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# Title

# Enhancement of catalytic activity of AgPd@Pd/TiO<sub>2</sub> nanoparticles under UV & visible photoirradiation<sup>†</sup>

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## Abstract

Effects of photoirradiation for the hydrogen production from formic acid (FA) decomposition were studied using  $Ag_{93}Pd_7@Pd/TiO_2$  (anatase (A) or P25 (P)) nanocatalysts. The catalytic activity was enhanced by a factor of 1.5–1.6 under UV & visible (Vis) photoirradiation at room temperature for both TiO<sub>2</sub> supports. It was explained by the formation of electron-rich Pd shell because of migration of photogenerated electrons from the TiO<sub>2</sub> surface. The catalytic activity of  $Ag_{93}Pd_7@Pd/TiO_2$  (A) was 1.7–7.3 times higher than that of  $Ag_{93}Pd_7@Pd/TiO_2$  (P) without and under photoirradiation at 27–90 °C. The catalytic activity of  $Ag_{93}Pd_7@Pd/TiO_2$  (A) under photoirradiation at 27°C, 468 mmol H<sub>2</sub> g catalyst<sup>-1</sup> h<sup>-1</sup>, is the best value ever reported in the all heterogeneous catalysts using TiO<sub>2</sub> (A) as photocatalysts at room temperature.

# Introduction

Hydrogen is a promising energy carrier that can be used to generate electricity in a fuel cell, with water being the only waste product. The search for effective techniques of hydrogen gas generation from liquid fuels has remained a difficult challenge for mobile hydrogen energy systems. Formic acid (FA) attracts great attention as such a liquid fuel because it has high energy density, nontoxicity, and excellent stability at room temperature. It is known that Pd-based catalysts involving core-shell and alloy types of catalysts are effective for the hydrogen production from FA decomposition at room temperature.<sup>1-6</sup> According to a systematic study on M@Pd (M = Ru, Rh, Pt, Ag, Au) core-shell nanocatalysts for hydrogen production from FA decomposition,<sup>7</sup> which gave higher catalytic activity than pure Pd/C catalysts, the best catalytic activity has been obtained from Ag@Pd catalysts for which a high initial hydrogen rate of about 4 L g<sup>-1</sup> h<sup>-1</sup> was achieved at room temperature. The highest catalytic activity of Ag@Pd core–shell nanocatalysts was explained by the largest electron transfer from Ag core to Pd shell because of the lowest work function of Ag (4.7 eV) among M compared with that of Pd (5.1 eV).

To enhance the catalytic activity, we have recently studied the preparation of Ag@Pd nanocatalysts loaded on TiO<sub>2</sub> nanoparticles using a microwave (MW)-polyol method,<sup>8</sup> where ethylene glycol (EG) was used as both solvent and reductant.<sup>9</sup> Based on spherical-aberration-corrected scanning transmission electron microscopy (Cs-corrected STEM), STEM-energy dispersed X-ray spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) data, product nanocatalysts consisted of Ag–Pd alloy core and Pd shell nanocrystals loaded on anatase type of TiO<sub>2</sub> nanoparticles. Ag and Pd atoms are partially alloyed with each other under heating at 176–178 °C. Therefore,  $Ag_{82}Pd_{18}$  alloy and Pd shell

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nanocatalysts were formed. Using TiO<sub>2</sub> support, about 4 times higher hydrogen production rate of  $16.00\pm0.89 \text{ Lg}^{-1} \text{ h}^{-1}$  than that without TiO<sub>2</sub> support was obtained.<sup>8</sup> The significant enhancement of catalytic activity of AgPd@Pd in the presence of TiO<sub>2</sub> was explained by further electron transfer from TiO<sub>2</sub> to Pd because the work function of TiO<sub>2</sub> (4.0 eV) is lower than those of Ag (4.7 eV) and Pd (5.1 eV).

