# Journal of Materials Chemistry A

# PAPER



Cite this: J. Mater. Chem. A, 2015, **3**, 4453

Efficient hydrogen production from formic acid using TiO<sub>2</sub>-supported AgPd@Pd nanocatalysts†

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We report here the significant enhancement of catalytic activity of Ag–Pd bimetallic nanocatalysts with the formation of Ag–Pd catalysts having an average diameter of  $4.2 \pm 1.5$  nm on TiO<sub>2</sub> nanoparticles using a two-step microwave (MW)–polyol method. Data obtained using XRD and STEM-EDS indicated that Ag-Pd bimetallic nanocatalysts consisted of Ag<sub>82</sub>Pd<sub>18</sub> alloy core and about 0.5 nm thick Pd shell, denoted as AgPd@Pd. The hydrogen production rate of AgPd@Pd/TiO<sub>2</sub> from formic acid,  $16.00 \pm 0.89 \text{ Lg}^{-1} \text{ h}^{-1}$ , was 23 times higher than that of bare AgPd@Pd prepared under MW heating at 27 °C. It was even higher by 2–4 times than the best Ag@Pd and CoAuPd catalysts at 20–35 °C reported thus far. The apparent activation energy of the formic acid decomposition reaction using AgPd@Pd catalyst decreased from 22.8 to 7.2 kJ mol<sup>-1</sup> in the presence of TiO<sub>2</sub>. Based on negative chemical shifts of the Pd peaks in the XPS data and the measured activation energies, the enhancement of catalytic activity in the presence of TiO<sub>2</sub> was explained by the lowered energy barrier in the reaction pathways because of the strong electron-donating effects of TiO<sub>2</sub> to Pd shells, which enhance the adsorption of formate to the catalyst and dehydrogenation from formate.

Received 18th December 2014 Accepted 5th January 2015 DOI: 10.1039/c4ta06988a

www.rsc.org/MaterialsA

# Introduction

Hydrogen gas  $(H_2)$  has been anticipated as a clean energy resource that can replace fossil fuels. However, at ordinary temperatures and normal pressures, H<sub>2</sub> is in a gaseous state that is not compatible with storage in a small space. This constraint limits miniaturization of efficient hydrogen production systems for mobile applications. To resolve this issue, a technique must be developed to extract H<sub>2</sub> instantly from liquid fuels on a small scale. As such a liquid fuel, formic acid has attracted great attention because it is produced by a combination of CO<sub>2</sub> and H<sub>2</sub>O with irradiation by sunlight and because it is generated as a primary product in artificial photosynthesis.<sup>1</sup> Some reports have described hydrogen production from the decomposition of formic acid using solid catalysts such as coreshell Au@Pd/C catalysts.<sup>2,3</sup> However, for formic acid dehydrogenation, such catalysts necessitate elevated temperatures (>80 °C). Moreover, the generation of CO gas greatly reduces catalytic activity. However, hydrogen production without CO production from formic acid at room temperature has been

reported recently using Ag@Pd core-shell and CoAuPd alloy catalysts.<sup>4,5</sup> Although hydrogen production rates of about 4 and 8 L g<sup>-1</sup> h<sup>-1</sup> have been achieved, higher catalytic activity without CO production is anticipated for practical application.

Reportedly, the catalytic activity of Pd nanoparticles for formic acid electrooxidation is enhanced in the presence of titanium dioxide (TiO<sub>2</sub>).<sup>6</sup> Therefore, it is expected that the catalytic activity of Ag@Pd core-shell nanocatalysts for formic acid decomposition in an aqueous solution can also be promoted by loading Ag@Pd core-shell nanocatalysts on TiO<sub>2</sub>. Usually, nanoparticles are loaded on an oxide semiconductor by sintering, which requires high-temperature treatment. It is difficult to load core-shell nanometals on an oxide semiconductor without alloying the core and shell metals. Based on previous results obtained for the catalytic activity of the Ag-Pd bimetallic system for formic acid decomposition,4 Ag@Pd core-shell nanocatalysts should not be alloyed because the catalytic property of the core-shell nanocatalyst is lost through alloying at high temperatures. To overcome this shortcoming, a new method must be used to synthesize core-shell nanoparticles directly on an oxide semiconductor.

