

## Preparation of Dihydroxy Naphthalene/TiO<sub>2</sub> Complex *via* Surface Modification and Their Photocatalytic H<sub>2</sub> Production Performances Under Visible Light

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The dihydroxy naphthalene/TiO<sub>2</sub> 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 TiO<sub>2</sub>. The visible-light absorbances of prepared dihydroxy naphthalene/TiO<sub>2</sub> 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 TiO<sub>2</sub> surface and H<sub>2</sub> production ability. The substitution pattern of dihydroxy naphthalene and CH<sub>3</sub>OH content could also influence the photocatalytic performance remarkably. The photocatalytic H<sub>2</sub> 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, TiO<sub>2</sub>, Substitution pattern, H<sub>2</sub> 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 CO<sub>2</sub>. 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 H<sub>2</sub> production from water splitting by Pt/TiO<sub>2</sub> system,<sup>1</sup> 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 H<sub>2</sub> from aqueous solutions with and without sacrificial reagents.<sup>2-5</sup> Among these photocatalysts, TiO<sub>2</sub>-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, TiO<sub>2</sub> absorbs the ultraviolet light which accounts for only small fraction of the solar light (3-5%). In photocatalytic H<sub>2</sub> 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 H<sub>2</sub> production ability, including transition metal doping,<sup>6,7</sup> combination with other semiconductors<sup>8</sup> or graphene,<sup>9,10</sup> formation of heterojunction,<sup>11</sup> and surface loading with noble metal.<sup>12-16</sup> Dholam *et al.*<sup>6</sup> prepared Cr- or Fe-doped TiO<sub>2</sub> composite thin films photocatalyst for H<sub>2</sub> production. They suggested that Fe doped TiO<sub>2</sub> exhibited higher H<sub>2</sub> 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.*<sup>7</sup> prepared Fe and Ni co-doped TiO<sub>2</sub> nanoparticles by alcohol-thermal method, and found that the co-doped catalyst showed much higher photocatalytic activity of H<sub>2</sub> evolution than that of pure and single doped TiO<sub>2</sub> 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.*<sup>8</sup> synthesized CdS quantum-dot sensitized TiO<sub>2</sub> nanowires for photocatalytic H<sub>2</sub> production. They suggested that the photogenerated electrons transferred from CdS to TiO<sub>2</sub>, whereas the formed holes stayed in the CdS, thus enhanced the quantum efficiency and activity. Graphene is a two-dimensional sp<sup>2</sup>-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.*<sup>9</sup> prepared TiO<sub>2</sub>-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 TiO<sub>2</sub> to separate the photogenerated electron/hole pairs effectively, thus improved the hydrogen production ability. Fan *et al.*<sup>10</sup> prepared TiO<sub>2</sub>-reduced graphene oxide (RGO) nanocomposites for photocatalytic hydrogen production. They proposed that the intimate contact between TiO<sub>2</sub> and RGO may accelerate the transfer of photogenerated electrons of TiO<sub>2</sub> 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.*<sup>11</sup> prepared AgIn<sub>5</sub>S<sub>8</sub>/TiO<sub>2</sub> heterojunction nanocomposite for H<sub>2</sub> production. They considered that the enhanced photoactivity can be ascribed to some AgIn<sub>5</sub>S<sub>8</sub> nanoparticles closely contacting the TiO<sub>2</sub> nanoparticles to form heterojunction structure, which results in an efficient charge separation at the interface, followed by fast diffusion of photoelectrons generated in AgIn<sub>5</sub>S<sub>8</sub> toward TiO<sub>2</sub>, 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.<sup>12</sup> In the past decades, many noble metals, such as Au, Pt, Ag, and Pd, have been tested and reported in numerous publications.<sup>13-17</sup> The results has been widely accepted that Pt/TiO<sub>2</sub> systems exhibited the best H<sub>2</sub> production ability.<sup>15</sup> However, the noble metals are too expensive to inhibit the practical application.

