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ARTICLE

Photocatalytic Ullmann coupling of aryl halides by a novel blended catalyst consisting of TiO_2 photocatalyst and Al_2O_3 supported Pd-Au bimetallic catalyst

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Ullmann coupling of aryl halides is a simple and efficient way to make symmetric biaryls. In this study, we have developed a novel blended catalyst system, consisting of a heterogeneous TiO_2 photocatalyst and a supported Pd metal catalyst, to carry out the photocatalytic Ullmann coupling of various aryl halides efficiently in mild conditions. A thorough study revealed that the reaction proceeds via a radical addition-elimination mechanism, involving TiO_2 photocatalysis and Pd metal catalysis. The two parts, i.e., TiO_2 photocatalyst particles and supported Pd nanoparticles, can cooperatively work with comparable yield and higher selectivity than the conventional Pd–loaded TiO_2 photocatalyst. The separation of Pd nanoparticles from the TiO_2 surface has some merits; it decreases the undesirable side reactions to improve biaryl selectivity and allows the modification of the metal catalyst, such as a fabrication of bimetallic catalyst, without affecting the property of the TiO_2 photocatalyst. Hence, the design of these blended catalysts is an attractive approach to fabricate both the photocatalyst and the metal catalyst parts independently and improve the entire catalytic performance.

Introduction

The biaryl moiety is the core of many versatile compounds, for example, natural products like Biphenomycin B (antibiotic),[1a] biologically active part of agrochemicals like Boscalid,[1b] and other pharmaceuticals.[1c] Further, the polyaromatic molecules found immediate use as dyes, organic conductors or semiconductors, ligands for the organometallic catalysts, and much more.[1d] So, it is necessary to develop effective strategies to make aryl-aryl bonds. Over the years, various reactions[2] like Ullmann reaction,[3] Gomberg-Bachmann reaction,[4] Scholl reaction,[5] Suzuki-Miyaura reaction,[6] and Stille reaction[7] have been developed to construct these bonds, nonetheless, due to its simplicity, Ullmann reaction remains a popular method.[8] The original report of this reaction required a Cu catalyst.[3a] The reaction was conducted at 373–633 K temperature range with or without a solvent. Although the use of a cheap and non-toxic metal like Cu was attractive, its stoichiometric amount and other harsh conditions have demanded milder methods. Thus, efforts are made to improve the catalysts, their amount and reaction conditions to perform the Ullmann reaction efficiently.

In our ongoing efforts to develop sustainable methodologies for C–C couplings, we found that heterogeneous metal (M) loaded TiO_2 photocatalysts, M/TiO_2, can catalyse these reactions in mild conditions.[9] The photogenerated holes on the TiO_2 photocatalyst successfully activated the C–H bonds in different organic molecules like acetonitrile, [9a, 9c] ethers,[9b, 9d, 9e] alkanes[9c, 9d] and alkenes[9c, 9e] to generate the carbon-centred radicals which selectively coupled to make the new C–C bonds. We also evidenced that the metal nanoparticles deposited on TiO_2 had a dual role in some of these reactions like for the C–C cross-coupling of aromatic compounds with acetonitrile[9a] and ether[9b], i.e., apart from being an electron receiver to decrease the recombination of photogenerated electron-hole pairs, they also catalysed the reaction between a photogenerated carbon-centred radical and an aromatic molecule, thus acting as co-catalysts. So, it is revealed that these reactions are a hybrid of TiO_2 photocatalysis and metal catalysis. This revelation provides an opportunity to improve the catalytic performance by modifying the two components, the deposited metal and the photocatalyst. However, the individual modification of one part is not so easy in M/TiO_2 samples. For example, due to an intimate contact, any attempt to change the state or electronic property of the metal (M) can also affect the properties of TiO_2. The physical properties of TiO_2 like surface area, crystalline phase, and so on, are crucial for its photocatalytic activity so that any change in these properties is undesirable.[10] As a possible solution to this problem, we have developed the concept of blended catalysts.[11] A blended catalyst is a physical mixture of a TiO_2 photocatalyst and a supported metal catalyst. As the metal nanoparticles and TiO_2 are separated, they can be modified independently, without affecting each other, to obtain high catalytic activity and selectivity. In the present work, we

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have examined the activity of a series of blended catalysts for the photocatalytic Ullmann coupling of aryl halides.

TiO$_2$ photocatalysis is widely employed for the degradation of aryl halides to arenes.[12] The photogenerated electrons in the TiO$_2$ samples reduce the aryl halide molecule to give arene while the solvent consumes the photogenerated holes as a reductant. But, the extension of this system to synthesise useful compounds like biaryls is still uncommon.[13] Here, we successfully developed an efficient photocatalytic method for the Ullmann coupling of various aromatic and heteroaromatic halides by using a heterogeneous TiO$_2$ sample. The reaction of iodobenzene to give biphenyl with a Pd/TiO$_2$ sample was thoroughly studied to elucidate the role of TiO$_2$ photocatalyst and Pd nanoparticles. The findings were used to develop a new type of catalytic system called the blended catalysts that consists of a TiO$_2$ photocatalyst physically mixed with an Al$_2$O$_3$ supported Au modified Pd catalyst. Lastly, additional experiments were carried out, like reaction with deuterated solvent, light intensity dependence, and temperature controlled reaction, to clarify the mechanism of the photocatalytic Ullmann coupling by the blended catalyst.

