NEW CATALYSTS FOR ORGANIC SYNTHESIS DRIVEN BY LIGHT AND EFFICIENT SORBENTS FOR REMOVAL OF RADIOACTIVE IONS FROM WATER

By

Sarina Sarina

BSc. (2006) & MSc. (2009)

Thesis completed under supervision of Prof. Huaiyong Zhu, submitted to Queensland University of Technology, in fulfilment of the requirements for the degree of

Doctor of Philosophy

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May 2013

ABSTRACT

Using sunlight to drive chemical reactions for producing fine chemicals is a great challenge facing scientists today. The core issue within this technology is to devise new photocatalytic processes in which reactions are driven by visible light. However, the commonly used titanium dioxide (TiO_2) photocatalysts appears not feasible for this purpose. TiO_2 photocatalysts absorb mainly ultraviolet (UV) irradiation. UV radiation account for about 4 % of the solar energy and the ability of the photocatalysts to utilise sunlight is limited. To drive reactions for synthesis of fine organic chemicals with sunlight, photocatalysts that can catalyze the reactions under visible and UV irradiation have to be devised. This project aims to develop such new photocatalysts. Since the inability of TiO_2 photocatalysts is intrinsically associated to the semiconductor electron structure, we may search for the new photocatalysts from other materials that absorb light in a different mechanism.

The first photocatalyst we found was gold nanoparticles (AuNPs) supported on zirconia, which can directly reduce nitroaromatic compounds to corresponding azo compounds when illuminated with incandescent light. For instance, 100 % nitrobenzene was reduced in 5 hours at 40°C, and more than 99 % of the product was azobenzene. AuNPs strongly absorb visible light due to the surface plasmon resonance (SPR) effect. The SPR absorption can excite electrons of the AuNPs, which are able to induce breakage of the N-O bonds in the molecules adsorbed on the nanoparticles at moderate temperatures. The reduction activity is sensitive to the intensity of the irradiation and atmosphere of the reaction. This photocatalytic process is a more efficient and greener approach than thermal reactions for the production of aromatic azo compounds, and allowed us to select the unstable intermediate in the thermal reaction.

We extended the application of AuNP photocatalyst into other reduction processes: deoxygenate epoxides to alkenes, reduce ketones to alcohols, and hydrogenate azobenzene to hydroazobenzene were also been realized by Au NP as photocatalysts at ambient temperatures under visible light or sunlight. Most importantly, this study revealed that the photocatalytic ability of such photocatalytic processes can be changed

by tuning wavelength of the incident light. The wavelength determined the energy of the excited electrons as well as their distribution over the high energy levels of Au NPs. The shorter the wavelength is, the higher the energy of the excited electrons. The electrons excited by light with wavelengths longer than 600 nm were only able to induce the reduction of azobenzene (reduction potential -1.1 eV), but could not induce the reduction of molecules with more negative reduction potentials, for example acetophenone and styrene oxide (-1.9 eV and -2.4 eV respectively). Obviously, the wavelength of light determined the reduction power of the Au NP photocatalysts. As the SPR absorption of the Au NPs is very weak in the range longer than 650 nm, the conversion of all the three reactants was negligible. This confirms again that the SPR absorption of Au NPs is essential to the catalytic activity.

Fully understanding on light absorption property and photocatalytic activity of noble metal NPs (mainly Au and Ag) not only allow us to develop SPR effect based new photocatalysts, but also provide the potential to design new photocatalyst structures of unprecedented efficiency. One approach that may be effective was to incorporate a metal component with an intrinsic catalytic ability into a Au NP to catalyze various chemical reactions with sunlight. Palladium (Pd) is known to be catalytically active for many reactions of important organic synthesis.

In our latest study, we developed a highly efficient photocatalyst structure of supported nanoparticles (NPs) of gold and palladium alloys that utilized incident light energy to catalyse the chemical syntheses at ambient temperatures. The alloy NPs strongly absorb both visible and UV light, energizing the alloy's conduction electrons. The energetic electrons of palladium sites at the NP surface significantly enhanced the intrinsic catalytic activity of palladium at ambient temperatures, which allowed the alloy NPs to efficiently catalyse numerous reactions such as: Suzuki-Miyaura cross coupling, oxidative addition of benzylamine, selective oxidation of aromatic alcohols to corresponding aldehydes and ketones, and phenol oxidation (under visible light). The performance of the photocatalysts depended on the Au:Pd ratio. The optimum performance for several reaction was observed when the molar ratio of Au:Pd is 1:1.86. We estimated the extent of the electron redistribution between Au and Pd, using a free electron gas model and work functions of Au and Pd, the redistribution approached its maximum at the ratio of 1:1. 86. It is also found that for the reactions when conducted in the dark Pd NPs exhibit substantial activity and even Au NPs show a low activity, the Au-Pd alloy NPs exhibited superior photocatalytic activity to both Au NPs and Pd

NPs. This revealed that the intrinsic catalytic activity of palladium has been significantly enhanced in the alloy NPs even at ambient temperature under light irradiation. This provided a general guiding principle for determining the applicability of the alloy NP photocatalysts as well as a clue for designing suitable photocatalysts made from gold alloyed with other transition metals. The knowledge acquired in this study may inspire further studies in new efficient photocatalysts and a wide range of organic synthesis driven by sunlight.

