Electronic Supplementary Information for

Visible light enhanced oxidant free dehydrogenation of aromatic alcohols using catalysts of Au-Pd alloy nanoparticles

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LEGENDS

Experimental Section

Table S1. A, Dehydrogenation of aromatic alcohols with the 3% Au-Pd@ZrO_2 catalysts of various Au:Pd mass ratios under visible light in air and in argon gas atmosphere. B, Dehydrogenation of aromatic alcohols with the 2% Au-Pd@ZrO_2 catalysts of various Au:Pd mass ratios under visible light in argon gas atmosphere.

Text S1. The calculation method of quantum yield.

Text S2. Estimation of Au-Pd alloy NPs' ionic property by free gas model.

Text S3. Density function theory (DFT) calculation of charge distribution in Au - Pd alloy nanoparticle.

Text S4. Calculation of apparent activation energy for all reactions.

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Experimental Section

Materials and Methods

Photocatalyst preparation: Catalysts with 3wt% of pure gold nanoparticles on ZrO_2 (labeled 3%Au), 3wt% of pure palladium nanoparticles on ZrO_2 (3%Pd) and three Au-Pd@ZrO_2 photocatalysts with different Au:Pd ratios on ZrO_2 were prepared by impregnation-reduction method. For example, 1.5%Au-1.5%Pd/ZrO_2 was prepared by the following procedure: 2.0 g ZrO_2 powder was dispersed into 15.2 ml of 0.01 M $HAuCl_4$ aqueous solution and 28.3 ml of 0.01 M $NaPdCl_3$ aqueous solution (0.05g of $PdCl_2$ was dissolved in 28.3ml of 0.02M NaCl solution under stirring) were added while magnetically stirring. 20 mL of 0.53 M lysine was then added into the mixture with vigorous stirring for 30 min. To this suspension, 10 mL of 0.35 M $NaBH_4$ solution was added dropwise in 20 min, followed by an addition of 10 mL of 0.3 M hydrochloric acid. The mixture was aged for overnight and then the solid was separated, washed with water and ethanol, and dried at 60 °C. The dried solid was used directly as catalyst. Catalysts with other Au:Pd ratios were prepared in a similar method but using different quantities of $HAuCl_4$ aqueous solution or $NaPdCl_3$ aqueous solution.

Catalyst Characterization: TEM study and Line profile analysis by energy dispersion X-ray spectrum technique of the photocatalysts were carried out on a Philips CM200 TEM with an accelerating voltage of 200 kV. The Au and Pd content of the prepared catalysts were determined by EDX technology using the attachment to a FEI Quanta 200 Environmental SEM. The element line scanning was conducted on a Bruker EDX scanner attached to JEOL-2200FS TEM with scanning beam diameter down to 1.0 nm. X-ray diffraction (XRD) patterns of the sample powders were collected using a Philips PANalytical X'pert Pro diffractometer. CuKα radiation (λ= 1.5418 Å) and a fixed power source (40 kV and 40 mA) were used. DR-UV-vis spectra of the sample powders were examined by a Varian Cary 5000 spectrometer.

Activity Test: The information of reaction system is given briefly as footnotes of Figure1. The suspension of catalyst powder, solvent and the reactant was placed in a chamber in which a 500 W Halogen lamp (from Nelson, wavelength in the range 400–750 nm) was used as a light source and the light intensity was usually 0.40 W/cm^2 (except for the experiments investigating the impact of the intensity), 50W high power LED lamps are applied as high intensity light source in the experiment of investigating impact of light intensity (0.6~1.2 W/cm^2). At given irradiation time intervals, 2 ml aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. The filtrates were analyzed in a Gas Chromatography (HP6890 Agilent Technologies) with a HP-5 column to measure the concentration change of alcohol and products.

Table S1. A, Dehydrogenation of aromatic alcohols with the Au-Pd@ZrO_2 catalysts of various Au:Pd mass ratios under visible light at oxygen gas atmosphere and argon gas atmosphere.

