Supporting Information

**Surface-Plasmon-Enhanced Transmetalation between Copper and Palladium Nanoparticle Catalyst**

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Experimental Part

Materials

The chemicals were purchased from commercial supplier Sigma-Aldrich and used as provided (unless otherwise noted): Copper powder (30-40 nm particle size, TEM), Palladium(II) chloride (PdCl₂, 99.999%), Sodium borohydride (NaBH₄, ≥98.0%), Iodobenzene (98%), Phenylacetylene (98%), Acetonitrile (anhydrous, 99.8%). Ultrapure water was used in all experiments.

Synthesis of Catalyst

Catalyst Preparation

The Cu NPs we used, which is commercially available, and composed by metallic copper core and CuO coating on the surface. The commercial Cu NPs were pretreated under a hydrogen atmosphere at 350°C for 4 h to secure the Cu NPs in a metallic state.

The Pd NPs/Al₂O₃ is readily prepared by impregnation-reduction methodology to load Pd NPs onto Al₂O₃ fibre powder. To prepare 3 wt% Pd NPs/Al₂O₃, 1.0 g of Al₂O₃ fibre powder was dispersed in 28 ml PdCl₂ solution (0.01 M) under magnetic stirring. To this suspension, 20 ml of 0.01 M NaBH₄ solution was added dropwise in 30 min. The mixture was aged overnight and then the solid was separated by centrifugation, washed with water and ethanol, and dried at 60°C. The dried solid was used directly as a catalyst. The metal concentration in the catalyst was confirmed by an inductively coupled plasma (ICP) atomic emission.

Characterization of Catalyst

The sizes, morphologies of the catalyst samples were characterized by TEM using a JEOL 2100 transmission electron microscope equipped with a Gatan Orius SC1000 CCD camera. Diffuse-reflectance UV/vis (DR UV/Vis) spectra of the sample powders were examined using a Varian Cary 5000 spectrometer with BaSO₄ as a reference. X-ray photoelectron spectroscopy (XPS) measurements were taken using a Kratos Axis Supra with a monochromatic AlKα source (1486.7 eV) with a 15 mA emission current and total power of 225 W. All the measurements were done using the charge neutraliser as a default. The base pressure in the analysis chamber was 1.0 × 10⁻⁸ Torrs. The binding energy scale of all spectra was calibrated by a rigid shift of all spectra to align adventitious carbon in the C 1s core level to 284.8 eV. Peak fitting of the high-resolution data was carried out using the Casa XPS software. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was performed using a Perkin Elmer 8300DV ICP fitted with an ESI SC-4DX autosampler and PrepFAST 2 sample handling unit for online internal reference standardization and auto-dilution of samples and calibration references. Nitric acid, purified by sub-boiling distillation, was used for the preparation of all references and blank solutions were used throughout the analysis.

Photocatalytic Reactions
The reaction mixture was stirred magnetically and irradiated using a halogen lamp with a wavelength in the range of 400−800 nm as the visible light source or light emitting diode (LED) lamps with different wavelengths, and the light intensity was measured. The temperature of the reaction system was carefully controlled with an air conditioner. The control reaction system in the dark was maintained at the same temperature to ensure that the comparison was meaningful. At given irradiation time intervals, 0.5 mL aliquots were collected and then filtered through a Millipore filter (pore size 0.45 μm) to remove the catalyst particulates. The liquid-phase products were analysed by gas chromatography (GC) using an Agilent 7820A gas chromatograph with an HP-5 column to measure the changes in the concentrations of reactants and products. An Agilent HP5977A mass spectrometer attached to an Agilent 7890B gas chromatograph with an HP-5MS column was used to identify the products.

Typical reaction conditions were as follows: 3 mL of 0.3 mmol phenylacetylene and 0.6 mmol iodobenzene in acetonitrile, 8 mg Cu NPs alone or 8 mg Cu NPs and 12 mg Pd NPs/Al₂O₃ mixture catalyst were added to the reaction tube, and the reaction was run at a temperature of 40°C under a 1 atm O₂ atmosphere for a reaction time of 6 h. The reactions with other catalysts and substrates were conducted under similar methods with some conditions changed slightly. The light intensity was measured using a power meter (Model 1918-R) from Newport Company and other reaction conditions were identical to those of typical reaction procedures.

