Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2016

Supporting Information for

Non-plasmonic Metal Nanoparticles as Visible Light Photocatalysts for Selective Oxidation of Aliphatic Alcohols with Molecular Oxygen at Near Ambient Conditions

Tana Tana,^a Xiao-Wei Guo,^b Qi Xiao,^a Yiming Huang,^a Sarina Sarina,^a Phillip Christopher,^b Jianfeng Jia,^c Haishun Wu^c and Huaiyong Zhu^{*a}

^a School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Brisbane, QLD 4001 (Australia)

^bKey Laboratory of Bio-Based Material Science and Technology, Ministry of Education, Northeast Forestry University, Harbin 150040 (China)

^c Department of Chemical & Environmental Engineering, University of California, Riverside, Riverside, California 92521 (United States)

^d School of Chemical and Material Science, Shanxi Normal University, Linfen 041004 (China)

*Corresponding author. E-mail: <u>hy.zhu@qut.edu.au</u>

Experimental Section

1. Preparation of catalysts.

I.1 <u>*Mg*-*Al HT*</u>. The Mg-Al HT with a Mg/Al ratio of 3 was produced using a sol-gel process following established procedures with some modification.^{1,2} First, Mg(NO₃)₂·6H₂O (115.4 g, 0.45 mol) and Al(NO₃)₃·9H₂O (56.3 g, 0.15 mol) were dissolved in 0.6 L of deionized water to form an acidic aqueous solution. Then NaOH (60.0 g, 1.5 mol) and Na₂CO₃ (26.5 g, 0.25 mol) were dissolved in 1.0 L of deionized water to form another alkaline solution. Both of these two solutions were heated to 75 °C. For the preparation of HT, the acidic and alkaline solutions were added dropwise simultaneously into 400 mL of deionized water at 75 °C to obtain the precipitation. The pH value was measured to be 10. The suspension was aged for 3 h at 85 °C under vigorous stirring. After being cooled down to room temperature, the gel suspension was filtered and transferred into an autoclave that was subsequently kept at 80 °C for 16 h. The hydrothermally treated gel was washed with deionized water (350 mL) until the washings reached a pH of 7. The resultant white precipitate was dried in an oven overnight at 80 °C and ground to a powder. The HT was calcined to 450 °C (heating rate 10 °C·min⁻¹) in a flow of 100 mL·min⁻¹ of dry air for 8 h in preparation, yielding mixed oxides of magnesium and aluminum, which were used for the subsequent ion exchange process.

1.2 <u>Phosphate-Modified HT (HT-PO₄ ³⁻)</u>. The calcined HT (2.0 g) was dispersed into 50 mL of Na₃PO₄ aqueous solution (0.02 mol/L), the suspension was stirred at room temperature for 12 h, the solid was washed and dried at 110 °C for 10 h, and the resultant solid was ground and denoted as HT-PO₄³⁻.

1.3 <u>Pd@HT-PO₄³⁻ Catalysts</u>. 5 wt% Pd@HT-PO₄³⁻ catalyst was prepared by an impregnation-reduction method. A 1.0 g portion of HT-PO₄³⁻ powder was placed in a 100 mL beaker, and PdCl₂ (47 mL, 0.01 M) aqueous solutions were added into the beaker under magnetic stirring at room temperature. Meanwhile, lysine (16 mL, 0.53 M) aqueous solution was added, and the suspension was kept stirring vigorously for 30 min. The pH value of the suspension was measured to be 8–9. Then, a freshly prepared NaBH₄ (6 mL, 0.35 M) aqueous solution was added dropwise over 20 min. After standing for 24 h, the solid was separated by centrifugation (3000 rpm), washed with deionized water (three times) and ethanol (once), and finally dried at 60 °C in a vacuum oven for 24 h. The dried sample can be used as the photocatalyst directly. All the other catalysts were prepared via the same methods with different quantities of PdCl₂ and HPtCl₄ aqueous solutions.

2. Catalyst Characterization.

The TEM study on the catalysts was conducted using a Philips CM200 JEOL 2100 TEM with an accelerating voltage of 200 kV. XRD patterns of the samples were recorded on a Philips PANalytical X'Pert PRO diffractometer using Cu K α radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 40 mA with a fixed slit. The metal contents of the prepared catalysts were determined by energy dispersion X-ray spectrum (EDS) technology using the attachment to a FEI Quanta 200 environmental scanning electron microscope (SEM). Diffuse reflectance UV-visible (DR-UV-vis) spectra of the sample powders were examined with a Varian Cary 5000 spectrometer with BaSO₄ as a reference.