For the practical application of AgPd@Pd/TiO<sub>2</sub> catalysts, even higher activity is required. Based on previous work on Ag–Pd bimetallic catalysts,<sup>7</sup> the catalytic activity of AgPd alloy catalyst was much lower than that of Ag@Pd core–shell catalysts. It is therefore expected that the catalytic activity of AgPd@Pd/TiO<sub>2</sub> can be enhanced by dealloying AgPd core. For this purpose, we prepared Ag<sub>100-x</sub>Pd<sub>x</sub>@Pd/TiO<sub>2</sub> (x = 7, 10, 15) catalysts having lower Pd content in AgPd alloy core in an aqueous solution under MW heating at 100 °C.<sup>10</sup> Results show that Ag<sub>100-x</sub>Pd<sub>x</sub>@Pd/TiO<sub>2</sub> (x = 7, 10, 15) catalysts obtained after heating for 30 min, 1 h, and 2 h, respectively, have much higher catalytic activity than that of Ag<sub>82</sub>Pd<sub>18</sub>@Pd/TiO<sub>2</sub> catalyst obtained in EG at higher temperature.<sup>8</sup> The best catalytic activity obtained for Ag<sub>93</sub>Pd<sub>7</sub>@Pd/TiO<sub>2</sub> catalyst, 46.03±2.27 L g<sup>-1</sup> h<sup>-1</sup>, was about three times higher than that of Ag<sub>82</sub>Pd<sub>18</sub>@Pd/TiO<sub>2</sub> prepared in EG.

TiO<sub>2</sub> has widely been used as photocatalysts for which charge separation due to the formation of excited electrons and hole pairs occurs on the TiO<sub>2</sub> surfaces.<sup>11-14</sup> In this study effects of photoirradiation on the hydrogen production from FA decomposition was studied using Ag<sub>93</sub>Pd<sub>7</sub>@Pd/TiO<sub>2</sub> catalyst to further enhance the catalytic activity. Hereafter, Ag<sub>93</sub>Pd<sub>7</sub>@Pd/TiO<sub>2</sub> catalyst is denoted as AgPd@Pd/TiO<sub>2</sub> for the sake of clarity. To ascertain effects of TiO<sub>2</sub> support, not only pure anatase TiO<sub>2</sub>, denoted as TiO<sub>2</sub> (A), prepared by MW-polyol method,<sup>8,10</sup> but also commercially obtained P25 type TiO<sub>2</sub>, denoted as TiO<sub>2</sub> (P), was used. This is the first report on effects of photoirradiation and TiO<sub>2</sub> (A or P) support for AgPd@Pd/TiO<sub>2</sub> catalysts in the hydrogen production from FA decomposition. TiO<sub>2</sub> has been used as photocatalyst or supports of AuPd, Au, Pd, Pt, Rh, Cu, CdS-TiO<sub>2</sub> photocatalysts for the hydrogen production from FA decomposition.<sup>15-19</sup> We demonstrate here that the catalytic activity of AgPd@Pd/TiO<sub>2</sub> under UV & visible (Vis) light irradiation is higher than the above photocatalysts loaded on TiO<sub>2</sub>.

#### Experimental

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AgPd@Pd/TiO<sub>2</sub> (A) was prepared using the same procedure as that reported previously.<sup>10</sup> In brief, TiO<sub>2</sub> nanoparticles were prepared by the hydrolysis of titanium tetraisopropoxide in 1,5-pentanediol under MW heating at 700 W for 60 min. In the first step, Ag core nanoparticles were formed in the presence of TiO<sub>2</sub> nanoparticles. 15 ml of distilled water containing 300 mg polyvinylpyrrolidone (PVP) and 12.26 mg AgNO<sub>3</sub> was mixed with the colloidal solution of 71.88 mg TiO<sub>2</sub> nanoparticles. The mixed solution was heated at 95 °C with MW irradiation at 120 W for 40 min under Ar bubbling. In the second step, 2 ml of distilled water containing 8.3 mg Pd(NO<sub>3</sub>)<sub>2</sub> was added to this solution temperature increased to about 100 °C under MW irradiation after about 1 min. When AgPd@Pd/TiO<sub>2</sub> (P) was prepared, TiO<sub>2</sub> (A) was replaced with commercially obtained TiO<sub>2</sub> (P: Nippon Aerosil Co. Ltd.) and then the same procedure was used for the synthesis of catalysts.