It is known that surface modification of TiO<sub>2</sub> 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,<sup>18</sup> reduction of heavy metals,<sup>19</sup> preparation of dye-sensitized solar cell,<sup>20,21</sup> and organic oxidation reaction.<sup>22</sup> However, only a few literature reported on the photocatalytic H<sub>2</sub> production by organic modified TiO<sub>2</sub>-based catalyst.<sup>23</sup> Ikeda *et al.*<sup>23</sup> reported the photochemical hydrogen evolution from aqueous triethanolamine solutions sensitized by binaphthol-modified TiO<sub>2</sub> 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 TiO<sub>2</sub>, and migrate the electrons to platinum deposits, where reduction of H<sup>+</sup> takes place to give H<sub>2</sub>. 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 TiO<sub>2</sub> complex was prepared for photocatalytic H<sub>2</sub> evolution. The obtained catalyst exhibited outstanding photocatalytic activity and stability under visible light. The H<sub>2</sub> production ability was remarkably improved with loading ultra low concentration of Pt, 0.02 wt %.

## Experimental

**Preparation and Characterization.** The raw material

(neat TiO<sub>2</sub>) was prepared as follows. 1.6 mL TiCl<sub>4</sub> was added dropwise to 15 mL ethanol to form solution. Ammonia was then added dropwise into the solution, and a TiO<sub>2</sub> precipitate was formed. The precipitation of TiO<sub>2</sub> was complete when the pH value reached the point of zero charge (PZC) of TiO<sub>2</sub>. 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/TiO<sub>2</sub>, a given amount of dihydroxy naphthalene with different substitution patterns was dissolved in 30 mL acetone to form solution (10 mmol/L). 1 g TiO<sub>2</sub> 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 TiO<sub>2</sub> 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/TiO<sub>2</sub> complexes, 1 g TiO<sub>2</sub> sample was added into aqueous methanol solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. 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 TiO<sub>2</sub> (wt %).

XRD patterns of the prepared TiO<sub>2</sub> samples were recorded on a Rigaku D/max-2400 instrument using Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). UV-Vis spectroscopy measurement was carried out on a Jasco V-550 spectrophotometer, using BaSO<sub>4</sub> as the reference sample. XPS measurements were conducted on a Thermo Escalab 250 XPS system with Al K $\alpha$  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.

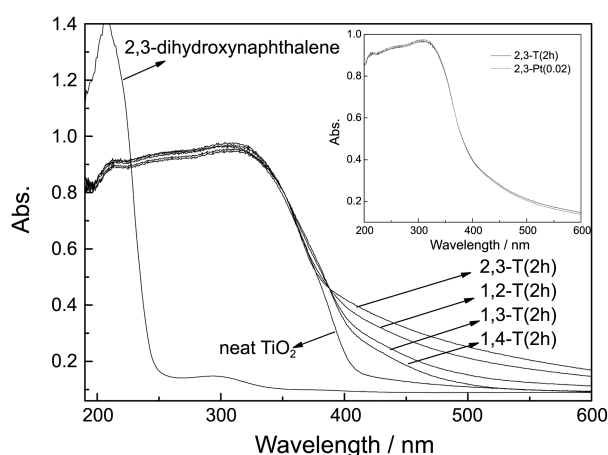
The coordination ability of hydroxynaphthalenes with different numbers and substitution patterns of hydroxyl groups on TiO<sub>2</sub> surface were evaluated from the concentration changes in solution before and after surface treatment. The initial concentration of hydroxynaphthalene in acetone was adjusted 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 O<sub>2</sub>. 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 CO<sub>2</sub>.

## Results and Discussion

The XRD patterns of prepared dihydroxy naphthalene/TiO<sub>2</sub> complex (not shown here) indicate that all TiO<sub>2</sub> 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.<sup>24</sup> 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 TiO<sub>2</sub> samples.

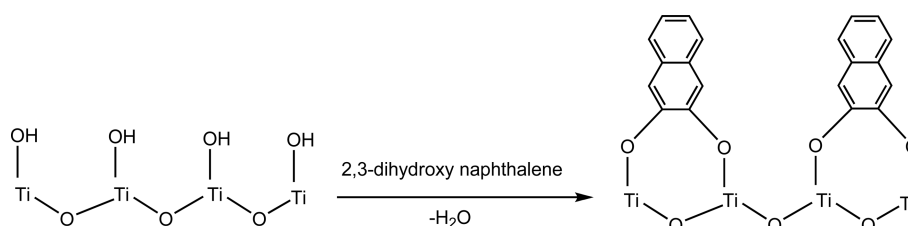
It is well-known that, in addition to the crystal phase structure, the optical properties of a photocatalytic material usually plays a dominant role in its activity. Figure 1 shows the UV-Vis spectra of neat TiO<sub>2</sub>, surface modified TiO<sub>2</sub>, 2,3-dihydroxynaphthalene, and Pt loaded (insert) TiO<sub>2</sub> sample. Obviously, neat TiO<sub>2</sub> and 2,3-dihydroxynaphthalene exhibited no absorption in the visible light region. Neat TiO<sub>2</sub> exhibited an absorption band below 400 nm corresponding to the band gap energy of anatase TiO<sub>2</sub>. 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 TiO<sub>2</sub>, 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 TiO<sub>2</sub> into the solution of 2,3-dihydroxynaphthalene, which indicates clearly the formation of surface complexes.<sup>25-27</sup> Janković *et al.* prepared benzene derivatives modified TiO<sub>2</sub>