Experimental section

Catalysts preparation

We have used various catalysts like metal loaded TiO$_2$ samples, M(x)/TiO$_2$, where x shows the metal loading amount in weight%, namely, Pd(3.0)/TiO$_2$, Au(3.0)/TiO$_2$ and Pd(2.0)Au(1.0)/TiO$_2$, and Al$_2$O$_3$ supported samples namely, Pd(3.0)/Al$_2$O$_3$, Au(3.0)/Al$_2$O$_3$, and Pd-Au bimetallic samples (Pd(x)Au(y)/Al$_2$O$_3$).

The M(3.0)/TiO$_2$ samples were prepared by a photodeposition method by using an anatase phase TiO$_2$ sample (Catalysis Society of Japan, JRC-TIO-8, 338 m^{2}g^{-1}) and aqueous metal precursor solutions like PdCl$_2$ (Kishida Chemicals, 99%) for Pd and HAuCl$_4$ (Kishida Chemicals, 99%) for Au. The Pd(3.0)/TiO$_2$ sample was prepared as follows. 4 g of the TiO$_2$ powder, dispersed in 300 mL ion-exchanged water, was irradiated for 30 min from a xenon lamp (PE300 BUV). Then, 100 mL methanol and 5.8 mL of an aqueous solution of PdCl$_2$ (10.1 mg mL^{-1} of Pd) were added, and the resultant suspension was stirred for 15 min in dark, followed by 1 h stirring under photoirradiation. The suspension was filtered off with suction, washed with ion-exchanged water, and dried at 323 K for 12 h to get the Pd(3.0)/TiO$_2$ sample. The Au(3.0)/TiO$_2$ sample was prepared by the same procedure by using 2.5 mL of an aqueous solution of HAuCl$_4$ (4.8 mg mL^{-1} of Au). For the Pd(2.0)Au(1.0)/TiO$_2$ bimetallic sample, 2 g TiO$_2$, 175 mL water, 50 mL methanol, and desired volume of aqueous solutions of PdCl$_2$ (6.12 mg mL^{-1} of Pd) and HAuCl$_4$ (4.8 mg mL^{-1} of Au) were used.

The Al$_2$O$_3$ supported bimetallic samples were prepared by using a previously reported method.[11] 2 g of the Al$_2$O$_3$ sample (Catalysis Society of Japan, JRC-ALO-7, gamma phase, 180 m^{2}g^{-1}) and the desired volume of the aqueous solutions of PdCl$_2$ (6.12 mg mL^{-1} of Pd) and HAuCl$_4$ (4.8 mg mL^{-1} of Au) were dispersed in 60 mL of ion-exchanged water, and the suspension was stirred at room temperature for 15 min. An aqueous NaOH

solution (1 M) was used to adjust the pH of the suspension to 10. The resultant slurry was stirred for 24 h at room temperature. Then, the contents were filtered off with suction and dried overnight at 323 K. The powder was reduced at 423 K under pure H$_2$ for 30 min to get the Pd(x)Au(y)/Al$_2$O$_3$ samples. The total loading amount of the metals on Al$_2$O$_3$ was fixed to 3 weight%. For comparison, the monometallic samples, Pd(3.0)/Al$_2$O$_3$ and Au(3.0)/Al$_2$O$_3$, were also prepared by the same procedure as the bimetallic samples. The Pd(x)Au(y)/Al$_2$O$_3$ samples were thoroughly characterised by different techniques like UV-DRS, TEM, powder XRD, and XAFS.[11] The results indicated an intimate contact between Pd and Au which affected their electron density and resulted in a slightly electron deficient Pd species and an electron rich Au species. As shown later in the results of activity tests, the co-existence of such species was beneficial for the selective and efficient Ullmann coupling of aryl halides.

Photocatalytic activity tests

Materials All chemicals were of analytical grade and used without any purification; iodobenzene (Nacalai Tesque), 3-iodotoluene (TCI Research Chemicals), 4-iodotoluene (TCI Research Chemicals), bromobenzene (TCI Research Chemicals), chlorobenzene (Wako Pure Chemicals), 5-bromopyrimidine (TCI Research Chemicals), 2-chloropyridine (Wako Pure Chemicals), 2-bromopyridine (TCI Research Chemicals), methanol (CH$_3$OH, Nacalai Tesque), methanol-d_4 (CD$_3$OD, Euriso-top), acetonitrile (CH$_3$CN, Nacalai Tesque), di-methylformamide (DMF, Nacalai Tesque), isopropyl alcohol (IPA, Nacalai Tesque), triethanolamine (TEA, Nacalai Tesque).