Except the noble metal nanoparticle photocatalysts, this thesis also includes development of new class of photocatalysts – surface complex grafted metal nanoparticles for radical induced selective oxidation of alkyl aromatics under light irradiation. The working mechanism is totally distinct from known semiconductor or noble metal nanoparticle photocatalyst. The selective oxidation of stable compounds such as toluene and xylenes to useful chemicals with molecular oxygen (O_2) has important applications in fine chemicals and pharmaceuticals production. However, it is difficult to activate stable carbon–hydrogen bonds for reaction under moderate conditions or to control the oxidation at high temperatures. For the approaches trialed to date, improved conversion through increased temperature and pressure significantly decreases product selectivity with runaway reactions giving over-oxidised products (such as CO_2). New means to achieve both higher conversions whilst retaining product selectivity need to be devised. The new class of photocatalysts: metal hydroxide nanoparticles grafted with alcohols, which can efficiently oxidize alkyl aromatic compounds with O_2 using visible or ultraviolet light or even sunlight to generate the corresponding aldehydes, alcohols and acids at ambient temperatures and gave very little over-oxidation. For example, using sunlight, toluene can be oxidized with a 23% conversion after 48 hours exposure with 85% of the product being benzaldehyde, minor amounts of alcohol and caroboxylic acid and only a trace of CO_2. The surface complexes grafted onto metal hydroxides can absorb light, generating free radicals on the surface, which then initiate aerobic oxidation of the stable alkyl aromatic molecules with high product selectivity. This mechanism was distinctly different from those of any known photocatalysts. The process wass also highly selective; for instance, only one of the two methyl groups of xylenes was oxidised (for conversions up to 49%) while the other remains intact. The use of the new photocatalysts as a controlled means to generate surface radicals through light excitation allowed us to drive the production of fine organic chemicals at ambient temperatures with sunlight. This may be especially valuable for temperature-sensitive reactions and is a greener process than many conventional heavy metal and thermal reactions.

Supporting information: In addition to the study on the new photocatalysts, the thesis involves research that developing efficient adsorbent from titanate nanostructures for removal of radioactive ions leaked into water as supporting information. Sodium tri-titanate ($Na_2Ti_3O_7$) nanofibers and nanotubes, consisting of negatively charged layers of TiO_6 octahedra and sodium ions between the layers, were used to purify the water contaminated by radioactive cesium ($^{137}Cs^+$) cations and iodine ($^{125}I^-$) anions. The prompt adsorption of $^{137}Cs^+$ ions from water (*via* ion-exchange with Na^+ ions) eventually triggered structural phase transition or deformation of the titanates, trapping the $^{137}Cs^+$ ions in the nanostructures because of stronger interaction between $^{137}Cs^+$ ions and the very thin TiO_6 octahedra layers. When the titanate nanostructures were dispersed in a silver nitrate solution at a pH above 7, well-dispersed silver oxide (Ag_2O) nanocrystals (5-10 nm in size) formed on them. These Ag_2O nanocrystals firmly anchored on the surface of titanate substrate because the crystals and the substrates join at the surfaces of crystallographic similarity. These Ag_2O nanocrystals can efficiently capture the I^- anions in fluids by forming AgI precipitate that also firmly attach to the adsorbent. The study show that the unique structural features of the titanate nanostructures played key roles in removal and trapping the ions from wastewater.

List of Publications

Journal Publications

1. **Sarina Sarina**, Huaiyong Zhu,* Esa Jaatinen, Qi Xiao, Hongwei Liu, Jianfeng Jia,‡Chao Chen, Jian Zhao, *Enhancing catalytic performance of palladium in gold and palladium alloy nanoparticles for organic synthesis reactions through visible light irradiation at ambient temperatures*, ***J. Am. Chem. Soc.*** 2013, 135, 5793-5801. (IF: 9.907)
2. **Sarina Sarina**, Huaiyong Zhu,* Zhanfeng Zheng, Steven Bottle, Jin Chang, Xuebin Ke, Jin-Cai Zhao, Yining Huang, Andre Sutrisno, Mathew Willans, Guoran Li, *Driving selective aerobic oxidation of alkyl aromatics by sunlight on alcohol grafted metal hydroxides*, ***Chem. Sci.***, 2012, 3, 2138-2146. (IF: 7.525)
3. **Sarina Sarina**, Eric R. Waclawik and Huaiyong Zhu*, *Photocatalysis on Supported gold and silver nanoparticles under ul-traviolet and visible light irradiation*, ***Green Chemistry***, accepted on 23 April, 2013. (IF: 6.32)
4. Dongjiang Yang, **Sarina Sarina**, Huaiyong Zhu,* Hongwei Liu, Zhanfeng Zheng, Mengxia Xie Suzanne V. Smith, and Sridhar Komarneni, *Capturing Radioactive* Cs^+ *and* I^- *from Water with Titanate Nanofibers and Nanotubes*. ***Angewandt Chemie International Edition***, 2011, 50, 10594-10598. (IF: 12.73)
5. Xuebin Ke, **Sarina Sarina**, Jian Zhao, Xingguang Zhang, Jin Chang, Huaiyong Zhu,* *Tuning the reduction power of supported gold nanoparticle photocatalyst for selective reductions by manipulating wavelength of visible light irradiation*, ***Chem. Commun.***, 2012, 48, 3509-3511. (IF: 6.169)
6. Arixin Bo, **Sarina Sarina**, Zhanfeng Zheng, Dongjiang Yang, Hongwei Liu, Huaiyong Zhu,* *Removal of Radioactive Iodine from Water Using* Ag_2O *Grafted Titanate Nanolamina as Efficient Adsorbent,* ***J. Hazad. Mater.*** 2013, 246-247, 199-205. (IF: 4.173)
7. Huaiyong Zhu,* Xuebin Ke, Xuzhuang Yang, **Sarina Sarina**, Hongwei Liu, *Reduction of nitroaromatic compounds on supported gold nanoparticles by visible*

