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## One-pot synthesis of secondary amines from alcohols and nitroarenes on TiO<sub>2</sub> loaded with Pd nanoparticles under UV irradiation<sup>+</sup>

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Photoirradiation ( $\lambda >_{300}$  nm) of TiO<sub>2</sub> loaded with Pd nanoparticles (2 wt%, ca. 5 nm diameter) in water containing benzyl alcohol and nitrobenzene at room temperature successfully produces the corresponding secondary amine (*N*-benzylaniline) with 96% yield. This is achieved via three consecutive catalytic reactions: (i) photocatalytic oxidation of alcohol (aldehyde formation) and reduction of nitrobenzene (aniline formation); (ii) catalytic condensation of the formed aldehyde with aniline on the TiO<sub>2</sub> surface (imine formation); and, (iii) photocatalytic hydrogenation of the formed imine (secondary amine formation). This catalytic system successfully produces several kinds of secondary amines, even those containing reducible substituents such as -CN, -COOH, or -CHO with >76% yields.

#### Introduction

Secondary amines are one of the most important classes of chemicals that are versatile intermediates for the synthesis of pharmaceuticals and agricultural chemicals.<sup>1</sup> These compounds are usually synthesized by N-alkylation of primary amines with alkyl halides. This method, however, requires stoichiometric or excess amount of inorganic bases with a concomitant formation of large amounts of inorganic salts as wastes.<sup>2,3</sup>

An alternative environmentally-friendly way for secondary amine synthesis is the N-alkylation of primary amines with alcohols as alkylating agents in the presence of transition metal catalysts, via the borrowing hydrogen (H) mechanism.<sup>4–8</sup> These systems promote three consecutive catalytic steps in one pot: (i) dehydrogenation of alcohol produces aldehyde and H atoms on the metal (H-metal species); (ii) catalytic condensation of the formed aldehvde with primary amine produces imine; and (iii) hydrogenation of the imine by the H-metal species produces secondary amine. Many homogeneous catalysts such as Pt, Ru, Ir complexes have been proposed so far,<sup>9-12</sup> but there are difficulties in the recovery and reuse of expensive catalysts. Heterogeneous systems have also been proposed with several catalysts such as  $PdO_x$  particles supported on  $Fe_2O_3$ ,<sup>13</sup> Pd particles supported on boehmite,<sup>14</sup> Ag clusters supported on  $Al_2O_3$ <sup>15</sup> Ru(OH)<sub>x</sub> or Cu(OH)<sub>x</sub> supported on  $Al_2O_3$ <sup>16,17</sup> Au particles supported on TiO2,18 Pd particles supported on MgO,19 and sulfated tungstate.<sup>20</sup> All of these systems selectively produce secondary amines, but need relatively high reaction temperatures (>363 K).

Another problem for these catalytic systems is the use of unstable "anilines" as substrates; they are oxidized very easily by autooxidation.<sup>21</sup> Alternative methods with stable substrates such as nitroarenes are necessary. Several homogeneous Ru catalysts promote one-pot synthesis of secondary amines from alcohols and stable nitroarenes.<sup>22–25</sup> Heterogeneous catalysts such as Ag particles supported on Al<sub>2</sub>O<sub>3</sub>,<sup>26</sup> Au particles supported Fe<sub>2</sub>O<sub>3</sub>,<sup>27</sup> TiO<sub>2</sub>,<sup>28</sup> or Ag-Mo nanorods<sup>29</sup> have also been proposed. They, however, still require relatively high reaction temperatures (>363 K). Improved methods capable of producing secondary amines at room temperature are therefore desired for green organic synthesis.

