Supporting Information

A Mild and Environmental Benign Strategy Towards Hierarchical CeO_2/Au Nanoparticle Assemblies with Crystal Facets Enhanced Catalytic Effects for Benzyl Alcohol Aerobic Oxidation

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Table S1. Particle size, ratio of the exposed crystal facets, surface area, pore size, and pore volume of of @CeO_2 spheres, @CeO_2 nanoparticle assemblies, and CeO_2 nanoparticles.

@CeO_2	d_{CeO2} (nm)	$I_{(200)/(111)}$	$I_{(220)/(111)}$	S_{BET} ($m^2 \cdot g^{-1}$)	D_{pore} (nm)	V_{pore} (cm^3/g)
Untreated	3.5	0.29	0.49	141.1	-	0.19
[Bmim][BF_4][a]	9.5	0.35	0.59	60.3	7.2	0.25
[Bmim][BF_4][b]	13.7	0.44	0.64	63.75	3.2	0.32
NH_4BF_4	11.4	0.43	0.61	62.8	3.5	0.27
$NaBF_4$	7.1	0.35	0.68	62.3	9.6	0.27
NH_4F	6.5	0.33	0.58	67.0	10.1	0.26

[a]CeO_2 nanoparticles obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] in the absence of SiO_2 sphere templates.

[b]@CeO_2 nanoparticle assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4].

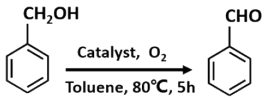
Table S2. XPS results for @CeO_2/Au spheres, @CeO_2/Au nanoparticle assemblies, and CeO_2/Au nanoparticles

@CeO_2/Au	Ce (%)	Ce^{3+}/Ce^{4+} (%)	F (%)	Au ^{0} (%)	Au^{n+} (%)
Untreated	18.9	20.2	-	77.1	22.9
[Bmim][BF_4][a]	19.8	31.5	15.7	82.3	17.7
[Bmim][BF_4][b]	20.0	29.0	8.4	70.5	29.5
NH_4BF_4	19.3	24.7	11.1	75.9	24.1
$NaBF_4$	19.7	23.2	12.0	80.3	19.7
NH_4F	19.1	22.8	9.6	79.0	21.0

[a]CeO_2/Au nanoparticles obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] in the absence of SiO_2 sphere templates.

[b]@CeO_2/Au nanocube assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4]

Table S3. The @CeO_2/Au etching by [Bmim][BF_4] for Oxidation of benzyl alcohol with different morphology and solvent.

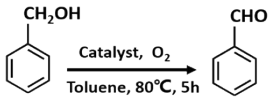


@CeO_2/Au	Au loading (wt %)	Solvent	Conversion (%)	Selectivity (%)
Untreated	2.47	toluene	62.1	82.6
[Bmim][BF_4][b]	1.67	toluene	89.6	91.1
[Bmim][BF_4][a]	2.44	toluene	43.3	85.5
[Bmim][BF_4][b]	1.67	trifluorotoluene	100	72.2

[a]CeO_2/Au nanoparticle assemblies obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] in the absence of SiO_2 sphere templates.

[b]@CeO_2/Au nanocube assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4].

Table S4. The different Au content of @CeO_2/Au etching by [Bmim][BF_4] for Oxidation of benzyl alcohol.



@CeO_2/Au	Au loading (wt %)	Solvent	Conversion (%)	Selectivity (%)
	0.85	toluene	52.1	83.2
[Bmim][BF_4][a]	1.16	toluene	73.4	84.7
	1.67	toluene	89.6	91.1

[a]@CeO_2/Au nanocube assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4].

Table S5. Comparison of catalytic performance of present @CeO_2/Au nanoparticle assemblies and other previously reported Au/CeO_2 based catalysts for benzyl alcohol aerobic oxidation.

Catalyst	Catalyst amount	Temperature (°C)	Time (h)	Solvent	Benzyl alcohol (mmoL)	Conversion (%)	Selectivity (%)	Ref.
@CeO_2/Au nanoparticle assemblies	0.1 g	80	5	Toluene	1	89.6	91.1	This work
@CeO_2/Au nanoparticle assemblies	0.1 g	90	3	Toluene	4	37.1	95.6	This work
Au/Sm-CeO_2	0.1 g	90	3	Toluene	4	27.41	>99	43
Au/CeO_2	0.1 g	130	2	--	0.1	64.5	86.2	44
Au-CeO_2@SBA-15	0.1g	90	3	Toluene	2.5	39	>99	45
Au/CeO_2	0.02g	90	8h	Chlorob -enzene	1	96	99	46

Table S6. The results of recyclability of @CeO_2/Au nanoparticle assemblies, @CeO_2/Au nanoparticle assemblies calcined at 300 ºC for 2 h, and CeO_2/Au nanopowders for oxidation of benzyl alcohol.