**Action Spectrum Experiments**

Light emitting diode (LED) lamps (Tongyifang, Shenzhen, China) with wavelengths 415±5 nm, 455±5 nm, 525±5 nm, 565±5 nm, 605±5 nm, 650±5 nm, 730±5 nm, 850±5 nm and 940±5 nm were used as the light source to investigate the catalytic performance under different wavelengths. The light intensity of the LED light sources used for the wavelength dependent experiments was 0.5 W/cm², and the light intensity was maintained constant for each wavelength dependent experiment. The other reaction conditions were kept identical with the halogen lamp (white light) photocatalytic reactions.
Figure S1. Influence of the mixing ratio between Cu NPs and Pd NPs in Sonogashira reaction.

The reactions were conducted over mixed Cu/Pd catalyst with different mixing ratio at 40°C for 6 h using 0.3 mmol phenylacetylene and 0.6 mmol iodobenzene in 3 ml acetonitrile. The irradiation intensity of white light was 0.6 W/cm².

The Sonogashira reaction performance depends on the mixing ratio between Cu NPs and Pd NPs is shown in Figure S1. The formation of cuprous phenylacetylide intermediate was rather fast. When the molar ratio of Cu to Pd was 148:1 and reaction time was 3 h, it’s still obvious to see the yellow-green cuprous phenylacetylide intermediate precipitation. With the reaction time further prolonged, the intermediate was consumed step by step due to its interaction with Pd NPs so that the yield of cross-coupling product increased. What’s more, the optimum molar ratio was 37:1 (Cu:Pd) which showed the highest yield of cross-coupling product.
Figure S2. The reactant conversion of Sonogashira reaction catalysed by the mixed Cu/Pd catalyst (a) and Cu NPs alone (b); The reactant conversion of Glaser reaction catalysed by mixed Cu/Pd catalyst (c) and Cu NPs alone (d) under white-light irradiation and in the dark at increasing temperatures, respectively.

The Sonogashira reaction catalysed by the mixed Cu/Pd catalyst and Cu NPs alone are conducted at increasing temperatures from 30°C to 90°C. Without irradiation, the highest conversion of Sonogashira coupling appear at 60-70°C and decrease gradually at increased temperatures (dash lines in Figure S2a). This indicated that heating is not always favoured by this reaction system - the thermal energy input shows a negative impact to the reaction above 70°C. The optimal reaction temperature shifted to lower temperature, 40°C, when irradiating with visible light, where the highest conversion rates of both reactants are observed. At 40°C, the conversion rate of photo-reaction (94% for alkyne and 40% of iodobenzene) is much higher than the rate of the reaction without light (below 20%), which demonstrated that the light irradiation accelerated the Sonogashira reaction very significantly at low temperatures. The photo-reaction conversion decline from 50°C and notably at temperature range 60-80°C is even lower than the thermal reaction. The results indicated that heat is not the main driver of the reaction.
Similarly, we also conducted Glaser reaction with reactant phenylacetylene only over Cu NP and Pd NP mixed catalyst and Cu NPs alone, respectively. The activation of phenylacetylene in Glaser reaction at various temperatures are similar to its activation in the Sonogashira reaction, the complete phenylacetylene conversion for Glaser coupling reaction is achieved on the mixed catalyst under light irradiation at 40°C, while the highest phenylacetylene conversion in the dark is about 30% even at 75°C. The elevated temperature also result in decrease in the conversion of phenylacetylene.

From this we surmise that the Glaser reaction and the Sonogashira coupling reaction have the same intermediate that forms when phenylacetylene is reacted over Cu NPs. The most likely candidate for this role would be the cuprous phenylacetylide. Cuprous phenylacetylide intermediates are well established as critical intermediates in Cu catalysed Glaser reactions (Table S1).\textsuperscript{[1]}
Figure S3. Diagram of the reactions of cuprous phenylacetylide under different conditions. (The panel on the right-hand side shows the GC patterns of the reaction mixtures.)

