



# Direct combination of hydrogen evolution from water and methane conversion in a photocatalytic system over Pt/TiO<sub>2</sub>



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## ABSTRACT

The CH<sub>4</sub> conversion under ambient condition remains a challenge over the past years, and the production of the ideal clean energy of H<sub>2</sub> is considered as an alternative method to meet the requirement of sustainable development. Herein, a new photocatalytic reaction system involved H<sub>2</sub> evolution from aqueous water and CH<sub>4</sub> conversion is established over Pt/TiO<sub>2</sub>. The synergistic effect between the two reactions of H<sub>2</sub> production and CH<sub>4</sub> conversion brings up the considerable quantum efficiencies of H<sub>2</sub> production to 4.7% without sacrificial agent and CH<sub>4</sub> conversion (the main products are C<sub>2</sub>H<sub>6</sub> and CO<sub>2</sub>) to 3.3% simultaneously. The introduction of Pt on the surface of TiO<sub>2</sub> particles facilitates the activation of CH<sub>4</sub> and •OH that can assist to produce methyl radical (•CH<sub>3</sub>), afterwards more C<sub>2</sub>H<sub>6</sub> (61.7% selectivity) is formed.

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## 1. Introduction

Methane (CH<sub>4</sub>), occupying the primary component of natural gas, is nearly ubiquitous in the world. As a fuel, the commercial use of CH<sub>4</sub> by directly burning will result in much worse global warming than CO<sub>2</sub> [1,2]. Recent, the conversion of CH<sub>4</sub> to other high value-added products has received increasing attention because of their sustainability for energy and environment [3–14]. These processes often demand the high pressure or high temperature reaction conditions. Photocatalysis technology is recognized as an alternative solution to meet the green conversion of CH<sub>4</sub>, since the solar energy is by far the largest exploitable resource [15]. Some important achievements, such as non-oxidative coupling of CH<sub>4</sub> to higher hydrocarbons (ethane, ethylene, propane, n- and i-butane) and H<sub>2</sub> [16–18], CH<sub>4</sub> reforming with CO<sub>2</sub> or H<sub>2</sub>O (gas) to syngas [19–23], partial oxidation of methane to methanol [24–30], and even to benzene [31] are developed in recent years. Among these works, the conversion of CH<sub>4</sub> to syngas and methanol are most studied in photocatalysis. For the desired product of alkanes, such as C<sub>2</sub>H<sub>6</sub>, the efficiency is still in a low level at present [28,29,32]. As a high-valued product, C<sub>2</sub>H<sub>6</sub> is an important industrial raw material to produce C<sub>2</sub>H<sub>4</sub>, halogenated ethane, and aromatic hydrocarbon

[33–39]. It is therefore necessary to find an effective strategy to improve the yield of C<sub>2</sub>H<sub>6</sub>.

The H<sub>2</sub> production from water has been a hot topic in photocatalysis, but the use of a sacrificial reagent is necessary [40–44], even in Pt/TiO<sub>2</sub> catalyst system. In addition, the improvement of efficiency via simultaneous utilization of photo-induced electron and hole for two different catalytic reactions is still a rarity. In this work, the two photocatalytic reactions of CH<sub>4</sub> conversion and water splitting into H<sub>2</sub> are introduced simultaneously in one system, and the high-valued products of H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> are gained, which has not been reported. Here the CH<sub>4</sub> is introduced as the sacrificial agent for hole as well as the useful reactant converted into other hydrocarbon. Through this way, the photo-induced electron and hole can be efficiently separated and adequately utilized, and a new strategy about the direct combination of H<sub>2</sub> evolution from water and CH<sub>4</sub> conversion with high efficiency photocatalytic performance is achieved successfully.

