

**Studies on photocatalysis of small organic molecules with
platinum-loaded titanium oxide**

Kexin Zou

Preface

The increasing environmental concerns and urgency for sustainable energy solutions have profoundly influenced my research path. Photocatalysis, as a technology that harnesses solar energy to drive chemical transformations, stands out as a promising and innovative approach. This study explores novel photocatalytic reactions involving platinum-loaded titanium oxide (Pt/TiO₂) and its unique catalytic mechanisms for transforming small organic molecules under mild conditions. The entire work was conducted under the supervision of Professor Hisao Yoshida at the Graduate School of Human and Environmental Studies, Kyoto University, JAPAN.

First and foremost, I would like to express my deepest gratitude to Professor Hisao Yoshida, whose invaluable guidance, patience, and expertise have significantly shaped my academic journey in photocatalysis. His unwavering support and insightful feedback have been instrumental in my development as a researcher, and I am deeply honored to have worked under his supervision. I am also sincerely thankful to Dr. Akira Yamamoto, the assistant professor in the Yoshida laboratory, for his dedication and inspiring perspectives, which have greatly influenced my research.

I extend my heartfelt appreciation to Ms. Yuri Bonnitche, the secretary in the Yoshida laboratory, for her diligent support, which has eased the daily challenges of our work. I am also greatly thankful to the senior members of the Yoshida laboratory, including Dr. Xing Zhu, Dr. Shimpei Naniwa, Ms. Shuting Li, Dr. Daichi Takami, Dr. Wirya Sarwana, and Dr. Surya Pratap Singh, for their invaluable guidance early in my career. Special thanks go to my colleagues, Dr. Yagna Prakash Bhoi, Mr. Hamada Salem El-Nagger, and Ms. Haifan Huang, for their valuable discussions. I am also grateful to all past and current members of the Yoshida laboratory for their kindness and support over the years.

I would like to acknowledge the Tatsunoko Foundation for providing me with a scholarship, enabling me to focus on my studies and research without financial concerns.

Finally, I express my deepest gratitude to my parents. Without their support, I would not have been able to study here. Their love and encouragement have been with me every step of the way.

This thesis concludes my six-and-a-half-year research journey at Kyoto University. I hope this work will contribute toward a more sustainable future.

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November 12th, 2024
Kyoto, JAPAN

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Chapter 1

General introduction

1.1 Overview of Titanium oxide photocatalysts

With the rapid growth of industry and human society, the use of fossil fuels has significantly increased. This rise in fossil fuel consumption has led to two major global issues: environmental pollution (such as toxic emissions and industrial waste) and the depletion of resources needed for renewable energy. Therefore, developing clean, safe, sustainable, and environmentally friendly energy technologies has become an urgent priority for researchers. [1] Solar energy is one of the most promising sources of clean and renewable energy on Earth, as it can be readily converted into electricity or chemical energy. For example, solar water splitting can produce clean hydrogen (H_2) fuel. Expanding the development and use of solar energy technologies is essential for tackling global environmental and energy challenges. Among these technologies, photocatalysis, *i.e.*, using solar energy to drive chemical and energy reactions, is now gaining much attention in these years. (**Fig. 1**)

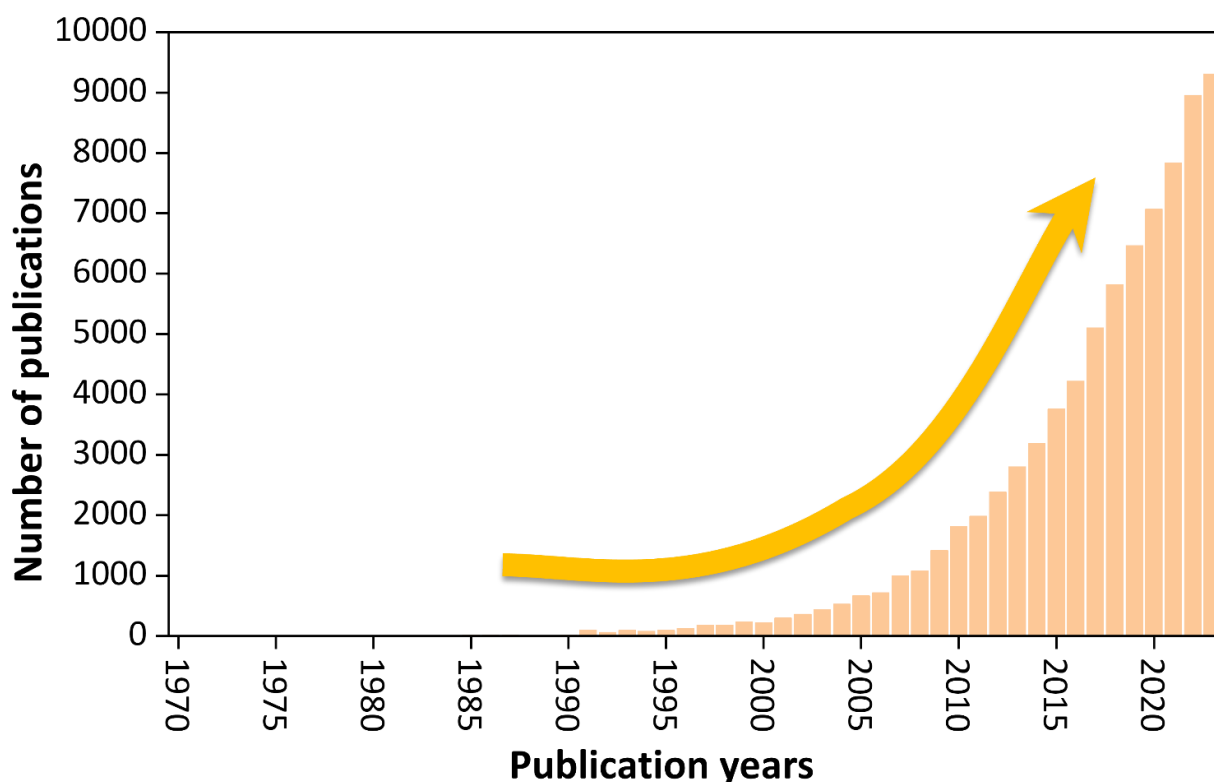


Fig. 1 Increasing publications related to photocatalysis since 1970. The data was recorded from the analyze results in web of science by searching “Photocatalysis” as the keyword on November 8th, 2024.

In photocatalysis, photocatalyst is a broad term for substances that exhibit catalytic action when exposed to photoirradiation. Of the many ways to categorize photocatalysts, they can be grouped based on the types of materials, including molecular photocatalysts and semiconductor photocatalysts. [2] For the case of molecular photocatalysts, the principle of this system can be described as molecular orbital theory (**Fig. 2 a**), where the alignment of the photocatalyst's highest occupied molecular orbitals (HOMO) or lowest unoccupied molecular orbitals (LUMO) with the reactant molecular orbitals is the most important factor. [3] For semiconductor photocatalysts, the energy band theory is most suitable. Among the electron-filled bands, the one with highest energy is the valence band (VB), and the lowest energy unfilled band in empty bands is called the conduction band (CB). [4] The energy difference between the VB and CB is called the band gap, which is also known as forbidden band because it cannot accommodate electrons. By light irradiation with energy over the band gap, electrons (e^-) in the VB are excited into the CB, and positive holes (h^+) are left in the VB. Then, each of these holes and electrons passes through the band to the surface of semiconductors, to initiate oxidation reaction and reduction reaction, respectively (**Fig. 2 b**).

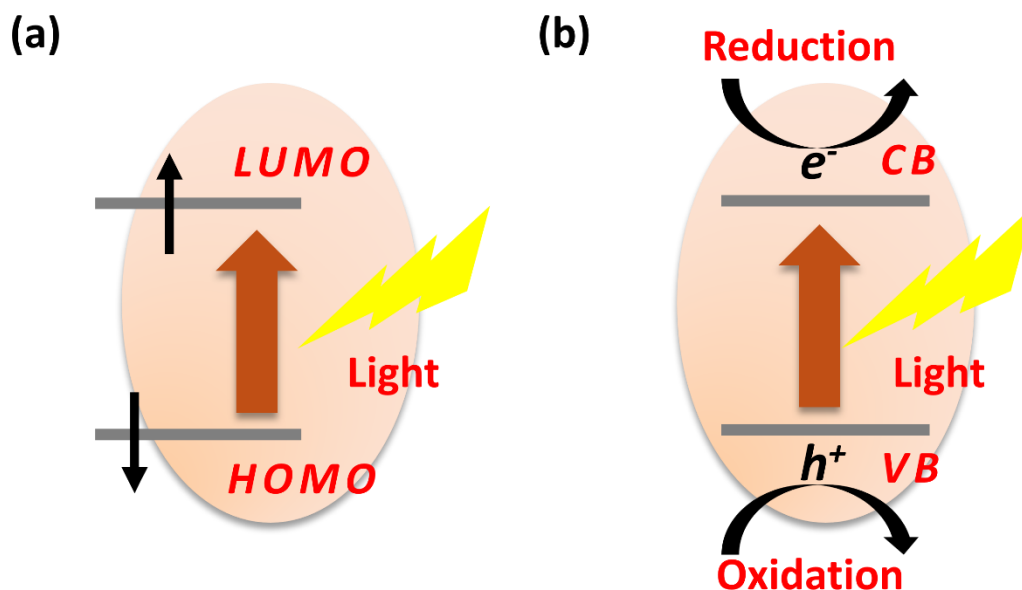


Fig. 2 Photoexcitation mechanism of (a) molecular photocatalysts and (b) semiconductor photocatalysts.

1.2 Broad applications of TiO₂ photocatalysts

Among those of semiconductor photocatalysts (TiO₂, ZnO, CdS, WO₃, g-C₃N₄, *etc.*), titanium oxide (TiO₂), due to its wonderful advantages such as durability, low cost, low toxicity, structural properties and high chemical stability, [5–7] has attracted growing interest in both academic and industrial fields. Historically, Fujishima and Honda reported the evolution of hydrogen and oxygen through photoelectrochemical water splitting with a TiO₂ photoanode and a platinum black electrode in 1972. [8] Since that, significant progress has been made in the field of photocatalysis, due to the extensive studies of TiO₂ photocatalyst across environmental and energy fields, including air cleaning, [9–12] metal anti-corrosion, [13,14] antibacterial activity, [15,16] *etc.* [17] In addition, the proper position of VB and CB (For initiating the oxidation reaction, the upper edge of VB should be more positive than the redox potential of substrates, and the lower edge of CB should be more negative than the redox potential of substrates for reduction reaction) provides a general oxidation and reduction ability with TiO₂ material (**Fig. 3**), make it a prototype photocatalyst for investigation on H₂ production and CO₂ conversion.

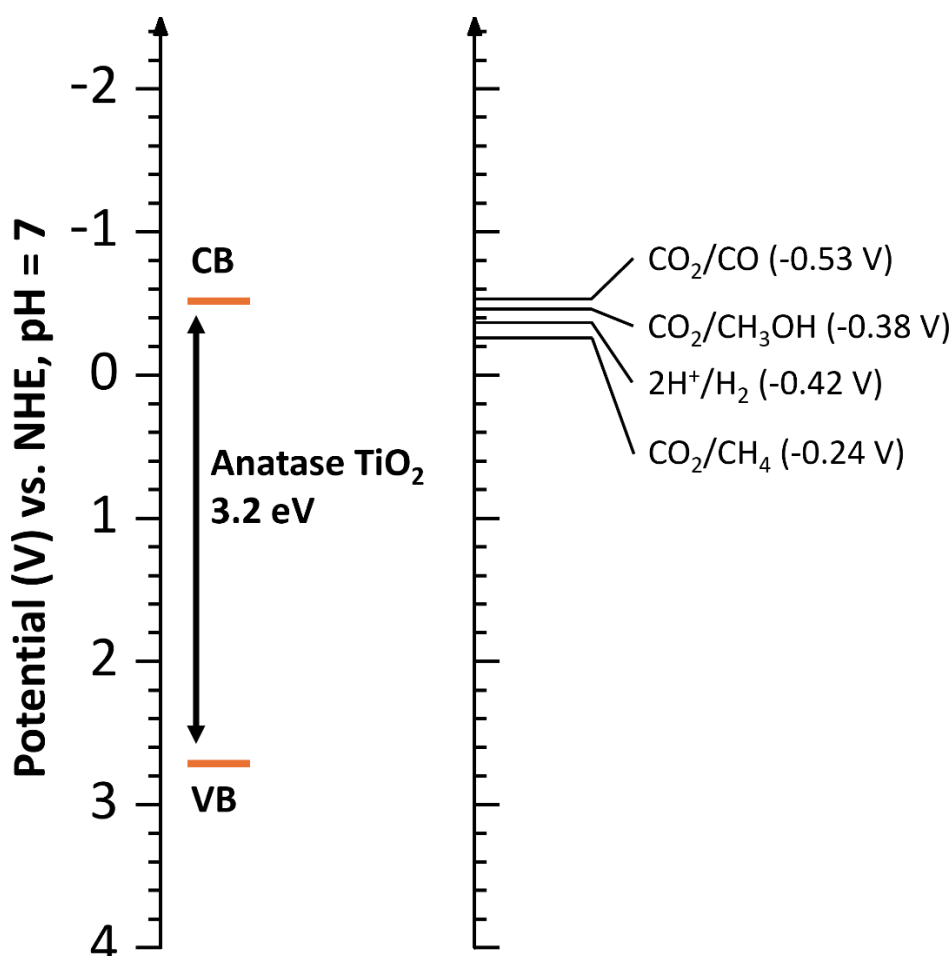


Fig. 3 Conduction band, valence band potentials, and band gap energies of anatase TiO₂ photocatalysts relative to the redox potentials at pH 7 of compounds involved in H₂ production and CO₂ conversion. The applied data are from ref. [18].

1.2.1 H₂ production

Producing hydrogen (H₂), a clean and renewable energy source, has become an important option to solve the severe environmental pollution and intensified climate change. [19] Nowadays, using solar energy to develop clean hydrogen is an alternative technique. In this regard, photocatalytic water splitting, a process that can convert light energy into hydrogen with photocatalyst materials, has been widely researched as an ideal method for producing chemical fuel. [20–22] Recently, many studies have been published, revealing a wide variety of TiO₂ based photocatalysts for their potential application in water splitting. **Table 1** summarized a few representative publications for photocatalytic H₂ production with TiO₂ based photocatalysts. [5] To obtain enhanced hydrogen evolution, various modifications have been made to TiO₂ photocatalyst in those studies, such as noble metal loading, [23–27] ion doping, [28,29] and composite of other semiconductors. [30,31] Another general strategy is the addition of sacrificial reagent into water, also known as hole scavengers, which can react to the photogenerated holes to prevent the rapid recombination of electrons and holes, resulting in an improved rate of hydrogen evolution.

Table 1 Photocatalytic H₂ evolution performance with various TiO₂ based photocatalysts. Adapted from ref. [5]

Photocatalysts (Dosage)	Sacrificial reagent	Irradiation source	Hydrogen evolution	Reference
Pt/TiO ₂ nanorods	/	300 W Xe lamp	1229 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[26]
Pt/TiO ₂	/	500 W Hg lamp	7410 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[27]
Co ₃ O ₄ /TiO ₂	/	300 W Xe lamp	41.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$	[31]
M/TiO ₂ /rGO :M = Au or Pt (50 mg/200 mL)	methanol	300 W Xe lamp	670 $\mu\text{mol h}^{-1}$	[23]
Cu/TiO ₂	methanol, glycerol	125 W mercury vapor lamp 400 W medium pressure lamp (365 nm maximum wavelength)	1–7 $\mu\text{mol min}^{-1}$	[24]
Pt/TiO ₂	methanol		1846 $\mu\text{mol h}^{-1}$ (1 wt% Pt)	[25]
Cobalt doped TiO ₂ (100 mg/ 50 mL)	glycerol	solar and UV light	11021 $\mu\text{mol h}^{-1}\text{g}^{-1}$	[28]
N doped TiO ₂	methanol	Xe lamp	760–4500 $\mu\text{mol h}^{-1}\text{m}^{-2}$	[29]
TiO ₂ /ZnO (0.1g/200 mL)	ethanol	High pressure Hg pen-lamp	1300 $\mu\text{mol h}^{-1}$	[30]

1.2.2 CO₂ conversion

Carbon dioxide is a greenhouse gas, which can contribute to global warming leading to climate change. [32] To help to solve the above issue, various kinds of TiO₂ based photocatalysts have been developed. In such systems, CO₂ can be activated and effectively converted into CO, CH₄ or CH₃OH. [33] **Table 2** listed recent works of photocatalytic CO₂ conversion with TiO₂ based photocatalysts. Similarly to H₂ production, modifications also are required for TiO₂ material to obtain enhanced yield of reduction product. Meanwhile, the band gap or the band edges can be tuned by modifications, so that different hydrocarbon products can be selectively obtained due to their different redox potential. [34,35]

It needs to be noted that due to the relatively wide band gap of TiO₂ photocatalyst (3.2 eV as anatase), only UV light can be utilized for the H₂ production and CO₂ conversion, which limits its further applications. To improve the sufficient use of solar energy, many researchers now are focusing on developing other visible light-responsive photocatalysts. [36–38] On the other hand, this chemically stable and inexpensive TiO₂ photocatalyst still has great potential on organic transformations, which will be introduced in the following section.

Table 2 photocatalytic CO₂ conversion with various TiO₂ based photocatalysts. Adapted from ref. [39]

Photocatalysts	Reaction conditions	Production yield (μmol/g)	Reference
Ag/TiO ₂	Irradiated under UV light for 6 h	Ag/TiO ₂ (CO = 69)	[40]
	Reaction with NaHCO ₃ solution	TiO ₂ (CO = 2.6)	
Ag/TiO ₂	Irradiated under UV light for 8 h	Ag/TiO ₂ (CH ₄ = 21.12)	[41]
	Reaction with H ₂ O	TiO ₂ (CH ₄ = 4)	
Pt/TiO ₂	Irradiated under UV light for 4 h	5 wt% Pt/TiO ₂ (CH ₄ = 10)	[42]
	Reaction with H ₂ O vapor	TiO ₂ (CH ₄ = 3.2)	
Au/TiO ₂	Irradiated under UV light for 6 h	0.2 wt% Au/TiO ₂ (CH ₄ = 8)	[43]
	Reaction with H ₂	TiO ₂ (CH ₄ = 3)	
Ce doped TiO ₂	Irradiated under UV light for 18 h	0.28 wt% Ce doped TiO ₂ (CH ₄ = 16)	[44]
	Reaction with NaOH solution	TiO ₂ (CH ₄ = 11)	
N doped TiO ₂	Irradiated under UV-vis light for 2 h	N doped TiO ₂ (CH ₃ OH = 20)	[45]
	Reaction with H ₂ O in liquid phase	TiO ₂ (no CH ₃ OH yield)	

1.2.3 Organic transformations

Organic transformations encompass a broad range of chemical reactions that convert organic substrates into value-added products. These transformations are critical in industries such as pharmaceuticals, agrochemicals, and fine chemicals. Traditional approaches for organic transformations often rely on harsh reaction conditions, including high temperatures, elevated pressures, and the use of hazardous reagents. These approaches, while effective, address significant challenges including high energy consumption, environmental concerns, and the generation of undesirable by-products. [46,47]

In recent years, there has been an increasing demand for more sustainable and environmentally friendly alternatives to traditional organic transformations. Photocatalysis has emerged as a promising solution to address the limitations associated with conventional methods. By harnessing light energy to activate photocatalysts, organic reactions can proceed under milder conditions (room temperature and atmospheric pressure), reducing energy inputs and minimizing the use of hazardous reagents. [48–50]

Among the various photocatalysts explored (**Table 3**), TiO₂ has garnered significant attention due to its several key advantages for organic transformations, including: 1) Chemical stability: TiO₂ is resistant to photodegradation and can maintain catalytic activity over extended reaction cycles; 2) Strong oxidative potential: The deep position of the valence band edge of TiO₂ enables efficient oxidation of organic substrates with chemical bonds activation; 3) Potential for dehydrogenative reactions: The position of the conduction band lies above the potential of the normal hydrogen electrode (standard zero potential), which enables the H₂ production during many organic transformations; 4) Environmental compatibility: Being a non-toxic and recyclable material, TiO₂ supports sustainable catalytic processes. [51] For TiO₂ photocatalyst, the applications for organic transformations can be classified as 3 types of reactions, *i.e.*, oxidations, reductions and bond construction reactions.

Table 3 Summary of the key properties of various photocatalysts used in organic transformations.

Photocatalyst	Band gap (eV)	Key advantages	Key limitations
TiO ₂ [51]	~3.2	High stability, non-toxic, strong oxidation	UV absorption, fast recombination
ZnO [52]	~3.3	High quantum efficiency	Photocorrosion in acidic conditions
CdS [53]	~2.4	Visible-light response	Toxicity, photocorrosion
g-C ₃ N ₄ [54]	~2.7	Visible-light activity, metal-free	Low charge mobility
WO ₃ [55]	~2.8	Visible-light absorption	Poor charge separation

1.2.3.1 Oxidations

The most discussed reactions would be oxidation of organic compounds with TiO₂ photocatalysts. For example, alcohols can be oxidized to the corresponding aldehydes, [56–58] the hydroxylation of aromatics to phenols, [59–61] the transformation of amino acids into nitrogen-containing heterocycles, [62–64] the epoxidation of olefines, [65–67] *etc.* In most of these reactions, molecular oxygen (O₂) is applied as the oxidant, which often leads to some undesirable overoxidation reactions. [68] Thus, to avoid the overoxidation and improve the selectivity, strategies like surface modification of TiO₂ photocatalyst [69] and the selection of incident wavelength [70–72] are applied.

1.2.3.2 Reductions

TiO₂ photocatalysts can be also employed in numerous reduction reactions. These reactions often rely on sacrificial reagents, such as alcohols, to inhibit back reactions. Compared to the conventional methods which usually use dangerous reducing agents such as hydrogen and carbon monoxide, photocatalysis provides a safer alternative. The most studies reactions are the reduction of nitroaromatics to the corresponding amines [73–77] and the reduction of aldehydes and ketones. [78,79] Recently, extensive studies also focus on the hydrogenation and semihydrogenation of alkenes and alkynes. [80–84] In above mentioned reduction reactions, the removal of O₂ significantly improves the reduction efficiency and selectivity, since O₂ behaves as a competitive scavenger of the electron on the TiO₂ surface and is converted to reactive oxygen radical (O₂^{•-}).

1.2.3.3 Bond construction reactions

Since photocatalysis readily produces radical species, it can be systematically utilized for the bond formation of organic compounds requiring radical reactions. There are many reports about the photocatalytic Minisci reactions to construct the C–C bond formation with TiO₂. [85–88] For instance, the addition of formamide to quinoline photocatalytically proceeded with the addition of H₂O₂ and H₂SO₄. The addition of H₂O₂ and H₂SO₄ is considered to accelerate the amide radical formation. Similar reactions of nitrogen-containing heterocycles with ethers have also been reported years ago. [85]

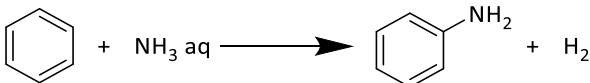
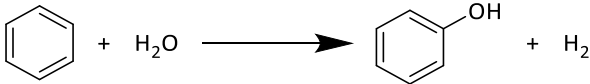
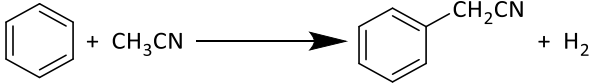
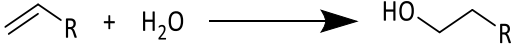
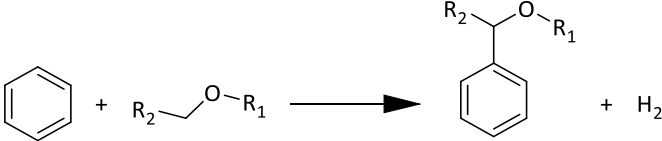
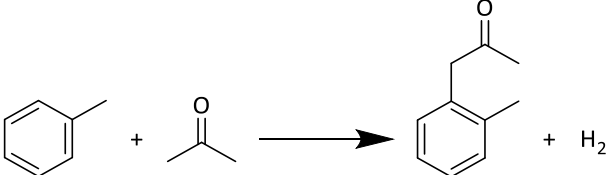
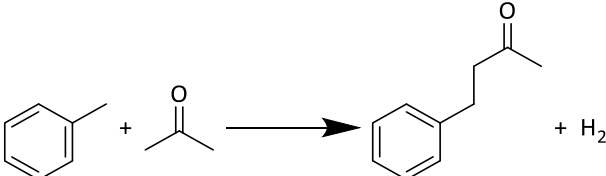
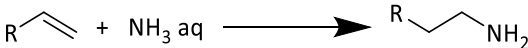
Another focused field is the C–N bond formation. Many authors reported that C–N coupling reaction can occur between amines and alcohols. [89–91] Upon photoirradiation of an alcohol solution containing primary or secondary amines with TiO₂ photocatalysts, the corresponding secondary or tertiary amines are formed. In these reactions, alcohols are oxidized by holes generated on the catalyst surface to yield the corresponding aldehydes or ketones. These intermediates subsequently react with amines to form imines, which are then reduced to produce the desired

amine products.

1.2.3.4 Reports from our laboratory

Our laboratory has been committed to developing photocatalytic bond constructions with metal-loaded TiO₂ (M/TiO₂) for years [92–112]. In our studies, we examined the direct activation of various small molecules to proceed the functionalization of aromatic rings, such as the amination of benzene by ammonia aqueous, the hydroxylation of benzene by water, the cyanomethylation of benzene by acetonitrile, the acetylation of toluene by acetone and so on with elucidation of their reaction mechanisms such as radical addition-elimination (RAE), radical-radical coupling (RRC). Most of the reactions are found to be the dehydrogenative type, *i.e.*, hydrogen gas is produced as the byproduct, which may contribute to sustainable energy solutions. Some of the representative publications were listed in **Table 4**.

Table 4 A part of photocatalytic bond constructions by small molecules reported by our laboratory.

Reactions	Photocatalysts	Reference
	Pt/TiO ₂	[93,95,98]
	Pt/TiO ₂	[92,94,98]
	Pd/TiO ₂	[96,101]
	Pt/TiO ₂ , Pd/TiO ₂	[97,99]
	Pd/TiO ₂	[96]
	Pd/TiO ₂	[109]
	Pt/TiO ₂	[109]
	Au/TiO ₂ , Pt/TiO ₂ , Pd/TiO ₂	[110]

1.3 Noble metal cocatalysts

As shown above, despite the broad applications of TiO₂ photocatalysts over various fields, the bare TiO₂ material itself is barely applied directly as it possesses some inherent shortcomings which limit its further exploitation. [113] The main problem is its fast and undesirable photogenerated electron–hole recombination reaction, which leads to a decreasing of photocatalytic activity. [114] One conventional protocol to solve the problem is the deposition of a number of noble metals (Pt, Pd, Ag, Au, *etc.*) on the TiO₂ surface as the Fermi level of loaded metal nanoparticles is lower than the conduction band of TiO₂, *i.e.*, the metal nanoparticles act as photoexcited electron receivers that inhibit the recombination of photogenerated electron–hole pairs, and thus improve the photocatalytic activity. [115,116] Besides that, in organic transformations, the addition of some noble metals has also been proved to effectively enhanced reaction yield and selectivity due to some specific catalytic effects. [94,99,100] Among the mentioned noble metals, Pt has gained a lot of attention from us due to its large work function (5.41 eV, bulk Pt, [117]) and possibly co-catalytic activity in a photocatalytic process, [102] which can be considered as an ideal metal to deposit on the TiO₂ surface in many reaction systems. [22,25,32]

1.4 Focus areas of this thesis

This thesis investigates three key reactions as case studies in photocatalysis with Pt/TiO₂, each addressing

distinct systematic challenges: (i) Benzene methylation by acetic acid: The functionalization of benzene is a crucial process in organic chemistry and industrial production. Traditional methods for benzene methylation are energy-intensive and often lack selectivity. This thesis explores a novel photocatalytic approach using acetic acid as the methylation agent on Pt/TiO₂ and investigates the methylation mechanism, aiming for efficient and selective benzene functionalization. [118] (ii) Direct C–N coupling of aniline to aminodiphenylamines: C–N coupling reactions are fundamental in the synthesis of pharmaceuticals and agrochemicals, yet they typically require harsh conditions. Here, we investigate the photocatalytic C–N coupling of aniline on Pt/TiO₂, offering a milder and potentially greener alternative to conventional methods for synthesizing aminodiphenylamines. [119] (iii) Coupling of hydrogen radicals catalyzed by Pt nanoparticles with TiO₂ photocatalyst: By using a unique flow reactor with a gas mixture of methanol and water in argon carrier, in which TiO₂ photocatalyst and separately supported Pt nanoparticles are located without physical contact, the ability of hydrogen radicals to couple after traveling significant distances from the TiO₂ photocatalyst surface offers an additional and critical role for Pt as a catalyst other than its traditional electron acceptor role in H₂ evolution. [120]

1.5 Research objectives and structure of the thesis

The primary objective of this research is to explore novel photocatalytic reactions for transforming small organic molecules using Pt/TiO₂. By focusing on the efficiency, selectivity, and mechanistic understanding of these reactions, this work aims to contribute to the development of sustainable and practical photocatalytic methods in synthetic chemistry.