Procedure of the activity tests The photocatalytic Ullmann coupling of aryl halides was carried out in a Pyrex test tube (70 mL) as a closed reactor. The desired catalyst sample was pre-treated with irradiation using a xenon lamp ($\lambda \geq 350$ nm) for 30 min under air atmosphere. Then, a solution of aryl halide (10 μL) in a solvent (2 mL) was added, the test tube was sealed with a silicon septum, and it was purged with argon gas for 10 min. The contents were stirred with light irradiation for the desired time. After the reaction, a part of the gaseous phase was analysed by GC-TCD (Shimadzu GC-8A). The liquid phase was filtered by using a syringe equipped with a PTFE filter and then analysed by GC-MS (Shimadzu GCMS-QP5050A) using decane as an internal standard.

Results and discussion

Photocatalytic Ullmann coupling of iodobenzene

Reaction with M(x)TiO$_2$ photocatalysts The photocatalytic Ullmann coupling of aryl halides was studied by examining the reaction of iodobenzene in acetonitrile. Table 1 shows the results. Biphenyl (**BP**), benzene (**B**), succinonitrile (**SN**), and benzyl cyanide (**BzCN**) were detected in the liquid phase while hydrogen was the only product detected in the gas phase. The reaction done with the pristine anatase TiO$_2$ photocatalyst (JRC-TIO-8, anatase phase) yielded benzene and succinonitrile only,

Table 1 Photocatalytic Ullmann coupling of iodobenzene in acetonitrile with different catalysts [a]
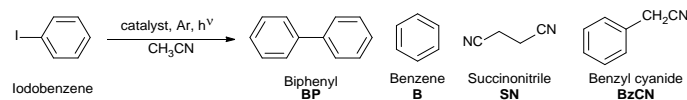
Entry	Catalyst		Products/μmol [b]				%Y [c]	%S [d]
	Photocatalyst	Metal catalyst	BP	B	SN	BzCN		
1	TiO_2	None	0.00	0.05	0.37	0.00	0.0	n.a. [e]
2	Pd(3.0)/TiO_2	None	0.87	0.68	0.65	0.29	2.0	64
3	Pd(2.0)Au(1.0)/TiO_2	None	0.57	0.40	0.00	0.09	1.3	70
4	TiO_2	Pd(3.0)/Al_2O_3	0.58	0.08	1.19	0.07	1.3	89
5 [f]	TiO_2	Al_2O_3	0.00	0.00	0.00	0.00	0.0	n.a.
6	TiO_2	Pd(2.5)Au(0.5)/Al_2O_3	0.49	0.05	0.53	0.16	1.1	82
7	TiO_2	Pd(2.0)Au(1.0)/Al_2O_3	0.98	0.07	1.11	0.17	2.2	89
8	TiO_2	Pd(1.5)Au(1.5)/Al_2O_3	0.51	0.04	1.04	0.16	1.1	84
9	TiO_2	Pd(0.5)Au(2.5)/Al_2O_3	0.13	0.05	0.63	0.05	0.2	72
10	TiO_2	Au(3.0)/Al_2O_3	0.07	0.02	0.39	0.00	0.2	88
11 [g]	None	Pd(2.0)Au(1.0)/Al_2O_3	0.00	0.00	0.00	0.00	0.0	n.a.
12	Pd(0.1)/TiO_2	Pd(2.0)Au(1.0)/Al_2O_3	1.27	0.74	1.16	0.41	2.8	69
13	Au(0.1)/TiO_2	Pd(2.0)Au(1.0)/Al_2O_3	1.04	0.91	0.95	0.53	2.3	59
14 [h]	TiO_2 (anatase-rutile)	Pd(2.0)Au(1.0)/Al_2O_3	1.21	0.18	0.23	0.27	2.7	84

[a] Reaction conditions: 10 μL (89.7 μmol) iodobenzene, 2 mL acetonitrile, and 25 mg of each catalyst (total 50 mg for the blended catalysts) were used, the reaction time was 30 min, wavelength and intensity of irradiated light were λ ≥ 350 nm, and I = 40 mW cm^{-2} (measured at 360 nm±10 nm), respectively. TiO_2 used was JRC-TIO-8 (anatase phase with large surface area, 335 m^{2}g^{-1}), except for the entry 14. [b] The amount of each product was determined from the calibration curve of their authentic sample. [c] %Y: GC-MS yield of biphenyl, **BP** (%) = 100 × [Experimental yield of **BP** (μmol)/theoretical yield of **BP** (μmol)]. [d] %S: Selectivity to **BP** (%) = 100 × [($2 \times P_{BP}$)/ (($2 \times P_{BP}$)+ P_B + P_{BzCN})], where P_X indicate the amount of the product **X** in μmol. [e] not applicable. [f] The reaction was carried out with bare Al_2O_3 sample. [g] The reaction was carried out without the TiO_2 photocatalyst under photoirradiation. [h] The reaction was carried out by using the TiO_2 sample containing a mixture of anatase and rutile phase (JRC-TIO-4, 50 m^2 g^{-1}).

while biphenyl and benzyl cyanide were not observed in this reaction (Table 1, entry 1). Pd loading on the TiO_2 photocatalyst was beneficial for the production of biphenyl (Table 1, entry 2). In fact, when compared to the pristine TiO_2 sample, the yield of all products increased in this reaction. It is passively considered that the well-known ability of the noble metal nanoparticles, like Pd, as an electron receiver on TiO_2 promotes the charge separation and increase the photocatalytic activity.[14]