and ultraviolet light, **Angewandt Chemie International Edition**, 2010, *49*, 9657-9661. (IF: 12.73)

8. Xuebin Ke, Xingguang Zhang, Jian Zhao, **Sarina Sarina**, Huaiyong Zhu,* *Selective reductions using visible light photocatalysts of supported gold nanoparticles*, ***Green Chemistry***, 2013, 15, 236-244. (IF: 6.32)
9. Dongjiang Yang, Hongwei Liu, Zhanfeng Zheng, **Sarina Sarina**, Huaiyong Zhu,* *Titanate-based Adsorbents for Radioactive Ions Entrapment from Water*, ***Nanoscale***, 2013, 5, 2232-2242. (IF: 5.914)
10. Zhanfeng Zheng, Jian Zhao, Yong Yuan, Hongwei Liu, Dongjiang Yang, **Sarina Sarina**, Hongjie Zhang, Eric R. Waclawika, Huaiyong Zhu,* *Tuning the Surface Structure of N-Doped TiO2 Nanofibres - an Effective Method to Enhance Photocatalytic Activities of Visible-Light-Driven Green Synthesis and Degradation,* ***Chemistry-A European Journal***, 2013, 19, 5731-5741. (IF: 5.925)
11. Jian Zhao, Zhanfeng Zheng, Steven Bottle, Alison Chou, **Sarina Sarina**, Huaiyong Zhu,* *Highly efficient and selective photocatalytic hydroamination of alkynes by supported gold nanoparticles using visible light at ambient temperature,* ***Chem. Commun.*** 2013, 49, 2676-2678. (IF: 6.169)

Conferences and Presentations

1. **Oral presentation**: GOLD2012 – the 6th International Conference, Tokyo/Japan, Sep. 05~08, 2012.

   Presentation title: *Contribution of Light Irradiation to Reduction of Activation Energy in Gold Nanoparticle Photocatalyzed reactions*

2. **Oral presentation**: ICC 2012 – 15th International Congress on Catalysis 2012, Munich/Germany, July 01~06, 2012.

   Presentation title: *Driving selective oxidation of aromatic alcohols with sunlight using photocatalysts of gold and palladium alloy nanoparticles*

Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature:

Date: 15/10/2013

~~Signature:~~

~~Date:~~

Acknowledgements

I would like to express my sincere gratitude and appreciation to my research supervisor team, Prof. Huaiyong Zhu, Dr. Xuebin Ke and Prof. Ray L. Frost, for their guidance, support and patience towards the completion of this work.

Grateful acknowledgements are to A/Prof. Esa Jaatinen, Prof. Steven Bottle, A/Prof. Eric R. Waclawik, Dr. Dongjiang Yang, Dr. Hongwei Liu, Dr. Zhanfeng Zheng and Prof. Jianfeng Jia for their collaboration, advice and valuable suggestion particularly in the method of conducting a research. Sincere thanks also goes to colleague students: Qi Xiao, Arixin Bo, Jian Zhao, Xingguang Zhang, Yiming Huang, Chao Chen and Jin Chang, who lent me a helping hand in conducting the lab works. My sincere appreciations also extend to Dr. Chris Carvalho, Leonora Newby, Dr. Wayde Martens, Dr. Llew Rintoul and other technicians who have provided assistance at instruments technology. Special thanks to Mr. Tony Raftery, Dr. Thor Bostrom, and Dr. Barry Wood (UQ) for the help with sample characterisation. I wish to thank the QUT Postgraduate Research Awards (PRA) Scholarship for supporting the tuition fee and living allowance. Appreciates also give to the funding from Australian Research Council (ARC) for the research.

