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### Selective Excitation of Pd-decorated Titania Enables Consecutive C–C Couplings and Hydrogenations under Ambient Conditions

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Here, we discovered that Pd decorated  $TiO_2$  (Pd@TiO<sub>2</sub>) enables consecutive photocatalytic Sonogashira C–C coupling and hydrogenation steps by simply adjusting the excitation conditions of the reaction. We demonstrated that by-products containing iodine species generated in the first reaction step can inhibit subsequent photocatalytic processes, but they can

#### Introduction

Common synthetic routes to fine chemicals rely on a series of steps, frequently involving a C-C coupling step to furnish unsaturated C-C bonds. These reactions are often coupled to their subsequent hydrogenation, commonly performed using H<sub>2</sub> gas.<sup>[1]</sup> The two steps are achieved using different reaction conditions and catalysts, reducing the atom and energy economy of the whole process. Simplifying the reaction conditions to combine the two steps in a less wasteful approach is difficult, as finding compatible synthetic sequences that can allow the use of simple reagents to construct more sophisticated molecules has proved challenging.<sup>[2]</sup> A recent example shows Sonogashira couplings can be coupled to hydrogenation reactions using a combination of heterobimetallic complexes<sup>[3]</sup> and a borohydride as the hydrogen source. Nevertheless, the homogeneous nature of this one-step process still requires the synthesis of complex organic ligands and makes palladium reusability virtually impossible. Incorporating multifunctional heterogeneous photocatalysts into consecutive transformations can improve the atom economy and environmental footprint of the process. An example demonstrates the

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be easily removed from solution to enable a compatible synthetic sequence for new C–C bond formation under mild reaction conditions. This work incorporates heterogeneous photocatalysts into consecutive transformations, promoting elegant reactions while meeting the demands of green chemistry.

Suzuki reaction and subsequent hydrogenation of a pyridine ring using heterogeneous Pd/C catalyst, where poisoning effects are overcome by adding excess of catalyst (Pd loadings between 10-80 mol%) in the second step.<sup>[4]</sup> Nevertheless, examples using a heterogeneous catalyst for sequential coupling and hydrogenation remain uncommon. Common heterogeneous photocatalysts include inorganic semiconductors, such as TiO<sub>2</sub>, which are frequently decorated with transition metals (e.g. Pd, Au, Ni, Cu) and employed in a variety of one-step organic transformations.<sup>[5]</sup> In this work we have demonstrated that an easy-to-separate heterogeneous photocatalyst based on Pd decorated TiO<sub>2</sub> (Pd@TiO<sub>2</sub>) can be used to trigger Sonogashira couplings and hydrogenations in a consecutive manner and using low Pd catalyst loadings (<2 mol%). Notably, Pd@TiO<sub>2</sub> has been previously used to photocatalyze a variety of organic reactions including C-C couplings, transfer hydrogenation, olefin isomerization, and benzylic arylation.<sup>[6]</sup> The photocatalyst has shown distinct reactivity under different irradiation regimes. Using Sonogashira C--C couplings in combination with hydrogenations we proved Pd@TiO<sub>2</sub> can trigger consecutive processes by simply adjusting illumination, in otherwise similar reaction conditions (Scheme 1). Sonogashira C–C coupling proceeds under blue light excitation ( $\lambda_{max}$ :



**Scheme 1.** Conventional two-step reaction versus consecutive photocatalysis involving a C–C coupling (Sonogashira coupling) followed by a transfer hydrogenation to yield alkenes or alkanes.  $R_1$ : Aryl or alkyl,  $R_2$ : Aryl.

450 nm), where TiO<sub>2</sub> is not excited, but it acts as a heterogeneous support for the Pd nanoparticles (Figure S6). The reaction is believed to proceed *via* a photothermal effect triggered by the Pd nanoparticles light absorption.<sup>[6c]</sup> In contrast, hydrogenations, in this case transfer hydrogenations, require UVA light excitation ( $\lambda_{max}$ : 365 nm), which can directly excite TiO<sub>2</sub>, creating exciton pairs within the semiconductor. The photoexcited holes are highly electrophilic and can activate C–H bonds<sup>[7]</sup> from certain solvents (e.g. alcohols), while electrons can form metal-H species from the resulting H<sup>+</sup>.

