

Heterogeneous Catalysis
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Surface-Plasmon-Enhanced Transmetalation between Copper and Palladium Nanoparticle Catalyst

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Abstract: Surface-plasmon-mediated phenylacetylide intermediate transfer from the Cu to the Pd surface affords a novel mechanism for transmetalation, enabling wavelength-tunable cross-coupling and homo-coupling reaction pathway control. C–C bond forming Sonogashira coupling and Glaser coupling reactions in O₂ atmosphere are efficiently driven by visible light over heterogeneous Cu and Pd nanoparticles as a mixed catalyst without base or other additives. The reaction pathway can be controlled by switching the excitation wavelength. Shorter wavelengths (400–500 nm) give the Glaser homo-coupling diyne, whereas longer wavelength irradiation (500–940 nm) significantly increases the degree of cross-coupling Sonogashira coupling products. The ratio of the activated intermediates of alkyne to the iodobenzene is wavelength dependent and this regulates transmetalation. This wavelength-tunable reaction pathway is a novel way to optimize the product selectivity in important organic syntheses.

Introduction

Transition-metal-catalysed carbon–carbon and carbon–heteroatom cross-coupling reactions are two of the most important reaction classes in modern synthetic organic chemistry.^[1] Since their initial discoveries, great progress has been made to address limitations in these reactions, increase efficiencies, and develop more environmentally friendly coupling procedures. For example, the addition of a Cu co-catalyst to the cross-coupling reaction between acetylenes and aryl or vinyl halides, was first proposed by Sonogashira and Hagihara to achieve the coupling reaction at ambient temperatures.^[2] Building on this, room-temperature photocatalytic processes have been developed in recent years for C–C coupling reactions based on metal catalysts that can harvest visible light.^[1c–e,3]

The widely accepted mechanism of Sonogashira coupling follows a multi-step reaction pathway of oxidative addition, transmetalation and reductive elimination, that proceeds by two synergistic catalytic cycles.^[2b,4] Metallic Cu can react with alkynes and the resultant cuprous acetylide species

inserts by transmetalation into the Pd catalytic cycle.^[4a] Transmetalation, defined as the transfer of an organic group from one metal center to another, is a rate-determining step in these metal-catalyzed cross-coupling reactions.^[5] Important to photocatalysis, sometimes these species, for example, cuprous phenylacetylide, (maximum absorption at 465 nm) can strongly absorb short wavelength light.^[6]

In establishing a photocatalytic cross-coupling process, we noted that Cu nanoparticles (NPs) which are a well-known plasmonic metal, effectively absorbs visible light through localized surface plasmon resonance (LSPR). This is where the conduction electrons of the NPs collectively oscillate when in resonance with the electromagnetic field of the incident light source. The Cu NPs LSPR absorption peak normally occurs around 560 nm.^[7] This LSPR absorption also generates energetic charges (hot electrons and holes) and intense electromagnetic fields in close proximity to the NPs, which may induce reactions of substances at or near the NP surface.^[8]

We hypothesized that by tuning the irradiation wavelength, light absorption by the Cu NPs LSPR and by cuprous

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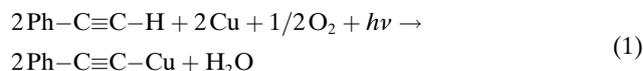
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phenylacetylide may accelerate a particular reaction pathway and thus favor a desired cross-coupling product. This approach has potential to expand the scope and address limitations with Sonogashira coupling (e.g. requirement for deoxygenated atmosphere and various additives) and advance knowledge in photocatalysis and coupling reactions. In this study, we report that by mechanically mixing Pd NPs deposited on Al₂O₃ nanofibers (Pd/Al₂O₃) with Cu NPs (abbreviated as mixed Cu/Pd, “/” – indicating that the two metals are not alloyed) we can generate a photocatalyst that can switch reaction pathway between Glaser homo-coupling and Sonogashira cross-coupling by changing the irradiation wavelength. Our investigations of the reaction mechanism is the first report on the impact of wavelength to the transmetalation step during the coupling reaction.

Results and Discussion

The Sonogashira reaction was conducted over the mixed Cu/Pd and proceeded in O₂ rich atmosphere and without the addition of base, ligands or other additives. Exceedingly mild reaction conditions of 40 °C and low intensity white light irradiation were required. The preparation, characterization and catalytic performance assessment of the catalysts are described in detail in the Supporting Information. In short, commercially available Cu NPs (Figure 1a) were reduced by H₂ at 350 °C for 4 h to ensure that the Cu NPs were in metallic state prior to the use when combined together with the Pd/Al₂O₃ catalyst (Figure 1b). The best catalytic performance was observed with a Cu:Pd molar

ratio of 37:1 (Figure S1). The synergistic effect of the Cu NPs and Pd NPs is of great interest since there was no thermal or photocatalytic reactivity detected when reactions were attempted using Pd/Al₂O₃ catalyst only, without base, ligands, and other additives (Table 1); and Cu NPs react with alkyne like a reactant, yielding cuprous phenylacetylide (Figure 1c):



Reaction (1) proceeds readily, and this results in high phenylacetylene conversions when the catalysts containing Cu NPs react in an oxidative atmosphere (Table 1). Considering this, we conducted the experiments with an iodobenzene:phenylacetylene molar ratio of 2:1 to bias the reaction towards cross-coupling.