Table of Contents

CHAPTER 1:

INTRODUCTION AND LITERATURE REVIEW

1.1 Introductory Remarks

This chapter includes one review articles:

Article 1 is an invited review by Green Chemistry (accepted on April, 2013, impact factor of this journal is 6.32), on the topic of supported noble metal nanoparticle photocatalysts under visible light and UV irradiation. Previously, the LSPR effect of noble metal NPs was utilized almost exclusively to improve the performance of semiconductor photocatalysts (for example, TiO_2 and Ag halides). While recently, a conceptual breakthrough was made: studies on light driven reactions catalysed by NPs of Au or Ag on photocatalytically inactive supports (insulating solids with very wide band gap) have demonstrated that these materials are a class of efficient photocatalysts working on mechanisms distinct from that of semiconducting photocatalysts. Recent progress in photocatalysis using Au and Ag NPs on insulator supports is reviewed in this article. We focus on the mechanism differences between insulator and semiconductor-supported Au and Ag NPs when applied in photocatalytic processes, and the influence of important factors: light intensity and wavelength, in particular estimations of light irradiation contribution, by calculating apparent activation energies of photo reactions and thermal reactions.

1.2 ARTICLE 1

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Photocatalysis on supported gold and silver nanoparticles under ultraviolet and visible light irradiation

Sarina Sarina, Eric R. Waclawik and Huaiyong Zhu*

Published on Green Chem., 2013, 15, 1814-1833.

Contributor	Statement of contribution
Student Author: Sarina Sarina	Collected all related information and references for the review, organised the contents and wrote the manuscript. Re-produced or revised all the figures and schemes for the paper.
Signature	
Date	
A/Prof. Eric R. Waclawik	Revised and polished the manuscript.
Prof. Huaiyong Zhu	Designed the content and structure of the paper, revised and polished the manuscript.

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

_Huaiyong Zhu________ ____________________ ______________________
Name Signature Date

CHAPTER 2:

SUPPORTED NOBLE METAL NANOPARTICLE PHOTOCATALYSTS FOR ORGANIC SYNTHESIS UNDER VISIBLE LIGHT IRRADIATION AT AMBIENT TEMPERATURE

2.1 INTRODUCTORY REMARKS

This chapter includes three articles:

Article 2 (this work published on *Angew. Chem. Int. Ed.* on 2010) is the first report of direct reduction of nitrobenzene to form azo compounds under visible light irradiation at ambient temperature over 3% Au NPs on ZrO_2. We found that over Au NP photocatalysts, series of nitro aromatics were completely reduced in 5 hours under visible light irradiation at 40°C, and the product was found to contain more than 99% azobenzene. This synthesis was conducted by other researchers under high pressure (5~9 bar) from aromatic azo compounds through a two-step, one-pot reaction with catalysts of AuNPs on TiO_2 or CeO_2 at 100 °C or above. In contrast, we realized a direct reduction of nitroaromatic compounds to their corresponding azo aromatic compounds via a photocatalytic process, which allow the synthesis of aromatic azo compounds be a much more controlled, simplified, and greener process. This gold photoreduction demonstrates the potential for utlising sunlight to drive the production of fine chemicals. My major contribution to this work is conducting part of the experiment and verifying the reaction mechanism.

In the article 3 (published in *Chem. Commun.* on 2012), we extended the application of Au NP photocatalyst into other reduction processes based on the finding of article 1. The reactions such as deoxygenate epoxides to alkenes, reduce ketones to alcohols, and hydrogenate azobenzene to hydroazobenzene are also been realized by Au NP as photocatalysts at ambient temperatures under visible light or sunlight. Most importantly, this study revealed that the photocatalytic ability of such photocatalytic processes can be changed by tuning wavelength of the incident light. The wavelength determines the energy of the excited electrons as well as their distribution over the high energy levels of Au NPs. The shorter the wavelength is, the higher the energy of the excited electrons. The electrons excited by light with wavelengths longer than 600 nm are only just able to induce the reduction of azobenzene (reduction potential -1.1 eV), but cannot induce the reduction of molecules with more negative reduction potentials, for example acetophenone and styrene oxide (-1.9 eV and -2.4 eV respectively). Obviously, the wavelength of light determines the reduction power of the photocatalysts. As the SPR absorption of the Au NPs is very weak in the range longer than 650 nm, the conversion of all the three reactants is negligible. This confirms again that the SPR absorption of Au NPs is essential to the catalytic activity.

Fully understanding on light absorption property and photocatalytic activity of noble metal NPs (mainly Au and Ag) not only allows us to develop SPR effect based new photocatalysts, but also provide the potential to design new photocatalyst structures of unprecedented efficiency. One approach that may be effective is to incorporate a metal component with an intrinsic catalytic ability into a gold NP to catalyze various chemical reactions with sunlight. Palladium (Pd) is known to be catalytically active for many reactions of important organic synthesis.

