

Electronic Supplementary Information

Direct Visible Photoexcitation on Palladium Nanocatalyst by Chemisorption with Distinct Size Dependence

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Experimental Procedures

Chemicals

Zirconium (IV) oxide (ZrO₂ nanopowder, <100 nm particle size, specific surface area ≥25 m²/g), palladium (II) chloride (PdCl₂, ReagentPlus[®], 99.0%), L-Lysine (≥98.0% TLC), sodium borohydride (NaBH₄, powder, ≥98.0%), iodobenzene (98%), styrene (ReagentPlus[®], ≥99.0%), sodium acetate (NaOAc, ACS reagent, ≥99.0%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), and all the chemical substrates with various substituent groups for the photocatalytic reaction scope study were purchased from Sigma-Aldrich Merck Australia. All the chemicals were used as received without further purification.

Preparation of catalysts

Preparation of Pd catalyst with large particle size

The Pd catalysts with large Pd NPs were prepared using the typical impregnation-reduction procedure. Briefly, taking the typical catalyst with 1.0 wt% Pd supported on ZrO₂ as an example, firstly 2.0 g of ZrO₂ nanopowder was dispersed into 18.7 mL of PdCl₂ (0.01 M) aqueous solution under vigorous stirring conditions at room temperature. A freshly prepared L-Lysine (5.3 mL, 0.1 M) aqueous solution was added dropwise into the above mixture, after completing the addition. The mixture was kept vigorous stirring for another 30 mins to achieve homogeneous mixing and pH value stabilization. The final pH value of the mixture solution was tested to be 8–9. To reduce Pd salt into metallic state, 2 mL of freshly prepared NaBH₄ (0.35 M) aqueous solution was added dropwise into the above prepared mixture. The mixture was then aged for 24 h. Finally, the solid sample was separated by centrifugation, washed with DI water (× 3, 40 mL each) and ethanol (× 1, 40 mL), and dried at 60 °C in a vacuum oven for 24 h. The collected powder sample was used directly as photocatalyst. Pd catalysts with the other Pd loading amounts (such as 0.5, 1.5, 3.0 and 5.0 wt%) were prepared via a similar method but using different quantities of PdCl₂ aqueous solution.

Preparation of Pd catalyst with small particle size

The Pd catalysts with small Pd NPs were prepared by the impregnation and followed by hydrogen reduction method. As a typical example, the catalyst with 0.5 wt% Pd supported on ZrO₂ was prepared by the following method: ZrO₂ nanopowder was dispersed into 0.94 mL of PdCl₂ (0.01M) aqueous solution, then kept stirring for 1 h at room temperature. The Pd adsorbed ZrO₂ nanopowder was dried in vacuum at 60 °C overnight. The collected sample was then calcined at 250 °C under hydrogen flow (10 sccm) for 30 mins.

Characterization of catalysts

The X-ray diffraction (XRD) patterns of the catalyst samples were measured on a PANalytical X'Pert PRO diffractometer (Philips) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) working at 40 mA and 40 kV (data collected range from 20° to 70° with a resolution of 0.01°). The diffuse reflectance UV-visible (DR UV-vis) spectra of the catalyst samples were measured using a Varian Cary 5000 spectrophotometer (Agilent) equipped with an integrating sphere using BaSO₄ as the reference. The

morphologies of the catalyst samples were analyzed using a transmission electron microscope (TEM, JEOL 2100) with an accelerating voltage of 200 kV. The Pd particle size distribution histogram was calculated based on 250 isolated particles from TEM images. The elemental composition of the catalyst samples was determined by energy dispersion X-ray (EDX) spectrum technology on a scanning electron microscope (SEM, FEI Quanta 200). The temperature-programmed infrared emission spectroscopy (IES) measurements were conducted on a Digilab FTS-60A spectrometer attached with a TGS detector, which was modified by replacing the IR source with an emission cell. Before the IES measurement, the catalyst samples were mixed with small amount of the reactants (iodobenzene or styrene, 10 mg each), and then dried in a vacuum oven at 60 °C for 48 h.