The purpose of this work is to design a heterogeneous catalytic system that promotes one-pot synthesis of secondary amines from alcohols and nitroarenes at room temperature. We used a semiconductor TiO<sub>2</sub> loaded with Pd particles (Pd/TiO<sub>2</sub>) as a catalyst under UV irradiation ( $\lambda > 300$  nm). Our hypothesis is briefly summarized in Scheme 1 and as follows. Photoexcited  $TiO_2$  oxidizes alcohol, producing aldehyde and protons (H<sup>+</sup>).<sup>30</sup> Photoexcited electrons reduce H<sup>+</sup> on the Pd particles and produce H atoms (H-Pd species).<sup>31</sup> These H-Pd species may reduce nitroarene and produce aniline. Catalytic condensation of the formed aniline and aldehyde by the Lewis acid sites on the surface of TiO<sub>2</sub> may produce imine.<sup>32</sup> The imine is then hydrogenated by the H-Pd species and is converted to the product secondary amine. These photocatalytic and catalytic sequences may therefore facilitate one-pot synthesis of secondary amine from alcohols and nitroarenes at room temperature.

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Scheme 1 Proposed pathway for secondary amine formation from alcohols and nitroarenes on the photoactivated  $Pd/TiO_2$  catalyst.

Here we report that the above hypothesis is realized by the  $Pd/TiO_2$  catalyst under UV irradiation, and several kinds of secondary amines are successfully obtained with high yields (>76%). We found that the reaction efficiency strongly depends on the amount of Pd loaded. The catalyst loaded with 2 wt % Pd, which contains about 5 nm Pd particles, exhibits very high activity for one-pot synthesis of secondary amines.

#### **Results and Discussion**

#### Preparation and characterization of catalysts

The Pd<sub>x</sub>/TiO<sub>2</sub> catalysts with different Pd loadings [x (wt%) = Pd / TiO<sub>2</sub> × 100] were prepared by impregnation of Pd(NO<sub>3</sub>)<sub>2</sub> onto P25 TiO<sub>2</sub> (anatase/rutile ratio = ~80/20; average particle size, 24 nm; BET surface area, 59 m<sup>2</sup> g<sup>-1</sup>) followed by reduction with H<sub>2</sub>.<sup>33,34</sup> Fig. 1 shows typical transmission microscopy (TEM) images of the respective Pd<sub>x</sub>/TiO<sub>2</sub> catalysts. All of them contain spherical Pd particles, and their sizes increase with the Pd loadings: the average diameters for x = 0.5, 1, 2, and 4 catalysts were 2.6, 4.1, 5.0, and 6.5 nm, respectively. As shown in Fig. 2, high-resolution TEM images of the catalysts revealed that these Pd particles can be indexed as *fcc* structures as same as bulk metallic Pd (JCPDS 46-1043). Fig. S1 (ESI†) shows the diffuse-reflectance UV-vis spectra of catalysts. The higher Pd loading catalysts exhibit increased absorbance at  $\lambda > 300$  nm due to the light scattering by the Pd particles.<sup>33,35</sup>

#### Photocatalytic activity

Photocatalytic reactions of benzyl alcohol and nitrobenzene were performed with respective catalysts. An water (4.5 mL) containing benzyl alcohol (0.5 mL), nitrobenzene (25  $\mu$ mol), and catalyst (10 mg) was photoirradiated by a Xe lamp at  $\lambda$  >300 nm under N<sub>2</sub> atmosphere (1 atm) at room temperature for 4 h. Table 1 summarizes the conversion of nitrobenzene and the yield of *N*-benzylaniline (1) and *N*-benzylidenaniline (2). Bare TiO<sub>2</sub> (entry 1) produces only a small amount of imine (2) and scarcely produces secondary amine (1). In contrast, Pd<sub>x</sub>/TiO<sub>2</sub> (entries 2–5) produce very large amount of 1. Increased Pd

loadings enhance the formation of **1**. Among them,  $Pd_2/TiO_2$  (entry 2) exhibits the highest activity: **1** is produced with almost quantitatively (96%). Further Pd loading ( $Pd_4/TiO_2$ ), however, decreases the activity (entry 5). As shown by entries 6 and 7, the catalysts loaded with other metal particles such as Pt and Ag show much lower **1** yields (<10%). In particular,  $TiO_2$  loaded with Au particles (Au<sub>2</sub>/TiO<sub>2</sub>; entry 8), which has been proposed for secondary amine synthesis from nitroarenes and ethanol, exhibit very low **1** yield (3%).<sup>36</sup> These data clearly suggest that Pd/TiO<sub>2</sub> catalyst is effective for one-pot synthesis of secondary amine from alcohol and nitroarene.



