head groups of micellar LAHC and the suspension of these interacted species in the solution as infinitesimally colloidal solid particles. After placing the transparent yellow sol in an oven at 80°C , a white gel was formed via the condensation process of the modified TIPT molecules attached to the LAHC head groups, and ACA was eliminated, as evidenced by the existence of a transparent yellow liquid layer on the gel. Complete gel formation was observed after a week, and the gel was then dried at 80°C to obtain dried TiO_2 (zero gel). The mesoporous TiO_2 photocatalyst was eventually obtained when the dried gel was calcined at 500°C , which was a sufficiently high temperature for both removing the LAHC template and crystallizing the photocatalyst [32].

3.2 Photocatalyst characterization results

To improve the visible light absorption ability of the TiO_2 photocatalysts, N-

doping was carried out by mixing urea, a simple N-containing molecule, with the synthesized TiO_2 and the commercial TiO_2 at various urea: TiO_2 molar ratios and various calcination temperatures. It was experimentally found that after the N-doping, the color of both TiO_2 photocatalysts clearly changed from white to yellow.

3.2.1 Pore structures of photocatalysts

The N_2 adsorption-desorption isotherms of the as-synthesized TiO_2 and N-doped synthesized TiO_2 exhibit the typical IUPAC type IV pattern with the presence of a hysteresis loop [34], as shown in Fig. 1. The hysteresis loop is ascribed to the existence of the mesoporous structure (mesopore size between 2-50 nm) in the sample. A sharp increase in the adsorption volume of N_2 was observed and located in the P/P_0 range of 0.5-0.9. This sharp increase can be assigned to the capillary condensation, indicating good homogeneity of the samples and fairly small pore sizes, since the P/P_0 position of the inflection point is pertaining to pore dimension. As illustrated in the inset of Fig. 1, the pore size distribution of the sample is quite narrow and monomodal, owing to the single hysteresis loop, implying that the synthesis technique used in this study can yield a mesoporous TiO_2 nanocrystal with a narrow pore size distribution. In contrast, for the commercial TiO_2 and N-doped commercial TiO_2 , the N_2 adsorption-desorption isotherms corresponded to the IUPAC type II pattern [34], as depicted in Fig. 2. It is apparent that the commercial TiO_2 exhibits non-mesoporous characteristic due to the absence of the hysteresis loop. No capillary condensation of N_2 into the pore was observed since the desorption isotherm was insignificantly different from the adsorption one. The pore size distribution of the commercial TiO_2 , as shown in the inset of Fig. 2, is quite broad. The average pore sizes of the commercial TiO_2 and N-doped commercial TiO_2 are quite large, and their pore size distributions not only exist in the mesoporous region but also mostly cover the macropore region (macropore size > 50 nm).

3.2.2 Textural properties of photocatalysts

The experimental results of the textural property characterization of the photocatalysts, including BET surface area, mean pore diameter, and total pore volume, are shown in Table 1. For any given N-doped mesoporous or N-doped commercial TiO₂ photocatalyst, the surface area tended to decrease with increasing urea:TiO₂ molar ratio at all calcination temperatures. For the N-doped mesoporous TiO₂, of which the isotherm exhibited typical IUPAC type IV, the mean pore diameter was quite similar to the pure mesoporous TiO₂, however the total pore volume decreased with increasing urea:TiO₂ molar ratio. For the commercial TiO₂, the mean pore diameter and total pore volume are usually not reported because it contains a large portion of macropores, which has a very broad pore size distribution with the pore diameters larger than 50 nm up to 200-250 nm.

3.2.3 Light absorption capability of photocatalysts

UV-visible spectroscopy was used to investigate the light absorption capability of the studied photocatalysts. The changes in the absorption spectra of N-doped mesoporous TiO₂ nanocrystal with different urea:TiO₂ molar ratios are exemplified in Fig. 3. The absorption band of pure mesoporous TiO₂ is in the range of 200-400 nm. The high light absorption band at low wavelengths in the spectra indicates the presence of the Ti species as tetrahedral Ti⁴⁺. This light absorption band is generally associated with the electronic excitation of the valence band O2p electron to the conduction band Ti3d level [35]. Its light absorption onset is approximately at 385 nm, which corresponds to the energy band gap of anatase TiO₂, 3.2 eV. For the N-doped mesoporous TiO₂, as also shown in Fig. 3, the light absorption band shifts to a wavelength longer than 400 nm (red shift), which is in the range of the visible light region. From the light absorption results, the N-doping technique can improve the visible light absorption capability of the mesoporous TiO₂ synthesized in this study. The

light absorption spectra of the N-doped commercial TiO_2 at different urea: TiO_2 molar ratios are shown in Fig. 4. The light absorption onset of the pure commercial TiO_2 begins at the wavelength longer than 400 nm, indicating that it can absorb visible light by itself without N-doping. This is because the commercial TiO_2 possesses both anatase and rutile phases, as shown by XRD patterns in the next part. Their energy band gap is approximately 3.2 and 3.0 eV for anatase and rutile TiO_2 , respectively, which can originally absorb both UV and visible ranges. It was therefore experimentally found that the N-doping cannot much enhance the visible light absorption capability of the commercial TiO_2 . As shown later from the XPS results, because the commercial TiO_2 possesses less capability of allowing the N-doping owing to its comparatively low surface N content, its visible light absorption is not obviously improved. By comparing between Fig. 3 and 4, the N-doping process gave the positive effect on the absorbance intensity, especially in UV light region, for the synthesized TiO_2 while giving the negative effect for the commercial TiO_2 , however the absorption of UV light with wavelength shorter than 400 nm requires no extensive consideration due to the utilization of only visible light for photocatalytic study. As shown later for the photocatalytic activity results, since both N-doped TiO_2 photocatalysts showed potential performance for photocatalytic H_2 production under visible light irradiation, it means that the photocatalysts can effectively capture the irradiated visible light for generating the excited electrons necessary for reducing protons to H_2 molecules. The possible reasons for these observations of absorbance intensity changes are still in doubt and need further clarified investigation.

3.2.4 Crystallinity and purity of photocatalysts

The XRD patterns of the N-doped mesoporous TiO_2 nanocrystal prepared at different urea: TiO_2 molar ratios and calcination temperatures are shown in Fig. 5, compared with that of the pure mesoporous TiO_2 photocatalyst, whereas those of the N-

doped commercial TiO_2 prepared at different urea: TiO_2 molar ratios and calcination temperatures are shown in Fig. 6, also compared with that of the pure commercial TiO_2 . As shown in Fig. 5, all samples of N-doped mesoporous TiO_2 prepared at a urea: TiO_2 molar ratio of 0.5:1, regardless of calcination temperature, show quite a similar XRD diffractogram with the pure mesoporous TiO_2 . The dominant peaks at 2θ at about 25.2, 37.9, 47.8, 53.8, and 55.0°, which represent the indices of (101), (004), (200), (105), and (211) planes (JCPDS Card No. 21-1272) [36], respectively, conform to the crystalline structure of anatase TiO_2 . At a temperature of 200°C, the biuret formation was first clearly observed at a urea: TiO_2 molar ratio of 3:1, as shown in Fig. 5. The biuret was also found at the urea: TiO_2 molar ratio of 1:1 in a very small amount due to the comparatively low peak intensity at this temperature ((c) in Fig. 5). A similar tendency of biuret formation was observed at a temperature of 250°C for the urea: TiO_2 molar ratios of both 1:1 and 3:1 ((f) and (g) in Fig. 5), but in extremely low amounts at the molar ratio of 1:1. In addition, cyanuric acid was apparently formed at this temperature. At 300°C, biuret formation was not observed at a molar ratio of 1:1 ((i) in Fig. 5), suggesting that biuret is decomposed at this temperature. At a molar ratio of 3:1 ((j) in Fig. 5), a large amount of cyanuric acid was observed, and biuret was observed in relatively low amounts when compared to 250°C at the same molar ratio. These results indicate that biuret starts to decompose to form cyanuric acid at temperatures higher than 200°C. Schaber et al. [37] explained about the decomposition of urea to produce many compounds depending on temperature. Two main products are biuret and cyanuric acid. Upon increasing temperature, biuret is formed at approximately 150 to 250°C. Cyanuric acid then appears in consecutive order at approximately 190 to 350°C. The formation of biuret and cyanuric acid due to the urea composition is shown in the following decomposition reactions.

doped commercial TiO₂, as shown in Fig. 6, the dominant peaks at 2θ of about 27.4, 36.1, 41.2, and 54.3°, which represent the indices of (110), (101), (111), and (211) planes (JCPDS Card No. 21-1276) [36], respectively, indicate the presence of the rutile phase, in addition to the presence of the anatase phase. Both biuret and cyanuric acid were observed in the same trend as the N-doped mesoporous TiO₂. The main difference between the mesoporous TiO₂ and the commercial TiO₂ photocatalysts was that the synthesized mesoporous TiO₂ is in only anatase form, whereas the commercial TiO₂ possesses the mixed phases of anatase (76.5%) and rutile (23.5%), of which the phase composition is calculated by the following equations [38]:

$$W_R = [1 + 0.8I_A/I_R]^{-1} \quad (7)$$

$$W_A = 1 - W_R \quad (8)$$

where I_A and I_R represent integrated intensities of anatase (101) and rutile (110) diffraction peaks, respectively, and W_A and W_R represent phase compositions of anatase and rutile, respectively.