**Figure 1.** UV-Vis spectra of neat TiO<sub>2</sub>, surface modified TiO<sub>2</sub>, 2,3-dihydroxynaphthalene, and Pt loaded (insert) TiO<sub>2</sub> sample.

catalyst and found the similar ligand-to-metal charge transfer phenomenon.<sup>25</sup> Eder *et al.* utilized benzyl alcohol (BA) as a surfactant to prepare carbon nanotube/TiO<sub>2</sub> and they inferred the coordination of BA hydroxyl groups with titanium atoms.<sup>26</sup> Shkrob *et al.* proved the complexation between chemical OH groups of polyols and uncoordinated titanium sites to form Ti<sup>IV</sup>-O-R groups by IR spectroscopy and XANES.<sup>27</sup> Therefore, we consider that the OH groups of dihydroxy naphthalene coordinate with the Ti-OH of the TiO<sub>2</sub> in a similar way as illustrated in Figure 2. For other dihydroxy naphthalene modified TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> and dihydroxy naphthalene was further investigated by XP spectra. Figure 3 shows the XP spectra of neat TiO<sub>2</sub> 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 TiO<sub>2</sub> and 2,3-T(2h) exhibited two peaks which could be assigned to Ti<sup>4+</sup> 2p<sub>3/2</sub> and Ti<sup>4+</sup> 2p<sub>1/2</sub> with the binding energy differences,  $\Delta E = E(\text{Ti } 2p_{1/2}) -$



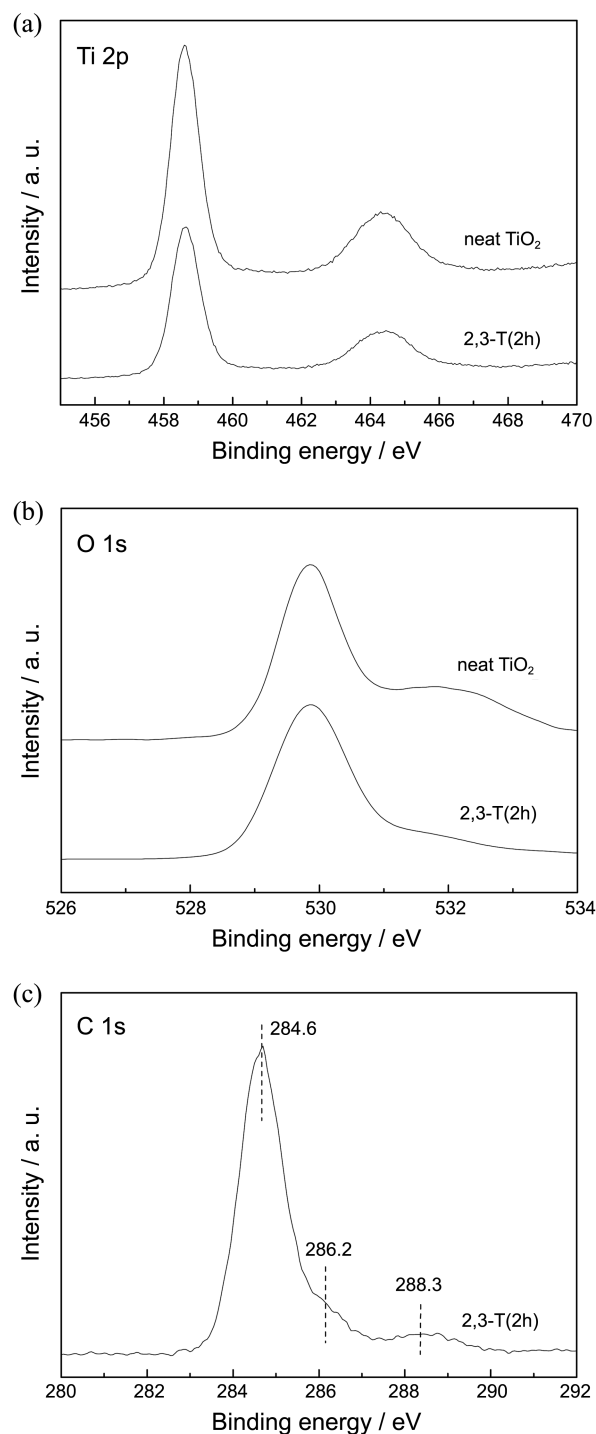
**Figure 2.** Schematic illustration of surface complexes formed by the coordination of 2,3-dihydroxy naphthalene on TiO<sub>2</sub> surface.