In this paper, we describe a two-step microwave (MW)–polyol method used to prepare Ag–Pd bimetallic core–shell nanocatalysts directly on TiO<sub>2</sub> nanoparticles. Actually, TiO<sub>2</sub> catalysts have been widely used as photocatalysts<sup>7,8</sup> and as photoelectrodes for dye-sensitized solar cells.<sup>9,10</sup> For such applications, TiO<sub>2</sub> nanoporous substrates such as nanoparticle films and TiO<sub>2</sub> nanotube arrays have been developed.<sup>11,12</sup> Therefore, the TiO<sub>2</sub> nanoporous substrates and techniques described in

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<sup>†</sup> Electronic supplementary information (ESI) available: Temperature profiles of reagent solutions in each experiment and STEM and STEM-EDS images of bare AgPd@Pd nanoparticles. See DOI: 10.1039/c4ta06988a

this work are expected to be useful for developing a practical hydrogen generation device from formic acid. For these reasons, the trial undertaken for this study represents a reasonable and practical challenge. Results show that MW heating is more effective than conventional oil-bath heating for preparing Ag-Pd/TiO<sub>2</sub> nanoparticles. The hydrogen production rate of Ag-Pd/TiO2 nanoparticles from formic acid without CO emission was higher than reported values<sup>4,5</sup> at room temperature. To clarify the enhancement of catalytic activity, nanocatalysts were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), TEM-energy dispersed X-ray spectroscopy (EDS), spherical-aberration-corrected scanning TEM (STEM), STEM-EDS, and X-ray photoelectron spectroscopy (XPS). A much higher catalytic activity with a lower apparent activation energy than that in previous reports4,5 has been obtained for hydrogen production from formic acid without CO emission at room temperature. The effects of the TiO<sub>2</sub> support on the enhancement of the catalytic activity are discussed on the basis of XPS data and the activation energies of formic acid decomposition.

## Experimental

### Preparation of TiO<sub>2</sub> nanoparticles

TiO<sub>2</sub> nanoparticles were prepared by the hydrolysis of titanium tetraisopropoxide (Ti(Oi-Pr)<sub>4</sub>) (Wako Pure Chemical Industries Ltd) in 1,5-pentanediol (Tokyo Chemical Industry Co. Ltd) under MW heating.13 3 mmol Ti(Oi-Pr)4 was added to 50 ml of 1,5-pentanediol. The solution was irradiated in the MW oven (Shikoku Keisoku Kogyo K.K.; µ type, maximum output power 750 W) at 200 W for 3 min. Then 2 ml distilled water was added to this solution and irradiated at 700 W for 1 h. The temperature profile of the reagent solution is shown in Fig. S1 (ESI<sup>†</sup>). The solution temperature increases to 175 °C after 3 min heating at 200 W. It drops to 150 °C after injection of distilled water and increases again to about 195 °C after 6 min at 700 W and becomes nearly constant after that. For the use of TiO<sub>2</sub> as a support for metallic nanoparticles in the next step, products were obtained by centrifuging the colloidal solution at 22 200g for 30 min. Then they were redispersed in ethylene glycol (EG) (Kishida Chemical Co. Ltd).

#### Preparation of Ag-Pd/TiO<sub>2</sub> nanoparticles

Ag–Pd bimetallic nanocatalysts were formed on  $TiO_2$  using a two-step heating method. First, Ag core nanoparticles were formed in the presence of  $TiO_2$  nanoparticles. 15 ml of EG solution containing 850 mg polyvinylpyrrolidone (PVP: average molecular weight of 40k in terms of monomer units) (Wako Pure Chemical Industries Ltd) and 12.26 mg AgNO<sub>3</sub> (Kishida Chemical Co. Ltd) were mixed with the colloidal solution of 17.25 mg TiO<sub>2</sub> nanoparticles. The mixed solution was heated with MW irradiation at 50 W for 20 min under Ar bubbling. Temperature profiles of the reagent solution under MW irradiation are shown in Fig. S2 (ESI†). In the second step, 2 ml of EG containing 16.5 mg Pd(NO<sub>3</sub>)<sub>2</sub> (Kishida Chemical Co. Ltd) was added to this solution and heated with MW irradiation at 250 W or using conventional oil-bath heating for 10 min under Ar bubbling. The temperature profiles of the solutions under MW heating and oil-bath heating are shown in Fig. S3 (ESI†). Finally, the prepared samples were separated from EG solution by centrifuging the obtained colloidal solution at 22 200*g* for 60 min. They were dispersed in distilled water. Then, PVP was removed from the Ag-Pd/TiO<sub>2</sub> surface by sonication for 30 min and PVP and Ag-Pd/TiO<sub>2</sub> were separated by centrifuging at 22 200*g* for 60 min. These processes were repeated six times for removing PVP adequately. Finally, the Ag-Pd/TiO<sub>2</sub> particles were dispersed in distilled water.

### Preparation of bare Ag-Pd nanoparticles

To examine the effects of  $\text{TiO}_2$ , bare Ag–Pd bimetallic nanocatalysts were also prepared using MW heating. 15 ml of EG solution containing 120 mg PVP and 12.26 mg AgNO<sub>3</sub> was heated with MW irradiation at 50 W for 20 min. Then, 2 ml of EG containing 16.5 mg Pd(NO<sub>3</sub>)<sub>2</sub> was added to this solution and heated with MW irradiation at 250 W for 10 min. The obtained Ag–Pd nanoparticles (called bare Ag–Pd (MW)) were precipitated in acetone, washed by sonication for 30 min, and then dried. These processes were repeated twice. Finally, they were dispersed in distilled water. The temperature profile of the solution under MW heating was the same as that in the preparation of Ag–Pd/TiO<sub>2</sub> under MW heating.