Additionally, the Pd nanoparticles on TiO_2 are evidenced to have a catalytic role in the photocatalytic C–C cross-coupling reactions in literature.[9b, 9c] So, attempts were made to modify the electronic state of Pd nanoparticles and examine their activity for the Ullmann coupling of iodobenzene. We fabricated Pd-Au bimetallic nanoparticles on the TiO_2 surface. However, the reaction carried out with the Pd(2.0)Au(1.0)/TiO_2 photocatalyst produced biphenyl with lower yield than the Pd(3.0)/TiO_2 sample (Table 1, entry 3). Among other possibilities, this could be due to the difficulty of the modification of the metal nanoparticles under mild conditions to avoid affecting the property of the TiO_2 photocatalyst. Thus, we examined a blended catalyst, consisting of the TiO_2 photocatalyst and an Al_2O_3 supported metal catalyst, for the photocatalytic Ullmann coupling of the iodobenzene (Table 1, entries 4–9). Al_2O_3 is a popular support to prepare small and well dispersed metal nanoparticle catalysts. It doesn't have any photocatalytic activity and has mild acidity which means it should not interfere in the photocatalysis of TiO_2 and preserve the properties of the metal nanoparticles. This approach enabled us to prepare and modify the metal catalyst individually, keeping the TiO_2 photocatalyst intact.

Reaction with blended catalysts A blended catalyst consisting of the pristine TiO_2 photocatalyst and a physically mixed Pd(3.0)/Al_2O_3 catalyst was examined for the photocatalytic Ullmann coupling of iodobenzene (Table 1, entry 4). The reaction gave biphenyl with high selectivity (89%), due to the decreased production of benzene. This result reaffirms that the efficient charge separation by the metal nanoparticles deposited on the TiO_2 photocatalyst is responsible for the high production rate of by-products like benzene, with the Pd(3.0)/TiO_2 and Pd(2.0)Au(1.0)/TiO_2 samples (Table 1, entries 2, and 3). The reaction carried out with the TiO_2 photocatalyst blended with the bare Al_2O_3 sample did not give any product, indicating that Al_2O_3 doesn't have any catalytic role in the reaction (Table 1, entry 5). These results prove that the Pd nanoparticles are required to form biphenyl, and they can participate in the reaction even when deposited on a photo inactive support like Al_2O_3. It is notable that by separating the metal nanoparticles from the TiO_2 surface, we could control the activities of TiO_2 and metal nanoparticles, which improved the selectivity to biphenyl from 64% to 89%.

Next, we focused to enhance the catalytic activity of Pd nanoparticles on Al_2O_3 by introducing the Au atoms to them. The resultant Pd-Au bimetallic samples on Al_2O_3 (Pd(x)Au(y)/Al_2O_3) were examined for the photocatalytic Ullmann coupling of iodobenzene along with the pristine TiO_2 photocatalyst (Table 1, entries 6–9). Similar to the monometallic Pd(3.0)/Al_2O_3 sample, these catalysts also exhibited a much higher selectivity to biphenyl compared to the reactions with the photocatalyst alone (Table 1, entries 1–3).

Among them, the blended catalyst consisting of the TiO$_2$ photocatalyst and the bimetallic Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst successfully gave the highest yield and selectivity to biphenyl (%Y=2.2, %S=89, Table 1, entry 7) in these conditions. The higher activity of this bimetallic sample over the monometallic Pd and Au samples (Table 1, entries 4 and 10) indicates the synergistic effect of the coexistence of the Pd and Au species. The TEM images of these bimetallic samples showed that the Pd and Au nanoparticles are small and well disperse on the Al$_2$O$_3$ support.[11] Further, UV-DRS revealed that the two metal atoms are in close contact with each other, rather than being independent species. This was also supported by XANES which revealed that the due to this proximity, electron density was transferred from Pd to Au to generate an electron deficient Pd species and an electron rich Au species. We believe that this electron deficient Pd species might be crucial for the Ullmann coupling reaction, as explained in later sections.

Although the Pd-Au bimetallic nanoparticles showing plasmonic excitation are reported to have photocatalytic activity for some reactions, [13a, 15] photoirradiation of the reaction mixture without the TiO$_2$ photocatalyst did not yield any product (Table 1, entry 11). The inactivity of these bimetallic samples could be due to various factors including the reaction conditions, as discussed later.

The replacement of the pristine TiO$_2$ photocatalyst to the metal loaded TiO$_2$ photocatalyst in the blended catalyst with a Pd or Au loaded TiO$_2$ sample increased the products' yield but was not helpful for the selective formation of biphenyl (Table 1, entries 12 and 13). Thus, the moderate photocatalytic activity of TiO$_2$ accompanied by the catalytic activity of the modified Pd nanoparticles was necessary for the selective Ullmann coupling of iodobenzene to biphenyl. The effect of the properties of the pristine TiO$_2$ photocatalyst part on the Ullmann coupling of iodobenzene was also studied (Table S1) where the crystalline phase and the surface area of TiO$_2$ were varied. The TiO$_2$

photocatalyst having a mixture of the anatase and rutile phases (JRC-TIO-4, which is equivalent to P-25) gave the highest yield of biphenyl (2.7%) with appreciable selectivity (84%) (Table 1, entry 14 and Table S1, entry 5). So, further reactions were performed with the pristine anatase-rutile TiO$_2$ photocatalyst (JRC-TIO-4) blended with the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst.