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**Fig. 2** High-resolution TEM images of  $Pd_2/TiO_2$  catalyst. (a) The incident beam direction is [0, -1, 1], and (b) this particle is a twinned one and the incident beam directions are [0, -1, 1] and [0, 1, -1], respectively.

#### **Reaction mechanism**

Secondary amine (1) is produced by tandem photocatalytic and catalytic reactions on Pd/TiO<sub>2</sub> (Scheme 1). The reaction is initiated by photoexcitation of TiO<sub>2</sub>, producing the electron ( $e^{-}$ ) and positive hole ( $h^{+}$ ) pairs.

$$\mathrm{TiO}_2 + h\nu \to \mathrm{e}^- + \mathrm{h}^+ \tag{1}$$

The  $h^+$  oxidize alcohol and produces aldehyde and  $H^+$ .

$$R_1 - CH_2OH + 2h^+ \rightarrow R_1 - CHO + 2H^+$$
(2)

The formed  $H^+$  are reduced on the surface of Pd particles by the  $e^-$  transferred from the TiO<sub>2</sub> conduction band, and converted to the surface H atoms (H–Pd species).<sup>33</sup>

$$H^{+} + e^{-} + Pd \rightarrow H - Pd$$
(3)

Nitrobenzene is reduced by the H–Pd species and transformed to the corresponding aniline.

$$R_2 - NO_2 + 6H - Pd \rightarrow R_2 - NH_2 + 2H_2O + 6Pd$$
(4)

Catalytic condensation of the formed aldehyde with aniline by the Lewis acid site on the  $TiO_2$  surface produces imine.<sup>32</sup>

$$R_1 - CHO + R_2 - NH_2 \xrightarrow{\longrightarrow} R_1 - CH = N - R_2 + H_2O$$
(5)

The formed imine is then hydrogenated by the H–Pd species and transformed to the product secondary amine.<sup>37</sup>

 $R_1-CH=N-R_2+2H-Pd \rightarrow R_1-CH_2-NH-R_2+2Pd \qquad (6)$ 

Fig. 3c shows the time-dependent change in the amounts of substrate and products during photoreaction of benzyl alcohol and nitrobenzene on the Pd<sub>2</sub>/TiO<sub>2</sub> catalyst. At the initial stage, photoirradiation decreases the amount of nitrobenzene (black), along with a formation of benzaldehyde (white) and aniline (3, blue). This suggests that, as shown by eqs. 1-4, photoexcitation of Pd/TiO<sub>2</sub> indeed promotes oxidation of alcohol (aldehyde formation) and reduction of nitrobenzene (aniline formation). The amount of aniline decreases with time, along with a formation of imine (2, green), suggesting that condensation of the formed aldehyde and aniline produces imine (eq. 5). The amount of imine then decreases, associated with a formation of product secondary amine (1, red). This suggests that, as shown by eq. 6, hydrogenation of imine produces the secondary amine. Photoirradiation for 4 h leads to almost complete conversion of nitrobenzene to 1. These substrate and product profiles suggest that the above reaction sequence (Scheme 1, eqs. 1–6) proceeds efficiently on the Pd<sub>2</sub>/TiO<sub>2</sub> catalyst. In addition, prolonged photoirradiation for >4 h scarcely changes the amount of 1, suggesting that further reaction of 1 does not occur. Furthermore, as shown in Table 1 (entry 4), the Pd<sub>2</sub>/TiO<sub>2</sub> catalyst, when reused for further photoreactions, shows almost the same activity as the fresh catalyst. This indicates that the catalyst is reusable without the loss of activity.

