

Preparation of Dihydroxy Naphthalene/TiO₂ Complex *via* Surface Modification and Their Photocatalytic H₂ Production Performances Under Visible Light

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Received March 18, 2013, Accepted April 12, 2013

The dihydroxy naphthalene/TiO₂ complexes with different substitution patterns were prepared by surface modification. X-ray diffraction, UV-Vis spectroscopy, photoluminescence, and X-ray photoelectron spectroscopy were used to characterize the prepared composite materials. The results indicated that the surface modification did not influence the crystallization of TiO₂. The visible-light absorbances of prepared dihydroxy naphthalene/TiO₂ complexes could be assigned to the ligand-to-metal charge transfer. The obtained catalyst exhibited outstanding photocatalytic activity and stability under visible light. A linear relationship existed between the percentages of hydroxynaphthalenes coordinated on TiO₂ surface and H₂ production ability. The substitution pattern of dihydroxy naphthalene and CH₃OH content could also influence the photocatalytic performance remarkably. The photocatalytic H₂ production ability was further improved after loading with ultra low concentration of Pt, 0.02 wt %. The possible mechanism was proposed.

Key Words : Dihydroxy naphthalene, TiO₂, Substitution pattern, H₂ evolution, Pt

Introduction

Fossil fuels are non-renewable energy sources, combustion of fossil fuels cause a series of global environmental problems, such as global warming by releasing of green house gas CO₂. Development of clean, environmental friendly, and sustainable none fossil fuel energy sources has drawn much attention and becomes an priority stratagem in the whole world. Nowadays, it is generally accepted that hydrogen is an ideal candidate for the replacement of the fossil fuels, because of its high combustion energy, and no environmental pollution. Since the first report on photocatalytic H₂ production from water splitting by Pt/TiO₂ system,¹ many kinds of materials and derivatives have been discovered as photocatalysts for this reaction, and this method is considered as one of the most effective to resolve such energy and environmental problems. Many photocatalysts have been reported to catalyze the evolution of H₂ from aqueous solutions with and without sacrificial reagents.²⁻⁵ Among these photocatalysts, TiO₂-based material is one of the most promising catalysts because of its: i) high resistance to photocorrosion in aqueous media, ii) low cost and easy availability, iii) environmental friendliness, iv) energy bands which are well-matched with the redox level of water, and v) electronic properties can be varied by modification. However, with a wide band gap energy of 3.0-3.2 eV, TiO₂ absorbs the ultraviolet light which accounts for only small fraction of the solar light (3-5%). In photocatalytic H₂ production from water splitting, prolonging life time of the photogenerated electrons is vital to enable the reduction of hydrogen ions to hydrogen. Whereas, the fast decay of electrons causes rapid recombination of charge carriers, which further restrains the photocatalytic efficiency.

Till now, many strategies have been proposed for the modification of the semiconductor so as to prolong the life time of the electrons and holes to improve the H₂ production ability, including transition metal doping,^{6,7} combination with other semiconductors⁸ or graphene,^{9,10} formation of heterojunction,¹¹ and surface loading with noble metal.¹²⁻¹⁶ Dholam *et al.*⁶ prepared Cr- or Fe-doped TiO₂ composite thin films photocatalyst for H₂ production. They suggested that Fe doped TiO₂ exhibited higher H₂ production rate than that of Cr doped catalyst, due to the ability of Fe ions to trap both electrons and holes, thus avoiding recombination, while Cr can only trap one type of charge carrier. Sun *et al.*⁷ prepared Fe and Ni co-doped TiO₂ nanoparticles by alcohol-thermal method, and found that the co-doped catalyst showed much higher photocatalytic activity of H₂ evolution than that of pure and single doped TiO₂ catalyst under visible light irradiation, due to the decreased recombination rate of the photo-induced electron-hole pairs and increased visible light absorption. Combination with other semiconductors is a effective method to separate the photogenerated electron/hole pairs and extend the absorption into visible light region. Wu *et al.*⁸ synthesized CdS quantum-dot sensitized TiO₂ nanowires for photocatalytic H₂ production. They suggested that the photogenerated electrons transferred from CdS to TiO₂, whereas the formed holes stayed in the CdS, thus enhanced the quantum efficiency and activity. Graphene is a two-dimensional sp²-hybridized carbon nanosheet, which possesses a large specific surface area, high mobility of charge carriers, and good mechanical strength, thus is used frequently to prepare functional nanomaterials. Cheng *et al.*⁹ prepared TiO₂-graphene nanocomposites for photocatalytic hydrogen production from splitting water. Due to its two-dimensional p-conjugation structure, graphene served as an