#### Characterization of product particles

For TEM, TEM-EDS (JEM-2100F; JEOL), STEM and STEM-EDS (JEM-ARM200F; JEOL), samples were prepared by dropping colloidal solutions of the products onto Cu grids. The average sizes of product particles were determined by measuring more than 100 particles in STEM images, although much larger particles than average ones were used for the EDS analyses of single particles to obtain clear images. The XRD patterns of the samples were measured using Cu K $\alpha$  radiation (SmartLab; Rigaku Corp.). The XPS data of the product were measured using Al K $\alpha$  radiation (AXIS-165; Shimadzu Corp.). The extinction spectra of the product solutions were measured using a spectrometer (UV-3600; Shimadzu Corp.) in the ultraviolet (UV)-visible (Vis)-near infrared (NIR) region.

# Hydrogen generation activity of Ag–Pd and Ag–Pd/TiO $_{\rm 2}$ nanocatalysts

The hydrogen production activity of the prepared samples was examined using the following method: the total gas volume from a stirred glass tube containing 20 ml of 0.25 M aqueous formic acid and the prepared sample (metallic catalyst weight of 5.8 mg) was measured using a gas burette. A schematic view of the measurement system is shown in Fig. S4 (ESI†). The hydrogen gas volume as production per gram of Ag–Pd catalyst per hour was calculated using eqn (1) and (2).<sup>5</sup>

$$x_{\rm a} = P_{\rm atm} V_{\rm gas} / RTn_{\rm FA},\tag{1}$$

where  $x_a$  is the conversion,  $P_{atm}$  stands for the atmospheric pressure,  $V_{gas}$  represents the generated volume of gas, *R* denotes

the universal gas constant, *T* is the room temperature (300 K), and  $n_{\rm FA}$  is the mole number of formic acid.

$$R_{\rm hydrogen} = V_{\rm gas}/2m_{\rm metal}t,$$
 (2)

where  $R_{\rm hydrogen}$  represents the initial rate of hydrogen generation when  $x_{\rm a}$  reaches 20%,  $m_{\rm metal}$  is the weight of the metallic catalyst, and t is the reaction time when  $x_{\rm a}$  reaches 20%.

The  $H_2$ ,  $CO_2$ , and CO gases were measured using a gas chromatograph (GC7100; J-Science): 10 ml of 1 M aqueous formic acid and the prepared sample (metallic catalyst weight of 0.97 mg) mixture were stirred for 30 min in a 110 ml glass tube filled with Ar gas. Then the atmosphere in the glass tube was measured. When the  $H_2$ ,  $CO_2$ , and CO concentrations were determined using GC, data were corrected using the standard gas, which was  $N_2$  gas containing 50 000 ppm  $H_2$ ,  $CO_2$ , and CO gas.

# Results and discussion

## Structural characterization of TiO<sub>2</sub> nanoparticles

Fig. 1a shows a typical TEM image of TiO<sub>2</sub> particles, where monodispersed nanoparticles with an average diameter of  $10 \pm 2$  nm are formed. Fig. 1b shows XRD patterns of the powder sample for which peaks are observed at  $2\theta = 25.3^{\circ}$ ,  $37.8^{\circ}$ ,  $48.1^{\circ}$ ,  $53.9^{\circ}$ , and  $55.1^{\circ}$ . These peaks can be indexed to {101}, {004}, {200}, {105}, and {211} facets of anatase-type of TiO<sub>2</sub> (PDF 00-021-1272). No peak of rutile-type TiO<sub>2</sub> is observed (PDF 01-076-0325). Apparently, the products are composed solely of anatasetype of TiO<sub>2</sub>.

## Structural characterization of Ag–Pd/TiO $_2$ nanoparticles

Ag–Pd/TiO<sub>2</sub> nanoparticles were prepared by two-step heating. In the first step, AgNO<sub>3</sub> was reduced in EG in the presence of TiO<sub>2</sub> at a relatively low reaction temperature of about 130 °C under MW heating at a low power of 50 W to obtain small Ag particles



Fig. 1 TEM and XRD pattern of  $\text{TiO}_2$  nanoparticles. (a) TEM and (b) XRD.

with a large specific surface area (Fig. S2, ESI<sup>†</sup>). In the second step,  $Pd(NO_3)_2$  was further reduced in EG to obtain Ag–Pd bimetallic particles on TiO<sub>2</sub> under MW heating at 250 W or oilbath heating. The reaction temperature was 176–178 °C (Fig. S3, ESI<sup>†</sup>), which was higher than that in the first step to make Ag–Pd particles adhere to a TiO<sub>2</sub> support strongly. Fig. 2a and 2b–d respectively portray STEM and STEM-EDS images of nanoparticles obtained from the reduction of AgNO<sub>3</sub> in the presence of TiO<sub>2</sub> nanoparticles after first MW heating. Spherical Ag nanoparticles with an average diameter of 2.6 ± 1.1 nm were formed. It is noteworthy that Ag nanoparticles were not loaded on TiO<sub>2</sub>, but were instead formed in EG solution. This fact was confirmed not only from TEM images but also from the colour of the solution, which was yellow after centrifugal separation because of the formation of spherical Ag particles.

