Light-induced Sonogashira C-C Coupling under Mild Conditions using Supported Palladium Nanoparticles

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ABSTRACT: The Sonogashira reaction can easily be photocatalysed by supported palladium nanoparticles. We demonstrate that the direct excitation of the PdNPs can catalyze the C-C coupling between different aryl iodides and acetylenes under very mild conditions in short reaction times. The catalyst is air and moisture tolerant and can be supported in a wide range of materials, including inert ones such as nanodiamonds. Study of the action spectrum demonstrates that direct excitation of the PdNP is required, and for example in the case of Pd@TiO₂ visible excitation works well, while UVA (368 nm) is ineffective due to TiO₂ shielding of the Pd absorption. The catalyst can be reused a couple of times, but when it loses activity it can be readily reactivated via a simple reductive photochemical strategy.

INTRODUCTION

The C-C coupling reactions are one of the most important strategies in synthetic organic chemistry. The idea of constructing complex molecular architectures from suitable tailored building blocks has been explored for decades. Palladium (Pd) catalysed cross-coupling reactions comprise one of the most efficient methods for the construction of C-C, C-N and C-O bonds.¹ These cross-coupling methodologies have revolutionized synthetic organic chemistry, having found widespread use in organic synthesis and material science, as well as playing an important role in pharmaceutical, agrochemical and fine chemical industries.² The metal-catalyzed Sonogashira coupling reactions lead to the formation of new C-C bonds and it is now the most important method for preparing aryl alkynes and conjugated enynes, which are key precursors in the synthesis of natural products, pharmaceuticals, and organic molecular materials.³ Pd complexes constitute the most commonly used catalysts; however, opinion remains divided with regard to the identity of the catalytically active species: are they the soluble metal complexes introduced, or the surfaces of metallic particles that are derived from such complexes.⁴ While homogeneous catalysts showed outstanding activity,⁵ the homogeneous catalysts has several drawbacks such as post reaction separation of the product from the catalyst, non-reusability, air and water sensitivity.⁶ The search for heterogeneous, reusable and efficient catalysts to replace the homogeneous ones promises practical solutions to many problems in catalysis. Gonzalez-Arellano *et al.* reported the use of a gold-ceria nanomaterial as a heterogeneous catalyst for this reaction, where Au(I) seems to be the catalytic active species, although Au(0) and Au(III) were the predominant components of the solid catalyst.⁷ Sagadevan *et al.* reported the use of CuCl

for photo-induced Sonogashira C-C Coupling at room temperature.⁸ However, the use of Cu halides is sensitive to air leading to formation of homo-coupling products (Glaser coupling)⁹. Additionally, the deficiency as well as the excess of copper intake raises some environmental and health concerns.¹⁰ Therefore, remarkable efforts have been dedicated to develop Sonogashira cross-coupling procedures in the absence of copper additives, so-called copper-free Sonogashira coupling.^{1d, 11}

In this respect, the use of supported PdNPs has been explored in the last few years because of their potential to replace Pd complexes as catalysts.¹² We have recently shown that Pd-based nanomaterials can be used as heterogeneous catalysts for alkene isomerization/hydrogenation reactions.¹³ A Pd on silica catalyst has been shown to catalyse the Sonogashira coupling under reflux (for example ethanol, but not methanol) or under microwave heating at temperatures up to 150°C.¹⁴

Our own interests have centered on photoinitiated reactions, trying to use very mild conditions that avoid potential reagent or product decomposition and help retain the integrity of the catalysts themselves. Further, with a view at potential imaging applications, the ability of light to provide temporal and spatial control is a very desirable feature. Today's advanced and inexpensive LED technologies allow reactions to be initiated under very mild conditions and with at least 10 times less power consumption than typical laboratory microwave ovens. Further, knowledge of the absorption spectra of reagents and products allows the selection of narrowband LED illuminators at benign wavelengths that prevent photodegradation of organics.

Here we show the use of supported PdNPs on different materials that can successfully catalyze Sonogashira C-C

couplings under visible light irradiation at room temperature. The successful use of different materials as catalyst supports, namely titanium dioxide (TiO₂), carbon nanodiamond (CND) or niobium oxide (Nb₂O₅), demonstrates the versatility of the photocatalytic activity of PdNP to work under ligand-free environment; an emerging field in catalysis. To the best of our knowledge, this is the first time that PdNP-decorated TiO₂ (Pd@TiO₂), CND (Pd@CND) or Nb₂O₅ (Pd@Nb₂O₅) are used as catalysts for the Sonogashira C-C couplings of different phenylacetylene and aryl iodides simply by using visible light (scheme 1), although we note the catalyst also works under thermal conditions. Both conditions selectively lead to the cross-coupling product without incorporation of ligands.