Catalysts	Cycle 1	Cycle 2	Cycle 3
CeO_2/Au nanoparticle assemblies	89.6 %	62.5 %	47.8 %
CeO_2/Au nanopowders	54.3 %	21.5 %	8.4 %
CeO_2/Au nanoparticle assemblies calcined at 300 ºC	91.3 %	85.4 %	73.7 %

Reaction conditions: benzylic alcohol (1 mmol), catalyst (100 mg), K_2CO_3 (1 mmol), toluene (10 mL), 5 h, 80 ºC, oxygen atmosphere. The product was determined by HPLC using biphenyl as an internal standard.

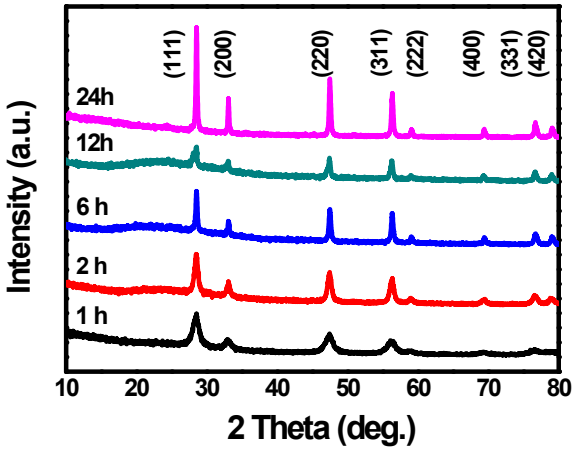


Figure S1. The XRD patterns of @CeO_2 nanoparticle assemblies obtained by etching with [Bmim][BF_4] at 160 ºC for different reaction times prolonged from 1-24 h.

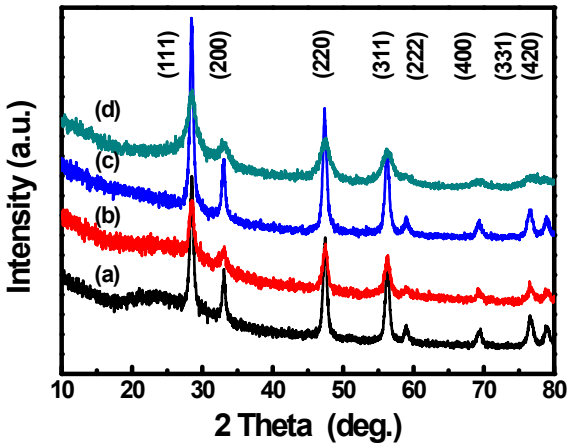


Figure S2. The XRD patterns of @CeO_2 nanoparticle assemblies obtained by etching @CeO_2 spheres with various fluorine-contained agents of (a) [Bmim][BF_4] (b) NH_4BF_4, (c) $NaBF_4$, and (d) NH_4F under hydrothermal condition at 160 ºC for 2 h.

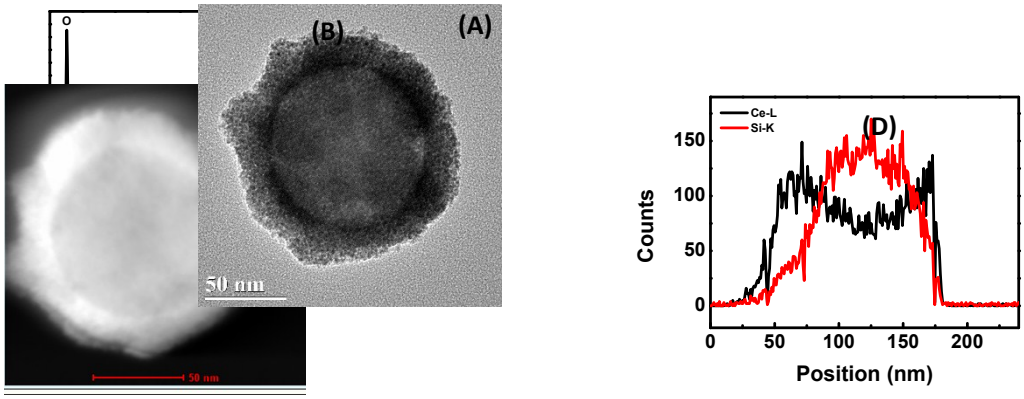


Figure S3. (A) TEM image, (B) EDX spectroscopy, (C) STEM, and (D) line scanning of SiO_2@CeO_2.