Fig. 3a–g show STEM and STEM-EDS images of products after second MW-heating for Pd shell formation. Fig. 3h shows line analysis data along the red line depicted in Fig. 3g. These images show that Ag–Pd bimetallic nanocatalysts with an average diameter of  $4.2 \pm 1.5$  nm were loaded uniformly on TiO<sub>2</sub> nanoparticles and 0.5 nm-thick pure Pd shell was formed on Ag or Ag–Pd alloy core metal. The Pd/Ag atomic ratio in whole Ag–Pd bimetallic nanocatalysts was determined as  $0.25 \pm 0.03$  from STEM-EDS analysis. Fig. 4a–g show STEM and STEM-EDS images of products using oil-bath heating for Pd shell formation. Fig. 4h shows line analysis data along the red line depicted in Fig. 4g. These images illustrate that the shape, size, and composition of the products using oil-bath heating. The average size was  $4.4 \pm 1.2$  nm, the thickness of the pure Pd shell was



Fig. 2 STEM and STEM-EDS image of Ag nanoparticles synthesized using microwave heating in the presence of  $TiO_2$  nanoparticles. (a) STEM image, (b) Ag component, (c) Ti component and (d) all components.



Fig. 3 STEM and STEM-EDS images of AgPd@Pd/TiO<sub>2</sub> (MW) nanocatalysts. (a) STEM image, (b) Ag and Pd components, (c) all components, (d) STEM image, (e) Ag component, (f) Pd component, (g) Ag and Pd components and (h) line analysis data along the red line shown in (g).

about 0.5 nm and the Pd/Ag atomic ratio in whole Ag–Pd bimetallic nanocatalysts was 0.25  $\pm$  0.02. On the other hand, there was a difference in the loading amount of catalysts on the TiO<sub>2</sub> support for the two heating methods. In the case of oilbath heating, there were some unloaded bare-Ag–Pd catalysts (see Fig. 4a–c) which were not observed in the products using MW-heating. Based on the data presented above, high-power MW heating at 250 W was required for strong adhesion of Ag–Pd nanoparticles to TiO<sub>2</sub>. Under MW irradiation at high power, it is likely that Ag–Pd nanoparticles are heated locally because of skin effects of nanoparticles under MW<sup>14</sup> so that Ag–Pd particles are strongly adhered to TiO<sub>2</sub> nanoparticles.

To examine crystal structures and composition of products in greater detail, we measured XRD patterns of bare Ag–Pd bimetallic nanoparticles prepared without the addition of TiO<sub>2</sub> support (Fig. 5a) and TiO<sub>2</sub>-supported Ag–Pd bimetallic nanoparticles (Fig. 5b). The observed XRD patterns of Ag and Pd components in bare Ag–Pd bimetallic and TiO<sub>2</sub>-supported Ag–Pd nanoparticles are similar, indicating that the presence of TiO<sub>2</sub> does not affect the crystal structure of Ag–Pd bimetallic particles. Aside from TiO<sub>2</sub> anatase-peaks, major peaks are observed at  $2\theta = 38.3^{\circ}$ ,  $44.7^{\circ}$ ,  $65.1^{\circ}$ , and  $78.1^{\circ}$  in both patterns. These peaks can be indexed to  $\{111\}, \{200\}, \{220\}, and \{311\}$ facets of the Ag component of fcc Ag-Pd bimetallic particles. All of these peaks shift to larger  $2\theta$  by 0.2–0.7° from those of pure fcc Ag crystals (PDF 01-087-0720:  $2\theta = 38.20^{\circ}$ ,  $44.40^{\circ}$ ,  $64.60^{\circ}$ , and 77.60° for {111}, {200}, {220}, and {311}, respectively) because of alloying that occurs between Ag and Pd. According to Vegard's law,<sup>15</sup> which is known to be applicable to Ag–Pd systems, <sup>16</sup> about 18  $\pm$  1% of Pd atoms are dissolved in Ag–Pd particles by alloying. Weak shoulder peaks are observed at  $2\theta =$ 40.1°, 46.7°, 68.1°, and 82.1°, corresponding to the {111}, {200}, {220}, and {311} facets of the Pd component of Ag–Pd bimetallic particles. Peak positions of the Pd component are close to those of pure Pd atoms (PDF 01-005-0681:  $2\theta = 40.12^{\circ}$ ,  $46.66^{\circ}$ ,  $68.09^{\circ}$ and 82.10°, respectively, for {111}, {200}, {220}, and {311}), indicating that a major Pd component exists as pure Pd shells over Ag-rich Ag<sub>82</sub>Pd<sub>18</sub> alloy cores. Based on XRD data, it was inferred that both Ag-Pd/TiO2 and Ag-Pd bimetallic particles consist of Ag<sub>82</sub>Pd<sub>18</sub>@Pd/TiO2 and Ag<sub>82</sub>Pd<sub>18</sub>@Pd core-shell particles and that the Ag : Pd atomic ratio in AgPd cores is independent of the presence of TiO<sub>2</sub> nanoparticles. Consequently, when we examined the catalytic activity of Ag<sub>82</sub>Pd<sub>18</sub>@Pd/TiO<sub>2</sub> and Ag<sub>82</sub>Pd<sub>18</sub>@Pd core-shell particles,