$E(\text{Ti } 2p_{3/2})$ , were around 5.7 eV.<sup>28</sup> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>. Ou *et al.*<sup>29</sup> reported that surface modification of TiO<sub>2</sub> with ascorbic acid caused a decrease of the surface hydroxyl groups. They considered that the ascorbic acid binding to surface hydroxyl groups of TiO<sub>2</sub> 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.<sup>30</sup> 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.<sup>31,32</sup> It has been reported that Ti-OH reacts with a phenolic groups of organic compounds, such as catechol,<sup>33</sup> salicylic acid,<sup>34</sup> and binaphthol,<sup>35</sup> to form Ti-O-C bonds on the TiO<sub>2</sub> surface. It is therefore possible that the TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> surface.

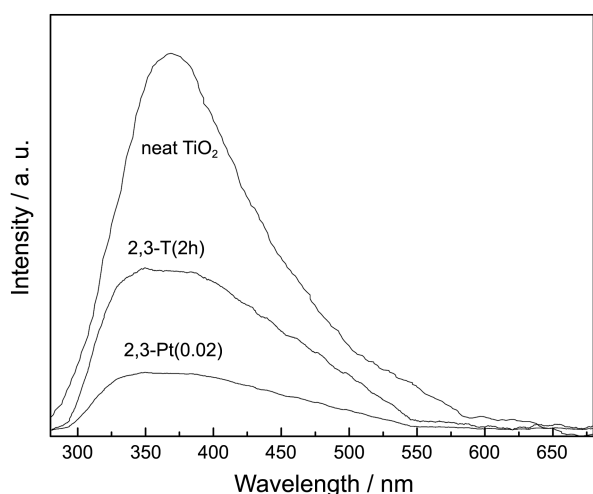
Figure 4 shows the PL spectra of prepared neat and surface modified TiO<sub>2</sub> catalysts. Obviously, 2,3-T(2h) exhibited much lower PL intensity than that of neat TiO<sub>2</sub>. It is known that a certain amount of chemical energy can be released during the recombination process of photo-induced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



**Figure 3.** XP spectra of neat TiO<sub>2</sub> 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 TiO<sub>2</sub>-based catalysts and the H<sub>2</sub> production abilities

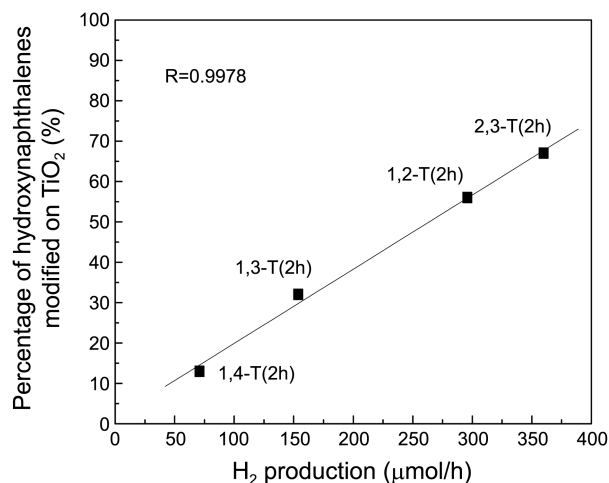
Sample	Percentage (%)	H <sub>2</sub> production (μmol·h <sup>-1</sup> )
neat TiO <sub>2</sub>	0	0
2,3-T(3h)	78	336
2,3-T(2h)	67	360
2,3-T(1h)	53	286
2,3-T(0.5h)	41	112
1,2-T(2h)	56	296
1,3-T(2h)	32	154
1,4-T(2h)	16	71
1-NT	6	22
2-NT	5	18