As a result, either  $H_2$  gas formation or transfer hydrogenation can be catalyzed under mild conditions (Figure S6). Given the change in reactivity exhibited by this catalyst under different excitation energies, we designed the method shown in Scheme 1: an aryl halide and terminal alkyne are subjected to the photocatalytic Sonogashira C–C coupling reaction under blue light, giving the cross-coupled alkyne. Switching the blue light for UVA light would furnish the corresponding alkene(ane) while the rest of the reaction components remain unchanged. Overall, the study offers an understanding of potential poisoning species and provides a solution that eliminates the need for excessive catalyst usage.

#### **Results and Discussion**

To test the consecutive reactions, we deposited Pd onto  $TiO_2$  (P25) using a magnetron sputtering approach,<sup>[8]</sup> resulting in Pd nanoparticles with a mean diameter of  $2.2\pm0.5$  nm (Figure 1a)



**Figure 1.** Characterisation of Pd@TiO<sub>2</sub>: (a) TEM image showing well-dispersed Pd nanoparticles (darker dots) onto P25 TiO<sub>2</sub>. Inset: Pd particle size distribution. (b) Pd 3d HR XPS spectrum.



Scheme 2. Photocatalytic Sonogashira coupling and photocatalytic transfer hydrogenation using  $Pd@TiO_2$ . Reaction conditions shown in the reaction arrow. Irradiance: 9 Wcm<sup>-2</sup> (blue) and 1.3 Wcm<sup>-2</sup> (UVA).

and 1.2 wt% Pd loading. High resolution TEM (HR-TEM) shows Pd d-spacing consistent with the presence of Pd(0) (Figure S4), whereas surface analysis *via* high resolution X-ray Photoelectron Spectroscopy (HR-XPS) of the Pd 3d signal reveals a composition of ~70% Pd(0) and ~30% Pd(II) (Figure 1b). The resulting material shows increased absorption across the visible region, consistent with previous reports (Figure S1).<sup>[6c]</sup> Further characterization analysis can be found in the accompanying ESI.

We first investigated the performance of Pd@TiO2 on photocatalytic Sonogashira coupling and photocatalytic transfer hydrogenation of model reagents when the reactions are performed separately, furnishing complete conversion to the desired product as shown in Scheme 2. Control experiments suggest the photocatalyst and light are essential for the reactions to take place (Tables S1–S2). In addition, the Sonogashira reaction proceeds to completion in the presence of dibenzocyclooctatetraene (DCT)<sup>[9]</sup> (Scheme S1), supporting the heterogeneous nature of the reaction. Then, we assayed the same reactions in a consecutive manner, i.e. upon completion of the Sonogashira reaction we adjusted the illumination conditions from blue light excitation to UVA light excitation to generate hydrogenation products. Nevertheless, this produced only trace amounts of the alkene product, with longer irradiation times having no effect on conversion. XPS analysis of the catalyst after reaction reveals the presence of a single iodine species on the catalyst surface, as observed in the I 3d HR-XPS spectrum (Figure 2a), where the signal at 618.4 eV could correspond to the presence of KI<sup>[10]</sup> or other unidentified iodine containing species. The C 1s HR-XPS spectrum shows two new peaks (Figure 2b) at high binding energies (BE = 292.5 eV and 295.3 eV), likely corresponding to K 2p<sub>3/2</sub> and K 2p<sub>1/2</sub> contributions from adsorbed potassium carbonate.<sup>[11,12]</sup> On the other hand, the signals corresponding to Pd 3d, O 1s and Ti 2p are shifted towards lower binding energies, with shifts of ca 0.8 eV for Pd and ca 0.5 eV for O and Ti (Figure 2c, d). These results suggest adsorbed organoiodide species are shielding both Pd



**Figure 2.** HR XPS spectra showing signals on the surface of  $Pd@TiO_2$  before and after Sonogashira reaction and after washing with methanol for (a) iodine species; (b) carbon species; (c) titanium species; and (d) palladium species.