**Fig. 4** STEM and STEM-EDS images of the AgPd@Pd nanocatalysts reduced by high-temperature (176  $^{\circ}$ C) oil-bath heating with TiO<sub>2</sub> nanoparticles. (a) STEM image, (b) Ag and Pd components, (c) all components, (d) STEM image, (e) Ag component, (f) Pd component, (g) Ag and Pd components, and (h) line analysis data along the red line shown in (g).



Fig. 5 XRD patterns of (a) bare AgPd@Pd and (b) AgPd@Pd/TiO\_2 prepared using the MW-polyol method.

only the effects of  $TiO_2$  were found through comparison with the two data. Hereinafter, for the sake of clarity, we respectively designate  $Ag_{82}Pd_{18}$ @Pd/TiO<sub>2</sub> and  $Ag_{82}Pd_{18}$ @Pd particles as AgPd@Pd/TiO<sub>2</sub> and AgPd@Pd.

The UV-Vis-NIR spectra of the products in each stage were measured (Fig. 6). Anatase-type  $TiO_2$  nanoparticles showed extinction below about 350 nm and a weak tail band from



Fig. 6 UV-Vis-NIR extinction spectra of  $TiO_2$  nanoparticles, mixture of Ag and  $TiO_2$  nanoparticles and AgPd@Pd/TiO\_2 nanocatalysts prepared using MW heating.

approximately 350 to about 600 nm. The SPR band of spherical silver particles is observed at around 400 nm,<sup>17</sup> whereas a long tail band without a prominent peak is found for Pd nanoparticles.<sup>18</sup> When Ag core particles are prepared in the presence of TiO<sub>2</sub> particles under MW heating at 50 W, aside from the TiO<sub>2</sub> peak, a typical SPR band of spherical Ag nanoparticles was observed in the 350-490 nm region with a peak at about 412 nm because of the formation of free spherical Ag particles in the supernatant in this stage. The extinction spectrum of AgPd@Pd/ TiO<sub>2</sub> particles comprises a long tail band from 200 nm to 1000 nm with a shoulder peak at about 400 nm. Generally speaking, the surface plasmon resonance (SPR) band of core-shell particles reflects optical properties of shell metals.19,20 Consequently, the long tail band and the peak at about 400 nm can be attributed respectively to the SPR bands of Pd and Ag components of AgPd@Pd/TiO2 particles.

To obtain chemical states of bare AgPd@Pd and AgPd@Pd/ TiO<sub>2</sub> nanocatalysts, XPS spectra were measured (Fig. 7). For comparison, binding energies of pure Pd and Ag metals are presented as vertical dotted lines. The XPS spectra, which provide information related to chemical states within several nanometer depth from the surface of nanoparticles, show that binding energies for Pd  $(3d_{5/2} \text{ and } 3d_{3/2})$  peaks in bare AgPd@Pd shift to lower values by about 0.6 eV compared to those of pure Pd ( $3d_{5/2} = 335.1$  eV,  $3d_{3/2} = 340.3$  eV). Taking account of the fact that AgPd@Pd particles are covered by pure Pd shells (Fig. S5, ESI<sup>†</sup>), these binding energy shifts originate from electron transfer from Ag to Pd because of a difference of work functions between Ag (4.7 eV) and Pd (5.1 eV). The binding energies of Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> in bare AgPd@Pd respectively shift to lower values by about 1.2 eV compared with those of pure Ag 3d ( $3d_{5/2} = 368.2 \text{ eV}$ ,  $3d_{3/2} = 374.2 \text{ eV}$ ). The binding energies of Ag 3d peaks in Pd rich (>90%) Ag-Pd alloys are known to shift to lower values by about 1 eV.21 It is therefore reasonable to assume that the peak shifts arise from the formation of the Ag-Pd alloy around the interface of the Ag-core and Pd-shell. It is noteworthy that the binding energies of Pd  $(3d_{5/2} \text{ and } 3d_{3/2})$  and Ag  $(3d_{5/2} \text{ and } 3d_{3/2})$  in AgPd@Pd/TiO<sub>2</sub> (MW) both shift to lower values by about 0.9 and 0.5 eV, respectively, compared with those of bare AgPd@Pd (MW). These shifts suggest that some electrons are transferred from TiO<sub>2</sub> to Pd and Ag because of the large difference of the work functions between Ag (4.7 eV) or Pd (5.1 eV) and TiO<sub>2</sub> (4.0 eV).