Morphologies, composition, and surface analyses of product particles were conducted using TEM, TEM–EDS, Cs-corrected STEM, STEM–EDS, atomic absorption spectrometry (AAS), XRD, and XPS data. The hydrogen production rate was determined using a gas burette. When effects of UV irradiation were studied, Xe Published on 25 August 2016. Downloaded by Northern Illinois University on 27/08/2016 08:57:54

lamp (Asahi Spectra Co.,Ltd., MAX 303 type: 250–385 nm mirror module) with a light guide was used (Fig. S1<sup>†</sup>). Irradiance of UV light in a reaction cell was measured as 580 W/m<sup>2</sup>. Further details of experimental and characterization methods of catalysts are described in electronic supplementary information<sup>†</sup>.

## **Results and discussion**

TEM images and XRD patterns of TiO<sub>2</sub> (A or P) particles are shown in Fig. S2<sup>†</sup> and S3<sup>†</sup>. Results show that TiO<sub>2</sub> support prepared by MW heating was solely anatase-type with an average diameter of  $10\pm2$  nm, whereas P25 type one is a 92 : 8 mixture of anatase and rutile types with an average diameter of  $27\pm8$  nm. Since particle sizes of TiO<sub>2</sub> (A) are smaller than those of TiO<sub>2</sub> (P), XRD patterns give broader peaks.

TEM and TEM–EDS images of AgPd@Pd/TiO<sub>2</sub> (A or P) are shown in Fig. 1 and Fig. S4<sup>†</sup>. AgPd@Pd/TiO catalysts with an average diameter of 4.6±0.9 nm were loaded uniformly on both TiO<sub>2</sub> (A or P) nanoparticles. This implies that little difference exists in the average diameter of AgPd@Pd catalysts loaded on TiO<sub>2</sub> (A) and TiO<sub>2</sub> (P) supports. To obtain further detailed information on crystal structures of products, Cs-corrected STEM and STEM-EDS images and their line analysis data are measured (Fig. 2A and 2B). Approximately 0.8 nm-thick Pd shells were formed on the AgPd core particles for both TiO<sub>2</sub> supports. The Pd/Ag ratios of AgPd@Pd/TiO<sub>2</sub> (A) and AgPd@Pd/TiO<sub>2</sub> (P) were estimated to be  $0.34\pm0.02$  from EDS data, which were in good agreement with those measured by AAS ( $0.35\pm0.02$ ). Almost the same sizes, morphologies, and composition of AgPd@Pd nanocatalysts were formed on TiO<sub>2</sub> (A) and TiO<sub>2</sub> (P) supports, indicating that TiO<sub>2</sub> (P) does not affect the nucleation and growth of AgPd@Pd nanoparticles.

Fig. 3 shows XRD patterns of AgPd@Pd/TiO<sub>2</sub> (A or P). Aside from anatase and rutile types of TiO<sub>2</sub> peaks, weak peaks derived from {200}, {220}, and {311} facets of fcc AgPd particles are observed. These peaks shift to larger 20 from those of pure fcc Ag crystals (red dotted lines in Fig. 3) because of alloying of Ag core and Pd.<sup>8,10</sup> A weak peak was observed around  $2\theta = 34^{\circ}$  in two samples indexed to {101} facets of PdO (PDF 01-088-2434). This result means that a small amount of PdO was formed under MW heating in aqueous solution.

To characterize chemical states of AgPd@Pd/TiO<sub>2</sub> (A or P) samples, XPS spectra were measured. The full XPS spectra are shown in Fig. S5<sup>†</sup>, where O 1s, Ti 2p, Ag 3d, and Pd 3d peaks are identified in both samples. In the expanded XPS spectra of the 330–345 eV range (Fig. 4a), besides Pd 3d peaks, weak PdO 3d peaks were observed. The binding energies of Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks in AgPd@Pd/TiO<sub>2</sub> (A or P) were almost identical and shift to lower values by about 1.0 eV compared to those of pure Pd (3d<sub>5/2</sub> = 335.1 eV, 3d<sub>3/2</sub> = 340.3 eV) shown by red dotted lines because of electron transfer from Ag and TiO<sub>2</sub> to Pd arising from differences of work functions among Ag (4.7 eV), TiO<sub>2</sub> (4.0 eV), and Pd (5.1 eV). Similarly, the binding energies of Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks in AgPd@Pd/TiO<sub>2</sub> (A or P) shift to lower values by about 1.2 eV compared with those of pure Ag 3d (3d<sub>5/2</sub> = 368.2 eV, 3d<sub>3/2</sub> = 374.2 eV) shown by red dotted lines (Fig. 4b). These negative chemical shifts suggest that some electrons are transferred from TiO<sub>2</sub> to Ag because of difference of the work functions between Ag and TiO<sub>2</sub>.