3.2.5 Oxidation state and surface N content of photocatalysts

The oxidation states and surface compositions of N, O, and Ti of the N-doped mesoporous TiO₂ and N-doped commercial TiO₂ nanocrystals were analyzed by XPS. The XPS results of the N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and calcination temperature of 250°C are exemplified in Fig. 7. Fig. 7(a) represents a typical XPS spectrum of Ti. The peaks of the Ti2p spectrum appeared with their centers at 458.4 and 464.0 eV, which correspond to the Ti2p_{3/2} and Ti2p_{1/2} levels, respectively. The peaks can denote the Ti⁴⁺ oxidation state, which agree well with the light absorption results. Fig. 7(b) shows the peak of the N1s spectrum centered at 400.8 eV, which can be ascribed to the molecularly chemisorbed nitrogen. Many recent

literatures also reported the presence of a broad N1s peak between 397 and 403 eV for N-doped TiO₂ photocatalysts prepared by various techniques [39-42]. Fig. 7(c) shows the deconvoluted peaks of the O1s (mesoporous TiO₂) spectrum with one centered at 529.7 eV, which is typical for the Ti-O-Ti environment and agrees with the O1s binding energy for TiO₂ molecule [43], and the other centered at 532.5 eV, which is typical for the Ti-O-H environment of the hydroxyl group on the photocatalyst surface [44]. Nosaka et al. [15] also investigated the N-doped TiO₂ photocatalyst with the XPS technique and observed that the peaks of the N1s spectrum appeared with their centers approximately at both 396 and 401 eV, correspondingly representing atomically substitutional nitrogen and molecularly chemisorbed nitrogen with comparatively low signal for the former. Although the N1s with a binding energy centered at 396 eV was not clearly observed for the samples in this study, it is believed to exist in a low amount. It has been analyzed that the peak centered at 396 eV is typical for N bound to Ti atoms, and the signal centered at 401 eV is typical for N bound to O, C, or N atoms. In combining with the light absorption results, it can be inferred that the molecularly chemisorbed nitrogen could contribute to the extended absorption into visible light region. The surface nitrogen compositions of all the investigated N-doped TiO₂ samples are summarized in Table 2. The presence of surface nitrogen on the as-synthesized mesoporous TiO₂ may be due to the imperfect removal of LAHC used as the surfactant template during the calcination step. For the pure commercial TiO₂, the presence of surface nitrogen is plausibly because of their production technique via spray combustion. During the combustion step, which is generally carried out with air, the commercial TiO₂ can inevitably be N-doped. For the N-doped mesoporous TiO₂ prepared at any given urea:TiO₂ molar ratio, the surface N content increases with increasing calcination temperature from 200 to 250°C, but decreases with further increasing to 300°C, as shown in Table 2. The trend of the surface N content for N-

doped mesoporous TiO_2 is quite different from that for N-doped commercial TiO_2 , of which at all urea: TiO_2 molar ratios, the surface N content tended to decrease with increasing the calcination temperature from 200 to 300°C. These results can probably be related to their pore characteristics. As the pore size of the synthesized TiO_2 exists entirely in the mesopore region, the formed N-containing compounds at 250°C, i.e. biuret and cyanuric acid, are easily trapped inside the pores due to the pore size limitation. However, with increasing the temperature to 300°C, biuret further decomposes to smaller compounds, and so they can be more thermally released from the pore structure at this high temperature. In contrast to the pore size of the commercial TiO_2 , which is mostly in the large macropore region, any compounds formed can be simultaneously released by the thermal removal process. At a higher temperature, this thermal removal phenomenon becomes more significant due to the greater amount of applied energy, resulting in less surface N content. Moreover, at any given calcination temperature, the surface N content increased with increasing urea: TiO_2 molar ratio for both the mesoporous TiO_2 and commercial TiO_2 , due to the presence of a higher amount of available urea molecules so as to increase the doping capability. When comparing these two types of TiO_2 , it is obvious that the surface N content of the mesoporous TiO_2 was considerably higher than that of the commercial TiO_2 at all preparation conditions, because of the higher surface area of the mesoporous TiO_2 , as well as other physical surface properties originating from the specific preparation technique.

3.3 Photocatalytic H_2 production activity results

The results of photocatalytic H_2 production over the photocatalysts are shown in Fig. 8. The photocatalytic activity in the absence of either light irradiation, photocatalyst, or methanol was also comparatively studied. It was found that there was no detectable H_2 production in their absence, indicating that all of them are very important for the photocatalytic H_2 production from water splitting. Moreover, without

N-doping, on both types of TiO₂ photocatalysts, extremely poor photocatalytic H₂ production activity was observed. As shown in Fig. 8, the N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C exhibits the highest H₂ production activity. For the series of the widely-known high photocatalytic activity commercial TiO₂, the best N-doping conditions were at a urea:TiO₂ molar ratio of 0.5:1 and a calcination temperature of 250°C.

At both calcination temperatures, 200 and 250°C, the photocatalytic H₂ production activity of the N-doped mesoporous TiO₂ tended to increase with increasing urea:TiO₂ molar ratio from 0.5:1 to 1:1 and then to decrease with further increasing molar ratio. It seems that for the N-doped mesoporous TiO₂ with a urea:TiO₂ molar ratio of 3:1, a huge amount of urea was decomposed to biuret (at 200 and 250°C) and further to cyanuric acid (250°C), and they could not be completely removed; consequently they remained inside the mesoporous structure, as shown in the XRD patterns (Fig. 5). Since both biuret and cyanuric acid are comparatively large molecules, they are easily trapped inside the pores of the synthesized mesoporous TiO₂, resulting in the decreased H₂ production activity due to less accessibility of the reactants to the photocatalyst surface (Table 1 and Fig. 8) despite the higher surface N content (Table 2). For any given urea:TiO₂ molar ratio, the photocatalytic activity of the N-doped mesoporous TiO₂ prepared at 300°C was different from those prepared at the other two calcination temperatures, 200 and 250°C. The H₂ production reached a maximum at a urea:TiO₂ molar ratio of 0.5:1 and gradually decreased as the molar ratio further increased. A possible explanation might be that at this high temperature, the biuret formed can be easily decomposed to cyanuric acid, iso-cyanic acid, and ammonia (Eq. (6)). The surface nitrogen may then also be released more, resulting in less surface N content (Table 2) and subsequently lowering the photocatalytic activity, as shown in Fig. 8. In addition, although the cyanuric acid formation at a molar ratio of 1:1 was not observed

from XRD, the decreased pore volume and increased amount of surface N content can be confirmed, as shown in Tables 1 and 2.

For the N-doped commercial TiO_2 photocatalyst calcined at 200°C , the photocatalytic H_2 production activity tended to increase with increasing urea: TiO_2 molar ratio from 0.5:1 to 1:1 and then to decrease with further increasing the molar ratio. At 250°C , the photocatalytic activity reached a maximum at a urea: TiO_2 molar ratio of 0.5:1 and gradually decreased as the urea: TiO_2 molar ratio further increased. At 300°C , the photocatalytic activity remained almost unchanged, even though the urea: TiO_2 molar ratio increased. Their activity was quite different from those of the N-doped mesoporous TiO_2 ones. It seems to be that the pore size is very important, greatly affecting the photocatalytic activity. As previously mentioned, the pore size of the commercial TiO_2 is mostly in the macropore region, having a pore size much greater than 50 nm in diameter. Because of the extremely large pore size of the commercial TiO_2 , it is much more capable of allowing the reactants to have access into and the products to leave from the pore structure than the mesoporous TiO_2 . This might lead to a much easier conversion of biuret (straight chain compound) to cyanuric acid (cyclic compound) according to Eq. (6). This effect is relatively dominant at high temperatures (250 and 300°C) because biuret can be easily transformed to cyanuric acid or even released into gas phase, consequently resulting in lowering the photocatalytic H_2 production activity of the N-doped commercial TiO_2 prepared at these conditions. At a calcination temperature of 300°C , in addition to the previous reason, the surface N content is another important parameter, which could be related to the constant photocatalytic activity. From the results of surface N content (Table 2), for any given urea: TiO_2 molar ratio at 300°C , the surface N content was lower than those at the other calcination temperatures with little difference between the urea: TiO_2 molar ratios of 0.5:1 and 1:1, resulting in the almost unchanged H_2 production activity. Moreover, even

though the surface N content of the commercial photocatalyst with a urea:TiO₂ molar ratio of 3:1 was much higher than those at the other two molar ratios, the photocatalytic H₂ production activity remained almost constant. The results suggest that the addition of nitrogen on the photocatalyst surface has to be optimized for a maximum H₂ production activity over both TiO₂ photocatalysts because the specific surface area can be significantly reduced with a higher amount of doped nitrogen.

In summary, the combination of porous structure and N-doping with their proper controls is definitely required for achieving the highest photocatalytic H₂ production activity over the TiO₂ photocatalyst.

4. Conclusions

Two types of N-doped TiO₂ photocatalysts, namely synthesized mesoporous TiO₂ and non-mesoporous commercial TiO₂, were comparatively studied for their photocatalytic H₂ production activity under visible light irradiation. The nanocrystalline mesoporous TiO₂ photocatalyst was synthesized by the surfactant-assisted templating sol-gel method using TIPT as the Ti precursor modified with the ACA agent and LAHC as the surfactant template to control its porosity structure. To modify the visible light absorption ability of the TiO₂ photocatalysts, N-doping was performed. The urea, as a source of N, was mixed with both TiO₂ photocatalysts at various urea:TiO₂ molar ratios and calcined at various calcination temperatures. The obtained N-doped TiO₂ photocatalysts could subsequently absorb visible light. The optimum preparation conditions of the N-doped mesoporous TiO₂ and N-doped commercial TiO₂ for achieving the highest photocatalytic H₂ production activity were a urea:TiO₂ molar ratio of 1:1 at a calcination temperature of 250°C and 0.5:1 at a calcination temperature of 250°C, respectively. However, the N-doped mesoporous TiO₂ prepared at such the optimum conditions exhibited relatively the best photocatalytic activity.

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Table 1 Summary of textural properties of the TiO₂ photocatalysts without and with N-doping prepared at various conditions

Calcination temperature (°C)	Urea:TiO ₂ molar ratio	BET surface area (m ² g ⁻¹)	Mean pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
-	Pure mesoporous TiO ₂	110.30	6.114	0.185
200	0.5:1	78.14	6.150	0.136
	1:1	35.36	6.156	0.070
	3:1	22.12	4.619	0.044
250	0.5:1	82.83	6.146	0.155
	1:1	38.52	6.129	0.080
	3:1	23.45	6.140	0.049
300	0.5:1	75.78	6.150	0.147
	1:1	73.98	6.161	0.137
	3:1	22.86	6.104	0.053
-	Pure Degussa P-25 TiO ₂	69.35	– ^(a)	– ^(a)
200	0.5:1	54.96	– ^(a)	– ^(a)
	1:1	53.26	– ^(a)	– ^(a)
	3:1	17.63	– ^(a)	– ^(a)
250	0.5:1	50.66	– ^(a)	– ^(a)
	1:1	44.63	– ^(a)	– ^(a)
	3:1	20.77	– ^(a)	– ^(a)
300	0.5:1	51.40	– ^(a)	– ^(a)
	1:1	26.21	– ^(a)	– ^(a)
	3:1	24.22	– ^(a)	– ^(a)

^(a) N₂ adsorption-desorption isotherms correspond to IUPAC type II pattern.