## 2. Experimental methods

### 2.1. Materials

The commercial P25 (Degussa) is used as TiO<sub>2</sub> precursor. H<sub>2</sub>PtCl<sub>6</sub> and CH<sub>3</sub>OH were purchased as A.R. grade chemicals from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. 5, 5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was obtained from J&K Chemical Ltd. The CH<sub>4</sub> (with purity ≥ 99.999%) was supplied by

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Fuzhou Xinhang gases co., Ltd. All of the reagents are used without further purification.

## 2.2. Sample preparation

The commercial  $\text{TiO}_2$  was dispersed in  $\text{H}_2\text{PtCl}_6$  solution with different mass fraction of Pt ( $x\% = 0.1\%, 0.3\%, 0.5\%, 1\%, 1.5\%, 2\%$ ). In the presence of  $\text{CH}_3\text{OH}$ , the mixture was irradiated by UV light of 254 nm for 1 h to produce Pt/ $\text{TiO}_2$ . Then resultant precipitate were harvested by centrifugation, then, washed with deionized water and absolute ethyl alcohol for several times. Finally, the obtained precipitate was dried at 80 °C in oven.

## 2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. The diffuse reflectance spectra (DRS) were performed on Varian Cary 500 UV–vis spectrophotometer with  $\text{BaSO}_4$  as the background ranging from 250 nm to 800 nm. The morphologies of the obtained products were observed by a transmission electron microscopy (TEM) (FEI Tecnai G2 F20 S-TWIN, operated at an accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) analysis was collected on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific) with monochromatic  $\text{Al K}\alpha$  radiation ( $E = 1486.2 \text{ eV}$ ). Electron spin resonance (ESR) spectra were obtained using a Bruker model A300 spectrometer with a Philip lamp of 254 nm as light source, and 5,5-dimethyl-L-pyrroline-N-oxide (DMPO) as trapper. All the samples are measured in suspension dispersed in various solutions. The sample is dispersed in purified methanol for detection of  $\cdot\text{O}_2^-$ , in deionized water for detection of  $\cdot\text{OH}$ , and in water dissolved  $\text{CH}_4$  for detection of  $\cdot\text{CH}_3$ .

## 2.4. Evaluation of photocatalytic properties

The photocatalytic activity of the catalyst was measured in a gas-liquid-solid system. 75 mg catalyst was dispersed in 75 mL  $\text{H}_2\text{O}$ , and the  $\text{CH}_4$  was filled upon the water with volume of 80 mL (including the gas circuit) at ordinary pressure. The reactant gas was circulated in the system with flow rate of 10 mL/min by a circulating pump. The reactant suspension was irradiated by UV lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). The reaction system was remained at 25 °C by thermostatic water around. After irradiation for 6 h, the concentration of the gas sample was monitored from the reactor using a gas chromatograph Model HP 6890 (Agilent Technologies Inc., USA) equipped with TDX-01, thermal conductivity detector and flame ionization detector. The schematic of the experimental set up for this work is shown in Fig. S1.

## 3. Results and discussion

### 3.1. Morphology and optical properties of the samples

The XRD patterns of the samples with different fraction of Pt ( $x\%$ ) are displayed in Fig. 1. The crystal phase of anatase and rutile  $\text{TiO}_2$  in the samples is respectively marked as \* and  $\blacktriangle$  according to the PDF no. 21–1272 and no. 21–1276 standard card. None of characteristic peaks belonging to Pt are observed due to its low proportion. And with the increasing of Pt proportion, a weak peak at 39.8° is detected, which can be indexed to the (111) plane of Pt (PDF no. 04-0802, labelled by  $\blacksquare$ ). The intensity of  $\text{TiO}_2$  peaks decreases with the amount increasing of Pt. This may be attributed to the shelter of Pt on the surface of  $\text{TiO}_2$  particles, or the aggregation inhibition of  $\text{TiO}_2$  particles caused by the participation of Pt.