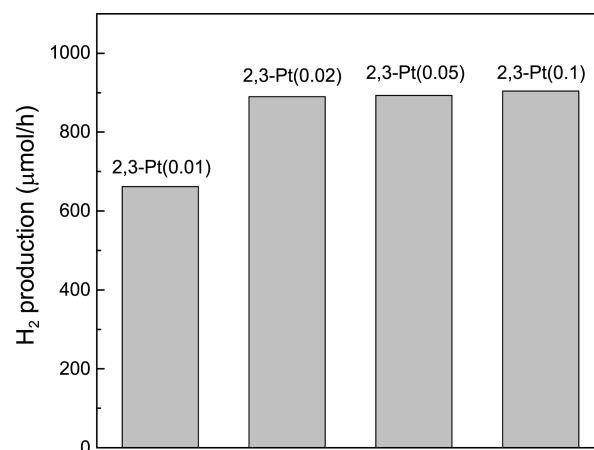
**Figure 4.** PL spectra of prepared neat and surface modified TiO<sub>2</sub> catalysts.

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.<sup>36</sup> Thus, it is possible that the photo-generated electrons transfer from TiO<sub>2</sub> conduction band to the surface of Pt, leading to the recombination rate of 2,3-Pt(0.02) further decreased.

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



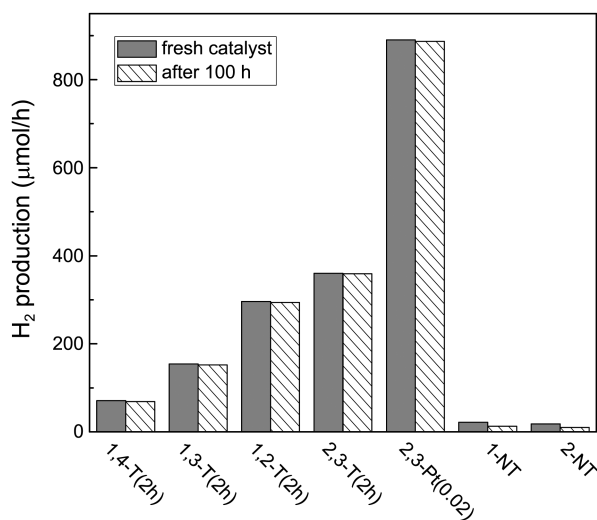
**Figure 5.** Relationship of H<sub>2</sub> production and percentages of corresponding hydroxynaphthalenes modified on TiO<sub>2</sub>.



**Figure 6.** Dependence of H<sub>2</sub> 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 H<sub>2</sub> production ability.

Figure 6 shows the H<sub>2</sub> production abilities of 2,3-dihydroxynaphthalene modified TiO<sub>2</sub> loaded with different amount of Pt. Obviously, the H<sub>2</sub> production abilities were remarkably increased after Pt loading. As suggested in the previous reports,<sup>23,37,38</sup> visible-light induced H<sub>2</sub> evolution originated from a sensitizing mechanism, which excited the localized electrons from the surface complexes into the conduction band continuum states of the TiO<sub>2</sub> semiconductor. The injected electrons in the TiO<sub>2</sub> particles migrate to the surface of Pt, where reduction of H<sup>+</sup> takes place to produce H<sub>2</sub>. Among the literatures reported Pt/TiO<sub>2</sub> catalyst for H<sub>2</sub> production, the optimal Pt contents were mainly in the region of 0.1-2 wt %.<sup>15,23,36,39</sup> However, in this investigation, no obvious H<sub>2</sub> 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/TiO<sub>2</sub> system can dynamic decrease the noble metal content which is beneficial to decrease the cost.



**Figure 7.** Photocatalytic stability of prepared TiO<sub>2</sub> catalysts.

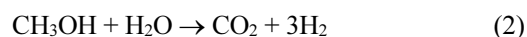
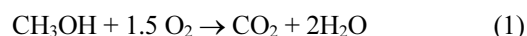
Figure 7 shows the photocatalytic stability of prepared TiO<sub>2</sub>-based catalysts. Dihydroxy naphthalene modified TiO<sub>2</sub> catalysts exhibited slight decrease in H<sub>2</sub> production ability after 100 h reaction compared with the fresh catalysts. For 2,3-Pt(0.02), lower than 1% decrease in H<sub>2</sub> 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 H<sub>2</sub> 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 TiO<sub>2</sub> surface during the reaction.