The thesis is structured into three main chapters, each addressing one of the focus areas mentioned above. Each chapter is presented as an independent study, including its own Introduction, Experimental details, Results and Discussion, and Conclusion. This format enables a comprehensive exploration of each reaction pathway while maintaining a cohesive narrative across the broader research themes of photocatalysis and sustainability.

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Chapter 2

Benzene methylation by acetic acid

Abstract

Photocatalytic functionalization of aromatic rings with simple small molecules has been intensively studied by using metal-loaded titanium oxide photocatalyst. In the present study, the photocatalytic direct methylation of benzene was examined by using acetic acid as a promising methylation reagent. Over 15% yield of toluene was achieved with a platinum-loaded TiO_2 photocatalyst (Pt/TiO_2) under light irradiation without any extra solvent. The kinetic investigations with isotopic compounds and temperature-controlled experiments elucidated that Pt nanoparticles on the TiO_2 surface have a dual role, i.e., working as an electron receiver to improve the charge separation and catalyzing a radical addition-elimination process to form toluene molecule. Two competitive reaction mechanisms were proposed in this reaction system.

2.1 Introduction

Methylation, as one of the most crucial processes in chemical modification, has been intensively researched over the past few decades. The most common method for methylation of aromatics is *via* directed ortho-metalation, [1,2] which entails a stoichiometric amount of strong base such as *n*-BuLi and the presence of heteroatoms as directing groups. Recently, numerous protocols were published focusing on methylation of aromatics driven by photo-energy method as it possesses advantages of cleanness, low-cost, and mild reaction conditions when compared with classic ways. Through the combination of an iridium photo-redox catalyst and a thiol organocatalyst, MacMillan designed a homogeneous catalytic system by using MeOH as the methyl radical source to functionalize six-membered-ring heteroarenes at room temperature to produce methylated products. [3] With addition of dichloromethane and trifluoroacetic acid, another photoinduced heteroarene methylation using MeOH as methyl radical source has also been reported. [4] Despite those breakthroughs have been achieved about methylation of aromatics, especially heteroarenes methylation mentioned above, the direct methylation of benzene, namely synthesis of toluene from benzene has not been reported in neither photo-induced way nor photocatalytic way due to the tremendous stability of benzene itself. Hence, a stable and efficient method for methylation of benzene is urged to be designed in mild environment.

On the other hand, when 50 mL of 9.0 v/v% acetic acid (CH_3COOH) aqueous solution was mixed with 100 mg of Pt/TiO₂, upon photoirradiation, methane (CH_4) and carbon dioxide (CO_2) were mainly produced, which was first reported as the photocatalytic decomposition reaction of acetic acid named the photo-Kolbe reaction in 1978. [5–7] Studies by electron spin resonance (ESR) measurements revealed that methyl radical ($\bullet\text{CH}_3$) and carboxymethyl radical ($\bullet\text{CH}_2\text{COOH}$) are generated from acetic acid and acted as intermediate roles in the photocatalytic reactions with Pt/TiO₂ in aqueous solution, [8–13] which demonstrated the possibility of acetic acid for being a source of the methyl group in the radical addition process.

In this work, we examined the methylation of benzene to form toluene by using acetic acid as a promising methylation reagent with platinum-loaded TiO₂ photocatalysts (Pt/TiO₂) under light irradiation. Kinetic experiments with isotopic compounds, and temperature-controlled reactions not only elucidated the mechanism of the methylation process, but also suggested that Pt nanoparticles on TiO₂ acted a dual role in toluene formation.

2.2 Experimental

2.2.1 Catalyst preparations

Various metal(M)-loaded titanium oxide photocatalysts, M(x)/TiO₂, were synthesized, where x shows a loading amount as weight percent (wt%), namely, Pt(0.1)/TiO₂, Pt(0.5)/TiO₂, Pt(1.0)/TiO₂, Pt(2.0)/TiO₂, Au(1.0)/TiO₂, Pd(1.0)/TiO₂ and Ag(1.0)/TiO₂, and an Al₂O₃-supported sample named Pt(1.0)/Al₂O₃ was also prepared.

The M(x)/TiO₂ samples were prepared by a photodeposition method by using commercial TiO₂ samples (Ishihara Sangyo Kaisha, ST-01, anatase, 300 m²g⁻¹) and aqueous metal precursor solutions like H₂PtCl₆ (Nacalai tesque, 99%), HAuCl₄ (Nacalai tesque, 99%), PdCl₂ (Kishida Chemical, 99%), and AgNO₃ (Kishida Chemical, 99%). As representatively, the procedure to prepare the Pt(1.0)/TiO₂ photocatalyst is described as follows. 1.0 g of TiO₂ powder was dispersed in 200 mL of ion-exchanged water and was irradiated with a xenon lamp (PE300BUV, 300 W) for 30 min with magnetically stirring. Then 50 mL of methanol and 530 μL of the H₂PtCl₆ solution (18.84 g L⁻¹ as Pt) were added to the suspension and the contents were stirred for 15 min without irradiation, followed by stirring for 1 h under light irradiation. This suspension was filtered with suction and was washed with 500 mL of ion-changed water 3 times. After drying for 12 h under 353 K in an electronic oven, a deep grey-coloured powder of the Pt(1.0)/TiO₂ sample was obtained. Other M(x)/TiO₂ samples were prepared by the same procedures mentioned above with the aimed metal precursor of different amount.

An impregnation method was applied for preparation of the Pt(1.0)/Al₂O₃ sample. 1.0 g of Al₂O₃ (the Catalysis

Society of Japan, JRC-ALO-7, γ -phase, $170 \text{ m}^2\text{g}^{-1}$) powder was dispersed in 200 mL of ion-exchanged water and was stirred for 30 min. Then the 530 μL of the H_2PtCl_6 solution (18.84 g L^{-1} as Pt) was added to the suspension and the contents were stirred for 1 h. Water was removed from the suspension by heating at 363 K in a water bath and the obtained bulk solid was powdered and dried under 353 K for 12 h. The $\text{Pt}(1.0)/\text{Al}_2\text{O}_3$ powder was finally collected after calcination at 773 K for 1 h by using an electric muffle furnace.

2.2.2 Photocatalytic reaction tests

2.2.2.1 Materials

All of the reagents employed in the photocatalytic reaction tests were of analytical grade and used without further purification: *n*-decane (Nacalai tesque, 98%), acetic acid (Nacalai tesque, 99.7%), acetic acid- d_1 (CH_3COOD , Tokyo Chemical Industry, 98%), acetic acid- d_4 (CD_3COOD , Cambridge Isotope Laboratories, 99.5%), benzene (Nacalai tesque, 99.7%), benzene- d_6 (C_6D_6 , Tokyo Chemical Industry, 99.6%), toluene (Tokyo Chemical Industry, 99.8%), biphenyl (Kishida Chemicals, 99%), *o*-xylene (Kishida Chemicals, 99%), and *p*-xylene (Kishida Chemicals, 99%).

2.2.2.2 Photocatalytic reaction tests

The photocatalytic reaction test was carried out in a capped test tube (20 mL) as a closed reactor. Without any optical filter, light irradiation from a xenon lamp (PE300BUV, 300 W) was conducted for 30 min to clean the surface of desired amount of photocatalyst (typically, 10 mg). Then, 4 mL (45 mmol) of benzene and 2.8 μL (50 μmol) of acetic acid were added as reactants, no extra solvent was introduced, and the test tube was plugged by a white silicone septum stopper and sealed. By using an argon gas bubbling flow (30 mL min^{-1}) for 30 min, the existed air was purged. The contents were stirred with light irradiation for the desired time (typically, 180 min) to promote the photocatalytic reaction. After the reaction, 0.5 mL of the gaseous phase was extracted and analyzed by GC-TCD (Shimadzu GC-8A). The liquid phase was filtered by using a syringe equipped with a PTFE membrane filter and then analyzed qualitatively and quantitatively by GC-MS (Shimadzu QP-2020) using *n*-decane as an internal standard.

2.2.2.3 Mechanistic studies

A few kinetic experiments were carried out by using deuterated benzene (benzene- d_6 , C_6D_6), monodeuterated acetic acid (acetic acid- d_1 , CH_3COOD) and deuterated acetic acid (acetic acid- d_4 , CD_3COOD) to get an insight into benzene methylation process. And to study the apparent activation energies to form each product, temperature-controlled experiments were conducted. The reaction temperature was controlled in a range of 299–312 K by a water bath with a cooling system.

2.3 Results and discussion

2.3.1 Outline of the photocatalytic methylation of benzene

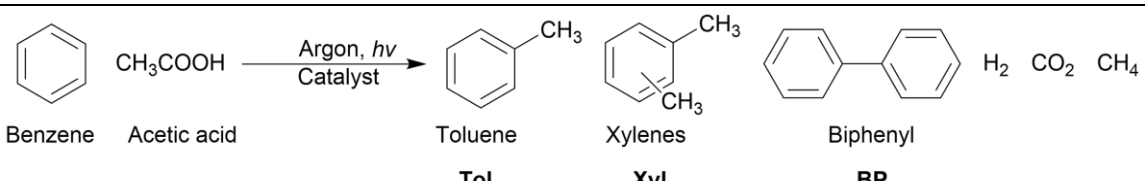
Table 1 shows the results of the photocatalytic reaction tests. When the $\text{Pt}(1.0)/\text{TiO}_2$ sample was used under the present conditions (See the footnote of **Table 1**), toluene (7.63 μmol , 15.3% yield) was observed as the target product (**Table 1**, entry 1). Some blank tests revealed that this direct methylation did not occur without light irradiation or without the photocatalyst (**Table 2**), meaning that this direct methylation was successfully promoted photocatalytically. In this reaction, *o*-xylene and *p*-xylene were also detected, which should be produced by the

successive methylation of toluene and the isomer ratio was roughly estimated as 53.3% and 46.7%, respectively. This will be discussed later. Observed by-products were biphenyl, hydrogen, methane, and carbon dioxide, indicating that homocoupling reaction of benzene and decomposition of acetic acid would take place competitively. Although the methylation and homocoupling give equimolar H_2 , the obtained amount of H_2 (32.0 μmol) was larger than the expected value (12.2 μmol) from the amount of the C–C coupling products: toluene, xylenes, and biphenyl. The excess amount of hydrogen would result from the formation of undetected products, like polyphenyls, that would be undetectable due to the large molecular weight leading to strong adsorption on the titanium oxide surface in the present conditions, [14] which was supported by a noticeable color change of the Pt(1.0)/TiO₂ sample from gray to dark brown during the photocatalytic reaction test. The scheme in **Table 1** summarized the reactions expected occurring in the reactor, except for the uncovered reactions resulting the excess amount of hydrogen. The balance of methyl group and CO₂ in the products, which was derived from acetic acid, was almost reasonable.

It also has to be mentioned that the present reaction conditions were selected from a series of optimization experiments, which included the metal-loading species on TiO₂, the loading amount of Pt on TiO₂, the applied weight of the Pt(1.0)/TiO₂ photocatalyst, the reaction time course, and the applied amount of acetic acid (**Tables 3–7**).

The reactions also occurred with the application of the bare TiO₂ photocatalyst (**Table 1, entry 2**). The yield of toluene was small such as 0.974 μmol and hydrogen was not detected. This suggests that Pt cocatalyst is efficient in enhancing the photocatalytic activity for the reaction of benzene conversion such as methylation and homocoupling, especially the formation of H_2 molecules. On the other hand, the methane and CO₂ were well obtained although the yields were somewhat lower than those with the Pt(1.0)/TiO₂ sample, which were formed through the decomposition of acetic acid. This means that the bare TiO₂ photocatalyst can activate acetic acid efficiently and the Pt cocatalyst can enhance the photocatalytic activity especially for the methylation and homocoupling of benzene with hydrogen formation.

Table 1 Photocatalytic methylation of benzene over various catalyst samples. ^a

										
	Benzene	Acetic acid		Toluene	Xylenes	Biphenyl				
				Tol	Xyl	BP				
Entry	Catalyst	Product ^b / μmol						Y(%) ^d	$S_1(\%)$ ^e	$S_2(\%)$ ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	Pt(1.0)/TiO ₂	7.63	0.508	3.52	32.0	18.4	28.4	15.3	29.3	68.4
2	TiO ₂	0.974	n.d.	0.270	n.d.	15.3	15.5	1.95	5.99	78.3
3	TiO ₂ + Pt(1.0)/Al ₂ O ₃	3.48	0.256	2.88	20.7	15.9	18.2	6.96	18.0	54.7
4	Pt(1.0)/Al ₂ O ₃	0 ^g	n.d. ^h	n.d.	n.d.	n.d.	n.d.	-	-	-

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol) were used as reactants without using solvent; Reaction time: 3 h; The incident light wavelength was limited > 330 nm by an optical filter; Irradiated light intensity was 30 mW cm^{-2} , measured at 360 ± 20 nm in wavelength; For **entries 1, 2 and 4**, 10 mg of catalyst was used; For **entry 3**, 10 mg of the bare TiO₂ sample and 10 mg of the Pt(1.0)/Al₂O₃ sample were applied; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene A_{Tol} was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, $Y(\%) = 100 \times A_{\text{Tol}}/(\text{introduced acetic acid})$, where A stands for the yielded amount of product; ^e Selectivity of toluene based on the acetic acid used for the formation of toluene and methane, $S_1(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{CH}_4})$; ^f Selectivity of toluene based on the benzene used for toluene and biphenyl formations, $S_2(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{BP}})$; ^g The detected amount of toluene was same as or less than the amount of the impurity in the used reagent of benzene; ^h n.d. = not detected.

Table 2 The results of some blank tests. ^a

Entry	Photoirradiation	Photocatalyst	Product ^b / μmol				
			Tol ^c	BP	H ₂	CH ₄	CO ₂
1	No	No	0.0 ^d	n.d. ^e	n.d.	n.d.	n.d.
2	No	Yes	0.0	n.d.	n.d.	n.d.	n.d.
3	Yes	No	0.0	n.d.	n.d.	n.d.	n.d.

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol) were used as reactants; Reaction time: 3 h; Photocatalyst: 10 mg of Pt(1.0)/TiO₂ (**entry 2**); The incident light wavelength was > 330 nm; Irradiated light intensity was 30 mW cm^{-2} , measured at 360 ± 20 nm (**entry 3**); ^b Tol = toluene, BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene A_{Tol} was calculated by subtracting the initial amount from the detected one; ^d The value of the produced toluene A_{Tol} same as or less than the value of the impurity was shown as zero; ^e n.d. = not detected.

In order to know the role of Pt cocatalyst, a physical mixture of the bare TiO₂ and Pt(1.0)/Al₂O₃ samples were examined for this reaction test, where Pt is loaded on not the TiO₂ photocatalyst but the photocatalytically inert Al₂O₃ support (**Table 1, entry 3**). It is quite interesting that this physical mixture exhibited higher photocatalytic activity than the bare TiO₂ sample for all these reactions and the product distribution was similar to that with the Pt(1.0)/TiO₂ photocatalyst although the yields were a little lower than those with the Pt(1.0)/TiO₂ photocatalyst, suggesting that the Pt species loaded on the alumina support functioned as a catalyst to enhance both the methylation

and homocoupling of benzene to yield toluene and biphenyl with H₂ formation. It was confirmed that the alumina-supported Pt catalyst could not produce any products without the TiO₂ photocatalyst in the present conditions (**Table 1, entry 4**), suggesting that the radical species generated on the TiO₂ photocatalyst could reach the alumina-supported Pt species and the Pt species functioned as a collaborative catalyst to promote the reactions with the radical species even when the Pt catalyst was not deposited on the TiO₂ photocatalyst.

As well known, the Pt cocatalyst can improve the carrier separation efficiency in TiO₂ photocatalyst and promote H₂ evolution. [15–18] As shown, the Pt loaded TiO₂ photocatalyst gave higher products yields of CO₂, which can be directly produced on the TiO₂ photocatalyst (mentioned later), than the physically separated one (**Table 1, entries 1 and 3**). This evidenced the role of Pt cocatalyst to accelerate the charge separation. The result with the physical mixture clarified that the Pt species can function as a catalyst to promote the reaction between the photocatalytically generated radical species and other molecules or radical species (**Table 1, entry 3**). Thus, it was elucidated that Pt played a dual role, i.e., (i) improving the carrier separation efficiency and (ii) acting like a collaborative catalyst for toluene formation. In the case with the Pt(1.0)/TiO₂ photocatalyst, the reaction selectivity to the methylation of benzene based on the converted acetic acid (S₁) and the selectivity of toluene among the benzene derivatives (S₂) were higher than those with the mixture (**Table 1, entries 1 and 3**). However, a CO-pulse adsorption measurement (**Table 8**) revealed that a better dispersion (36.6%) and smaller particle size (0.679 nm) of Pt nanoparticles on Al₂O₃ surface than on the TiO₂ surface (15.4%, 1.62 nm). Usually, the highly dispersed Pt cocatalyst loaded on Al₂O₃ support might catalyze more efficiently than that on the TiO₂ surface with the same loading amount (1.0 wt%), but the results were opposite. The reasons why the Pt nanoparticles directly located on the surface of the TiO₂ photocatalyst provided more sufficient photocatalytic activity are as follows: 1) Pt nanoparticles on the TiO₂ surface plays a significant role as an electron acceptor to enhance the photocatalytic activity, 2) the distance between Pt catalyst and TiO₂ photocatalyst are short, 3) the supporting effect of TiO₂ and Al₂O₃ on the catalytic property of Pt catalyst might also be taken into consideration.

Table 3 Reaction tests with various metal-loaded TiO₂ photocatalyst samples. ^a

Entry	M(1.0)/TiO ₂	Product ^b / μmol						<i>Y</i> (%) ^d	<i>S</i> ₁ (%) ^e	<i>S</i> ₂ (%) ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	Ag	1.72	n.d. ^g	17.4	20.6	21.2	19.2	3.44	7.50	9.00
2	Pd	2.47	n.d.	7.78	13.6	19.4	20.0	4.94	11.3	24.1
3	Au	3.15	0.0492	13.1	24.1	18.2	18.8	6.30	14.8	19.4
4	Pt	6.26	0.106	14.7	37.8	14.5	21.9	12.5	30.2	29.9

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol) were used as reactants; Photocatalyst: 50 mg of M(1.0)/TiO₂; Reaction time: 3 h; The incident light wavelength was > 330 nm; Irradiated light intensity was 30 mW cm⁻², measured at 360 $\pm$ 20 nm; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene and BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene *A*_{Tol} was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, *Y* (%) = 100 $\times$ *A*_{Tol}/(introduced acetic acid), where *A* stands for the yielded amount of product; ^e Selectivity of toluene to methane, *S*₁ (%) = 100 $\times$ *A*_{Tol}/(*A*_{Tol} + *A*_{CH₄}); ^f Selectivity of toluene to biphenyl, *S*₂ (%) = 100 $\times$ *A*_{Tol}/(*A*_{Tol} + *A*_{BP}); ^g n.d. = not detected.

Table 4 Reaction tests with the Pt(*x*)/TiO₂ photocatalysts. ^a

Entry	Pt loading <i>x</i> (wt%)	Product ^b / μmol						<i>Y</i> (%) ^d	<i>S_I</i> (%) ^e	<i>S₂</i> (%) ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	0.1	3.16	0.212	4.72	27.2	16.6	19.0	6.32	16.0	40.1
2	0.5	3.73	0.286	6.56	37.0	14.6	20.1	7.46	20.4	36.2
3	1.0	6.26	0.217	14.7	37.8	14.5	21.9	12.5	30.2	29.9
4	2.0	4.89	0.211	9.14	15.4	16.5	22.3	9.78	22.9	34.9

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL, 50 μmol) were used as reactants; Photocatalyst: 50 mg of Pt(*x*)/TiO₂, *x* stands for wt % of Pt based on TiO₂ weight; Reaction time: 3 h; The incident light wavelength was > 330 nm; Irradiated light intensity was 30 mW cm⁻², measured at 360 ± 20 nm; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene *A_{Tol}* was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, *Y* (%) = 100 × *A_{Tol}*/(introduced acetic acid), where *A* stands for the yielded amount of product; ^e Selectivity of toluene to methane, *S_I* (%) = 100 × *A_{Tol}*/(*A_{Tol}* + *A_{CH4}*); ^f Selectivity of toluene to biphenyl, *S₂* (%) = 100 × *A_{Tol}*/(*A_{Tol}* + *A_{BP}*).

Table 5 Results of reaction test with different amount of the Pt(1.0)/TiO₂ photocatalysts. ^a

Entry	Photocatalyst weight / mg	Product ^b / μmol						<i>Y</i> (%) ^d	<i>S_I</i> (%) ^e	<i>S₂</i> (%) ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	2.0	6.16	0.523	0.569	29.6	15.8	27.1	12.3	28.1	91.5
2	5.0	7.41	0.489	1.55	32.2	19.0	29.6	14.8	28.1	82.7
3	10	7.63	0.508	3.52	32.0	18.4	28.4	15.3	29.3	68.4
4	25	6.36	0.307	8.18	34.2	19.4	25.8	12.7	24.7	43.7
5	50	6.26	0.109	14.7	37.8	14.5	21.9	12.5	30.2	29.9

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL, 50 μmol) were used as reactants; Photocatalyst: Pt(1.0)/TiO₂; Reaction time: 3 h; The incident light wavelength was > 330 nm; Irradiated light intensity was 30 mW cm⁻², measured at 360 ± 20 nm; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene *A_{Tol}* was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, *Y* (%) = 100 × *A_{Tol}*/(introduced acetic acid), where *A* stands for the yielded amount of product; ^e Selectivity of toluene to methane, *S_I* (%) = 100 × *A_{Tol}*/(*A_{Tol}* + *A_{CH4}*); ^f Selectivity of toluene to biphenyl, *S₂* (%) = 100 × *A_{Tol}*/(*A_{Tol}* + *A_{BP}*).

Table 6 Results of the photocatalytic reaction test with various reaction times. ^a

Entry	Time / min	Product ^b / μmol						$Y(\%)$ ^d	$S_I(\%)$ ^e	$S_2(\%)$ ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	10	1.14	0.0852	0.115	12.9	10.6	16.0	2.28	9.71	90.8
2	30	3.46	0.254	0.446	21.8	19.4	28.6	6.92	15.1	88.6
3	60	5.40	0.437	1.38	26.8	18.7	28.3	10.8	22.4	79.6
4	120	6.26	0.579	2.37	28.7	18.9	28.5	12.5	24.9	72.5
5	180	7.63	0.508	3.52	32.0	18.4	28.4	15.3	29.3	68.4
6	360	7.54	0.579	4.47	34.6	18.7	27.0	15.1	28.7	62.8

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol) were used as reactants; Photocatalyst: 10 mg Pt(1.0)/TiO₂; The incident light wavelength was $> 330\text{ nm}$; Irradiated light intensity was 30 mW cm^{-2} , measured at $360 \pm 20\text{ nm}$; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene A_{Tol} was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, $Y(\%) = 100 \times A_{\text{Tol}}/(\text{introduced acetic acid})$, where A stands for the yielded amount of product; ^e Selectivity of toluene to methane, $S_I(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{CH}_4})$; ^f Selectivity of toluene to biphenyl, $S_2(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{BP}})$. ^g Conversion of introduced acetic acid = $100 \times (A_{\text{Tol}} + 2 \times A_{\text{Xyl}} + A_{\text{CH}_4})/(\text{introduced acetic acid})$.

Table 7 Results of the photocatalytic reaction test with various amounts of acetic acid. ^a

Entry	Acetic acid / μmol	Product ^b / μmol						$Y(\%)$ ^d	$S_I(\%)$ ^e	$S_2(\%)$ ^f
		Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂			
1	50	7.63	0.508	3.52	32.0	18.4	28.4	15.3	29.3	68.4
2	100	13.0	1.12	4.68	25.2	35.9	47.8	13.0	26.6	73.5
3	500	70.0	7.78	3.22	110	159	307	14.0	30.6	95.6

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid were used as reactants; Photocatalyst: 10 mg Pt(1.0)/TiO₂; Reaction time: 3 h; The incident light wavelength was $> 330\text{ nm}$; Irradiated light intensity was 30 mW cm^{-2} , measured at $360 \pm 20\text{ nm}$; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the employed benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene A_{Tol} was calculated by subtracting the initial amount from the detected one; ^d Yield of toluene, $Y(\%) = 100 \times A_{\text{Tol}}/(\text{introduced acetic acid})$, where A stands for the yielded amount of product; ^e Selectivity of toluene to methane, $S_I(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{CH}_4})$; ^f Selectivity of toluene to biphenyl, $S_2(\%) = 100 \times A_{\text{Tol}}/(A_{\text{Tol}} + A_{\text{BP}})$. ^g Conversion of introduced acetic acid = $100 \times (A_{\text{Tol}} + A_{\text{Xyl}} + A_{\text{CH}_4})/(\text{introduced acetic acid})$.

Table 8 Results of CO-pulse adsorption measurements for evaluation of Pt nanoparticle size. ^a

Entry	Catalyst	Adsorbed CO $\mu\text{mol g-catalyst}^{-1}$	Pt dispersion %	Pt particle size ^b nm
1	Pt(1.0)/TiO ₂	7.89	15.4	1.62
2	Pt(1.0)/Al ₂ O ₃	18.8	36.6	0.679

^a The CO-pulse adsorption measurement was conducted to obtain the dispersion and particle size of Pt nanoparticles. The detailed steps are as follows: the catalyst is first treated in an argon gas flow at 673 K for 15 min, and then reduced in a flow of H₂ at 673 K for 15 min followed by purge with argon for 15 min, then the catalyst is cooled down to room temperature in a flow of argon, and a series of CO pulses are injected with an interval of 3 min until the amount of exit CO pulses reaches a steady state value. In this method, it is assumed that the adsorption stoichiometry of CO to Pt particles was 1:1; ^b Pt particle size stands for the mean Pt particle diameter on the TiO₂ or Al₂O₃ surface.

2.3.2 Kinetic experiments

Table 9 shows the results of kinetic experiments by using isotopic compounds. When the same amount of benzene and deuterated benzene were mixed with acetic acid, both toluene and deuterated toluene were obtained (**Table 9, entry 1**), and the k_H/k_D ratio were clearly higher than unity (1.85), corresponding to a kinetic isotope effect (KIE). This result suggests that the photocatalytic C–H bond dissociation of benzene to give the phenyl radical species ($\bullet\text{C}_6\text{H}_5$) [19] would affect the toluene formation rate, suggesting that this radical formation is the rate-determining step (RDS) for toluene production in the present conditions (this will be discussed later). The almost same k_H/k_D value (2.04 and 2.00) for biphenyl production regardless of the presence or absence of acetic acid (**Table 9, entries 1 and 2**) also hinted that the phenyl radical species was generated by the C–H bond cleavage in benzene, and this step was the RDS for biphenyl production.

Table 9 Results of the photocatalytic reaction tests with isotopic compounds. ^a

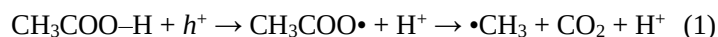
Entry	Substrates		Tol ^b / μmol			BP ^c / μmol			k_H/k_D ^d
	Benzene	Acetic acid	Tol-h	Tol-d	k_H/k_D	BP-h	BP-d ₅	BP-d ₁₀	
1	C ₆ H ₆ (50%) C ₆ D ₆ (50%)	CH ₃ COOH	1.53	0.826	1.85 ^e	0.0733	0.0752	0.0167	2.04
2	C ₆ H ₆ (50%) C ₆ D ₆ (50%)	-	-	-	-	0.128	0.135	0.0304	2.00
3	C ₆ H ₆	CH ₃ COOH	2.67	-	-	0.218	-	-	-
4	C ₆ H ₆	CH ₃ COOD	1.92	-	1.39 ^f	0.231	-	-	-
5	C ₆ H ₆	CH ₃ COOD (50%) CD ₃ COOD (50%)	1.30	1.25	1.04 ^e	0.267	-	-	-

^a Reaction conditions: Photocatalyst was 10 mg of the Pt(1.0)/TiO₂ sample; The incident light wavelength was > 330 nm; Irradiated light intensity was 30 mW cm⁻², measured at 360 ± 20 nm in wavelength; Reactants: For **entry 1**, benzene (2.0 mL, 22 mmol), benzene-d₆ (2.0 mL, 22 mmol) and acetic acid (2.8 μL , 50 μmol); For **entry 2**, benzene (2.0 mL, 22 mmol), benzene-d₆ (2.0 mL, 22 mmol); For **entry 3**, benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol); For **entry 4**, benzene (4.0 mL, 45 mmol) and acetic acid-d₁ (2.8 μL , 50 μmol); For **entry 5**, benzene (4.0 mL, 45 mmol), acetic acid-d₁ (1.4 μL , 25 μmol) and acetic acid-d₃ (1.4 μL , 25 μmol); ^b Tol = toluene, Tol-h = toluene, Tol-d = deuterated toluene; ^c BP = biphenyl, BP-h = C₆H₅–C₆H₅, BP-d₅ = C₆H₅–C₆D₅, BP-d₁₀ = C₆D₅–C₆D₅; ^d $k_H/k_D = (2 \times A_{\text{BP-h}} + A_{\text{BP-d5}}) / (2 \times A_{\text{BP-d10}} + A_{\text{BP-d5}})$; ^e $k_H/k_D = A_{\text{Tol-h}} / A_{\text{Tol-d}}$; ^f $k_H/k_D = (\text{production from non-deuterated reactants}) / (\text{production from deuterated reactant})$.