Scheme 1. Sonogashira C-C coupling catalyzed by supported PdNPs under mild conditions.

The selection of TiO₂ as a support is known to affect tandem reactions in which the change of the irradiation source can give different outcomes.¹³ We have also examined the action spectrum, that is, discover which spectral region drives the photocatalytic reaction. This photochemical mechanistic tool demonstrates that in this system the catalytic process is centered exclusively on the Pd nanoparticles and that the support is essentially inactive, except in the case of Nb₂O₅ where abundant acid sites may cause a small rate reduction.

RESULTS AND DISCUSSION

The use of PdNP-decorated materials (TiO₂, CND and Nb₂O₅) has been explored for the selective cross-coupling of iodobenzene and phenylacetylene under both reflux and visible light irradiation. The Sonogashira reaction was investigated under conventional heating (thermal conditions) using methanol as solvent under air or under Ar atmosphere. The results summarized in table 1 show that Pd and heating are needed for the reaction to proceed (entries *i-iv*). Although previous report suggest that higher temperatures are needed,¹⁴ here we show that methanol boiling point (65 °C) is sufficient for the reaction to proceed. The efficiency of the catalyst with different supports slightly changes, with TiO₂ as the most promising one. While the reaction works best under argon, it is reasonably air tolerant.

Table 1. Different experimental conditions tested for the thermal-induced Sonogashira C-C coupling using Pd-decorated materials.

	Catalyst	Conditions	% Conv	% Yield ^a
i	none	65 °C, Ar	0	ND
ii	TiO ₂	65 °C, Air	0	ND
iii	Pd@TiO ₂	RT, Ar	0 (57)	0 ^b (50)
iv	Pd@TiO ₂	65 °C, Air	66	47 ^c
v	Pd@TiO ₂	65 °C, Ar	>99	82 ^c

vi	Pd@CND	65 °C, Air	71	35 ^c
vii	Pd@Nb ₂ O ₅	65 °C, Air	75	24 ^c

Reactions conditions: 1 eq. of Iodobenzene, 1.3 eq. of Phenylacetylene, 2 eq. of K₂CO₃, 4 mL methanol, 15 mg catalyst. ^aYields were determined by GC-FID using *t*-butylbenzene as an external standard. ^bUnder dark conditions, values between brackets were run at 42 °C. ^cTraces of alkyne homo-coupling were found.

The Sonogashira coupling was also evaluated under different conditions upon visible light irradiation (465 nm LED) as summarized in Table 2. Thus, the photocatalytic reaction only proceeds when Pd-decorated materials are irradiated with visible light (465 nm LED). Further, the reaction is dependent on the presence of PdNP to selectively favour the C-C sp-sp² hetero-coupling (Table 2, entries *i-v*). The role of the base was also evaluated and the best conditions were found when the aryl iodide and the phenylacetylene were mixed together with Pd@TiO₂ (Pd-loading ~1.3 wt%) catalyst using methanol as solvent, 2 equivalents of K₂CO₃ and irradiated for 5 h under Argon atmosphere (Table 2, entry *v-ix* and Figure S1). It is known that K₂CO₃ in MeOH can generate a stronger base, methoxide,¹⁵ and this might explain why other bases such as TEA (Table 2, entry *iv*) cannot perform as well. Changing the catalyst support for a known inert and rather transparent material such as crystal nanodiamonds (CND, Pd-loading ~1.7 wt% by ICP-OES), the yield of the reaction remains the same (*cf.* entries *v* and *x*, Table 2). The use of niobium oxide as a support considerably drops the yield of the reaction (Table 2, entry *xi*), presumably due to interaction of the base with the acid sites on the surface of the support.¹⁶ Accordingly, the material has slightly low Pd-loading (0.7 wt% by ICP-OES) comparing with TiO₂ or CND, although all materials were prepared under the same conditions. In addition, TEM images show that the particle size (~3 nm) is slightly bigger than those found in the other two supports (Figure S3). Interestingly, the photoinitiated cross coupling reaction also shows air tolerance although more time is needed to achieve complete conversion (Table 2, entry *ix*). Additional experiments run in different solvents (Table S2) show the reaction is highly favored in polar protic solvents (e.g. Methanol), possibly due to the K₂CO₃ solubility,¹⁵ although small conversion and lower selectivity has been found using non-protic polar solvents (*i.e.* THF, AcN). The reaction is also moisture tolerant (Table 2, entry *viii*). The intensity of the irradiation also affects the product yield (Table 2, entry *vi*) suggesting a photochemical process involved in the reaction (*vide infra*). The optimum amount of catalyst was determined ~1.5 mol% as shown in Figure S2. Finally, other metal nanoparticles (Cu, Au) were tested under the same reaction conditions (Table 2, entries *xii-xv*). Cu-based catalyst has shown alkyne homo-coupling product formation⁹ and only moderate yields of the desired product. Decomposition of the catalyst within the time of reaction was also detected in the case of copper. Although there are reports on the excellent performance of AuNPs towards Sonogashira couplings,^{7, 17} commercial Au@TiO₂ leads to negligible conversion under the very mild conditions used in our system.