Article 4 (Published on J. Am. Chem. Soc. on 2013) reported a highly efficient photocatalyst structures of supported nanoparticles (NPs) of gold and palladium alloys that utilize incident light energy to catalyse the chemical syntheses at ambient temperatures. The alloy NPs strongly absorb both visible and UV light, energizing the alloy's conduction electrons. The energetic electrons of palladium sites at the NP surface significantly enhanced the intrinsic catalytic activity of palladium at ambient temperatures, which allows the alloy NPs to efficiently catalyse numerous reactions such as: Suzuki-Miyaura cross coupling, oxidative addition of benzylamine, selective oxidation of aromatic alcohols to corresponding aldehydes and ketones, and phenol oxidation (under visible light). The performance of the photocatalysts depends on the Au:Pd ratio. The optimum performance for several reaction was observed when the molar ratio of Au:Pd is 1:1.86. We estimated the extent of the electron redistribution between Au and Pd, using a free electron gas model and work functions of Au and Pd, the redistribution approaches its maximum at the ratio of 1:1. 86. It is also found that for the reactions when conducted in the dark Pd NPs exhibit substantial activity and even Au NPs showed a low activity, the Au-Pd alloy NPs exhibited superior photocatalytic activity to both Au NPs and Pd NPs. This reveals that the intrinsic catalytic activity of palladium is significantly enhanced in the alloy NPs even at ambient temperature under light irradiation. This provides a general guiding principle for determining the applicability of the alloy NP photocatalysts as well as a clue for designing suitable photocatalysts made from gold alloyed with other transition metals. The knowledge acquired in this study may inspire further studies in new efficient photocatalysts and a wide range of organic synthesis driven by sunlight.

2.2 ARTICLE 2

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Reduction of nitroaromatic compounds on supported gold nanoparticles by visible and ultraviolet light

Huaiyong Zhu,* Xuebin Ke, Xuzhuang Yang, Sarina Sarina, and Hongwei Liu

Published on *Angew. Chem. Int. Ed., 2010, 49, 9657-9661.*

Contributor	Statement of contribution
Student Author: Sarina Sarina	Conducted part of the data collection: such as photocatalytic activity test, catalyst recycling test and optimising of reaction atmosphere etc. Also contributed for confirming the intermediate product structure and collected literatures for reaction mechanism study; draw the scheme.
Signature	
Date	
Prof. Huaiyong Zhu	Proposed the idea, designed the study, wrote and revised the manuscript.
Dr. Xuebin Ke	Discovered the photocatalytic reaction, organize and designed the experiments, wrote the manuscript.
Prof. Xuzhuang Yang	Improved the method of catalyst preparation and the photocatalytic activity.
Dr. Hongwei Liu	Provided detailed TEM analysis.

Principal Supervisor Confirmation

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____Huaiyong Zhu____ ______________________ ________________________
Name Signature Date

2.3 ARTICLE 3

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Tuning the reduction power of supported gold nanoparticle photocatalysts for selective reductions by manipulating the wavelength of visible light irradiation

Xuebin Ke, Sarina Sarina, Jian Zhao, Xingguang Zhang, Jin Chang and Huaiyong Zhu*

Published on Chem. Commun., 2012, 48, 3509-3511.

Contributor	Statement of contribution
Student Author: Sarina Sarina	Conducted the data collection of reduction of ketones to alcohols, calculated the contribution of light irradiation to the three reactions and proposed the relationship between activation energy of all reactions and effective wavelength range. Designed and drawn the two figures of reaction mechanism.
Signature	
Date	
Dr. Xuebin Ke	Organize and designed the experiments, wrote the manuscript.
Jian Zhao	Conducted the data collection of hydrogenation of azobenzene and draw the schemes.
Xingguang Zhang	Conducted the data collection of deoxygenation of epoxides to alkenes.
Jin Chang	Contributed for the data analysis.
Prof. Huaiyong Zhu	Proposed the idea, designed the study, wrote and revised the manuscript.

Principal Supervisor Confirmation

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____Huaiyong Zhu_____ ______________________ ________________________
Name Signature Date

2.4 ARTICLE 4

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Enhancing catalytic performance of palladium in gold and palladium alloy nanoparticles for organic synthesis reactions through visible light irradiation at ambient temperatures

Sarina Sarina, Huaiyong Zhu,* Esa Jaatinen, Qi Xiao, Hongwei Liu, Jianfeng Jia, Chao Chen and Jian Zhao

Published on J. Am. Chem. Soc. 2013, 135, 5793-5801.

Contributor	Statement of contribution
Student Author: Sarina Sarina	Organize and designed the experiments, prepared photocatalysts and conducted the data collection of aromatic alcohol oxidation, designed and arranged the data collection of coupling reaction and oxidation of benzylamine, and revealed and confirmed the mechanism of visible light enhancement in the Au-Pd alloy structure. Wrote the manuscript.
Signature	
Date	
Prof. Huaiyong Zhu	Proposed the idea, designed the study, revised the manuscript.
A/Prof. Esa Jaatinen	Provide discussion and calculation data on mechanism and polish the manuscript.
Qi Xiao	Conducted part of the data collection.
Dr. Hongwei Liu	Provided detailed TEM analysis.
A/Prof. Jianfeng Jia	Provide DFT calculation data on mechanism
Chao Chen	Conducted part of the data collection.
Jian Zhao	Conducted part of the data collection.