As shown in Table 1, light irradiation of the system markedly promotes the reactions on the mixed Cu/Pd, giving 61 % of the cross-coupling product and 39 % of the homo-coupling product. In the absence of light irradiation, a much lower conversion rate, only $\approx 1/5$ that of the photocatalytic reaction was observed. Under irradiation using only the Cu NP catalyst a product selectivity of 91 % was biased towards phenylacetylene homo-coupling (Glaser reaction) and only 9 % of the Sonogashira cross-coupling product detected. No biphenyl product occurred under the base-free conditions employed. In the absence of light irradiation, negligible phenylacetylene conversion (1 %) occurred over the Cu NPs, demonstrating that the phenylacetylene reaction on the Cu surface occurs only with photo-excitation.

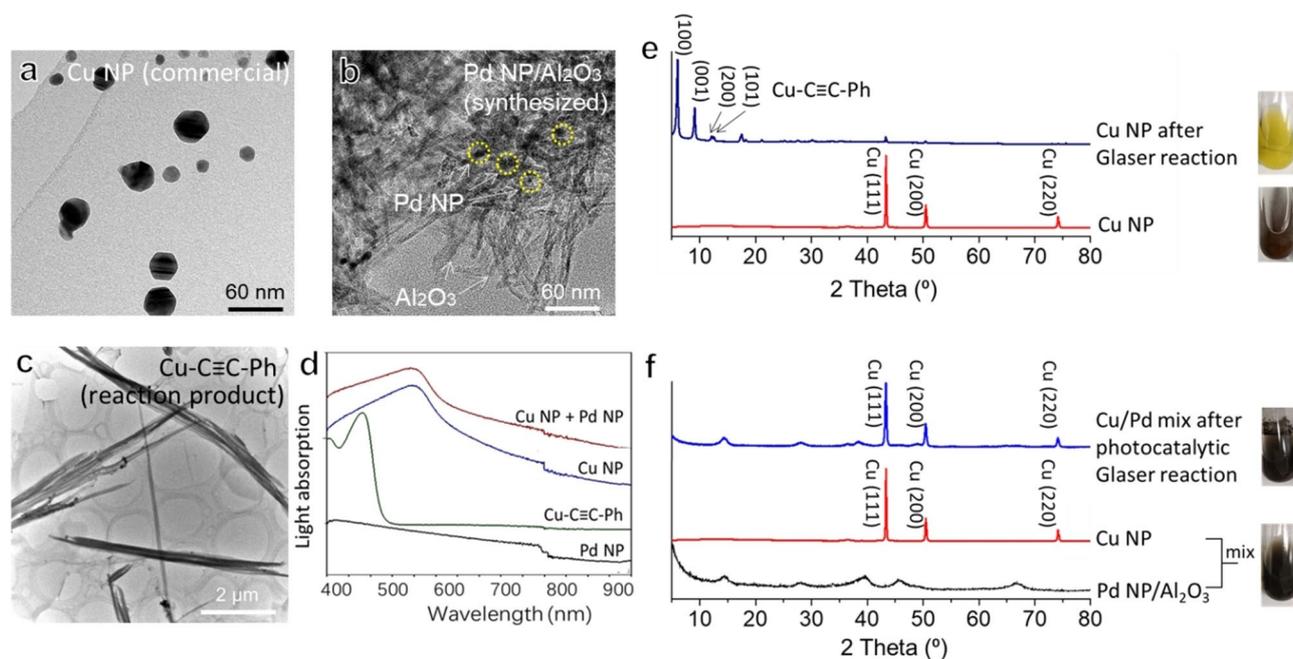
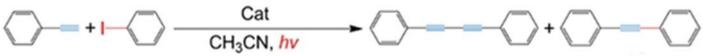


Figure 1. Characterization of catalysts and intermediate. a)–c) TEM image of Cu NPs, Pd NPs/Al₂O₃ and intermediate product cuprous phenylacetylide. d) UV/Vis light absorption of the above samples. e) XRD analysis of Cu NPs catalyst before and after Glaser reaction, inserts are the photos of the reaction system catalysed by Cu NPs catalyst. f) XRD analysis of mixed Cu/Pd catalyst before and after Glaser reaction, inserts are the photos of the reaction system catalysed by mixed Cu/Pd catalyst.

Table 1: Photocatalytic performance for the Sonogashira reaction. (The values in the parentheses are the conversions in the dark.)


Entry	Catalyst	Atm.	Conversion of alkyne %		Selectivity % Photo-reaction		Selectivity % Dark-reaction	
			Photo-reaction	(Dark-reaction)	Homo-coupling	Cross-coupling	Homo-coupling	Cross-coupling
1 ^a	Cu NPs	O ₂	99	(1)	91	9	-	-
2 ^b	Pd NPs	O ₂	0	(0)	-	-	-	-
3 ^c	Cu NPs+Pd NPs	O ₂	93	(18)	39	61	23	77
4 ^c	Cu NPs+Pd NPs	Ar	6	(1)	0	100	0	100
5 ^c	Cu NPs+Pd NPs	Air	38	(16)	27	73	22	78

[a] The reactions were conducted at 40 °C for 6 h using 0.3 mmol phenylacetylene and 0.6 mmol iodobenzene in 3 mL acetonitrile and 8 mg of Cu NP catalyst. The irradiation intensity of white light was 0.6 W cm⁻². [b] 12 mg Pd/Al₂O₃ catalyst was used. [c] The mixed catalyst of 8 mg Cu NPs and 12 mg Pd/Al₂O₃ was used.