ChemCatChem 2023, 15, e202300528 (2 of 6)



8673899

NPs and TiO<sub>2</sub> surfaces and could be the cause for catalyst deactivation in the transfer hydrogenation step. Fortunately, subjecting the poisoned catalyst to several washing cycles in methanol proved effective to clean the surface, as subsequent XPS analysis showed the disappearance of both iodine and the associated carbon signals. The washing also restored the initial position of the Ti 2p and O 1s signals to within 0.2 eV. As expected, Pd 3d signals remain shifted by ~0.5 eV towards low binding energies compared to fresh catalyst, which has been attributed to the reduction of Pd species (Pd(0) 75% after reaction) under the reaction conditions.<sup>[61]</sup>

With this information we decided to test the consecutive reaction after separating the 'poisoned' catalyst from the



Sonogashira step and replacing it with washed or fresh catalyst. Unfortunately, this still yielded to only trace products, indicating some of the upstream by-products remaining in solution can poison the transfer hydrogenation step. Therefore, we evaluated the potential effect of homogeneous species generated during the Sonogashira step. The main differences between the two steps are the presence of a base and iodine species that can be generated upon C-C coupling completion. Table 1 shows the presence of K<sub>2</sub>CO<sub>3</sub> halves the conversion of the alkyne into alkene (only 50% conversion and yields after 5 h of irradiation), whereas incorporation of iodine (I<sub>2</sub>) quenches the reaction almost completely (7% yield after 5 h). It is interesting to note that the presence of iodide species does not appear to have any negative effect on conversion in the Sonogashira reaction, as the concentration of the starting reagents can be increased by 2.5 times without any observed loss in conversion (Table S3).

As mentioned before, reintroducing the washed (or fresh) catalyst proved ineffective in allowing the transfer hydrogenation step to proceed (Table 2, entry 2). This is likely due to the presence of the soluble iodide species carried over from the upstream reaction, which can simply re-adsorb onto the surface of the catalyst, thereby quenching the reaction. Thus, iodide species must be removed from solution before re-introduction of the catalyst. To achieve this, the reaction mixture was passed through alumina plugs directly after separation. Introduction of washed catalyst to this filtered mixture proved effective in allowing the transfer hydrogenation step to proceed, giving excellent conversion of the alkyne to the corresponding alkene

Table 2. Optimisation of the sequential photocatalytic Sonogashira reaction coupled to a transfer hydrogenation reaction. <sup>[a]</sup>									
$R_{3} \overset{I}{4} \overset{I}{5} \overset{I}{5} \overset{R_{2}CO_{3}}{\underset{Pd@TiO_{2}\\CH_{3}OH, N_{2}\\455 nm, 30 min}{\underset{Step 1}{\overset{R_{3}}{\overset{R_{4}}{\overset{Pd@TiO_{2}}{\underset{R_{3}}{\overset{R_{4}}{\overset{Pd@TiO_{2}}{\underset{R_{3}}{\overset{R_{4}}{\overset{R_{4}}{\overset{Pd@TiO_{2}}{\underset{R_{3}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{\overset{R_{4}}{R$									
Entry	R <sub>3</sub>	$R_4$	<b>6</b> Yield [%]ª	Catalyst	Step 2 time [h]	<b>6</b> Conversion [%]	<b>7</b> Yield [%]	E/Z	<b>8</b> Yield [%]
1	OCH₃	Ph	96	Unwashed, reused	5	< 1	Trace	N/A	ND
2	OCH₃	Ph	78	Washed, reused	5	< 1	trace	N/A	ND
3 <sup>b</sup>	$OCH_3$	Ph	88 (86)	Washed, reused	5	76 (100)	66 (>99)	1:4 (1:5)	trace
4 <sup>b</sup>	OCH₃	Ph	79	Fresh	5	98	40	1:3	59
5 <sup>b,c</sup>	Н	Ph	<sup>f</sup> 79	Washed, reused	5	92	89	1:6	trace
6 <sup>c,d</sup>	Н	Ph	<sup>f</sup> N/A	Washed, reused	5	88	85	1:3	trace
7 <sup>b</sup>	OCH₃	Ph	98	Fresh	2	96	84	1:3	trace
8 <sup>b,e</sup>	OCH₃	$C_6H_{11}$	65	Fresh	3	100	ND	N/A	99
9 <sup>b,e</sup>	OCH₃	$C_6H_{11}$	55	Fresh	0.33	64	58	1:15	Trace

