Supporting information

Colloidal platinum nanoparticles dispersed by polyvinylpyrrolidone and poly(diallyldimethylammonium chloride) with high catalytic activity for hydrogen production based on formate decomposition

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1. Materials

The colloidal platinum nanoparticles dispersed by PVP (Pt-PVP) was purchased from Tanaka Holdings Co. Ltd. Pt concentration in Pt-PVP was estimated to be 4.0 wt. %. The particle size of Pt-PVP was estimated to be *c.a*. 2.0 nm using transmission electron microscope (TEM) image shown in the analysis table published by Tanaka Holdings Co., Ltd. A cationic polymer, poly(diallyldimethylammonium chloride) (PDADMA) (20 wt. % in H_2O) was purchased from Sigma-Aldrich. Co. Ltd.

2. Experimental procedure

The outline of the experimental procedure is shown in Fig. S1.

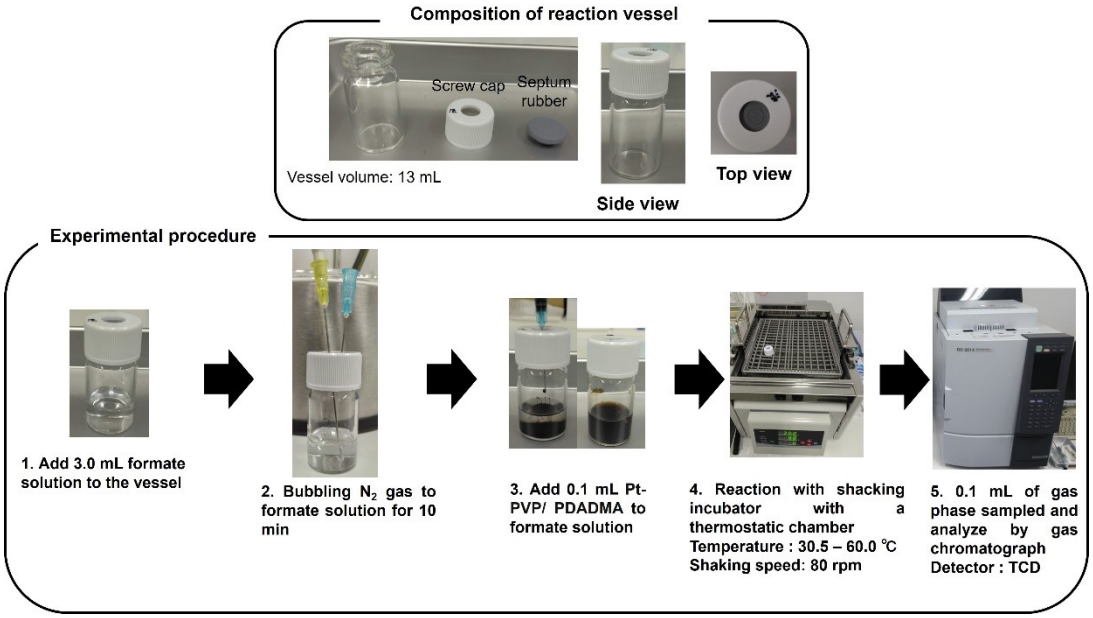

Fig. S1. The outline of experimental procedure for H_2 and CO_2 production based on the formate decomposition with Pt-PVP/PDADMA.

The reaction vessel consists of a glass sample bottle, a screw cap and a septum rubber. The volume of vessel is 13.0 mL. First, add 3.0 mL of formate aqueous solution (0.9 mmol; pH 1.9-4.0) the reaction vessel and then bubbling nitrogen gas into formate aqueous solution for 10 min. Next, add 0.1 mL of Pt-PVP or Pt-PVP/ PDADMA (content of platinum nanoparticles: 0.4 mg) to formate aqueous solution by using a syringe. The reaction is carried out using the shacking incubator with a thermostatic chamber (EYELA NTS-4000, TOKYO RIKAKIKAI Co. Ltd.). The reaction temperature is adjusted between 30.5 and 60 °C. The shaking speed is adjusted to be 80 rpm. 0.1 mL of the gas phase of the reaction vessel was sampled with a gas-tight syringe and analyzed by gas chromatography (GC-2014, SHIMADZU Corporation) with a

thermal conductivity detector (TCD). Activation charcoal column (column length: 3 mm I.D. × 2 m) was equipped for detecting those gasses. The temperature of injection, column and detector were adjusted to be 100.0, 70.0 and 100.0 °C respectively. Ar gas was used by carrier gas and the flow rate was 30.0 mL min^{-1}.

3. Detection for H_2 and CO_2 using gas chromatography

The amount of H_2 and CO_2 production was determined by gas chromatograph (GC-2014, SHIMADZU Corporation) with a TCD. The retention time for H_2 was detected at 0.9-2.0 min. The signal intensity changes in the various amount of H_2 (0 – 2.2 μmol) were shown in Fig. S2.

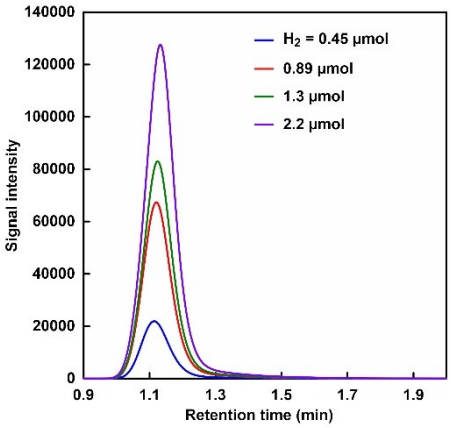

Fig. S2. Chart of chromatogram of H_2 (0 – 2.2 μmol).