It is known that hydrogen is produced from  $H_2O$  in the presence of metal/TiO<sub>2</sub> photocatalysts under photoirradiation.<sup>12</sup> It may also be produced from decomposition of FA in the presence of TiO<sub>2</sub> photocatalysts without the presence of metallic catalysts.<sup>15</sup> In order to examine contribution of the above reactions, hydrogen

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production was examined under photoirradiation into AgPd@Pd/TiO<sub>2</sub> catalysts in an aqueous solution without FA and into an aqueous solution of a TiO<sub>2</sub> + HCOOH mixture without AgPd@Pd/TiO<sub>2</sub> catalysts. In the former condition, effects of hydrogen generation from H<sub>2</sub>O decomposition on AgPd@Pd@TiO<sub>2</sub> catalysts under UV & Vis photoirradiation was examined, whereas those from FA decomposition on TiO<sub>2</sub> photocatalysts was examined in the latter case. No H<sub>2</sub> + CO<sub>2</sub> gas emission was observed without FA or AgPd@Pd/TiO<sub>2</sub> catalysts, indicating that the contribution of above background processes is negligible under photoirradiation in our conditions. We also examine pre-irradiation effects of UV & Vis light. Before catalytic reaction, we irradiated UV & Vis light for 30 min, and then the hydrogen production from FA decomposition was measured. No significant difference was obtained between pre-irradiated sample and that without photoirradiated one. It was therefore concluded that pre-irradiation effects, such as UV cleaning on the surface of catalysts, are unimportant.

The initial H<sub>2</sub> production rate ( $R_{initial}$ ) of AgPd@Pd/TiO<sub>2</sub> (A or P) samples was measured using the following method: total gas volume from a stirred glass tube containing 20 ml of 0.25 M aqueous FA and the prepared sample (metallic catalyst weight of 5.1 mg and TiO<sub>2</sub> support weight of 23.0 mg) was measured using a gas burette (see Fig. S1†). Detailed gas analyses for CO<sub>2</sub>, H<sub>2</sub>, and CO were performed on a gas chromatograph and no CO emission was detected using GC for all samples at 27–90 °C. Temporal variation of total gas (H<sub>2</sub> + CO<sub>2</sub>) generation by decomposition of FA in the presence of AgPd@Pd/TiO<sub>2</sub> (A or P) at various temperatures from 27 °C to 90 °C was measured without or under photoirradiation (Fig. 5). Table 1 shows the  $R_{initial}$  values obtained from equation (S1) of ESI† along with reported data for Ag-Pd bimetallic systems.<sup>7,8</sup> The  $R_{initial}$  values of AgPd@Pd/TiO<sub>2</sub> (A or P) without

photoirradiation at 27 °C were larger than those of Ag@Pd and AgPd@Pd without catalyst support and Ag@Pd/C at 20-35 °C.<sup>7,8</sup> The R<sub>initial</sub> value of AgPd@Pd/TiO<sub>2</sub> (A) increases from 44.1 L g<sup>-1</sup> h<sup>-1</sup> at 27 °C to 382 L g<sup>-1</sup> h<sup>-1</sup> at 90 °C without photoirradiation. Under UV irradiation, it increases from 70.1 L g<sup>-1</sup> h<sup>-1</sup> to 404 L g<sup>-1</sup> h<sup>-1</sup> at 90 °C. This indicates that the catalytic activity is enhanced by a factor of 1.6 at 27 °C under photoirradiation, however, the degree of enhancement decreases with increasing the reaction temperature from 1.6 to 1.1 at 27–90  $^{\circ}$ C. The catalytic activity of AgPd@Pd/TiO<sub>2</sub> (P) was smaller than that of AgPd@Pd/TiO<sub>2</sub> (A) by factors of 1.7-7.1 at 27-90 °C without photoirradiation. It should be noted that a similar enhancement of the catalytic activity is observed for  $AgPd(@Pd/TiO_2 (P))$  by photoirradiation. Its  $R_{initial}$  value under photoirradiation is larger than that without photoirradiation by a factor of 1.5 at 27 °C and the enhancement degree decreases to a factor of 1.2 at 90  $^{\circ}$ C. On the basis of above findings, the degree of enhancement of the catalytic activity by photoirradiation is similar (1.5–1.6) between AgPd@Pd/TiO<sub>2</sub> (A) and AgPd@Pd/TiO<sub>2</sub> (P) at 27  $^{\circ}$ C and decreases to 1.1–1.2 for both TiO<sub>2</sub> (A and P) supports at 90  $^{\circ}$ C.