Table 2 Summary of surface N content of the TiO₂ photocatalysts prepared at different

conditions

Calcination temperature (°C)	Urea:TiO ₂ molar ratio	Surface N content (wt.%)	
		Mesoporous TiO ₂	Commercial TiO ₂
-	0:1	4.72 ^(a)	2.59 ^(a)
200	0.5:1	5.77	3.96
	1:1	20.11	5.01
	3:1	21.28	7.73
250	0.5:1	8.70	3.21
	1:1	26.23	4.68
	3:1	32.61	7.93
300	0.5:1	7.11	2.35
	1:1	11.23	2.91
	3:1	30.25	7.17

^(a) Pure TiO₂

Figure Captions

Fig. 1. N₂ adsorption-desorption isotherm and pore size distribution (inset) of (a) the as-synthesized mesoporous TiO₂ and (b) the N-doped synthesized TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and calcined at 250°C.

Fig. 2. N₂ adsorption-desorption isotherm and pore size distribution (inset) of (a) the commercial TiO₂ and (b) the N-doped commercial TiO₂ prepared at a urea:TiO₂ molar ratio of 0.5:1 and calcined at 250°C.

Fig. 3. UV-visible spectra of (a) pure nanocrystalline mesoporous TiO₂ and (b)-(d) N-doped mesoporous TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and 3:1, respectively, prepared at a calcination condition of 250°C.

Fig. 4. UV-visible spectra of (a) commercial TiO₂ and (b)-(d) N-doped commercial TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at calcination condition of 250°C.

Fig. 5. XRD patterns of (a) pure mesoporous TiO₂, and (b)-(d) N-doped mesoporous TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at a calcination condition of 200°C, (e)-(g) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 250°C, and (h)-(j) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 300°C (A: Anatase TiO₂, B: Biuret, C: Cyanuric acid).

Fig. 6. XRD patterns of (a) commercial TiO₂, (b)-(d) N-doped commercial TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at a calcination condition of 200°C, (e)-(g) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 250°C, and (h)-(j) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 300°C (A: Anatase TiO₂, R: Rutile TiO₂, B: Biuret, C: Cyanuric acid).

Fig. 7. XPS spectra of (a) Ti2p, (b) N1s, and (c) O1s of N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C.

Fig. 8. Photocatalytic H₂ production activity of (a) N-doped mesoporous TiO₂ and (b) N-doped commercial TiO₂ prepared with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1 and at different calcination temperatures of 200, 250, and 300°C (Reaction conditions: 0.2 g photocatalyst, 150 ml distilled water, 50 ml methanol, and 5 h irradiation time).

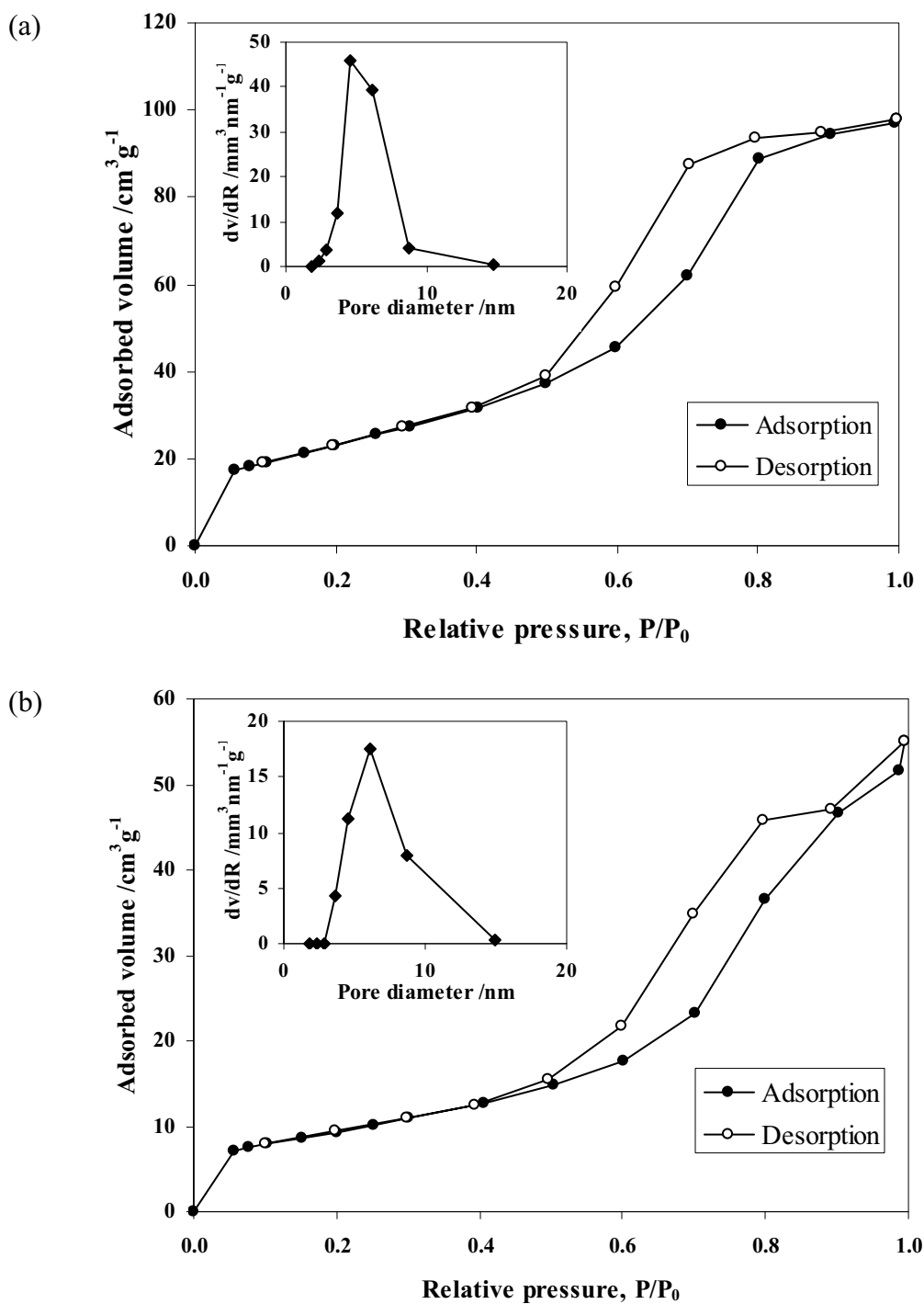


Fig. 1. N_2 adsorption-desorption isotherm and pore size distribution (inset) of (a) the as-synthesized mesoporous TiO_2 and (b) the N-doped synthesized TiO_2 prepared at a urea: TiO_2 molar ratio of 1:1 and calcined at 250°C .

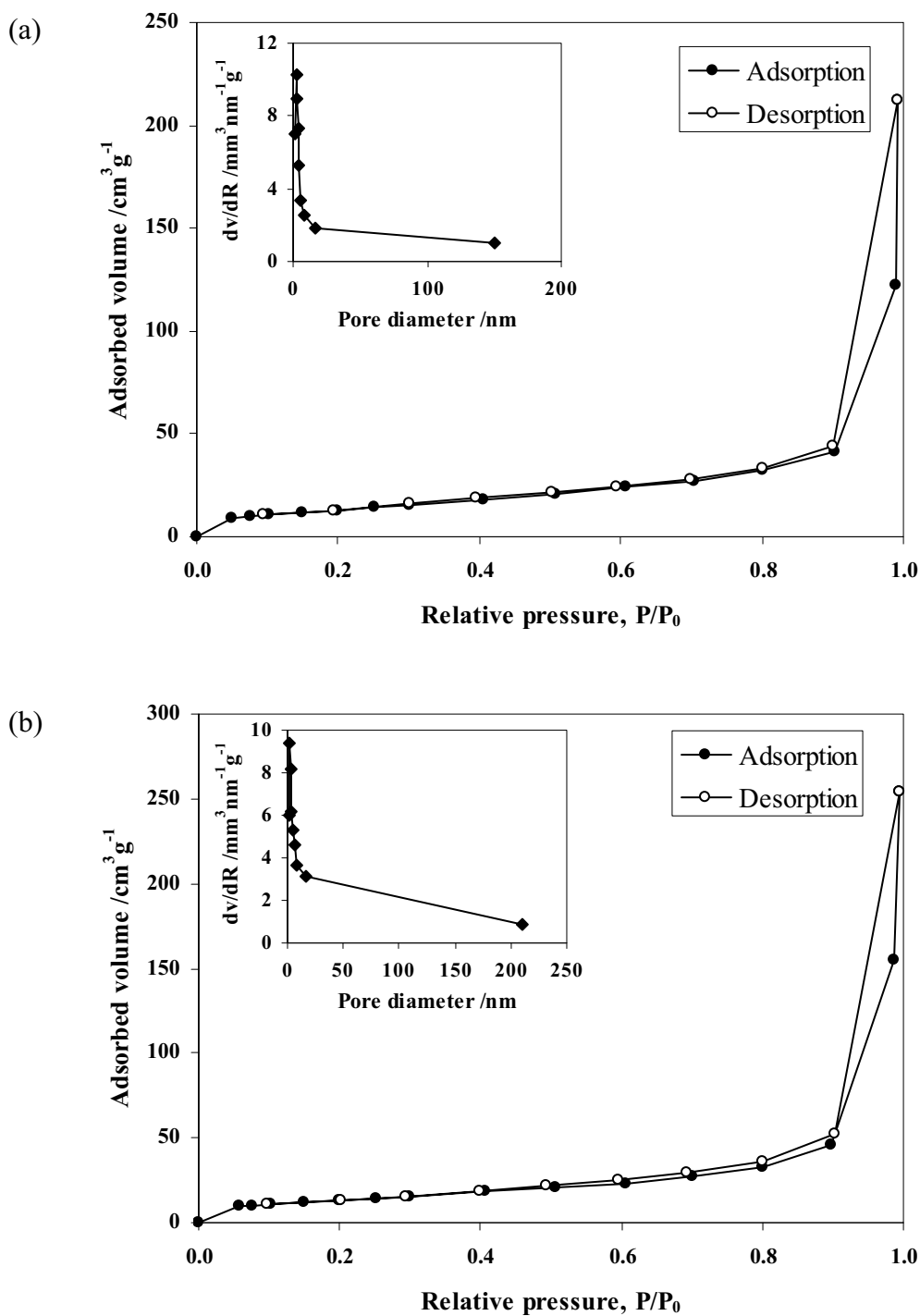


Fig. 2. N₂ adsorption-desorption isotherm and pore size distribution (inset) of (a) the commercial TiO₂ and (b) the N-doped commercial TiO₂ prepared at a urea:TiO₂ molar ratio of 0.5:1 and calcined at 250°C.

