Supplementary information for

Selective photocatalytic oxidation of aromatic alcohols to aldehydes in an aqueous suspension of gold nanoparticles supported on cerium(IV) oxide under irradiation of green light

Experimental procedure

Commercial CeO_2 powders having a cubic structure were supplied by Kanto Chemical and Kojundo Chemical Laboratory. The CeO_2 powder from Kanto Chemical branded as NanoTek^R with > 99.5% purity and the CeO_2 powder from Kojundo Chemical Laboratory is highly pure (>99.99%) and fine spherical having an average diameter of 0.2 μm. Loading of Au on CeO_2 was performed by the photodeposition method. Bare CeO_2 powder (198 mg) was suspended in water (10 cm^3) in test tubes and the test tubes were sealed with rubber septums under argon (Ar). Aqueous solutions of citric acid (30 μmol) and tetrachloroauric acid ($HAuCl_4$, as 2 mg Au) were injected into the sealed test tubes and then photoirradiated at λ >300 nm by a 400-W high-pressure mercury arc (Eiko-sha, Osaka, Japan) under Ar with magnetic stirring in a water bath continuously kept at 298 K. The Au source was reduced by photogenerated electrons in the conduction band of CeO_2, and Au metal was deposited on CeO_2 particles, resulting in the formation of Au/CeO_2. The resultant powder was washed repeatedly with distilled water and then dried at 310 K overnight under air. The dried Au/CeO_2 powder (50 mg) was suspended in distilled water (5 cm^3), bubbled with O_2, and sealed with a rubber septum. Benzyl alcohol (33 μmol) was injected into the suspension and then irradiated with visible light of a green light-emitting diode (HDMS8G, Hayashi Watch Works, Tokyo, maximum energy at 530 nm, designated green LED hereafter). Since an LED consumes less energy than that of a fluorescent lamp, LEDs have been preferably used as light sources of photochemical processes in industry and advertisement in commerce because of their low energy consumption. Recently, LEDs have also been used for lighting in offices in buildings and in living rooms, kitchens and bathrooms in houses because LEDs, especially white LEDs, are now supplied at low cost. The amount of carbon dioxide (CO_2) in the gas phase and the amounts of benzyl alcohol and benzaldehyde in the liquid phase were measured using gas chromatographs. No apparent differences in photoabsorption and photocatalytic activity were observed between the two commercial CeO_2 powders after Au loading.

Results

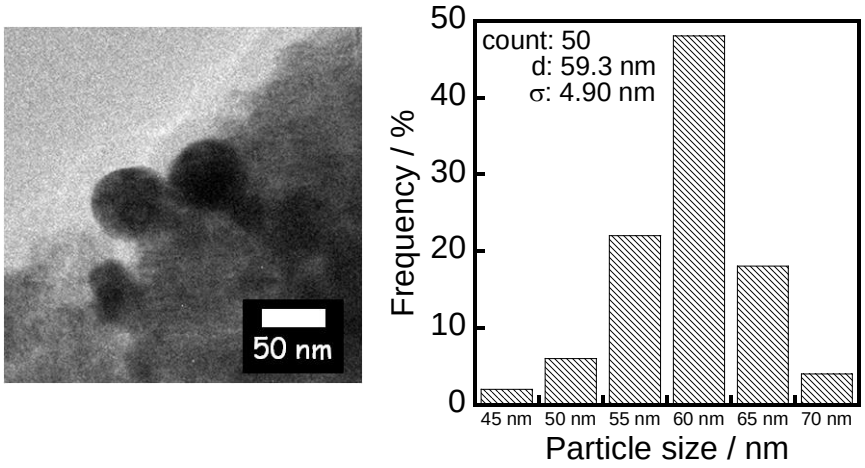


Fig. S1 TEM photograph of 1.0 wt% Au/CeO_2 (left) and size distribution of Au particles (right).