acceptor of the photogenerated electrons of TiO₂ to separate the photogenerated electron/hole pairs effectively, thus improved the hydrogen production ability. Fan *et al.*¹⁰ prepared TiO₂-reduced graphene oxide (RGO) nanocomposites for photocatalytic hydrogen production. They proposed that the intimate contact between TiO₂ and RGO may accelerate the transfer of photogenerated electrons of TiO₂ to RGO surface, suppressing the recombination of charge carriers. When two different semiconductors contact each other closely, the "heterojunction" is formed. Because of the different semiconductor properties, the space potential difference will be formed in both side of the heterojunction, which is beneficial to electron/hole separation. Li *et al.*¹¹ prepared AgIn₅S₈/TiO₂ heterojunction nanocomposite for H₂ production. They considered that the enhanced photoactivity can be ascribed to some AgIn₅S₈ nanoparticles closely contacting the TiO₂ nanoparticles to form heterojunction structure, which results in an efficient charge separation at the interface, followed by fast diffusion of photoelectrons generated in AgIn₅S₈ toward TiO₂, thus is beneficial for separating the photogenerated carriers in space and improving the photoactivity. The enhancement of the photocatalytic activity by loading with noble metal is attributed to the formation of a Schottky barrier at the metal/semi-conductor interface, which leads to electron trapping and efficient charge separation.¹² In the past decades, many noble metals, such as Au, Pt, Ag, and Pd, have been tested and reported in numerous publications.¹³⁻¹⁷ The results has been widely accepted that Pt/TiO₂ systems exhibited the best H₂ production ability.¹⁵ However, the noble metals are too expensive to inhibit the practical application.

It is known that surface modification of TiO₂ with organic matter is an important method to improve the light respond range and quantum efficiency, thus has been widely used for degradation of organic contaminations,¹⁸ reduction of heavy metals,¹⁹ preparation of dye-sensitized solar cell,^{20,21} and organic oxidation reaction.²² However, only a few literature reported on the photocatalytic H₂ production by organic modified TiO₂-based catalyst.²³ Ikeda *et al.*²³ reported the photochemical hydrogen evolution from aqueous triethanol-amine solutions sensitized by binaphthol-modified TiO₂ loaded with 0.1 wt % Pt under visible light. They proposed that visible-light excited the surface complex, inject the electrons from the complex to TiO₂, and migrate the electrons to platinum deposits, where reduction of H⁺ takes place to give H₂. However, the photoactivity of reused catalyst was much lower than that of fresh one, indicating the catalyst stability need to be improved. Here, a dihydroxy naphthalene modified TiO₂ complex was prepared for photocatalytic H₂ evolution. The obtained catalyst exhibited outstanding photocatalytic activity and stability under visible light. The H₂ production ability was remarkably improved with loading ultra low concentration of Pt, 0.02 wt %.

Experimental

Preparation and Characterization. The raw material

(neat TiO₂) was prepared as follows. 1.6 mL TiCl₄ was added dropwise to 15 mL ethanol to form solution. Ammonia was then added dropwise into the solution, and a TiO₂ precipitate was formed. The precipitation of TiO₂ was complete when the pH value reached the point of zero charge (PZC) of TiO₂. More ammonia was added dropwise until the pH of the mixture reached 8. The formed suspension was stirred for 30 min, and then transferred into a 30 mL stainless steel autoclave, which was then heated to 180 °C and kept for 24 h. The solid product was separated by filtration, followed by washing, and drying at 60 °C for 8 h.

For preparation of dihydroxy naphthalene/TiO₂, a given amount of dihydroxy naphthalene with different substitution patterns was dissolved in 30 mL acetone to form solution (10 mmol/L). 1 g TiO₂ sample was added into above solution and stirred for 2 h at 298 K. The obtained product was centrifuged, and washed with acetone for several times. Then the sample was dried at 60 °C for 12 h to remove the acetone completely. The obtained surface modified TiO₂ sample was denoted as x,y-T(2h), in which, x and y stand for the substitution site of dihydroxyl. For comparison, 2,3-T(0.5h), 2,3-T(1h), and 2,3-T(3h) were prepared following the same procedure described above but stirred for 0.5, 1, and 3 h respectively. When monohydroxy derivatives of naphthalene, *i.e.*, 1-naphthol (1-NAP) and 2-naphthol (2-NAP) was used to replace dihydroxy naphthalene following the same procedure as in the synthesis of 2,3-T(2h), the product is denoted as 1-NT and 2-NT. For preparation of Pt loaded dihydroxy naphthalene/TiO₂ complexes, 1 g TiO₂ sample was added into aqueous methanol solution of H₂PtCl₆·6H₂O. The suspension was irradiated with a 500 W mercury high-pressure immersion lamp for 6 h under vigorous stirring for photodeposition. After irradiation, the samples were washed twice with water, centrifuged, dried at 70 °C for 10 h and carefully grinded. The obtained sample was surface treated following the same procedure as in the synthesis of 2,3-T(2h), and denoted as 2,3-Pt(x), in which, x stands for the weight percentage of Pt to TiO₂ (wt %).