Figure 2 illustrates how mixed Cu/Pd causes significant changes in the photocatalytic performance as a function of irradiation wavelength, affecting both the product selectivity (Figure 2a and b) and the reaction rate (Figure 2c). Most

importantly, a significant product selectivity switch from homo-coupling (diyne, blue symbols) to cross-coupling (diphenylacetylene, red symbols) was detected as the irradiation wavelength was increased, as shown in Figure 2b.

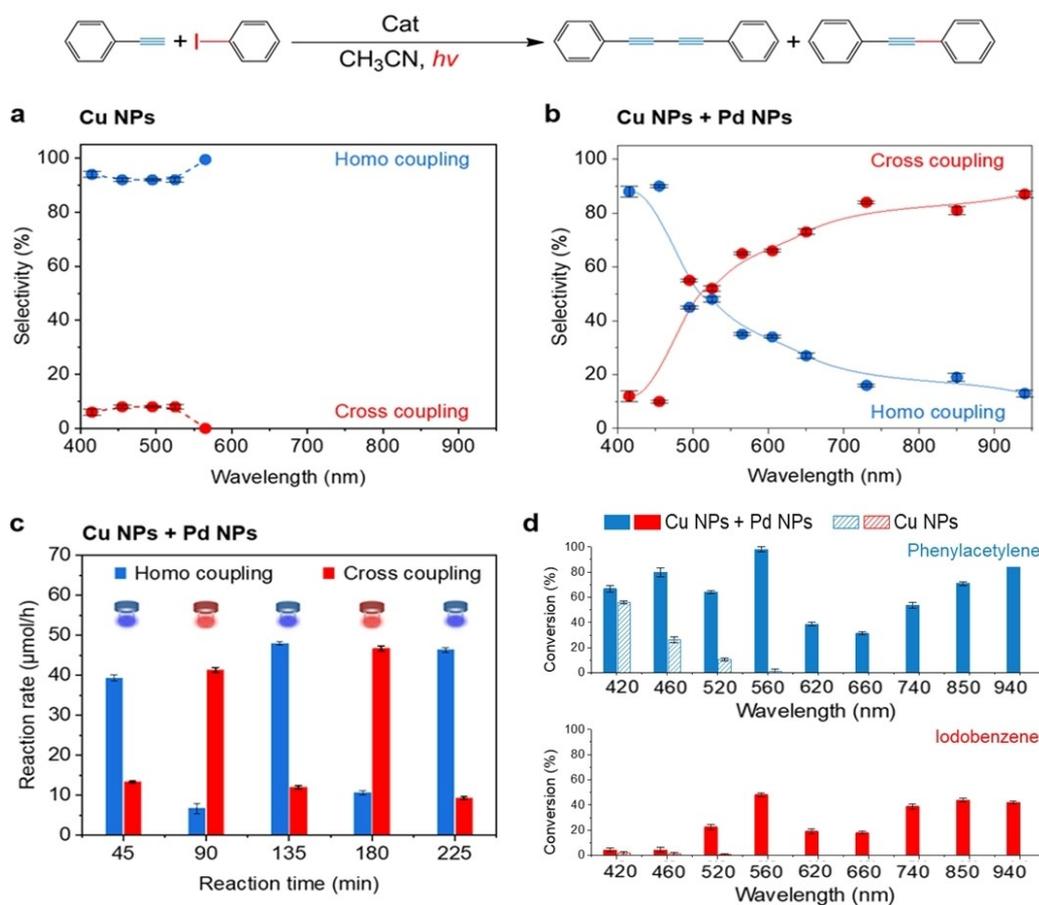


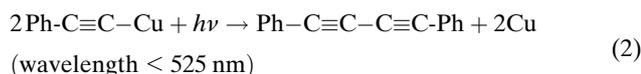
Figure 2. Impact of light irradiation wavelength on the Sonogashira reaction using the Cu NP catalyst and the mixed Cu/Pd catalyst. a), b) Product selectivity dependence on the irradiation wavelength over Cu NP catalyst and mixed Cu/Pd catalyst. c) Repeatedly switching product selectivity by blue-on (455 ± 5 nm) and red-on (850 ± 5 nm) cycles. d) Photo-enhanced reactant conversion dependent on irradiation wavelength over the mixed catalyst (the phenylacetylene conversion of thermal control reaction is subtracted).

The long wavelength irradiation selectively favors Sonogashira coupling in an oxygen-rich environment, occurring without base and other additives. This effective photocatalytic performance was not observed when other metal nanoparticles were mixed with the Cu NPs (Tables S1 and S2). Under irradiation with wavelengths longer than 730 nm, over 80 % diphenylacetylene formed through Sonogashira cross-coupling. By contrast, using wavelengths shorter than 455 nm (blue light irradiation), near 90 % of the product is diyne arising from Glaser homo-coupling of phenylacetylene. Leaching tests indicate that the reaction occurs in the heterogeneous phase: the reaction stops after removal of the solid catalyst, confirming that the heterogeneous phase is required to complete the catalytic cycle (Table S3). Photo-enhanced reactant conversion depends on irradiation wavelength over the Cu/Pd mixed catalyst (Figure 2d, the conversion of thermal control reaction is subtracted).

Transmission electron microscopy (TEM) images in Figure 1a show that the Cu NPs were in the form of 30–40 nm spherical particles before reacting with phenylacetylene, and the precipitate observed after the reaction under white light consisted of nanobelt-shaped structures, which is consistent with the formation of cuprous phenylacetylidyne (Figure 1c).^[6] This was confirmed by the XRD patterns of the Cu NP catalysts before and after reaction, shown in Figure 1e.