Principal Supervisor Confirmation

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___Huaiyong Zhu______ ______________________ ________________________
Name Signature Date

CHAPTER 3:

DRIVING SELECTIVE AEROBIC OXIDATION OF ALKYL AROMATICS BY SUNLIGHT ON ALCOHOL GRAFTED METAL HYDROXIDES

3.1 Introductory Remarks

This chapter includes one articles:

Article 5 reported new block of photocatalysts – surface complex grafted metal nanoparticles for radical induced selective oxidation of alkyl aromatics under light irradiation. The working mechanism is totally distinct from known semiconductor or noble metal nanoparticle photocatalyst

The selective oxidation of stable compounds such as toluene and xylenes to useful chemicals with molecular oxygen (O_2) has important applications in fine chemicals and pharmaceuticals production. However, it is difficult to activate stable carbon–hydrogen bonds for reaction under moderate conditions or to control the oxidation at high temperatures. For the approaches trialled to date, improved conversion through increased temperature and pressure significantly decreases product selectivity with runaway reactions giving over-oxidised products (such as CO_2). New means to achieve both higher conversion whilst retaining product selectivity need to be devised. Herein we report a new class of photocatalysts: metal hydroxide nanoparticles grafted with alcohols, which can efficiently oxidize alkyl aromatic compounds with O_2 using visible or ultraviolet light or even sunlight to generate the corresponding aldehydes, alcohols and acids at ambient temperatures and give very little over-oxidation. For example, using sunlight, toluene can be oxidized with a 23% conversion after 48 hours exposure with 85% of the product being benzaldehyde, minor amounts of alcohol and caroboxylic acid and only a trace of CO_2. The surface complexes grafted onto metal hydroxides can absorb light, generating free radicals on the surface, which then initiate aerobic oxidation of the stable alkyl aromatic molecules with high product selectivity.

This mechanism is distinctly different from those of any known photocatalysts. The process is also highly selective; for instance, only one of the two methyl groups of xylenes is oxidised (for conversions up to 49%) while the other remains intact. The use of the new photocatalysts as a controlled means to generate surface radicals through light excitation allows us to drive the production of fine organic chemicals at ambient temperatures with sunlight. This may be especially valuable for temperature-sensitive reactions and is a greener process than many conventional heavy metal and thermal reactions.

3.2 ARTICLE 5

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Driving selective aerobic oxidation of alkyl aromatics by sunlight on alcohol grafted metal hydroxides

Sarina Sarina, Huaiyong Zhu,* Zhanfeng Zheng, Steven Bottle, Jin Chang, Xuebin Ke, Jin-Cai Zhao, Yining Huang, Andre Sutrisno, Mathew Willans, Guoran Li

Published on *Chem. Sci., 2012, 3, 2138-2146.*

Contributor	Statement of contribution
Student Author: Sarina Sarina	Found the oxidation of alkyl aromatics over the new catalyst, conducted most of data collection, proposed the reaction mechanism and designed reactions to confirm the mechanisms. Wrote the manuscript.
Signature	
Date	
Prof. Huaiyong Zhu	Proposed the idea, designed the study, revised the manuscript.
Dr. Zhanfeng Zheng	Analyzed the EPR data.
Prof. Steven Bottle	Give discussion on the mechanism study, revised and polished the manuscript.
Jin Chang	Contributed to FT-IR data analysis.
Dr. Xuebin Ke	Contributed to data analysis.
Jin-Cai Zhao	Give discussion on the mechanism study, revised and polished the manuscript.
Prof. Yining Huang, Andre Sutrisno Mathew Willans,	Provided detailed solid state NMR data and analysis.
Dr. Guoran Li	Contributed to data collection and analysis.

Principal Supervisor Confirmation

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CHAPTER 4: SUPPORTING INFORMATION

CAPTURE OF RADIOACTIVE CESIUM AND IODIDE IONS FROM WATER BY USING TITANATE NANOFIBERS AND NANOTUBES

4.1 INTRODUCTORY REMARKS

This chapter includes two articles:

Article 6 is an invited review by Nanoscale (published on March, 2013. The impact factor of the journal is 5.914). Titanate-based materials, such as crystalline silicotitanate (CST), monosodium titanate (MST), peroxotitanate (PT), sodium trititante (T3), and sodium hexatitanate (T6), have been developed as adsorbents for radioactive ions from water due to their excellent ion-exchange capacities and high stability. In this feature article, we start with a brief discussion of the conventional CST, MST and PT adsorbents, and then summarize the recent process on the removal of radioactive cations and anions by using advanced intelligent T3 and T6 nanoadsorbents, in particular the one-dimensional (1D) nanofibril and nanotubular adsorbents.