XRD patterns of the prepared TiO₂ samples were recorded on a Rigaku D/max-2400 instrument using Cu-K α radiation (λ = 1.54 Å). UV-Vis spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using BaSO₄ as the reference sample. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al K α radiation as the exciting source. The binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. PL spectra were measured at room temperature with a fluorospectrophotometer (FP-6300) using an Xe lamp as excitation source.

The coordination ability of hydroxynaphthalenes with different numbers and substitution patterns of hydroxyl groups on TiO₂ surface were evaluated from the concentration changes in solution before and after surface treatment. The initial concentration of hydroxynaphthalene in acetone was adjusted to 10 mmol/L. After modification, the residual quantities of hydroxynaphthalene in acetone was monitored by gas chromatography.

Photocatalytic Reaction. The photocatalytic experiments were performed in an outer-irradiation and air-tight Pyrex glass reactor, connected to a water-cooling system. In a typical run, 1 g photocatalyst was suspended in an aqueous solution of methanol (5 vol %) used as the hole scavenger under stirring. Prior to the photocatalytic reaction, the suspension was purged with Ar gas for 20 min to get rid of O₂. A 500 W Xe lamps with UV cutoff filter ($\lambda > 420$ nm) were used as light source. The reaction products were analyzed on-line by thermal conductivity detectors on a micro-gas chromatography (Model Agilent P200 Series) allowing detection and quantification of hydrogen, oxygen, CO, and CO₂.

Results and Discussion

The XRD patterns of prepared dihydroxy naphthalene/TiO₂ complex (not shown here) indicate that all TiO₂ samples were pure anatase phase with characteristic diffractions at 25.2° (1 0 1), 37.8° (0 0 4), 48.1° (2 0 0), 54.7° (1 0 5), and 62.7° (2 1 1) (JCPDS No. 21-1272). The particle sizes were calculated by their XRD patterns according to the Debye-Scherrer equation.²⁴ The result showed that the samples are all around 10 nm in size. This indicated that the surface modification treatment did not change the phase composition and particle sizes of TiO₂ samples.

It is well-known that, in addition to the crystal phase structure, the optical properties of a photocatalytic material usually plays a dominant role in its activity. Figure 1 shows the UV-Vis spectra of neat TiO₂, surface modified TiO₂, 2,3-dihydroxynaphthalene, and Pt loaded (insert) TiO₂ sample. Obviously, neat TiO₂ and 2,3-dihydroxynaphthalene exhibited no absorption in the visible light region. Neat TiO₂ exhibited an absorption band below 400 nm corresponding to the band gap energy of anatase TiO₂. 2,3-Dihydroxynaphthalene displayed a strong absorption peak at 220 nm and a weak absorption band around 300 nm. However, the new absorption was observed in the visible-light region around 400–700 nm for 2,3-dihydroxynaphthalene modified TiO₂, 2,3-T(2h). These visible-light absorbances could be assigned to the ligand-to-metal charge transfer (LMCT) of the surface complexes formed between the surface Ti atoms and the phenolic compounds (surface-attached ligands). The clear solution immediately turned orange when immerse TiO₂ into the solution of 2,3-dihydroxynaphthalene, which indicates clearly the formation of surface complexes.^{25–27} Janković *et al.* prepared benzene derivatives modified TiO₂

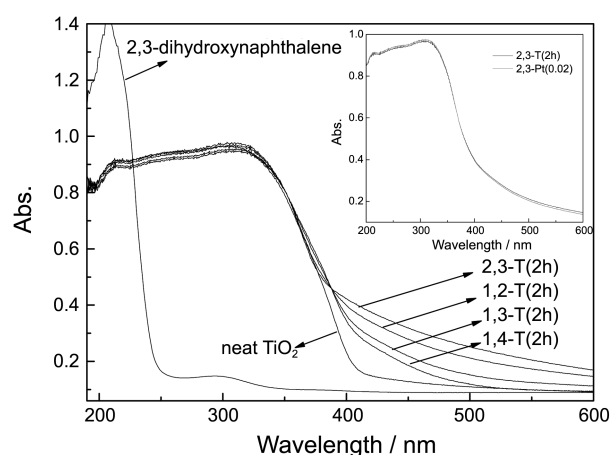


Figure 1. UV-Vis spectra of neat TiO₂, surface modified TiO₂, 2,3-dihydroxynaphthalene, and Pt loaded (insert) TiO₂ sample.