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

**Table 2.** Photocatalytic production of 2,3-Pt(0.02) under different CH<sub>3</sub>OH amount

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

O<sub>2</sub> reacted with CH<sub>3</sub>OH to form 47 μmol·h<sup>-1</sup> CO<sub>2</sub>. Accordingly, 11 μmol·h<sup>-1</sup> CO<sub>2</sub> came from methanol reforming reaction, which produced 33 μmol·h<sup>-1</sup> H<sub>2</sub>. It is noted that 1.2 μmol·h<sup>-1</sup> 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 H<sub>2</sub> production. Therefore, it is deduced that the appropriate methanol content is 5 vol %, which can scavenge O<sub>2</sub> or holes, and limit the reverse H<sub>2</sub>+1/2O<sub>2</sub> → H<sub>2</sub>O reaction without poisoning the noble metal, leading to the high H<sub>2</sub> production ability.



## Conclusion

The dihydroxy naphthalene/TiO<sub>2</sub> 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 TiO<sub>2</sub> surface and H<sub>2</sub> production ability. 2,3-T(2h) exhibited the best photocatalytic H<sub>2</sub> production ability among the prepared dihydroxy naphthalene/TiO<sub>2</sub> catalysts, which is probably due to the high percentages of 2,3-dihydroxynaphthalene coordinated on TiO<sub>2</sub> surface. After loading with ultra low concentration of Pt (0.02 wt %), the H<sub>2</sub> production ability was further improved. The obtained dihydroxy naphthalene modified TiO<sub>2</sub> catalysts exhibited much better photocatalytic stability than that of monohydroxy naphthalene modified TiO<sub>2</sub> 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 TiO<sub>2</sub> surface. The appropriate methanol content is 5 vol %, which can scavenge O<sub>2</sub> or holes, and limit the reverse H<sub>2</sub>+1/2O<sub>2</sub> → H<sub>2</sub>O reaction without poisoning the noble metal, leading to the high H<sub>2</sub> production ability.