Fig. 7 XPS spectra for AgPd@Pd/TiO<sub>2</sub> (MW) nanoparticles and bare AgPd@Pd (MW) nanoparticles, (a) Pd  $3d_{3/2.5/2}$  and (b) Ag  $3d_{3/2.5/2}$ .

# Hydrogen generation activity of AgPd@Pd and AgPd@Pd/TiO $_2$ nanoparticles

Fig. 8 presents the catalytic activities of AgPd@Pd/TiO<sub>2</sub> (MW), bare AgPd@Pd (MW), a mixture of bare AgPd@Pd (MW) and TiO<sub>2</sub>, and AgPd@Pd/TiO<sub>2</sub> (oil) nanoparticles as counterparts for H<sub>2</sub> generation from formic acid decomposition. The H<sub>2</sub> generation rates, obtained from relationships (1) and (2), are presented in Table 1. Corresponding reported data of Ag@Pd and CoAuPd catalysts<sup>4,5</sup> are given for comparison. The hydrogen production rate of AgPd@Pd/TiO<sub>2</sub> (MW) sample was 16.00 L g<sup>-1</sup> h<sup>-1</sup> at room temperature (27 °C), which is about four times higher than that of Ag@Pd catalysts at 20 °C (3.67 L g<sup>-1</sup> h<sup>-1</sup>)<sup>4</sup> and about two times higher than that of CoAuPd catalysts at 25 °C (7.9 L g<sup>-1</sup> h<sup>-1</sup>).<sup>5</sup> It was about 23 times higher than that of bare AgPd@Pd (MW). The average size of bare AgPd@Pd (MW)



Fig. 8 Gas generation by decomposition of formic acid (0.25 M, 20 ml) versus time in the presence of (a) AgPd@Pd/TiO<sub>2</sub> (MW) nanoparticles, (b) bare AgPd@Pd (MW) nanoparticles, (c) the mixture of bare AgPd@Pd (MW) and TiO<sub>2</sub> nanoparticles, and (d) AgPd@Pd/TiO<sub>2</sub> (oil) nanoparticles at 27 °C.

 Table 1
 Hydrogen production rates from the catalytic decomposition

 of formic acid in water at different temperatures

Catalyst	Temperature (°C)	$H_2$ gas volume (L g <sup>-1</sup> h <sup>-1</sup> )
AgPd@Pd/TiO2 (MW)	27	$16.00 \pm 0.89$
AgPd@Pd/TiO <sub>2</sub> (MW)	40	$16.80 \pm 0.52$
AgPd@Pd/TiO <sub>2</sub> (MW)	60	$17.89 \pm 0.38$
AgPd@Pd/TiO <sub>2</sub> (MW)	70	$21.26 \pm 0.77$
AgPd@Pd/TiO <sub>2</sub> (MW)	90	$26.73 \pm 0.53$
Bare AgPd@Pd (MW)	27	$0.71\pm0.06$
Bare AgPd@Pd (MW)	40	$1.19\pm0.09$
Bare AgPd@Pd (MW)	60	$1.98\pm0.18$
Bare AgPd@Pd (MW)	70	$2.54\pm0.30$
Bare AgPd@Pd (MW)	90	$3.34\pm0.22$
Mixture of AgPd@Pd	27	$2.14\pm0.21$
(MW) and TiO <sub>2</sub>		
AgPd@Pd/TiO <sub>2</sub> (oil)	27	$11.76\pm0.32$
Ag@Pd (ref. 4)	20	3.67
Ag@Pd (ref. 4)	35	4.58
CoAuPd (ref. 5)	25	7.9

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was 4.3  $\pm$  1.2 nm (Fig. S5, ESI<sup>†</sup>). These sizes were nearly the same as those of AgPd@Pd/TiO<sub>2</sub> (MW) nanocatalysts (4.2  $\pm$  1.5 nm). Therefore, the much higher catalytic activity of AgPd@Pd/TiO<sub>2</sub> (MW) cannot be explained simply by the increase in the specific surface area of nanocatalysts. It can, however, be attributed to enhancement by the assistance of the TiO<sub>2</sub> support. To examine the catalytic activity of pure TiO<sub>2</sub> nanoparticles in formic acid decomposition, formic acid was mixed with TiO<sub>2</sub> nanoparticles without the addition of AgPd@Pd (MW) nanocatalysts. Then the gas emissions were observed. No H<sub>2</sub> or CO<sub>2</sub> gas emission was observed using only TiO<sub>2</sub> nanoparticles. This result led us to conclude that TiO<sub>2</sub> does not act as a catalyst in formic acid decomposition in the absence of AgPd@Pd nanocatalysts.