Figure S3 shows that in the dark cuprous phenylacetylide remains stable. But adding Pd NPs loaded on Al₂O₃ or ZrO₂ (Pd/Al₂O₃ or Pd/ZrO₂) to the suspension of cuprous phenylacetylide, yields 16% homo-coupling product, diyne, and metallic Cu. The characteristic peaks in the XRD pattern of cuprous phenylacetylide disappeared under light irradiation (Figure 1, main text), Cu was regenerated from the cuprous phenylacetylide. The transmetalation step is initiated by the dissociation of the neutral ligand and the transfer of acetylide from Cu(I) to Pd(II) was almost barrierless.[2]

Ph-≡C-C≡C-Cu + Pd → Ph-≡C-C≡C-Pd + Cu

(enhanced by 400-940 nm)  (3)

Reaction (3) describes transmetalation of Ph-≡C- species from Cu NPs to the Pd NPs. The transmetalation is supported by X-ray photoelectron spectroscopy (XPS) analysis in Figure 3a (main text). Subsequently the coupling reaction takes place on Pd NP surface:

2Ph-≡C-Pd → Ph-≡C-C≡C-Ph + 2Pd

(enhanced by 400-940 nm)  (4)
**Figure S4.** TEM images of Cu NPs before reaction (a); Cu NPs after Glaser reaction (b), almost fully transformed into cuprous phenylacetylide; mixture of Cu NPs and Pd NPs/ZrO$_2$ after Glaser reaction (c).

We used Pd NPs/ZrO$_2$, instead of Pd NPs/Al$_2$O$_3$ to show the morphology change clearly by avoiding the confusion between fibril-like cuprous phenylacetylide and Al$_2$O$_3$ fibres.
We also investigated the reusability of the mixture of Cu NPs and Pd NPs as catalyst. The used catalyst was recovered, washed simply with ethanol, and then directly applied in cycling reactions without further treatment or regeneration. The recycled Cu NPs and Pd NPs from Glaser reaction exhibited good reusability, as shown in Figure S5, the reaction conversion was maintained over 95% without dropping activity considerably for more than five cycles.

Besides, the Cu NPs and Pd NPs recycled from Sonogashira reaction showed lower conversion of both reactants and much more homocoupling product (90% selectivity), due to the transformation of Cu into Cul.
Figure S6. XRD pattern of the powder specimen collected from the Sonogashira reaction over the mixed Cu/Pd catalyst.
Figure S7. Gas chromatogram of Diphenylacetylene (cross-coupling product) and 1,4-Diphenylbutadiyne (homo-coupling product) in model Sonogashira reaction.
**Figure S8.** Mass spectra of Diphenylacetylene (cross-coupling product) and 1,4-Diphenylbutadiyne (homo-coupling product) in model Sonogashira reaction.
Table S1. Impact of the different metal NPs to the photocatalytic performance for the Glaser reaction. (The values in parentheses are the data of reaction in the dark.)

| Entry | Catalyst                  | Atm. | Conversion % | Selectivity % |
|-------|---------------------------|------|--------------|---------------|
| 1^a   | Blank                     | O₂   | 0 (0)        | - (-)         |
| 2^a   | Al₂O₃                     | O₂   | 0 (0)        | - (-)         |
| 3^ax  | Cu NPs+Al₂O₃              | O₂   | 50 (1)       | 96 (-)        |
| 4^a   | Pd NPs/ZrO₂               | O₂   | 0 (0)        | - (-)         |
| 5^a   | Cu NPs+TEMPO              | O₂   | 11           | 100           |
| 6^a   | Cu NPs+Pd NPs/Al₂O₃       | Ar   | 3            | 100           |
| 7^a   | Cu NPs+Pd NPs/ZrO₂        | O₂   | 78 (5)       | 100 (100)     |
| 8^ax  | Cu NPs+Au NPs/ZrO₂        | O₂   | 47 (1)       | 96 (-)        |
| 9^ax  | Cu NPs+Ag NPs/ZrO₂        | O₂   | 49 (1)       | 97 (-)        |
| 10^ax | Cu NPs+Pt NPs/ZrO₂        | O₂   | 40 (1)       | 98 (-)        |
| 11^ax | Cu NPs+Ir NPs/ZrO₂        | O₂   | 44 (1)       | 96 (-)        |
| 12^ax | Cu NPs+Ni NPs/ZrO₂        | O₂   | 40 (1)       | 95 (-)        |

^a The reactions were conducted at 40°C for 6 h using 0.3 mmol phenylacetylene in 3 mL acetonitrile. The irradiation intensity of white light was 0.6 W/cm². The values in the parentheses are the conversion and selectivity in the dark reaction. The × means the system was turbid after reaction. The conversion and selectivity were calculated from the amounts of products formed and reactants converted as measured by gas chromatography (GC).
Table S2. Photocatalytic performance for the Sonogashira reaction control experiments. (The values in parentheses are the data of reaction in the dark.)