Photocatalytic reactions

The photocatalytic Heck reaction was carried out in a 10 mL reaction tube (Pyrex, ϕ 10 mm). For detailed reaction receipt, see reaction conditions in relevant figure captions. After loading catalyst, chemicals and solvent, the reaction tube was sealed with a rubber septum cap. The reaction tube was evacuated and then back filled in with argon gas (repeated 3 times). Then the reaction was irradiated by visible light source (Nelson Industries: tungsten linear halogen lamp 500 W, wavelength in the range 400–750 nm) under continuous magnetic stirring. The light intensity of the light source was calibrated to 0.5 W/cm² prior to each experiment using a PM100D optical power and energy meter (Thorlabs). The reaction temperatures were carefully controlled through air cooling. The thermal (dark) reactions were conducted using a water bath at certain setting temperatures. The reaction tube was wrapped with aluminum foil to avoid exposure of the reaction to light. After completion of the reaction, the reaction mixture was filtered to remove solid catalysts and then analyzed by a gas chromatography (GC, Agilent 7820A, HP-5 column). The reaction products were identified by a mass spectrometer (Agilent HP5977A) attached to GC (Agilent 7890B, HP-5MS column).

Action spectrum experiments

The light emitting diode (LED) light source used for the action spectrum experiments was described and discussed in our previous work.¹ The LED light intensity was calibrated to 0.2 W/cm² prior to each experiment using a PM100D optical power and energy meter (Thorlabs). The apparent quantum yield (AQY) was calculated using the following equation:

$$AQY (\%) = \frac{Y(\text{light}) - Y(\text{dark})}{n(\lambda)} \times 100\%$$

where $Y_{(\text{light})}$ and $Y_{(\text{dark})}$ are the number of products formed under light irradiation and dark conditions, respectively. $Y = y \times$ the mole of reactant \times Avogadro constant, where the y is the reaction yield. $n_{(\lambda)}$ is the number of incident photons involved in the reaction, which can be calculated by $n_{(\lambda)} = E/e$ (E is the total energy input involved in the reaction, and e is the energy of one incident photon at the specific wavelength).

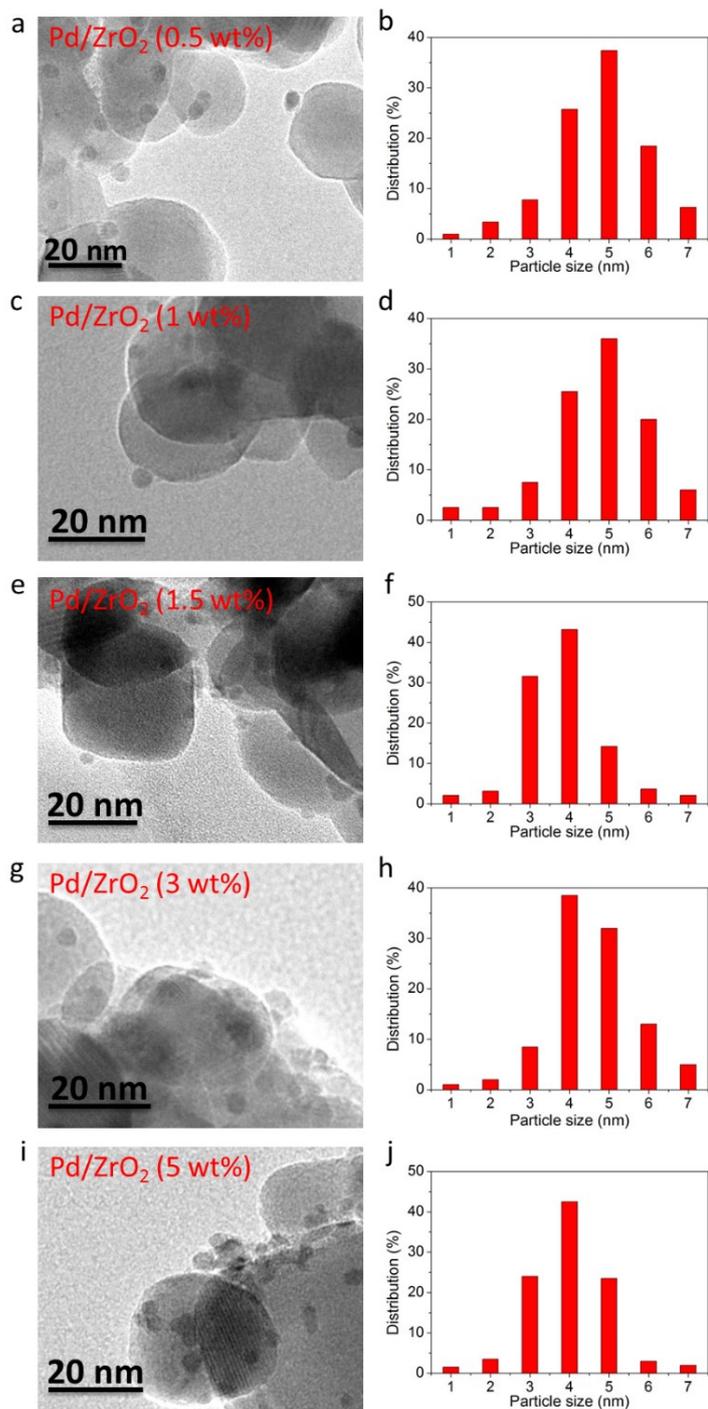


Figure S1. (a, c, e, g, and i) TEM images of the Pd/ZrO₂ photocatalysts (large particles) with various Pd loading amounts. (b, d, f, h, and j) Particle size distribution of the Pd NPs based on the statistical analysis from TEM images.