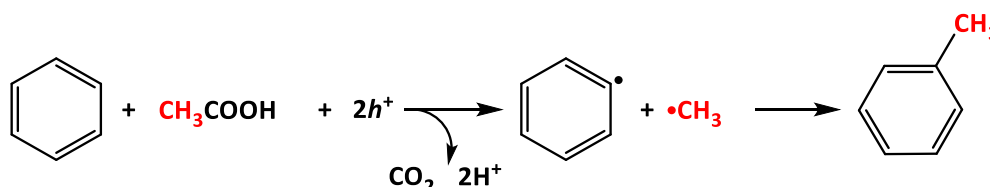
When acetic acid-d₁ (CH₃COOD) and benzene were applied, no deuterated toluene was obtained (**Table 9, entry 4**), which suggests that the methyl group in toluene was all from the methyl group in acetic acid. By comparing the produced toluene amount in the presence of acetic acid and acetic acid-d₁ (**Table 9, entries 3 and 4**), a KIE ($k_H/k_D = 1.39$) was also confirmed, which suggested that the photocatalytic dissociation of O–H bond in acetic acid to produce radical species (CH₃COO $\bullet$) and proton (H⁺) also affected toluene production rate, suggesting this step is also suggested to be the RDS for toluene formation in the present conditions. It would be explained that unlike acetic acid aqueous [5,6], the acetic acid molecule in benzene solvent would tend to be adsorbed in a molecule form (CH₃COOH) on the TiO₂ surface rather than an acetate anion form (CH₃COO⁻) and thus the molecule is directly oxidized by a photo-generated hole to become acetoxyl radical species (CH₃COO $\bullet$) with releasing a proton. The unstable acetoxyl radical species immediately releases CO₂ molecule to become methyl radical ($\bullet\text{CH}_3$).

When acetic acid-d₁ (CH₃COOD) and acetic acid-d₄ (CD₃COOD) were introduced in benzene solvent at the same time, almost the same amount of toluene (C₆H₅–CH₃) and toluene-d₃ (C₆H₅–CD₃) were obtained (**Table 9, entry 5**), i.e., $k_H/k_D = 1.04$, revealing that no C–H bond cleavage took place on the methyl group of the acetic acid molecule during the toluene formation process, meaning another possible radical species (carboxymethyl

radical, $\bullet\text{CH}_2\text{COOH}$) mentioned above did not contribute to the methylation. Thus, the following mechanism is proposed for a methyl radical formation from an acetic acid molecule in an organic solvent (eq. 1):



These results elucidated that both phenyl radical species and methyl radical species were formed in the reaction mixture and the toluene could be produced by the coupling of the methyl radical and phenyl radical (a $k_H/k_D = 1.85$ in **Table 9, entry 1**) as the **Scheme 1** shows:



Scheme 1 Toluene molecule formation through the coupling of methyl radical and phenyl radical.

Considering the following order of the bond dissociation energy as shown: $\text{C}_6\text{H}_5\text{-H}$ (472 kJ mol^{-1}) $>$ $\text{H}_3\text{CCOO-H}$ (443 kJ mol^{-1}) $>$ $\text{H-CH}_2\text{COOH}$ (399 kJ mol^{-1}) $>$ $\text{H}_3\text{C-COOH}$ (385 kJ mol^{-1}) [20], and if both benzene and acetic acid were activated to form corresponding radical species, the RDS in the radical–radical coupling reaction (**Scheme 1**) should be the most difficult step, i.e., the C–H bond fission of benzene molecules (472 kJ mol^{-1}). The result shown in **Table 9, entry 1** is consistent with this consideration. However, the results shown in **Table 9, entries 3** and **4** indicated the O–H bond dissociation of acetic acid seemed to be another RDS, which may look like a contradiction according to this thermodynamically consideration. But it should be noted here that this conclusion could not rule out another possibility, i.e., the presence of another competitive reaction mechanism such as a radical addition-elimination mechanism as discussed later.

2.3.3 Temperature-controlled experiments

To investigate the apparent thermal activation energy of various products in this photocatalytic reaction system, temperature-controlled photocatalytic reactions were conducted at 299–312 K with applying the bare TiO_2 sample and the $\text{Pt}(1.0)/\text{TiO}_2$ sample (**Table 10**). In the presence of the bare TiO_2 photocatalyst, toluene and methane were formed, and their amounts increased with increasing reaction temperature from 299 K to 307 K. The pseudo-Arrhenius plots for the product formation rate obtained from the data at 299–307 K gave the apparent thermal activation energies for the productions of toluene and methane such as $E_a(\text{Tol})=172 \text{ kJ mol}^{-1}$ and $E_a(\text{CH}_4)=41.5 \text{ kJ mol}^{-1}$, respectively on the bare TiO_2 photocatalyst (**Fig. 1a**). These apparent thermal activation energies in photocatalytic reaction indicate that some thermal activation steps are present in the photocatalytic reaction, confirming that after the initial photoexcitation in TiO_2 photocatalyst the most elementary steps are thermal (dark) processes, such as adsorption of reactants, electron migration, elementary redox reactions, and desorption of the redox products and final products. Especially, the higher activation energy for the toluene production might be related to a certain chemical reaction step, suggesting the difficulty of not the adsorption nor desorption but the benzene methylation by the bare TiO_2 photocatalyst.

Table 10 Results of the photocatalytic reaction tests at different temperatures. ^a

Entry	Sample	Temp. / K	Product ^b / μmol					
			Tol ^c	Xyl	BP	H ₂	CH ₄	CO ₂
1	TiO ₂	299	0.0124	n.d. ^d	n.d.	n.d.	0.759	n.d.
2		305	0.0338	n.d.	n.d.	n.d.	0.880	n.d.
3		308	0.0641	n.d.	n.d.	n.d.	1.31	n.d.
4		312	0.240	n.d.	n.d.	n.d.	1.45	n.d.
5	Pt(1.0)/TiO ₂	299	1.09	0.0179	0.136	3.25	7.62	6.86
6		303	1.90	0.0333	0.189	4.65	8.52	8.34
7		307	2.07	0.0487	0.213	4.90	10.9	10.8

^a Reaction conditions: benzene (4.0 mL, 45 mmol) and acetic acid (2.8 μL , 50 μmol) were used as reactants; Photocatalyst used was 10 mg; Reaction time was for 10 min; The incident light wavelength was $> 330\text{ nm}$; Irradiated light intensity was 30 mW cm^{-2} , measured at $360 \pm 20\text{ nm}$ in wavelength; ^b Tol = toluene, Xyl = *o*-xylene and *p*-xylene, BP = biphenyl; ^c Since the benzene reagent contained toluene as an impurity (0.625–1.12 μmol of toluene in 1 mL of benzene), the produced amount of toluene A_{Tol} was calculated by subtracting the initial amount from the detected one; ^d n.d. = not detected.

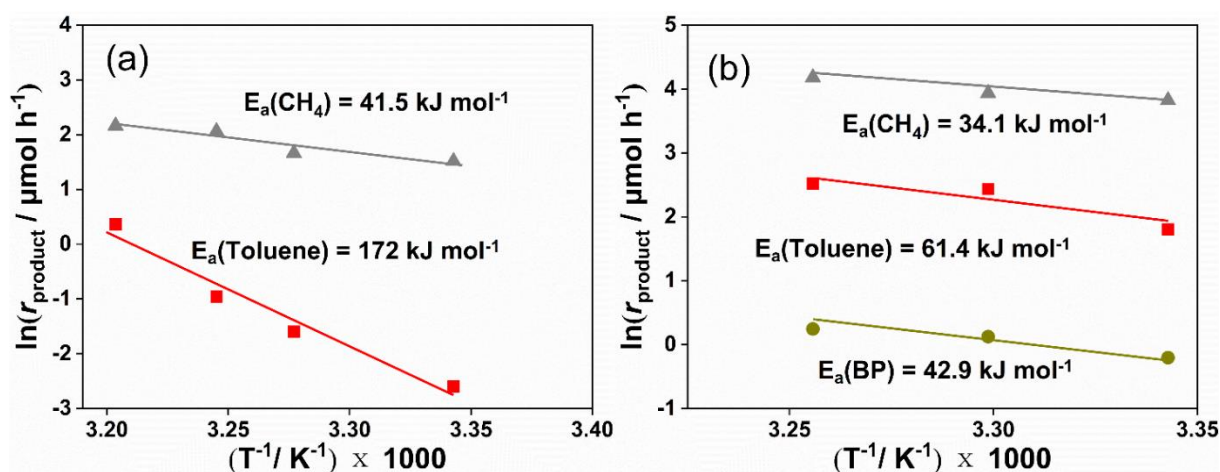
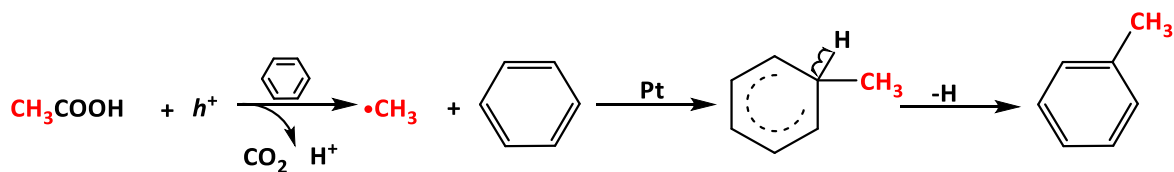


Fig. 1 Pseudo-Arrhenius plots of the products formation rate $\ln(r_{\text{product}})$ for the temperature-controlled reactions with 10 mg of the bare TiO₂ photocatalyst (a) and 10 mg of the Pt(1.0)/TiO₂ photocatalyst (b). Data are from **Table 10**. The amount of products at the first 10 min was used for the calculation of the formation rate of products. Other reaction conditions are given in the footnote of **Table 10**.

On the other hand, the Pt(1.0)/TiO₂ photocatalyst gave toluene, biphenyl, and methane and their apparent activation energies calculated were $E_a(\text{Tol})=61.4$, $E_a(\text{BP})=42.9$, and $E_a(\text{CH}_4)=34.1\text{ kJ mol}^{-1}$, respectively (**Fig. 1b**). It was noticed that the activation energy for toluene production with the Pt(1.0)/TiO₂ photocatalyst was clearly lower than that with the bare TiO₂ photocatalyst. This means that the RDS among the thermal processes for the toluene formation on the bare TiO₂ was much accelerated by the Pt species deposited on the TiO₂ surface. It is proposed that the Pt species well catalyzed the thermal RDS and reduced the apparent activation energy, which consisted with the results shown in **Table 1, entry 3**. In the photocatalytic dehydrogenative cross-coupling reactions, metal catalysts such as Pd, Pt and Pd–Au nanoparticles deposited on the surface of TiO₂ photocatalyst promote the reactions between benzene and other organic compounds such as acetonitrile [21,22], ether [23,24], and acetone [25], between THF and alkane [26], and between aryl halides [27], where these metal nanoparticles catalyze a C–C formation step between molecule and radical species through the radical addition-elimination mechanisms. Thus, also in the present case, the reaction between benzene and methyl radical would be catalyzed by the Pt species in

the same mechanism (Scheme 2).



Scheme 2 Toluene formation catalyzed by Pt nanoparticles.

On the other hand, the activation energy for methane production was not so much changed. The formation of methane would start from the hole oxidation of acetic acid (eq. 1), followed by the reactions of the methyl radical and hydrogen radical or other organic compounds, which would not require the catalysis by the Pt species. As mentioned, compared with the physical separation case (**Table 1, entry 3**), the Pt cocatalyst deposited on the TiO₂ surface gave higher CO₂ formation (**Table 1, entry 1**), which evidences one role of the Pt cocatalyst as an electron receiver to enhance the charge separation for more efficient photocatalysis. However, the activation energy in the presence of the Pt species was slightly lower, suggesting that the Pt species might also accelerate the formation of methyl radical or the radical-radical coupling between methyl radical and hydrogen radical and so on.

2.3.4 Proposed reaction mechanisms

Based on those observations in the kinetic study and so on, we must consider at least two possible reaction mechanisms. One is a radical-radical coupling (RRC) process, and another is a radical addition-elimination (RAE) process, where the latter can proceed in the aid of catalysis by the Pt cocatalyst.

The former can be proposed as follows (**Fig. 2**). (i) The photoexcitation of the TiO₂ photocatalyst generates electrons and holes. The holes move to the TiO₂ surface while the electrons move to Pt nanoparticles. (ii) The holes can oxidize acetic acid molecule to generate corresponding methyl radical species, CO₂ gas, and proton (eq. 1) while benzene molecule was oxidized to form phenyl radical and proton. The electrons on the Pt cocatalyst can reduce the protons to hydrogen radicals (H•). (iii) One methyl radical and one phenyl radical can combine to give a toluene molecule, and (iv) the two hydrogen radicals can combine to form hydrogen gas. This RRC mechanism for the toluene formation is apparently a two-photon process, and the RDS should be the photooxidation of benzene to give phenyl radical species (**Table 9, entry 1**). According to the results of the reaction test with the bare TiO₂ photocatalyst sample, this radical-radical coupling would proceed photocatalytically even without assistance by metal catalyst, though the yield of toluene was limited. In this process, the platinum nanoparticles loaded on the TiO₂ surface rather acted as the electron acceptors to drastically accelerate the charge separation efficiency than directly took part in the toluene formation as catalysts.

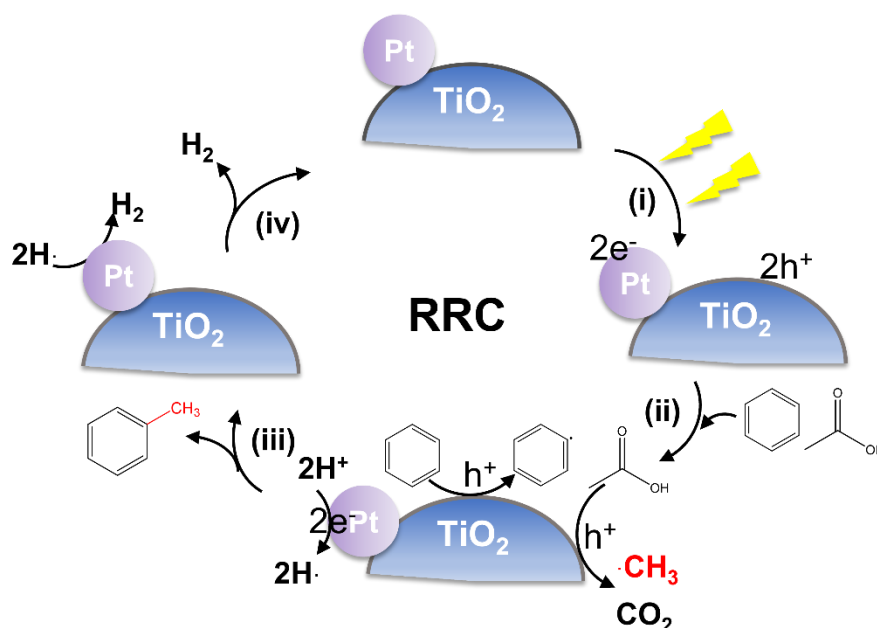


Fig. 2 Proposed RRC mechanism for the photocatalytic methylation of benzene.

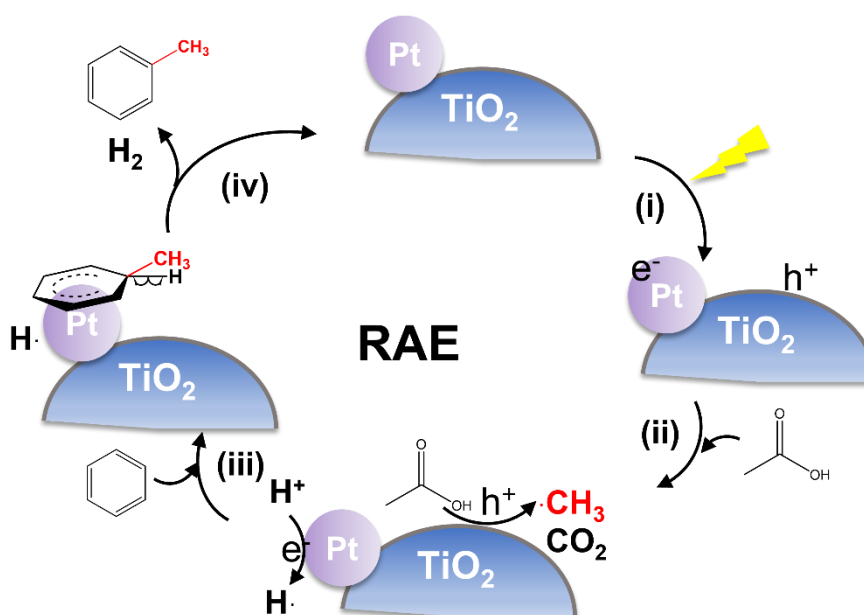


Fig. 3 Proposed RAE mechanism for the photocatalytic methylation of benzene.

The latter, the RAE mechanism is described in **Fig. 3**. (i) The photoexcitation of the TiO_2 photocatalyst generates electrons and holes. The holes move to the TiO_2 surface while the electrons move to the Pt cocatalyst. (ii) The generated holes only oxidize acetic acid molecule to give methyl radical, CO_2 gas, and H^+ . The electrons on the Pt cocatalyst can reduce the protons to $\text{H}^\bullet$. (iii) With the catalysis by the Pt cocatalyst, benzene molecule adsorbed on the Pt species was activated, and then methyl radical species can attack the catalytically activated benzene ring to generate a sp^3 -type radical transition state. (iv) After the elimination of a $\text{H}^\bullet$ from this transition state (or, additional hole oxidation might release a proton, and this proton is reduced by additional electron at the Pt species to form hydrogen radical), toluene as the methylation product is produced, and the two hydrogen radicals can combine to form hydrogen gas. This is a one-photon (or two-photon) process, and the RDS should be the photooxidation of acetic acid molecule to generate methyl radical species as mentioned above (eq. 1, **Table 9**, **entries 3 and 4**) and the thermal RDS corresponds would be the catalysis by the Pt catalyst.

As mentioned above, the successive methylation of toluene gives xylenes (**Table 1**), where the isomer ratio of 53.5% and 46.7% for *o*-xylene and *p*-xylene. This orientation determined by the methyl group as an electron donating substituent suggests that the successive methylation corresponds to an electrophilic substitution, which was observed also in photocatalytic hydroxylation of benzene promoted with electrophilic surface radical species. [14] Thus, two possible mechanisms are proposed for the xylene formation; one is that the photoformed hole oxidizes the electron-rich carbon at *ortho-para* positions to form radical species and proton, followed by the reaction with a methyl radical in the RRC mechanism, and another is that, if methyl radical has electrophilic property, the methyl radical may attack the *ortho-para* positions to start the RAE mechanism. Further investigation is necessary for the latter possibility.

The mechanisms for the biphenyl formation are similarly explained. After the phenyl radical formation by the photogenerated holes, it would react with another phenyl radical in the RRC mechanism or benzene molecules on the Pt catalyst through the RAE mechanism.

The reason why the Pt catalyst exhibited higher selectivity when located on the TiO₂ surface than that on the alumina support (**Table 1, entries 1 and 3**) is discussed here. One possibility is that in the former case, since the Pt catalyst is located close to the hole-oxidation sites, the reaction can efficiently occur. Another possibility is that the Pt catalyst can become negatively charged due to electron donation from the TiO₂ semiconductor, especially under photoirradiation, which may contribute to the efficient catalysis. This point also requires further investigation.

2.4 Conclusion

In this study, we successfully found a novel protocol for the synthesis of toluene from benzene using acetic acid as the methylation reagent with bare TiO₂ and metal-loaded TiO₂ photocatalysts. Comparing to the limited toluene production and the methyl radical based selectivity with the bare TiO₂ sample, higher yield and selectivity such as 15.3% and 68.4% (based on benzene), respectively was achieved with the Pt(1.0)/TiO₂ photocatalyst sample. The kinetic study demonstrated that both the phenyl radical and the methyl radical were formed during the formation of toluene molecules. Then the results of temperature-controlled experiments and the photocatalytic reaction test with a physical mixture of the TiO₂ and Pt(1.0)/Al₂O₃ samples revealed that besides the well-known electron acceptor role, Pt nanoparticles also catalyzed the toluene production.

According to the findings of the investigation, it can be proposed that two competitive pathways contribute to the formation of toluene molecules. Once the methyl radical species was generated from acetic acid by the oxidation of photogenerated holes, it can either (i) combine with the phenyl radical species originated from photooxidation to yield toluene molecules or (ii) attack the catalytically activated benzene ring directly on Pt nanoparticles to form a sp³-type radical transition state, forwarding the elimination of a H• from this transition state (or, hole oxidation, releasing proton, and reduction of the proton by photoexcited electron) to complete the benzene methylation process.

The results obtained offer novel insights into aromatic ring methylation, potentially expanding the utility of aromatic compounds across various fields, including pharmaceuticals and materials science. Moreover, understanding the dual role of Pt nanoparticles could pave the way for the development of more efficient heterogeneous catalytic systems in the future.

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Chapter 3

Direct C–N coupling of aniline to aminodipheylamines

Abstract

Aminodiphenylamines (ADPAs) and their derivatives have been known to be used as dye intermediates and antioxidant of rubber. Due to its high demand in industrial production, the synthetic methods have been widely developed. In the present study, a photocatalytic asymmetric homocoupling route was examined, *i.e.*, the photocatalytic C–N coupling of aniline in an alkaline solution with a Pt-loaded titanium oxide (Pt/TiO₂) photocatalyst. Nearly 20% of yield and 77% of selectivity were achieved with the Pt/TiO₂ photocatalyst for 30 min. It was found that this C–N bond formation showed a high dependence on the pH of solvent and irradiation light wavelength, *i.e.*, the reaction can only proceed when pH > 11.79, and an incident light wavelength of 365 nm gave a high ADPAs selectivity. The mechanistic studies by using isotopic compounds suggested that the rate-determining step (RDS) for ADPAs production would be the formation of a transition complex with the rehybridization to sp³ on the aromatic ring of aniline. The UV-vis spectra analysis and Arrhenius plots further revealed the presence of three formation routes of ADPAs in the present system: The first one begins with the hole-oxidation of aniline by TiO₂ photocatalyst excited by UV light, the second one starts with one electron transfer from N atom in aniline to Ti in TiO₂, which only occurred with an incident light wavelength of 365 nm, and the last one is the oxidation of aniline molecules by hydroxyl radicals as a minor route

3.1 Introduction

The formation of carbon-nitrogen (C–N) bond is a fundamental process in organic chemistry, underpinning the synthesis of a wide array of compounds, including pharmaceuticals, agrochemicals, and natural products. [1–3] Traditionally, C–N bond formation has been achieved through various classical methods such as nucleophilic substitution, [4–6] reductive amination, [7–10] the Buchwald-Hartwig [11–13] and Ullmann coupling reactions. [14–16] These methods have been proven effective, however, they often require harsh reaction conditions like high refluxing temperatures, bio-toxicity of aldehydes, organic halides. As the demand for more sustainable chemical processes continues to grow, there is a pressing need to develop green and mild synthetic methods for C–N bond formation.

Recent developments of photocatalysis have opened new avenues for C–N bond formation, [17] offering a more environmentally friendly and versatile alternative to traditional methods. Titanium oxide (TiO₂), as the most common heterogeneous photocatalyst, due to its high chemical stability and low cost, has been developed successfully to construct C–N bond for a few synthetic applications, for example, *N*-alkylation [18–20] and *N*-heterocycle formation. [21,22] Our group also reported direct aromatic ring amination [23,24] and alkenes hydroamination [25] by ammonia aqueous with metal loaded TiO₂ photocatalysts.

On the other hand, aniline has been applied for manufacturing of dyes, rubber, polymers, pharmaceuticals, and so on. [26,27] Many attempts have been made to photocatalytically convert it into some value-added products, such as azobenzene, azoxybenzene, and nitrosobenzene. [28–30] In this study, we examined asymmetric homocoupling of aniline, *i.e.*, the direct C–N coupling of aniline to produce 2-aminodiphenylamines (ADPA) and 4-aminodiphenylamines (4-ADPA), which have highly demand for dye intermediates and rubber antioxidants, with platinum-loaded TiO₂ photocatalyst (Pt/TiO₂) under UV light illumination. A series of experiments revealed the high pH dependence and wavelength dependence of these ADPAs formation. Kinetic experiments with isotopic compounds and temperature-controlled reactions elucidated the formation mechanism under the present conditions.

3.2 Experimental

3.2.1 Materials

A commercial TiO₂ sample (Ishihara Sangyo Kaisha, ST-01, anatase, 300 m² g^{−1}) and aqueous metal precursor solutions including H₂PtCl₆ (Nacalai Tesque, 99%), HAuCl₄ (Nacalai Tesque, 99%), PdCl₂ (Kishida Chemical, 99%), and AgNO₃ (Kishida Chemical, 99%) were applied for catalysts preparation without further purification. All of reagents employed in the photocatalytic reaction tests were commercially purchased and used without further purification: sodium hydroxide solution (NaOH (aq), Nacalai Tesque, 1 mol L^{−1} and 0.1 mol L^{−1}), hydrochloric acid solution (HCl (aq), Nacalai Tesque, 0.1 mol L^{−1}), acetonitrile (Nacalai Tesque, 99.5%), 1-octanol (Kishida Chemicals, 99.5%), aniline (Nacalai Tesque, 99%), aniline-*d*₅ (Cambridge Isotope Laboratories, ≥98%), aniline-*d*₇ (Cambridge Isotope Laboratories, ≥98%), azobenzene (Sigma-Aldrich, 96%), hydrazobenzene (Tokyo Chemical Industry, >98%), 2-aminodiphenylamine (Tokyo Chemical Industry, >98%), 4-aminodiphenylamine (Tokyo Chemical Industry, >98%).

3.2.2 Preparation of catalysts

A typical photodeposition method was used to synthesize various metal(M)-loaded titanium oxide photocatalysts, $M(x)/TiO_2$, where x shows a loading amount of the metal cocatalyst as weight percent (wt%) of the photocatalyst. The preparation procedure of representative $Pt(1.0)/TiO_2$ photocatalyst is described as follows. 1.0 g of TiO_2 powder was dispersed in 200 mL of ion-exchanged water and was irradiated with a xenon lamp (PE300BUV, 300 W) for 30 min with magnetically stirring to clean the TiO_2 surface. Then, 50 mL of methanol and 530 μL of prepared H_2PtCl_6 solution (18.84 g L^{-1} as Pt) were added to the suspension as a hole scavenger and a metal precursor, respectively. The contents were stirred for 15 min without irradiation, followed by stirring for 1 h under light irradiation. The resulted suspension was filtered with suction and was washed with 500 mL of ion-changed water 3 times. After drying over 12 h at 353 K in an electronic oven, a grey-colored powder of the $Pt(1.0)/TiO_2$ sample was obtained. The XRD pattern (**Fig. 1**) of the prepared $Pt(1.0)/TiO_2$ sample suggested the anatase phase of TiO_2 remains after Pt loading, and no characteristic peaks of Pt were observed, which may attribute from a small loading amount and the small size of Pt nanoparticles. The TEM images revealed that the average diameter of highly dispersed Pt nanoparticles was 2.06 nm (**Fig. 2**). Due to the Pt loading, comparing to the bare TiO_2 sample, this $Pt(1.0)/TiO_2$ sample showed a strong visible light absorption in the DR UV-vis spectrum. (**Fig. 3**). Other $M(x)/TiO_2$ samples were prepared by the same procedure mentioned above with the different amount of desired metal precursor.