The catalytic activity has often been given by initial turnover frequency  $(TOF_{initial})$  given in equation (S2) of ESI<sup>†</sup>. The  $TOF_{initial}$  values obtained in this study at 27–90 °C are given in Table 1. In Table S1<sup>†</sup> are compared  $TOF_{initial}$  values obtained in this study at 27 °C with reported data at 20–30 °C.<sup>6,7,20-30</sup> The  $TOF_{initial}$  values of AgPd@Pd/TiO<sub>2</sub> (A) and AgPd@Pd/TiO<sub>2</sub> (A) + light are larger than those of AgPd@Pd/TiO<sub>2</sub> (P) and AgPd@Pd/TiO<sub>2</sub> (P) + light by factors of 1.6 and 1.5, respectively. The  $TOF_{initial}$  value of AgPd@Pd/TiO<sub>2</sub> (A) at 27 °C is larger than that of Ag<sub>50</sub>Pd<sub>50</sub> alloy at 20 °C by a factor of 1.34,<sup>7</sup> whereas it is comparable to that of Ag<sub>42</sub>Pd<sub>58</sub> alloy at 25 °C.<sup>6</sup> The highest  $TOF_{initial}$  value of AgPd@Pd/TiO<sub>2</sub> (A) + light,

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306 mol H<sub>2</sub> mol metal catalyst<sup>-1</sup> h<sup>-1</sup>, is larger than most of previous data. However, it is by 8–20% smaller than those of AuPd-MnO<sub>x</sub>/ZIF-8-rGO (382.1 mol H<sub>2</sub> mol metal catalyst<sup>-1</sup> h<sup>-1</sup>) and AgPd-Hs/G (333 mol H<sub>2</sub> mol metal catalyst<sup>-1</sup> h<sup>-1</sup>).<sup>21,24</sup> This shows that the AgPd@Pd/TiO<sub>2</sub> (A) + light catalyst is one of best performance catalysts for the hydrogen production from FA decomposition at room temperature.

The catalytic activity is also estimated by  $H_2$  production rate per the entire photocatalyst including support using equation (S3) of ESI<sup>†</sup>. Results obtained at room temperature are listed in Table S2<sup>†</sup> along with other reported data using TiO<sub>2</sub> photocatalysts.<sup>14-19</sup> Until now AuPd/TiO<sub>2</sub> nanowire (NW) was the best performance catalyst using TiO<sub>2</sub> (A) photocatalyst with a H<sub>2</sub> production rate of 17.7 mmol H<sub>2</sub> g catalyst<sup>-1</sup> h<sup>-1</sup>.<sup>15</sup> It should be noteworthy that the H<sub>2</sub> production rate of AgPd@Pd/TiO<sub>2</sub> (A or P) under photoirradiation, 468 or 64.0 g catalyst<sup>-1</sup> h<sup>-1</sup>, are 26 or 3.6 times larger than that of AuPd/TiO<sub>2</sub> NW. Present results show that AgPd@Pd (A or P) nanoparticles loaded on TiO<sub>2</sub> support is the best combination between metals and TiO<sub>2</sub> support when metals/TiO<sub>2</sub> photocatalyst is used for hydrogen generation from FA decomposition at room temperature.