Screening of solvents and additives The photocatalytic Ullmann coupling of iodobenzene to give biphenyl was carried out in various protic and aprotic solvents like methanol (CH$_3$OH), isopropyl alcohol (IPA), triethanolamine (TEA), acetonitrile (CH$_3$CN) and dimethylformamide (DMF) (Fig. 1). Among them, the alcoholic solvents like methanol (CH$_3$OH) and isopropyl alcohol (IPA) gave the highest yield of biphenyl. However, the biphenyl selectivity in these reactions was low due to the enhanced formation of benzene. The high reactivity of alcoholic solvents could be related to their hole scavenging activity which suppresses the electron-hole recombination and promotes the photocatalytic reduction.[16] Since methanol gave the highest yield of biphenyl, further experiments were performed in it.

To improve the selectivity to biphenyl, NaOH was added to the reaction mixture (Fig. 2 and Table S2†). The results show that Na$^+$ ions, which can remove the halide anion like I$^-$ from the reaction mixture, promoted the production of phenyl radical.[12b] The amount of biphenyl indeed increased with the increase of NaOH and was the maximum for the addition of 100 μL of NaOH (1 M), with 65% yield and 89% selectivity to biphenyl (Table S2, entry 4). However, further increase of NaOH was not helpful as the selectivity to biphenyl decreased.

Substrate scope for the photocatalytic Ullmann coupling

Various aromatic (Table 2, entries 1–5) and heteroaromatic (Table 2, entries 6–8) aryl halides successfully underwent the
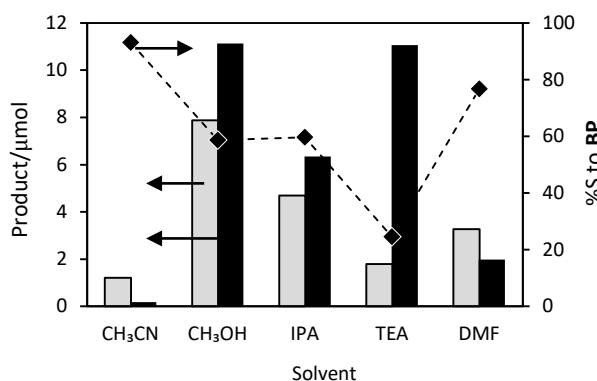

Fig. 1 Screening of the solvents for the photocatalytic Ullmann coupling of iodobenzene with the TiO$_2$ photocatalyst blended with the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst. Reaction conditions: 2 mL methanol, 10 μL iodobenzene, and 25 mg each of the TiO$_2$ (JRC-TIO-4) photocatalyst and the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst (total 50 mg of catalyst); other conditions were same as Table 1. Grey bar: the amount of **BP**, black bar: the amount of **B**, and diamond: the selectivity to **BP** (%).
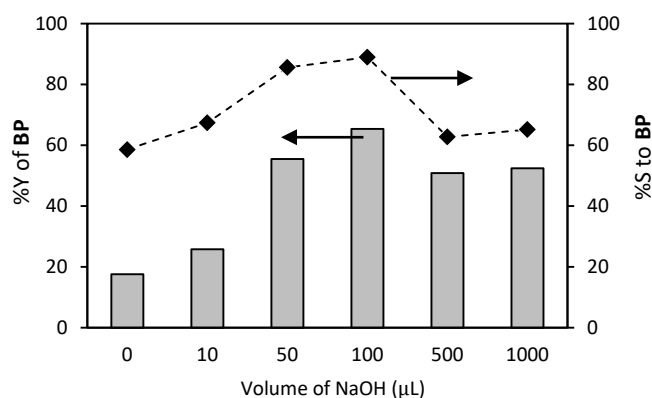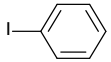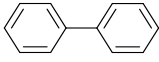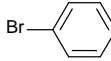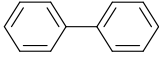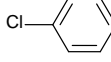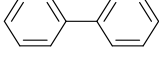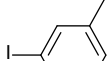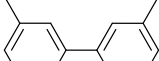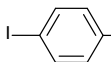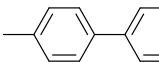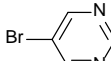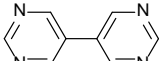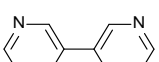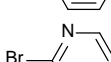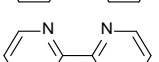

Fig. 2 Effect of NaOH on the photocatalytic Ullmann coupling of iodobenzene with a TiO$_2$ photocatalyst blended with the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst. Reaction conditions: 2 mL methanol, 10 μL iodobenzene, 25 mg each of the TiO$_2$ (JRC-TIO-4) photocatalyst and the Pd(2.0)Au(1.0)/Al$_2$O$_3$ cataly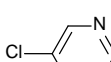st (total 50 mg of catalyst), and different amount of 1 M NaOH solution; other conditions were same as Table 1. Grey bar: the yield of **BP** (%) and diamond: the selectivity to **BP** (%).