Table 1. Catalyst properties and results for one-pot synthesis of secondary amine from nitrobenzene and benzyl alcohol under UV irradiation.

+ NO <sub>2</sub>	ОН	l hv (>300 nm), 4 h catalyst (10 mg)		+ N	+ NH2
25 µmol	0.5 mL	water (4.5 mL), N <sub>2</sub> , 298 K	1	2	3

Entry		Size of metal particles / nm <sup>a</sup>	Nitrobenzene conv. / %	Yields / % <sup>b</sup>		Amount of product formed (µmol)		
	Catalyst			1	2	Benzaldehyde	Toluene	3
1	TiO <sub>2</sub>		86	0	28	35.2	< 0.1	12.8
2	Pd <sub>0.5</sub> /TiO <sub>2</sub>	$2.6 \pm 0.5$	>99	56	30	61.8	1.0	2.0
3	$Pd_1/TiO_2$	$4.1\pm0.9$	>99	64	25	65.6	1.1	1.8
4	Pd <sub>2</sub> /TiO <sub>2</sub>	$5.0 \pm 0.9$	>99	96	3	70.5	2.6	<0.1
	1st reuse		>99	96	3	68	2.8	0
	2nd reuse		>99	95	4	67.1	3.0	0
	3rd reuse		>99	94	5	65.3	2.8	0
	4th reuse		>99	92	7	63.8	3.1	0
5	Pd <sub>4</sub> /TiO <sub>2</sub>	$6.5 \pm 1.3$	>99	71	11	68.0	6.3	4.1
6	Pt <sub>2</sub> /TiO <sub>2</sub>	$3.1 \pm 0.8^{c}$	60	2	13	27.0	< 0.1	6.9
7	Ag <sub>2</sub> /TiO <sub>2</sub>	$4.6 \pm 1.2^{c}$	88	8	8	28.8	< 0.1	9.0
8	Au <sub>2</sub> /TiO <sub>2</sub>	$3.7 \pm 0.5^{c}$	95	3	14	33.0	< 0.1	9.3

<sup>*a*</sup> Average diameter of metal particles determined by TEM observations. <sup>*b*</sup> = [product formed ( $\mu$ mol)] / [initial amount of nitrobenzene (25  $\mu$ mol)] × 100. <sup>*c*</sup> TEM images of the catalysts and size distribution of metal particles are summarized in Fig. S2 (ESI†)

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Fig. 3 Time-dependent change in the amounts of substrate and products during photoreaction of benzyl alcohol and nitrobenzene with (a) Pd<sub>0.5</sub>/TiO<sub>2</sub>, (b) Pd<sub>1</sub>/TiO<sub>2</sub>, (c) Pd<sub>2</sub>/TiO<sub>2</sub>, (d) Pd <sub>4</sub>/TiO<sub>2</sub> catalysts, respectively. The reaction conditions are identical to those in Table 1. (e) The data obtained on Pd<sub>2</sub>/TiO<sub>2</sub> catalyst in benzyl alcohol (5 mL) without water.

#### Effect of Pd loadings

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As shown in Table 1, the  $Pd_2/TiO_2$  catalyst shows the highest activity for secondary amine formation, and the catalysts with lower or higher Pd loadings show decreased activity. Effect of the Pd amount on the respective reaction steps in Scheme 1 was therefore studied. Fig. 3 shows the time-course profiles for the amounts of substrate and products during the photoreaction of benzyl alcohol and nitrobenzene on the catalysts with different Pd loadings. All of the catalysts lead to complete disappearance of nitrobenzene by 4 h reaction. This indicates that, on all of the catalysts, photocatalytic reduction of nitrobenzene (aniline formation) occurs efficiently. Fig. S3 (ESI<sup>†</sup>) shows the time profiles for the amounts of substrate and products during the photoreaction with aniline as a starting material in a benzyl alcohol solution on Pd<sub>2</sub>/TiO<sub>2</sub>. The formation rate of secondary amine is similar to that obtained with nitrobenzene as a starting material (Fig. 3c). These data clearly suggest that the reactions (eqs. 2-4) are not the rate-determining steps for secondary amine formation. Condensation of the formed aniline and aldehyde (eq. 5) is also not the rate-determining step. This is confirmed by stirring aniline and benzaldehyde in the dark condition. As shown in Fig. S4 (ESI<sup>†</sup>), the yield of imine (2) is scarcely affected by the amount of Pd loaded. This is because the reaction is catalyzed by the Lewis acid site on the TiO2 surface.32