The hydrogen production rate of AgPd@Pd/TiO<sub>2</sub> (MW) was eight times higher than that of the mixture of bare AgPd@Pd (MW) and TiO<sub>2</sub> nanoparticles. This result indicates that strong adhesion of AgPd@Pd (MW) and TiO<sub>2</sub> nanoparticles using MW heating is necessary to enhance the synergy effects between AgPd@Pd and TiO<sub>2</sub>. Moreover, the hydrogen production rate of AgPd@Pd/TiO<sub>2</sub> (MW) was 1.4 times higher than that of AgPd@Pd/TiO<sub>2</sub> (oil). The average size of AgPd@Pd/TiO<sub>2</sub> (oil) was 4.4  $\pm$  1.2 nm (see Fig. 4a–c). These sizes were nearly the same as those of AgPd@Pd/TiO<sub>2</sub> (MW) nanocatalysts (4.2  $\pm$  1.5 nm). This fact demonstrates that MW heating is more effective than conventional oil-bath heating for strong adhesion between AgPd@Pd nanoparticles and TiO<sub>2</sub> nanoparticles.

Hydrogen gas production rates were measured at various temperatures using AgPd@Pd/TiO<sub>2</sub> (MW) and bare AgPd@Pd (MW) catalysts (Table 1). The results show that the hydrogen production rate of bare AgPd@Pd (MW) increases more with increasing temperature from 27 to 90 °C than that of AgPd@Pd/TiO<sub>2</sub> (MW).

It is known that the chemical decomposition of formic acid proceeds *via* two main pathways, *i.e.*, the dehydrogenation reaction to form  $CO_2 + H_2$  and the dehydration reaction to form  $CO + H_2O$ 

$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2: \Delta G = -48.4 \text{ kJ mol}^{-1}$$
(3)

HCOOH 
$$\rightarrow$$
 CO + H<sub>2</sub>O:  $\Delta G = -28.5 \text{ kJ mol}^{-1}$  (4)

Although  $H_2$  and  $CO_2$  emissions from reaction (3) were observed, no CO emission from reaction (4) was detected using GC for AgPd@Pd/TiO<sub>2</sub> at 27–90 °C. Based on GC detection, the concentration of CO, which reduces the catalytic activity of AgPd@Pd/TiO<sub>2</sub>, was estimated as <10 ppm. The apparent activation energies of reaction (3) using AgPd@Pd/TiO<sub>2</sub> (MW) and bare AgPd@Pd (MW) catalysts were estimated from the following relationship.

$$\ln(R_{\rm hvdrogen}) = -E_{\rm a}/RT + C \tag{5}$$

In this equation,  $R_{hydrogen}$  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 as 7.2 and 22.8 kJ mol<sup>-1</sup>, respectively, for AgPd@Pd/TiO<sub>2</sub> (MW) and bare AgPd@Pd (MW)



Fig. 9 Plots of  $ln(R_{hydrogen})$  vs. 1000/T for AgPd@Pd/TiO<sub>2</sub> (MW) and bare AgPd@Pd (MW) nanocatalysts.

catalysts (see Fig. 9). The  $E_a$  value of bare AgPd@Pd (MW) catalyst is lower than those of Pd/C (53.7 kJ mol<sup>-1</sup>)<sup>22</sup> and Ag@Pd (30 kJ mol<sup>-1</sup>).<sup>4</sup> It is noteworthy that the  $E_a$  value of AgPd@Pd/TiO<sub>2</sub> (MW) is lower by a factor of three than that of bare AgPd@Pd (MW) catalyst. It is the lowest value ever reported in the literature.

### Reaction mechanism of dehydrogenation of formic acid over AuPd@Pd/TiO<sub>2</sub>

Based on previous DFT calculations on intermediate species,<sup>23,24</sup> formate is an important intermediate in formic acid decomposition on metallic catalysts. A possible decomposition scheme of formate on AgPd@Pd/TiO2 is shown in Fig. 10. Decomposition starts by activating the C-H bond of formate adsorbed on the catalytic surface. Under our conditions, monodentate formate (species A) transforms efficiently to more stable bidentate formate (species B), in which both oxygen atoms bind to the catalyst surface. Otherwise CO is formed through decomposition of monodentate formate (species A).<sup>4</sup> Bidentate formate (species B) decomposes into CO<sub>2</sub><sup>\*</sup> + H<sup>\*</sup> (species C), where X\* denotes intermediates adsorbed onto the surface. Recombination of two H\* and CO<sub>2</sub><sup>\*</sup> leaving from the surface results in the formation of  $CO_2 + H_2$  gases (species D). Based on theoretical calculations on potential energy surfaces (PESs) of the formic acid decomposition reaction, the energy barrier from species B to species C is highest. It is the ratedetermining step. Hu et al.24 calculated energy barriers between species B and C for Pt, Pd, Rh, and Au catalysts using {111} facets of metallic surfaces and found that a low energy barrier height for Pd is qualitatively consistent with the high hydrogen



Fig. 10 The schematic diagram of formic acid decomposition pathways on the Pd surface of AqPd@Pd/TiO<sub>2</sub>.

production rate from formic acid. Moreover, when they calculated PESs of Pd–Ag bilayer systems, the energy barrier of the last process becomes lower than that of pure Pd metal because the migration energy of H\* to the top surface of Pd decreases in the presence of Ag cores.