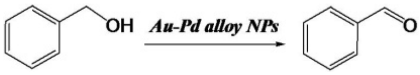
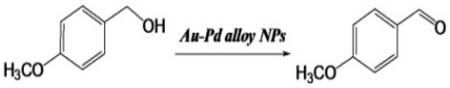
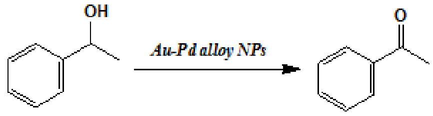
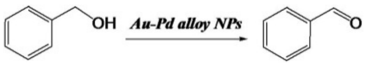
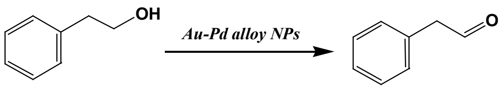
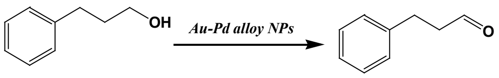
Reactant	**Au:Pd** Mass ratio	**Atmosphere**	**Yield / %**		**Selec. / %**		**Q.Y. / %**
			Light	Dark	Light	Dark	
	3% (1:1)	O_2	100[b]	44	99	100	5.2
		Degas, Ar	100	43	100	100	5.3
	3% (1:2)	O_2	89[b]	28	98	98	5.6
		Degas, Ar	93	31	98	99	5.7
	3% (1:3)	O_2	78[b]	32	96	98	4.3
		Degas, Ar	80	29	99	100	4.7
	3% (3:1)	O_2	68[b]	27	99	100	3.8
		Degas, Ar	66	28	98	99	3.5
	3% (1:0)	O_2	7[b]	3	100	100	0.4
		Degas, Ar	10	4	99	100	0.6
	3% (0:1)	O_2	22[b]	20	99	99	0.2
		Degas, Ar	23	20	100	97	0.3
	3% (1:1)	O_2	100[d]	56	94	96	0.0
		Degas, Ar	99	54	98	99	0.0
	3% (1:2)	O_2	75[d]	39	96	98	4.1
		Degas, Ar	78	40	97	99	4.2
	3% (1:3)	O_2	68[d]	36	95	98	3.3
		Degas, Ar	65	38	100	98	3.5
	3% (3:1)	O_2	59[b]	21	99	99	3.0
		Degas, Ar	58	24	97	100	2.5
	3% (1:0)	O_2	26[d]	10	98	99	3.5
		Degas, Ar	24	12	96	99	3.1
	3% (0:1)	O_2	29[d]	22	92	96	1.5
		Degas, Ar	31	25	100	99	1.1
	3% (1:1)	O_2	98	31	95	99	6.2
		Degas, Ar	94	40	99	97	5.0
	3% (1:2)	O_2	76	29	97	96	4.4
		Degas, Ar	79	33	99	98	4.3
	3% (1:3)	O_2	64	31	97	99	3.1
		Degas, Ar	66	30	96	100	3.3
	3% (3:1)	O_2	55	25	98	99	2.8
		Degas, Ar	58	27	97	98	2.9
	3% (1:0)	O_2	11	6	100	100	0.5
		Degas, Ar	8	6	99	100	0.2
	3% (0:1)	O_2	25	26	96	97	---
		Degas, Ar	26	19	99	99	0.6

Table S1. B, Dehydrogenation of aromatic alcohols with the 2% Au-Pd@ZrO_2 catalysts of various Au:Pd mass ratios under visible light in argon gas atmosphere.

Reactant	**Au:Pd**		**Yield / %**		**Selec. / %**		**Q.Y. / %**
	Mass ratio		Light	Dark	Light	Dark	
	2% (1:4)	Degas, Ar	30	12	98	99	0.8
	2% (1:2)	Degas, Ar	53	19	96	100	1.6
	2% (1:1)	Degas, Ar	73	15	97	99	2.7
Degas, Ar	2% (2:1)	Degas, Ar	50	12	96	99	1.8
	2% (4:1)	Degas, Ar	42	15	100	98	1.3
	2% Au	Degas, Ar	3	0	100	---	0.1
	2% Pd	Degas, Ar	9	3	98	100	0.3
	2% (1:4)	Degas, Ar	16	10	100	100	0.3
	2% (1:2)	Degas, Ar	28	12	99	100	0.7
	2% (1:1)	Degas, Ar	65	7	98	100	2.7
	2% (2:1)	Degas, Ar	39	13	97	99	1.2
	2% (4:1)	Degas, Ar	28	12	100	99	0.7
	2% Au	Degas, Ar	4	0	100	---	0.2
	2% Pd	Degas, Ar	12	4	96	99	0.4
	2% (1:4)	Degas, Ar	10	6	96	98	0.2
	2% (1:2)	Degas, Ar	16	9	94	99	0.3
	2% (1:1)	Degas, Ar	31	6	96	100	1.2
	2% (2:1)	Degas, Ar	11	5	98	100	0.3
	2% (4:1)	Degas, Ar	8	3	99	99	0.2
	2% Au	Degas, Ar	4	1	98	100	0.1
	2% Pd	Degas, Ar	5	3	96	97	0.1