The apparent activation energies were estimated from the following relation using  $R_{\text{initial}}$  data given in Table 1.

$$\ln(R_{\text{initial}}) = -E_a/RT + C \tag{1}$$

In that equation,  $R_{initial}$  is the initial rate of hydrogen generation,  $E_a$  is the apparent activation energy, and C is a constant. The  $E_a$  values were estimated respectively as 30, 25, 47, and 43 kJ mol<sup>-1</sup> for AgPd@Pd/TiO<sub>2</sub> (A), AgPd@Pd/TiO<sub>2</sub> (A) + UV & Vis, AgPd@Pd/TiO<sub>2</sub> (P), and AgPd@Pd/TiO<sub>2</sub> (P) + UV & Vis (Fig. S6†). The  $E_a$  values

of AgPd@Pd/TiO<sub>2</sub> (A) and AgPd@Pd/TiO<sub>2</sub> (A) + UV & Vis catalysts are smaller than those of AgPd@Pd/TiO<sub>2</sub> (P) and AgPd@Pd/TiO<sub>2</sub> (P) + UV & Vis one by factors of 1.6–1.7. The lower  $E_a$  value obtained using AgPd@Pd/TiO<sub>2</sub> (A) than that using AgPd@Pd/TiO<sub>2</sub> (P) agrees with the higher catalytic activity of the former catalyst. The  $E_a$  values decrease by 4–5 kJ mol<sup>-1</sup> under photoirradiation for AgPd@Pd/TiO<sub>2</sub> (A or P). The enhancement of catalytic activity under photoirradiation also agrees with the decrease in the activation energy.

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The active site of FA decomposition in this study is not on  $TiO_2$  photocatalysts but it is on the Pd shell of AgPd@Pd, because no FA decomposition occurs under photoirradiation to FA/TiO<sub>2</sub> photocatalysts without loading AgPd@Pd nanoparticles. Based on XPS measurements (Fig. 4), electronic states of Pd component in AgPd@Pd/TiO<sub>2</sub> (A) and AgPd@Pd/TiO<sub>2</sub> (P) catalysts without photoirradiation were almost identical. According to our previous studies,<sup>8,10</sup> the higher catalytic activity of AgPd@Pd/TiO<sub>2</sub> (A) catalysts than that of AgPd@Pd (A) ones without photoirradiation has been explained by electron donating effects of  $TiO_2$  (A) support to Pd shell in AgPd@Pd (A). Photocatalytic behavior of TiO<sub>2</sub> under photoirradiation has extensively been studied.<sup>11-14</sup> According to such results, electron-hole pairs are formed on the surface of TiO2 under UV & Vis photoirradiation. As shown in Fig. 6, photogenerated electrons in the TiO<sub>2</sub> conduction band can transfer to the Pd shell of AgPd@Pd/TiO<sub>2</sub> catalysts because of larger work function of Pd (5.1 eV) than those of TiO<sub>2</sub> (4.0 eV) and Ag (4.7 eV), whereas the photogenerated holes remain in the valence band due to the electron-sink effect.<sup>15</sup> The formation of further electron-rich Pd shell under photoirradiation will be a main reason for the enhancement of catalytic activity by UV & Vis photoirradiation. We found that effects of photoirradiation decrease with increasing the reaction temperature. With increasing

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the reaction temperature, the migration rate of photogenerated electrons from  $TiO_2$  to Pd will increase. However, the recombination rate between electron-hole pairs may also increase with increasing the reaction temperature, so that total numbers of electrons which can arrive at the surface of Pd shell may decrease. Thus the degree of enhancement of catalytic activity decreases with increasing the reaction temperature.

We found that the catalytic activity of AgPd@Pd particles depends strongly on the  $TiO_2$  support. The catalytic activity of AgPd@Pd/TiO<sub>2</sub> (A) is higher than that of AgPd@Pd/TiO<sub>2</sub> (P) both without and under photoirradiation, even though the content of TiO<sub>2</sub> (rutile: R) in TiO<sub>2</sub> (P) is small (8%). This implies that a small amount of TiO<sub>2</sub> (R) greatly affects the catalytic activity of AgPd@Pd particles. Photocatalytic activity of TiO<sub>2</sub> (A or R) has been studied.<sup>31-33</sup> The rate of electronhole recombination for  $TiO_2$  (A) and  $TiO_2$  (R) particles has been determined and was found to be greater for rutile in all cases, varying between one and over three orders of magnitude depending on the method used. The  $E_a$  value of AgPd@Pd/TiO<sub>2</sub> (A) is about half of that of AgPd@Pd/TiO<sub>2</sub> (P). The larger catalytic activity of smaller  $E_a$ value of AgPd@Pd/TiO<sub>2</sub> (A) may be linked to the difference in slower electron-hole recombination rate on  $TiO_2$  (A) surface than that on  $TiO_2$  (R) one. According to previous studies on the catalytic activity of Pd/TiO<sub>2</sub>,<sup>34-38</sup> Pd/TiO<sub>2</sub> (A) demonstrated a greater activity than Pd/TiO<sub>2</sub> (R) in selective hydrogenation reactions due to the superior metal supporting behavior of  $TiO_2$  (R). The higher catalytic activity has been explained by its high specific surface area and strong interaction with metal nanoparticles.<sup>39,40</sup> Thus additional reasons for the higher catalytic activity of  $AgPd@Pd/TiO_2$  (A) than that of  $AgPd@Pd/TiO_2$  (P) may be high specific surface area and strong interaction of  $TiO_2$  (A) with AgPd@Pd.