Reaction conditions: iodoanisole (0.12 mmol), alkyne (0.16 mmol), potassium carbonate (0.24 mmol),  $Pd@TiO_2$  (15 mg, 1.2 wt% Pd, Pd = 1.4 mol% of limiting reagent), methanol (4 mL), nitrogen atmosphere, 455 nm excitation at 9.0 Wcm<sup>-2</sup> for 30 min, followed by 365 nm excitation at 1.3 Wcm<sup>-2</sup>. <sup>a</sup>Yields and conversions determined by GC-FID using tridecane as the external standard. Unwashed: catalyst is used straight from step 1. Washed: catalyst is washed between steps 1 and 2. <sup>b</sup>Reaction mixture filtered through 3 alumina plugs. Brackets show values obtained after rescaling the transfer hydrogenation reaction to account for catalyst loss. <sup>c</sup>Transfer hydrogenation step rescaled to account for catalyst loss during separation. <sup>d</sup>Transfer hydrogenation reaction performed with catalyst reused in entry 5 using diphenylacetylene (0.12 mmol) as starting material. <sup>e</sup>Blue light irradiation time 1 hour. ND: Not Detected.



time of 1 hour, giving a good yield of the alkyne product. Transfer hydrogenation was also successful after passing the supernatant through alumina plugs, and the introduction of fresh catalyst. Transfer hydrogenation of the alkyne was considerably faster than in the previous case, giving total conversion of the alkyne within 3 hours, with a near quantitative yield of the alkane as the sole product (Table 2, entry 8). Selectivity towards alkene product was also controlled via UV irradiation time (Table 2, entry 9). Conclusions Overall, we have demonstrated a versatile heterogeneous photocatalyst (Pd@TiO<sub>2</sub>) can trigger consecutive photocatalytic processes under mild reaction conditions by simply changing the illumination. We uncovered the effect of the upstream byproducts on catalyst deactivation and developed an easy separation methodology to carry on consecutive reactions. The mild reaction conditions utilized in this work (room temperature, atmospheric pressure, solvent as H source, low catalyst loadings) are almost identical between the two steps, with the major difference being the excitation wavelength, reinforcing the key role light plays in photocatalysis providing easy ways to manipulate product selectivity. This work represents a significant step forward in the development of sustainable synthetic methodologies. It provides a framework for the design of future photocatalytic processes that can be used in sequential transformations, including adaptation to continuous flow processes, which could offer further productivity and efficiency.

#### **Experimental Section**

#### Materials and instrumentation

Chemicals and solvents were purchased from Merck or Fisher Scientific and used without further purification. P25  $TiO_2$  was purchased from Sigma Aldrich.

GC-FID analyses were conducted using a Thermo scientific Trace 1310 gas chromatograph equipped with a Thermo scientific TG-17MS column (length 30 m, internal diameter 0.25 mm, film thickness 0.25  $\mu m$ ). GC-MS analyses were conducted using a Thermo scientific Trace 1300 gas chromatograph equipped with an ISQ LT single quadrupole mass spectrometer, and a Restek Rtx-1701 column (length 30 m, internal diameter 0.25 mm, film thickness  $0.25 \,\mu\text{m}$ ) or a Thermo scientific TG-17MS column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 µm). TEM images showing nanoparticle distribution were collected using a JEOL-2100+ TEM equipped with a GATAN Oneview camera. HR-TEM images showing d-spacing of the materials were collected using a JEOL-2100F FEG-TEM equipped with a GATAN K3 camera. 'Lacey' carbon covered 200 mesh Cu grids, purchased from Agar scientific, were used. Analysis of TEM images was conducted using GATAN DigitalMicrograph3 and Fiji/ImageJ software.<sup>[9]</sup> Palladium nanoparticle size was measured manually as low contrast between palladium NPs and metal oxide support prevented the use of automated techniques. XPS data was collected using a Kratos AXIS Ultra DLD instrument using monochromated aluminium K $\alpha$  emission at 120 W and a Thermo Scientific K-Alpha x-ray spectrometer