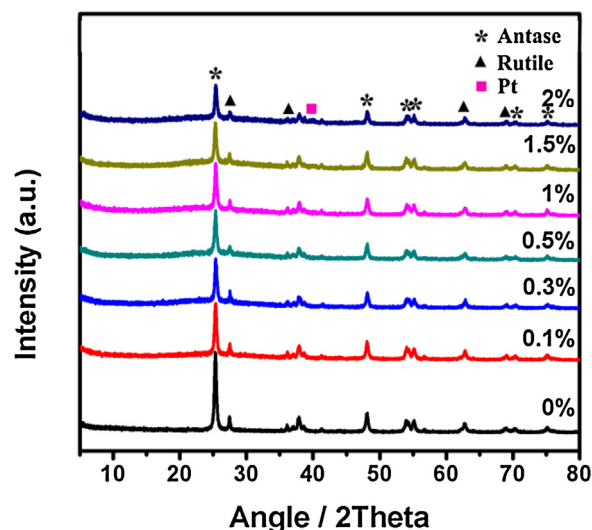


Fig. 1. The XRD patterns of the  $x\%$  Pt/ $\text{TiO}_2$ .

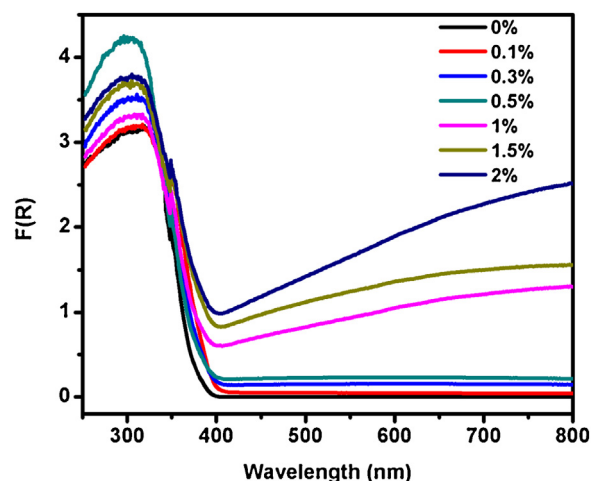


Fig. 2. The UV–vis diffuse reflectance spectra of the  $x\%$  Pt/ $\text{TiO}_2$ .

The optical character of the samples was studied by using UV–vis diffuse reflectance spectra (see Fig. 2). It shows that  $\text{TiO}_2$  only absorbs the light in the UV region ( $\lambda < 400 \text{ nm}$ ), based on which the UV light is used as exciting light source. The introduction of the Pt increases the absorption in the visible light region, and the absorption is positive increased with the proportion of Pt. Besides, the introduction of Pt slightly shifts the absorption edge of the  $\text{TiO}_2$  to longer wavelength. The results indicate that the Pt is successfully loaded on the  $\text{TiO}_2$  particles.

XPS was carried out to further investigate the surface compositions and chemical states of 0.5% Pt/ $\text{TiO}_2$  and  $\text{TiO}_2$  (Fig. 3). From the results spectra of Ti 2p and O 1s of lattice oxygen at 529.8 eV, it shows peak-shifting to the higher binding energy, which can be the evidence for the interaction between Pt and  $\text{TiO}_2$ . The peak shifting to the lower binding energy of the oxygen of surface hydroxyl at 531.6 eV [45,46] indicates that Pt is interaction with surface oxygen. The fitted two pairs of Pt peaks are indexed to two states of Pt elements ( $\text{Pt}^0$ ,  $\text{Pt}^{2+}$ ).

The morphology nature of 0.5% Pt/ $\text{TiO}_2$  is characterized by transmission electron microscopy (TEM) in Fig. 4a. The dispersing Pt particles are smaller as compared to  $\text{TiO}_2$  particles. The identification of lattice fringes indicates the coexistence of anatase (A) and rutile (R)  $\text{TiO}_2$ , as shown in Fig. 4b. The particle with a deeper contrast of which the diameter is about 5 nm, obtains the lattice fringe

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