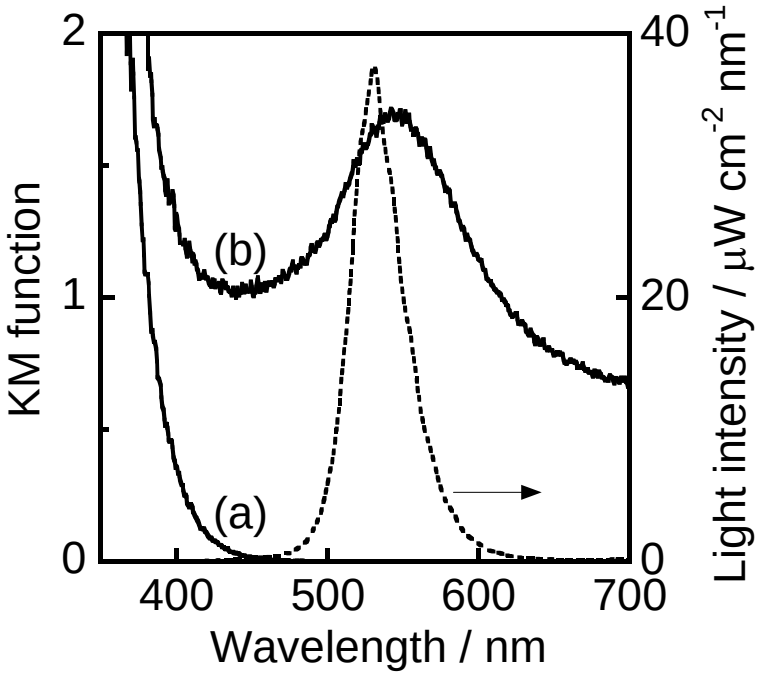


Fig. S2 Absorption spectra of (a) CeO_2 and (b) 1 wt% Au/CeO_2 and visible light irradiated to reaction systems (benzyl alcohol in aqueous suspensions of various powders) from a green LED (broken line).

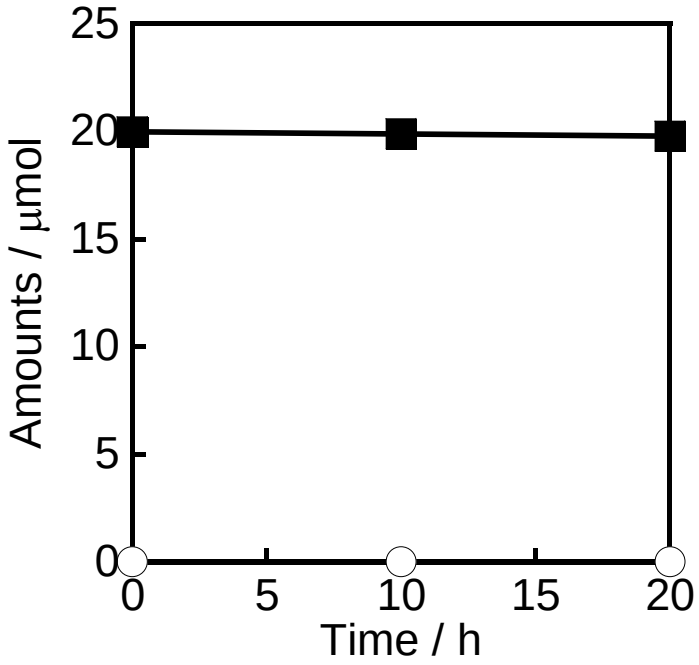


Fig. S3 Time courses of the amounts of benzaldehyde (squares) and CO_2 (circles) in an aqueous suspension of 1.0 wt% Au/CeO_2 under irradiation of green light from an LED.