# Conclusions

Effects of UV & Vis photoirradiation were studied for the hydrogen production from FA decomposition using  $Ag_{93}Pd_7@Pd/TiO_2$  nanocatalysts. Both anatase and commercially obtained P25 types of TiO<sub>2</sub> were examined as supports. The catalytic activity of AgPd@Pd/TiO<sub>2</sub> (A or P) was enhanced by a factor of 1.5–1.6 under UV & Vis photoirradiation at room temperature. It was explained by the formation of electron-rich Pd shell owing to migration of photogenerated electrons from the TiO<sub>2</sub> (A or P) surface to Pd shell. The degree of enhancement decreased from 1.5–1.6 to 1.1–1.2 with increasing reaction temperature from 27 °C to 90 °C probably because of increase in the recombination rate between electron-hole pairs. The catalytic activity of AgPd@Pd/TiO<sub>2</sub> (A) under photoirradiation was 1.8–7.3 times higher than that of Ag<sub>93</sub>Pd<sub>7</sub>@Pd/TiO<sub>2</sub> (A) as photocatalysts. Therefore AgPd@Pd/TiO<sub>2</sub> (A) photocatalyst is applicable to efficient hydrogen production systems intended for mobile applications.

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#### Notes and references

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† Electronic Supplementary Information (ESI) available. Experimental details, TEM, and lists of hydrogen production rates from FA decomposition. See DOI: 10.1039/b000000x/

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Catalyst	Temperature	H <sub>2</sub> gas volume	TOF
	(°C)	$(L g^{-1} h^{-1})$	(h <sup>-1</sup> )
AgPd@Pd/TiO <sub>2</sub> (A)	27	44.1 ± 1.3	193
AgPd@Pd/TiO <sub>2</sub> (A) + light	27	$70.1 \pm 2.1$	306
AgPd@Pd/TiO <sub>2</sub> (A)	40	$94.8 \pm 2.8$	414
AgPd@Pd/TiO <sub>2</sub> (A) + light	40	$117 \pm 4$	509
AgPd@Pd/TiO <sub>2</sub> (A)	60	$147 \pm 7$	642
AgPd@Pd/TiO <sub>2</sub> (A) + light	60	$159\pm 8$	695
AgPd@Pd/TiO <sub>2</sub> (A)	70	$236 \pm 12$	1031
AgPd@Pd/TiO <sub>2</sub> (A) + light	70	299 ± 15	1307
AgPd@Pd/TiO <sub>2</sub> (A)	90	$382 \pm 19$	1669
AgPd@Pd/TiO <sub>2</sub> (A) + light	90	$404\pm20$	1765
AgPd@Pd/TiO <sub>2</sub> (P)	27	$6.2 \pm 0.2$	27
AgPd@Pd/TiO <sub>2</sub> (A) + light	27	$9.6 \pm 0.3$	42
AgPd@Pd/TiO <sub>2</sub> (P)	40	$32.8\pm1.0$	143
AgPd@Pd/TiO <sub>2</sub> (A) + light	40	$40.2 \pm 1.2$	176
AgPd@Pd/TiO <sub>2</sub> (P)	60	65.6 ±3.3	287
AgPd@Pd/TiO <sub>2</sub> (A) + light	60	$75.7 \pm 3.8$	331
AgPd@Pd/TiO <sub>2</sub> (P)	70	$141 \pm 7$	614
AgPd@Pd/TiO <sub>2</sub> (A) + light	70	$143 \pm 7$	624
AgPd@Pd/TiO <sub>2</sub> (P)	90	$176 \pm 9$	768
AgPd@Pd/TiO <sub>2</sub> (A) + light	90	219 ± 11	955
$Ag@Pd^{a}$	20	$3.67\pm0.05$	
$Ag@Pd^a$	35	$4.58\pm0.05$	
Ag@Pd/C <sup>a</sup>	20	$4.23\pm0.05$	
AgPd@Pd <sup>b</sup>	27	$0.71 \pm 0.06$	