Table 2 Substrate scope for the photocatalytic Ullmann coupling with blended catalyst consisting of the TiO_2 photocatalyst and the $Pd(2.0)Au(1.0)/Al_2O_3$ catalyst. [a]

Entry	Aryl halide	t/min [b]	Product	Product/μmol [c]	%Y	%S
1	I—⟨benzene⟩	60	biphenyl	31.9	71	72
2	Br—⟨benzene⟩	60	biphenyl	17.6	37	40
3	Cl—⟨benzene⟩	60	biphenyl	7.6	15	20
4 [d]	I—⟨methyl-benzene⟩	30	dimethylbiphenyl	28.3	73	80
5 [d]	I—⟨methyl-benzene⟩	30	dimethylbiphenyl	3.28	84	75
6 [e]	Br—⟨pyrimidine⟩	60	bipyrimidine	31.8	48	66
7 [f]	Cl—⟨pyridine⟩	60	bipyridine	11.0	21	41
8	Br—⟨pyridine⟩	60	bipyridine	40.2	77	67

[a] Reaction conditions: 10 μL of aryl halide, 2 mL methanol, 100 μL (1 M) NaOH, and 25 mg each of $Pd(2.0)Au(1.0)/Al_2O_3$ and TiO_2 (JRC-TIO-4). Other conditions and %Y and %S calculations were same as Table 1. [b] Reaction time. [c] The product amount was determined from the calibration curve of its authentic sample, unless otherwise mentioned. [d] 1.7 mg of aryl halide was used. The amount of biaryl was determined from the calibration curve of biphenyl. [e] 21.2 mg of aryl halide was used, the amount of biaryl was determined from the calibration curve of 2,2'-bipyridine. [f] Amount of biaryl was determined from the calibration curve of 2,2'-bipyridine.

photocatalytic Ullmann coupling to give the corresponding biaryls by using the blended catalyst consisting of the TiO_2 (JRC-TIO-4) photocatalyst and the $Pd(2.0)Au(1.0)/Al_2O_3$ catalyst. The dehalogenation reaction also proceeded in these conditions, which gave the corresponding arenes and decreased the selectivity to biaryls. For mono-substituted benzene, the biphenyl yield decreased with the increase of the carbon-halogen (C–X) bond dissociation energy in the order iodobenzene > bromobenzene > chlorobenzene (Table 2, entries 1–3). These results indicate that the dissociation of the C–X bond in aryl halides might be a crucial step in biaryl formation. The iodine substituted arenes provided the Ullmann coupling products with high yield and high selectivity such as 71–84% and 72-80%, respectively (Table 2, entries 1, 4, and 5).

Mechanistic studies

Reaction with deuterated methanol As shown in Fig. 1, the yield of benzene and biphenyl varied significantly with the nature of the solvent. To elucidate the role of the solvent in the reaction, the photocatalytic Ullmann coupling of iodobenzene was carried out in deuterated methanol (CD_3OD) (Table S3)†. This reaction gave a much smaller yield of benzene than that with unsubstituted methanol (CH_3OH) (Table S3, entries 1 and 2). The k_H/k_D value was > 1, indicating a normal kinetic isotope effect (KIE). Besides, the GC-MS analysis of the reaction mixture indicated that the mass number of the molecular ion peak of benzene was 79, which is larger than that of usual benzene (78) by unity, suggesting the incorporation of D from the solvent (CD_3OD). These results indicate that the cleavage of the C–H

bond in methanol is the rate determining step for benzene formation and that hydrogen in benzene is derived from the solvent. The amount of biphenyl, on the contrary, slightly increased in this reaction and the k_H/k_D value was < 1, indicating an inverse KIE. This result indicates that the formation of benzene and biphenyl is a competitive reaction, so that when the amount of benzene decreased, that of biphenyl increased. The phenyl radical generated via the reduction of iodobenzene can either be consumed to produce benzene or converted to biphenyl by reacting with another iodobenzene molecule. Replacing methanol with its deuterated counterpart will impede the former and promote the latter to give a high yield of biphenyl.

Temperature controlled reactions The Ullmann coupling of iodobenzene to give biphenyl required both TiO_2 and metal nanoparticles, such as monometallic Pd and bimetallic Pd-Au. The necessity of the metal nanoparticles and their activity even on Al_2O_3 hints at their catalytic role in the reaction and to confirm it we studied the effect of temperature on the photocatalytic reaction. The experimental details are mentioned in the ESI†. The photocatalytic Ullmann coupling of iodobenzene with the TiO_2 (JRC-TIO-4) photocatalyst blended with the $Pd(2.0)Au(1.0)/Al_2O_3$ catalyst was done at different temperatures. The amount of both biphenyl and benzene increased with temperature (Table S4, entries 1–3). Further, the products were not formed in the reaction carried out at high temperature without the light irradiation. Similar experiments were done with the pristine TiO_2 (JRC-TIO-4) photocatalyst. The