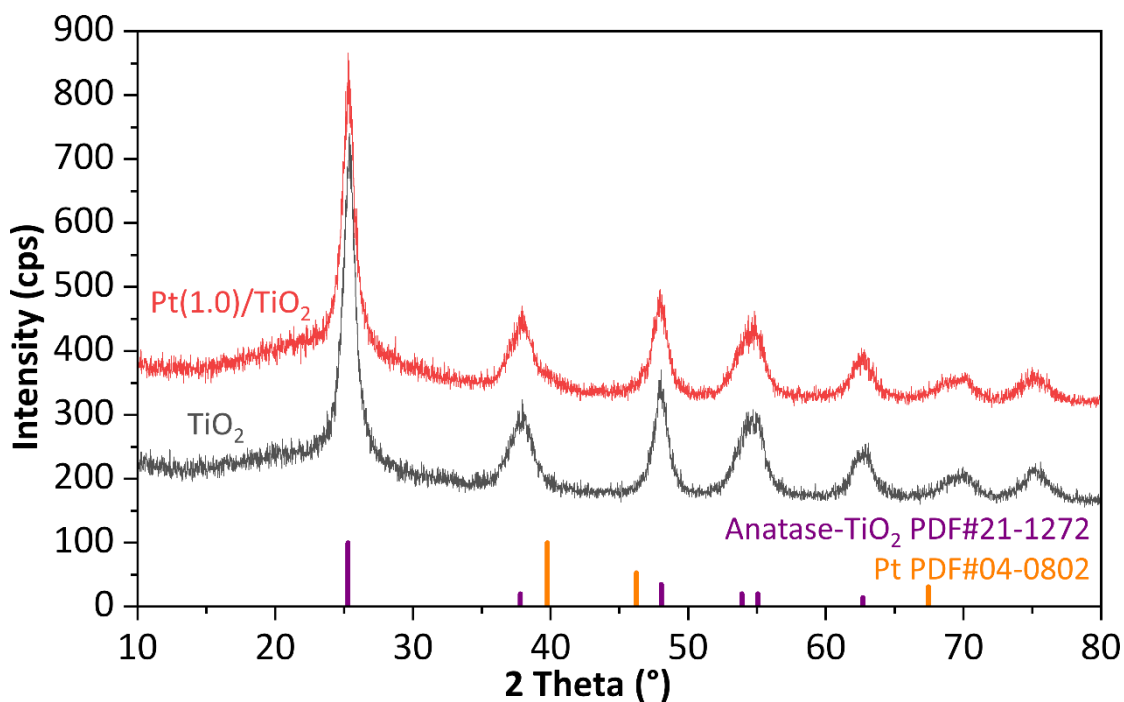


Fig. 1 XRD pattern of the $Pt(1.0)/TiO_2$ and TiO_2 samples with the reference data for anatase TiO_2 (PDF#21-1272) and Pt (PDF#04-0802). The TiO_2 phase of the $Pt(0.1)/TiO_2$ sample did not change after Pt loading. No characteristic peaks of Pt were observed for the $Pt(0.1)/TiO_2$ sample, which would be due to a small loading amount and a small size of Pt species.

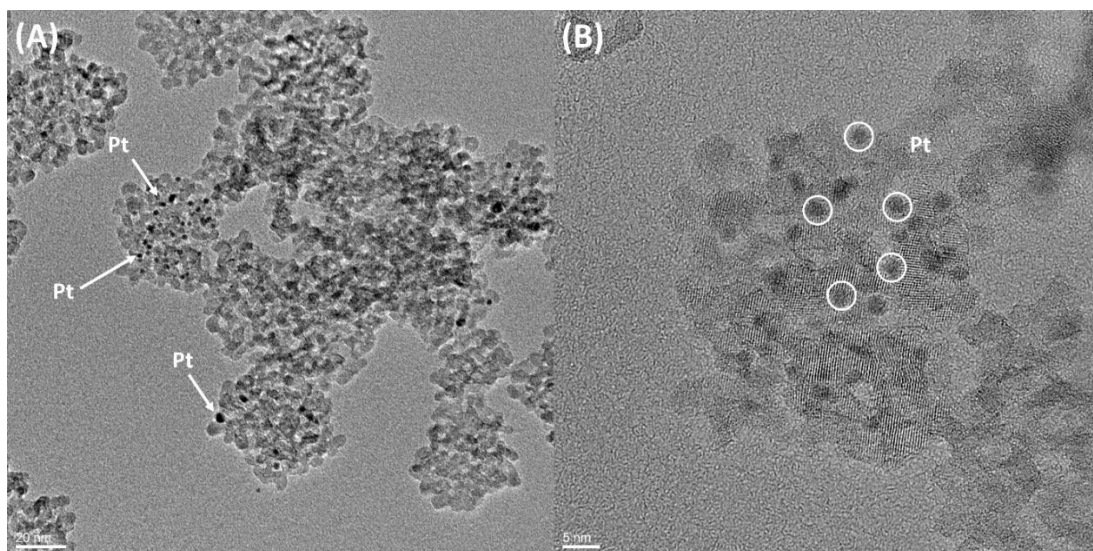


Fig. 2 (A) The TEM image of the Pt(1.0)/TiO₂ sample and (B) the enlarged TEM image showing Pt nanoparticles. The average size of Pt nanoparticles was 2.06 nm.

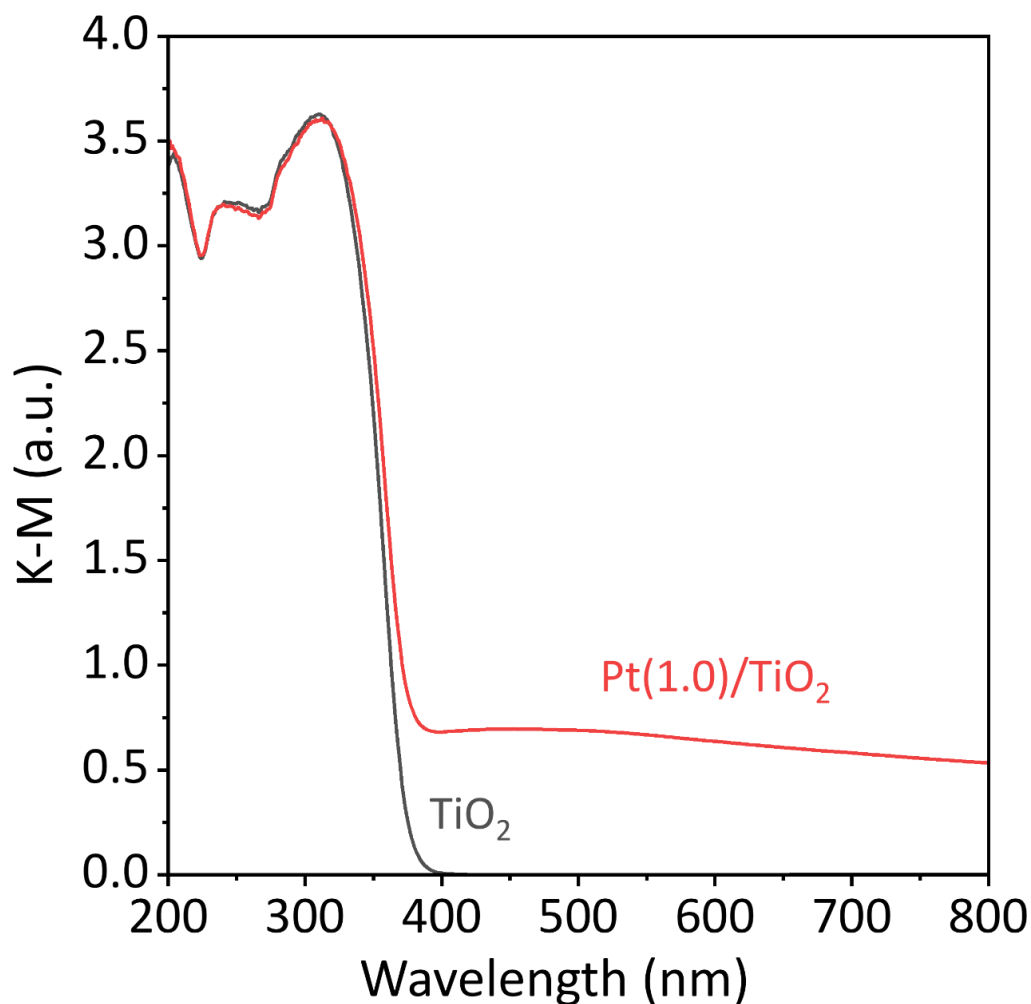


Fig. 3 DR UV-vis spectra of the bare TiO₂ and Pt(1.0)/TiO₂ samples. The Pt(1.0)/TiO₂ sample shows a similar light absorption as bare TiO₂ sample in UV region with an enhanced absorption in visible light range due to the loaded platinum on the TiO₂ surface, which gave the catalyst a greyish color.

3.2.3 Photocatalytic reaction tests

The photocatalytic reaction test was carried out in a sealed test tube (20 mL) as a closed reactor. A typical experiment was as follows. As a pretreatment, light irradiation from a xenon lamp (PE300BUV, 300 W) was conducted without any optical filter for 30 min to clean the surface of 50 mg of Pt(1.0)/TiO₂ photocatalyst. Then, 4 mL of 0.1 mol L⁻¹ NaOH (aq) was added as solvent, and 4.6 μ L (50 μ mol) of aniline was added as the only reactant by a micropipette. And the test tube was plugged by a silicone septum stopper and sealed. By using an argon gas bubbling flow (30 mL min⁻¹) for 20 min, the existed air was purged. The contents were stirred with another UV-LED light irradiation (LC-L1V3 spotlight source) for the desired time (typically, 30 min) to promote the photocatalytic reaction. During the reaction, the reaction temperature was controlled at 298 K by a water bath with a cooling system. After the reaction, the suspension was firstly diluted by CH₃CN and filtered by using a syringe equipped with a PTFE membrane filter. The obtained liquid phase was then analyzed qualitatively and quantitatively by GC-MS (Shimadzu QP-2020) and GC-FID (Shimadzu GC-2014) using 1-octanol as an internal standard. In some of reaction tests, 0.5 mL of the gaseous phase was extracted and analyzed by GC-TCD (Shimadzu GC-8A) to detect the production of H₂ gas after reactions.

3.2.4 Mechanistic studies

To propose the formation mechanism of detectable products, a few kinetic experiments were carried out by using aniline-*d*₅ (C₆D₅NH₂) and aniline-*d*₇ (C₆D₅ND₂). And the apparent activation energies of each detectable products were calculated from a series of temperature-controlled experiments. The reaction temperature was controlled in a range of 296–306 K.

3.2.5 Characterization

X-ray diffraction (XRD) patterns of samples were measured at room temperature using a Shimadzu Lab X XRD-6000 with Cu K α radiation (40 kV, 30 mA). The transmission electron microscopy (TEM) images were taken by a JEM-2200FS. The diffuse reflectance (DR) UV-vis spectra of the powder samples were recorded by using a JASCO V-770 spectrophotometer equipped with an integrating sphere, where BaSO₄ was used as a reference. The same spectrophotometer was also applied to measure the UV-vis spectra of liquid sample in a transmittance mode.

3.3 Results and discussion

3.3.1 Outline of the photocatalytic reaction tests

Table 1 shows the results of photocatalytic reaction tests. When the Pt(1.0)/TiO₂ sample was used in the present conditions (See the footnote), 2-aminodiphenylamine (2-ADPA, 8.99% yield) and 4-aminodiphenylamine (4-ADPA, 10.5% yield) were observed as main products (**Table 1, entry 1**). Our previous study has reported another simple C–N bond coupling reaction [31], *i.e.*, the photocatalytic amination of benzene by ammonia (NH₃) to form aniline, where the N–H bond in an ammonia can be activated by photogenerated holes (*h*⁺) on Pt/TiO₂ photocatalyst to form an amide radical ($\bullet$ NH₂) and it attacks aromatic ring to form C–N bond. This mechanism would be possibly applicable in the present study. The control experiment results listed in **Table 2** revealed that this C–N bond formation from aniline did not occur without photoirradiation or without photocatalyst, indicated that the formation of ADPAs (2-ADPA and 4-ADPA) was photocatalytically promoted. Another isomer of ADPA, *i.e.*, 3-aminodiphenylamine (3-ADPA), was not found in the resulting mixture, which may be attributed to the electron donating property of amino group (–NH₂) in aniline. After the formation of ADPAs, the successive reaction can occur since the amino group in ADPAs can be activated again and yield some oligomers or polyanilines when the

reaction time was extended, and thus led to a decrease of ADPAs selectivity (from 77.0% at 30 min to 37.3% at 720 min, **Fig. 4**). The UV-vis spectra of the solutions after the reaction showing a broad absorption peak from 500 nm to 600 nm (**Fig. 5**) confirmed the formation of oligomers or polyanilines. [32,33] Another observed organic byproduct was azobenzene (AZB), a N=N bond coupling product resulting from the activation of amino group, which was already reported in some studies about the photocatalytic oxidation of aniline. [30,34–36] In those reported studies, other byproducts were confirmed, such as benzoquinone, nitrosobenzene, and aminophenol, while they were not found in the present study, probably due to the absence of O₂ molecule and a relatively high concentration of aniline in NaOH aqueous solutions (12.5 mmol L⁻¹), where the radical reactions have great chance of occurring between aniline-related species. A series of optimization experiments in different initial concentrations of aniline were conducted. The results were listed in **Table 3** and plotted in **Fig. 6**, where the 12.5 mmol L⁻¹ of aniline showed best yield and selectivity for ADPAs and was applied as the standard concentration in this study. Under the present reaction conditions, only H₂ (6.09 μmol) was detected as a gaseous product, no O₂ that might be possibly formed in water splitting was found. The calculated H₂ evolution (7.16 μmol) from the obtained ADPAs (5.02 μmol) and AZB (1.07 μmol) was close to the detected one, which hinted that such H₂ production was possibly from a dehydrogenative C–N and N=N coupling of aniline. However, in **Table 1, entry 2**, without adding any aniline, 6.42 μmol of H₂ and zero of O₂ was found, which suggested that such H₂ evolution was probably from the decomposition of alkaline water as reported in the absence of aniline (eqs. 1 and 2). [37–40] Since aniline is more easily oxidized by photogenerated holes in TiO₂ photocatalyst than water (eq. 3), aniline can be oxidized instead of water, *i.e.*, the presence of aniline would inhibit the water oxidation and produce ADPAs and AZB with H₂ as the only gas observation. In both cases (**Table 1, entries 1 and 2**), the exact pH of reaction suspensions remained almost no change after the photocatalytic tests (12.69 and 12.70 respectively).



To elucidate the solvent effect, some reaction tests were conducted with other solvents, such as acetonitrile (CH₃CN), H₂O and HCl (*aq*). In CH₃CN (**Table 1, entry 3**), only trace amount of ADPAs and 0.353 μmol of AZB were obtained, which suggested that the photogenerated holes (*h*⁺) can hardly activate the aniline molecules to form C–N bond and N–N bond under present conditions. And the observed small amount of H₂ production (2.22 μmol) was due to photocatalytic dehydrogenative formation of succinonitrile (NCCH₂–CH₂CN) and 4-aminobenzeneacetonitrile (NCCH₂–C₆H₅NH₂), from the homo-coupling of CH₃CN and the cross-coupling of aniline and CH₃CN respectively, [41–43] as they were qualitative distinguished by GC-MS in a trace amount.

When the pH of the aqueous solvent was 3.29, 6.58, and 11.79 respectively (**Table 1, entries 4–6**), no detectable organic products. A slightly increased amount of H₂ production was confirmed when pH was 11.79. Considering the pK_a of aniline is 4.63, [44] in the acidic condition (**Table 1, entry 4**, pH = 3.29), most of aniline molecules were existed in an anilinium cation form (C₆H₅NH₃⁺), which were unfavourable to be adsorbed on the positively charged TiO₂ surface due to the electric charge repulsion (the isoelectric point of TiO₂ is around 6) and the difficulty of the N–H bond activation in the positively charged amino group by holes. While the results in **Table 1, entries 5 and 6** hinted that without the enough concentration of OH⁻ in the solution, even the aniline molecules were in usual form (C₆H₅NH₂), the photocatalytic conversion can hardly proceed. Furthermore, the reaction tests under various aqueous solutions with different pH confirmed that the ADPAs and AZB can be obtained only at the pH > 11.79 (**Table 4, entries 7–11**). The requirement on high concentrated OH⁻ solution may be related with the following possible processes, *i.e.*, (i) abstraction of the hydrogen atom by OH⁻ from the aniline radical cation species to generate anilino radical species (C₆H₅NH•, pK_a of 7) [45] (eqs. 4 and 5); (ii) The photooxidation of OH⁻ by holes to produce hydroxyl radical species (•OH) (eq. 6), and the formed •OH can attack aniline molecules to give the same anilino radical species (eq. 7). In a study about photocatalytic oxidation of aniline to AZB in the presence of O₂, the author observed the same pH dependence on the AZB formation (8.3 < pH < 12.3) in a low aniline

concentration basic solution (0.0215 mmol L⁻¹) and confirmed that the holes were the primary oxidants to active aniline molecules rather than hydroxyl radicals, [30] which also supports the present case with the higher aniline concentration (12.5 mmol L⁻¹). Thus, the first case would be more likely; the hydrogen abstraction requires high pH conditions (eq. 5). The optimistic pH with highest selectivity to ADPAs (77.0 %) was found at 12.70 and decreased to 39.3 % at 13.43 (**Table 4, entries 9–11**) because of an obvious photocatalyst aggregation with the increasing of pH as observation.



Various photocatalysts were examined under the best conditions for the photocatalytic reactions (**Table 1, entries 7–10**). For the bare TiO₂ sample (**Table 1, entry 7**), there was no detectable organic products but 0.0461 μmol of H₂, suggesting that both the formation of the coupling products and the photocatalytic H₂ production require cocatalyst that contribute to efficient charge separation. The Ag(1.0)/TiO₂, Pd(1.0)/TiO₂, and Au(1.0)/TiO₂ photocatalyst samples exhibited relatively low activities (**Table 1, entries 8–10**), which indicated that Pt would be the most effective loaded metal cocatalyst for the coupling products and hydrogen formation. It was also consistent to our previous report that Pt/TiO₂ photocatalyst well promotes the ammonia decomposition through N–H bond activation to nitrogen and hydrogen. [46] The highest H₂ evolution with the Pt(1.0)/TiO₂ sample also consists with our previous study that Pt nanoparticles can play a catalytic role for the coupling of hydrogen radical species to yield H₂ molecules. [47]

Table 1 Photocatalytic conversion of aniline over various photocatalysts and solvents ^a

Aniline 2-Aminodipheylamine 2-ADPA 4-Aminodipheylamine 4-ADPA Azobenzene AZB									
Entry	Photocatalyst	Solvent	<i>C</i> (%) ^c	<i>Y</i> (%) ^d				<i>S</i> (%) ^e	H ₂ (μmol)
		(solvent pH) ^b			2-ADPA	4-ADPA	AZB		
1	Pt(1.0)/TiO ₂	NaOH (<i>aq</i>) ^f (pH = 12.70)	25.3	8.99	10.5	4.16	77.0	6.09	
2 ^g	Pt(1.0)/TiO ₂	NaOH (<i>aq</i>) (pH = 12.70)	/	/	/	/	/	6.46	
3	Pt(1.0)/TiO ₂	CH ₃ CN	1.63	tr. ^h	tr.	0.353	0	2.22	
4	Pt(1.0)/TiO ₂	HCl (<i>aq</i>) ⁱ (pH = 3.29)	0	n.d. ^j	n.d.	n.d.	/	0.844	
5	Pt(1.0)/TiO ₂	H ₂ O ^k (pH = 6.58)	0	n.d.	n.d.	n.d.	/	0.916	
6	Pt(1.0)/TiO ₂	NaOH (<i>aq</i>) ^l (pH=11.79)	1.82	n.d.	n.d.	n.d.	/	2.13	
7	TiO ₂	NaOH (<i>aq</i>) (pH = 12.70)	0	n.d.	n.d.	n.d.	/	0.0461	
8	Ag(1.0)/TiO ₂	NaOH (<i>aq</i>) (pH = 12.70)	3.21	1.00	0.927	0	60.1	0.0670	
9	Pd(1.0)/TiO ₂	NaOH (<i>aq</i>) (pH = 12.70)	4.58	1.19	1.01	0	48.1	1.10	
10	Au(1.0)/TiO ₂	NaOH (<i>aq</i>) (pH = 12.70)	2.52	0.934	0.679	0.851	64.1	1.63	

^a Reaction conditions: 50 mg of photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of different solvents were applied; Reaction time: 30 min; The wavelength of the incident UV-LED light was at 365 ± 5 nm in wavelength, the irradiated light intensity was 1035 mW cm⁻² when measured at 360 ± 20 nm in wavelength; ^b The actual solvent pH was measured by a pH meter; ^c Conversion of aniline, *C* (%) = 100 × (introduced aniline – aniline remnant after the reaction)/(introduced aniline); ^d Yield of detectable products, *Y* (%) = 100 × *A*_(2-ADPA, 4-ADPA, AZB) × 2/(introduced aniline), where *A*_(2-ADPA, 4-ADPA, AZB) stands for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. ^e Selectivity to 2-ADPA and 4-ADPA based on consumed aniline, *S* (%) = 100 × (*A*_(2-ADPA) + *A*_(4-ADPA)) × 2/ (introduced aniline – aniline remnant); ^f The commercial-purchased 0.1 mol L⁻¹ of NaOH (aq) was applied; ^g The reaction was proceeded without adding aniline as reactant; ^h tr. = not detected in GC-FID, but appeared characteristic mass peak in GC-MS; ⁱ The applied HCl (aq) was diluted from 0.1 mol L⁻¹ of HCl (aq); ^j n.d. = not detected in GC-MS and GC-FID; ^k Ion-changed water was applied; ^l The applied NaOH (aq) was diluted from 0.1 mol L⁻¹ of NaOH (aq).

Table 2 The results of some blank tests. ^a

Entry	Photoirradiation	Photocatalyst	C (%) ^b	Y (%) ^c		
				AZB	2-ADPA	4-ADPA
1	No	No	0	n.d. ^d	n.d.	n.d.
2	No	Yes	0	n.d.	n.d.	n.d.
3	Yes	No	0	n.d.	n.d.	n.d.

^a reaction conditions: 50 mg of Pt(1.0)/TiO₂ photocatalyst was used (**entry 2**); 4.6 μ L (50 μ mol) of aniline was introduced as the reactant, the actual amount was measured by electronic balance before each reaction; 4 mL of 0.1 mol L⁻¹ of NaOH (aq) were applied; Reaction time: 30 min; The incident UV-LED light wavelength was around 365 $\pm$ 5 nm, the irradiated light intensity was 1035 mW cm⁻², measured at 360 $\pm$ 20 nm in wavelength (**entry 3**); ^b Conversion of aniline, C (%) = 100 $\times$ (introduced aniline – aniline remnant after reaction)/(introduced aniline); ^c Yield of detectable products, Y (%) = 100 $\times$ A_(2-ADPA, 4-ADPA, AZB) $\times$ 2/(introduced aniline), where A_(2-ADPA, 4-ADPA, AZB) stands for the yielded amount of 2-ADPA, 4-ADPA, and AZB respectively; ^d n.d. = not detected.

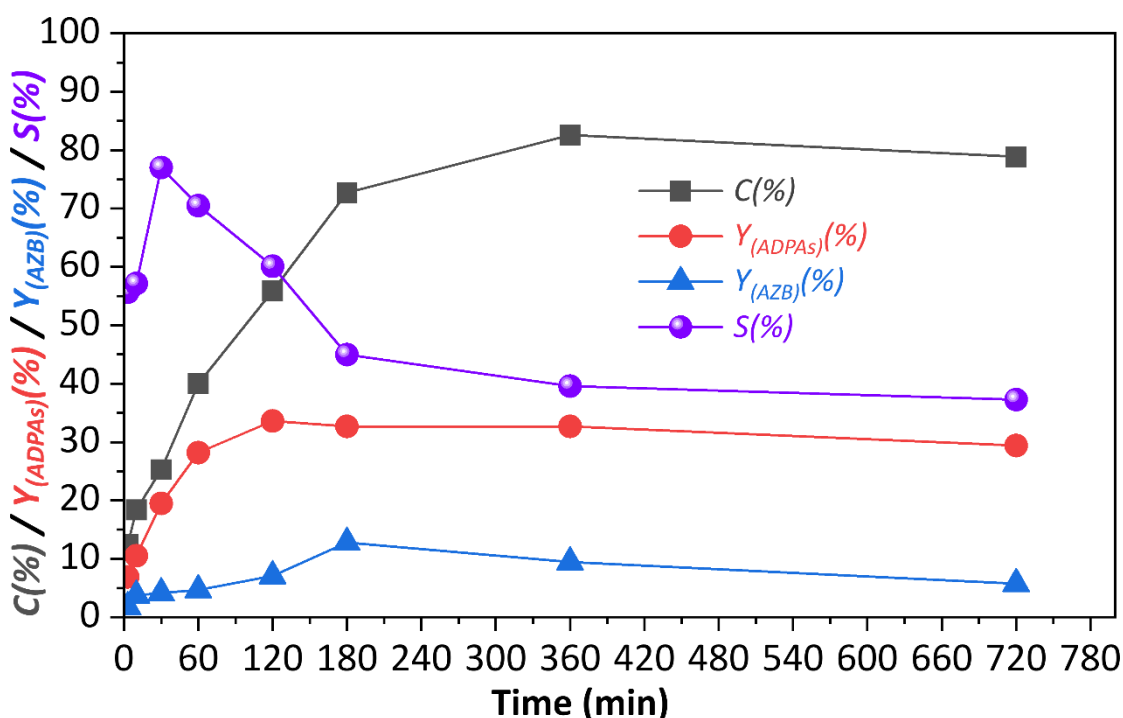


Fig. 4 Results of the photocatalytic reaction test with various reaction times. Reaction conditions: 50 mg of Pt(1.0)/TiO₂ photocatalyst was used; 4.6 μ L (50 μ mol) of aniline was introduced as the reactant; 4 mL of 0.1 mol L⁻¹ NaOH (aq, pH = 12.70) was applied; The incident UV-LED light wavelength was around 365 $\pm$ 5 nm, the irradiated light intensity was 1035 mW cm⁻² when measured at 360 $\pm$ 20 nm in wavelength; C (%) = 100 $\times$ (introduced aniline – remained aniline after reaction)/(introduced aniline); Y_(ADPAs) (%) = 100 $\times$ (A_(2-ADPA) + A_(4-ADPA)) $\times$ 2/(introduced aniline), Y_(AZB) (%) = 100 $\times$ A_(AZB) $\times$ 2/(introduced aniline), where A_(2-ADPA, 4-ADPA, AZB) stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively; S (%) = 100 $\times$ (A_(2-ADPA) + A_(4-ADPA)) $\times$ 2/(introduced aniline – remained aniline). The highest Y_(ADPAs) was observed at 120 min with a yield of 33.6%. The highest S (%) was found at 30 min with a selectivity of 77.0%.

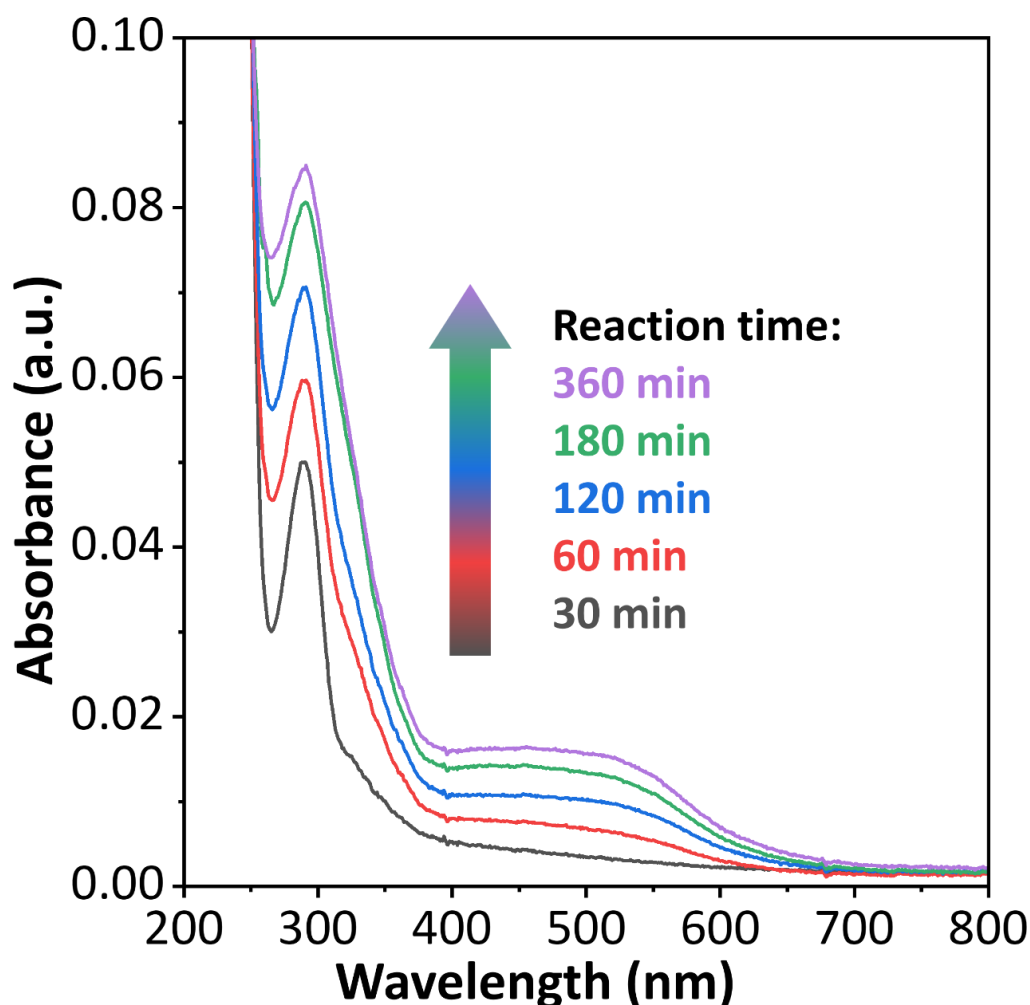


Fig. 5 Transmitted UV-vis spectra of the after-reaction solutions with various reaction times. All the solution samples were diluted 150 times with acetonitrile to avoid saturated light absorption in UV region. Other reaction conditions are given in the footnote of **Fig. 4**.