However, when the Cu NPs and Pd NP/Al₂O₃ mixture were used to catalyze Glaser reaction, the Cu NPs remained in a metallic state (Figure 1f). In the same reaction system, the product selectivity can be repeatedly switched (Figure 2c) over a mixed Cu/Pd photocatalyst by switching the irradiation wavelength used. When the system was irradiated with blue light (455 ± 5 nm) for 45 min, the homo-coupling of phenylacetylene was observed to proceed at a rate of 39 μmol h⁻¹ and cross-coupling of phenylacetylene and iodobenzene at a rate of 13 μmol h⁻¹. When the same system was subsequently irradiated with red light (850 ± 5 nm) for 45 min, the reaction rate of the homo-coupling was reduced to 7.3 μmol h⁻¹ while the rate of the cross-coupling reaction increased to 42 μmol h⁻¹. This unique property demonstrates that a simple change in the irradiation wavelength diverts the reaction pathway from homo-coupling to cross-coupling. Pd NP catalyst can work under short wavelengths irradiation with the assistance of semiconductor support (e.g. TiO₂) for Ullmann coupling reaction in the presence of a base in argon atmosphere.^[9] By cooperating with Cu NPs, the light absorption of the catalyst dramatically extends into visible light and near-infrared wavelengths, as shown in this work.

For the Glaser reaction, the cuprous phenylacetylidyne produced via Reaction (1), decomposes under light irradiation, yielding Cu and diyne:



The irradiation of wavelengths ≤ 525 nm promotes the catalytic reactions of Glaser coupling (predominant) and Sonogashira coupling (minor) over Cu NPs without any

base, additives or elevated temperatures. In the long-wavelength range (> 525 nm), Cu NPs alone exhibit negligible catalytic activity for both reactants. Even the intense light absorption arising from the LSPR effect of Cu NPs (peak at 560 nm) did trigger or contribute to the conversion of either of the reactants on the illuminated Cu NP catalyst. In sharp contrast, over the mixed Cu/Pd, products are generated at all wavelengths from 400 to 960 nm (Figure 2b). This implies that mixing Pd NPs with Cu NPs substantially reduces the activation energy barriers of the conversions. A transmetalation process should be involved in the system, linking the reactions on Cu NPs and Pd NPs, respectively.

The scope of this photocatalytic Sonogashira cross-coupling over the mixed Cu/Pd with blue light (455 ± 5 nm) and red light (850 ± 5 nm) was investigated (Table 2). The product selectivity of the reactions with a variety of substrates produced similar wavelength-dependent switchable performance: under blue light irradiation, the main product is homo-coupling of alkynes and under red light irradiation, the cross-coupling product predominantly formed. The reaction system with the mixed Cu/Pd is also applied for the synthesis of indole compound.

The potential of the plasmonic metal Cu NPs photo-thermal effects influencing the reaction was also investigated. The results demonstrate that both the Glaser and Sonogashira couplings are not temperature-dependent but wavelength-sensitive instead (Figure S2). We also investigated whether the Glaser reaction and the Sonogashira reaction have the same intermediate that forms when phenylacetylene reacted over Cu NPs.

Reaction (1) proceeds rather slowly in the dark and in the presence of O₂ (Entry 2 in Table S4) but rapidly proceeds (a yellow precipitate observable within 10 min) when under irradiation of white light (Entry 1 in Table S4); to yield a yellow-green precipitate (insert of Figure 1e) that also makes the reaction mixture turbid. This precipitate was identified as cuprous phenylacetylidyne based on assignment of its X-ray diffraction (XRD) pattern (Figure 1e).

Cuprous phenylacetylidyne is stable in the dark (Figure S3) and under irradiation of wavelengths ≥ 525 nm. But addition of Pd NPs loaded on Al₂O₃, or ZrO₂ (Pd/Al₂O₃ or Pd/ZrO₂) to the suspension of cuprous phenylacetylidyne, yielded 16 % homo-coupling product, diyne, and metallic Cu. The characteristic peaks in the XRD pattern of cuprous phenylacetylidyne disappeared under light irradiation (Figure 1f, also see Figure S4) and copper was regenerated. Hence the recycled Cu/Pd mixed catalyst from the Glaser reaction exhibits good reusability, as shown in Figure S5. The reaction conversion efficiency was retained at over 95 % without a noticeable drop in activity after more than five cycles.

Reaction (3) describes the transmetalation of the Ph-C≡C- species from Cu NPs to Pd NPs. This transmetalation is supported by X-ray photoelectron spectroscopy (XPS) analysis in Figure 3, discussed later.

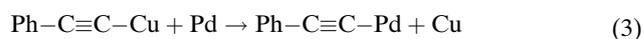
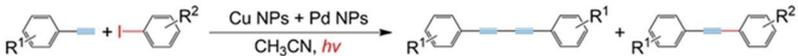
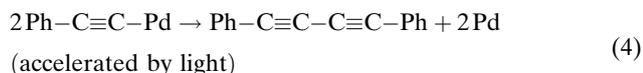


Table 2: The substrate scope for a photocatalytic Sonogashira reaction using a mixed Cu/Pd catalyst.