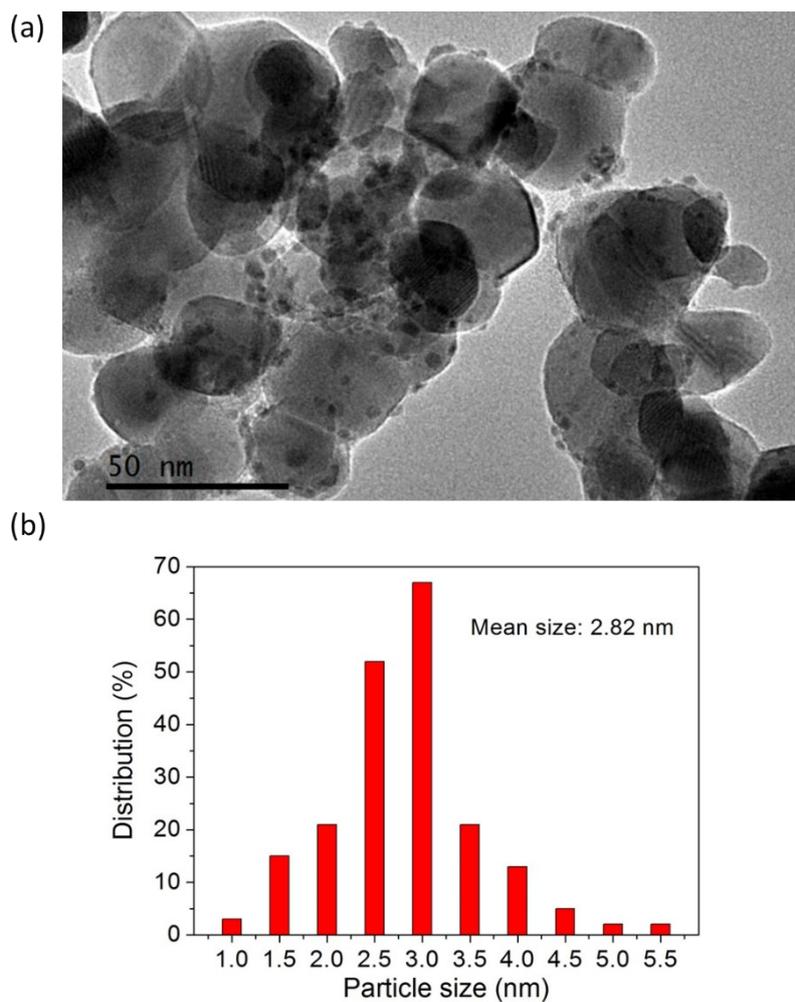


Figure S2. Additional TEM image of the 0.5 wt% Pd/ZrO₂ catalyst (small particles), and particle size distribution of the Pd NPs based on the statistical analysis from TEM images.

