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Supplementary Information

Enhancement of catalytic activity of AgPd@Pd/TiO_2 nanoparticles under UV and visible photoirradiation

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Characterizations of nanocatalysts

Transmission electron microscopy (TEM, JEM-2100F; JEOL) and corresponding energy dispersive X-ray (EDX) spectrometry were applied for microstructure and composition analyses. Spherical-aberration-corrected scanning TEM (Cs-corrected STEM, JEM-ARM200F; JEOL) and corresponding EDX spectrometry were applied for more detailed analyses. Amorphous carbon coated copper grids were used as the sample supporters. The average sizes of product particles were determined by measuring more than 100 particles in TEM and STEM images. Amorphous carbon coated copper grids were used as the sample supporters. The composition of AgPd@Pd/TiO_2 nanocatalysts was analyzed using atomic absorption spectrometry (AA-7000; Shimadzu Corp.). Before measurement, AgPd@Pd/TiO_2 nanocatalysts were dissolved into sulfuric acid and this solution was filtered for removing TiO_2 nanoparticles. The Pd/Ag atomic ratio was estimated from the concentrations of Ag and Pd ions in the solution. Powder X-ray diffraction (XRD) patterns of the samples were measured using Cu Kα radiation operating at 45 kV and 200 mA (SmartLab; Rigaku Corp.). X-ray photoelectron spectrometry (XPS) was conducted using Al Kα radiation (AXIS-165; Shimadzu Corp.). The calibration was carried out using a carbon peak which was derived from tape used for stabilizing samples at XPS measurement before analyzing. Since drift of peaks due to charge up was observed for the AgPd@Pd/TiO_2 (P) sample, only the first scan data with low signal to ratio was used. Such a drift was not observed for the AgPd@Pd/TiO_2 (A) sample, so that data with better signal-to-noise ratio were obtained by averaging several scan data. Detailed analyses for CO_2, H_2, and CO were performed on a gas chromatograph (GC7100; J-Science).

Measurement of hydrogen production under light irradiation

Hydrogen production rate from decomposition of formic acid was measured using the apparatus shown in Fig. S1.

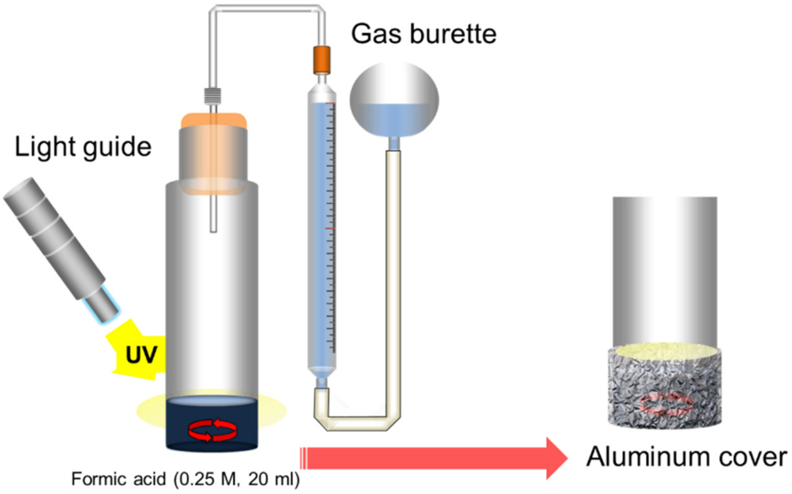

Fig. S1 Gas burette measurements for the production of H_2 from FA decomposition under UV + Vis photoirradiation

Determination of initial hydrogen formation rate and TOF_{initial}

R_{initial}(L H_2 g metal catalyst^{-1} h^{-1}), TOF_{initial} (mol H_2 mol metal catalyst^{-1} h^{-1}), and H_2 production rate (mmol H_2 g catalyst^{-1} h^{-1}) were estimated from the following equations.

$$R_{\mathrm{initial}} = V_{\mathrm{gas}}/2m_{\mathrm{metal}}t, \qquad \text{(S1)}$$