Table 3 The photocatalytic reaction tests with different concentrations of aniline. ^a

Entry	c_0^b (mmol L ⁻¹)	r^c ($\mu\text{mol min}^{-1}$)	C (%) ^d	Y (%) ^e			S (%) ^f
				2-ADPA	4-ADPA	AZB	
1	0.859	0.0815	71.1	tr. ^g	tr.	tr.	0
2	5.10	0.223	32.7	5.15	5.86	1.09	33.6
3	12.5	0.435	25.3	8.99	10.5	4.16	77.0
4	41.1	0.490	8.89	2.46	3.45	0.763	66.6
5	128	0.803	4.67	1.16	1.46	0.414	56.2

^a Reaction conditions: 50 mg of the Pt(1.0)/TiO₂ photocatalyst was used; Different amount of aniline was introduced as the reactant; 4 mL of 0.1 mol L⁻¹ NaOH (*aq*, pH = 12.70) was applied; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{-2} when measured at 360 ± 20 nm in wavelength; Reaction time was 30 min. ^b initial concentration of aniline, $c_0 = (\text{introduced amount of aniline})/(\text{introduced volume of aniline and NaOH (aq)})$; ^c consumption rate of aniline, $r = (\text{introduced aniline} - \text{remained aniline after reaction})/(\text{reaction time})$; ^d Conversion of aniline, $C (\%) = 100 \times (\text{introduced aniline} - \text{remained aniline after reaction})/(\text{introduced aniline})$; ^e Yield of detectable products, $Y (\%) = 100 \times A_{(2\text{-ADPA}, 4\text{-ADPA}, \text{AZB})} \times 2/(\text{introduced aniline})$, where $A_{(2\text{-ADPA}, 4\text{-ADPA}, \text{AZB})}$ stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. ^f Selectivity to 2-ADPA and 4-ADPA based on consumed aniline, $S (\%) = 100 \times (A_{(2\text{-ADPA})} + A_{(4\text{-ADPA})}) \times 2/(\text{introduced aniline} - \text{remained aniline})$; ^g tr. = not detected in GC-FID, but appeared characteristic mass peak in GC-MS.

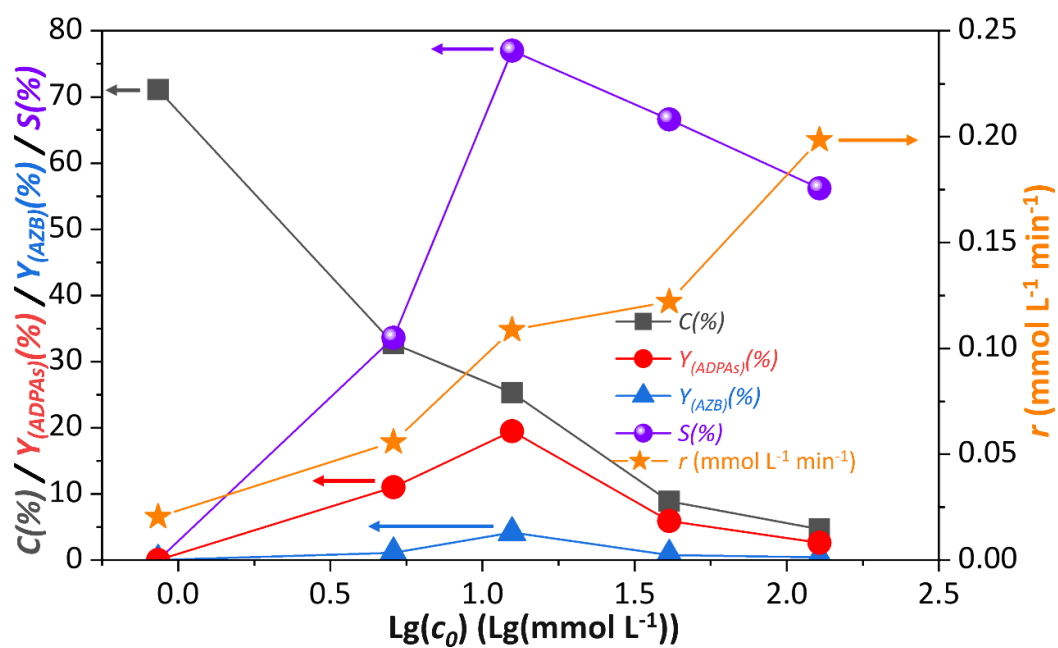


Fig. 6 Results of the photocatalytic reaction test with different concentrations of aniline. The reaction conditions were described in the footnote of **Table 3**.

Table 4 Photocatalytic conversion of aniline under various aqueous solutions with different pH. ^a

Entry	pH ^b	C (%) ^c	Y (%) ^d			S (%) ^e	H ₂ (μmol)
			2-ADPA	4-ADPA	AZB		
1	3.29	0	n.d. ^f	n.d.	n.d.	/	0.844
2	5.62	0	n.d.	n.d.	n.d.	/	1.11
3	6.58	0	n.d.	n.d.	n.d.	/	0.916
4	7.74	0	n.d.	n.d.	n.d.	/	1.11
5	10.35	0	n.d.	n.d.	n.d.	/	1.47
6	11.79	1.82	n.d.	n.d.	n.d.	/	2.13
7	12.01	30.5	7.40	10.1	0.488	57.4	n.m. ^g
8	12.21	30.1	9.65	11.7	1.84	70.9	6.94
9	12.70	25.3	8.99	10.5	4.16	77.0	6.09
10	13.01	25.8	8.36	9.06	3.72	67.5	5.92
11	13.43	24.9	4.57	5.21	3.17	39.3	5.62

^a Reaction conditions: 50 mg of the Pt(1.0)/TiO₂ photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of different aqueous solvents with different pH were applied; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm⁻² when measured at 360 ± 20 nm in wavelength; Reaction time was 30 min; ^b The exact pH was measured by a pH meter. For acidic solutions, HCl (aq) with different concentration (**entries 1 and 2**) and ion-changed water were used; For basic solutions, NaOH (aq) with different concentration (**entries 4–11**) were added; ^c Conversion of aniline, C (%) = 100 × (introduced aniline – remained aniline after reaction)/(introduced aniline); ^d Yield of detectable products, Y (%) = 100 × A_(2-ADPA, 4-ADPA, AZB) × 2/(introduced aniline), where A_(2-ADPA, 4-ADPA, AZB) stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. ^e Selectivity to 2-ADPA and 4-ADPA based on consumed aniline, S (%) = 100 × (A_(2-ADPA) + A_(4-ADPA)) × 2/ (introduced aniline – remained aniline); ^f n.d. = not detected in GC-MS and GC-FID; ^g n.m. = not measured.

3.3.2 Wavelength dependency for products formation

As shown in **Fig. 7A**, the formation of APDAs showed a strong dependence toward the incident light wavelength. **Fig. 7B** shows the transmittance of the optical filters and the absorption band of TiO₂. When the reaction was conducted with visible light irradiation (>400 nm), no detectable product was found, as no corresponding light absorption for TiO₂ photocatalyst (**Figs. 3 and 7B**). When UV light was irradiated, the total yield of detectable products increased with the increase of the light absorption of TiO₂ that realized by extending permitting wavelength. It is notable that the product selectivity was also varied with the light conditions and the best selectivity to ADPAs, $S(\%) = 74.1$ was achieved when the bandpass filter permitting around 365 nm light was applied. Such kind of high selectivity may be related to two reasons as follows. One is the avoidance of potential photolysis of aniline and ADPAs. As their UV-vis spectra shown in **Fig. 8**, no absorption was found for aniline and ADPAs in the region of longer than 350 nm in wavelength. The other is a specific photoexcitation of aniline adsorbed on the TiO₂ surface. The **Fig. 9** revealed that when a small amount of aniline mixed with the TiO₂ powder, an adsorption edge shift was observed in the DR UV-vis spectrum (**Fig. 9 a and b**). The difference spectrum between them clearly suggested that a specific absorption band appeared around at 365 nm due to the interaction between aniline and TiO₂ surface (**Fig. 9c**). This band is different from the absorption bands of aniline or products in their UV-vis spectra (**Fig. 8**), suggesting that a surface complex consisting of aniline and TiO₂ surface would be formed and photoexcited by the light of 365 nm in wavelength.

Similar interaction between adsorbates and TiO₂ has already been reported, like benzylamine, [48] pyridine, [49] and ammonia [50] on TiO₂ surface. In those studies, the photocatalytic reaction can be selectively mediated in visible light irradiation via photoexcitation at the N–Ti coordinate bond, where electron of N atom is excited by a charge transfer to Ti belonging to the conduction band of TiO₂. Thus, for the present photocatalytic conversion of aniline to ADPAs, it is necessary to consider two formation routes, the one proceeds by the light in the range of 320–400 nm in wavelength with the photoexcitation of TiO₂ photocatalyst, and the other is the selective reaction promoted by the light of around 365 nm in wavelength starting from the photoexcitation at the N–Ti coordinate bond. This will be discussed in detail later. It is also noticed that there was a broad absorption edge from 400 nm to 500 nm (**Fig. 9**, inset), which probably arise from a formation of a ligand-to-metal charge-transfer (LMCT) complex of aromatic ring adsorbed on TiO₂ surface with a $[\text{Ti}^{4+} \cdots \pi]$ interaction, [51,52] which gave a light brownish color of the TiO₂ sample adsorbing aniline.

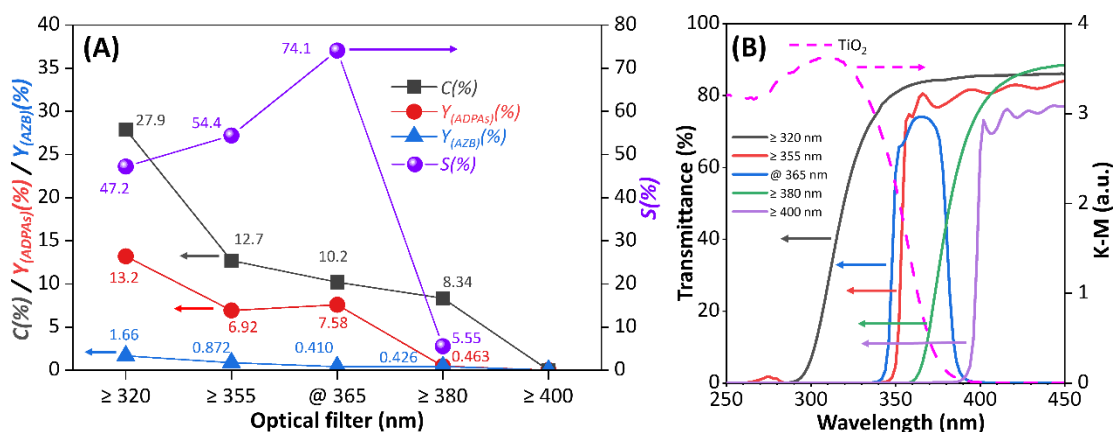


Fig. 7 (A) Results of photocatalytic tests for aniline conversion by using various optical filters. (B) left y-axis: The transmission spectrum of each optical filter used in the photocatalytic test, where permitted wavelength of long pass filters was longer than 320, 355, 380, and 400 nm, respectively and that of the band-pass filter was around 365 nm; Right y-axis: DR UV-vis spectra of the TiO₂ sample. Reaction conditions: 50 mg of the Pt(1.0)/TiO₂ photocatalyst; 4.6 μ L (50 μ mol) of aniline was introduced as the reactant, the actual amount was measured by electronic balance before each reaction; 4 mL of NaOH (aq, pH = 13); the xenon lamp was applied as light source with different filters. The original irradiated light intensity was 50 mW cm⁻², measured at 360 $\pm$ 20 nm in wavelength; Reaction time: 30 min. $C (%) = 100 \times (\text{introduced aniline} - \text{remained aniline after the reaction}) / (\text{introduced aniline})$; $Y_{(ADPA)} (%) = 100 \times (A_{(2-ADPA)} + A_{(4-ADPA)}) \times 2 / (\text{introduced aniline})$, $Y_{(AZB)} (%) = 100 \times A_{(AZB)} \times 2 / (\text{introduced aniline})$, where $A_{(2-ADPA)}$, $A_{(4-ADPA)}$, $A_{(AZB)}$ stands for the yielded amount of 2-ADPA, 4-ADPA, and AZB respectively; $S (%) = 100 \times (A_{(2-ADPA)} + A_{(4-ADPA)}) \times 2 / (\text{introduced aniline} - \text{remained aniline})$.

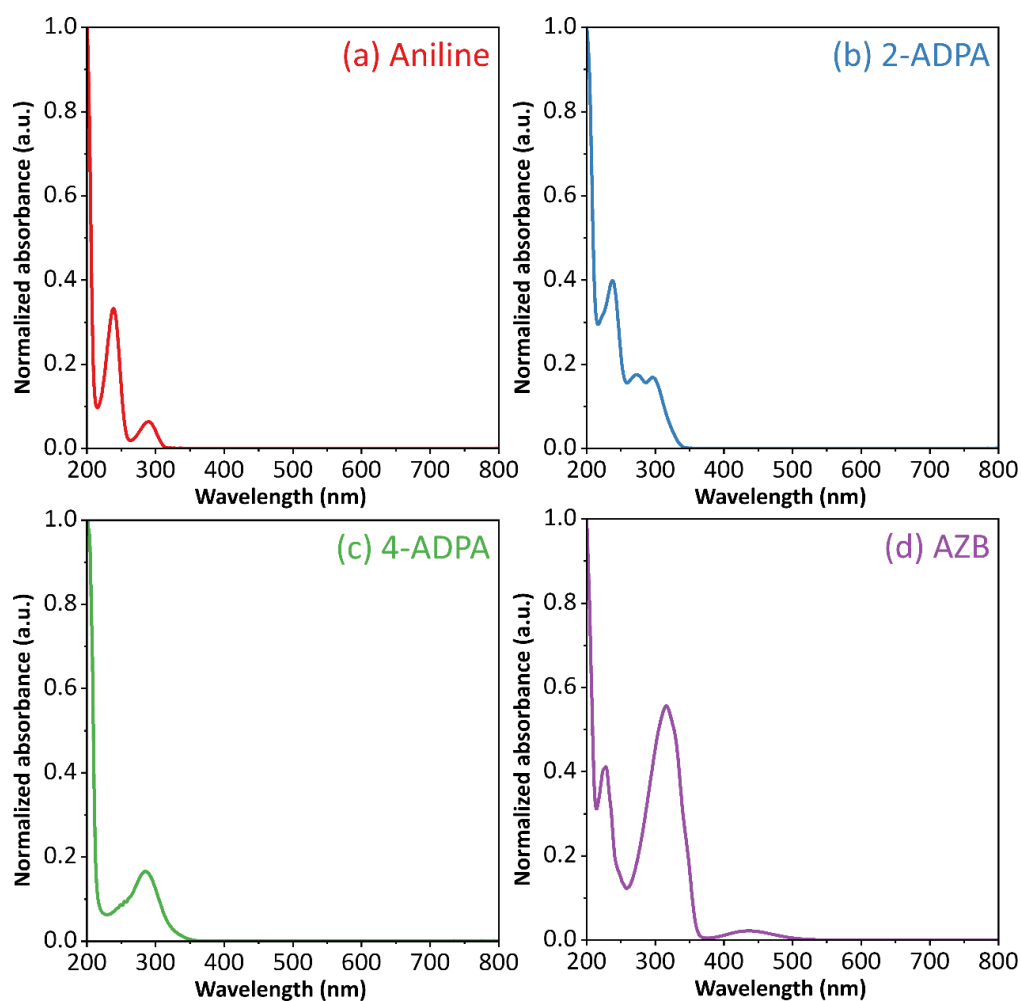


Fig. 8 Transmitted UV-vis spectra of aniline, 2-ADPA, 4-ADPA, and AZB samples. All the samples were prepared as acetonitrile solutions to avoid the saturated absorbance in UV region. Each spectrum was normalized to its maximum absorbance.

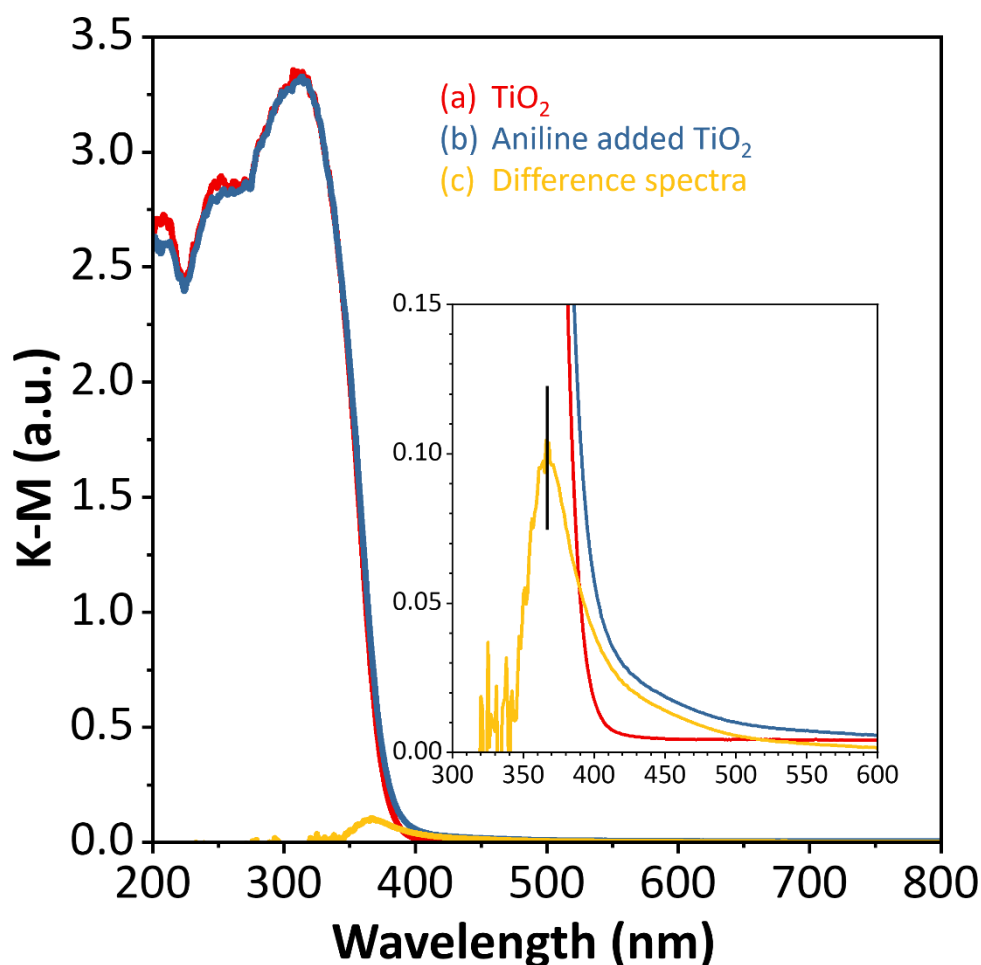
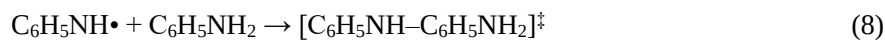


Fig. 9 The DR UV-Vis spectra of (a) TiO_2 powder, (b) aniline adsorbed TiO_2 powder (200 μmol of aniline mixed with 200 mg of TiO_2 powder), and (c) their difference spectra. The inset shows enlarged plot from 300 nm to 600 nm.

3.3.3 Kinetic experiments

To get insight into the formation mechanism of 2-ADPA and 4-ADPA, three parallel reactions were conducted by applying aniline (aniline- h_7) and deuterated anilines (aniline- d_5 and aniline- d_7) as reactants (**Table 5, entry 2**). When aniline- d_5 was the reactant, no kinetic isotope effect (KIE) was observed on the ADPAs ($k_H/k_D = 1.03$, **Table 5, entry 2**). This result indicated that cleavage of C–H bond in aromatic ring of aniline was not the rate-determining step (RDS) for the formation of 2-ADPA and 4-ADPA. However, the ratio of 2-ADPA production to 4-ADPA production in the case of aniline- d_5 changed from 0.872 (**Table 5, entry 1**) to 0.999 (**Table 5, entry 2**), even the total yield of ADPAs remained no change, suggesting that when aniline- d_5 was as the reactant, the *ortho* product (2-ADPA) was more favorably produced than *para* product (4-ADPA). It could be explained by the bond length difference between the C–H of the aniline and the C–D of aniline- d_5 . In the deuterated molecule, the C–D bond is shorter than the C–H bond, which provides a lower steric effect when another aniline- d_5 molecule approaches the *ortho* site to form a sp^3 -type transition complex as mentioned later. Also, no KIE was observed for ADPAs production when aniline- d_7 molecule was used ($k_H/k_D = 1.06$, **entry 3**), suggesting that the N–H bond cleavage was not the RDS for ADPAs formation. Considering the bond dissociation energy (BDE) of $\text{C}_6\text{H}_5\text{NH-H}$ (386 kJ mol^{-1}) is weaker than that of $\text{H-C}_6\text{H}_4\text{NH}_2$ (472 kJ mol^{-1} as $\text{H-C}_6\text{H}_5$ in benzene), [53] if both two bonds in aniline were able to be activated to form corresponding radical species, the RDS should be the most difficult step, *i.e.*, the C–H bond fission of aromatic ring in aniline molecule. However, the presented k_H/k_D value shown in **Table 5, entries 2 and 3** were almost unity. This pointed out another possible mechanism, *i.e.*, the formed anilino radical attacks

another aniline molecule to give a transition complex with rehybridization (eq. 8), such as sp^2 to sp^3 in a radical addition-elimination mechanism like in our previous studies. [31,54,55]



On the other hand, a secondary KIE was found for the production of AZB for aniline-*d*5 reactant ($k_H/k_D = 1.13$, **Table 5, entry 2**). Considering that the formation of AZB is only related to the N–H bond breaking in aniline, such value over-unity but close to the unity would be due to stabilization effect of D atoms on the aromatic ring. A clear KIE was shown in **Table 5, entry 3** on AZB production ($k_H/k_D = 1.83$) hinted that dissociation of one of several N–H bonds was the RDS in the process of AZB formation.

Table 5 Results of photocatalytic reaction tests with isotopic compounds (The schemes are described below). ^a

(1)				
	Aniline- <i>h</i> 7	2-ADPA- <i>h</i>	4-ADPA- <i>h</i>	AZB- <i>h</i>
(2)				
	Aniline- <i>d</i> 5	2-ADPA- <i>d</i> 9	4-ADPA- <i>d</i> 9	AZB- <i>d</i>
(3)				
	Aniline- <i>d</i> 7	2-ADPA- <i>d</i> 12	4-ADPA- <i>d</i> 12	AZB- <i>d</i> '

Entry	Substance	Y (%) ^b			<i>ortho/para</i> ^f	<i>k_H/k_D</i> (ADPAs)	<i>k_H/k_D</i> (AZB)
		2-ADPA ^c	4-ADPA ^d	AZB ^e			
1	aniline- <i>h</i>	9.24±0.245	10.6±0.153	4.49±0.296	0.872	-	-
2	aniline- <i>d</i> 5	9.58±0.219	9.59±0.226	3.96±0.0636	0.999	1.03 ^g	1.13 ⁱ
3	aniline- <i>d</i> 7	9.09±0.490	8.97±0.220	2.16±0.662	1.01	1.06 ^h	1.83 ^j

^a Reaction conditions: 50 mg of Pt(1.0)/TiO₂ photocatalyst was used; 4.6 μL (50 μmol) of aniline-*h* (**entry 1**), aniline-*d*5 (**entry 2**), and aniline-*d*7 (**entry 3**) were introduced as the reactants respectively, the actual amount of aniline was measured by electronic balance before each reaction; 4 mL of NaOH (*aq*, pH = 13) was added as solvent; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm⁻², measured at 360 ± 20 nm in wavelength; Reaction time: 30 min; For aniline-*d*5 (**entry 2**) and aniline-*d*7 (**entry 3**), the corresponding deuterated products were confirmed by GC-MS; ^b Yield of products was presented with standard deviation, $Y(\%) = 100 \times A_{(2-ADPA, 4-ADPA, AZB)} \times 2 / (\text{introduced aniline})$, where $A_{(2-ADPA, 4-ADPA, AZB)}$ stands for the yielded amount of non-deuterated or deuterated 2-ADPA, 4-ADPA, and AZB respectively; ^c yield of 2-ADPA (2-ADPA-*h*, **entry 1**) and deuterated 2-ADPA (2-ADPA-*d*9 in **entry 2** and 2-ADPA-*d*12 in **entry 3**); ^d yield of 4-ADPA (4-ADPA-*h*, **entry 1**) and deuterated 4-ADPA (4-ADPA-*d*9 in **entry 2** and 4-ADPA-*d*12 in **entry 3**); ^e yield of AZB (AZB-*h*, **entry 1**) and deuterated AZB (AZB-*d* in **entry 2** and AZB-*d*' in **entry 3**); ^f The ratio of produced 2-ADPA to 4-ADPA, $ortho/para = Y_{(2-ADPA)} / Y_{(4-ADPA)}$; ^g $k_H/k_D = (Y_{(2-ADPA-h)} + Y_{(4-ADPA-h)}) / (Y_{(2-ADPA-d9)} + Y_{(4-ADPA-d9)})$; ^h $k_H/k_D = (Y_{(2-ADPA-d9)} + Y_{(4-ADPA-d9)}) / (Y_{(2-ADPA-d12)} + Y_{(4-ADPA-d12)})$; ⁱ $k_H/k_D = Y_{(AZB-h)} / Y_{(AZB-d)}$; ^j $k_H/k_D = Y_{(AZB-d)} / Y_{(AZB-d')}$.

3.3.4 Temperature controlled experiments

To investigate the apparent thermal activation energy (E_a) of various products in this photocatalytic reaction, temperature-controlled photocatalytic reactions were conducted at 296–306 K. The pseudo-Arrhenius plots for products formation rate gave the apparent thermal activation energies for the productions of 2-ADPA, 4-ADPA, and AZB to be 15.9 kJ mol⁻¹, 7.57 kJ mol⁻¹, and 72.7 kJ mol⁻¹, respectively (**Fig. 10**). The quite low E_a value for ADPAs formation suggests that such kind of C–N bond formation process would be a purely photocatalytic process like our previous researches for photocatalytic C–C bond formation and C–N bond formation [25,56] with Pt(1.0)/TiO₂ photocatalyst.

Meanwhile, for the formation of AZB, a relatively high E_a value indicates that besides the photoenergy, the thermal energy also assisted at least one step, which is the thermally RDS step. According to the kinetic experiments,

probably one of the N–H bond dissociation processes for the AZB production was promoted by the thermal energy. In literatures, [30,34–36] it has been well-known that in the photocatalytic oxidation reaction of aniline, AZB was a main product formed through a hydrogen abstraction process of hydrazobenzene (HyAZB) by O_2 (if existed), h^+ (eq. 9) and $OH^\bullet$ (eq. 10). Considering that the anilino radicals were the predominant active aniline-related species in present conditions, the HyAZB should be mainly produced from the radical coupling of two anilino radicals, and then oxidized into AZB (eq. 11). If the first photocatalytic N–H bond dissociation in amino group ($-NH_2$) of aniline to anilino radical species was the RDS for AZB formation, a similar E_a value of AZB as the E_a of 2-ADPA and 4-ADPA would have been observed. The obviously different E_a value indicated that the RDS should be only in the formation process from HyAZB to AZB with a N–H bond dissociation, which could be accelerated by thermal energy.