catalyst and found the similar ligand-to-metal charge transfer phenomenon.²⁵ Eder *et al.* utilized benzyl alcohol (BA) as a surfactant to prepare carbon nanotube/TiO₂ and they inferred the coordination of BA hydroxyl groups with titanium atoms.²⁶ Shkrob *et al.* proved the complexation between chemical OH groups of polyols and uncoordinated titanium sites to form Ti^{IV}-O-R groups by IR spectroscopy and XANES.²⁷ Therefore, we consider that the OH groups of dihydroxy naphthalene coordinate with the Ti-OH of the TiO₂ in a similar way as illustrated in Figure 2. For other dihydroxy naphthalene modified TiO₂ catalysts with different substitution patterns, the similar visible-light absorption around 400–700 nm were observed, indicated the surface complexes were formed in all the dihydroxynaphthalene modified TiO₂ catalysts. It is noted that the visible light absorption increased obviously in the order: 1,4-T(2h) < 1,3-T(2h) < 1,2-T(2h) < 2,3-T(2h). This indicated that the substitution pattern of dihydroxy naphthalene play a important role on the visible light absorption. Besides, no obvious difference between the spectra of 2,3-T(2h) and 2,3-Pt(0.02) was observed (Figure 1 insert), probably due to the tiny loading amount of Pt.

The nature of the interaction between TiO₂ and dihydroxy naphthalene was further investigated by XP spectra. Figure 3 shows the XP spectra of neat TiO₂ and 2,3-T(2h) in the region of Ti 2p (A), O 1s (B), and C 1s (C). In the Ti 2p region (Figure 3(a)), both neat TiO₂ and 2,3-T(2h) exhibited two peaks which could be assigned to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2} with the binding energy differences, $\Delta E = E(\text{Ti } 2p_{1/2}) -$

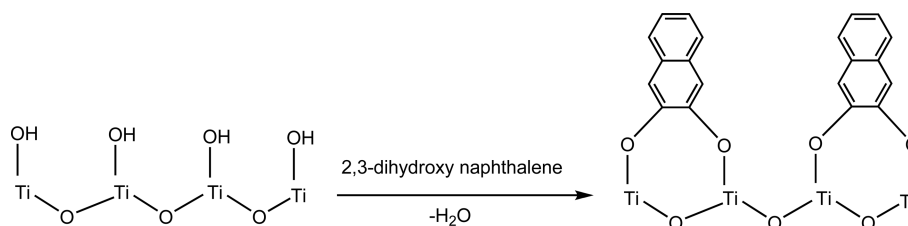


Figure 2. Schematic illustration of surface complexes formed by the coordination of 2,3-dihydroxy naphthalene on TiO₂ surface.

$E(\text{Ti } 2p_{3/2})$, were around 5.7 eV.²⁸ An decrease in peak intensity for 2,3-T(2h) is probably due to the coverage of Ti atoms after surface modification by dihydroxy naphthalene. In the O 1s region (Figure 3(b)), the XPS peaks of neat TiO₂ and 2,3-T(2h) around 530 and 532 eV are attributed to crystal lattice oxygen (Ti-O) and surface hydroxyl group (O-H). It is noted that the surface hydroxyl content of 2,3-T(2h) is obvious lower than that of neat TiO₂. Ou *et al.*²⁹ reported that surface modification of TiO₂ with ascorbic acid caused a decrease of the surface hydroxyl groups. They considered that the ascorbic acid binding to surface hydroxyl groups of TiO₂ to form bidentate complexes was responsible for the decrease of the surface hydroxyl groups. Similarly, the Ti-OH groups may react with dihydroxy naphthalene to form Ti-O-C bonds, resulting in a decrease in the number of surface hydroxyl groups, as shown in Figure 2. In Figure 3(c), the peaks in the C 1s region were deconvoluted into three contributions located at 284.6, 286.2, and 288.3 eV, respectively. Those at 284.6 and 286.2 eV are attributed to the C=C and C-(C/H) group of dihydroxy naphthalene.³⁰ The small peak at higher binding energy (288.3 eV) may be attributed to the electron deficiency of the C atom in the Ti-O-C structure.^{31,32} It has been reported that Ti-OH reacts with a phenolic groups of organic compounds, such as catechol,³³ salicylic acid,³⁴ and binaphthol,³⁵ to form Ti-O-C bonds on the TiO₂ surface. It is therefore possible that the TiO₂ surface is modified by the formation of Ti-O-C bonds rather than by physical adsorption of dihydroxy naphthalene.