The current results show that the hydrogen production rate is greatly enhanced in the presence of TiO<sub>2</sub> for the AgPd@Pd system. Large negative chemical shifts were observed for XPS peaks of Pd (3d<sub>5/2,3/2</sub>) atoms for AgPd@Pd/TiO<sub>2</sub> compared with those for AgPd@Pd. The work function has been regarded as an important parameter of the catalytic system for the formic acid decomposition system over M@Pd (M = Ag, Rh, Au, Ru, Pt) core-shell catalysts. The catalytic activity increases concomitantly with decrease of the work function.4 Therefore, the best activity has been obtained for Ag@Pd. We found here that the catalytic activity of AgPd@Pd particles is greatly enhanced in the presence of TiO<sub>2</sub> having a further lower work function. Larger negative chemical shifts in XPS peaks for AgPd@Pd/TiO<sub>2</sub> than those of bare AgPd@Pd show that more electrons were transferred from TiO<sub>2</sub> to Pd shells in the presence of TiO<sub>2</sub>. Consequently, the high catalytic activity of AgPd@Pd/TiO<sub>2</sub> originates from a larger amount of electron transfer not only from Ag cores but also from the TiO<sub>2</sub> support to Pd shells. The current results show that the apparent activation energy of reaction (3) using AgPd@Pd catalyst decreases by a factor of three in the presence of TiO<sub>2</sub>. The greater degree of electron transfer from the Pd layer to intermediate species A-C in the presence of TiO<sub>2</sub> strengthens the adsorption of formates and decreases the energy barriers of hydrogen formation and proton diffusion over catalysts.

## Conclusions

Using a two-step MW-polyol method, TiO2-supported AgPd@Pd core-shell nanoparticles having an average diameter of 4.2  $\pm$ 1.5 nm were prepared. In the first step, AgNO<sub>3</sub> was reduced at a low MW power of 50 W to prepare a mixture of small Ag nanoparticles and TiO<sub>2</sub> nanoparticles. In the second step, Ag<sub>82</sub>Pd<sub>18</sub>@Pd/TiO<sub>2</sub> particles were prepared by reducing  $Pd(NO_3)_2$  in the presence of a mixture of Ag and TiO<sub>2</sub> nanoparticles at a high MW power of 250 W. For comparison, AgPd@Pd/TiO2 particles were prepared using conventional oilbath heating. To examine the effects of TiO<sub>2</sub>, bare AgPd@Pd were synthesized under MW heating in the absence of TiO<sub>2</sub>. The initial hydrogen formation rate of AgPd@Pd/TiO2 from formic acid, 16.00  $\pm$  0.89 L g<sup>-1</sup> h<sup>-1</sup>, was about 23 times higher than that of bare AgPd@Pd. It was 2-4 times higher than the reported best Ag@Pd and CoAuPd catalysts at 20-35 °C. The catalytic activity of AgPd@Pd/TiO<sub>2</sub> particles prepared by MW heating is higher than that prepared under oil-bath heating in the second step because of stronger adhesion of AgPd@Pd catalysts on TiO<sub>2</sub>. Consequently, the MW-polyol method is a promising new mode for the loading of uniform metallic nanocatalysts on a TiO<sub>2</sub> support adhered strongly to TiO<sub>2</sub>. The apparent activation energy of dehydrogenation of formic acid by AgPd@Pd catalysts decreased from 22.8 kJ mol<sup>-1</sup> to 7.2 kJ mol<sup>-1</sup> in the presence of the TiO<sub>2</sub> support. When XPS spectra of the catalyst were

observed, larger negative chemical shifts were observed for Pd peaks of AgPd@Pd/TiO<sub>2</sub> in comparison with those of bare AgPd@Pd because of electron-donating effects of TiO<sub>2</sub> to Pd shells. Based on the findings presented above, the marked enhancement of catalytic activity of AgPd@Pd/TiO<sub>2</sub> was attributed to electron transfer from TiO<sub>2</sub> to AgPd@Pd/catalysts, promoting C-H cleavage of formic acid over the surface of AgPd@Pd/TiO<sub>2</sub> nanocatalysts. In fact, CO emission, which reduces catalytic activity of AgPd@Pd/TiO<sub>2</sub>, was not observed at 27–90 °C. Our method, which provides a novel preparation route for core–shell AgPd@Pd nanocatalysts on TiO<sub>2</sub> particles with high catalytic activity, is applicable for efficient hydrogen production systems intended for mobile applications.

## Acknowledgements

We thank Mrs Keiko Uto of our institute for her advice related to the preparation of  $TiO_2$  nanoparticles using MW heating. This work was supported by JSPS KAKENHI (grant nos 25286003 and 25550056) and by the Management Expenses Grants for National University Corporations from MEXT.

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