#### (Table 2, entry 3). The absorption profile of the reaction filtrate shows slightly higher absorption at 350 nm before (Figure S8) alumina plug filtration, which could reduce the number of photons reaching the catalyst but cannot account for the complete shutdown of the reaction observed. This further supports the presence of soluble species in the reaction filtrate, and not their absorption profile, are responsible for the poisoning effect. Further, inspection of the catalyst's surface via attenuated total reflectance infrared spectroscopy (ATR-IR) and thermal gravimetric analysis (TGA) suggest small quantities of hydrocarbons (< 2 wt%) are present in the unwashed catalysts compared to the fresh catalyst (Figure S9-S10 and Table S4). On the other hand, introduction of fresh catalyst yielded quantitative conversion of the alkyne in 5 hours, to the corresponding alkene and alkane (Table 2, entry 4). This suggests the reused catalyst furnishes the semi hydrogenation product only, potentially due to catalyst poisoning, which is how selectivity control is frequently achieved in traditional hydrogenations.<sup>[13]</sup> To explore this further, we reused the catalyst in a second cycle in the transfer hydrogenation of diphenylacetylene and obtained similar conversion and yield (Table 2, entry 5-6) at different reaction times (Figure 3). Noteworthy, we detected only traces of the alkane product, suggesting that although catalyst activity towards transfer hydrogenation can be recovered by catalyst washing, catalyst poisoning (or deactivation) during the Sonogashira step may be permanent. It is important to highlight that the catalysts' metal loadings remain constant throughout all catalytic cycles explored (see table S5). The content of Pd(0) after the last catalytic cycle (step 2) is ca. 70% (Figure S11) with slight increase of metal particle size, from 2.2 to 2.8 nm (Figure S12). Furthermore, the selectivity towards the alkene or alkane

Furthermore, the selectivity towards the alkene or alkane products can be tuned by irradiation. That is, reducing the UV irradiation time to 2 hours allows the selectivity to be flipped entirely towards the alkene product, providing a good yield and only minor traces of the alkane (Table 2, entry 7). This offers extra control on the reaction outcome *via* light excitation.

The viability of the consecutive reaction was also tested using aliphatic terminal alkynes using iodoanisole and 1-octyne as the starting materials. The Sonogashira reaction between these reagents was successful with a slightly increased reaction



**Figure 3.** Kinetics of transfer hydrogenation upon reuse of the  $Pd@TiO_2$  catalyst after the Sonogashira reaction to produced diphenylacetylene: (a) first transfer hydrogenation cycle (Table 2, Entry 5); and (b) second transfer hydrogenation cycle (Table 2, Entry 6). The rapid production of stilbene, followed by no further conversion to bibenzyl, suggests that residual catalyst poisoning or deactivation makes the reaction selective towards semi hydrogenation product.



8673899

with a monochromated aluminium source at 1486 eV. XPS analysis was carried out using CasaXPS software (version 2.3.24) and all fittings obtained using Gaussian-Lorentzian line shapes and a Shirley baseline, and calibrated to the C 1s signal at 284.8 eV. ICP-OES was conducted using a Perkin Elmer Optima 2000 DV. Pd emissions at 340.458 nm and 363.470 nm were used for quantification. Solutions were prepared by digestion of catalysts (ca. 10 mg) overnight in aqua regia, followed by dilution to 10 mL in 5% HCl solution after removal of solids by centrifugation. Thermal gravimetric analysis (TGA) was performed in a TA Q500 Thermogravimetric Analyser. All samples were measured using a platinum pan and in the presence of air. Experimental parameters were as follows: 10 min isothermal hold at room temperature, ramp from room temperature to 1000°C at 10°C/min, followed by a final 10 min isothermal hold at 1000 °C. Diffuse reflectance data was obtained using an Agilent Cary 4000 UV-Vis spectrophotometer equipped with an integrating sphere. A LuzChem LED illuminator equipped with an LEDi-HBL (blue, 455 nm) or LEDi-UV7 (UVA, 365 nm) was used for photocatalytic reactions. A StellarNet Black-Comet SR spectroradiometer was used to determine irradiance values. Temperature of reactions were determined using an IR thermometer and were generally 60-65°C under blue light, and 30–35 °C under UV light.