The coordination ability of hydroxynaphthalenes, which have different numbers and substitution patterns of hydroxyl groups, was evaluated and shown in Table 1. It is reasonable that the percentage of coordinated 2,3-dihydroxynaphthalene increased with increasing the treatment time. Besides, the coordination percentages of 2,3-T(2h) and 1,2-T(2h) were more than 50%, indicating the adjacent hydroxyl groups are more suited for formation of stable bidentate structures, as shown in Figure 2. For 1,3-T(2h) and 1,4-T(2h), larger steric hindrance make it more difficult to coordinate on TiO₂ surface, leading to the lower coordination percentages. It is noted that the coordination percentages of 1-NT and 2-NT were much lower than that of hydroxynaphthalenes possess-

ing two hydroxyl groups. This is probably due to that the formed monodentate structure is unstable compared with the bidentate structure formed by dihydroxy naphthalene and easy to remove from the TiO₂ surface.

Figure 4 shows the PL spectra of prepared neat and surface modified TiO₂ catalysts. Obviously, 2,3-T(2h) exhibited much lower PL intensity than that of neat TiO₂. It is known that a certain amount of chemical energy can be released during the recombination process of photo-induced charge

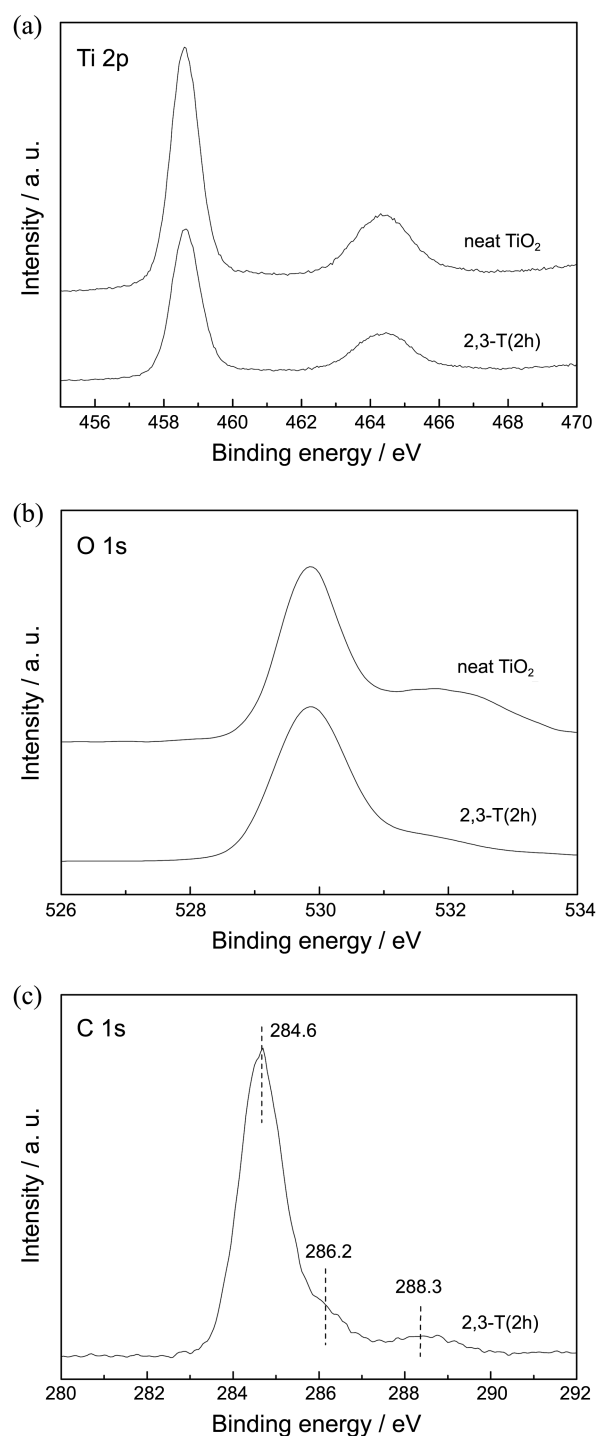


Figure 3. XP spectra of neat TiO₂ and 2,3-T(2h) in the region of Ti 2p (a), O 1s (b), and C 1s (c).