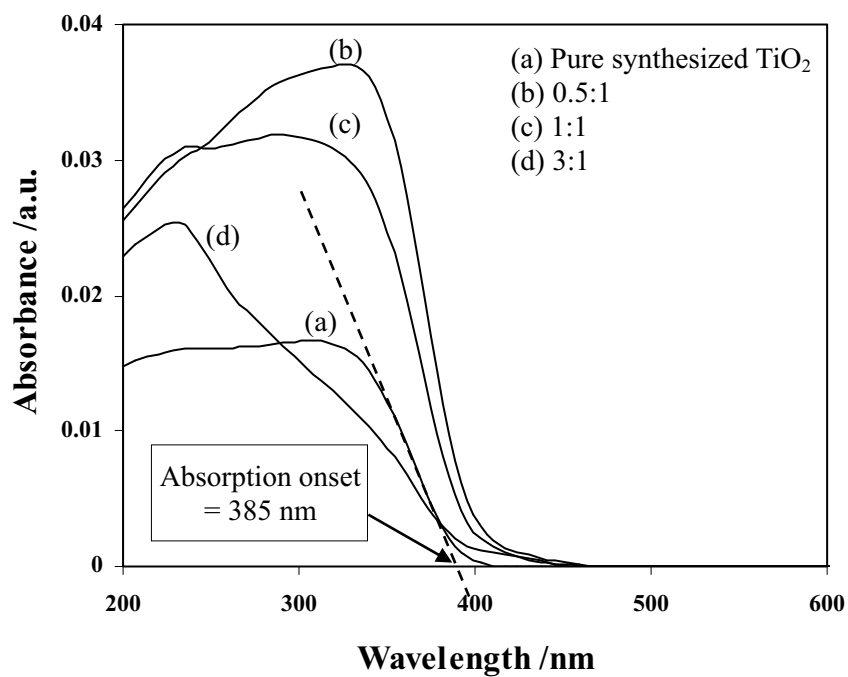


Fig. 3. UV-visible spectra of (a) pure nanocrystalline mesoporous TiO₂ and (b)-(d) N-doped mesoporous TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and 3:1, respectively, prepared at a calcination condition of 250°C.

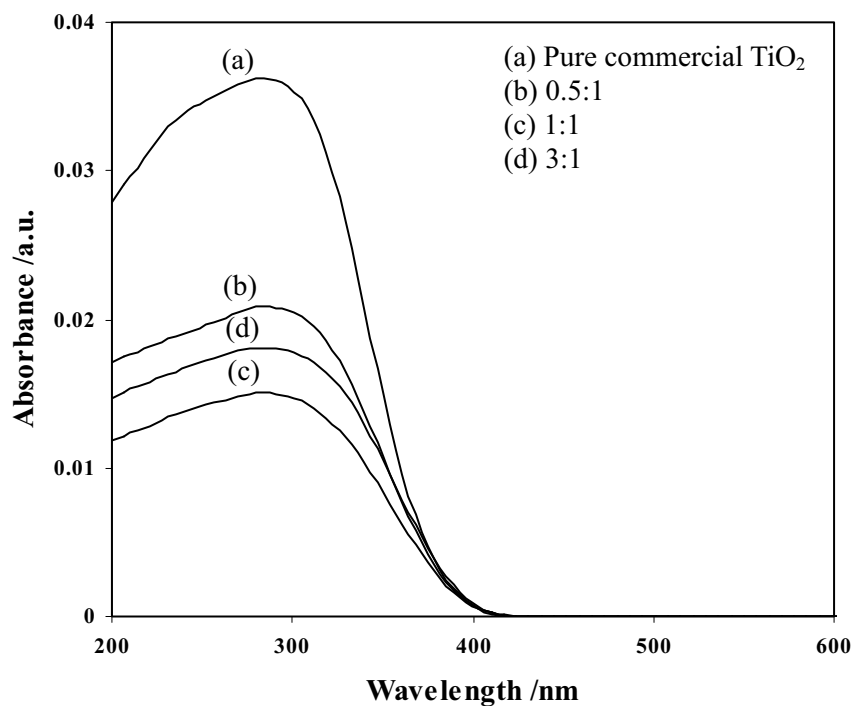


Fig. 4. UV-visible spectra of (a) commercial TiO₂ and (b)-(d) N-doped commercial TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at a calcination condition of 250°C.

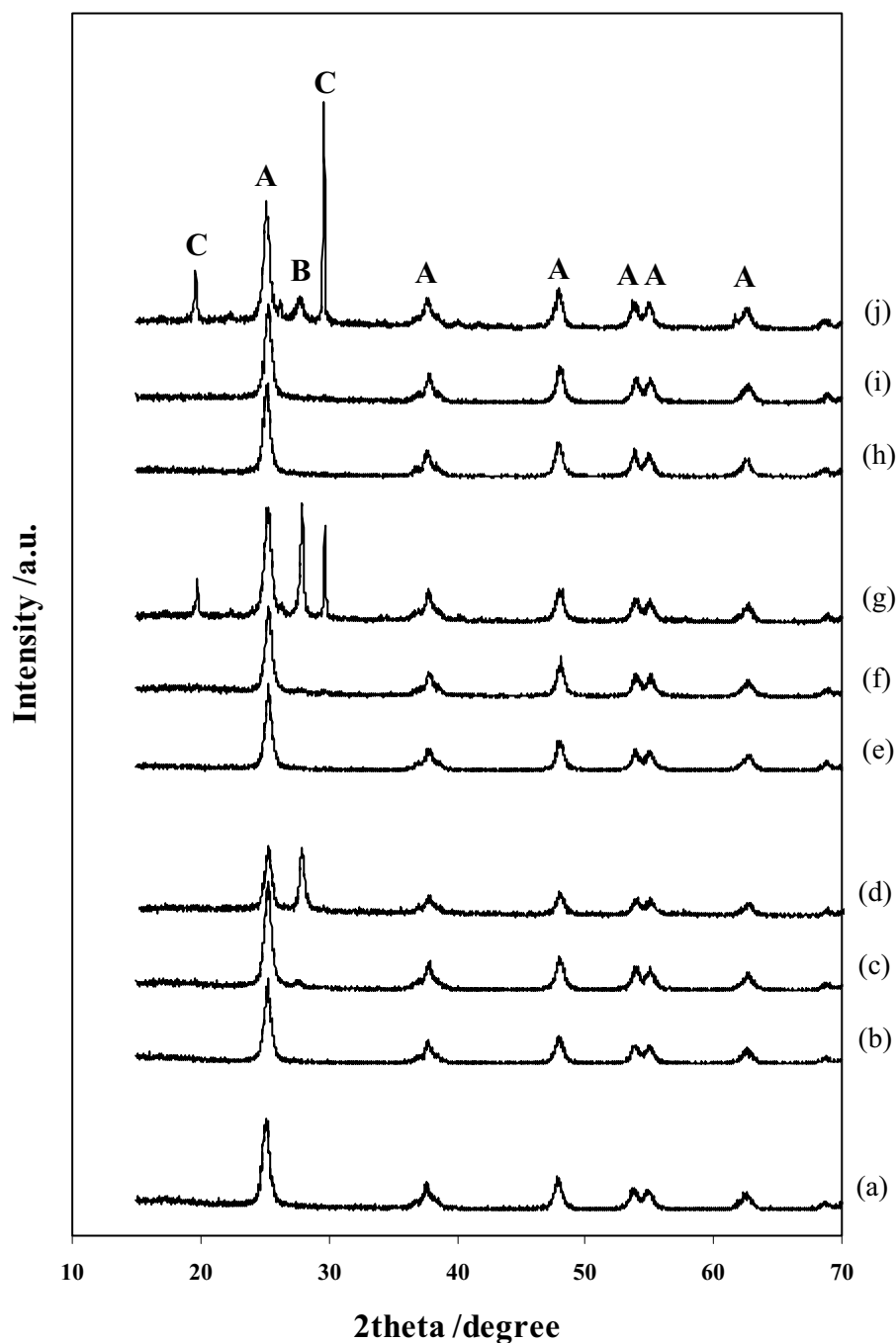


Fig. 5. XRD patterns of (a) pure mesoporous TiO_2 , and (b)-(d) N-doped mesoporous TiO_2 with different urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at a calcination condition of 200°C, (e)-(g) urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 250°C, and (h)-(j) urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 300°C (A: Anatase TiO_2 , B: Biuret, C: Cyanuric acid).