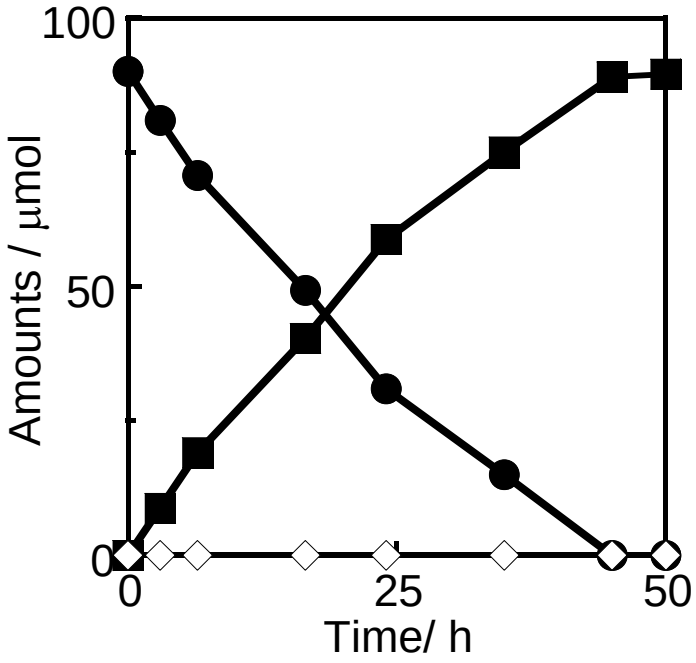


Fig. S4 Time courses of the amounts of benzyl alcohol (circles), benzaldehyde (squares) and CO_2 (diamonds) in an aqueous suspension of 1.0 wt% Au/CeO_2 under irradiation of green light from an LED.

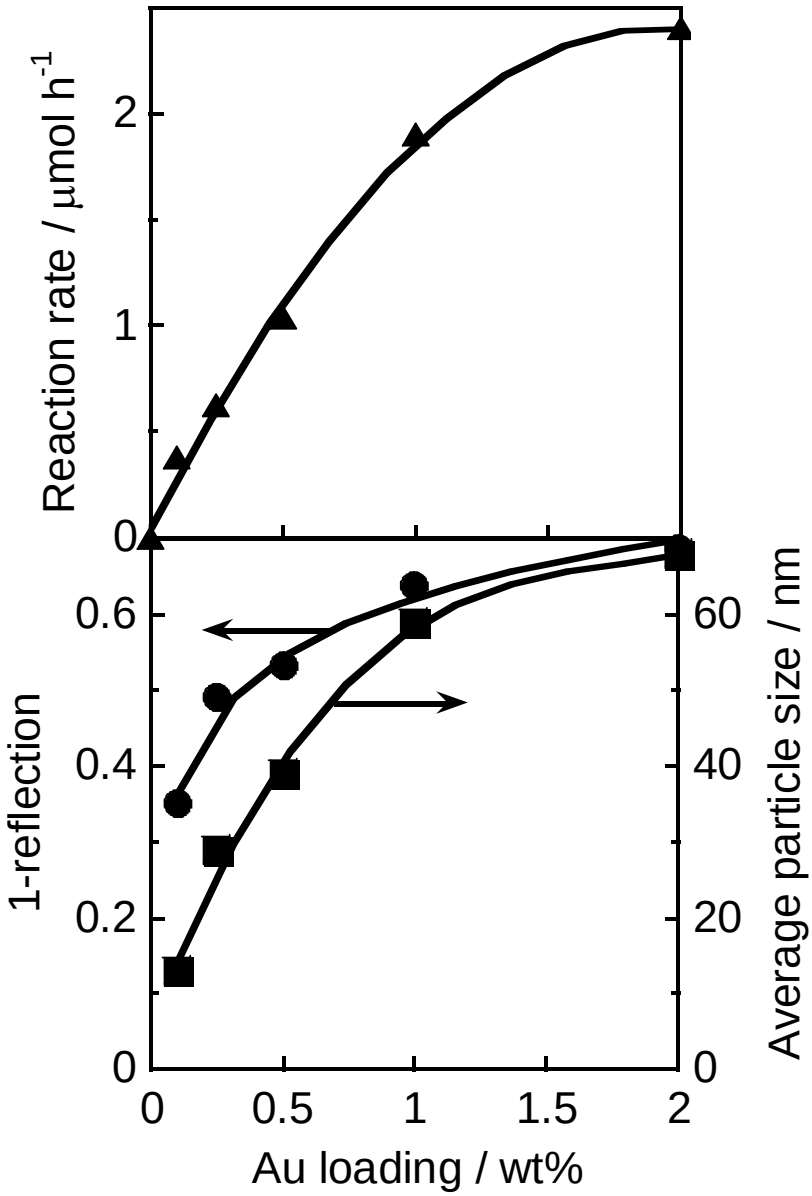


Fig. S5 Effect of Au loading on average particle size of Au loaded on CeO_2 (squares), photoabsorption properties of Au/CeO_2 (circles) and rate of production of benzaldehyde from aqueous solutions of benzyl alcohol in the presence of Au/CeO_2 and O_2 under irradiation of green light from an LED (triangles).