![Chemical diagram of the Sonogashira reaction]

| Entry | Catalyst | Atm. | Conversion A | Conversion B | Selectivity AA | Selectivity AB |
|-------|----------|-----|--------------|--------------|----------------|----------------|
| 1     | Blank    | O₂  | 0(0)         | 0(0)         | 0(-)           | 0(-)           |
| 2     | Al₂O₃    | O₂  | 0(0)         | 0(0)         | 0(-)           | 0(-)           |
| 3<sup>x</sup> | Cu NPs+Al₂O₃ | O₂  | 99(1)       | 4(0)         | 92(-)         | 8(-)           |
| 4     | Pd NPs/ZrO₂ | O₂  | 0(0)         | 0(0)         | 0(-)           | 0(-)           |
| 5     | Pd NPs/Al₂O₃ | O₂  | 0(0)         | 0(0)         | 0(-)           | 0(-)           |
| 6     | Pd NPs/Al₂O₃ (75°C) | O₂  | 0(0)         | 0(0)         | 0(-)           | 0(-)           |
| 7     | Pd NPs/Al₂O₃ (iodobenzene) | O₂  | 0(0)       | 0(0)         | 0(-)           | 0(-)           |
| 8     | Pd NPs/Al₂O₃ (740 nm NIR) | O₂  | 0(0)      | 0(0)         | 0(-)           | 0(-)           |
| 9     | Pd NPs/Al₂O₃ (850 nm NIR) | O₂  | 0(0)       | 0(0)         | 0(-)           | 0(-)           |
| 10    | Cu NPs+Pd NPs/Al₂O₃ (18 h dark) | O₂  | (54)   | (16)         | (54)         | (46)           |
| 11    | Cu NPs+Pd NPs/Al₂O₃ (4 h dark) | O₂  | (12)   | (7)          | (26)         | (74)           |
| 12<sup>x</sup> | Cu NPs+Au NPs/ZrO₂ | O₂  | 85(1)    | 4(0)         | 90(-)         | 10(-)          |
| 13<sup>x</sup> | Cu NPs+Ag NPs/ZrO₂ | O₂  | 83(1)    | 3(0)         | 93(-)         | 7(-)           |
| 14<sup>x</sup> | Cu NPs+Pt NPs/ZrO₂ | O₂  | 72(1)    | 3(0)         | 92(-)         | 8(-)           |
| 15<sup>x</sup> | Cu NPs+Ir NPs/ZrO₂ | O₂  | 78(1)    | 4(0)         | 90(-)         | 10(-)          |
| 16<sup>x</sup> | Cu NPs+Ni NPs/ZrO₂ | O₂  | 76(1)    | 5(0)         | 88(-)         | 12(-)          |

All of these reactions were conducted at 40°C for 6 h using 0.3 mmol phenylacetylene and 0.6 mmol iodobenzene in 3 ml acetonitrile (except for the specially marked in parentheses). The irradiation intensity of white light was 0.6 W/cm². The values in the parentheses are the conversion and selectivity in the dark reaction. The × means the system was turbid after reaction. The conversion and selectivity were calculated from the amounts of products formed and reactants converted as measured by gas chromatography (GC).

All the supported metal NP catalysts used here were 3 wt% metal NPs loaded on the Al₂O₃ or ZrO₂ and the dosages in reaction were 12 mg. And the dosage of Cu NP catalyst was 8 mg.
Table S3. The ICP results of leaching metal in the reaction solution.

| Sample                                  | Cu          | Pd          |
|-----------------------------------------|-------------|-------------|
| Reaction solution from Glaser reaction | Release 0.2%| Release 0.28%|
| Reaction solution from Sonogashira reaction | -          | Release 0.30%|

Samples were collected after Glaser reaction and Sonogashira reaction with mixed Cu/Pd catalyst and filtrated with 0.45 µm polymer filter.

In addition, an inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the reaction solution indicated that only 0.2% of Cu and 0.28% of Pd and 0.30% of Pd were leached separately in Glaser and Sonogashira coupling reactions, as shown in Table S3. The negligible metal loss is the reason for the good reusability of the photocatalyst. The Al₂O₃ fibres solidly bond the NPs, avoiding the loss of Pd NPs.