The rate-determining step in the reaction sequence is the hydrogenation of imine by the H–Pd species (eq. 6). As shown in Fig. 3c, on the  $Pd_2/TiO_2$  catalyst, the imine (**2**, green) is rapidly consumed by 4 h photoreaction, but lower or higher Pd loading catalysts (Fig. 3a, b, d) are ineffective for imine hydrogenation.

This is further confirmed by the photoreaction of imine (2) as a starting material in benzyl alcohol with respective catalysts. As shown in Fig. 4, the secondary amine (1, black) is produced very efficiently on the  $Pd_2/TiO_2$  catalyst, but other catalysts exhibit lower amine yields. The results clearly indicate that the  $Pd_2/TiO_2$  catalyst promotes efficient hydrogenation of imine (2) to amine (1) and, hence, facilitates consecutive catalytic sequences shown in Scheme 1.



Fig. 4 The yields of secondary amine (1) formed by photoirradiation of a benzyl alcohol solution containing imine (2) and respective  $Pd_x/TiO_2$  catalysts.

The lower activity for imine hydrogenation on lower Pd loadings catalysts ( $Pd_{0.5}/TiO_2$  and  $Pd_1/TiO_2$ ) is due to the smaller number of surface Pd atoms, as observed in related systems.<sup>38</sup> This may produce a smaller number of H–Pd species and result in inefficient hydrogenation activity. In contrast,  $Pd_4/TiO_2$  may

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have a larger number of surface Pd atoms, but shows lower hydrogenation activity. This dilemma is probably caused by hydrogenation of "alcohols". As shown in Fig. 4, photoreaction of imine (2) in benzyl alcohol with respective catalysts also produces toluene (gray). This indicates that H-Pd species promote hydrogenolysis of benzyl alcohol as well as imine hydrogenation. The amount of toluene formed increases with the Pd loadings. The Pd4/TiO2 catalyst produces much larger amount of toluene than Pd<sub>2</sub>/TiO<sub>2</sub>, although the amount of secondary amine (1) formed is much smaller. The enhanced formation of toluene on higher Pd loading catalyst is also confirmed by the photoreaction of benzyl alcohol and nitrobenzene (Table 1). These data suggest that, on Pd4/TiO2, alcohols react preferentially with the H-Pd species: this may suppress imine hydrogenation.

The preferential reaction of alcohols on Pd<sub>4</sub>/TiO<sub>2</sub> is probably due to the size of Pd particles. It is well known that<sup>39-42</sup> metal particles contain different types of surface atoms located at the vertex, edge, square, and triangle sites, each of which shows different activity for the reactions. The number of these atoms changes substantially with the particle size. As shown in Table 1, Pd<sub>4</sub>/TiO<sub>2</sub> possesses larger Pd particles than other catalysts. These Pd particles probably contain a larger number of specific surface Pd atoms that promote preferential reaction of alcohols, resulting in inefficient imine hydrogenation. As a result of this, Pd<sub>2</sub>/TiO<sub>2</sub> with appropriate size of Pd particles (ca. 5 nm) exhibits the highest activity for imine hydrogenation.

It must be noted that the use of water as solvent affects strongly on the catalytic activity. Fig. 3e shows the time profiles of the substrate and products during reaction of nitrobenzene in benzyl alcohol without water in the presence of Pd<sub>2</sub>/TiO<sub>2</sub> catalyst. The rate of secondary amine formation is much slower than that obtained with water (Fig. 3c). The water addition probably suppresses the adsorption of alcohols onto the Pd surface. This may accelerate the reduction reactions.