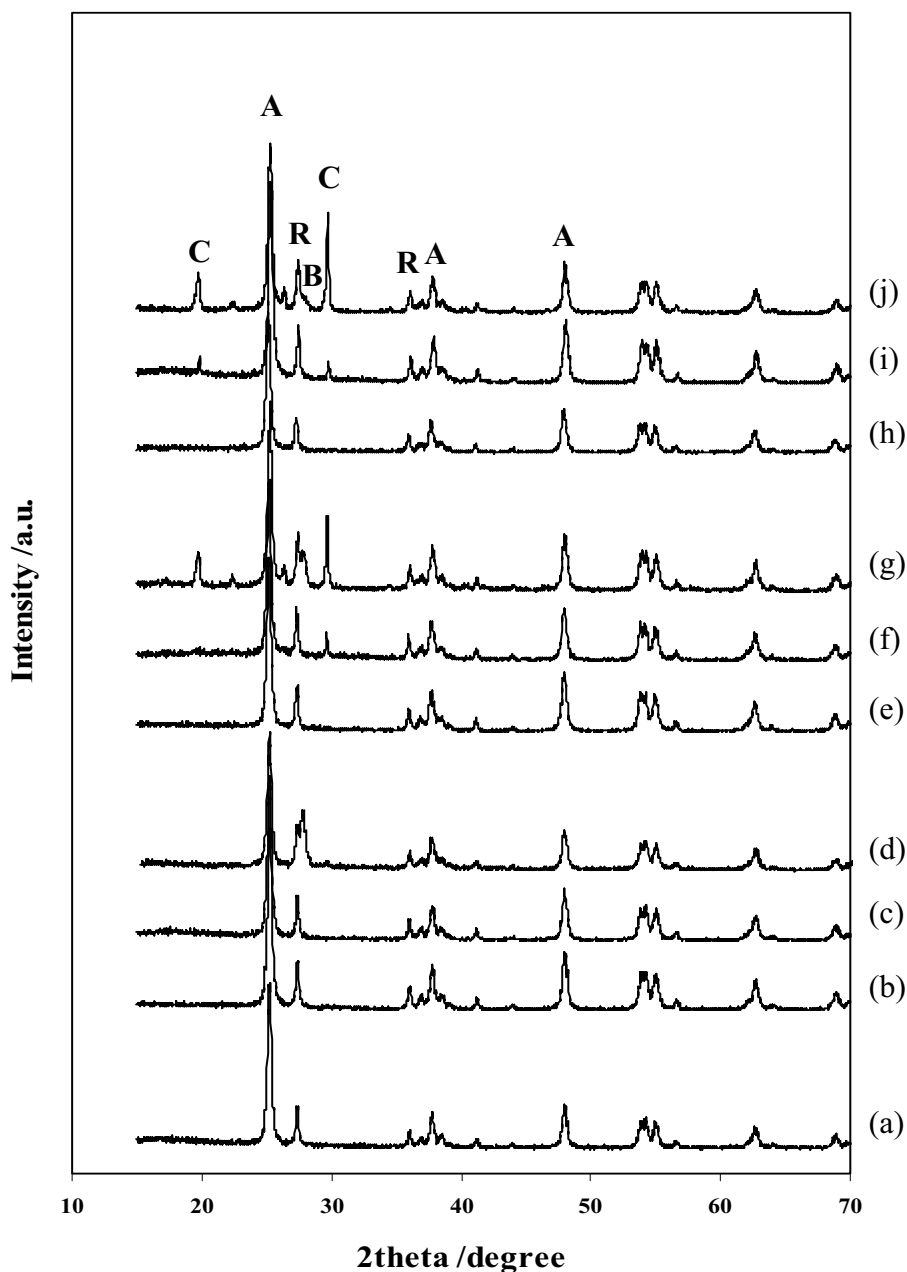


Fig. 6. XRD patterns of (a) commercial TiO₂, (b)-(d) N-doped commercial TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at a calcination condition of 200°C, (e)-(g) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 250°C, and (h)-(j) urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 300°C (A: Anatase TiO₂, R: Rutile TiO₂, B: Biuret, C: Cyanuric acid).

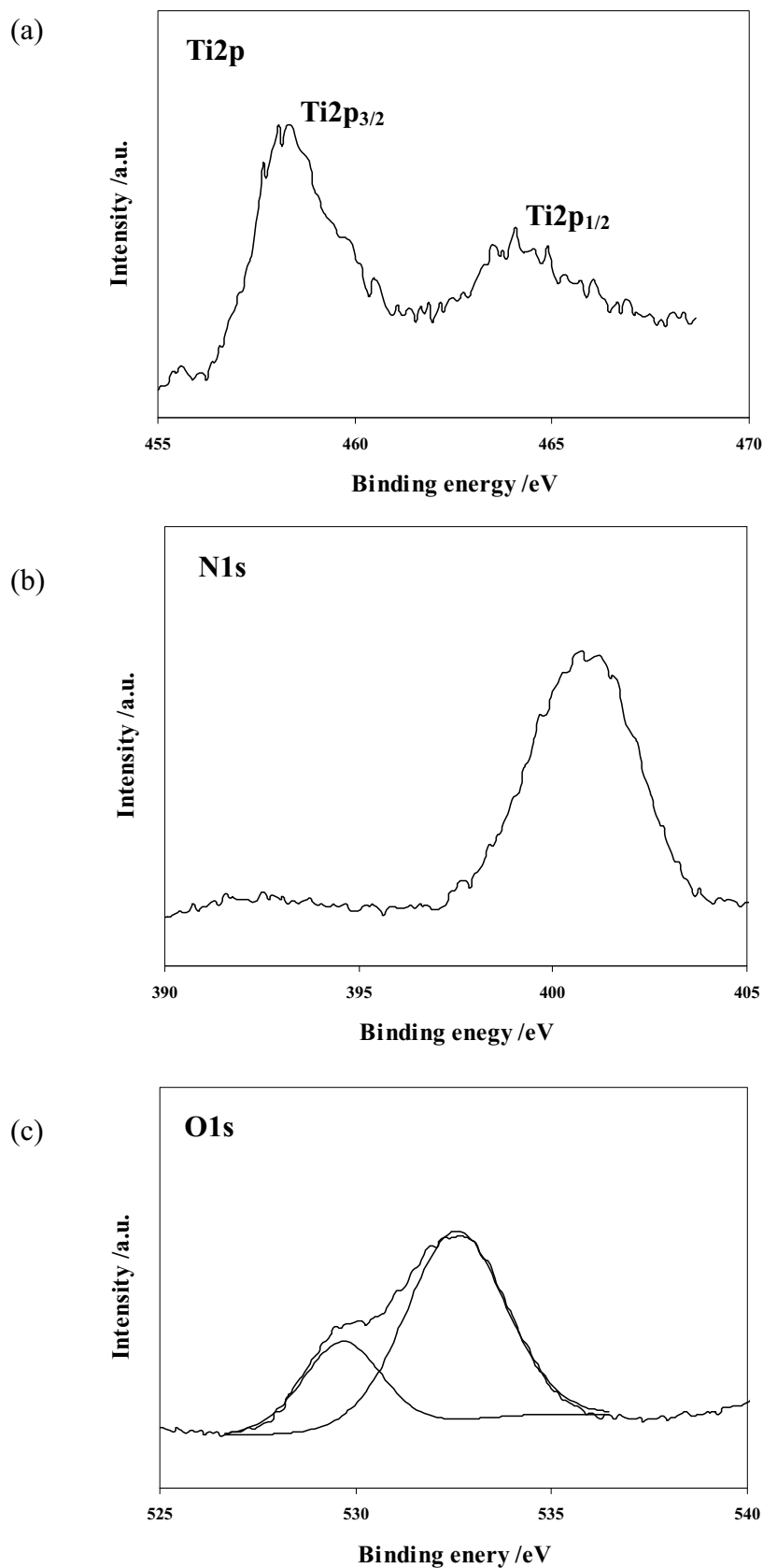


Fig. 7. XPS spectra of (a) Ti2p, (b) N1s, and (c) O1s of N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C.

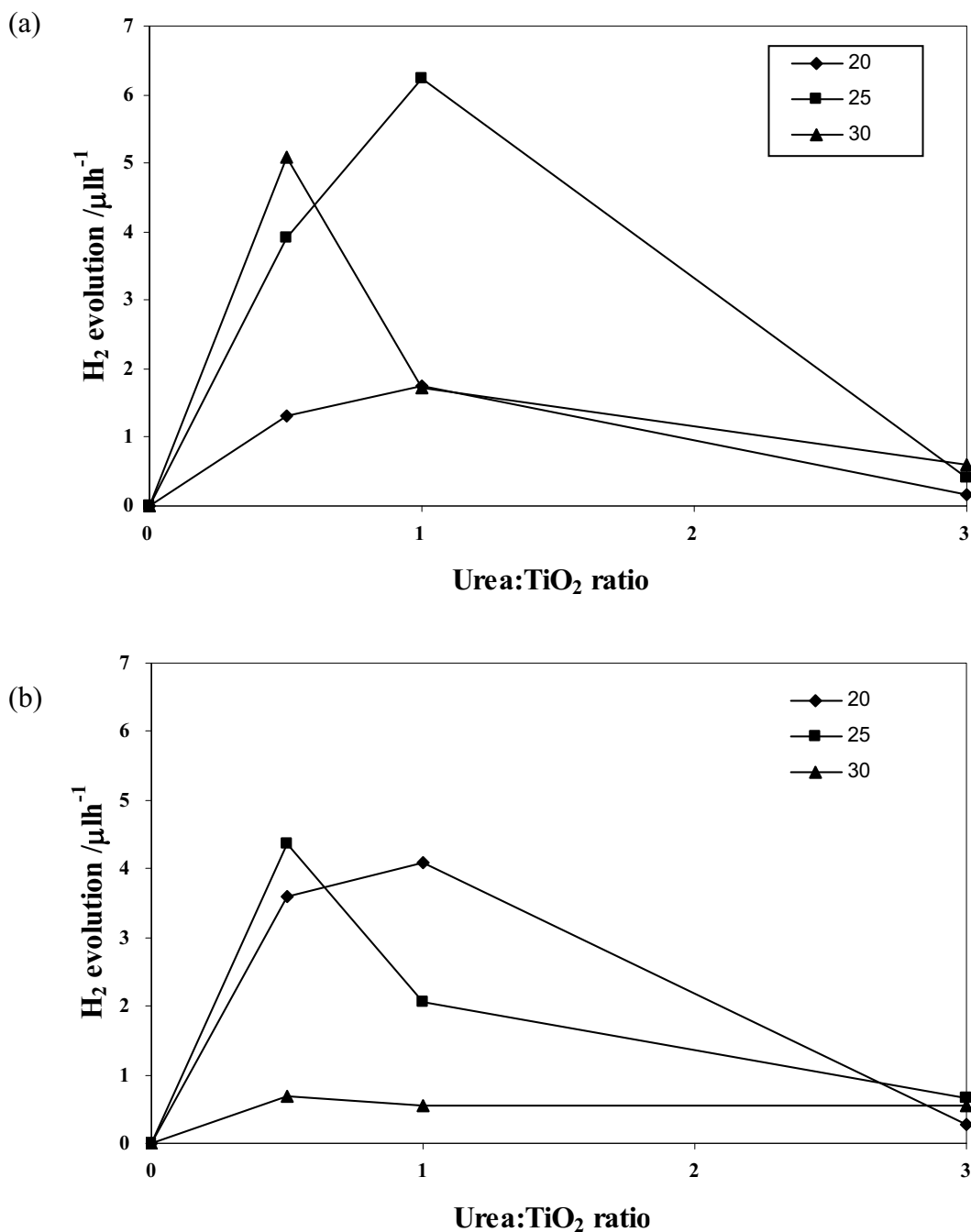


Fig. 8. Photocatalytic H₂ production activity of (a) N-doped mesoporous TiO₂ and (b) N-doped commercial TiO₂ prepared with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and, 3:1 and at different calcination temperatures of 200, 250, and 300 °C (Reaction conditions: 0.2 g photocatalyst, 150 ml distilled water, 50 ml methanol, and 5 h irradiation time).