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### References

1. Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
2. Zong, X.; Yan, H. J.; Wu, G. P.; Ma, G. J.; Wen, F. Y.; Wang, L.; Li, C. *J. Am. Chem. Soc.* **2008**, *130*, 7176.
3. Kudo, A.; Sekizawa, M. *Chem. Commun.* **2000**, 1371.
4. Kudo, A.; Kato, H. *Chem. Phys. Lett.* **2000**, *331*, 373.
5. Maeda, K.; Domen, K. *J. Phys. Chem. C* **2007**, *111*, 7851.
6. Dholam, R.; Patel, N.; Adami, M.; Miotello, A. *Int. J. Hydrogen Energ.* **2009**, *34*, 5337.
7. Sun, T.; Fan, J.; Liu, E. Z.; Liu, L. S.; Wang, Y.; Dai, H. Z.; Yang, Y. H.; Hou, W. Q.; Hu, X. Y.; Jiang, Z. Y. *Powder Technol.* **2012**, *228*, 210.
8. Wu, G. S.; Tian, M.; Chen, A. C. *J. Photochem. Photobiol. A: Chem.* **2012**, *233*, 65.
9. Cheng, P.; Yang, Z.; Wang, H.; Cheng, W.; Chen, M. X.; Shangguan, W. F.; Ding, G. F. *Int. J. Hydrogen Energ.* **2012**, *37*, 2224.
10. Fan, W. Q.; Lai, Q. H.; Zhang, Q. H.; Wang, Y. *J. Phys. Chem. C* **2011**, *115*, 10694.
11. Li, K.; Chai, B.; Peng, T. Y.; Mao, J.; Zan, L. *ACS Catal.* **2013**, *3*, 170.
12. Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem Rev.* **1995**, *95*, 735.
13. Meyer, S.; Saborowski, S.; Schäfer, B. *ChemPhysChem* **2006**, *7*, 572.
14. Vasileia, M. D.; Paraskevi, P.; Dimitris, I. K. *Chem. Eng. J.* **2011**, *170*, 433.
15. Rosseler, O.; Shankar, M. V.; Du, M. K.; Schmidlin, L.; Keller, N.; Keller, V. *J. Catal.* **2010**, *269*, 179.
16. Onsuratoom, S.; Chavadej, S.; Sreethawong, T. *Int. J. Hydrogen Energ.* **2011**, *36*, 5246.
17. Wu, X. M.; Song, Q. Q.; Jia, L. S.; Li, Q. B.; Yang, C.; Lin, L. Q. *Int. J. Hydrogen Energ.* **2012**, *37*, 109.
18. Kim, S.; Choi, W. *J. Phys. Chem. B* **2005**, *109*, 5143.
19. Kim, G.; Choi, W. *Appl. Catal. B: Environ.* **2010**, *100*, 77.
20. Park, H.; Kim, W.; Jeong, H.; Lee, J.; Kim, H.; Choi, W. *Sol. Energ. Mat. Sol. C* **2011**, *95*, 184.
21. Chou, C.; Yang, R.; Yeh, C.; Lin, Y. *Powder Technol.* **2009**, *194*, 95.
22. Tachikawa, T.; Yoshida, A.; Tojo, S.; Sugimoto, A.; Fujitsuka, M.; Majima, T. *Chem. Eur. J.* **2004**, *10*, 5345.
23. Ikeda, S.; Abe, C.; Torimoto, T.; Ohtani, B. *J. Photochem. Photobiol. A: Chem.* **2013**, *160*, 61.
24. Lin, J.; Lin, Y.; Liu, P.; Meziani, M. J.; Allard, L. F.; Sun, Y. P. *J. Am. Chem. Soc.* **2002**, *124*, 11514.
25. Janković, I. A.; Šaponjić, Z. V.; Comor, M. I.; Nedeljković, J. M. *J. Phys. Chem. C* **2009**, *113*, 12645.
26. Eder, D.; Windle, A. H. *Adv. Mater.* **2008**, *20*, 1787.
27. Shkrob, I. A.; Sauer, M. C.; Gosztola, D. *J. Phys. Chem. B* **2004**, *108*, 12512.
28. Yu, J. G.; Zhao, X. J.; Zhao, Q. N. *Mater. Chem. Phys.* **2001**, *69*, 25.
29. Ou, Y.; Lin, J. D.; Zou, H. M.; Liao, D. W. *J. Mol. Catal. A* **2005**, *241*, 59.
30. Biniak, S.; Szymański, G.; Siedlewski, J.; Świątkowski, A. *Carbon* **1997**, *35*, 1799.
31. Li, X. Y.; Wang, D. S.; Cheng, G. X.; Luo, Q. Z.; An, J.; Wang, Y. H. *Appl. Catal. B: Environ.* **2008**, *81*, 267.
32. Su, B. T.; Liu, X. H.; Peng, X. X.; Xiao, T.; Su, Z. X. *Mater. Sci. Eng. A* **2003**, *349*, 59.
33. Liu, Y.; Dadap, J. I.; Zimdars, D.; Eisenthal, K. B. *J. Phys. Chem. B* **1999**, *103*, 2480.
34. Regazzoni, A. E.; Mandelbaum, P.; Matsuyoshi, M.; Schiller, S.; Bilmes, S. A.; Blesa, M. A. *Langmuir* **1998**, *14*, 868.
35. Ikeda, S.; Abe, C.; Torimoto, T.; Ohtani, B. *J. Photochem. Photobiol. A* **2003**, *160*, 61.
36. Khan, M. A.; Akhtar, M. S.; Woo, S. I.; Yang, O. *Catal. Commun.* **2008**, *10*, 1.
37. Liu, Y.; Dadap, J. I.; Zimdars, D.; Eisenthal, K. B. *J. Phys. Chem. B* **1999**, *103*, 2480.
38. Ikeda, S.; Abe, C.; Torimoto, T.; Ohtani, B. *Electrochem.* **2002**, *70*, 442.
39. Daskalaki, V. M.; Panagiotopoulou, P.; Kondarides, D. I. *Chem. Eng. J.* **2011**, *170*, 433.
40. Iwase, A.; Kato, H.; Kudo, A. *Catal. Lett.* **2006**, *108*(1-2), 7.
41. Zalas, M.; Laniecki, M. *Sol. Energ. Mat. Sol. C* **2005**, *89*, 287.