reaction gave only benzene whose yield did not change much with temperature (Table S4, entries 5–7). The apparent activation energy (E_a) with the blended catalyst system was 16.2 kJ mol^{-1} for biphenyl (Fig. S1a) and 8.7 kJ mol^{-1} for benzene (Fig. S1b) while that with the bare TiO$_2$ photocatalyst was 1.8 kJ mol^{-1} for benzene (Fig. S1c). The increase in the yield of biphenyl and benzene with temperature in the presence of the Pd-Au bimetallic catalysts compared to the reaction containing only the pristine TiO$_2$ photocatalyst indicates that the thermal energy is used by the bimetallic nanoparticles which might catalyse some reaction steps that lead to these products. In addition, since the value for biphenyl (16.2 kJ mol^{-1}) was higher than that for the benzene (8.7 kJ mol^{-1}), it is suggested that the formation of biphenyl requires the catalysis. However, it cannot proceed in dark, meaning it requires light irradiation.

Although it is difficult to point out the exact nature of the metal catalysis at this moment, the following proposals are made based on the previous studies and additional experiments. Some reports suggest that Pd nanoparticles can activate the aromatic ring in the direct DCC between arenes and radical species of acetonitrile[9a,9c] and ethers.[9b,11] The catalysis facilitates the attack of the radical species on the arene and yields the cross-coupling product. Additionally, some studies report the activation of a carbon-halogen (C–X) bond by the noble metals like Pd by oxidative addition or injection of a hot electron produced by plasmonic excitation into the C–X bond.[12a,17] Control experiments (Table S5) revealed that, under the suitable reaction conditions of solvent and additives, Pd and Au nanoparticles have the plasmonic catalytic activity which can reduce iodobenzene molecule to produce benzene, although the biphenyl yield is low in the reaction done without the TiO$_2$ photocatalyst (Table S5, entries 2 and 3). Even in this condition the catalytic activity of Pd nanoparticles is indispensable for the biphenyl formation (Table S5, entry 2). Eventually, a synergy of TiO$_2$ photocatalysis and Pd metal catalysis is necessary to obtain a high yield of biphenyl (Table S5, entry 4). Thus, it is proposed that the catalytic nature of the metal nanoparticles would predominantly contribute to the photocatalytic Ullmann coupling to assist the reaction between the aryl radical and aryl halide while the plasmonic nature of metal nanoparticles would also contribute additionally.

Light intensity dependence Since the reaction mixture contains many phenyl radicals, it is possible that two of these radicals easily combine to produce biphenyl. To confirm the possibility of a radical coupling path for biphenyl formation, we studied the light intensity dependence of the reaction.

The photocatalytic Ullmann coupling of iodobenzene with the blended catalysts consisting of the TiO$_2$ (JRC-TIO-4) photocatalyst and the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst was carried out at different light intensities. Fig. 3 shows the results. The amount of both products, benzene and biphenyl, increased with the light intensity. The amount of benzene increased linearly (Fig. 3a), while that of biphenyl initially increased with the intensity and became constant at high intensities (Fig. 3b). These results suggest that the formation of benzene is a photocatalytic process in a first order. The amount of biphenyl, on the contrary, was less sharp than benzene and became
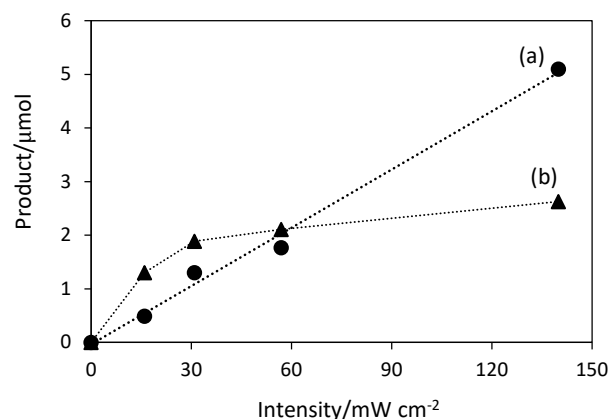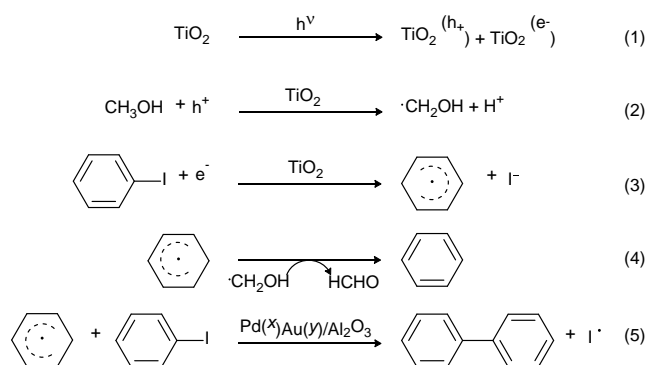