Table 2. Different experimental conditions tested for the light-induced Sonogashira C-C coupling using Pd-decorated materials.

	Catalyst	Base	Atm	% Conv	% Yield ^a
i	none	K ₂ CO ₃	Ar	0	ND
ii	TiO ₂	K ₂ CO ₃	Ar	0	ND
iii	Pd@TiO ₂	none	Ar	0	ND
iv	Pd@TiO ₂	TEA	Ar	38 (53)	30 (40)
v	Pd@TiO ₂	K ₂ CO ₃	Ar	>99	80-86
vi ^b	Pd@TiO ₂	K ₂ CO ₃	Ar	70	34
vii ^c	Pd@TiO ₂	K ₂ CO ₃	Ar	37	35
viii ^d	Pd@TiO ₂	K ₂ CO ₃	Ar	100	68
ix	Pd@TiO ₂	K ₂ CO ₃	Air	54(>99)	52 (80)
x	Pd@CND	K ₂ CO ₃	Ar	>99	78
xi	Pd@Nb ₂ O ₅	K ₂ CO ₃	Ar	53	36
xii	Cu@TiO ₂	K ₂ CO ₃	Air	>99	38 ^e
xiii	Cu@TiO ₂	K ₂ CO ₃	Ar	>99	30 ^e
xiv	Au@TiO ₂	K ₂ CO ₃	Air	0	ND ^f
xv	Au@TiO ₂	K ₂ CO ₃	Ar	0	ND ^f

Values between brackets correspond to 24 h of reaction. Reactions conditions: 1 eq. of Iodobenzene, 1.3 eq. of Phenylacetylene, 2 eq. of base, 4 mL methanol, 15 mg catalyst. Irradiation: 465 nm LED set at 1 W/cm². ^aYields were determined by GC-FID using *t*-butylbenzene as an external standard. ^bIrradiation at 0.2 W/cm². ^c1 eq. of K₂CO₃. ^dSolvent= 9:1 CH₃OH:H₂O. ^eAlkyne homo-coupling was found as the major product, catalyst decomposition was also detected. ^fIrradiation source: four 532 nm LEDs each of them working at 0.56 W/cm². No conversion detected under conventional heating conditions.

It is important to highlight that homo-coupling products from the aryl iodide reagents were not detected under the conditions studied. Indeed, no coupling products were detected if only one of the reagents is subjected to the reaction conditions (Table S3), which further confirms the selectivity of this catalyst towards cross-coupling reaction. Additionally, the alkyne product shows strong stability under the reaction conditions, despite the well-known reductive properties of the catalyst under light.^{13, 18} Interestingly, phenylacetylene can undergo deuterium incorporation under these conditions when the reaction is run in deuterated methanol. This clearly indicates that the H-Pd surface interaction is strong enough to deprotonate the alkyne and form the corresponding carbanion, a strong base able to act as a nucleophile, or in the absence of substrate, to trap D¹⁹ (Scheme 2).

Scheme 2. Proposed mechanism for Sonogashira coupling or phenylacetylene deuteration in the absence of aryl iodides and in the presence of CD₃OD.

In order to investigate further the photocatalytic activity of this material, the action spectrum of the Pd@TiO₂ photocatalyst was measured. This technique is widely used in photobiology and recently introduced by us in an example of heterogeneous photocatalysis.²⁰ An action spectrum can be described as a plot of the apparent quantum yield of the reaction versus the wavelength of the incident photons when the same number of einsteins is delivered to the sample.²⁰ An action spectrum can help differentiate if the photoreaction is simply the consequence of a lowering of the semiconductor band gap or due to the absorption band of Pd@TiO₂ that extends to longer wavelengths (*ca.* 740 nm in this case). Thus, if the mechanism involves direct Pd excitation (sometimes referred as direct photocatalysis),²⁰ the action spectrum will simply resemble the absorption profile of the photocatalyst. Then, the action spectrum can be obtained by plotting the apparent quantum yield (ν_0/Φ) versus the wavelength of the incident photons (see calculations in SI). As can be seen in Figure 1, the catalytic performance in the visible region overlaps with the diffuse reflectance spectrum of the Pd@TiO₂ catalyst, suggesting the light-induced Sonogashira coupling involves the direct excitation of PdNP. This is in agreement with reported photocatalytic mechanism of nonplasmonic metallic nanoparticles, where the intensity and the light wavelength can interfere with the photothermal product yields.²¹ Interestingly, the photonic efficiency of the reaction suddenly drops to zero when irradiation below 400 nm is used. This can be readily rationalized as the light absorption efficiency of TiO₂ increases below 400 nm effectively shielding the PdNP from light absorption and therefore the generated heat is not localized at the Pd centers. However, when Pd@CND is used similar catalytic efficiencies are found using both UV light or blue light (Table 3). This further confirms the idea of TiO₂ role as a simple support that can be easily replaced by inert materials such as CND.