Entry	Catalyst	Additive	Incident light	Ester yield (%)
1	HT-PO ₄ ³⁻	_	visible	0
		_	dark	0
2	5 wt% Pd@ZrO ₂	_	visible	7
		_	dark	0
3	5 wt% Pd@ZrO ₂	K ₃ PO ₄	visible	49
		K ₃ PO ₄	dark	7
4	5 wt% Pd@HT-CO ₃ ²⁻	_	visible	74
		_	dark	7
5	5 wt% Pd@HT-CO ₃ ²⁻	K ₃ PO ₄	visible	100
		K ₃ PO ₄	dark	13
6	5 wt% Pd@HT-PO ₄ ³⁻	_	visible	84
		_	dark	18

Table S1. Activity test of different supports and base additive for oxidative esterification of 1-octanola

^a Reaction conditions: photocatalyst, 50 mg; reactant, 0.1 mmol; solvent, 2 mL of α, α, α -trifluorotoluene; additive, 20 mg; 1 atm of O₂; environment temperature, 60 °C; reaction time, 24 h; and light intensity, 0.6 W/cm².

As shown in Table S1, PO_4^{3-} modified HT itself did not show any catalytic activity for the oxidative esterification of 1-octanol, indicating that alcohol oxidation took place on the metal NPs. HT-PO₄³⁻ significantly increases the catalytic performance of Pd NPs compared to ZrO₂. The well-defined, double layered structure characteristic of HT-PO₄³⁻ has relatively high specific surface area than ZrO₂. We also found that a moderate amount of basic sites on the supports can result in better catalytic performance for alcohol oxidation reaction, and PO₄³⁻ is superior to other basic sites for the catalytic performance.³ Thus with the effective basic sites of support material and the photocatalytic properties of NPs, this photocatalytic system were able to direct oxidize the aliphatic alcohols to corresponding aldehydes and esters without any base additive.

	ОН —	Photocatalyst, hv 1 atm O_2 , 60°C, 24h	0	~~~	
Entry	Photocatalyst	Conversion	onversion Product selectivity (%)		
	(@ HT-PO ₄ ³⁻)	(%)	Ester	Aldehyde	
1	1 wt% Pd	44 (24)	56 (0)	44 (100)	
2	3 wt% Pd	64 (23)	96 (0)	4 (100)	
3	5 wt% Pd	84 (55)	100 (32)	0 (68)	
4	1 wt% Pt	16 (6)	0 (0)	100 (100)	
5	3 wt% Pt	48 (26)	0 (0)	100 (100)	
6	5 wt% Pt	62 (42)	0 (0)	100 (100)	

Table S2. Influence of Different Metal Amount on Catalytic Performance for Selective Oxidation of 1-Octanol^a

^a Reaction conditions: photocatalyst, 50 mg; reactant, 0.1 mmol; solvent, 2 mL of α,α,α -trifluorotoluene; 1 atm of O₂; environment temperature, 60 °C; reaction time, 24 h; and light intensity, 0.6 W/cm². The conversion and selectivity were calculated based on the product formed and reactant consumed as measured by gas chromatograph (GC). The values in parentheses are the results in the dark.



Fig. S1 (a) High-resolution TEM (HR-TEM) image of the Pd NPs. (b) High-resolution TEM (HR-TEM) image of the Pt NPs.



Fig. S2 (A Scanning electron microscopy (SEM) image of a typical 5 wt% Pd@HT-PO₄³⁻ sample and the corresponding energy dispersive spectrometer (EDX) mapping of O, Mg, Al, P and Pd elements. (B EDX spectrum. All elemental components (Pd, P, Mg, Al) of the Pd@HT-PO₄³⁻ are homogeneously distributed throughout the sample.



Fig. S3 XRD patterns of the photocatalysts. The X-ray diffraction patterns for all samples indicate the well-defined, layered structure characteristic of HT.



Fig. 4 Dependence of the catalytic activity of $Pd@HT-PO_4^{3-}$ photocatalyst for the oxidative esterification of 1-octanol on the intensity of irradiation. The light contribution = $[(Y_{light} - Y_{dark})/Y_{light}] \times 100\%$, where Y_{light} and Y_{dark} are the product yields under irradiation and controlled in the dark, respectively.

The numbers with percentages in Fig. S4 show the visible irradiation contribution to the ester production yields, while the product yield obtained in the dark is regarded as the thermal contribution. The light contribution is determined by subtracting the yields of reaction in the dark from those of reactions under light irradiation at 50°C. It can be seen that The light contribution for the photocatalytic reaction is as high as 73.3% when the irradiance is only 0.2 W/cm² (about 2 suns), and it increased to 91.4% when the irradiance is 0.6 W/cm². Under irradiation of higher intensity, more photons contribute to driving the reactions, resulting higher yields.⁴ As discussed later, the light irradiation can enhance the photocatalytic activity by two possible pathways.