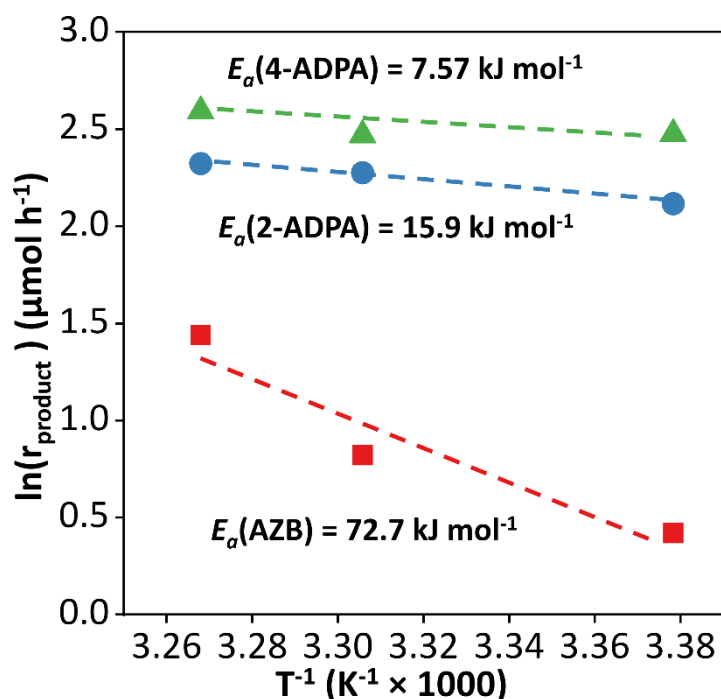
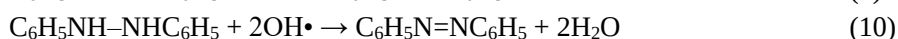


Fig. 10 Pseudo-Arrhenius plots of the products formation rate $\ln(r_{\text{product}})$ for the temperature-controlled reactions. The amount of products at the first 3 min was used for the calculation of the formation rate of products. Reaction conditions: 50 mg of Pt/TiO₂ photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant, the actual amount was measured by electronic balance before each reaction; 4 mL of 0.1 mol L⁻¹ of NaOH (aq) was applied as solvent; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm⁻², measured at 360 ± 20 nm in wavelength.

3.3.5 Proposed reaction mechanism

In previous reports, it was well-studied that the photocatalytic activation of aniline started from the photogenerated hole (h^+) oxidation into the $C_6H_5NH_2^+$ (aniline radical cation) (eq. 4). [30,34,35] In this study, in addition to the conventional photocatalytic route, the high selectivity for ADPAs under 365 nm incident light and the corresponding absorption band in the UV-vis spectra, which are attributed to the surface complex formed by aniline and the TiO₂ surface, suggest an alternative mechanism, *i.e.*, the photoexcitation of surface complex with a single electron transfer from nitrogen atom in aniline to titanium atom in TiO₂, which resulted in an extra route for

$\text{C}_6\text{H}_5\text{NH}_2^+$ radical cation production (eq. 12). Following by a reaction of the $\text{C}_6\text{H}_5\text{NH}_2^+$ radical cation with OH^- , the anilino radical was formed in alkaline environment (eq. 5). Then the 2-ADPA and 4-ADPA can be produced after the attack of the anilino radical to another aniline molecule by a radical addition-elimination process (eqs. 8 and 13), which is the same process after the conventional photocatalytic route. As another possibility, a radical-radical coupling of anilino radical and 2-aminophenyl radical or 4-aminophenyl radical ($\bullet\text{C}_6\text{H}_4\text{NH}_2$) cannot be eliminated, which is however quite less possible due to the low concentration of the aminophenyl radical species as the reaction intermediate. Considering the BDE of $\text{C}_6\text{H}_5\text{NH}-\text{H}$ (386 kJ mol^{-1}) and that of $\text{H}-\text{C}_6\text{H}_4\text{NH}_2$ (472 kJ mol^{-1} as $\text{H}-\text{C}_6\text{H}_5$ in benzene), [53] the formation of $\bullet\text{C}_6\text{H}_4\text{NH}_2$ is relatively difficult so that the possibility of the ADPA formation via a radical-radical coupling mechanism would be quite low.

Based on those observations in the mechanistic study and so on, the three possible mechanisms for ADPA production are proposed here: The first is a conventional photocatalytic route (**Scheme 1A**). (i) The UV light photoexcitation of the TiO_2 photocatalyst by the light of 320–400 nm in wavelength generates electrons and holes. The holes move to the TiO_2 surface while the electrons move to Pt nanoparticles (eq. 1). And the adsorbed aniline molecule on the TiO_2 surface is oxidized by the photogenerated holes to give aniline radical cation (eq. 4); (ii) The formed aniline radical cation is oxidized by OH^- to give anilino radical (eq. 5). (iii) Then, anilino radical reacts with another aniline molecule by attacking the *ortho* or *para* position of the aromatic ring to generate a sp^3 -type radical transition complex. (iv) After the elimination of a $\text{H}\bullet$ from this transition state, the 2-ADPA or 4-ADPA molecule as the C–N coupling product is formed (eqs. 8 and 13).

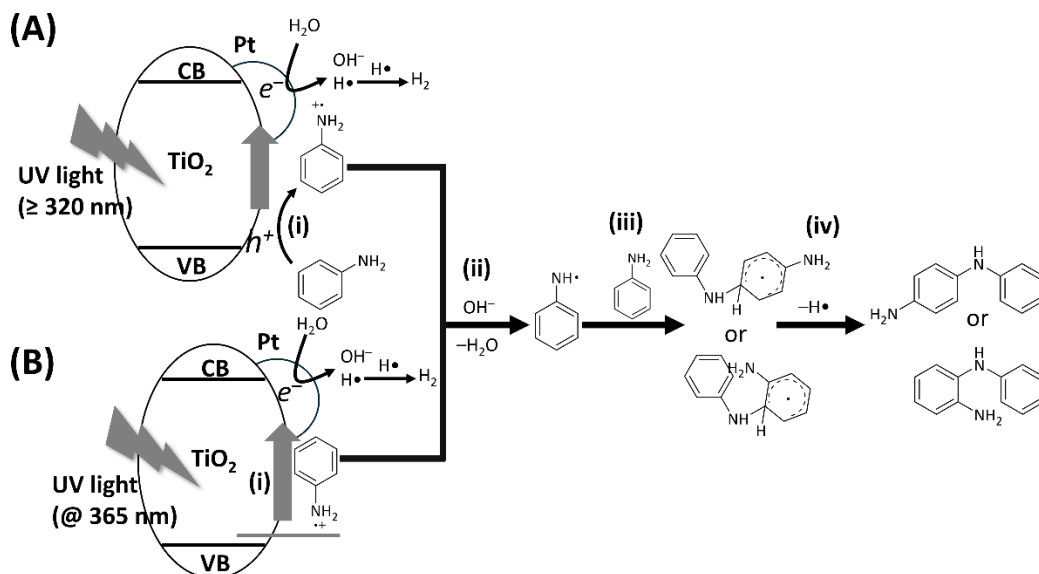
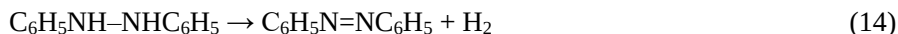
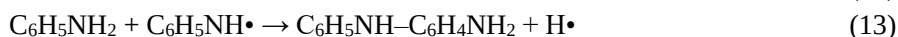
The second route starts from the photoexcitation of the surface complex (**Scheme 1B**). (i) On the TiO_2 surface, the adsorbed aniline molecule is excited by a 365 nm UV light with a single electron transfer from nitrogen atom in aniline to the titanium atom in TiO_2 , corresponding the formation of an adsorbed aniline radical cation (eq. 12). (ii–iv) Then the successive steps are the same as **Scheme 1A**.

As mentioned in the previous section, a minor route by hydroxyl radicals is also considered here. The $\bullet\text{OH}$ radical is photocatalytically generated from the reaction of OH^- and holes (eq. 6). Aniline molecule is oxidated by the $\bullet\text{OH}$ radical to produce anilino radical and water (eq. 7). The subsequent reactions proceed in the same manner as described above.

Considering the relatively small value of E_a for both 2-ADPA and 4-ADPA, they are photocatalytically formed without assistance of thermal catalytic step. The whole C–N bond coupling reaction is a one-photon or two-photon process, and the RDS should be the formation step of the sp^3 -type radical transition state (eq. 8). The small thermal activation energy contributes to thermal step in photocatalytic reaction process proposed in literature.⁵⁷ In the above proposed mechanisms (**Scheme 1**), the final common step, i.e., the elimination of a H radical in the sp^3 -type radical transition complex to give ADPA was considered to initiate in three possible routes. The first one is the additional oxidation by the photogenerated holes on the TiO_2 surface to the transition complex, which changes the charge distribution of the C–H bond and results in the release of a proton. The second route is the hydrogen abstraction by hydroxyl radicals ($\bullet\text{OH}$). The reactive $\bullet\text{OH}$ species may react with the H atom to form H_2O . The above two possibilities both required one extra photon, i.e., the direct utilize of holes and the $\bullet\text{OH}$ species formation from the oxidation of OH^- by holes, which make the formation of ADPA a two-photon process. The last one is the catalysis of Pt. It is well-known that Pt nanoparticles can catalyze the C–H bond cleavage, as demonstrated in processes like the catalytic dehydrogenation of propane. [58] In this study, it is possible that the Pt directly catalyzes the elimination of H atoms in that sp^3 -type radical transition complex.

The formation of AZB has been reported from a successive hole oxidation of HyAZB in the photocatalytic oxidation of aniline. In the present anaerobic conditions, the produced two anilino radicals combine to form a HyAZB molecule (eq. 11), followed by hydrogen abstraction to yield an AZB molecule. This hydrogen abstraction would be promoted by thermal-assisted RDS (eq. 14) or photocatalysis (eqs. 9 or 10).

It is worth noting that hydrogen was also observed as the only detected gaseous product. The process is described in eq. 2 and **Scheme 1**. The water molecules consumed, and hydroxide ions generated in this reductive hydrogen evolution process are quantitatively balanced when considering the hydroxide ions, water, and hydrogen radicals involved in the formation of ADPA and AZB.



Scheme 1 Proposed one-photon mechanism for ADPA formation; (A) a general photocatalytic route under UV light (≥ 320 nm), (B) a single electron transfer route from the N atom to the Ti atom at an incident light wavelength of 365 nm, including the following steps, (i) formation of aniline radical cation, (ii) formation of anilino radical, (iii) formation of sp^3 transition states, and (iv) formation of the products. When a proton was released from the transition state, a two-photon process would occur.

3.4 Conclusions

In this study, we successfully found a photocatalytic way to synthesize 2-ADPA and 4-ADPA from aniline under a high pH solution. After 30 min reaction, a 19.5% of yield and 77.0% of selectivity were achieved with Pt(1.0)/TiO₂ photocatalyst. The limited pH condition ($\text{pH} > 11.79$) was found to yield a great amount of ADPAs. And the DR UV-vis spectra revealed that a specific absorption peak at 365 nm when aniline was adsorbed on the TiO₂ surface, which provided a related high ADPAs selectivity in the same wavelength. The kinetic study suggested that neither the dissociation of C–H bond nor the N–H dissociation in aniline is the RDS during the ADPAs formation. Then the results of temperature-controlled experiments revealed that production of 2-ADPA and 4-ADPA is a typical photocatalytic process.

According to the above findings and previous studies, it can be proposed three tentative pathways for the formation of anilino radical. (i) In a typical photocatalytic pathway, the aniline is oxidized by photogenerated holes under UV light irradiation to form aniline radical cation species, then the anilino radical species can be formed by the reaction with OH[•]. (ii) Under an incident photoirradiation of 365 nm wavelength, the adsorbed aniline molecule is photoexcited with a single electron transfer from nitrogen atom in aniline to the titanium atom in TiO₂, corresponding the formation of an adsorbed aniline radical cation. Then this radical cation can react with OH[•] to give anilino radical. (iii) As a minor route, the OH[•] reacts with holes to give reactive hydroxyl radical species. After the hydrogen-abstraction by the hydroxyl radical species, the anilino radical species is given. The anilino radical formed by the above pathways attacks another aniline molecule to generate a sp^3 -type radical transition state, which process is the RDS, followed by the hydrogen radical elimination (or hole oxidation, releasing proton, and reduction of the proton by photoexcited electron). Finally, this photocatalytic asymmetric homocoupling reaction gives 2-ADPA or 4-ADPA through the C–N bond formation.

The results obtained provide a deeper understanding of photocatalytic C–N coupling, potentially broadening the selectively synthetic strategy for more practical N contained compounds.

3.5 Reference

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Chapter 4

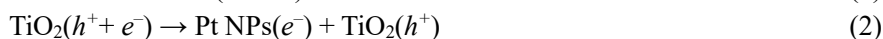
Coupling of hydrogen radicals catalyzed by Pt nanoparticles after traveling several millimeters from TiO₂ photocatalyst

Abstract

Pt nanoparticles (NPs) loaded on TiO₂ photocatalyst as cocatalyst is well-known for significantly enhancing photocatalytic H₂ production from an aqueous methanol solution since Pt NPs in contact with the TiO₂ surface can improve the charge separation by accepting photoexcited electrons. In this study, another catalytic role of Pt NPs was clearly evidenced by a simple method, using a flow reactor and gas mixture of methanol and water in argon carrier, in which TiO₂ photocatalyst and separately supported Pt NPs are located without physical contact. It was demonstrated that hydrogen radical species, generated on the TiO₂ photocatalyst, are capable of migrating through a quartz wool layer of several millimeters in length and reach the Pt NPs on alumina support, where coupling of the hydrogen radical to form H₂ molecules is catalytically promoted by the Pt NPs.

4.1 Introduction

As mentioned in **General introduction**, bare TiO₂ photocatalyst can hardly be applied for H₂ production due to its rapid charge recombination. To enhance the photocatalytic hydrogen evolution with TiO₂, many efforts have been made recently, such as the morphology modification [1,2], application of heterojunction structure like TiO₂/CdS/CdSe [3,4] and elements doping like nitrogen (N) [5] and tungsten (W) [6], *etc.* Among all of the methods, the following two conventional protocols are proved simple and effective, *i.e.*, loading noble metals such as platinum nanoparticles (Pt NPs) on the TiO₂ surface as a cocatalyst [7–10] and adding sacrificial reactive reagent like methanol into water [11]. Through a combination of them, the H₂ evolution on Pt NPs loaded TiO₂ photocatalyst in methanol aqueous can be described as follows. The photoirradiation of TiO₂ generates photoexcited electrons (e^-) and holes (h^+) in its conduction and valence bands (eq. 1). Since the bottom of the conduction band of TiO₂ is higher than Fermi level of Pt NPs, photogenerated electrons are transferred from TiO₂ to Pt NPs attached on the TiO₂ surface (eq. 2). Protons (H^+) in the aqueous solution can be reduced by electrons on Pt NPs into hydrogen radicals ($H^\bullet$) (eq. 3). Then two hydrogen radicals react to form H₂ gas, possibly on the Pt surface (eq. 4). On the other hand, holes are efficiently consumed for methanol photooxidation to constantly reduce the recombination of electrons and holes in the TiO₂ photocatalyst (eq. 5).



It has been quite acceptable that Pt NPs receive the photogenerated electrons from TiO₂ (eq. 2) and provide surface active sites for protons reduction (eq. 3) and on which the coupling of hydrogen radicals takes place (eq. 4). However, it is still ambiguous about whether the Pt NPs contribute to the coupling of hydrogen radicals catalytically or not. Here, to experimentally investigate the possible role of Pt NPs in the radical coupling (eq. 4), we examined the catalytic performance of physically separated Pt NPs on an Al₂O₃ support from the surface of TiO₂ photocatalyst. Even when they are free from their physical contact in a flow reactor, the Pt NPs enhanced H₂ generation from a gas mixture of methanol and water. Hydrogen radicals generated on the TiO₂ photocatalyst can migrate even the long distance in a millimeter scale (0~8 mm), where quartz wool and gas mixture were present, and reach Pt NPs to be coupled. Based on our observations, it is evidenced that Pt NPs catalyze the coupling of hydrogen radicals to form H₂ molecules.

4.2 Experimental

4.2.1 Catalyst preparations

Various platinum-loaded titanium oxide photocatalysts were synthesized by a photodeposition (PD) method and an impregnation (IMP) method [12,13], by which Pt NPs can be formed on TiO₂ [14,15]. A commercial TiO₂ sample, ST-01 (Ishihara Sangyo Kaisha, anatase, 300 m² g⁻¹, ca. 7 nm) was used as photocatalyst. In the PD method, 1.0 g of TiO₂ powder was dispersed in 200 mL of ion-exchanged water and was irradiated with a xenon lamp (PE300BUV, 300 W) for 30 min with magnetically stirring. Then 50 mL of methanol (Nacalai tesque Inc., ≥ 99.8 %) and the desired amount of the H₂PtCl₆ solution (Nacalai tesque Inc., ≥ 98.5 %, the prepared solution was 18.84 g L⁻¹ as Pt) were added to the suspension. The contents were stirred for 15 min without irradiation and stirred for 1 h under light irradiation. This suspension was filtered with suction and was washed with 500 mL of ion-changed water 3 times. After drying for 12 h under 353 K in an electronic oven, a white or grey-colored powder of the

Pt(*x*)/TiO₂(PD) sample was obtained, where *x* shows a loading amount as weight percent (wt%) and the color of the sample depending on the loading amount. For the preparation of Pt(*x*)/TiO₂(IMP), 1.0 g of TiO₂ powder was dispersed in 200 mL of ion-exchanged water and stirred for 30 min. Then the desired amount of H₂PtCl₆ solution (18.84 g L⁻¹ as Pt) was added to the suspension and the contents were stirred for 1 h. Water was removed from the suspension by heating at 353 K in a water bath and the obtained bulk solid was powdered and dried under 353 K for 12 h. The Pt(*x*)/TiO₂(IMP) powder was finally collected after calcination at 773 K for 1 h and reduction with hydrogen gas at 423 K for 30 min. The XRD pattern (**Fig. 1**) of the prepared Pt(0.1)/TiO₂(PD) sample (273 m² g⁻¹, **Table 1**) and Pt(0.1)/TiO₂(IMP) sample (99.1 m² g⁻¹, **Table 1**) suggested the anatase phase of TiO₂ remains even after Pt loading. For both samples, no characteristic peaks of Pt were observed, which would originate from a small loading amount and the small size of Pt NPs. The Pt(0.1)/TiO₂(PD) sample showed almost the same UV-vis spectrum as the bare TiO₂ sample, indicating that the Pt species did not change the photoabsorption by TiO₂ (**Fig. 2**).

The platinum-loaded aluminium oxide samples (Pt(*x*)/Al₂O₃) were prepared by the same impregnation method (IMP) mentioned above with aluminium oxide of γ -phase as a support (JRC-ALO-7, the Catalysis Society of Japan, 180 m² g⁻¹). As for the present Pt(3.0)/Al₂O₃ sample (180 m² g⁻¹, **Table 1**), the successful loading of Pt was confirmed by XRD (**Fig. 3**), and highly dispersed Pt nanoparticles with an average size of 2.5 nm were observed by TEM (**Fig. 4**). A strong light absorption in both UV and visible light range was appeared compared to the bare Al₂O₃ sample, giving a greyish color of catalyst, which is due to the relatively high Pt loading amount (**Fig. 5**) [16].

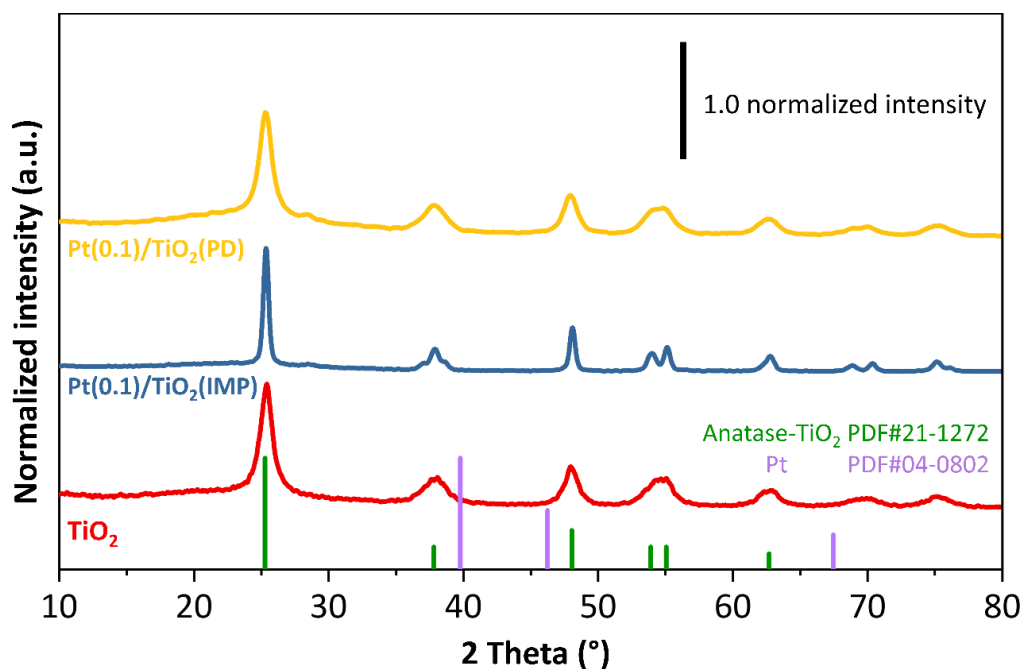


Fig. 1 XRD pattern of the Pt(0.1)/TiO₂(PD), Pt(0.1)/TiO₂(IMP), and TiO₂ samples. All the XRD profiles were normalized from its maximum intensity. The TiO₂ phase of the Pt(0.1)/TiO₂(PD) and Pt(0.1)/TiO₂(IMP) samples did not change after Pt loading, according to the characteristic peaks of anatase TiO₂ (PDF#21-1272). For the Pt(0.1)/TiO₂(IMP) sample, the calcination step in preparation would improve the crystallization of TiO₂ as clearer characteristic peaks of anatase TiO₂ (PDF#21-1272) were observed. No characteristic peaks of Pt (PDF#04-0802) were observed for Pt(0.1)/TiO₂(PD) and Pt(0.1)/TiO₂(IMP), which may be due to a small loading amount and a small size of Pt species.

Table 1 The specific surface area (S_a) of various catalyst samples.

Entry	Sample	S_a (m ² g ⁻¹) ^a
1	TiO ₂	300 ^b
2	Pt(0.1)/TiO ₂ (PD)	273
3	Pt(0.1)/TiO ₂ (IMP)	99.1
4	Pt(3.0)/TiO ₂ (IMP)	100
5	Al ₂ O ₃	180 ^c
6	Pt(3.0)/Al ₂ O ₃	180

^a Measured by BET method. ^b Provided by Ishihara Sangyo Kaisha. ^c Provided by the Catalysis Society of Japan.

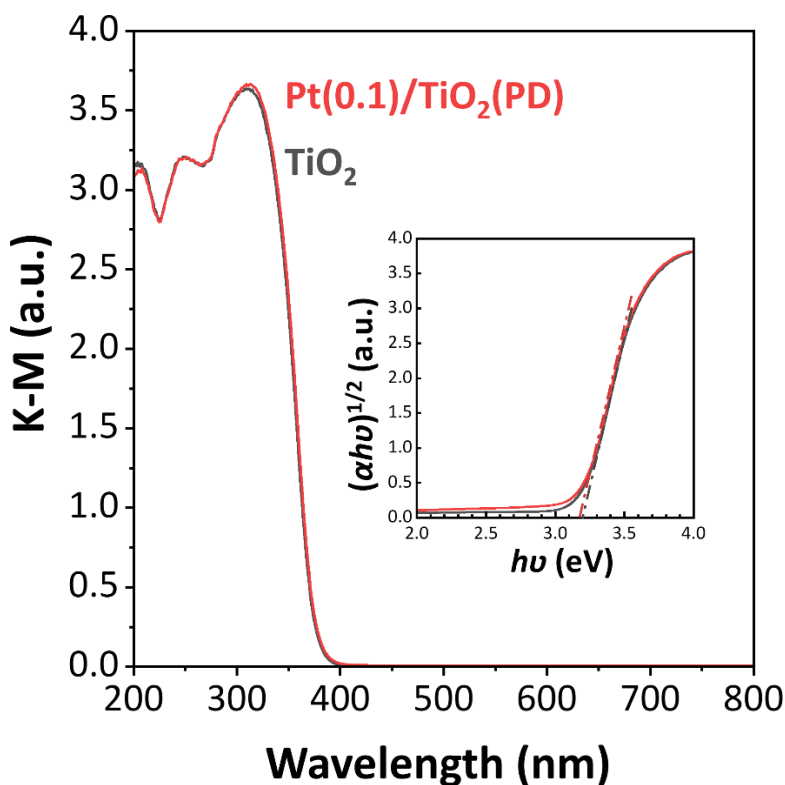


Fig. 2 DR UV-vis spectra of the bare TiO_2 and $\text{Pt}(0.1)/\text{TiO}_2(\text{PD})$ samples. According to the calculation in the inset graph, the $\text{Pt}(0.1)/\text{TiO}_2(\text{PD})$ exhibited slightly shifted band edge from 3.20 eV to 3.18 eV due to the loading Pt loading on the TiO_2 surface.

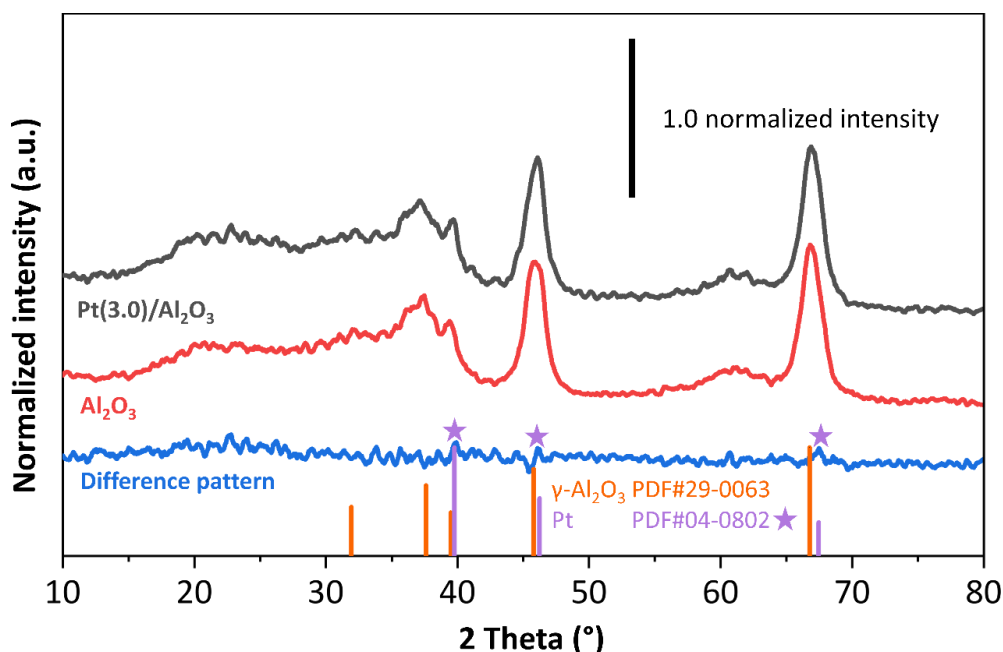


Fig. 3 XRD pattern of the $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ and Al_2O_3 samples and their difference pattern. All the XRD profiles were normalized from its maximum intensity. The Al_2O_3 phase of the Al_2O_3 support did not change even after the calcination and reduction process to prepare the $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ sample, which is indicated by the unchanged characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ (PDF#29-0063). The difference pattern suggested a successful Pt loading for the $\text{Pt}(3.0).\text{Al}_2\text{O}_3$ sample, as small characteristic peaks of Pt (PDF#04-0802) were observed.