Entry	Alkyne	Aryl-halide	Blue light 455 nm		Red light 850 nm	
			Conv.%	Sel. (%) Homo-/Cross-coupling	Conv.%	Sel. (%) Homo-/Cross-coupling
1	H	OCH ₃	54	79/21	17	12/88
2	H	CH ₂ OH	35	87/13	68	32/68
3	H	NH ₂	60	78/22	54	36/64
4	H	COCH ₃	87	72/28	63	32/68
5	H	CH ₃	98	70/30	42	18/82
6	CH ₃ O	H	99	62/38	32	13/87
7	CH ₃	H	99	69/31	48	16/84
8	F-(CH ₃)	H	65	58/42	36	22/78
9	C ₂ H ₄ -	H	69	88/12	48	24/76
10	CH(OH)	H	15	79/21	37	7/93
11 ^a	HOC(CH ₂) ₆ C≡CH	H	76	83/17	84	36/64
12 ^a	CH ₃ (CH ₂) ₅ C≡CH	H	24	93/7	46	19/81

The reactions were conducted in 1 bar O₂ gas at 40 °C for 6 h using 0.3 mmol alkyne and 0.6 mmol aryl halide in 3 mL acetonitrile and the mixture of 8 mg Cu NPs and 12 mg Pd/Al₂O₃ as catalysts. The irradiation intensity was 0.5 W cm⁻². [a] Substrates 11 and 12 are aliphatic alkynes.



Notably, in the dark, the performance of the mixed Cu/Pd (Entry 3 in Table 1) is much better than that of solely Cu NPs (Entry 1 in Table 1). This corroborates that Pd NPs are involved in the reaction both in light and dark conditions, through reducing the activation energy barrier to reaction. In addition, irradiation of visible and near-infrared light appears to accelerate the transmetalation step. There appears to be a synergetic effect occurring with the mixed Cu/Pd NP system that provides favors with transmetalation, likely through lowering reaction activation energy barrier that increases the rate of reaction relative to Cu NPs-only reactions in the dark, at temperatures $\leq 40^\circ\text{C}$.

We found that in the dark, cuprous phenylacetylide did not react with iodobenzene. Adding Pd/Al₂O₃ to the mixture of cuprous phenylacetylide and iodobenzene produced homo-coupling (25 %) and cross-coupling (75 %) products and CuI. Thus, activation of iodobenzene appears to occur on the Pd NP surface, which for most Pd-catalyzed coupling reactions, is thought to involve a Ph-Pd-I intermediate.^[10] Also, the transmetalation of the Ph-C≡C- species intermediate allows both coupling reactions to take place on Pd/Al₂O₃. Reductive elimination from Pd NPs (Reaction 4) follows the transmetalation.

The XPS spectra in Figure 3 are consistent with this rationale. The high-resolution XPS (HR-XPS) in Figure 3

shows the binding energy peaks of metallic Cu at 932.5 and 952.25 eV (S1). These peaks shift to 933.4 and 953.2 eV in the specimen obtained from the reaction between Cu NPs and phenylacetylene (S3), and a satellite peak at 948.9 eV is observed. The changes indicate that Cu in the product exists in a higher oxidation state (+1),^[6] which is likely to be cuprous phenylacetylide.

Comparing the XPS spectrum of the system containing phenylacetylene and Pd NPs (S4) with that of Pd NPs alone (S2), there are no obvious shifts of Pd binding energies. In both spectra, there are peaks at 335.0 eV (3d 5/2) and at 340.26 eV (3d 3/2), indicating Pd exists in a metallic state in the two samples. In the spectrum for the system containing the mixed Cu/Pd and phenylacetylene (S5), however, the binding energy of Pd shifts significantly with peaks now seen at 336.19 eV (3d 5/2) and 341.47 eV (3d 3/2), corresponding to Pd^{II} state. This change supports the idea that transmetalation of Ph-C≡C- species from Cu NPs to Pd NPs occurs. This transmetalation is expected to take place after phenylacetylene activation on Cu NPs.

Comparing the XPS spectra of iodine in the sample mixture (S8) with the Cu NP-only sample (S6) and Pd NPs-only sample (S7), we find that the iodine signal of S8 is much more pronounced than that found from S6 and S7, suggesting that iodobenzene activation is enhanced through a combined effect of mixed Cu/Pd. However, the activation using either Cu or Pd separately is ineffective. The iodine XPS signals measured using the mixed Cu/Pd includes signals from CuI as well as the activation of iodobenzene on

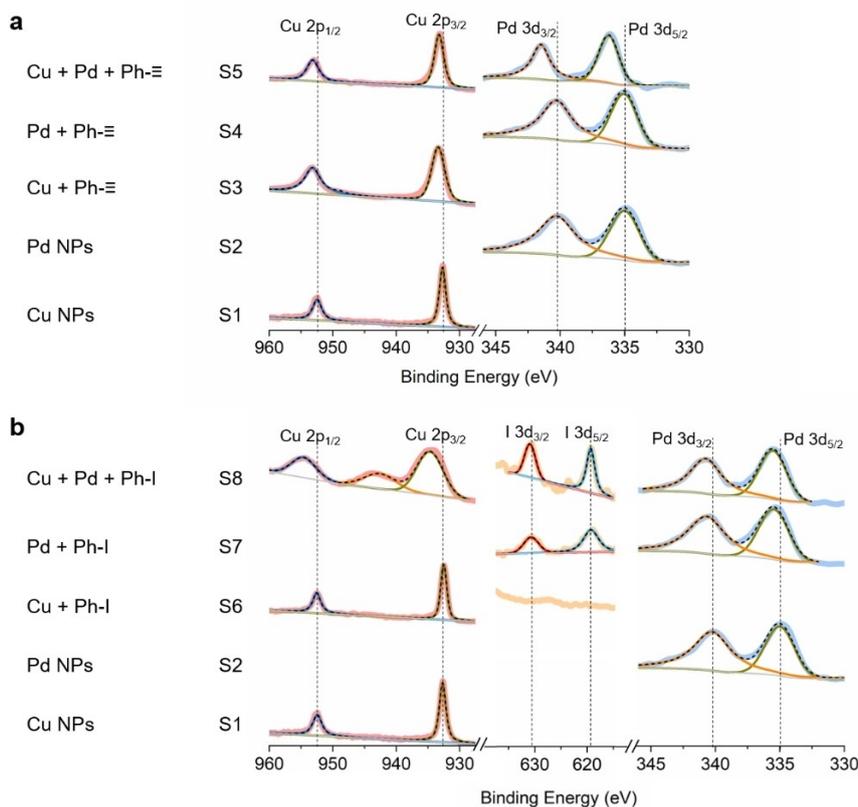
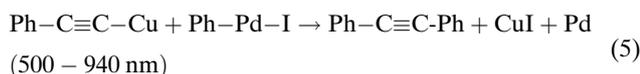