 Table 1
 Hydrogen production rates from catalytic decomposition of formic acid

 in water at different temperatures without and under UV & Vis photoirradiation.

<sup>a</sup> Ref. 7.

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<sup>b</sup> Ref. 8.

# **Figure Captions**

**Fig. 1** TEM and TEM–EDS images of the (A) AgPd@Pd/TiO<sub>2</sub> (A) and (B) AgPd@Pd/TiO<sub>2</sub> (P) nanocatalysts: (a) TEM image, (b) Ag component, (c) Pd component, (d) Ti component, and (e) Ag-Pd-Ti components, (f) EDS data.

**Fig. 2** Cs-corrected STEM, STEM-EDS images, and line analyses along blue lines in 2e1 and 2e2 of the (A) AgPd@Pd/TiO<sub>2</sub> (A) and (B) AgPd@Pd/TiO<sub>2</sub> (P) nanocatalysts.

**Fig. 3** The XRD patterns of (A)  $AgPd@Pd/TiO_2$  (A) and (B)  $AgPd@Pd/TiO_2$  (P) nanocatalysts. Red dots are anatase, whereas green dots are rutile.

**Fig. 4** XPS spectra for (A) AgPd@Pd/TiO<sub>2</sub> (A) and (B) AgPd@Pd/TiO<sub>2</sub> (P) nanocatalysts: (a) Pd  $3d_{3/2,5/2}$  and (b) Ag  $3d_{3/2,5/2}$ .

**Fig. 5** (a) Gas generation by decomposition of formic acid (0.25 M, 20 mL) vs. time in the presence of (A) AgPd@Pd/TiO<sub>2</sub> (A) and (B) AgPd@Pd/TiO<sub>2</sub> (P) nanocatalysts at 27–90  $^{\circ}$ C without and under photoirradation.

**Fig. 6** Enhancement mechanism of catalytic activity of AgPd@Pd/TiO<sub>2</sub> under UV irradiation.

# **Table of contents**

Hydrogen production rate of  $AgPd@Pd/TiO_2$  nanocatalysts from formic acid decomposition was enhanced by 50–60% at room temperature under photoirradiation.

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Fig. 1 TEM and TEM-EDS images of the (A) AgPd@Pd/TiO2 (A) and (B) AgPd@Pd/TiO2 (P) nanocatalysts: (a) TEM image, (b) Ag component, (c) Pd component, (d) Ti component, and (e) Ag-Pd-Ti components, (f) EDS data.



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Fig. 2 Cs-corrected STEM, STEM-EDS images, and line analyses along blue lines in 2e1 and 2e2 of the (A) AgPd@Pd/TiO2 (A) and (B) AgPd@Pd/TiO2 (P) nanocatalysts.



Fig. 3. M. Tsuji et al.

Fig. 3 The XRD patterns of (A) AgPd@Pd/TiO2 (A) and (B) AgPd@Pd/TiO2 (P) nanocatalysts. Red dots are anatase, whereas green dots are rutile.



Fig. 4. M. Tsuji et al.

Fig. 4 XPS spectra for (A) AgPd@Pd/TiO2 (A) and (B) AgPd@Pd/TiO2 (P) nanocatalysts: (a) Pd 3d3/2,5/2 and (b) Ag 3d3/2,5/2.



Fig. 5 (a) Gas generation by decomposition of formic acid (0.25 M, 20 mL) vs. time in the presence of (A) AgPd@Pd/TiO2 (A) and (B) AgPd@Pd/TiO2 (P) nanocatalysts at 27–90 ∘C without and under photoirradation.



Fig. 6. M. Tsuji et al.

Fig. 6 Enhancement mechanism of catalytic activity of AgPd@Pd/TiO2 under UV irradiation.



76x40mm (150 x 150 DPI)