Calculation of Au surface area

Average particle size of Au: D [nm]
Volume of an Au particle: V_p [m^3]
Surface area of an Au particle: S_P [m^2]
Density of Au: ρ [g m^{-3}]
Weight of an Au particle: W_P [g]
Atomic weight of Au: M_W [g mol^{-1}]
Amount of substance of Au in an particle: n_P [mol]
Weight of Au in 50 mg Au/CeO_2: W_A [g]
Amount of substance of Au in 50 mg Au/CeO_2: n_A [mol]
Number of Au particles in 50 mg Au/CeO_2: N_A
Surface area of Au particles in 50 mg Au/CeO_2: S_A [m^2]

$$V_p = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3$$

$$S_P = 4\pi\left(\frac{D}{2}\right)^2$$

$$W_p = V_p\rho$$

$$n_p = \frac{W_P}{M_W}$$

$$n_A = \frac{W_A}{M_W}$$

$$N_A = \frac{n_A}{n_P}$$

$$S_A = S_P N_A$$

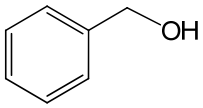
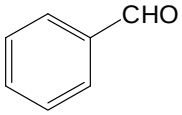
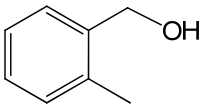
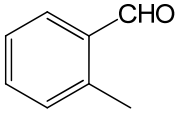
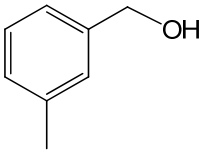
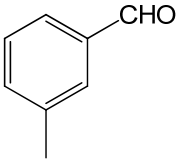
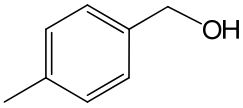
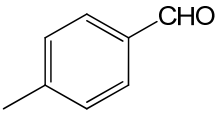
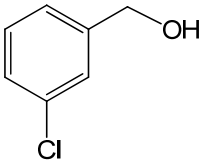
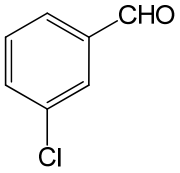
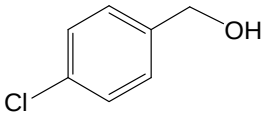
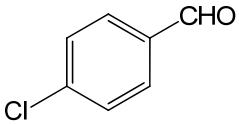
Equation S1

Table S1 Oxidation of benzyl alcohol in an aqueous suspension of 1 wt% Au/CeO_2 under irradiation of green light from an LED in the presence of O_2[a]

Entry	Photocatalyst	Times of usage[b]	Light intensity /mW cm^{-2}	Time / h	Conv.[c] / %	Selectivity[c] / %
1	Au/CeO_2	Fresh	1.7	10	52	> 99
2	Au/CeO_2	Fresh	1.7	20	> 99	> 99
3	Au/CeO_2	Second	1.7	20	> 99	> 99
4	Au/CeO_2	Third	1.7	20	> 99	> 99
5	Au/CeO_2	Fresh	0 (dark)	20	trace	-
6	CeO_2	Fresh	1.7	20	trace	-
7	non	--	1.7	20	trace	-
8	CeO_2	Fresh	(1.7) (Blue LED)	20	trace	-

[a] Benzyl alcohol: 33 μmol, Au/CeO_2: 50 mg, Water: 5 cm^3, O_2: 1 atm, LED: maximum energy at 530 nm. [b] Recovered from the reaction mixture by simple filtration and then used. [c] Determined by GC using the internal standard method.

Table S2 Oxidation of various alcohols in an aqueous suspension of 1 wt% Au/CeO_2 under irradiation of green light from an LED in the presence of O_2[a]

Entry	Substrate	Product	Time / h	Conv.[b] / %	Selectivity[b] / %
1			20	> 99	> 99
2			20	> 99	> 99
3			20	> 99	> 99
4			20	> 99	> 99
5			20	95	> 99
6			20	92	> 99

[a] Benzyl alcohols: 33 μmol, Au/CeO_2: 50 mg, Water: 5 cm^3, O_2: 1 atm, LED: maximum energy at 530 nm. [b] Determined by GC using the internal standard method.