Figure 3. High-resolution XPS patterns of the catalytic reaction systems after white light irradiation. a) Catalyst after phenylacetylene adsorption on surface. b) Catalyst after iodobenzene adsorption on its surface. (S1) Cu NPs; (S2) Pd NPs; (S3) Cu NPs + phenylacetylene + $h\nu$; (S4) Pd NPs + phenylacetylene + $h\nu$; (S5) mixed Cu/Pd + phenylacetylene + $h\nu$; (S6) Cu NPs + iodobenzene + $h\nu$; (S7) Pd NPs + iodobenzene + $h\nu$; (S8) mixed Cu/Pd + iodobenzene + $h\nu$.

Pd surface (Ph–Pd–I). The iodine on Pd surface is removed by reaction with cuprous phenylacetylide:



The Ph- species on the Pd surface is available for reaction with the Ph–C≡C– delivered from cuprous phenylacetylide, via transmetalation, yielding the cross-coupling product. The observation of diffraction peaks arising from CuI in the XRD pattern of the powder specimen collected from the Sonogashira reaction over the mixed Cu/Pd (Figure S6) supports this theory. The coupling reactions and subsequent reductive elimination of the coupling products proceeds more readily on the Pd NPs than on the Cu NPs. Thus, the activation energy barrier of the elimination would be lower for the mixed Cu/Pd than that for the Cu NP catalyst alone (see Figure 4). With the lowered barriers the transmetalation and the coupling reaction on Pd can be promoted by light irradiation of all wavelengths from 400 to 960 nm (Figure 2b). The light-promoted transmetalation route provides rational explanation to the different action spectra given by the Cu NPs and mixed Cu/Pd catalyst in both of Glaser coupling (Figure 4) and Sonogashira coupling

(Figure 5). The XPS analysis evidences the transmetalation process from Cu to Pd surface.

The wavelength dependence of the Glaser reaction shows that a high diyne yield from the homo-coupling of phenylacetylene occurs under light irradiation of wavelengths < 525 nm (Figure 4a). The photon energy associated with the LSPR effect of Cu NPs (peak at 560 nm) is not sufficient to cross the Glaser reaction activation energy barrier in the case of the Cu NP catalyst. Figure 4b shows this energy requirement schematically. The irradiation of 415 ± 5 nm wavelength can generate hot electrons with higher energy by excitation of the electrons in cuprous phenylacetylide, which promotes the Cu–C bond cleavage and the subsequent coupling of Ph–C≡C– species.

Over mixed catalyst, the Glaser reaction is accelerated by light irradiation with longer wavelengths > 525 nm (Figure 4c), where the highest product yield is observed at LSPR absorption of Cu NPs. The high yields and match between the action spectrum and light absorption spectrum, indicating that the activation energy barrier to the Glaser reaction over the mixed Cu/Pd catalyst is lower than over the Cu-only NP catalyst. The reaction activation barrier is likely decreased, due to the Ph–C≡C– species transferring from Cu to Pd surface, so that hot electrons excited by LSPR