Table 2.	le 2. One-pot synthesis of various kinds of secondary amines on the photoactivated Pd <sub>2</sub> /TiO <sub>2</sub> catalyst <sup>a</sup>					
Run	Alcohol	Nitroarene	<i>t /</i> h	Nitroarene conv. / %	Product	GC yield / % <sup>b</sup>
1	∕∩н		2	>99	_n_	99
2	∽∽он		5	>99		99
3	Он	O <sub>2</sub> N-	5	>99		99
4			4	>99	C-A-C)	96
5 <sup><i>c</i></sup>			72	>99		85 (85 <sup>d</sup> )
6		0 <sub>2</sub> N-	5	>99		98
7		O <sub>2</sub> N-OMe	5	>99	C A OMe	91
8 <sup>e</sup>	СОН	O <sub>2</sub> N-	8	>99	Он	85
9		O <sub>2</sub> N-CN	6	>99	C - CN	92
10 <sup>e</sup>		O <sub>2</sub> N-COOH	12	95	А-С-соон	76
11 <sup>e</sup>	O	O <sub>2</sub> N-CHO	12	95	Судосно	87
12		O <sub>2</sub> N-CI	6	>99	C-H-C)	57 <sup>f</sup>
13 <sup>e</sup>		0 <sub>2</sub> N-	6	>99		95 <sup>g</sup>

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#### Synthesis of various secondary amines

The Pd<sub>2</sub>/TiO<sub>2</sub> catalyst is applicable for the synthesis of various types of secondary amines. The results are summarized in Table 2. Reaction of aliphatic alcohols and nitrobenzene (entries 1–3) produces the secondary amines with almost quantitative yields (99%), as is the case for the benzyl alcohol/nitrobenzene system (entry 4). A large scale reaction is also successfully carried out. As shown by entry 5, 0.5 mmol of nitrobenzene is transformed to the secondary amine with 85% isolated yield although the reaction requires relatively long photoirradiation time (72 h). Reactions of nitrobenzene with -CH<sub>3</sub>, -OCH<sub>3</sub>, and -OH groups (entries 6-8) also gave the products with very high yields  $(\geq 85\%)$ . Nitrobenzenes with reducible substituents such as -CN, -COOH, and -CHO (entries 9-11) are converted to the secondary amines with high yields ( $\geq$ 76%) while retaining the substituents as they are. There are, however, some unsuccessful examples; reaction of p-chloronitrobenzene (entry 12) mainly gave the dechlorinated product because H-Pd species also promote dehalogenation.<sup>33</sup> In addition, reaction of *p*-nitrostyrene (entry 13) produced ethyl-substituted product via the hydrogenation of vinyl group by the H-Pd species.<sup>40,41</sup> These results suggest that Pd2/TiO2 facilitates one-pot synthesis of several kinds of secondary amines, although some cases are unsuccessful due to the subsequent hydrogenation of functional groups.

#### Conclusion

We found that Pd<sub>2</sub>/TiO<sub>2</sub> catalyst facilitates one-pot synthesis of secondary amines from alcohols and nitroarenes under UV light, via tandem photocatalytic and catalytic reactions consisting of (i) photocatalytic oxidation of alcohol (aldehydes formation) and reduction of nitroarenes (anilines formation); (ii) catalytic condensation of the formed aldehydes and anilines; and, (iii) photocatalytic hydrogenation of the formed imines (secondary amines formations). Several secondary amines are successfully produced with high yields. The present system employs Xe lamp as a light source with large electricity consumption. Use of LED light or sunlight is required for practical synthesis although the intensity of UV light contained in these light sources is weaker than that in Xe lamp. Activity improvement of the catalyst is therefore necessary for practical applications. Nevertheless, the present system have several advantages: (i) easily recoverable and recyclable heterogeneous catalyst; (ii) mild reaction conditions (room temperature and atmospheric pressure); and, (iii) cheap and stable substrates (alcohol and nitroarenes). The present system based on the tandem photocatalytic and catalytic actions, therefore, have a potential to be a powerful method for one-pot green synthesis of secondary amines.