In this equation, R_{initial} represents the initial rate of hydrogen generation when conversion x_a reaches 20%, V_{gas} is the volume of the initial generated gas (H_2 + CO_2), when x_a reaches 20%, m_{metal} is the weight of the metallic catalyst, and t is the reaction time when x_a reaches 20%. For obtaining average value, measurements were taken at least three times.

$$TOF_{\mathrm{initial}} = P_{\mathrm{atm}}V_{\mathrm{gas}}/2RTM_{\mathrm{metal}}t, \qquad \text{(S2)}$$

Where TOF_{initia} is the initial turn over frequency of reaction, when x_a reaches 20%, and M_{metal} is the mole number of metal catalyst.

$$H_2 \text{ production rate} = 1000P_{\mathrm{atm}}V_{\mathrm{gas}}/2RTm_{\mathrm{catalyst}}t, \qquad \text{(S3)}$$

Where m_{catalyst} is the weight of total catalyst including support.

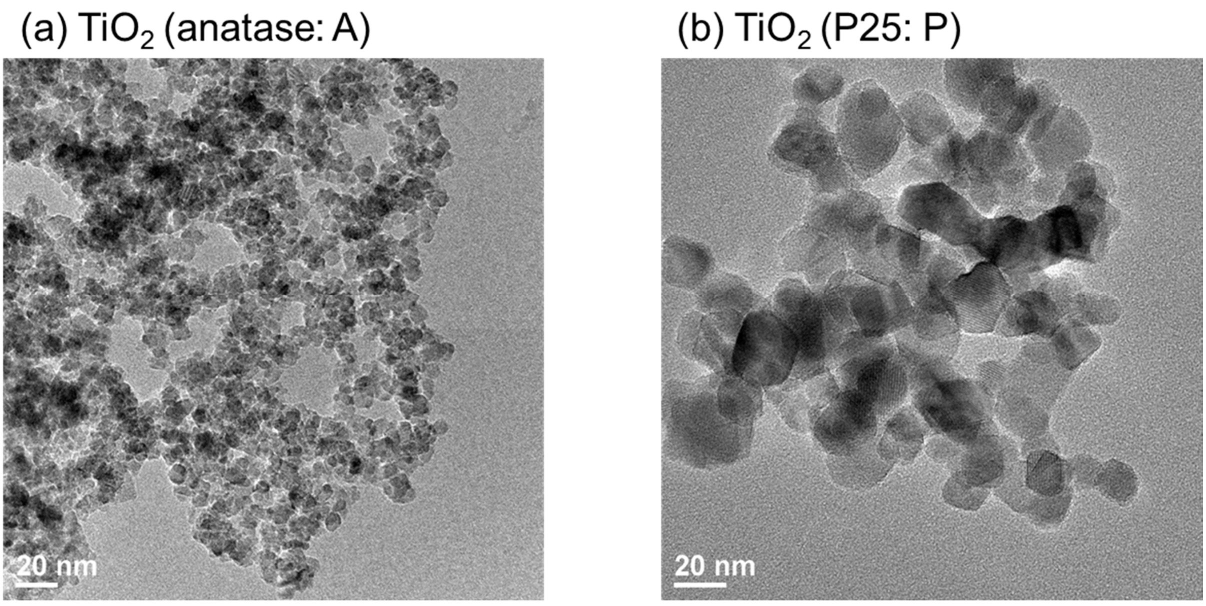

Fig. S2 TEM images of (a) TiO_2 (anataze: A) and (b) TiO_2 (P25: P).