Furthermore, the filtrated reaction solutions from Glaser reaction catalysed by Cu NPs and mixed Cu/Pd catalyst, and Sonogashira reaction catalysed by Cu NPs showed no catalytic activity under light irradiation and in the dark. But the reaction solution from Sonogashira reaction catalysed by mixed Cu/Pd catalyst could convert phenylacetylene into diyne under the light irradiation due to the partially dissolved CuI in the reaction solution. These results confirming that the reactions are catalysed by the Cu NPs and Pd NPs on their surface and not ions leached into the reaction solution even though trace leaching occurs.³
Table S4. Impact of the Pd loading to the photocatalytic performance for the Glaser reaction.

| Entry | Catalyst | Atm. | Light | Conversion % | Yield % | Selectivity % |
|-------|----------|------|-------|--------------|---------|---------------|
| 1<sup>a</sup> | Cu NPs | O<sub>2</sub> | Visible | 60 | 57 | 95 |
| 2<sup>a</sup> | Cu NPs | O<sub>2</sub> | Dark | 1 | 0 | - |
| 3<sup>a</sup> | Cu NPs | Ar | Visible | 3 | 2 | 67 |
| 4<sup>b</sup> | Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Visible | 0 | 0 | - |
| 5<sup>b</sup> | Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Dark | 0 | 0 | - |
| 6<sup>c</sup> | Cu NPs+Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Visible | 99 | 99 | 100 |
| 7<sup>c</sup> | Cu NPs+Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Dark | 8 | 8 | 100 |
| 8<sup>d</sup> | Cu NPs+0.5 Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Visible | 62 | 61 | 98 |
| 9<sup>e</sup> | Cu NPs+1.5 Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Visible | 55 | 55 | 100 |
| 10<sup>f</sup> | Cu NPs+2 Pd NPs/Al<sub>2</sub>O<sub>3</sub> | O<sub>2</sub> | Visible | 32 | 32 | 100 |

<sup>a</sup>The reactions were conducted in O<sub>2</sub> atmosphere at 40°C using 3 mL acetonitrile with 0.3 mmol of phenylacetylene substrate and 8 mg of Cu NP catalyst. <sup>b</sup>12 mg Pd/Al<sub>2</sub>O<sub>3</sub> was used. <sup>c</sup>mixture of 8 mg Cu NPs and 12 mg Pd/Al<sub>2</sub>O<sub>3</sub> was used. <sup>d</sup>mixture of 8 mg Cu NPs and 6 mg Pd@Al<sub>2</sub>O<sub>3</sub> was used. <sup>e</sup>mixture of 8 mg Cu NPs and 18 mg Pd/Al<sub>2</sub>O<sub>3</sub> was used. <sup>f</sup>mixture of 8 mg Cu NPs and 24 mg Pd/Al<sub>2</sub>O<sub>3</sub> was used. The irradiation intensity was 0.6 W/cm<sup>2</sup> and reaction time was 6 h. The conversion and selectivity were calculated from the amounts of products formed and reactants converted as measured by gas chromatography (GC).
Table S5. The photocatalytic performance for the Glaser reaction and Sonogashira reaction in different solvents.

![Diagram]

| Entry | Catalyst  | Reactant | Solvent  | Conversion | Selectivity |
|-------|-----------|----------|----------|------------|-------------|
|       |           |          | A        | B          | AA          | AB          |
| 1     | Cu/Pd     | A        | 1,4-Dioxane | 71         | -           | 100         | -           |
| 2     | Cu/Pd     | A        | Isopropanol | 44         | -           | 100         | -           |
| 3     | Cu/Pd     | A        | Toluene   | 89         | -           | 100         | -           |
| 4     | Cu/Pd     | A+B      | Toluene   | 56         | 5           | 70          | 30          |
| 5     | Cu/Pd     | A+B      | DMF       | 85         | 2           | 92          | 8           |
| 6     | Cu/Pd     | A+B      | THF       | 2          | -           | 100         | -           |

The reactions were conducted in 1 bar O$_2$ gas at 40°C for 6 h using 0.3 mmol phenylacetylene and 0.6 mmol iodobenzene in 3 ml solvent and the mixture of 8 mg Cu NPs and 12 mg Pd/Al$_2$O$_3$ as catalyst. The irradiation intensity was 0.5 W/cm$^2$. 
References

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