Table 3. Comparison of the use of CND and TiO₂ as supports and their catalytic performance upon excitation using different irradiation wavelengths.

	Catalyst	λ (nm)	% Conv	% Yield
i	Pd@CND	465	100	78
ii	Pd@CND	368	100	80
iii	Pd@TiO ₂	465	100	82
iv	Pd@TiO ₂	368	100	18*

Conditions: 4 h irradiation at 1 W/cm². *Mixture of by-products includes around 35 % of stilbene.

Figure 1. Comparison of the acquired action spectrum (pink dots) and the diffuse reflectance spectra of the TiO_2 (red), the Pd@TiO_2 (black), and the difference spectrum (blue). Conditions: 2 hours of irradiation, irradiance of 0.19 W cm^{-2} (See SI).

The scope of the catalytic activity has been explored with a diverse group of aryl iodides and alkynes, as shown in Table 4. Notice that for *para* substituted aryl iodides, both electron withdrawing- and electron donating groups, show excellent yields. As expected, *ortho* substituted analogs show lower yields under the same reaction time.

Table 4. Scope of the reaction using different substituted aryl iodides and phenylalkyne and 1.5 wt % Pd@TiO_2 .

	R_1	R_2	% Conv	% Yield ^a
i	H	<i>p</i> - CO_2CH_3	>99	92 ^b
ii	H	<i>p</i> - OCH_3	>99	99 ^b
iii	H	<i>o</i> - OCH_3	60(80)	60(80) ^b
iv	H	<i>p</i> - NH_2	>99	99
v	H	<i>p</i> - NO_2	>99	99 ^b
vi	H	<i>o</i> - CH_3	48 (80)	43 ^b (67)
vii	H	<i>o</i> - NH_2	50(60)	44 ^b (52)
viii	H	<i>p</i> - CF_3	>99	99 ^b
ix	H	H	>99	82
x	<i>p</i> - NH_2	H	>99	99
xi	<i>p</i> - OCH_3	H	>99	99
xii	<i>o</i> - NH_2	H	55(59)	39(50)
xiii	<i>p</i> - CH_3	H	>99	>99

^aYields were determined by GC-FID using *t*-butylbenzene as an external standard. ^bIsolated yields.

The photocatalyst can be reused twice with good performance (Table 5). The catalytic activity drops down drastically after the second cycle, but ICP-OES analyses of the reaction mixtures show no Pd-leaching from the catalyst. XPS studies suggest accumulation of alkyne hydrogenation products on the surface as the likely cause for poisoning (Figure S5). In order to restore the catalytic activity, an

easy recovery phototreatment¹³ using I-2959 and UVA light can be performed (See SI). Further analysis of the material before and after reaction suggest particle size increase and changes on the oxidation state of Pd species. Those can be reverted by phototreatment with I-2959 (Figures S4 and S5), recovering the catalytic activity of the material.

Table 5. Catalyst reusability for the reaction under conditions described in Table 4, entry iii.

	Cycle	Conversion (%)	Yield (%)
i	1	100	99
ii	2	75	75
iii	3	<5	Traces
iv	4 ^a	100	78

^aAfter catalyst recovery treatment with I-2959.

CONCLUSIONS

We demonstrated that supported PdNPs can act as photocatalysts for Sonogashira coupling independently of the material chosen as a support. Mild conditions, good tolerance for air and moisture, spatial and temporal control are some of the assets that can be highlighted for this material. Interestingly, the catalyst can perform as well under regular thermal conditions as under photocatalytic conditions. Particularly, Pd@TiO_2 drives the Sonogashira reaction within short reaction times (usually 5 h) with unprecedented yields under mild conditions. The performance of the photocatalyst matches very well the absorption profile of the supported PdNP.

ASSOCIATED CONTENT

Supporting Information

Experimental details, instrumentation used, and characterization of materials (PDF). The Supporting Information is available free of charge on the ACS Publications website.

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