#### Preparation of Pd@TiO<sub>2</sub> catalyst

P25 titanium dioxide (1000 mg) was placed in a custom-built AJA magnetron sputterer. A 99.99% pure palladium target was used, set at a work distance of 90 mm and with a target tilt of 0.3". Argon was used as the gas source, at a work pressure of 3 mTorr and a flow rate of 10 sccm. The gun used a DC power supply with the power held at 20 W. A pre-deposition time of 60 seconds and a deposition time of 60 minutes was used.

#### Photocatalytic Sonogashira coupling reaction

Pd@TiO<sub>2</sub> (15 mg), 4-iodoanisole (28 mg, 0.12 mmol) and potassium carbonate (33 mg, 0.24 mmol, 2 equiv.) were placed in a flask under a nitrogen atmosphere. Then, methanol (4 mL) and phenylacetylene (18  $\mu$ L, 0.16 mmol, 1.3 equiv.) were added and the flask was sealed. The mixture was then sonicated for 15 minutes and followed by irradiation under blue light (455 nm, irradiance = 9.0 W/cm<sup>2</sup>) with vigorous stirring for 30 minutes. The reaction was then analysed and products quantified via GC-FID, using tridecane as the external standard. Products were confirmed using GC-MS.

#### Photocatalytic transfer hydrogenation reaction

 $Pd@TiO_2$  (15 mg) and diphenylacetylene (44.6 mg, 0.25 mmol) were placed in a flask under nitrogen atmosphere. Methanol (4 mL) was added and the flask was sealed and sonicated for 15 minutes. The reaction mixture was then irradiated under UVA light (365 nm, irradiance = 1.3 W/cm<sup>2</sup>) with vigorous stirring. The reaction was analysed and products quantified via GC-FID, using tridecane as the external standard. Products were confirmed using GC-MS.

## Sequential photocatalytic Sonogashira/transfer hydrogenation reaction

 $Pd@TiO_2$  (15 mg), 4-iodoanisole (28 mg, 0.12 mmol) and potassium carbonate (33 mg, 0.24 mmol, 2 equiv.) were placed in a flask under nitrogen atmosphere. Methanol (4 mL) and alkyne (0.16 mmol, 1.3 equiv.) were addd and the flask was sealed and sonicated for 15 minutes. The reaction mixture was then irradiated under blue light

(455 nm, irradiance=9.0 Wcm<sup>-2</sup>) with vigorous stirring for 30 minutes or 1 hour. Pd@TiO<sub>2</sub> was then removed via centrifugation, and the supernatant passed through 3 alumina plugs (diameter ~5 mm, length ~50 mm). In the case of reuse of the catalyst, the retrieved Pd@TiO<sub>2</sub> was washed with methanol (5×4 mL), dried in a vacuum dessiccator, and weighed. The reaction mixture was rescaled to acount for catalyst loss during the separation process. In the case of fresh catalyst, fresh Pd@TiO<sub>2</sub> (15 mg) was added to the reaction mixture. The reaction mixture was degassed under nitrogen, followed by a further 15 minutes of sonication. The reaction mixture was then irradiated under UVA light (365 nm, irradiance= 1.3 Wcm<sup>-2</sup>) for up to 5 hours. The reaction was analysed and products quantified via GC-FID, using tridecane as the external standard.

#### **Supporting Information**

Supporting information is provided as a separate PDF file. Additional references cited within the supporting information.  $^{[6a,c,9,14]}$ 

#### **Author Contributions**

R.Z.W. carried out the experimental work presented in the study, collected TEM images for nanoparticle distribution and size, conducted analysis on acquired data and drafted the initial manuscript. L.T.N. produced the Pd@TiO<sub>2</sub> materials and assisted with TEM analysis. W.J.C. collected HR-TEM images showing d-spacings of the materials and performed TGA analysis. J.A.F. assisted with supervision and reviewing and editing of the manuscript. A.E.L. conceived the study, led the supervision, acquired XPS data, worked on reviewing and editing the manuscript. All authors read and approved the final manuscript.

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#### **Conflict of Interests**

The authors declare no conflict of interest.

ChemCatChem 2023, 15, e202300528 (5 of 6)



The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Sonogashira coupling · transfer hydrogenations · photocatalysis · sequential reactions · palladium

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