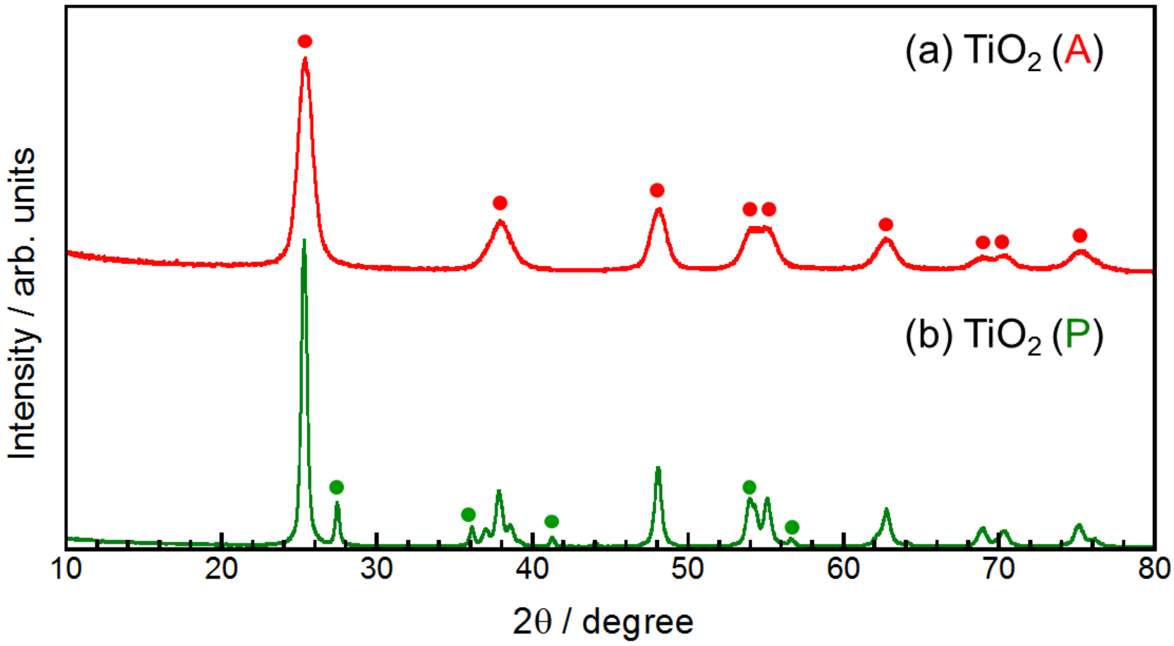

Fig. S3 XRD patterns of (a) TiO_2 (A: red dots, anatase) and (b) TiO_2 (P: green dots, rutile).

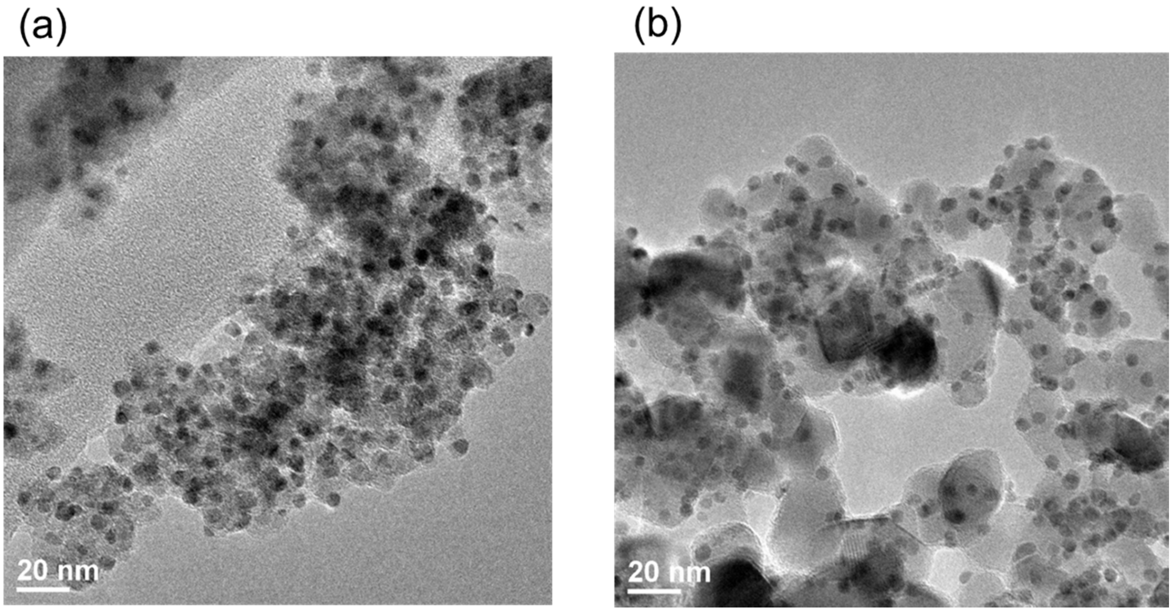

Fig. S4 TEM images of (a) AgPd@Pd/TiO_2 (A) and (b) AgPd@Pd/TiO_2 (P).