Text S1. The calculation method of quantum yield

The light intensity measured at the reaction system was 0.30 W/cm^2 (which included both the absorbed and scattered light). The overall energy of the photons of the irradiation on the reaction system was derived from the product of the light intensity and section area of the reactor, which under irradiation. The overlap of the light source and the absorption spectrum of catalysts provide the distribution of the absorbed photons over the wavelength range between 400 nm and 800 nm, as shown in figure below. We could estimate the mean wavelength of the absorbed photons from the distribution (after being normalized). The mean energy of the photons could be calculated from the mean wavelength. The number of the photons introduced in the reaction system in our study was calculated from the ratio of the overall energy of the photons and mean energy of the photons. The number of molecules formed was determined during the reaction course. Thus the apparent quantum yield was from the ratio of the number of molecules formed to the number of the photons introduced in the reaction system.

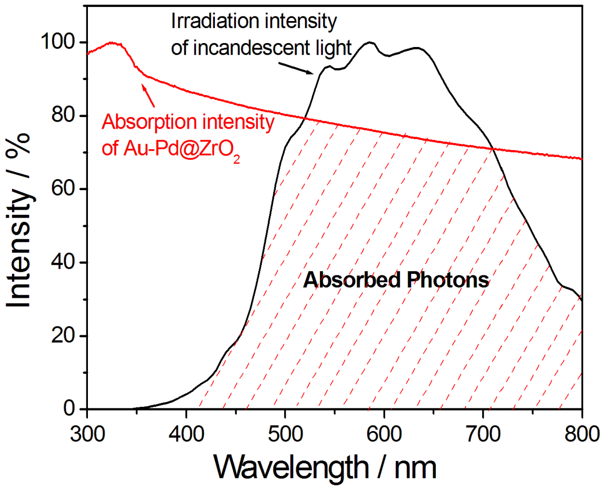


Figure. Absorption intensity of Au-Pd alloy NPs on ZrO$_2$ (a) and irradiation intensity of incandescent light (b). The overlapped area indicated the distribution of the absorbed photons.

Text S2. Estimation of Au-Pd alloy NPs' ionic property by free gas model.

The electron redistribution of the Au-Pd bond is dependent on the magnitude of the electron transferred between the two metals. An estimate of magnitude of the charge transferred can be obtained with the free electron gas model (1), with the change in the number of electrons given by:

$$\Delta N = D(\varepsilon_{F,Au})\Delta a = D(\varepsilon_{F,Pd})\Delta b \qquad (1)$$

where D(ε$_F$) is the density of electron states at the Fermi energies for the two metals and:

$$\Delta a = \Phi_{Pd} - \Phi^* \qquad (2a)$$

$$\Delta b = \Phi^* - \Phi_{Au} \qquad (2b)$$

$$\Delta a + \Delta b = \Phi_{Pd} - \Phi_{Au} \qquad (2c)$$

where Φ_{Pd} and Φ_{Au} are the work functions of pure palladium and gold, respectively, and Φ* is the work function of the alloy once charge equilibrium is reached.(see Scheme 2). Effectively Δa and Δb give the shift in Fermi level (chemical potential) of the two metals at their interface upon contact. The density of states of a free electron gas at the Fermi level is given by (*3*):

$$D(\varepsilon_F) = \frac{3N}{2\varepsilon_F}$$

where N is the number of electrons, so for the two metals the densities are:

$$D(\varepsilon_{F,Au}) = \frac{3N_{Au}}{2\varepsilon_{F,Au}} \qquad (3a)$$

$$D(\varepsilon_{F,Pd}) = \frac{3N_{Pd}}{2\varepsilon_{F,Pd}} \qquad (3b)$$

Combining Equations 3a and 3b with Equation 1 the ratio Fermi level shift is given by:

$$\frac{\Delta a}{\Delta b} = \frac{N_{Pd}}{N_{Au}} \frac{\varepsilon_{F,Au}}{\varepsilon_{F,Pd}} \qquad (4)$$

In the alloy systems in this study, the relative concentration of Pd and Au is varied. If the relative concentration of Pd in the alloy is *x*, then that of Au will be 1-*x* and Equation 4 becomes:

$$\frac{\Delta a}{\Delta b} = \frac{x}{1-x}\frac{\varepsilon_{F,Au}}{\varepsilon_{F,Pd}} \tag{5}$$

