Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supplementary Information

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

Akanksha Tyagi,[a] Akira Yamamoto[a,b] and Hisao Yoshida *[a,b]

[a] Graduate School of Human and Environmental Studies, Kyoto University, Yoshida Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan.
[b] Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8520, Japan.
*E-mail: yoshida.hisao.2a@kyoto-u.ac.jp

Table of contents

1. Screening of TiO_2 samples

Table S1 shows the result of the photocatalytic Ullmann coupling of iodobenzene done with a blended catalyst consisting of different TiO_2 samples and the Pd(2.0)Au(1.0)/Al_2O_3 catalyst. The various TiO_2 samples were obtained from the Catalysis Society of Japan. For the anatase TiO_2, the amount of the biphenyl (**BP**) increased with increasing the surface area (Table S1, entries 1–3). For the TiO_2 samples with similar surface area (Table S1, entries 3–5), the amount of biphenyl was maximum for the sample having a mixture of rutile and anatase (Table S1, entry 5).

Table S1 Ullmann coupling of iodobenzene in acetonitrile with a Pd(2.0)Au(1.0)/Al_2O_3 catalyst blended with different TiO_2 photocatalysts [a]

Entry	Catalyst	Phase	Specific surface area/ m^2g^{-1}	Product / µmol				%Y	**%S**
				BP	**B**	**SN**	**BzCN**		
1	JRC-TIO-8	anatase	335	0.98	0.07	1.11	0.17	2.2	89
2	JRC-TIO-10	anatase	128	0.77	0.09	0.24	0.09	1.7	89
3	JRC-TIO-1	anatase	75	0.31	0.22	0.00	0.17	0.7	61
4	JRC-TIO-6	rutile	50	0.24	0.03	0.05	0.03	0.5	89
5	JRC-TIO-4	anatase + rutile	50	1.21	0.18	0.23	0.27	2.7	84

[a] Reaction conditions: 2 mL acetonitrile, 10 µL (89.7 µmol) iodobenzene and 25 mg each catalyst (total 50 mg of catalyst) were used for the reaction. The reaction time was 30 min. The wavelength of the irradiated light was λ≥350 nm and the light intensity was 40 mW cm^{-2} (measured at 360 ± 60 nm). For products' abbreviations, yield (%Y), and selectivity (%S) calculations, please see Table 1 in the main text.

2. Addition of NaOH

Table S2 shows the effect of NaOH addition to the Ullmann coupling of iodobenzene in methanol. The amount of biphenyl (**BP**) increased with the addition of NaOH, and for 100 µL of NaOH the yield and selectivity to biphenyl became 65% and 80%, respectively (Table S2, entry 4). Further addition of NaOH increased benzene (**B**) production which decreased both %Y and %S to biphenyl. The reasons for the improved yield and selectivity of biphenyl upon NaOH addition could be similar to the previous reports.[S1] The Na^+ ions might be responsible for removing iodide anion, which would help the formation of phenyl radical and facilitate its further reactions. Also, the OH^- ions might consume H^+ and supress benzene formation which would improve the %S to biphenyl.

Table S2 Effect of NaOH addition to the photocatalytic Ullmann coupling of iodobenzene with a TiO_2 (anatase and rutile) photocatalyst blended with the Pd(2.0)Au(1.0)/Al_2O_3 catalyst [a]

Entry	Volume of NaOH added / µL	Product / µmol		%Y	**%S**
		BP	**B**		
1	0	7.9	11.1	18	59
2	10	11.6	11.2	29	67
3	50	24.9	8.4	56	86
4	100	29.3	7.3	65	89
5	500	22.9	27.1	51	63
6	1000	23.5	25.1	52	65

[a] Reaction conditions: 2 ml methanol was used for the reaction. Other reaction conditions were same as Table S1.

3. Reaction in deuterated methanol

The photocatalytic Ullmann coupling of iodobenzene was carried out in deuterated methanol. As mentioned in the main text, this result suggested that formation of benzene and biphenyl might be a competitive reaction.

Table S3 Photocatalytic Ullmann coupling of iodobenzene in deuterated methanol with the TiO_2 (anatase and rutile) photocatalyst and Pd(2.0)Au(1.0)/Al_2O_3 catalyst [a]

Entry	Solvent	Product / µmol		k_H/k_D [b]	
		BP	**B**	**BP**	**B**
1	CH_3OH	3.9	16.2	-	-
2	CD_3OD	4.7	6.3	0.8	2.5

[a] Reaction conditions: 5 µL (44.9 µmol) iodobenzene, 1 mL solvent (CH_3OH or CD_3OD) were used for the reaction. Other conditions were same as Table S1. [b] k_H/k_D for each product = [Product amount in entry 1 (µmol)/ product amount in entry 2 (µmol)].

4. Temperature controlled reactions

The photocatalytic Ullmann coupling of iodobenzene was carried out at different temperatures to confirm the involvement of Pd metal catalysis in the biphenyl formation. The reaction temperature was maintained by using a water bath, and the remaining procedure was the same as the general procedure mentioned in the main text. Table S4 shows the results of the experiments carried out with the blended catalyst consisting of the TiO_2 (anatase and rutile) photocatalyst and the Pd(2.0)Au(1.0)/Al_2O_3 catalyst (Table S4, entries 1–4) and the pristine TiO_2 photocatalyst alone (Table S4, entries 5–7). Figure S1 shows the pseudo Arrhenius plots and the apparent activation energies (E_a) as the results of these experiments.