Table 1. Percentages of hydroxynaphthalenes coordinated on TiO₂-based catalysts and the H₂ production abilities

Sample	Percentage (%)	H ₂ production (μmol·h ⁻¹)
neat TiO ₂	0	0
2,3-T(3h)	78	336
2,3-T(2h)	67	360
2,3-T(1h)	53	286
2,3-T(0.5h)	41	112
1,2-T(2h)	56	296
1,3-T(2h)	32	154
1,4-T(2h)	16	71
1-NT	6	22
2-NT	5	18

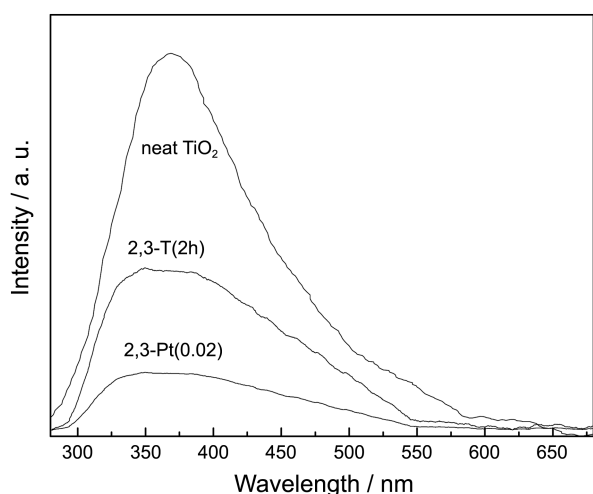


Figure 4. PL spectra of prepared neat and surface modified TiO₂ catalysts.

carriers, which would further transform possibly to heat or light energy. The light energy can be dissipated as radiation, which results in a luminescence emission of semiconductor material, giving a PL signal. In general, the lower the PL intensity, the lower the recombination rate of photo-induced electron-hole pairs, thus the higher the photocatalytic activity. Therefore, the recombination rate of electron-hole pairs was decreased by hydroxynaphthalene modification. Moreover, the PL intensity of 2,3-Pt(0.02) was much lower than that of 2,3-T(2h). It is known that the noble metal Pt can act as sink for photoinduced charge carriers and promotes interfacial charge transfer process.³⁶ Thus, it is possible that the photo-generated electrons transfer from TiO₂ conduction band to the surface of Pt, leading to the recombination rate of 2,3-Pt(0.02) further decreased.

The photocatalytic H₂ production abilities of prepared TiO₂-based catalysts under visible light irradiation were shown in Table 1. Neat TiO₂ exhibited no H₂ production ability. 1-NT and 2-NT showed poor activities, whereas dihydroxy naphthalene modified TiO₂ catalysts exhibited outstanding activities. 2,3-T(2h) showed the best H₂ production ability, 360 $\mu\text{mol}\cdot\text{h}^{-1}$. Further increase the 2,3-dihydroxynaphthalene percentage caused a decreased H₂ production ability, 336 $\mu\text{mol}\cdot\text{h}^{-1}$. This is probably due to the excess coordinated aromatic molecules occupied the TiO₂ surface, leading to the strong steric hindrance. Therefore, surface modification with a suitable amount of dihydroxy naphthalene is crucial for the enhancement of H₂ production due to the easy access of reactant and product without the steric hindrance of surface-attached ligands. Besides, the H₂ production abilities of prepared dihydroxy naphthalene/TiO₂ catalysts increased in the order: 1,4-T(2h) < 1,3-T(2h) < 1,2-T(2h) < 2,3-T(2h), which is consistent with the order of percentages of hydroxynaphthalenes coordinated on TiO₂. In order to further understand the relationship of coordination amount and H₂ production ability, Figure 5, relationship of H₂ production and percentages of corresponding hydroxynaphthalenes modified on TiO₂ was given. Interestingly, a linear relationship

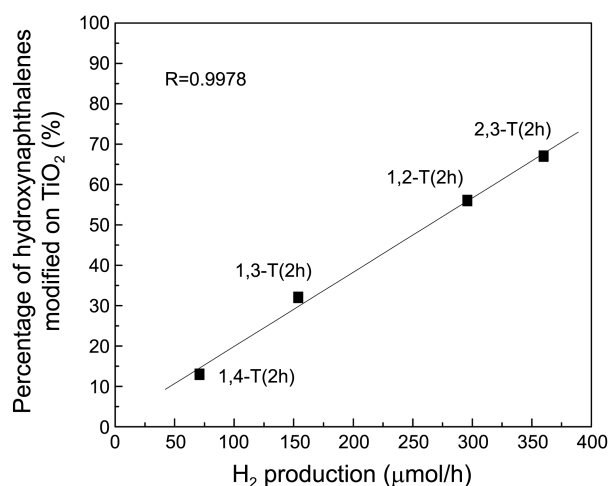


Figure 5. Relationship of H₂ production and percentages of corresponding hydroxynaphthalenes modified on TiO₂.