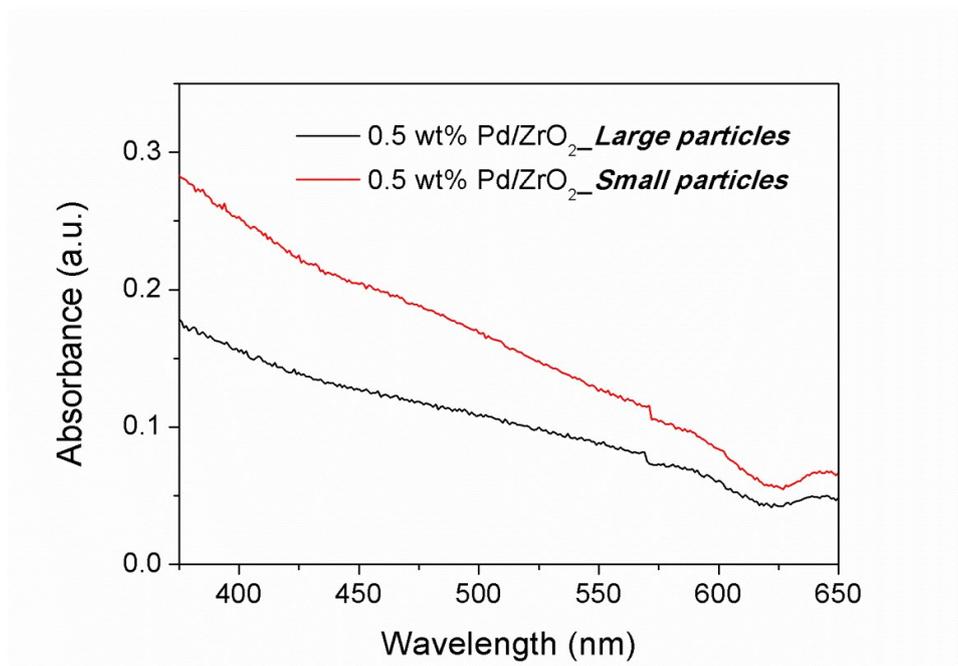


Figure S3. DR UV-vis spectra of the 0.5 wt% Pd NPs/ZrO₂ catalyst with different particle sizes.

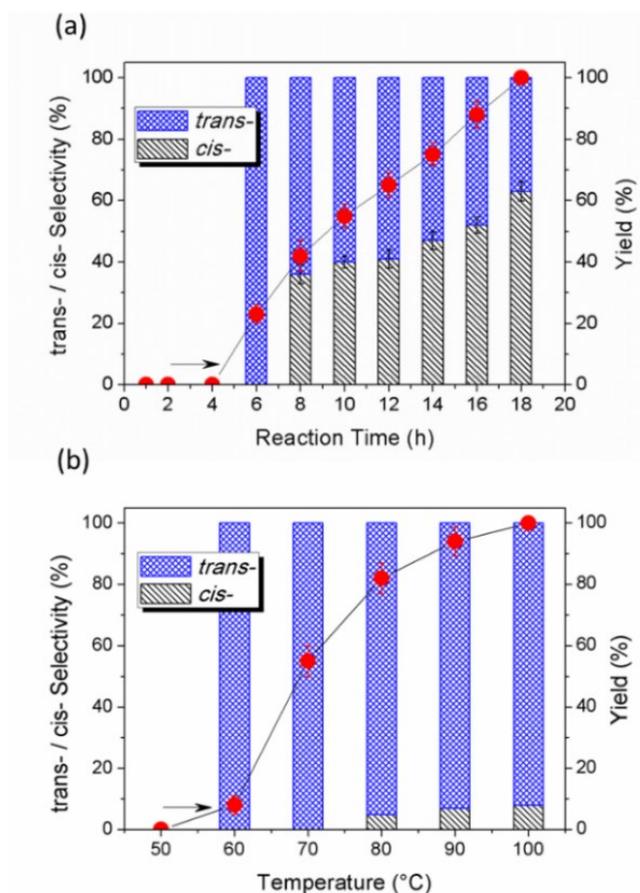
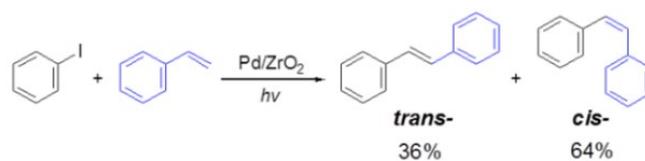


Figure S4. The top scheme shows the photoisomerization of the product of Heck reaction. (a) The time course for the product yield and trans-/cis- selectivity under visible light irradiation at 50 °C. (b) The dependence of reaction temperatures on the trans-/cis- selectivity for the thermal (dark) reactions, reaction time 17 h.

The cis-/trans- photoisomerization of stilbene is one of the most extensively investigated subjects in photochemistry, both experimentally and theoretically.^{2,3} Both the cis→trans and trans→cis photoisomerizations can take place in stilbene, and the cis- and trans- isomers are typically produced in approximately equal amounts. However, there are some striking differences between the cis→trans and trans→cis isomerization processes.² The isomerization proceeds much faster in the former (~2 ps) than in the latter (10~200 ps), and there is a relatively large barrier (~3 kcal/mol) on the trans→cis isomerization path, while the cis→trans reaction involves a negligible barrier or a barrierless process.² Because of the sterically hindered and less stable nature in the cis-isomer, typically the trans-isomer is the major product in the Heck reactions.