ภาคผนวก ค

Extended abstract of The 4th Asia Pacific Congress on Catalysis

Probing factors affecting photocatalytic H₂ evolution over nanocrystalline mesoporous Pt/TiO₂ prepared by single-step sol-gel process with surfactant template

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ABSTRACT

Nanocrystalline Pt/TiO₂ photocatalyst possessing mesoporous characteristic and narrow monomodal pore size distribution was synthesized and utilized to study photocatalytic H₂ evolution from water. A single-step sol-gel process with surfactant template acting as mesopore-directing agent was employed to load Pt onto the mesoporous TiO₂. The effects of various operational parameters, including solution pH, photocatalyst concentration, sacrificial reagent type, and sacrificial reagent concentration on the photocatalytic H₂ evolution activity over the mesoporous TiO₂ loaded with optimum Pt content were studied. The optimum values of solution pH, photocatalyst concentration, and sacrificial reagent concentration, as well as appropriate type of sacrificial reagent were experimentally obtained.

1. INTRODUCTION

Direct production of hydrogen from photocatalytic splitting of water over semiconductors utilizing solar light energy has attracted much attention aiming to searching a suitable source of hydrogen for future clean energy supply. TiO₂ has been intensively used in photocatalysis including photocatalytic H₂ evolution. Noble metals behaving as cocatalysts have been used to disperse on TiO₂ surface in order to expedite the photoinduced electron transport upon band gap excitation. A multitude of interests have been focused on Pt loading on TiO₂ to enhance photocatalytic H₂ evolution activity [1]. In this study, nanocrystalline mesoporous TiO₂ was prepared by a surfactant-assisted templating sol-gel process. Single-step sol-gel method was used to load Pt cocatalyst onto TiO₂ photocatalyst during sol-gel preparation. The nanocrystalline mesoporous Pt/TiO₂ was applied for photocatalytic H₂ evolution. The effects of several operational parameters on photocatalytic H₂ evolution activity were mainly investigated.

2. EXPERIMENTAL

For the photocatalyst synthesis procedure [2], a specified amount of tetraisopropyl orthotitanate (TIPT) was mixed with acetylacetone (ACA) and 0.1 M laurylamine hydrochloride (LAHC) aqueous solution in an orderly manner. The mixed solution was stirred at 40°C until obtaining transparent yellow sol. Then, a necessary amount of hydrogen hexachloroplatinate(IV) hydrate in methanol was added into the sol, and

the final mixture was further aged at 40°C. Afterwards, the gel was formed by placing the sol-containing solution into an oven at 80°C for a few days, dried overnights at 80°C, and calcined at 500°C. The photocatalyst was methodically characterized by XRD, N₂ adsorption-desorption analysis, and TEM. Studies of the photocatalytic H₂ evolution reaction over the synthesized photocatalyst was carried out in a closed-gas system. A specified amount of photocatalyst was suspended in an aqueous solution of sacrificial reagents under various reaction conditions within a Pyrex glass reactor. The reaction was started by exposing the photocatalytic system with light irradiated from 300 W high-pressure Hg lamp. The gaseous H₂ evolved was periodically collected and analyzed by a gas chromatograph equipped with thermal conductivity detector.

3. RESULTS AND DISCUSSION

The XRD pattern of the synthesized photocatalyst shows that the diffractogram was indexed to anatase TiO₂. The absence of diffraction peaks of Pt indicates that Pt was in a very high dispersion degree. The particle sizes of both Pt and TiO₂ from TEM analysis are in the region of 1-2 and 10-15 nm, respectively. The N₂ adsorption-desorption isotherm exhibited IUPAC type IV pattern with single hysteresis loop, which is a prevalent characteristic of mesoporous material [3]. The pore size distribution was also very narrow and monomodal, suggesting a good quality of the sample.

The photocatalytic H₂ evolution results over the nanocrystalline mesoporous TiO₂ loaded with various Pt contents show that optimum Pt loading was 0.6 wt%. The optimization results over the reveal that the mild acidic pH values in the range of 5-6 were favorable for the photocatalytic H₂ evolution reaction. Methanol was found to be the most efficient sacrificial reagent among several types of sacrificial reagent investigated. The optimum concentrations photocatalyst and methanol were found to be 0.91 g/l and 2.25 M, respectively.

4. CONCLUSIONS

Photocatalytic activity for H₂ evolution was investigated over nanocrystalline mesoporous TiO₂ photocatalyst loaded with Pt cocatalyst by the single-step sol-gel process with surfactant template. The optimum conditions for obtaining the highest photocatalytic activity over the nanocrystalline mesoporous TiO₂ loaded with 0.6 wt% Pt were at solution pH of 5-6, photocatalyst concentration of 0.91 g/l, and methanol concentration of 2.25 M.

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**Abstract of The 2nd International Conference on Advances in Petrochemicals and
Polymers**

Use of Pt/N-Doped Titania for Photocatalytic Hydrogen Evolution from Water under Visible Light Irradiation

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To date, there have been a multitude of studies on the production of hydrogen from direct water splitting using the most investigated semiconductor photocatalyst, titania (TiO₂), because hydrogen has been considered as a clean-burning fuel. Moreover, this process takes advantage of the utilization of available and abundant resources, water and sunlight, which is believed to be a sustainable source of future energy supply. However, TiO₂-composed systems require some modifications in order to improve the photocatalytic activity under visible light, which is the main portion of sunlight exposing the earth surface, such as anion doping of TiO₂. In this study, N-doped mesoporous TiO₂ and N-doped non-mesoporous commercial TiO₂, Degussa P-25, prepared at different N-doping content and calcination temperatures, as well as the effect of Pt loading were investigated for photocatalytic H₂ evolution under visible light irradiation. It was experimentally found that N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C exhibited the highest efficiency. For the N-doped P-25, the preparation conditions of the molar ratio of 0.5:1 and the temperature of 250°C is the best, but still less photocatalytically active than such the N-doped mesoporous TiO₂ prepared at optimum conditions. Pt loading onto the N-doped mesoporous TiO₂ via incipient wetness impregnation method was performed to improve the photocatalytic activity, exhibiting the optimum Pt loading content of 1.3 wt.%.

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Photocatalytic Production of Hydrogen from Water over Pt/N-Doped Titania under Visible Light Irradiation

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Abstract

To date, there have been a multitude of studies on the production of hydrogen from direct water splitting using the most investigated semiconductor photocatalyst, titania (TiO₂), because hydrogen has been considered as a clean-burning fuel. Moreover, this process takes advantage of the utilization of available and abundant resources, water and sunlight, which are believed to be sustainable sources of future energy supply. However, TiO₂-composed systems require some modifications in order to improve the photocatalytic activity under visible light, which is the main portion of sunlight exposing the earth surface, such as anion doping of TiO₂. In this study, the preparation of N-doped mesoporous TiO₂ and N-doped non-mesoporous commercial TiO₂, Degussa P-25, prepared at different N-doping content and calcination temperatures, as well as the effect of Pt loading, were investigated for photocatalytic H₂ evolution under visible light irradiation. It was experimentally found that N-doped mesoporous TiO₂ prepared at a urea:TiO₂ molar ratio of 1:1 and a calcination temperature of 250°C exhibited the highest efficiency. For the N-doped P-25, the preparation condition of the molar ratio of 0.5:1 and the temperature of 250°C is the best, but still less photocatalytically active than such the N-doped mesoporous TiO₂ prepared at the optimum conditions. Pt loading onto the N-doped mesoporous TiO₂ via incipient wetness impregnation method was performed to improve the photocatalytic activity, exhibiting the optimum Pt loading content of 1.3 wt.%.

1. INTRODUCTION

H₂ is considered to be an alternative fuel for replacing conventional energy resources, such as coal, natural gas, and fossil fuel, which are gradually depleting, because it is clean energy, unlike the conventional ones, which produce CO₂ that can cause global warming upon their combustion. The combustion of H₂ can generate energy, and the only by product is water or water vapor. Moreover, it can be used in many applications, especially a fuel for fuel cells.

The photocatalytic water splitting is a promising process for producing H₂ since water is used as reactant, which is an abundantly available substrate. Moreover, the solar energy as an energy resource is used for H₂ production from water. It can be considered as an ideal process since the sunlight is also renewable resource. The photocatalytic H₂ evolution from water over photocatalyst can achieve when the photocatalyst directly absorbs light with energy equal or higher than its energy band gap, and then the electrons are excited from the valance band (VB) to the conduction band (CB) and reduce photons to H₂ molecules (Serpone & Pelizzetti, 1989; Hoffmann *et al*, 1995). Among various semiconductors, TiO₂ is the most investigated photocatalyst because it is chemically stable, non-corrosive, environmentally friendly, and cost-effective. Despite the positive attributes of TiO₂, there are few drawbacks associated with its use: (i) charge carrier recombination occurs easily and (ii) the band gap absorption does not allow the utilization of visible light. In order to solve the former problems, the combination with other technologies, such as noble metal loading and hole scavenger addition, are necessary. To improve visible light absorption ability of TiO₂, anion doping, such as nitrogen-doped TiO₂, is an effective method to enhance visible light response (Asahi *et al*, 2001).

The mesoporous materials have attracted much attention in the area of catalysis because of their large surface area and narrow pore size distribution (Rouquerol *et al*, 1999). The sol-gel process is an effective method for synthesis of mesoporous materials. Moreover, in combination with a surfactant template, the sol-

gel process allows the formation of mesoporous oxide with controlled porosity. In this study, the photocatalytic H₂ evolution from water by comparatively using N-doped mesoporous and N-doped non-mesoporous TiO₂ (commercial Degussa P-25 TiO₂) photocatalysts under visible light irradiation without and with Pt loading was investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

All chemicals/materials used in this research are as follows. Tetraisopropyl orthotitanate (TIPT, Ti(OCH(CH₃)₂)₄), (synthesis grade, MERCK), as Ti precursor and acetylacetone (ACA, CH₃COCH₂COCH₃), (synthesis grade, Rasayan), as a modifying ligand were used for synthesized TiO₂ photocatalyst. Laurylamine hydrochloride (LAHC, CH₃(CH₂)₁₁NH₂·HCl), (synthesis grade, MERCK), was used as surfactant template to control porosity. Urea (NH₂CONH₂), (Laboratory Reagent, UNILAB), and hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O), (analytical grade, ALDRICH), were used as N and Pt sources, respectively. Methanol (CH₃OH), (Anhydroscan, LAB-SCAN Analytical Sciences), was used as hole scavenger or electron donor for photocatalytic H₂ evolution. Commercial Degussa P-25 TiO₂ was selected for comparative study of photocatalytic H₂ evolution.