The study in article 7 demonstrates that the titanate NTs and NFs are superior materials for removal radioactive ions in water because of their unique structural properties. Their 1D structure provides a large external surface, not only assuring a high removal efficiency even at large feed flux, but also allowing trouble-free separation of the used adsorbents after ion removal for safe disposal. The titanates can uptake large amount of cations because their large exchange capacity. The layers in the nanostructure are so thin that make the layer structure metastable and uptake of large ions can cause phase transition and structural deformation, which can be utilized to trap cations in the nanostructure permanently for safe disposal. Also the surface of the titanate nanostructures have crystallographic similarity to some lattice planes of the Ag_2O and AgI crystals, and these crystals can solidly bonded to the titanate substrates through coherent interfaces. Finally the fibers and tubes can be fabricated readily from TiO_2 with low cost. These structural features that contribute to the uptake and trapping ions can also be useful for developing other efficient adsorbents for the removal of radioactive ions from wastewater.

4.2 ARTICLE 5

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Titanate-based Adsorbents for Radioactive Ions Entrapment from Water

Dongjiang Yang, Hongwei Liu, Zhanfeng Zheng, Sarina Sarina, Huaiyong Zhu*

Published on Nanoscale, 2013, 5, 2232-2242.

Contributor	Statement of contribution
Student Author: Sarina Sarina	Contributed to revising the manuscript and provide part of the figures.
Signature	
Date	
Prof. Dongjiang Yang	Organize and wrote the manuscript.
Dr. Hongwei Liu	Provide all TEM analysis.
Dr. Zhanfeng Zheng	Contributed to structure analysis of the materials, revised the manuscript.
Prof. Huaiyong Zhu	Organize, revised and polished the manuscript.

Principal Supervisor Confirmation

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Huaiyong Zhu		
Name	Signature	Date

4.3 ARTICLE 7

Statement of Contribution of Co-Authors

Publication title and date of publication or status:

Capturing Radioactive Cs^+ and I^- from Water with Titanate Nanofibers and Nanotubes

Dongjiang Yang, Sarina Sarina, Huaiyong Zhu,* Hongwei Liu, Zhanfeng Zheng, Mengxia Xie
Suzanne V. Smith, and Sridhar Komarneni

Published on Angew. Chem. Int. Ed., 2011, 50, 10594-10598.

Contributor	Statement of contribution
Student Author: Sarina Sarina	Synthesized all adsorbent material, completed data collection of all adsorption study, part of the data is collected in ANSTO with radioactive isotops, and draw Figure 1 to the paper.
Signature	
Date	
Prof. Dongjiang Yang	Organize and designed the experiments, wrote the manuscript
Prof. Huaiyong Zhu	Proposed the idea, designed the study, revised the manuscript.
Dr. Hongwei Liu	Provide all TEM analysis.
Dr. Zhanfeng Zheng	Contributed to structure analysis of the materials, revised the manuscript.
Prof. Mengxia Xie	Conducted ICP measurement of the Cs^+ ions.
Prof. Suzanne V. Smith	Supervise the experiment in ANSTO.
Prof. Sridhar Komarneni	Revised and polished the manuscript.

Principal Supervisor Confirmation

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CONCLUSIONS & FUTURE WORK

The main results of the research in this thesis are concluded as below:

1. AuNP absorb visible light by SPR effect, and the high energetic electrons can drive photocatalytic reactions including both oxidation and reduction. The direct reduction of nitroaromatic compounds to their corresponding azo compounds, realized by a photocatalytic process over AuNPs catalysts under light irradiation at moderate reaction condition, this allows the synthesis of aromatic azo compounds by a more controlled, simplified, and greener process.
2. To better understand the common feature of visible light driven reduction process on supported AuNP photocatalysts, the application of AuNP is successfully extended to three other reduction processes: deoxygenate epoxides to alkenes, reduce ketones to alcohols, and hydrogenate azobenzene to hydroazobenzene, which are also been realized by AuNP as photocatalysts at ambient temperatures under visible light or sunlight. An important correlation between the irradiation wavelength and the reduction ability of AuNP is revealed firstly: the electrons excited by light with wavelengths longer than 600 nm are only just able to induce the reduction of azobenzene (reduction potential -1.1 eV), but cannot induce the reduction of molecules with more negative reduction potentials, for example acetophenone and styrene oxide (-1.9 eV and -2.4 eV respectively). While the light with wavelength longer than 550 nm could drive the reduction of acetophenon and azobenzene, but cannot drive the styrene oxide deoxygenation. This is because the wavelength determines the energy of the excited electrons as well as their distribution over the high energy levels of AuNPs. The shorter the wavelength is, the higher the energy of the excited electrons. These results demonstrated that the photocatalytic ability of such photocatalytic processes over noble metal NPs can be changed by tuning wavelength of the incident light, which is a distinct feature compared with the traditional semiconductor photocatalysts. Similar law should be found in oxidation process. We described in our previous study that, Au NPs can absorb both UV and visible light but in different mechanisms. Under visible light irradiation, part of the conduction electrons in the 6sp band of surface Au NPs, get energy from light by the SPR effect, and migrate to the higher energy level of 6sp band, this is an intraband migration. Since some