As seen from **Figure S4a**, mainly trans-isomer formed during the early stage of the reaction, and the selectivity to cis-isomer increased during the time course. This suggests that the catalytic cross-coupling is followed by the

photoisomerization from trans-isomer to cis-isomer. The photocatalytic system gives mainly cis-isomer product, while the conventional heating system yields trans-isomers. To further confirm this important feature, we tested the reaction in the dark but under thermal heating at 60~100 °C. As can be seen clearly in **Figure S4b**, the selectivity was mainly trans-isomer even when elevated to a temperature of 100 °C. The heating has weak influence over the selectivity to cis-isomer, while the visible light irradiation can efficiently induce the photoisomerization through rotation around the C=C double bond in stilbene molecule. The photoisomerization mechanism can be explained by the double-bond-shift of stilbene on Pd NPs, which follows the similar pathway reported by Hashimoto *et al.* for the photoisomerization of 1-butene over Pd-loaded TiO₂.⁴ In the present study, we can obtain cis-isomer as the main product in one-pot process through a photocatalytic Heck reaction.

Table S1. The optimization of the photocatalytic reaction conditions for Heck cross-coupling reaction.^a

Entry	Base	Solvent	Atmosphere	Yield (%)
1	NaOAc	DMF	Ar	100
2	NaOAc	DMF	Air	65
3	NaOAc	DMF	O ₂	Trace
4	Na ₂ CO ₃	DMF	Ar	95
5	KOH	DMF	Ar	100
6	NaOH	DMF	Ar	86
7	K ₂ CO ₃	DMF	Ar	91
8	NaCl	DMF	Ar	18
9	Na ₂ SO ₄	DMF	Ar	17
10	NaOAc	DMSO	Ar	95
11	NaOAc	BTF	Ar	Trace
12	NaOAc	CH ₂ Cl ₂	Ar	Trace
13	NaOAc	DMA	Ar	36
14	NaOAc	Acetonitrile	Ar	9
15	NaOAc	IPA	Ar	4

^a Reaction conditions: Pd/ZrO₂ photocatalyst 50 mg, iodobenzene 0.1 mmol, styrene 0.12 mmol, solvent 2 mL, base 0.6 mmol, environment temperature 50 ± 2 °C, reaction time 17 h. The visible light intensity was 0.5 W/cm². The yields were calculated from the product formed and the reactant converted measured by GC. DMF: dimethyl formamide; DMSO: dimethylsulfoxide; BTF: trifluorotoluene; DMA: dimethylacetamide; IPA: isopropyl alcohol.

Table S2. The reusability of 1.0 wt% Pd/ZrO₂ photocatalyst for Heck reaction under visible light irradiation.^a

Entry	Runs	Yield (%)
1	1	93
2	2	91
3	3	86
4	4	83
5	5	83

^a Reaction conditions: photocatalyst 50 mg, iodobenzene 0.1 mmol, styrene 0.12 mmol, solvent DMF 2 mL, 1 atm Ar, additive AcONa 50 mg, environment temperature 50 ± 2 °C, reaction time 17 h. The visible light intensity was 0.5 W/cm². The product yields were calculated from the product formed and the reactant converted measured by gas chromatography (GC).

For practical applications of heterogeneous catalyst, the reusability is a very important factor, particularly when precious metals are used. Therefore, in order to clarify this issue, the performance of our catalytic systems was tested for the iodobenzene and styrene model chemical transformation up to five consecutive cycles and the results are illustrated in **Table S2**. The reaction conditions were kept identical for each run and after each reaction cycle, the catalyst was separated by centrifugation, washed with acetone once and then dried for subsequent reactions. The results indicate that the catalyst can be reused without losing significant activity and the product selectivity can be maintained >99%. The observed slightly decrease in catalytic activity was possibly due to the loss of Pd NPs during washing after each run.

Table S3. The catalytic activity of Pd NPs on different supports for Heck reaction.^a

Entry	Catalyst	Incident light	Yield (%)
1	Pd@ZrO ₂ (1 wt%)	Visible	100
		Dark	0
2	Pd@CeO ₂ (1 wt%)	Visible	91
		Dark	0
3	Pd@TiO ₂ (1 wt%)	Visible	100
		Dark	0
4	Pd@Al ₂ O ₃ (1 wt%)	Visible	82
		Dark	0

^a Reaction conditions: photocatalyst 50 mg, iodobenzene 0.1 mmol, styrene 0.12 mmol, solvent DMF 2 mL, 1 atm Ar, additive AcONa 50 mg, environment temperature 50 ± 2 °C, reaction time 17 h. The visible light intensity was 0.5 W/cm². The yields were calculated from the product formed and the reactant converted measured by GC.

References

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