Table S4 Temperautre controlled photocatalytic Ullmann coupling of Iodobenzene with different catalysts [a]

Entry	Temperature / K	Catalyst	Product / µmol	
			BP	**B**
1	304.2	TiO_2 + Pd(2.0)Au(1.0)/Al_2O_3	7.7	12.2
2	309.2	TiO_2 + Pd(2.0)Au(1.0)/Al_2O_3	8.7	13.3
3	313.2	TiO_2 + Pd(2.0)Au(1.0)/Al_2O_3	9.3	13.4
4 [b]	313.2	TiO_2 + Pd(2.0)Au(1.0)/Al_2O_3	0.0	0.0
5	305.2	TiO_2	0.0	22.5
6	309.2	TiO_2	0.0	22.0
7	314.2	TiO_2	0.0	22.9

[a] Reaction conditions: 2 mL methanol, 10 µL iodobenzene, 100 µL NaOH, 25 mg each of the TiO_2 (anatase and rutile) photocatalyst and the Pd(2.0)Au(1.0)/Al_2O_3 catalyst were used for a 1 h reaction. Other conditions were same as Table S1. [b] The reaction was performed in the dark.

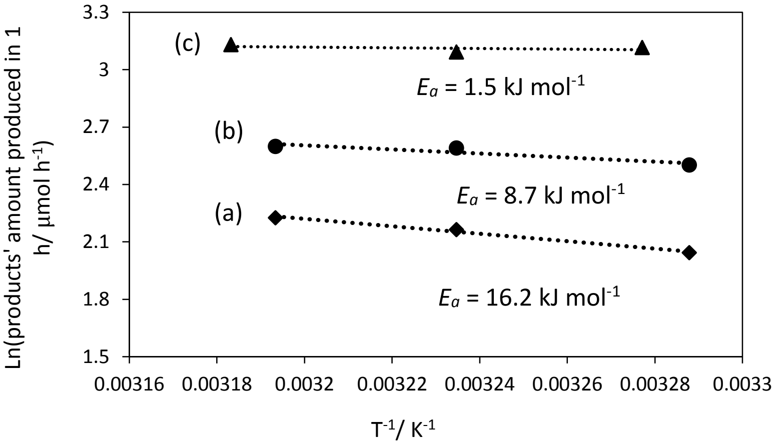

Fig. S1 Pseudo Arrhenius plots of temperature controlled photocatalytic Ullmann coupling of iodobenzene for (a) biphenyl and (b) benzene production with the blended catalyst consisting of the TiO_2 (anatase and rutile) photocatalyst and the Pd(2.0)Au(1.0)/Al_2O_3 catalyst, and (c) benzene formation with the pristine TiO_2 (anatase and rutile) photocatalyst.

5. Control experiments

Table S5 shows the results of control experiments. The reactions were carried out in methanol by using NaOH as an additive under photoirradiation for 30 min. The reaction done with the pristine TiO_2 photocatalyst yielded benzene predominantly, and biphenyl was a minor product (Table S5, entry 1). This result suggests that although the photogenerated electrons on TiO_2 might reduce iodobenzene to produce phenyl radicals, these radicals don't give biphenyl via radical coupling in this condition. Surprisingly, the photoirradiation of the Pd(3.0)/Al_2O_3 and Au(3.0)/Al_2O_3 catalysts without the TiO_2 photocatalyst (Table S5, entries 2 and 3) yielded benzene, while only the Pd(3.0)/Al_2O_3 catalyst gave biphenyl. These results indicate that the Pd and Au nanoparticles can function as plasmonic photocatalysts to generate hot electrons which can reduce iodobenzene to a phenyl radical that furnishes benzene. However, Pd catalysis is crucial for biphenyl formation, suggesting that it could activate a molecule of iodobenzene and promote its reaction with the photogenerated phenyl radical to yield biphenyl. Although Au is inactive for biphenyl formation, its presence in the vicinity of Pd, like in Pd(*x*)Au(*y*)/Al_2O_3 bimetallic samples, promotes the catalytic activity of Pd. However, the reaction requires both the TiO_2 photocatalysis and Pd catalysis to achieve high biphenyl yield as shown in Table S5, entry 4.

Table S5 Control experimnets to clarify the catalysis by metal nanoprticles [a]

Entry	Catalyst	Product / µmol		%Y	**%**S
		BP	**B**		
1	TiO_2 (anatase and rutile)	0.1	27	0.2	0.3
2	Pd(3.0)/Al_2O_3	6.4	4.8	14	57
3	Au(3.0)/Al_2O_3	0.0	2.7	n.a. [b]	n.a.
4	TiO_2 (anatase and rutile) + Pd(2.0)Au(1.0)/Al_2O_3	29.3	7.3	65	89

[a] The reactions were carried out with different catalysts. Reaction conditions: 10 µl iodobenzene, 2 ml methanol, 100 µl NaOH, 25 mg of each catalyst (50 mg the blended catalysts). The reaction time was 30 min. Other conditions were same as Table S1. [b] Not applicable.

References

S1. (a) K. Fuku, K. Hashimoto and H. Kominami, *Catal. Sci. Technol.*, 2011, 1, 586; (b) Y. Shiraishi, Y. Takeda, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Chem. Commun.*, 2011, 47, 7863.