By combining Equation 5 with Equations 2c and 1, the total change in electron concentration can be evaluated:

$$\Delta N = \frac{3}{2}\frac{x}{\varepsilon_{F,Pd}}\frac{\left(\Phi_{Pd} - \Phi_{Au}\right)}{1+\frac{x}{1-x}\frac{\varepsilon_{F,Au}}{\varepsilon_{F,Pd}}}K = \frac{3}{2}\frac{x}{5.6}\frac{\left(5.6-5.3\right)}{1+\frac{x}{1-x}\frac{5.3}{5.6}}K \tag{6}$$

where K is a constant of proportionality. Therefore, the net increase in electron concentration on the Pd outer-shell of the nanoparticle will be:

$$\Delta N = K'\frac{0.4x}{1+\frac{x}{1-x}0.9} \sim 0.4K'x\left(1-x\right) \tag{7}$$

Text S3. Density function theory (DFT) calculation of charge distribution in Au - Pd alloy nanoparticle.

An Au_{32} cluster and a corresponding $Au_{12}Pd_{20}$ alloy cluster were constructed to mimic the Au and Au-Pd nanoparticles. The geometry of the Au_{32} and $Au_{12}Pd_{20}$ were optimized by PBE[1] method of density functional theory implemented in CP2K[2] code. The Molecular optimized double zetha-valence Shorter Range basis sets[3] with a polarization function was used to describe the valance orbitals and Goedecker-Teter-HutterPseudo-potential[4]was used to describe the core electrons.The excited state calculations on as optimized structures were performed in the framework of Time-Dependent density functional theory with B3LYP[5,6] functional provided by Gaussian09 package[7]. In this stage, Lanl2dz basis set[8]was selected to describe the atomic orbital of Au and Pdatoms.The excited states with excited wavelength of 534nm for Au32 and 532 nm for $Au_{12}Pd_{20}$were considered in our calculations. The optimized geometry of the Au_{32} and $Au_{12}Pd_{20}$ clustersand the natural charge distributions[9] of them in ground state and considered excited statewere depicted in Figure 8.

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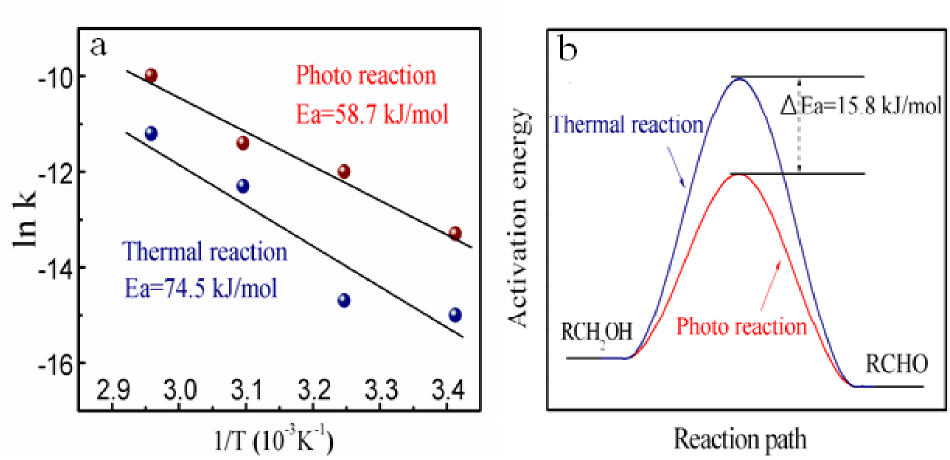
Text S4. Calculation of apparent activation energy

Panel a shows the Arrhenius plots for benzyl alcohol dehydrogeneition in dark (Thermal reaction) and under light irradiation (Photo-reaction). The conversion rates of the catalytic oxidation were used for the calculation of the reaction rate *k*. Arrhenius equation is applied for calculating apparent activation energy based on reaction rate *k*: $k=Ae^{-Ea/RT}$. Panel b schematically illustrates the difference in activation energy between the dark reaction and the reaction under light irradiation.



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Text S5. DFT simulation of $PhCH_2OH^-$ transient anion:

To model the $PhCH_2OH^-$ transient anion, all the associated species were optimized at the level of density functional theory (DFT) with Becke's [1] three-parameter exchange and Lee-Yang-Parr correlation functional [2] implemented in Gaussian 09 package [3]. 6-311++G(d,p) basis set was employed to describe the orbital of all atoms involved. The energy to break the bond between C and α-H in $PhCH_2OH$ was calculated favouring the reaction of $PhCH_2OH = PhCHOH + H$, while in $PhCH_2OH^-$ favouring the reaction of $PhCH_2OH^- = PhCHOH + H^-$.

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