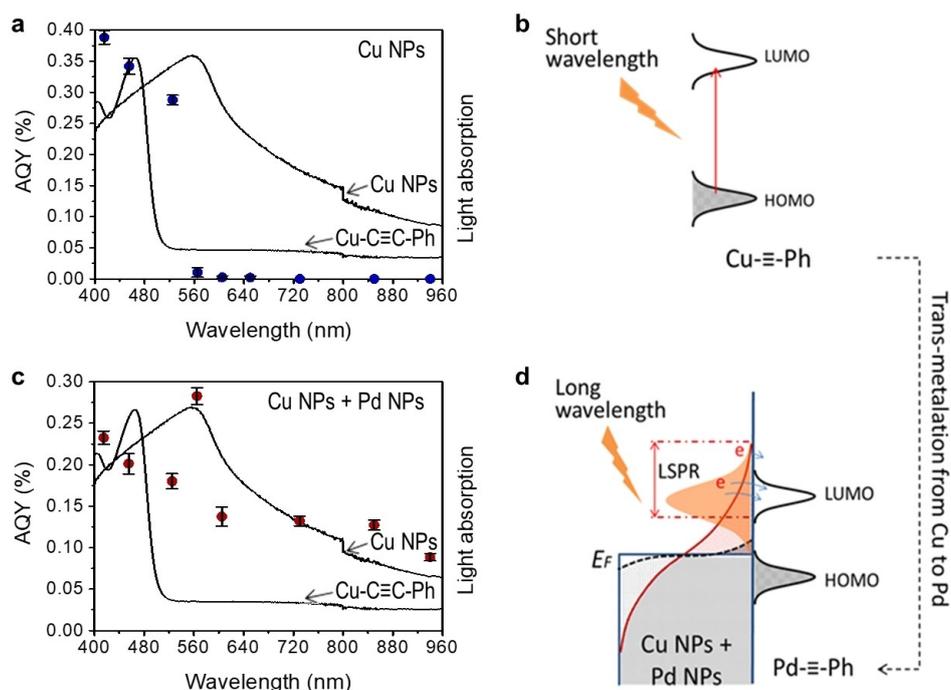


Figure 4. a), b) Action spectra (the apparent quantum yield, AQY, plot against the wavelengths) of the Glaser coupling reaction over Cu NP catalyst and the mixed Cu/Pd catalyst, respectively. b) and d) are the energy diagram of (a) and (c).

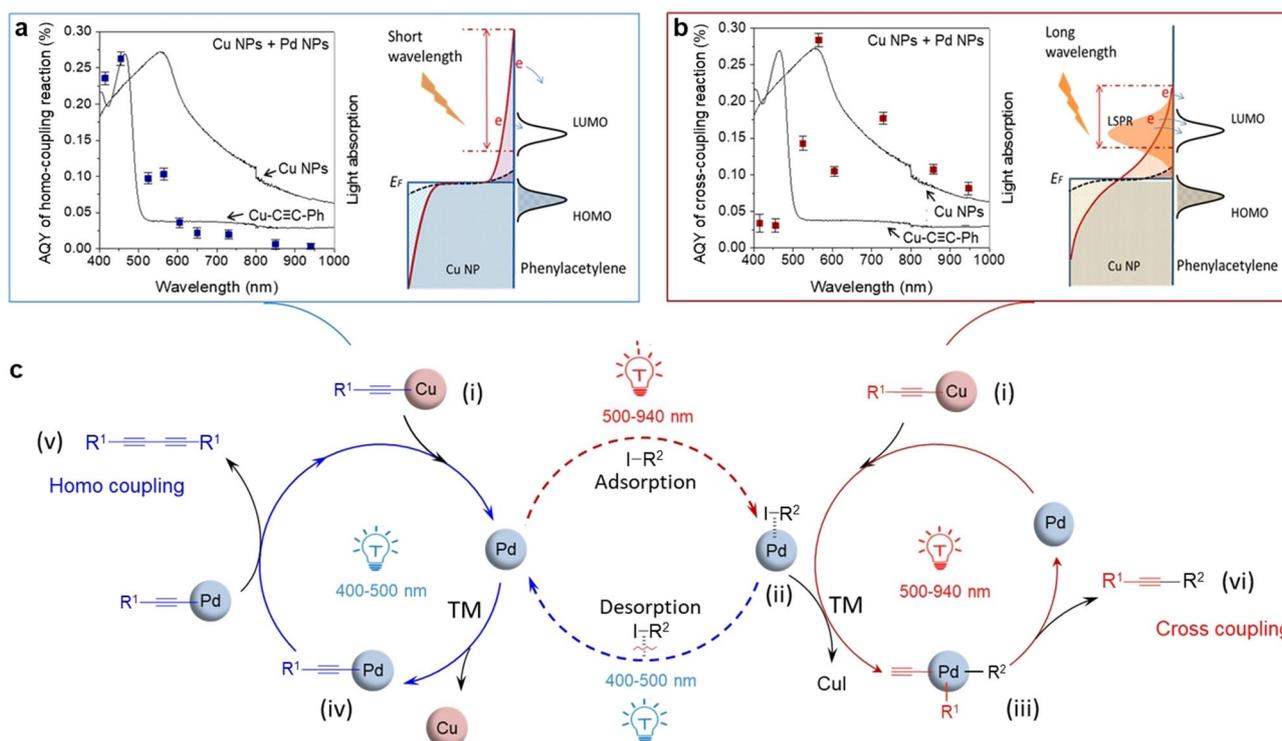


Figure 5. Action spectra and energy diagram of the Sonogashira coupling reaction over mixture Cu/Pd NP catalyst. a) Under short wavelength irradiation, the formation of homo-coupling reaction. b) Under long wavelength irradiation, the formation of cross-coupling reaction. c) Scheme of proposed mechanism for wavelength switchable Sonogashira coupling photocatalyzed by Cu/Pd mixed metal nanoparticle catalyst, the blue circle shows the mechanism under short wavelength irradiation and the red circle shows the mechanism under the long wavelength irradiation. TM: transmetalation.

absorption of Cu NPs can contribute to the homo-coupling, switching the reaction product distribution.

The distinct wavelength dependence of Glaser coupling reaction when catalyzed by Cu and mixed Cu/Pd catalyst discussed above, clearly demonstrated the transmetalation of Ph–C≡C– between Cu and Pd, and showed this transmetalation step enhanced by the LSPR absorption of Cu NPs.