electrons shifted to higher energy level, there must be some positively charged vacancies are left in the lower energy level. These positive vacancies can capture electrons from organic molecule adsorbed on them and oxidize it. While, the UV light is much more powerful than visible light, so it can excite the 5d electrons to the 6sp electron band, we call this interband excitation of electrons. This resulted the positive vacancies are left in the 5d electron band. This means we can adjust the wavelength of incident light we use for reaction to control the catalytic ability of Au NPs in oxidation reactions. A new study should be proposed that can correlate the irradiation wavelength and the photocatalytic ability of Au NPs in various oxidation reactions. Degradation of SRB, oxidation of methanol and formaldehyde can be processed over 3% Au NPs supported on ZrO_2 under visible light irradiation with optical filters are used to block irradiation below a certain wavelength, for example, if we use a filter of 490nm cut-off wavelength, means the reaction will be driven by the light with wavelength between 490nm-800nm (by filtering out wavelength shorter than 490nm). This future work aims to extend the unique feature of Au NP photocatalysts – wavelength controllable photocatalytic activity – into oxidation process and thus will give out the possibility of application in more organic synthesis.

3. An effective approach to broad the application of AuNP photocatalysts is to incorporate a metal with an intrinsic catalytic ability as an alloy with the Au NP base, to catalyse various chemical reactions with sunlight. For example, palladium (Pd) is known to be catalytically active for many reactions of important organic synthesis because of its affinity to many organic molecules. We successfully realized the coupling of light absorption of AuNP and catalytic property of Pd in alloy structure and drive several kinds of organic reactions, such as Suzuki-Miyaura coupling, oxidative addition of benzylamine to form imine, selective oxidation of aromatic alcohols and phenol degradation. This provides a general guiding principle for determining the applicability of the alloy NP photocatalysts as well as a clue for designing suitable photocatalysts made from gold alloyed with other transition metals. The knowledge acquired in this study may inspire further studies in new efficient photocatalysts and a wide range of organic synthesis driven by sunlight. The component of the new photocatalysts, especially the light harvesting component, should not be limited to Au only. Many other noble metal

NP with SPR effect, for example, Ag and Cu, can also be alloyed with Pd to form new photocatalyst structure.

4. The surface complexes grafted onto the metal hydroxide surface are stable and able to absorb main components of sunlight: visible and UV light. The surface complex catalyze the selective oxidation by an efficient mechanism that employs light absorption by the complexes to yield highly reactive surface radicals ($–O–\dot{C}H_2–R$), and these surface radicals initiate the aerobic oxidation of the organic molecules in contact with them. By this pathway this new photocatalytic oxidation process is able to oxidize aliphatic C–H bonds associated with α-hydrogens in stable alkyl aromatics and aromatic alcohols at ambient temperature and pressure. The process is selective, in that toluene can be oxidized to benzaldehyde and lesser amounts of benzoic acid and benzyl alcohol, and only one of the methyl groups of xylenes is oxidized, with the other group remaining unchanged. The oxidation ability of the photocatalysts can be tuned through selection of the metal element and the alcohols grafted. The reaction speed of the selective oxidation using the new photocatalysts is unsatisfactory, research aiming to increase the speed and reactant conversion of the photocatalytic process is under way. The discovery of this new class of photocatalysts for organic synthesis reveals a new photocatalytic mechanism for the controlled transformation of specific functional groups. The prospect of sunlight irradiation driving the transformation has potential to deliver greener industrial processes especially for temperature-sensitive synthesis.

   The main challenge for this surface complex photocatalysts is the relatively low efficiency. Further study will be conducted for promoting the photocatalytic rate of surface complex photocatalysts. More effort should be done to extend the application of surface complex photocatalysts to different type of organic synthesis that prefer moderate reaction conditions (ambient temperature and atmospheric pressure).

5. The results of radioactive ions adsorbent study, we demonstrates that the titanate NTs and NFs are superior materials for removal radioactive ions in water because of their unique structural properties. Their 1-demential structure provides a large external surface, not only assuring a high removal efficiency even at large feed flux, but also allowing trouble-free separation of the used adsorbents after ion removal for safe disposal. The titanates can uptake large amount of cations because their

large exchange capacity. The layers in the nanostructure are so thin that make the layer structure metastable and uptake of large ions can cause phase transition and structural deformation, which can be utilized to trap cations in the nanostructure permanently for safe disposal. Also the surface of the titanate nanostructures have crystallographic similarity to some lattice planes of the Ag_2O and AgI crystals, and these crystals can solidly bonded to the titanate substrates through coherent interfaces. Finally the fibers and tubes can be fabricated readily from TiO_2 with low cost. These structural features that contribute to the uptake and trapping ions can also be useful for developing other efficient adsorbents for the removal of radioactive ions from wastewater.

Based on the current achievement, we may propose that the other materials with layered structure, such as sodium vanadate, hydrotalcite etc. all can be designed to efficient adsorbents for the removal of radioactive ions (including cations and anions) from water. Since the titanate, vanadates and hydrotalcite are the common minerals in Australia, the adsorbents can be readily developed from these low cost raw materials.