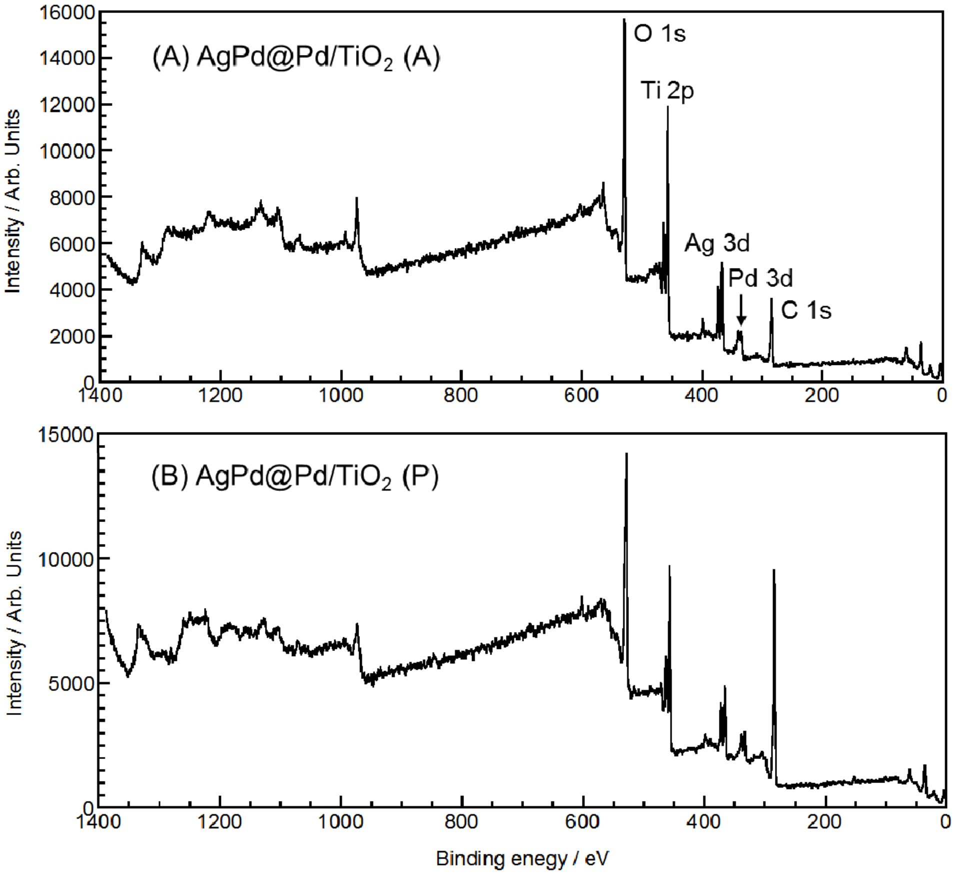

Fig. S5. XPS spectra of AgPd@Pd/TiO_2 (A) and (b) AgPd@Pd/TiO_2 (P).