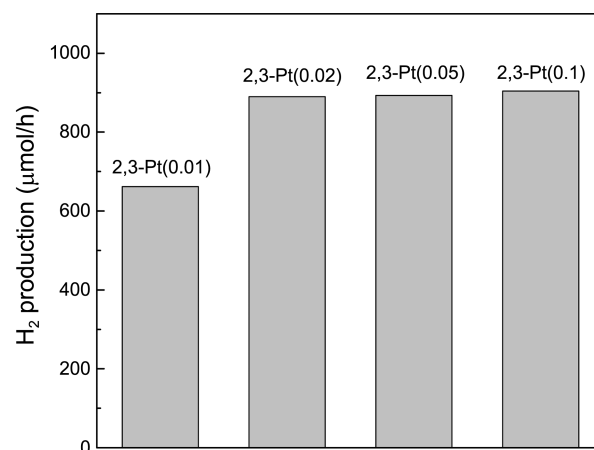


Figure 6. Dependence of H₂ production on amount of Pt deposits.

between them was obtained ($R = 0.9978$). Therefore, it is indicated that the coordination amount plays an significant important role on the H₂ production ability.

Figure 6 shows the H₂ production abilities of 2,3-dihydroxynaphthalene modified TiO₂ loaded with different amount of Pt. Obviously, the H₂ production abilities were remarkably increased after Pt loading. As suggested in the previous reports,^{23,37,38} visible-light induced H₂ evolution originated from a sensitizing mechanism, which excited the localized electrons from the surface complexes into the conduction band continuum states of the TiO₂ semiconductor. The injected electrons in the TiO₂ particles migrate to the surface of Pt, where reduction of H⁺ takes place to produce H₂. Among the literatures reported Pt/TiO₂ catalyst for H₂ production, the optimal Pt contents were mainly in the region of 0.1–2 wt %.^{15,23,36,39} However, in this investigation, no obvious H₂ production increase was observed when the Pt content beyond 0.02 wt %. This optimal Pt content is much lower than that in the previous reports, indicating such Pt loaded dihydroxy naphthalene/TiO₂ system can dynamic decrease the noble metal content which is beneficial to decrease the cost.

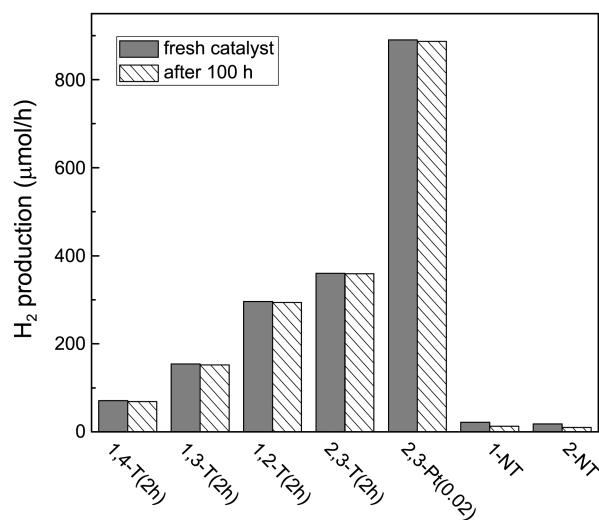


Figure 7. Photocatalytic stability of prepared TiO₂ catalysts.

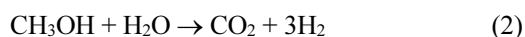
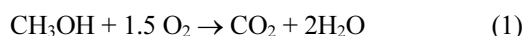
Figure 7 shows the photocatalytic stability of prepared TiO₂-based catalysts. Dihydroxy naphthalene modified TiO₂ catalysts exhibited slight decrease in H₂ production ability after 100 h reaction compared with the fresh catalysts. For 2,3-Pt(0.02), lower than 1% decrease in H₂ production ability was observed after 100 h reaction, indicating that the activity of 2,3-Pt(0.02) is stable under visible light irradiation. For 1-NT and 2-NT, obvious decrease in H₂ production ability, 41% and 44%, were shown after 100 h reaction. This is probably due to that the formed monodentate structure is unstable and easy to remove from the TiO₂ surface during the reaction.