2.2. Synthesis procedure

The nanocrystalline mesoporous TiO₂ photocatalyst was synthesized via the surfactant-assisted templating sol-gel method (Sreethawong *et al*, 2005). Firstly, tetraisopropyl orthotitanate (TIPT) as a titanium precursor was mixed with acetylacetone (ACA) at the molar ratio of unity. To control porosity, laurylamine hydrochloride (LAHC) aqueous solution was added into the TIPT/ACA solution with the molar ratio of TIPT to LAHC of 4. The mixture was continuously stirred at 40°C overnight to obtain transparent yellow sol. The gel was formed by placing the sol into the oven at 80°C for a week. Then, the gel was dried overnight at 80°C and then calcined at 500°C for 4 h to remove LAHC template and obtain nanocrystalline mesoporous TiO₂. After that, the synthesized mesoporous TiO₂ and Degussa P-25 TiO₂ powder was mixed with urea at various urea:TiO₂ molar ratios by using an agate mortar. The powders were then calcined at 200–300°C for 2 h. In order to improve the photocatalytic activity, Pt was loaded onto the N-doped TiO₂ photocatalyst via incipient wetness impregnation method and then calcined at 200°C for 6 h.

2.3. Characterization techniques

A nitrogen adsorption system (Quantachrome Autosorb 1) was employed to measure adsorption–desorption isotherms at liquid nitrogen temperature of -196°C. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) approaches were utilized to determine specific surface area, mean pore size and pore size distribution. The sample was degassed at 150°C for 2 h to remove physisorbed gases prior to measurement. The sample morphology was observed by a transmission electron microscope (JEOL 2000CX) operated at 200 kV. X-ray diffraction (XRD) was used to identify the structure and composition of crystalline photocatalyst. A Rigaku RINT 2000 XRD system generating monochromated CuKα radiation with continuous scanning mode at the rate of 5°/min and operating conditions of 40 kV and 30 mA was used to obtain XRD patterns. A Shimadzu UV-2550 UV-Visible spectrophotometer was exploited to record diffuse reflectance spectra of the samples at room temperature with BaSO₄ as the reference. The surface composition was analyzed by an X-ray photoelectron spectroscopy (XPS). A MgKα source emitting X-ray energy of 1253.6 eV was used as X-ray source.

2.4. Photocatalytic H₂ evolution system

A specified amount of all prepared photocatalysts (0.2 g), namely N-doped synthesized TiO₂, N-doped Degussa P-25, and Pt-loaded N-doped TiO₂, was suspended in an aqueous methanol solution (50 ml CH₃OH and 150 ml distilled water) by means of magnetic stirrer within a reactor made of Pyrex glass. The mixture was deaerated by purging with Ar gas for 45 min in dark environment. The reaction was started by exposing the mixture with visible light irradiation from a 300 W Xe arc lamp emitting light with wavelength longer than 400 nm. The gaseous H₂ evolved was periodically collected by a gas-tight syringe and analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

3. RESULTS AND DISCUSSION

3.1. Photocatalyst characterizations

To study mesoporous and non-mesoporous structures of the TiO₂ photocatalysts, N₂ adsorption-desorption analysis was used. The N₂ adsorption-desorption isotherms of the synthesized TiO₂ exhibited typical IUPAC type IV pattern with hysteresis loop, indicating mesoporous structure (Rouquerol *et al*, 1999), as shown in Figure 1. The pore size distribution is quite narrow with mean pore diameter in the mesopore region (pore diameter between 2-50 nm). For the commercial Degussa P-25 TiO₂, N₂ adsorption-desorption isotherms correspond to IUPAC type II pattern (Rouquerol *et al*, 1999), exhibiting non-mesoporous characteristics due to the absence of hysteresis loop, as shown in Figure 1. The pore size distribution is quite broad since their pore size distributions not only exist in the mesoporous region but also mostly cover the macropore with pore diameter larger than 50 nm.

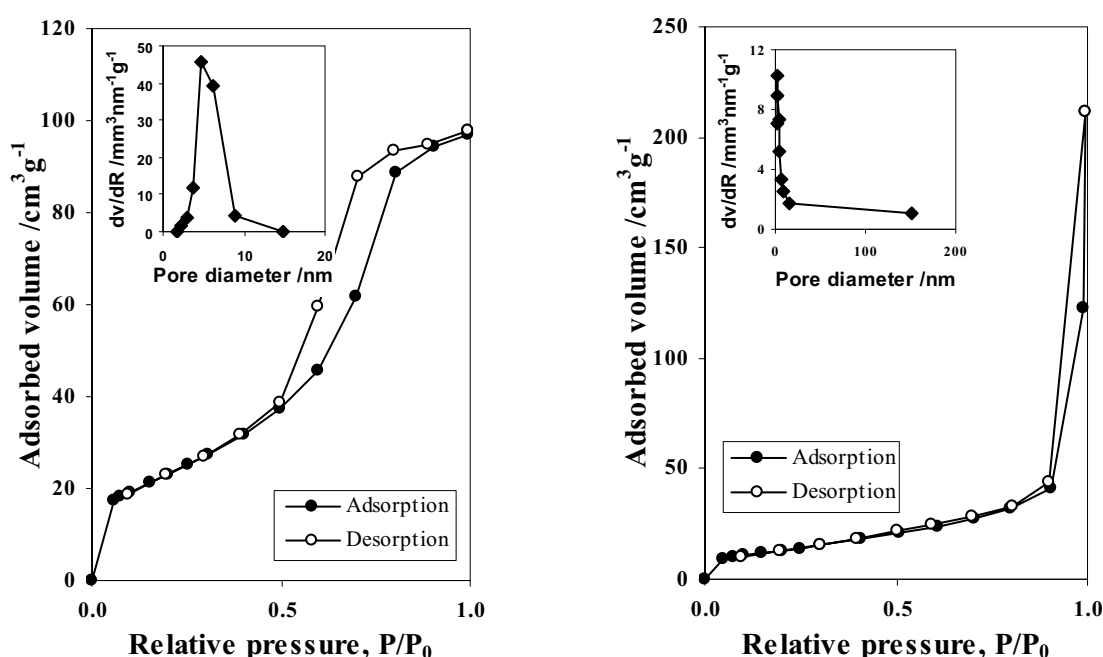


Figure 1 N₂ adsorption-desorption isotherms and (inset) pore size distribution of (left) the synthesized mesoporous TiO₂ calcined at 500°C for 4 h and (right) the commercial Degussa P-25 TiO₂.

To investigate the visible light absorption ability of the photocatalysts, UV-Vis spectroscopy was used. For pure mesoporous TiO₂, its absorption onset is approximately at 385 nm, corresponding to UV region. For the N-doped mesoporous TiO₂, the absorption band shifts to wavelength longer than 400 nm, corresponding to the visible region. So, the N-doping method can improve the visible light absorption ability of TiO₂. For the pure commercial Degussa P-25 TiO₂, the absorption onset begins at the wavelength longer

than 400 nm. Because the commercial Degussa P-25 TiO₂ possesses both anatase and rutile phases, their energy band gaps are approximately 3.2 and 3.0 eV for anatase and rutile TiO₂, respectively, which can help absorb both UV and visible regions. Consequently, the absorption onsets between pure and N-doped commercial Degussa P-25 TiO₂ are slightly different.

Surface area analysis was used to characterize the textural property of photocatalyst, as shown in Table 1. For all mesoporous and commercial Degussa P-25 TiO₂ photocatalysts, the surface area tended to decrease with increasing the urea:TiO₂ molar ratio at different calcination temperatures. The possible explanation is that the urea as N precursor can be decomposed to many components depending on temperature. Two main components are biuret and cyanuric acid (Schaber *et al*, 1999). The appearance of biuret and cyanuric acid affected to the decrease in the surface area. For the N-doped mesoporous TiO₂, the mean pore diameter was quite similar to the pure mesoporous TiO₂, and the total pore volume decreased with increasing urea:TiO₂ molar ratio. For the commercial Degussa P-25 TiO₂, the mean pore diameter and total pore volume are always not reported because it mostly consists of macropore with pore diameter larger than 50 nm.

Table 1. Summary of textural properties of the TiO₂ photocatalysts without and with N-doping prepared at various conditions

Calcination temperature/°C	Urea:TiO ₂ molar ratio	BET surface area/m ² g ⁻¹	Mean pore diameter/nm	Total pore volume/cm ³ g ⁻¹
	Pure mesoporous TiO ₂	110.30	6.114	0.185
200	0.5:1	78.14	6.150	0.136
	1:1	35.36	6.156	0.070
	3:1	22.12	4.619	0.044
250	0.5:1	82.83	6.146	0.155
	1:1	38.52	6.129	0.080
	3:1	23.45	6.140	0.049
300	0.5:1	75.78	6.150	0.147
	1:1	73.98	6.161	0.137
	3:1	22.86	6.104	0.053
	Pure Degussa P-25 TiO ₂	69.35	– (a)	– (a)
200	0.5:1	54.96	– (a)	– (a)
	1:1	53.26	– (a)	– (a)
	3:1	17.63	– (a)	– (a)
250	0.5:1	50.66	– (a)	– (a)
	1:1	44.63	– (a)	– (a)
	3:1	20.77	– (a)	– (a)
300	0.5:1	51.40	– (a)	– (a)
	1:1	26.21	– (a)	– (a)
	3:1	24.22	– (a)	– (a)

^(a)N₂ adsorption-desorption isotherm corresponds to IUPAC type II pattern.

The formation of biuret and cyanuric acid was confirmed by XRD analysis, as shown in Figure 2. The dominant peak of all mesoporous TiO₂ is at about 25° (JCPDS Card No. 21-1272) (Smith, 1960), which exhibits anatase phase. For all commercial Degussa P-25 TiO₂, the dominant peaks are about at 25 and 27° (JCPDS Card No. 21-1276) (Smith, 1960), which exhibit both anatase and rutile phases, respectively. At temperature of 200°C, the biuret formation was first clearly observed. At temperature of 250°C, the cyanuric acid was initially formed. At 300°C, the cyanuric acid formation was highly observed, and the biuret formation was observed with relatively less amount when compared to the temperature of 250°C at the same molar ratio of urea to titania. These results indicate that the cyanuric acid was formed at a temperature higher than 200°C, above which the biuret started decomposing.