Fig. 3 Intensity dependence for (a) benzene and (b) biphenyl formation during the photocatalytic Ullmann coupling of iodobenzene with the blended catalyst consisting of the TiO$_2$ (JRC-TIO-4) photocatalyst and the Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst. Reaction conditions: 2 mL of a stock solution of iodobenzene (52 μL) in methanol (10.5 mL), 100 μL (1 M) NaOH, and 25 mg each of TiO$_2$ (JRC-TIO-4) photocatalyst and Pd(2.0)Au(1.0)/Al$_2$O$_3$ catalyst (total 50 mg). The reaction time was 6 min. Wavelength (λ) of the irradiated light was limited to 365±20 nm and the intensity was measured at 360±10 nm.

constant at higher intensities, indicating that the rate limiting step varies with the reaction condition and the production of the phenyl radical is not the crucial step for biphenyl formation at higher intensities. If biphenyl formation was a radical coupling reaction, the photocatalytic generation of phenyl radical would be a critical step, and then the increase in the biphenyl yield with intensity would be much steeper, like a second-order reaction. As this was not the case, the possibility of a radical coupling mechanism was ruled out as a main route. The present result shows that at low light intensity the photocatalysis would be the slowest step while at high light intensity the other thermal process such as the catalytic process by the metal part would be the rate determining step. Thus, a possible reaction mechanism for the biphenyl formation follows a radical addition-elimination route instead of a radical coupling. **Proposed reaction mechanism** The above results are summarized in Scheme 1 to propose the following reaction mechanism for the photocatalytic Ullmann coupling of iodobenzene in methanol (CH$_3$OH) with the blended catalyst consisting of the TiO$_2$ photocatalyst and Pd(x)Au(y)/Al$_2$O$_3$ bimetallic catalysts. (1) The photoexcitation of TiO$_2$ generates the excited electrons and holes in the conduction band and the valance band, respectively. (2) The hole oxidises methanol to generate its carbon centred radical and a proton (H$^+$). (3) The electron can reduce iodobenzene to give phenyl radical and iodide anion (I$^-$). (4) The phenyl radical can abstract proton from the solvent to yield benzene as the by-product. The rate determining step for the benzene formation would be the step 2, since the reaction rate decreased when deuterated methanol was employed (Table S3) and proportionally increased with increasing the light intensity. (5) When the photogenerated

$$TiO_2 \xrightarrow{h\nu} TiO_2{}^{(h_+)} + TiO_2{}^{(e-)} \quad (1)$$

$$CH_3OH + h^+ \xrightarrow{TiO_2} \cdot CH_2OH + H^+ \quad (2)$$

$$\text{C}_6\text{H}_5\text{I} + e^- \xrightarrow{TiO_2} \text{C}_6\text{H}_5\cdot + I^- \quad (3)$$

$$(4)$$

$$(5)$$

Scheme 1 Proposed mechanism for the photocatalytic Ullmann coupling of iodobenzene with a TiO_2 photocatalyst blended with the Pd(*x*)Au(*y*)/Al$_2$O$_3$ catalyst.

phenyl radical attacks on another iodobenzene molecule activated on the surface of the Pd-Au bimetallic catalysts (Pd(*x*)Au(*y*)/Al$_2$O$_3$), the transition state complex is formed, as shown in equation 6, followed by the elimination of the iodide anion (I$^-$) from the transition state complex, which gives biphenyl as the aimed product. This process would be mainly metal catalysed including the possible plasmonic effect. Thus, it is proposed that the biphenyl formation is completely a radical addition-elimination process, which would be a hybrid of the TiO_2 photocatalysis and the Pd metal catalysis.

$$(6)$$
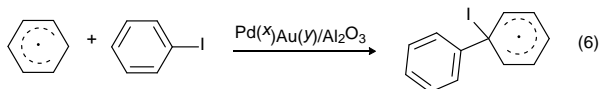
Conclusion

In the present work, we have developed an innovative catalytic system to carry out the efficient and selective photocatalytic Ullmann coupling of different aryl halides to give biaryls, where the yield and selectivity reached 15–84% and 20–89%, respectively for 30–60 min reactions. Remarkably, a 60 min reaction of iodobenzene gave 98% conversion with 72% selectivity to biphenyl.

Our study revealed that the reaction catalysed by the Pd/TiO$_2$ photocatalyst or the pristine TiO$_2$ photocatalyst physically mixed with the Pd(*x*)Au(*y*)/Al$_2$O$_3$ catalyst followed a radical addition-elimination path. The photogenerated electrons on the TiO$_2$ photocatalyst reduced the aryl halide molecule to generate the corresponding radical species, while the Pd-Au bimetallic nanoparticles activated another aryl halide molecule and facilitated its reaction with the photogenerated aryl radical to yield biaryl. The separation of the metal co-catalysts like Pd and Au from the TiO$_2$ surface significantly suppressed the undesirable production of an arene, while the presence of the metal nanoparticles as an Al$_2$O$_3$ supported catalyst yielded biphenyl with high selectivity.

This study has provided new insights into the mechanism of the photocatalytic organic reactions, and the role of metal nanoparticles, deposited on the photocatalyst, in the reactions. Also, the novel blended catalytic system developed here has opened a wide possibility to design efficient catalytic systems by independently modifying the photocatalyst and the metal catalyst parts, and improve the catalytic performance.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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