#### Experimental

#### Materials

All of the reagents used were supplied from Wako, Tokyo Kasei, and Sigma-Aldrich, and used without further purification. Water was purified by the Milli Q system. JRC-TIO-4 TiO<sub>2</sub> (equivalent to Deggusa P25 TiO<sub>2</sub>) were kindly supplied from the Catalyst Society of Japan.

 $Pd_x/TiO_2$  catalysts [x (wt%) =  $Pd/TiO_2 \times 100$ ; x = 0.5, 1, 2, 4] were prepared as follows:<sup>43</sup> TiO<sub>2</sub> (1.0 g) and  $Pd(NO_3)_2$  (10.9, 21.9, 44.2, or 90.2 mg) were added to water (40 mL), and the solvents were evaporated with vigorous stirring at 353 K for 12 h. The obtained powders were calcined at 673 K under air flow (0.5 L min<sup>-1</sup>) and then reduced at 673 K under H<sub>2</sub> flow (0.2 L min<sup>-1</sup>). The heating rate and the holding time at 673 K for these treatments were 2 K min<sup>-1</sup> and 2 h, respectively. Ag<sub>2</sub>/TiO<sub>2</sub> and Pt<sub>2</sub>/TiO<sub>2</sub> were prepared in a similar manner to Pd<sub>x</sub>/TiO<sub>2</sub> with AgNO<sub>3</sub> (16 mg) or H<sub>2</sub>PtCl<sub>6</sub>•6H<sub>2</sub>O (54 mg) as metal precursors.

 $Au_2/TiO_2$  was prepared by a deposition-precipitation method as follows:<sup>44</sup> HAuCl<sub>4</sub>•4H<sub>2</sub>O (45.8 mg) was added to water (50 mL). The pH of the solution was adjusted to 7 by an addition of 1 M NaOH. TiO<sub>2</sub> (1.0 g) was added to the solution and stirred vigorously at 353 K for 3 h. The particles were recovered by centrifugation and washed with water. They were calcined at 673 K under an air flow (0.5 L min<sup>-1</sup>).

#### Photoreaction

Each of the respective catalysts (10 mg) was added to an alcohol/water mixture (0.5/4.5 mL/mL) containing a nitroarene within a Pyrex glass tube (20 cm<sup>3</sup>;  $\phi$  16.5 mm). The tube was sealed using a rubber septum cap, and N<sub>2</sub> gas bubbled through the solution. The tube was photoirradiated with magnetic stirring by a Xe lamp (2 kW; Ushio Inc.). The temperature of the solution during photoirradiation was about 298 K, and the light intensity was 18.2 W m<sup>-2</sup> (at 300–400 nm). The gas phase product was analyzed by GC-TCD (Shimadzu; GC-8A). The resulting solution was extracted with diethyl ether (2 × 2 mL), and the obtained solution was analyzed by GC-FID (Shimadzu; GC-1700). The amounts of substrate and products were determined with authentic samples.

#### Analysis

The total amounts of metals on the respective catalysts were determined by an X-ray fluorescence spectrometer (Seiko Instruments, Inc.; SEA 2110). Diffuse reflectance UV-vis spectra were measured on an UV-vis spectrophotometer (Jasco Corp.; V-550 with Integrated Sphere Apparatus ISV- 469) with BaSO<sub>4</sub> as a reference. TEM observations were carried out using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.<sup>45</sup>

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#### Notes and references

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**Manuscript title:** One-pot synthesis of secondary amines from alcohols and nitroarenes on TiO<sub>2</sub> loaded with Pd nanoparticles under UV irradiation

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**Graphical Abstract** 



TiO<sub>2</sub> loaded with Pd nanoparticles, when irradiated by UV light in alcohols with nitroarenes, successfully produces the corresponding secondary amines with almost quantitative yield, via tandem photocatalytic and catalytic actions.