Fig. S5 Time course for the reaction conversion and product selectivity (blue, ester; gray, aldehyde) of the oxidative esterification of 1-octanol using 5 wt% Pd@HT-PO₄³⁻ photocatalyst under irradiation with 400 nm LED (a), 620 nm LED (b), and in the dark (c) at 50 °C.



Fig. S6 IES spectra of 1-pentanol adsorbed on different catalysts. Experiment condition: 1-pentanol (0.04 g) was added onto the prepared catalyst (0.2 g), then dried at 60 °C under vacuum.



Fig. S7 FT-IR spectra of the liquid 1-Pentanol and Octanal.

Table S3. The calculated adsorption energy

	Adsorption energy (eV)		
	On Pd surface	On Pt surface	
1-Butanol	2.85	2.61	
Butanal	2.67	2.25	



Fig. S8 ATR FT-IR spectra of octanal adsorbed on Pd and Pt NPs at different temperatures. Experiment condition: Octanal (0.04 g) was added onto the prepared catalysts (0.1 g), then dried at 60 $^{\circ}$ C, 80 $^{\circ}$ C and 100 $^{\circ}$ C under vacuum.

ATR FT-IR spectra of octyl aldehyde adsorbed on HT-PO₄³⁻, Pd and Pt NPs were collected after dried at different temperature. As shown in Fig. S7, the peak at 1726 cm⁻¹ related to C=O stretching of aldehyde, shifted significantly to lower wavenumber of 1693 cm⁻¹ in the spectra of octanal adsorbed on Pd and Pt NPs, compared to that of HT-PO₄³⁻ support. This means C=O bond of aldehyde has better interaction with metal NPs and results a strong absorption on Pd and Pt photocatalysts. With the temperature increased, the C=O stretching peak become broadening significantly for the Pd and Pt NPs, while the peak remains for the support, was due to the strong interaction metal NPs and aldehyde. Both C=O peak shift and broadening with temperature increase indicate that the strong adsorption ability of transition metal NPs.



Fig. S9 The catalytic activities of the oxidative esterification of 1-octanol using $Pd@HT-PO_4^{3-}$ photocatalyst at different temperatures under visible-light irradiation and in the dark. The numbers with percentages show the light contribution.

Another unique feature of metal NP photocatalysts is that the metal NPs can absorb thermal energy and photon energy simutaneously and combine them to achieve sufficient photocatalytic activity.⁵⁻¹⁰ As shown in Fig. S9, higher product yields were achieved at slightly higher reaction temperature. Thus, one can utilise this property by moderate temperature increasing to achieve optimal photocatalytic reaction efficiency. It is also noted that the light contribution decreases as the reaction temperature was raised. This is because, at higher temperatures, both of the reactant molecules and catalyst gain energy from external heating, which will reduce the energy requirement from irradiation to overcome the activation barrier.

Reference

- 1 M. C. I. Bezen, C. Breitkopf and J. A. Lercher, Acs. Catal., 2011, 1, 1384.
- 2 J. Orthman, H. Y. Zhu and G. Q. Lu, Sep. Purif. Technol., 2003, 31, 53.
- 3. Q. Xiao, Z. Liu, A. Bo, S. Zavahir, S. Sarina, S. Bottle, J. D. Riches, H. Y. Zhu, J. Am. Chem. Soc., 2015, 137, 1956.
- 4 P. Christopher, H. Xin and S. Linic, *Nat. Chem.*, 2011, **3**, 467.
- 5 S. Sarina, E. R. Waclawik and H. Y. Zhu, Green. Chem., 2013, 15, 1814.
- 6 S. Sarina, H. Y. Zhu, E. Jaatinen, Q. Xiao, H. W. Liu, J. F. Jia, C. Chen and J. Zhao, J. Am. Chem. Soc., 2013, 135, 5793.
- 7 S. Sarina, H. Y. Zhu, Q. Xiao, E. Jaatinen, J. F. Jia, Y. M. Huang, Z. F. Zheng and H. S. Wu, *Angew. Chem., Int. Edit.*, 2014, **53**, 2935.
- 8 Q. Xiao, E. Jaatinen and H. Y. Zhu, Chem. -Asian J., 2014, 9, 3046.
- 9 Q. Xiao, S. Sarina, A. X. Bo, J. F. Jia, H. W. Liu, D. P. Arnold, Y. M. Huang, H. S. Wu and H. Y. Zhu, *ACS. Catal.*, 2014, **4**, 1725.
- 10 Q. Xiao, S. Sarina, E. Jaatinen, J. F. Jia, D. P. Arnold, H. W. Liu and H. Y. Zhu, *Green Chem.*, 2014, **16**, 4272.