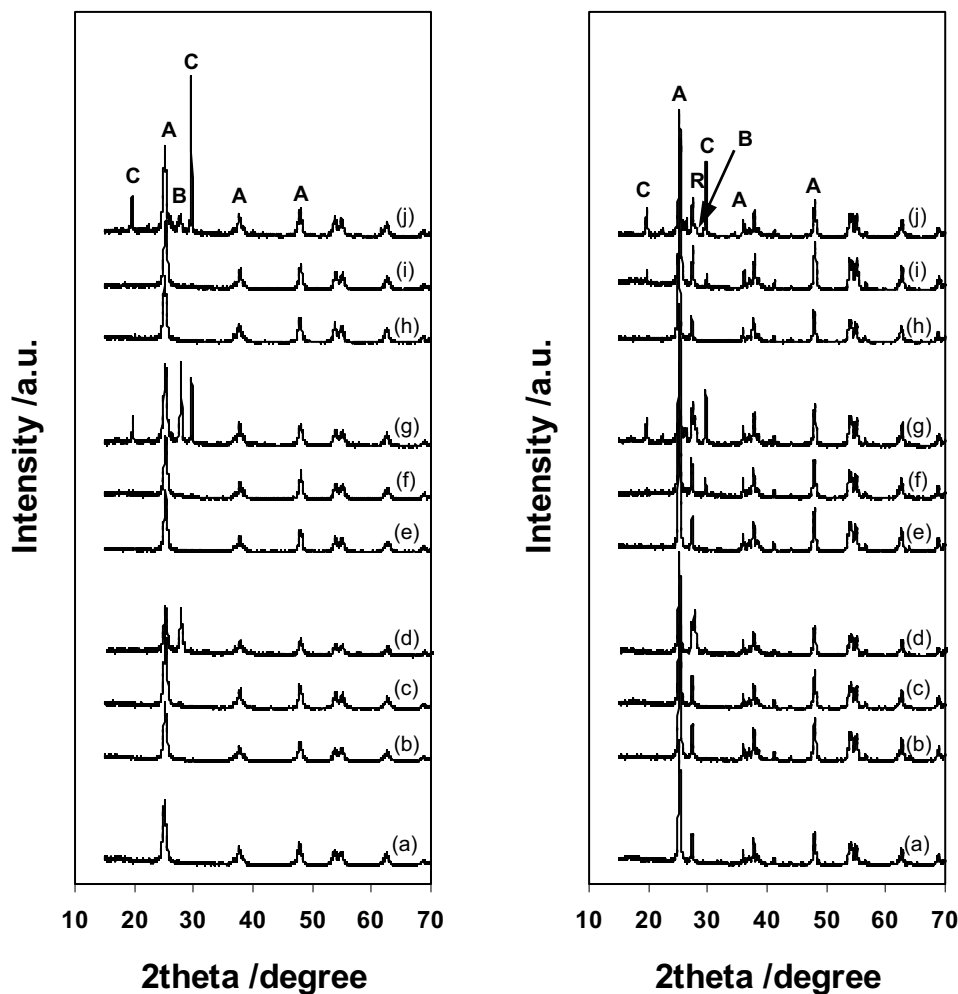


Figure 2 XRD patterns of (left) mesoporous TiO_2 and (right) commercial Degussa P-25 TiO_2 : (a) pure TiO_2 , and (b)-(d) N-doped TiO_2 with different urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, prepared at calcination conditions of 200°C for 2 h, (e)-(g) urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 250°C for 2 h, (h)-(j) urea: TiO_2 molar ratios of 0.5:1, 1:1, and, 3:1, respectively, at 300°C for 2 h (A: Anatase TiO_2 , R: Rutile, B: Biuret, C: Cyanuric acid).

To determine the surface N content and oxidation state, XPS analysis was used. It can be found that the surface N content increased with increasing the urea: TiO_2 molar ratio for both the mesoporous TiO_2 and commercial Degussa P-25 due to the presence of higher amount of urea molecules as to increase the doping capability, as shown in Table 2.

Table 2 The summary of surface N content of N-doped photocatalyst

Calcination temperature/°C	Urea:mesoporous TiO ₂ molar ratio	Surface N content/wt%	Urea:Degussa P-25 molar ratio	Surface N content/wt%
	Pure mesoporous TiO ₂	4.72	Pure Degussa P-25 TiO ₂	2.59
200	0.5:1	5.77	0.5:1	3.96
	1:1	20.11	1:1	5.01
	3:1	21.28	3:1	7.73
250	0.5:1	8.70	0.5:1	3.21
	1:1	26.23	1:1	4.68
	3:1	32.61	3:1	7.93
300	0.5:1	7.11	0.5:1	2.35
	1:1	11.23	1:1	2.91
	3:1	30.25	3:1	7.17

3.2. Photocatalytic H₂ evolution results

For photocatalytic H₂ evolution study, the photocatalytic activity in the absence of light irradiation, photocatalyst, or methanol was initially studied. It was found that there was no detectable H₂ evolution in the absence of them, indicating that all of them are necessarily important for the photocatalytic H₂ evolution. The highest H₂ evolution activities of N-doped mesoporous TiO₂ and N-doped Degussa P-25 TiO₂ were obtained at the urea:TiO₂ molar ratio of 1:1 prepared at a calcination temperature of 250°C and 0.5:1 with a calcination temperature 250°C, respectively, as shown in Figure 3. Interestingly, the mesoporous one gave better photocatalytic activity. So, the mesoporous TiO₂ prepared at this optimum condition was taken to study the effect of Pt cocatalyst loading in order to improve the H₂ evolution activity of the system. The Pt was loaded onto the TiO₂ photocatalyst by using incipient wetness impregnation method. In order to understand the role of Pt, the brief mechanism of photocatalytic H₂ evolution over Pt/TiO₂ is first explained. The reaction is initiated by the photoexcitation of TiO₂ particles, which leads to the formation of electron hole pairs. Photogenerated conduction band electrons can be transferred to electron acceptor, H⁺. With Pt on TiO₂ photocatalyst, Pt can rapidly trap electrons, and hydrogen can be produced on Pt by reduction reaction. Likewise, valence band holes can be filled by the electron donor, CH₃OH, resulting in the great prevention of photoinduced charge recombination (Kawai & Sakata, 1980; Bamwenda *et al*, 1995).

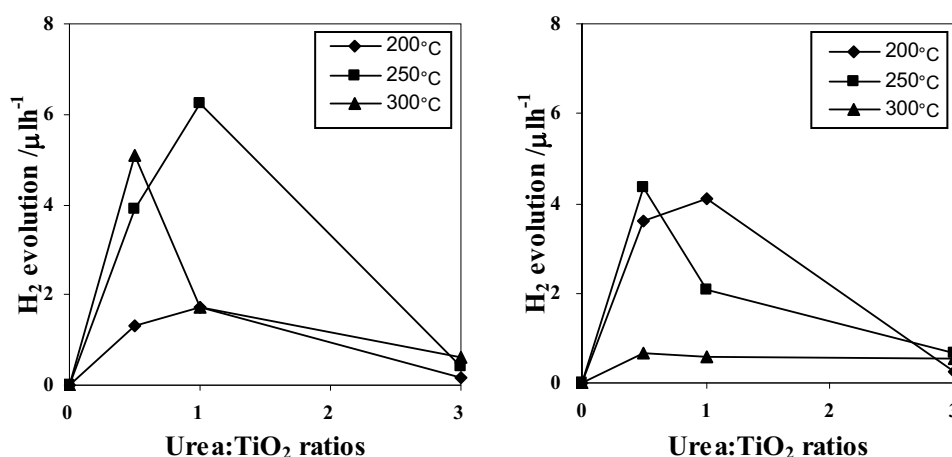


Figure 3 The H₂ evolution of (left) N-doped mesoporous TiO₂ and (right) N-doped commercial Degussa P-25 TiO₂ with different urea:TiO₂ molar ratios of 0.5:1, 1:1, and 3:1 prepared at different calcination temperatures of 200, 250, and 300°C (Reaction conditions: photocatalyst, 0.2 g; distilled water, 150 ml; methanol, 50 ml; and irradiation time, 5 h).

The H₂ evolution activity significantly increased with increasing the nominal Pt loading content up to 1.3 wt.%, then after this optimum point, the H₂ evolution activity decreased, as shown in Table 3. This result can be related to surface Pt content, which was analyzed by XPS, and it was found that the surface Pt content also reached the maximum at the nominal Pt content of 1.3 wt.%. The possible explanation is that TiO₂ particles may carry more Pt nanoclusters, which are very important for the removal of photogenerated electrons from TiO₂ for the reduction reaction and lead to an increase of the photocatalytic activity. After reaching a maximum, the H₂ evolution activity decreased due to too much Pt nanoclusters on TiO₂. These clusters would shield the photosensitive TiO₂ surface, and subsequently reduce the surface concentration of the electrons and holes available for the reactions. Another explanation is that at high metal loadings, the deposited metal particles may act as the recombination centers for the photoinduced species (Courbon *et al*, 1984).

Table 3. Summary of the effect of Pt loading onto N-doped mesoporous TiO₂ on surface Pt content and photocatalytic H₂ evolution (Reaction conditions: photocatalyst, 0.2 g; distilled water, 150 ml; methanol, 50 ml; and irradiation time, 5 h)

Nominal Pt loading/wt%	Surface Pt content/wt%	H ₂ evolution/ μlh^{-1}
0	0	6.23
0.4	0.80	8.05
0.8	3.69	15.19
1.0	3.23	17.89
1.1	3.30	17.95
1.3	4.73	26.40
1.4	3.25	11.75
1.6	3.71	8.04

4. CONCLUSIONS

In this work, two types of TiO₂ photocatalyst, the mesoporous TiO₂ synthesized by surfactant-assisted templating sol-gel method and commercial Degussa P-25 TiO₂, were comparatively used for photocatalytic H₂ evolution under visible light irradiation in a form of N-doped TiO₂. The results of N₂ adsorption-desorption analysis revealed that the synthesized TiO₂ photocatalyst possessed mesoporous structure (mesopore size between 2-50 nm), whereas the commercial Degussa P-25 TiO₂ possessed non-mesoporous structure. To modify the visible light absorption ability of TiO₂ photocatalyst, N-doping onto TiO₂ photocatalyst was performed. The urea as a source of N was mixed with the TiO₂ photocatalysts at various urea:TiO₂ molar ratios and calcined at various calcination temperatures. The optimum preparation conditions of the N-doped mesoporous and Degussa P-25 TiO₂ were the urea:TiO₂ molar ratio of 1:1 at calcination temperature of 250°C and 0.5:1 at calcination temperature of 250°C, respectively. However, the N-doped mesoporous TiO₂ prepared at such the optimum condition exhibited the best H₂ evolution activity. To improve the photocatalytic H₂ evolution activity, Pt was loaded onto this N-doped mesoporous TiO₂ by incipient wetness impregnation method. The optimum Pt loading content was 1.3 wt%, providing the highest photocatalytic H₂ evolution activity. It was clearly found that the surface Pt content greatly influenced on the H₂ evolution activity.

5. ACKNOWLEDGMENTS

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