When Sonogashira coupling is catalyzed by the mixed Cu/Pd the reaction shows a significant product selectivity, dependent on wavelength (Figure 5): The shorter wavelengths resulted in diyne as the major product from phenylacetylene homo-coupling (Figure 5a). Shorter wavelength irradiation appears to promote formation of Ph–C≡C– species via cleavage of Cu–C bond in cuprous phenylacetylide on Cu NPs (Figure 2d). This increases the concentration of Ph–C≡C– species near the Pd surface through transmetalation of the Ph–C≡C– species to the Pd NPs. The consequent high local concentration of Ph–C≡C– species may suppress iodobenzene adsorption at the surface of Pd NPs, resulting in high phenylacetylene conversions but very low iodobenzene conversions (Figure 2d). Another possibility is that short wavelength irradiation induces iodobenzene desorption. The iodobenzene conversion over the mixed Cu/Pd at wavelengths ≤ 455 nm is even lower than that which occurs in the dark (Entry 11 of Table S2 and Figure 2d), which allow a high selectivity to the homo-coupling reaction product.

A salient feature of this catalysis process, is that the highest yield of Sonogashira coupling over the mixed catalyst is delivered using the wavelength of LSPR absorption of Cu NPs, as shown in Figure 5b. The overall quantity of cuprous phenylacetylide formed on Cu NP surface is increased under the influence of the LSPR effect (Figure 4c) and thus the quantity of cuprous phenylacetylide transferred to Pd surfaces for Reaction (5) can be expected to be higher. The coupling of Ph- species and Ph–C≡C– species on the surface of Pd NPs proceeds more readily than on the surface of Cu NPs, and the efficiency is the highest at LSPR wavelength than at the other wavelengths (Figure 5b). Nevertheless, when employing shorter wavelength light, the formation of a large quantity of cuprous phenylacetylide near the surface of Pd NPs lowers levels of Ph–Pd–I to favor homo-coupling over cross-coupling (Figure 5a). Thus, low yield of the cross-coupling product and high selectivity to homo-coupling product are observed in a short wavelength range (Figure 2 and Figure 5a). This could be due to competitive adsorption of Ph–C≡C– transferred from Cu, or possible iodobenzene desorption induced by short wavelengths, leading to high selectivity to homo-coupling and the product distribution observed.

Under NIR (wavelength > 730 nm) irradiation, the phenylacetylene conversion on the mixed Cu/Pd decreases to $\approx 16\%$ and is much lower than under visible light (Figure 5). The substantially reduced cuprous phenylacetylide quantity benefits the iodobenzene activation on Pd surface. The iodobenzene conversion on the mixed Cu/Pd under NIR irradiation is much higher than occurs under short wavelengths < 455 nm and the ratio of the amount of

cuprous phenylacetylide compared to the activated iodobenzene on Pd surface approaches that optimal for high selectivity to the product of the Sonogashira cross-coupling (Figure 2d). This is the key factor for determining which pathway the reaction takes, which can therefore be switchable by the wavelength.

On the basis of the above discussion, we propose a mechanism of the wavelength-switchable Sonogashira cross-coupling in 1 bar O₂ gas catalyzed by the illuminated mixed catalyst as shown below in Figure 5c.

We propose that phenylacetylene reacts with Cu NPs under O₂ atmosphere (Reaction 1), as oxidative addition, yielding cuprous phenylacetylide (i) on the Cu surface.^[7c,11] O₂ facilitates abstraction of the acetylenic hydrogen by the metal.^[12] Highly efficient iodobenzene activation on the Pd NPs surface could form the intermediate aryl iodide surface complex Ph–Pd–I (ii).^[11,13] The cuprous phenylacetylide (i) reacts with surface complex Ph–Pd–I (ii) via transmetalation of Ph–C≡C– from Cu to Pd, forming a Pd surface complex (iii)^[11c,2b,4a,14] (Red circle; TM: transmetalation). Iodine on Pd is removed by forming CuI during the transmetalation.^[4a,b] The irradiation with short wavelength light (blue light, 400–500 nm) promotes the rapid formation of cuprous phenylacetylide (i) and its subsequent transmetalation (Blue circle), forming Pd surface complex (iv). This results in a large quantity of cuprous phenylacetylide that suppresses the iodobenzene activation, and so the homo-coupling compound (v) predominantly forms as a major final product by reductive elimination. In contrast, when longer wavelength irradiation is employed (Red circle), the formation of cuprous phenylacetylide is decreased while the iodobenzene activation is enhanced, thereby favoring cross-coupling product (vi).^[11c,d,1,2b,15] Visible light and NIR irradiation can promote the transmetalation because of the low energy barriers involved. Thus, the intense LSPR light absorption of Cu NPs results in the highest yield at 560 nm for both homo-coupling and cross-coupling over the mixed Cu/Pd. The enhanced transmetalation accelerates the conversion of both reactants. This mechanism suggests an exciting opportunity to tune the product selectivity by changing wavelength.

Conclusion

In summary we report a new approach to catalyze Glaser homo-coupling and Sonogashira cross-coupling reactions under mild conditions, efficiently, with visible and near-infrared light irradiation, that can switch the reaction pathway between homo-coupling and cross-coupling by simply changing the irradiation wavelength. Moreover, we have found, fundamentally, that light irradiation promotes the transmetalation of the intermediate species formed on Cu NPs to Pd surface. Thus, it is possible to apply long wavelength irradiation to promote the Sonogashira coupling selectively in an O₂ atmosphere (O₂ facilitates the reaction, see Table 1). These findings demonstrate how light irradiation can promote fundamental steps, such as the transmetalation in catalysis, to reduce energy barriers of coupling

reactions. This mechanism promises opportunities for flexible, mixed catalysts that switch of key reaction pathways by changing irradiation wavelength, inspiring development of efficient photocatalytic processes tailored to important targets for fine chemical syntheses.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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