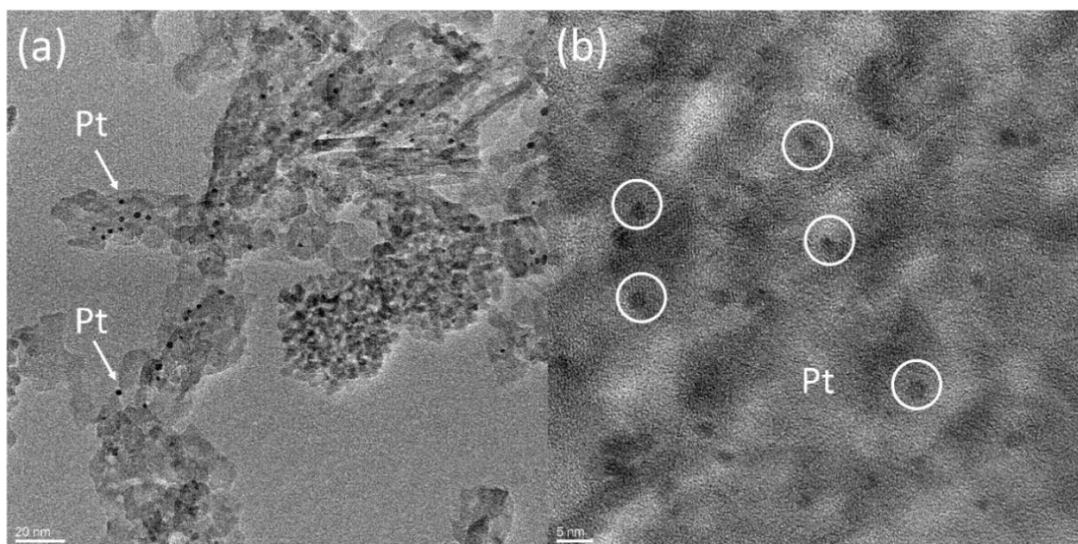


Fig. 4 (a) TEM image of the mixture of the TiO_2 and $\text{Pt(3.0)/Al}_2\text{O}_3$ samples (25 mg each) and (b) the localized magnified TEM image for observing Pt nanoparticles. The average size of Pt nanoparticles was 2.5 nm.

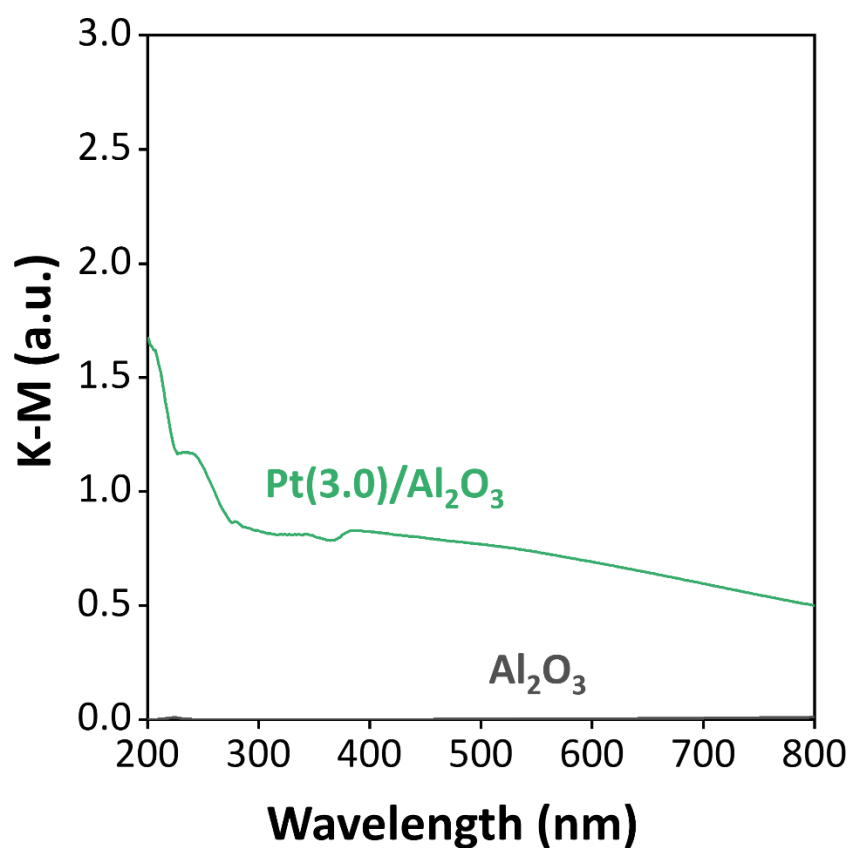


Fig. 5 DR UV-Vis spectra of the bare Al_2O_3 and $\text{Pt(3.0)/Al}_2\text{O}_3$ samples. The bare Al_2O_3 sample showed no light adsorption in the range of 200 nm to 800 nm. The improved absorption of the $\text{Pt(3.0)/Al}_2\text{O}_3$ sample was observed in the same wavelength range due to the high amount of Pt loading and the greyish color of catalyst.

4.2.2 Photocatalytic H₂ evolution from aqueous solutions

Photocatalytic reaction test for hydrogen production from an aqueous methanol solution was carried out in a test tube (20 mL). Without any optical filter, light irradiation from a xenon lamp (PE300BUV, 300 W) was conducted for 30 min to clean the surface of photocatalyst (25 mg). Then, 4 mL of methanol solution (40 vol%) was added, and the test tube was plugged by a silicone septum stopper and sealed. The existing air was purged by using a bubbling flow of argon gas (30 mL min⁻¹) for 15 min. The contents were stirred under photoirradiation through an optical filter (permitted wavelength: $\lambda \geq 360$ nm) for 30 min to promote photocatalytic H₂ production. After the reaction, 0.5 mL of the gaseous phase was extracted and analyzed by GC-TCD (Shimadzu GC-8A).

The photocatalytic reaction test from an aqueous solution of acetic acid was also carried out in a closed test tube. The reaction procedure and analysis procedure were similar to reactions in aqueous methanol. In these tests, 20 vol% of acetic acid was applied.

4.2.3 Photocatalytic H₂ evolution in a gas flow reactor

The photocatalytic reaction test for H₂ evolution from a gas mixture of methanol and water was carried out in a flow reactor (**Fig. 6**). The TiO₂ photocatalyst powder and Pt(3.0)/Al₂O₃ catalyst powder were first pressed under 40 MPa for 1 min, which gave their thin pellets. The pellet obtained was crushed and sifted using 25 mesh and 50 mesh sieves. The remaining granules on the 50-mesh sieve were used for the reaction tests. The desired amount of catalyst granules (25 mg each) was placed in a quartz tube reactor (10 cm of length and 4 mm of inner diameter) in a designated order. A constant argon gas flow through a vessel containing an aqueous methanol (40 vol%) made vapor of methanol and water. The total flow rate of the mixed gas containing of methanol and water vapor was controlled at 10 mL min⁻¹, in which the flow rate of methanol and water were estimated as 940 and 594 $\mu\text{mol h}^{-1}$, respectively. A xenon lamp (PE300BUV, 300W) was used as a light source for photoirradiation with the optical filter ($\lambda \geq 360$ nm) from the side of the quartz tube reactor. The light intensity was 50 mW cm⁻² which was measured in the range of 360 ± 20 nm in wavelength. The temperature of the reactor became 333 K due to the photoirradiation. The gas product, H₂ was analyzed by online GC-TCD (Shimadzu GC-8A).

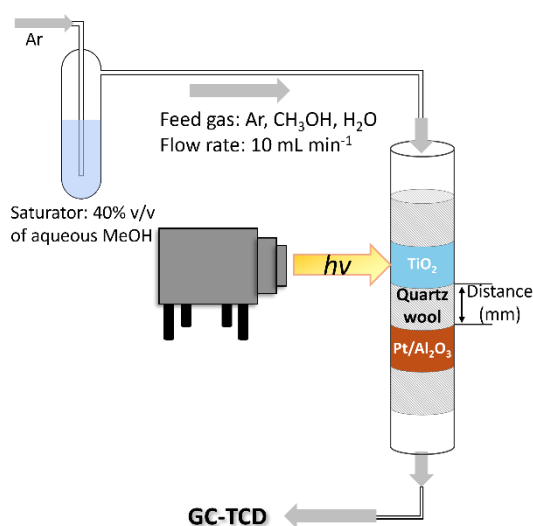


Fig. 6 Schematic of a flow reactor system employed in the photocatalytic hydrogen evolution test.

4.2.4 Characterization

The transmission electron microscopy (TEM) images were taken by JEM-2200FS. X-ray diffraction (XRD)

patterns of the samples were recorded at room temperature using a Shimadzu Lab X XRD-6000 with Cu K α radiation (40 kV, 30 mA). The Brunauer–Emmett–Teller (BET) specific surface area was measured by using adsorbed amount of N₂ on the sample surface at 77 K using a Quantachrome Monosorb MS-21. The diffuse reflectance (DR) UV-vis spectra were recorded by using a JASCO V-770 spectrophotometer equipped with an integrating sphere, where barium sulphate (BaSO₄) was used as a reference. Pt L_{III}-edge XANES spectra were recorded in a transmission mode and a fluorescence mode at room temperature at the BL01B1 facility of SPring-8 (Hyogo, Japan) using a Si(111) double crystal monochromator.

4.3 Results

4.3.1 Methanol solution

Fig. 7 shows the results of photocatalytic H₂ production tests from the aqueous solution of methanol. Without any platinum loading on its surface, the 25 mg of TiO₂ sample gave quite limited H₂ production (26.0 μ mol) (**Fig. 7a**). It has been understood that the low activity was due to a low charge separation efficiency of TiO₂ photocatalyst. In addition, the lack of metal catalyst on TiO₂ surface would also have a significant impact as discussed later. When TiO₂ powder (25 mg) was mixed with Al₂O₃ powder (25 mg), it showed slightly lower H₂ production than unmixed TiO₂ powder, where the Al₂O₃ powder would disturb the light absorption of TiO₂ photocatalyst due to the light diffusion even though it has no absorption and no photocatalytic activity due to the wide band gap (ca. 8.2 eV) (**Fig. 7b**). However, when mixing TiO₂ with the Pt(x)/Al₂O₃ catalyst (denoted as Pt(x)/Al₂O₃+TiO₂), this dual catalyst sample exhibited large amount of H₂ generation (**Fig. 7c**). The H₂ production gradually increased with increasing the loading amount of Pt (from 0.1 to 3.0 wt%) on the Al₂O₃ support, and the optimal dual catalyst was the powder mixture of the TiO₂ and Pt(3.0)/Al₂O₃ sample, which led to a 165 μ mol of H₂ production for 30 min. On the other hand, both the single Pt(3.0)/Al₂O₃ sample and bare Al₂O₃ sample in the absence of TiO₂ photocatalyst (**Fig. 7d**) gave no H₂ production, indicating that coexistence of the TiO₂ photocatalyst and Pt NPs loaded on the Al₂O₃ carrier is necessary for the large amount of H₂ production. In some previous studies, similar results were also found that when Pt black powder or commercial Pt NPs powder mixed with TiO₂ powder, an improved H₂ evolution was observed compared to the bare TiO₂ sample [17,18].

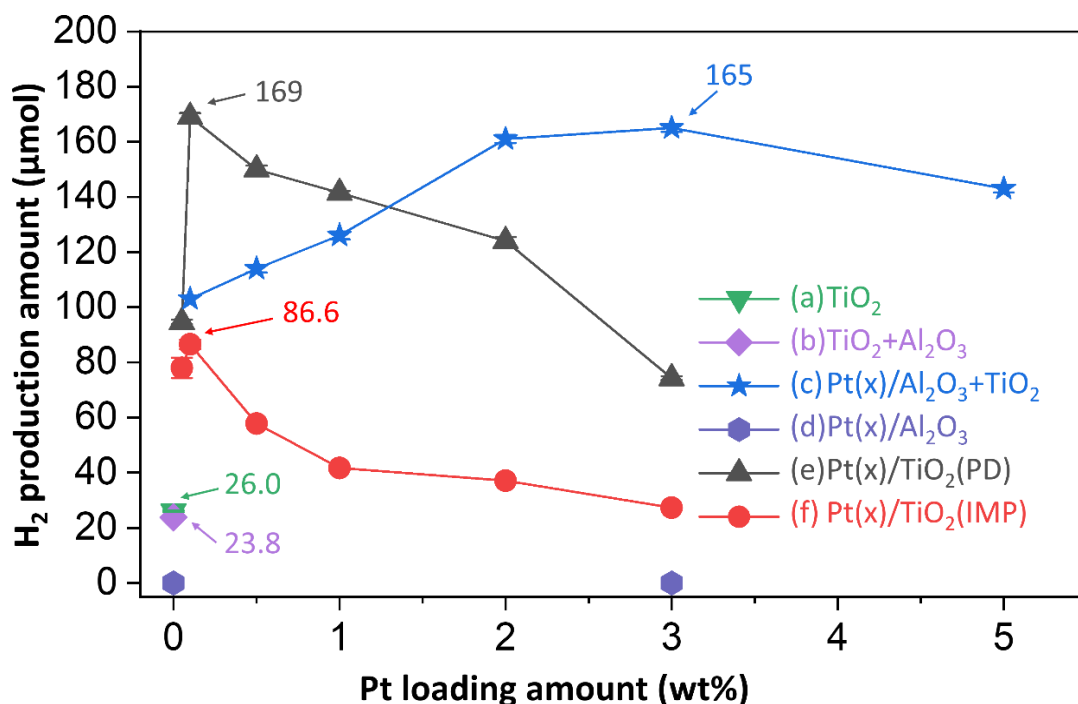


Fig. 7 Photocatalytic production amount of hydrogen for 30 min from aqueous methanol (4 mL, 40 vol%) with various catalyst samples. The weight of catalyst sample was 25 mg for each single catalyst (TiO₂, Al₂O₃, Pt(x)/TiO₂(PD), Pt(x)/TiO₂(IMP), and Pt(3.0)/Al₂O₃) and 50 mg (25 mg each) for the dual catalysts (TiO₂+Al₂O₃ and Pt(x)/Al₂O₃+TiO₂). The incident light wavelength was ≥ 360 nm; Irradiated light intensity was 30 mW cm⁻² when measured at 360 ± 20 nm in wavelength. Results of most of the samples are shown with error bars, except for the Pt(1.0)/TiO₂(IMP), Pt(2.0)/TiO₂(IMP), Pt(3.0)/TiO₂(IMP), Al₂O₃, and Pt(3.0)/Al₂O₃ samples. Error bars represent standard deviation of the H₂ production amount, which are smaller than the symbols in the range of 0.212–3.68.

For the comparison, the Pt(x)/TiO₂(PD) samples (**Fig. 7e**) and the Pt(x)/TiO₂(IMP) samples (**Fig. 7f**) were both applied for the photocatalytic reaction tests. Among the Pt(x)/TiO₂(PD) samples, the highest H₂ production was observed with the Pt(0.1)/TiO₂(PD) sample (169 μmol) and continued to decline due to the possibly aggregation of Pt particles. The Pt(x)/TiO₂(IMP) samples showed a relatively low performance even compared with mixture of Pt(x)/Al₂O₃ and TiO₂ samples of the same Pt loading amount, which will be discussed here.

Fig. 8 shows Pt L_{III}-edge XANES spectra of the Pt(3.0)/TiO₂(IMP) and Pt(3.0)/Al₂O₃+TiO₂ samples, before and after the photocatalytic reaction test. In both samples, Pt species were loaded with calcination and reduction. For both samples before the photocatalytic reaction tests, the shape of XANES spectra was almost same to each other and different from that of metallic Pt foil, suggesting that Pt species existed in the form of Pt oxide similarly (**Fig. 8A**). After the photocatalytic reaction test, these samples exhibited obvious changes in the spectra which were similar to metallic one (**Fig. 8A**). The 1st derivative of Pt L_{III}-edge XANES spectra (**Fig. 8B**) revealed that the oxidized Pt species on both catalyst samples were partially reduced after using in the photocatalytic reactions, where the oxidation state of Pt species on TiO₂ surface was more closed to metallic Pt(0) than that on the Al₂O₃ surface. According to the estimation in **Fig. 9**, after photocatalytic reactions, the ratio of Pt to PtO₂ was close to 8:2 for Pt(3.0)/TiO₂(IMP), and 6.5:3.5 for the Pt(3.0)/Al₂O₃+TiO₂ sample. It is explained that the Pt species on the TiO₂ photocatalysts was reduced by the photoexcited electrons (e^-) supplied from the TiO₂ surface during the photocatalytic reactions [19,20]. Note that the reduction of the Pt species also occurred not only on the TiO₂ surface but also on the Al₂O₃ surface although the Pt species on the Al₂O₃ support was less reduced than that directly deposited on the TiO₂ surface. This implies two possibilities; one is the potential contact of TiO₂ particles to the Pt NPs on the Al₂O₃ support allowing the electron transfer from the former to the latter and another is that the hydrogen radical can migrate and reach the Pt species on the Al₂O₃ support to reduce them. This also will be discussed later.

Another possible reason for the lower H_2 production activity observed in the $Pt(x)/TiO_2(IMP)$ samples, compared to the $Pt(x)/Al_2O_3+TiO_2$ samples, could be the drastic changes in state of TiO_2 caused by the calcination at 773 K. This is supported by the observed decrease of the BET specific surface area (S_a) of $Pt(3.0)/TiO_2(IMP)$, which dropped from $300\text{ m}^2\text{ g}^{-1}$ into $98.0\text{ m}^2\text{ g}^{-1}$ after calcination (**Table 1**) [21]. Whereas the BET specific surface area of the $Pt(3.0)/Al_2O_3$ support was not changed by the calcination ($180\text{ m}^2\text{ g}^{-1}$) and it was larger than the calcined TiO_2 (**Table 1**), allowing high dispersion of Pt on the Al_2O_3 support. And the relatively high surface area of Al_2O_3 support may assist the formation of hydrogen molecules, which will be mentioned later [22].

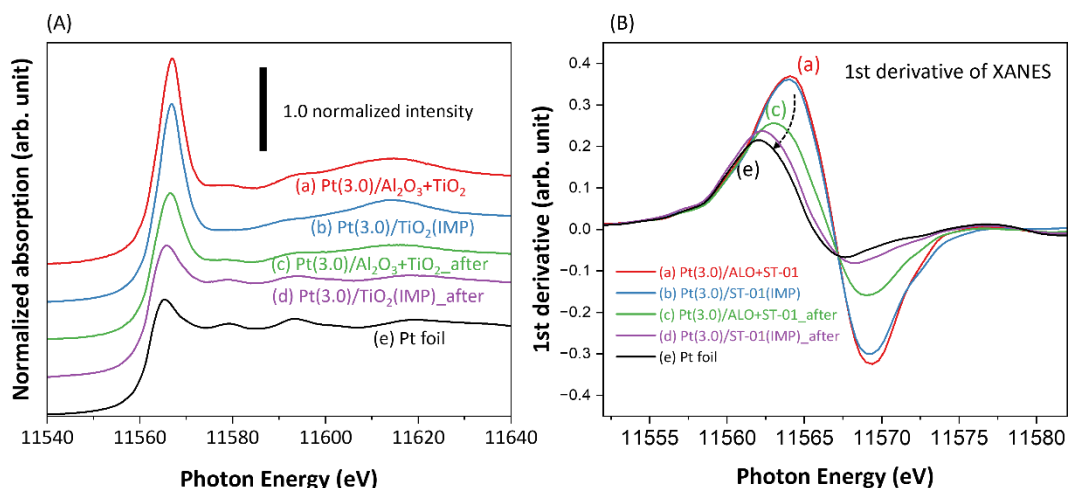


Fig. 8 (A) Pt L_{III}-edge XANES spectra of the $Pt(3.0)/TiO_2(IMP)$ sample and the dual $Pt(3.0)/Al_2O_3+TiO_2$ sample before and after the photocatalytic reaction tests in the aqueous methanol solution and (B) their 1st derivative curves. For both $Pt(3.0)/TiO_2(IMP)$ and $Pt(3.0)/Al_2O_3+TiO_2$ samples, it was indicated that the Pt was reduced after the photocatalytic reaction tests, although the oxidation state of Pt species on TiO_2 surface was more closed to metallic Pt(0) than that on the Al_2O_3 surface.

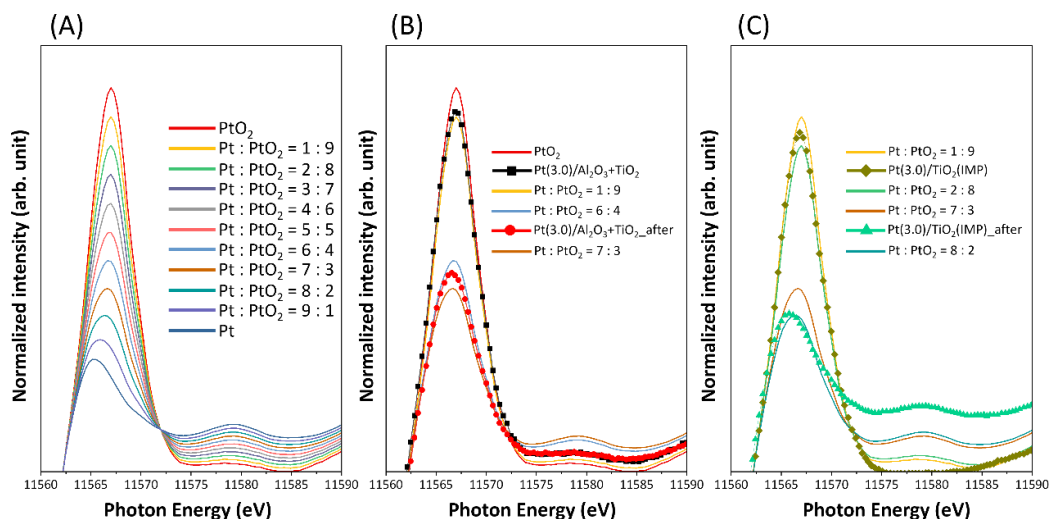


Fig. 9 (A) Simulated Pt L_{III}-edge XANES spectra with different composition of Pt and PtO_2 . The spectrum of Pt used for the calculation was that of a Pt foil, the spectrum of PtO_2 was that of the $Pt(3.0)/Al_2O_3$ sample prepared by the impregnation method (2.1 Catalyst preparations) but without proceeding H_2 reduction. The calculated spectra were plotted by summing the spectra of Pt and PtO_2 with different ratio. (B) XANES spectra of the $Pt(3.0)/Al_2O_3+TiO_2$ sample before and after the photocatalytic reaction test in the aqueous methanol solution. The ratio of Pt to PtO_2 before the reaction test was 1:9, that after the reaction test was 3.5:6.5. (C) XANES spectra of the $Pt(3.0)/TiO_2(IMP)$ sample before and after the photocatalytic reaction test in the aqueous methanol solution. The ratio of Pt to PtO_2 before the reaction test was close to 2:8 while that after the reaction test was 8:2 approximately.

4.3.2 Acetic acid solution

Photocatalytic decomposition of acetic acid to methane (CH₄) and carbon dioxide (CO₂) has been known as photo-Kolbe reaction (eq. 6) [23–25], which involves hydrogen radical formation as an intermediate. It starts with hole oxidation of acetic acid to form carbon dioxide (eq. 7) and reduction of proton (eq. 3), followed by radical-radical coupling of hydrogen radical and methyl radical to form methane (eq. 8) and methyl radical coupling can give ethane depending on the conditions [26,27]. During this photo-Kolbe reaction in aqueous solution, if coupling of hydrogen radical takes place, H₂ can be formed as a byproduct (eq. 4).



Table 2 shows the results of the photocatalytic reaction tests in an aqueous solution of acetic acid. Here, we used the Pt loaded catalyst samples showing the best performance in the H₂ evolution tests from the methanol solution, *i.e.*, the Pt(0.1)/TiO₂(PD) photocatalyst and the Pt(3.0)/Al₂O₃+TiO₂ catalyst, as well as the samples of the comparable Pt loading amount, the Pt(3.0)/TiO₂(PD) and Pt(3.0)/TiO₂(IMP) samples (**Fig. 7**). In this condition, gaseous products detected were limited to H₂, CH₄, and CO₂. Since H₂ and CH₄ were competitively formed by the reaction with hydrogen radical species (eqs. 4 and 8), the reaction selectivity was also listed as S_{H₂} (See the caption of **Table 2** for the definition). The bare TiO₂ photocatalyst gave CH₄ and CO₂ as the main products and H₂ as a minor byproduct (**Table 2, entry 1**), where the inconsistent stoichiometric ratio of products implied formation of other undetected products in the aqueous solution like methanol and other hydroxylated organic compounds [28]. In this result, the reaction selectivity for H₂ production was only 5.9 %. In contrast, the Pt(0.1)/TiO₂(PD) photocatalyst, which exhibited the highest H₂ evolution activity in methanol aqueous solution among all Pt(x)/TiO₂ samples, demonstrated significantly higher activity than the bare TiO₂ photocatalyst (**Table 2, entry 2**). Specifically, it generated 6 times more CH₄, 7 times more CO₂, and 42 times more H₂. The hydrogen selectivity reached 32 %, indicating that the addition of Pt NPs not only extremely improved the activities of TiO₂ photocatalyst for acetic acid decomposition (eq. 6) but also further boosted the H₂ production. On the other hand, the mixture of the Pt(3.0)/Al₂O₃ and TiO₂ samples gave similarly larger numbers of H₂ and CH₄ than the bare TiO₂ photocatalyst, and the H₂ selectivity reached 38 % (**Table 2, entry 3**). The Pt(3.0)/TiO₂(PD) and Pt(3.0)/TiO₂(IMP) photocatalysts, promoted H₂ generation compared to the bare TiO₂, but not as good as the Pt(0.1)/TiO₂(PD) photocatalyst and the combination of the Pt(3.0)/Al₂O₃+TiO₂ catalysts. (**Table 2, entries 4 and 5**)

These results indicate that the presence of Pt in the reaction system significantly enhances the photocatalytic activity, particularly promoting the coupling of two hydrogen radicals (eq. 4) over the coupling of methyl and hydrogen radicals (eq. 8). In other words, Pt preferentially catalyzes the coupling of hydrogen radicals to form H₂. And to achieve the best performance in these conditions, the required loading of Pt cocatalyst on the TiO₂ photocatalyst and the Al₂O₃ support were 0.1 and 3.0 wt%, respectively. These would be explained by the difference of the function: In the former, Pt cocatalyst function as both electron receiver and catalyst while the latter works as catalyst.

Moreover, the combination of Pt/Al₂O₃ with TiO₂ boosted overall photocatalytic performance by improving the hole oxidation of acetic acid (**Table 2, entry 3**). This suggested that the TiO₂ fine particles (ca. 7 nm in size) could directly contact with the Pt NPs loaded on the Al₂O₃ support, donating photoexcited electrons to the Pt NPs. Consequently, the TiO₂ photocatalyst could efficiently utilize holes to oxidize acetic acid, producing CH₄ and CO₂. However, the improved selectivity to H₂ formation supports an alternative possibility of hydrogen radical migration from TiO₂ photocatalyst to Pt NPs. The higher amount of H₂ production and S_{H₂} observed with the Pt(3.0)/Al₂O₃+TiO₂ sample (**Table 2, entry 3**) compared to the Pt(0.1)/TiO₂(PD) sample (**Table 2, entry 2**) would be attributed to the larger loading amount of Pt NPs catalyst and potentially higher dispersion of Pt NPs on the

Al₂O₃ support with the high specific surface area (**Table 1**). The Pt(3.0)/Al₂O₃ sample did not yield any gaseous products in the absence of TiO₂ photocatalyst (**Table 2, entry 6**), meaning that it cannot form any radical species from acetic acid under the light irradiation.

Table 2 Photocatalytic H₂ production from aqueous acetic acid over various catalyst samples. ^a

Entry	Catalysts	Product / μ mol			S _{H₂} (%) ^b
		H ₂	CH ₄	CO ₂	
1	TiO ₂	0.201	6.43	4.74	5.88
2	Pt(0.1)/TiO ₂ (PD)	8.61	36.2	33.3	32.2
3	Pt(3.0)/Al ₂ O ₃ +TiO ₂	9.48	30.9	30.2	38.0
4	Pt(3.0)/TiO ₂ (PD)	3.42	30.7	27.5	18.2
5	Pt(3.0)/TiO ₂ (IMP)	2.37	28.9	26.6	14.1
6	Pt(3.0)/Al ₂ O ₃	0	0	0	/

^a 4 mL of 20 vol% of aqueous acetic acid was used. Reaction time was 30 min. For reactions with a single catalyst (**entries 1, 2, and 4–6**), the weight of catalyst was 25 mg; For reactions with the dual catalyst sample (**entry 3**), 25 mg of each catalyst was used; The incident light wavelength was ≥ 360 nm; Irradiated light intensity was 30 mW cm⁻² when measured at 360 ± 20 nm in wavelength. ^b Selectivity to H₂, based on the generated hydrogen radical: $S_{H_2}(\%) = 100 \times 2N_{H_2}/(2N_{H_2} + N_{CH_4})$, where N_{H_2} and N_{CH_4} are the obtained amount of H₂ and CH₄, respectively.

4.3.3 A flow system

From the results in the above two H₂ generation reaction systems, roles of Pt NPs sites should be divided into 3 parts, *i.e.*, receiving electrons from the photoexcited TiO₂ according to the potential difference (eq. 2), reducing protons by the electrons (eq. 3), and catalyzing the coupling of hydrogen radicals (eq. 4). In the present study, a flow reactor was employed to elucidate the third role of the catalytic sites in coupling hydrogen radical species more clearly.