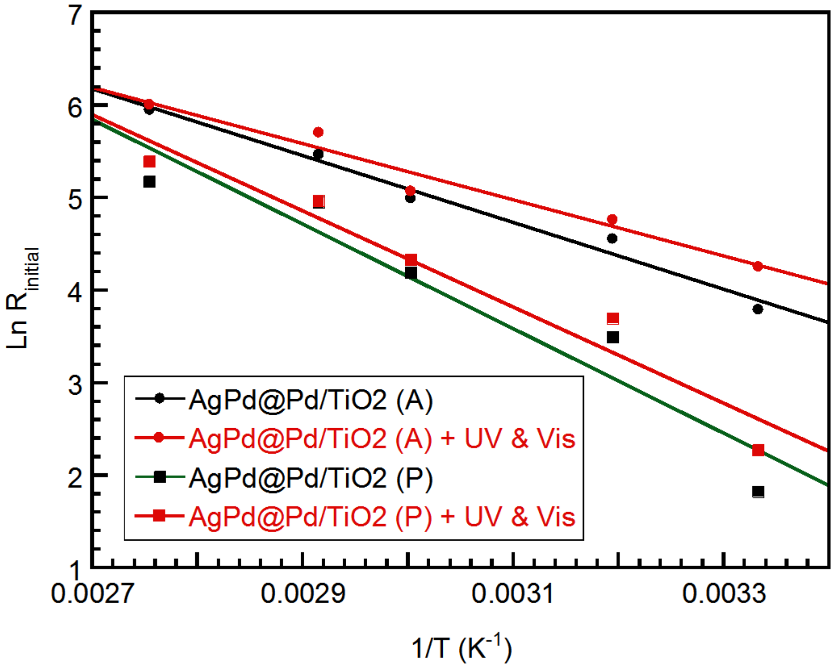

Fig. S6 Arrhenius plots of hydrogen production rate vs 1/T for AgPd@Pd/TiO_2 (A or P) catalysts without photoirradiation and under UV and vis photoirradiation.

Table S1 Initial TOF values for the decomposition of FA over various heterogeneous catalysts at low temperature.

Catalyst	Temperature (^{o}C)	$TOF_{initial}$ (mol H_2 mol metal catalyst^{-1} h^{-1})[a]	Ref.
$Ag_{93}Pd_7$@Pd/TiO_2 (A)	27	193	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (A) + light	27	306	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (P)	27	27.1	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (P) + light	27	41.9	This work
CoAuPd/DNA-rGO[b]	25	102.4	20
AuPd-MnOx/ZIF-8-rGO[c]	25	382.1	21
Au@Pd/N-mrGO[d]	25	104.5	22
Pd-poly(allyl-amine)	22	61.5	23
AgPd-Hs/G[e]	25	333	24
AgPd/rGO	25	105.2	25
Citric acid modified Pd/C	25	143.1	26
$Ag_{50}Pd_{50}$	20	144	7
$Ag_{42}Pd_{58}$	25	198	6
CoAuPd/C	25	80	27
Ag@Pd	20	125	7
Ag@Pd/C	20	192	7
Pd/C	30	228	28
AgAuPd/rGO	25	57.6	29
Pd-MnO_x/SiO_2-NH_2	30	290	30

[a] mol catalyst without support

[b] DNA–reduced-graphene-oxide

[c] ZIF-8 framework ($Zn(MeIM)_2$, MeIM = 2-methylimidazole)

[d] nitrogen-doped mildly reduced graphene oxide

[e] hollow spheres anchored on graphene

Table S2 Hydrogen production rate from formic acid decomposition by using photocatalysts under light irradiation at room temperature.

Catalyst	Light	H_2 production (mmol H_2 g catalyst^{-1} h^{-1})[a]	Ref.
$Ag_{93}Pd_7$@Pd/TiO_2 (A)	no	294	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (A) + light	UV + Vis	468	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (P)	no	41.3	This work
$Ag_{93}Pd_7$@Pd/TiO_2 (P) + light	UV + Vis	64.0	This work
AuPd/TiO_2 (A) nanowire (NW)	AM1.5, 1 sun	17.7	15
Au/TiO_2 (A) NW	AM1.5, 1 sun	3.9	15
TiO_2 (A) NW	AM1.5, 1 sun	10.9	15
Pd/TiO_2 (A) NW	AM1.5, 1 sun	0.80	15
Pt/TiO_2 (A)	UV	1.62	16
Rh-N/TiO_2 (A)	230-440 nm	0.746	17
Cu/TiO_2 (A)	UV	0.83	18
CdS-TiO_2 nanotube/TiO_2	>430 nm	0.56	19

[a] g catalyst: the mass of the entire photocatalyst including support used for reaction.