Figure S3 shows the relationship between the amount of H_2 and the detection peak area using gas chromatograph.

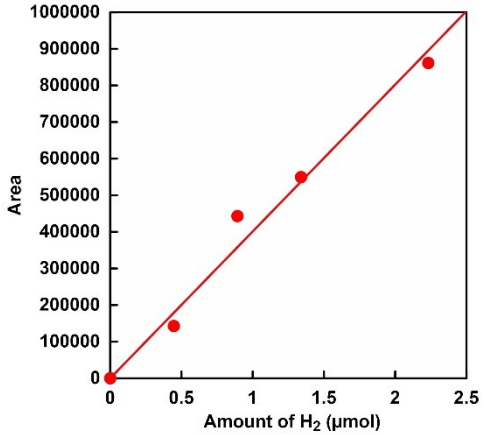

Fig. S3. Relationship between the amount of H_2 and the detection peak area using gas chromatograph.

As shown in Fig. S3, the amount of H_2 and the detected peak area showed a good linear relationship (correlation coefficient: r^2=0.992) as following equation (S1).

$$\text{Peak area} = 4.012\times10^5\times H_2\ (\mu\text{mol}) \quad \text{(S1)}$$

The retention time for CO_2 was detected at 15.5-20.0 min. The signal intensity changes in the various amount of CO_2 (0 – 2.2 μmol) were shown in Fig. S4.

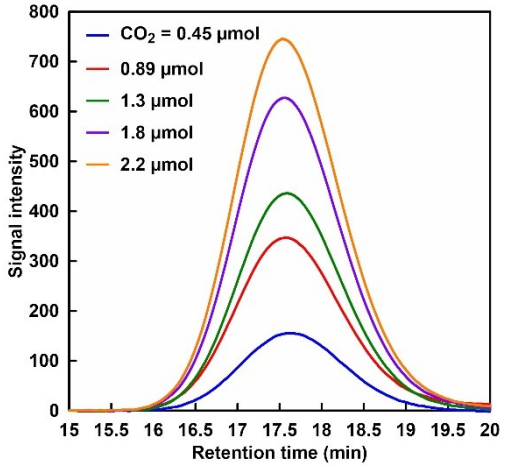

Fig. S4. Chart of chromatogram of CO_2 (0 – 2.2 μmol).

Figure S5 shows the relationship between the amount of CO_2 and the detection peak area using gas chromatograph.

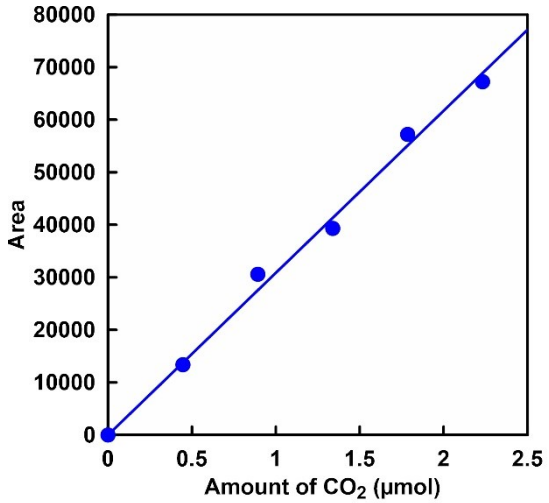

Fig. S5. Relationship between the amount of CO_2 and the detection peak area using gas chromatograph.

As shown in Fig. S5, the amount of CO_2 and the detected peak area showed a good linear relationship (correlation coefficient: r^2=0.998) as following equation (S2).

$$\text{Peak area} = 3.085\times10^4\times CO_2\ (\mu\text{mol}) \quad \text{(S2)}$$

4. IR spectrum measurement for Pt-PVP or Pt-PVP/PDADMA

IR spectra of Pt-PVP, Pt-PVP /PDADMA and PDADMA were obtained with FT/IR-6600 (JASCO) by Attenuated Total Reflection (ATR) method. Fig. S6 shows the IR spectra of Pt-PVP, Pt-PVP /PDADMA and PDADMA.

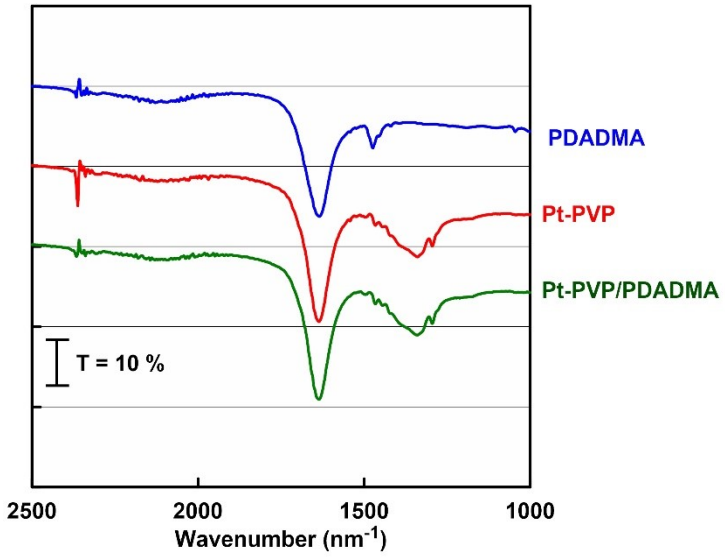

Fig. S6. IR spectra of Pt-PVP, Pt-PVP /PDADMA and PDADMA.