In this reaction system, to avoid the possible direct contact providing interparticle electron transfer from the photoexcited TiO₂ surface to Pt NPs and successive reduction of protons (eqs. 2 and 3), the quartz wool layer was added between the TiO₂ granules and the Pt(3.0)/Al₂O₃ granules, and the length of this quartz wool layer in millimeter order was defined as the distance between these two catalysts (**Fig. 10**). **Fig. 11A** displays the H₂ formation rate obtained in several setups with various distance between the TiO₂ and Pt(3.0)/Al₂O₃ samples and so on. The combination of the TiO₂ and Pt(3.0)/Al₂O₃ samples with and without quartz wool layer (**Fig. 11A(a–e)**) showed higher H₂ production rate than both the TiO₂ photocatalyst without Pt NPs and the bare Al₂O₃ support (**Fig. 11A(f and g)**). It is worth noting that even though the Pt NPs were spatially separated from TiO₂ surface, the Pt NPs on the Al₂O₃ support contributed to the high H₂ formation rate. Especially, the separated samples with 2 mm of the quartz wool layer (**Fig. 11A(b)**) exhibited 13 times higher H₂ formation rate than that on the TiO₂ sample without the Pt/Al₂O₃ sample (**Fig. 11A(f)**). In this setup, photoexcited electrons cannot reach the Pt NPs on the Al₂O₃ support since both quartz wool (SiO₂) and Al₂O₃ are insulators. This strongly suggests that the free hydrogen radicals generated on the bare TiO₂ photocatalyst should migrate through the quartz wool layer to land on the Pt NPs in the Pt/Al₂O₃ sample, where the Pt NPs catalyzed the coupling of the adsorbed hydrogen radicals to form H₂ molecules (eq. 4). In addition, the H₂ production rate clearly depended on the distance of the two parts, the TiO₂ and Pt(3.0)/Al₂O₃ samples, *i.e.*, the closer distance provided the higher H₂ generation rate. It can be explained that if the photocatalytically formed hydrogen radicals could not become H₂ molecules on the TiO₂ photocatalyst in the absence of Pt NPs, the H• radicals possibly disappear due to the reaction with other molecules such as methanol and formaldehyde (a product of hole oxidation of methanol) and other H• radical, during the migration. The mixture of the TiO₂ photocatalyst and the Pt(3.0)/Al₂O₃ catalyst showed higher H₂ formation (**Fig. 11A(h)**), which is quite

reasonable because the mixture had more closed distance between TiO_2 photocatalyst and Pt NPs and reduced the vein disappearance of the formed $\text{H}\cdot$ radicals. The $\text{Pt}(0.1)/\text{TiO}_2(\text{PD})$ photocatalyst showed the best H_2 production rate among them (**Fig. 11A(i)**) according to the efficient transfer of electrons from the photoexcited TiO_2 to the Pt NPs deposited on the surface (eq. 2) and the efficient reduction of protons to $\text{H}\cdot$ radicals (eq. 3) and successive their coupling on the same surface of the Pt NPs (eq. 4), which provides efficient use of the photogenerated electrons and $\text{H}\cdot$ radicals on the Pt NPs catalyst to form H_2 molecules.

When the amount of the $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ granules increased from 0 to 25 mg in the spatially separated system, the H_2 evolution was also enhanced (**Fig. 11B**). A small amount of the $\text{Pt}/\text{Al}_2\text{O}_3$ sample such as 10 mg was not enough to convert all available $\text{H}\cdot$ radicals to H_2 and 25 mg of the sample was enough for full conversion of $\text{H}\cdot$ radicals to H_2 at the distance of 4 mm. More than 25 mg of the $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ granules showed no positive effect for H_2 evolution anymore.

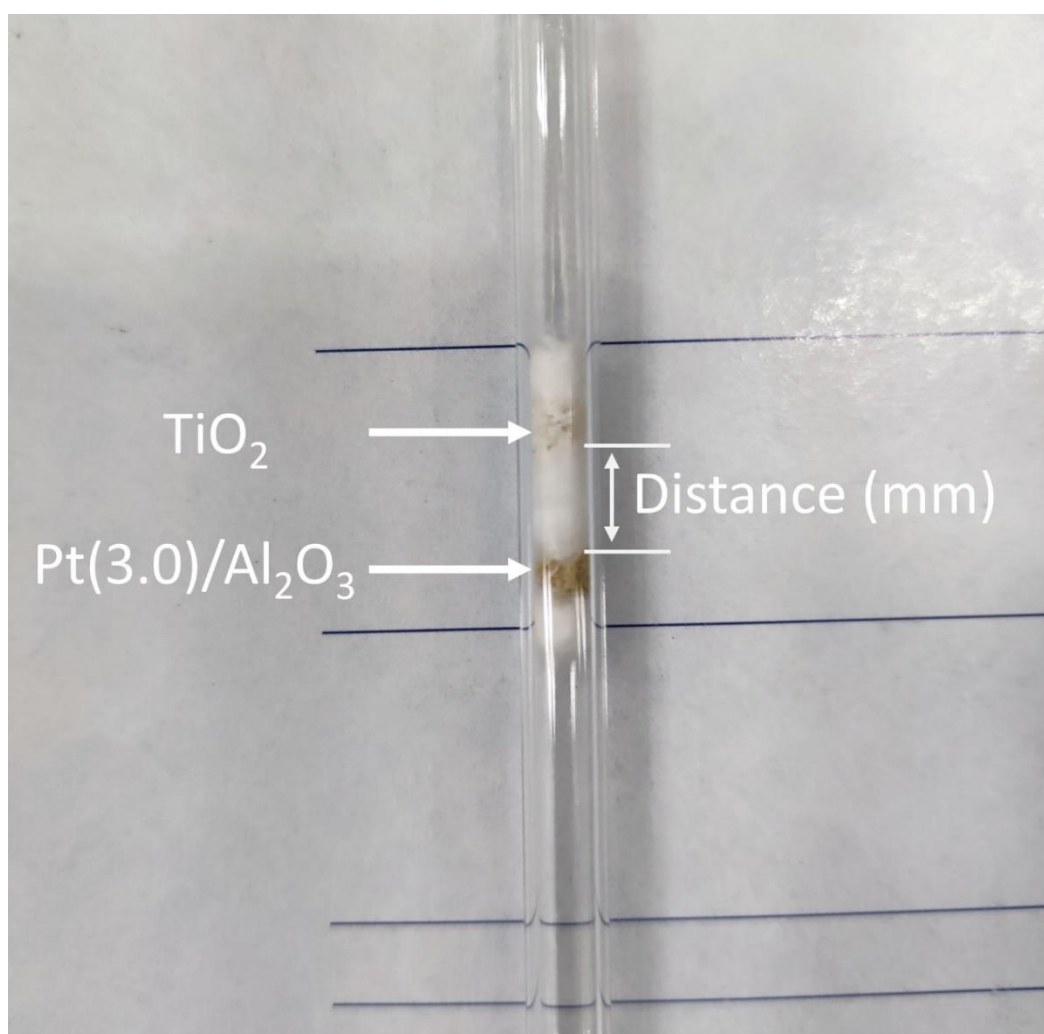


Fig. 10 An example of the catalysts setup for the flow reactor. 25 mg of the TiO_2 granules and 25 mg of the $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ granules were applied. The length of the inserted quartz wool layer, defined as distance between the sample layers, was 8 mm in this figure.

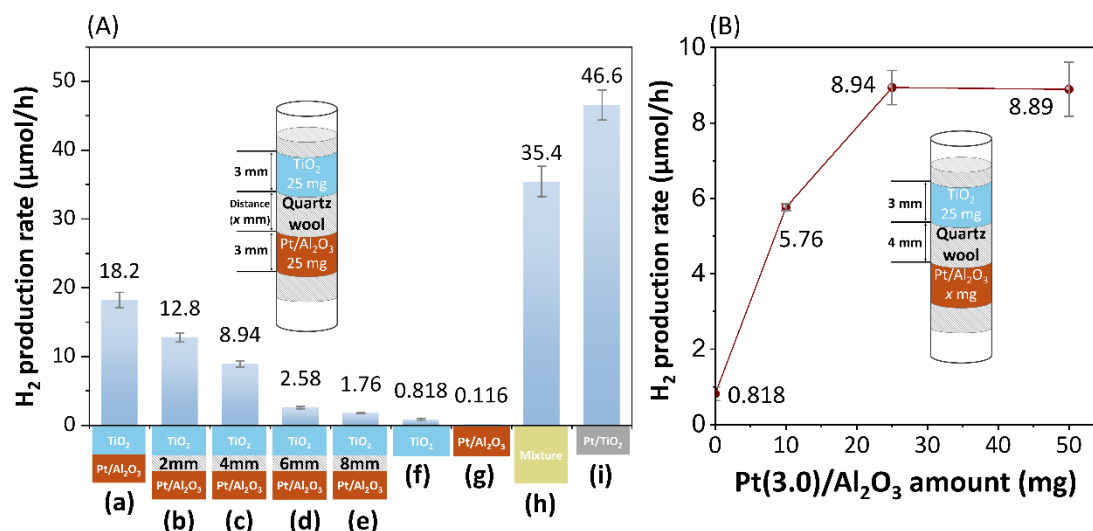


Fig. 11 Photocatalytic hydrogen production from gaseous methanol and water over various setups of catalyst samples. (A) Combination of the TiO₂ and Pt(3.0)/Al₂O₃ samples (25 mg of granules with 3 mm of thickness for each) with various distance of (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 mm between them provided by the quartz wool layer as well as (f) the TiO₂ sample, (g) the Pt(3.0)/Al₂O₃ sample, (h) the physical mixture of the TiO₂ and Pt(3.0)/Al₂O₃ samples (25 mg of granules for each, 6 mm of thickness), and (i) the Pt(0.1)/TiO₂(PD) sample (25 mg of granules, 3 mm of thickness). (B) The effect of the weight of the Pt(3.0)/Al₂O₃ sample (10, 25, and 50 mg of granules samples with the thickness of 1.2, 3, and 6 mm, respectively) in the combination with the TiO₂ (25 mg of granules with 3 mm of thickness) and 4 mm of the quartz wool layer, where the plot at 0 mg of the Pt(3.0)/Al₂O₃ sample corresponds to the use of only the TiO₂ sample shown in **Fig. 11A**f. Reaction conditions: The total flow rate was 10 mL min⁻¹ and flow rates of methanol and water were 940 and 594 μmol/h, respectively; The incident light wavelength was ≥ 360 nm; Irradiated light intensity was 50 mW cm⁻² that was measured at 360 ± 20 nm in wavelength. The gas sampling was carried out at 30 min after the start of the photoirradiation. Error bars represent standard deviation of the H₂ production rate from several reactions. Data for most of the samples, except the Al₂O₃ sample, are shown with error bars. Error bars represent standard deviation of the H₂ production rate, the range is 0.0636–2.19.

4.4 Discussion

In a literature, Joo, et al., proposed the role of metal nanoparticles such as Au NPs as a catalyst for coupling of hydrogen radical to produce H₂ molecules in photocatalytic water splitting. In their study, an Au@SiO₂ core-shell material mixed with TiO₂ photocatalyst enhanced H₂ production from 10 vol% of methanol aqueous compared with pure TiO₂ photocatalyst, which is similar results to the present study. Hydrogen radicals migrate through SiO₂ shell of nanometer scale such as 15 nm. In the present study, at first, a physical mixture of TiO₂ photocatalyst and Al₂O₃-supported Pt NPs was examined in magnetically stirred aqueous solutions of methanol and acetic acid, where Pt NPs were confirmed to function as a catalyst for H₂ evolution (**Fig. 7** and **Table 2**) but the physical contact between the metal and TiO₂ photocatalyst was also suggested by the decreased charge recombination and the increased hole oxidation to form CH₄ and CO₂ on the TiO₂ photocatalyst in the presence of the Al₂O₃-supported Pt NPs in the aqueous solution of acetic acid (**Table 2, entry 3**). When a flow reactor system was utilized to spatially separate the TiO₂ photocatalyst and the Al₂O₃-supported Pt NPs by quartz wool on the millimeter scale, it was observed that hydrogen radicals generated on TiO₂ photocatalyst could migrate through the quartz wool layer along with the reactant mixture. These hydrogen radicals subsequently recombined into H₂ molecules via catalysis on the Pt NPs. The distance between the TiO₂ photocatalyst and Pt NPs, ranging from 0 mm to 8 mm, significantly influenced the rate of H₂ production. These results evidenced that hydrogen radicals can survive millimeter-scale distances in the presence of quartz wool, methanol, and other reactants. However, their concentration gradually diminished due to reactions with species such as methanol, formaldehyde, and possibly other hydrogen radicals, within both the TiO₂

and quartz layers (see **Fig. 11A(f)**). Further, the fact that catalytic conversion was well related to the amount of the Pt(3.0)/Al₂O₃ granules (**Fig. 11B**) supports the role of Pt NPs to adsorb hydrogen radicals and catalyze the coupling, where the Al₂O₃ support of high specific surface area may assist the adsorption and migration of hydrogen radicals to the Pt NPs in a reverse spillover process [22].

Based on these observations in our study and past literature, we propose plausible mechanisms for the enhanced H₂ production from aqueous methanol with a physically and spatially separated dual catalysts. Firstly, in an aqueous solution, the reactions take place on physical mixture of TiO₂ photocatalyst and Pt/Al₂O₃ catalyst in two mechanisms as described below.

One is the electron transfer mechanism on a physical contact model (**Fig. 12A**). (i) The photoexcitation of the TiO₂ photocatalyst generates electrons (e^-) and holes (h^+) and both of them move to the TiO₂ surface if they survive by avoiding the recombination. (ii) The holes at the surface can oxidize methanol molecules (CH₃OH) to give protons (H⁺) and oxidized products such as formaldehyde (HCHO). While an interparticle electron transfer from the TiO₂ surface to the Pt NPs on Al₂O₃ surface occurs due to a sufficient contact between each catalyst in aqueous solution, then the electrons on the Pt NPs can reduce H⁺ to give hydrogen radical species (H•). (iii) The coupling of two H• radicals on the Pt NPs surface produces one H₂ molecule. In this mechanism, like as conventional Pt/TiO₂ photocatalyst, the Pt NPs on Al₂O₃ function as both electron receivers to suppress the charge recombination and catalysts for the coupling of hydrogen radicals.

Another is the hydrogen radical transfer mechanism for the spatially separate model (**Fig. 12B**). (i) The photogenerated electrons and holes move to the surface of TiO₂ photocatalyst. (ii) The H⁺ is formed through the oxidation of methanol by holes, and the H⁺ is reduced by electron to produce H• radical on the surface of the TiO₂ photocatalyst. (iii) The formed H• radicals migrate and meet on the Pt NPs, where the coupling of radicals catalytically takes place to generate H₂ molecules.

As for the dual catalysts spatially separated with quartz wool in the gas flow reactor (**Fig. 6**), no physical contact can be considered between the TiO₂ photocatalyst and Pt NPs catalyst. In this case, the reaction proceeds in the hydrogen radical transfer mechanism (**Fig. 13**): (i) Upon the photoirradiation, hydrogen radical and oxidized products from methanol are generated in the TiO₂ photocatalyst layer, (ii) The generated H• radical can migrate from the TiO₂ layer to the Al₂O₃ surface in the quartz wool layer providing the distance of a millimeter scale. The number of H• radicals gradually decrease during this migration due to the reaction with molecules such as methanol and other H• radicals to some extent, (iii) H• radicals adsorbed by the Al₂O₃ surface can move to Pt NPs catalyst to form H₂ molecules.

In the present study, the catalytic effect of Pt NPs in photocatalytic H₂ evolution was experimentally evidenced. Here, it should be mentioned that in some novel photocatalytic organic reactions, the catalytic role of metal cocatalyst has been reported: Pd NPs on TiO₂ photocatalyst catalyzed a reaction between benzene molecules and cyanomethyl radical in photocatalytic cyanomethylation [19], and Pt, gold (Au), and palladium (Pd) loaded on Al₂O₃ support were confirmed to similarly catalyze between molecule and radical species to form the target molecules in several photocatalytic reactions such as methylation [30] and cyanomethylation of benzene [31], and cross-coupling with ether [20,32], and also Pd-Au bimetal catalyst for other reactions [33,34]. Thus, it might be a general property of these precious metal NPs, *i.e.*, metal NPs can catalyze the reaction of radical species, including the H• radical. Hopefully, this catalytic property of precious metal NPs in radical-promoting reactions such as photocatalysis will shed light on the development of more efficient heterogeneous catalytic systems in the future.

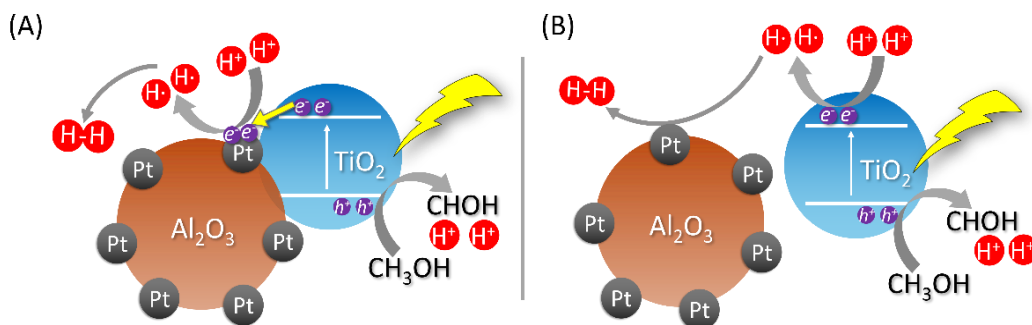


Fig. 12 Two proposed mechanisms of photocatalytic H_2 production with physically separated TiO_2 photocatalyst and $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst in aqueous methanol. (A) the electron transfer mechanism for a physical contact model. In this mechanism, the photogenerated electrons on TiO_2 surface transfer to Pt NPs on Al_2O_3 surface by contact; (B) the hydrogen radical transfer mechanism for a physically separate model. Without any contact, photocatalytically generated $\text{H}^\bullet$ radical species on TiO_2 surface migrate and combine each other to produce H_2 molecules on the surface of Pt NPs catalyst.

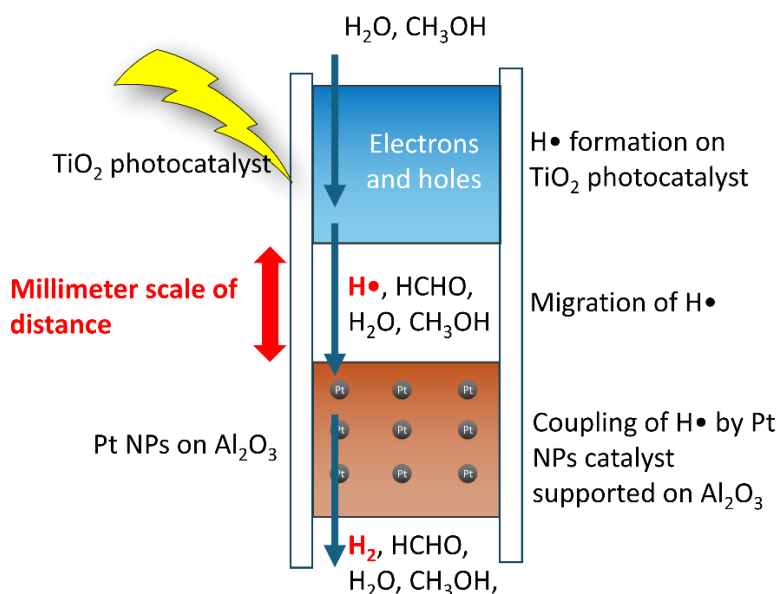


Fig. 13 Proposed reaction scheme in a gas flow reactor for photocatalytic H_2 production in the hydrogen radical transfer mechanism, which evidences the catalytic role of Pt NPs. $\text{H}^\bullet$ radical species formed by the photocatalytic reduction of H^+ on TiO_2 surface can migrate several millimeters to Al_2O_3 support and combine each other to generate H_2 molecules with Pt NPs catalysts.

4.5 Conclusion

Although Pt NPs attached on the TiO_2 surface is widely recognized as the electron receiver from TiO_2 photocatalyst reducing the recombination of electrons and holes to enhance the photocatalytic activity, the present study revealed an additional and critical role for Pt as a catalyst in H_2 evolution. Unique experiments by using a flow reactor with spatially separated catalysts evidenced the catalytic function for H_2 evolution.

While even the powder mixture of TiO_2 and $\text{Pt}/\text{Al}_2\text{O}_3$ highly enhanced H_2 production and selectivity in the reaction systems with aqueous solutions, it was not clearly distinguished the catalytic activity of Pt NPs from the contribution to enhance the charge separation from TiO_2 photocatalyst due to possible physical contact. Employing the flow reactor with spatially separated catalysts, the TiO_2 photocatalyst and the $\text{Pt}/\text{Al}_2\text{O}_3$ sample without contact,

provided clear and unequivocal evidence of the catalytic role of Pt cocatalyst for H₂ evolution. In the conditions, the photocatalytically generated hydrogen radicals can migrate through the intermediate space filled with quartz wool of millimeter scale such as 8 mm and reach the Pt NPs loaded on the Al₂O₃ support, where Pt NPs can act as a catalyst to promote the coupling of hydrogen radicals to release H₂ molecules like as a reverse spillover process. The Al₂O₃ support would assist in collecting the hydrogen radical species by adsorption and supply them to Pt NPs.

This study presents a fresh perspective on the catalytic contribution of Pt NPs to H₂ evolution by promoting hydrogen radical coupling. The findings in this work have broad implications and could be applicable to other photocatalytic systems, thereby advancing the development of efficient photocatalytic H₂ production methods.

4.6 References

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Chapter 5

General conclusion

5.1 Summary of research goals and approach

This thesis sets out to explore innovative photocatalytic methods for transforming small organic molecules using platinum-loaded titanium oxide (Pt/TiO₂). Recognizing the need for selective, efficient, and sustainable chemical transformations, this work examined three distinct reactions: benzene methylation by acetic acid, direct C–N coupling of aniline to aminodiphenylamines, and hydrogen radical coupling catalyzed by Pt nanoparticles with TiO₂ photocatalyst. Each study was designed to probe the capabilities of Pt/TiO₂ photocatalysts in catalyzing reactions under mild conditions, ultimately contributing to the advancement of sustainable photocatalysis.

5.2 Key findings and contributions of this thesis

In this thesis, the author yielded significant findings that highlight the potential of Pt/TiO₂ in diverse catalytic applications:

5.2.1 Benzene methylation by acetic acid

The photocatalytic direct methylation of benzene was developed by using acetic acid as a promising methylation reagent. Over 15% yield of toluene was achieved after 3 h with a Pt/TiO₂ photocatalyst under light irradiation without any extra solvent. The kinetic investigations with isotopic compounds and temperature-controlled experiments elucidated that Pt nanoparticles on the TiO₂ surface have a dual role, *i.e.*, working as an electron receiver to improve the charge separation and catalyzing a radical addition-elimination process to form toluene molecule. Two competitive reaction mechanisms were proposed in this reaction system. This study offered novel insights into aromatic ring methylation method, and hopefully, understanding the dual role of Pt nanoparticles may shed light on developing more efficient heterogeneous catalytic systems in the future.

5.2.2 Direct C–N coupling of aniline to aminodiphenylamines

A photocatalytic direct synthesis route of 2-aminodiphenylamine (2-ADPA) and 4-aminodiphenylamine (4-ADPA) from aniline was examined. In this study, 19.5% of yield and 77.0% of selectivity were achieved after 30 min with Pt/TiO₂ photocatalyst in an NaOH solution of pH = 12.70. The UV-vis spectra revealed a specific adsorption of aniline on the TiO₂ surface which resulted in high selectivity at an incident wavelength of 365 nm. The mechanistic study and others suggested that the aniline can be activated either through oxidation by the photogenerated holes or a single electron transfer from the N atoms in aniline to Ti in TiO₂. A radical addition-elimination mechanism was proposed for this C–N bond coupling reaction. This study demonstrated the potential of Pt/TiO₂ photocatalyst for selective C–N bond coupling, and offered a milder, environmentally friendly approach compared to traditional C–N bond coupling reactions.

5.2.3 Coupling of hydrogen radicals catalyzed by Pt nanoparticles after traveling several millimeters from TiO₂ photocatalyst

For photocatalytic H₂ production reaction, the catalytic role of Pt nanoparticles (NPs) was examined by a simple method using Pt loaded on an Al₂O₃ support, which was physically and spatially separated from TiO₂ photocatalyst. In both photocatalytic reactions with aqueous methanol and acetic acid, it was both found that H₂ production was much enhanced with the mixture sample of TiO₂ and Pt(3.0)/Al₂O₃ when compared to bare TiO₂ sample (6.3 and 47 times). And results in acetic acid suggested that the Pt NPs could not only directly contact with TiO₂ particles and receive photogenerated electrons to improve the formation of methane, but also preferentially enhanced H₂ selectivity (6.5 times) as the bare TiO₂ sample. In a photocatalytic reaction system with a flow of gas

mixture of methanol and water vapor in argon carrier, TiO_2 and $\text{Pt}(3.0)/\text{Al}_2\text{O}_3$ physically and spatially separated in this sequence by a quartz wool layer in millimeter scale (2 mm) gave 13 times higher H_2 production rate than TiO_2 without Pt NPs. We proposed that in such photocatalytic H_2 production reactions, Pt NPs can specifically catalyze the coupling of H radicals to H_2 molecules. This finding is not only interesting from a mechanistic perspective but also highlights potential applications in hydrogenation reactions and other processes involving free radical species.

5.3 Potential implications and limitations of this thesis

The findings of this thesis underscore the versatility of Pt-loaded TiO_2 as a photocatalyst for diverse organic transformations. These studies demonstrate that photocatalysis can provide a selective and energy-efficient alternative to traditional synthesis methods. By enabling reactions under milder, more sustainable conditions, this work contributes to the field of green chemistry and highlights the potential for photocatalytic methods in industrial catalysis and environmental applications.

While this research demonstrates promising results, several limitations warrant consideration. Notably, limited yield and selectivity, the potential successive reactions when prolonged light exposure, and relatively high cost of platinum precursor. Furthermore, the lack of functional group tolerance study, the non-activity in visible light range may pose challenges for scalability. Addressing these limitations will be essential to successfully transition these laboratory-scale findings into practical, large-scale applications.

5.4 Future developments

The findings of this thesis open several avenues for future research: (i) Catalyst development: Further improvements in the Pt-loaded TiO_2 catalyst could focus on enhancing stability and reusability, as well as exploring alternative co-metal loadings to increase activity under visible light. (ii) Expanding reaction scope: Similar photocatalytic approaches could be applied to a broader range of small organic molecules, expanding the scope of functionalization and coupling reactions. This could include reactions with various alkylating agents, amines, or even larger aromatic compounds. (iii) Mechanistic studies: More detailed mechanistic studies on radical dynamics, particularly the long-range coupling observed in the hydrogen radical study, would deepen our understanding of radical interactions in photocatalytic systems and could inspire new applications in hydrogenation and radical coupling reactions.

5.5 Conclusion

In conclusion, this thesis has demonstrated the utility of Pt-loaded TiO_2 photocatalyst in achieving selective, efficient photocatalytic transformations of small organic molecules as representative model cases. By advancing methods that are both sustainable and practical, this research contributes to the growing field of green chemistry and offers promising pathways for future photocatalytic innovations. It is hoped that these findings will inspire continued exploration into photocatalysis, driving forward the development of sustainable solutions for modern chemical synthesis.

List of publications

Chapter 2

- [1] Kexin Zou, Akira Yamamoto, Hisao Yoshida
Benzene methylation by acetic acid with platinum-loaded titanium oxide photocatalyst
Catalysis Today, 2024, **425**, 114354.

Chapter 3

- [2] Kexin Zou, Akira Yamamoto and Hisao Yoshida.
Direct C–N coupling of aniline to aminodiphenylamines with platinum-loaded titanium oxide photocatalyst
Catalysis Science & Technology, 2025, Advance Article [<https://doi.org/10.1039/D4CY01413H>]

Chapter 4

- [3] Kexin Zou, Akira Yamamoto, Hisao Yoshida.
Coupling of hydrogen radicals catalyzed by Pt nanoparticles after traveling several millimeters from TiO₂ photocatalyst
International Journal of Hydrogen Energy, 2024, **91**, 989-996

Other publications

- [4] Akira Yamamoto, Shinsuke Goto, Kexin Zou, Hisao Yoshida
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- [5] Gunik Lee, Riko Maruyama, Kexin Zou, Haifan Huang, Kin-ichi Oyama, Hisao Yoshida, Jun Kumagai
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