It is known that CH₃OH acts as an effective sacrificial reagent by scavenging O₂ or holes, limiting the reverse H₂+1/2O₂ → H₂O reaction, and increasing charge separation,⁴⁰ as shown in Eq. (1). Besides, under anaerobic conditions, CH₃OH can also undergo photocatalytic reforming to produce H₂ and CO₂, according to Eq. (2).⁴¹ This means that the produced H₂ is uncertain issued completely from photocatalytic water splitting. Therefore, the photocatalytic production of 2,3-Pt(0.02) under different CH₃OH amount were analyzed and shown in Table 2. When the CH₃OH amount was 1 vol %, the H₂ production ability was obvious decreased to 210 μmol·h⁻¹. The O₂ production was 103 μmol·h⁻¹, slightly lower than the academic value (105 μmol·h⁻¹). This indicated this CH₃OH amount is insufficient to scavenging formed O₂ and reverse H₂+1/2O₂ → H₂O reaction, leading to the poor H₂ production ability. The H₂ and O₂ production achieved 890 and 431 μmol·h⁻¹ when increase CH₃OH amount to 5 vol %. The academic value of O₂ production was 445 μmol·h⁻¹, indicating 14 μmol·h⁻¹ O₂ reacted with CH₃OH according to Eq. (1) to form 9.3 μmol·h⁻¹ CO₂. The total CO₂ production was 11.2 μmol·h⁻¹, indicating 1.9 μmol·h⁻¹ CO₂ came from Eq. (2). Thus, the produced H₂ from Eq. (2) was only 5.7 μmol·h⁻¹, indicating most H₂ came from photocatalytic water splitting. When the CH₃OH amount was increased to 20 vol %, the H₂ and O₂ production decreased to 560 and 210 μmol·h⁻¹. Therefore, 70 μmol·h⁻¹

Table 2. Photocatalytic production of 2,3-Pt(0.02) under different CH₃OH amount

CH ₃ OH amount (vol %)	H ₂ (μmol·h ⁻¹)	O ₂ (μmol·h ⁻¹)	CO ₂ (μmol·h ⁻¹)	CO (μmol·h ⁻¹)
1	210	103	1.1	-
5	890	431	11.2	-
20	560	210	58	1.2

O₂ reacted with CH₃OH to form 47 μmol·h⁻¹ CO₂. Accordingly, 11 μmol·h⁻¹ CO₂ came from methanol reforming reaction, which produced 33 μmol·h⁻¹ H₂. It is noted that 1.2 μmol·h⁻¹ CO was detected (Table 2), which should come from methanol reforming. It is well-known that the metal sites are easily poisoned by CO because of its strong adsorption on noble metals. Such noble metal poisoning was probably the main reason for decreased H₂ production. Therefore, it is deduced that the appropriate methanol content is 5 vol %, which can scavenge O₂ or holes, and limit the reverse H₂+1/2O₂ → H₂O reaction without poisoning the noble metal, leading to the high H₂ production ability.



Conclusion

The dihydroxy naphthalene/TiO₂ complexes with different substitution patterns were prepared by surface modification. These visible-light absorbances could be assigned to the ligand-to-metal charge transfer of the surface complexes formed between the surface Ti atoms and the phenolic compounds (surface-attached ligands). A linear relationship existed between the percentages of hydroxynaphthalenes coordinated on TiO₂ surface and H₂ production ability. 2,3-T(2h) exhibited the best photocatalytic H₂ production ability among the prepared dihydroxy naphthalene/TiO₂ catalysts, which is probably due to the high percentages of 2,3-dihydroxynaphthalene coordinated on TiO₂ surface. After loading with ultra low concentration of Pt (0.02 wt %), the H₂ production ability was further improved. The obtained dihydroxy naphthalene modified TiO₂ catalysts exhibited much better photocatalytic stability than that of monohydroxy naphthalene modified TiO₂ catalysts. This is probably due to that the formed bidentate structure is more stable compared with the monodentate structure formed by monohydroxy naphthalene, and not easy to remove from the TiO₂ surface. The appropriate methanol content is 5 vol %, which can scavenge O₂ or holes, and limit the reverse H₂+1/2O₂ → H₂O reaction without poisoning the noble metal, leading to the high H₂ production ability.

Acknowledgments. This work was supported by National Natural Science Foundation of China (No. 41071317, 30972418), National Key Technology R & D Programme of China (No. 2007BAC16B07, 2012ZX07505-001), the Natural

Science Foundation of Liaoning Province (No. 20092080). And the publication cost of this paper was supported by the Korean Chemical Society.

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