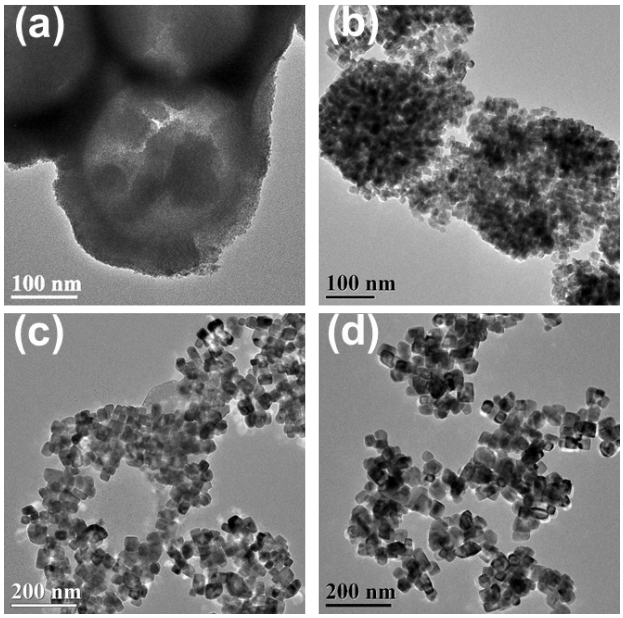


Figure S4. The TEM images of @CeO_2 nanoparticle assemblies obtained by etching @CeO_2 with [Bmim][BF_4] at 160 ºC for different reaction times (a) 1 h, (b) 2 h, (c) 4 h, and (d) 6 h.

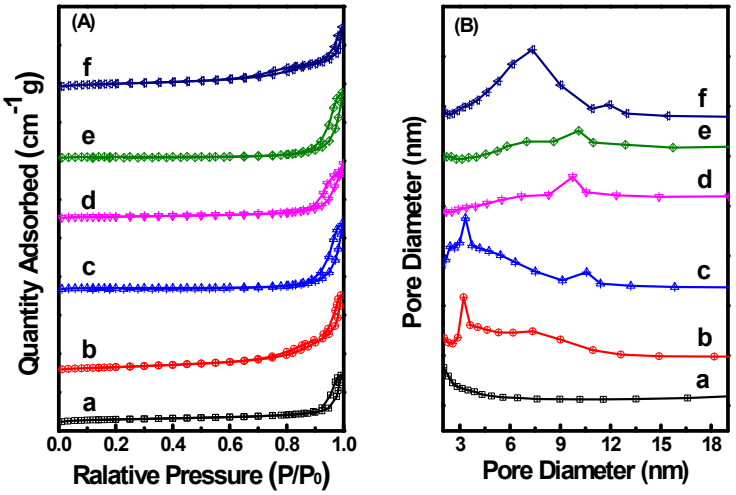


Figure S5. (A) N_2 absorption and desorption isomers and (B) BJH measurements of (a) @CeO_2 spheres without etching treatment, @CeO_2 nanoparticle assemblies obtained by etching @CeO_2 spheres with different fluorine-contained agents of (b) [Bmim][BF_4], (c) NH_4BF_4, (d) $NaBF_4$, and (e) NH_4F under hydrothermal condition at 160 ºC for 2 h and (f) CeO_2/Au nanoparticle obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] h in the absence of SiO_2 sphere templates under hydrothermal condition at 160 ºC for 2 h.

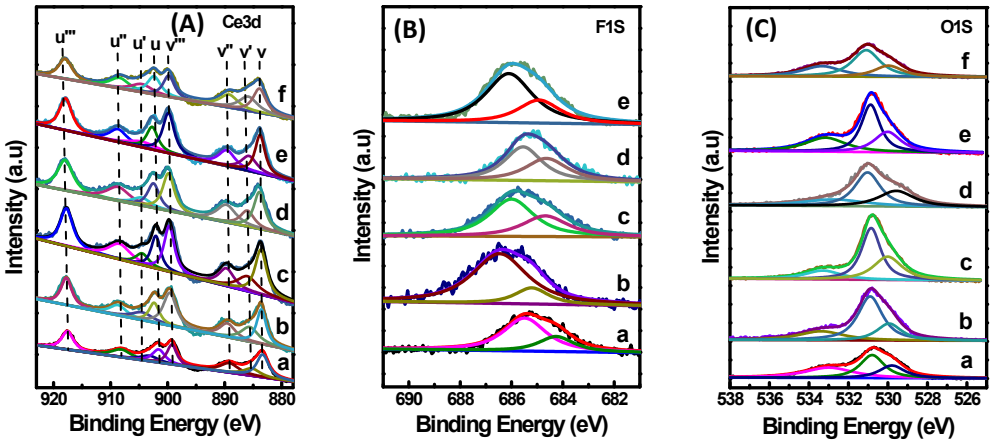


Figure S6. Experimental and fitting core-level XPS spectra of (A) Ce3d, (B) F1S, and (C) O1S of @CeO_2 spheres (a) without etching treatment and @CeO_2/Au nanoparticle assemblies obtained by etching @CeO_2/Au spheres with different fluorine-contained agents of (b) [Bmim][BF_4], (c) NH_4BF_4, (d) $NaBF_4$, and (e) NH_4F under hydrothermal condition at 160 ºC for 2 h and (f) CeO_2/Au nanoparticles obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] in the absence of SiO_2 sphere templates under hydrothermal condition at 160 ºC for 2 h.

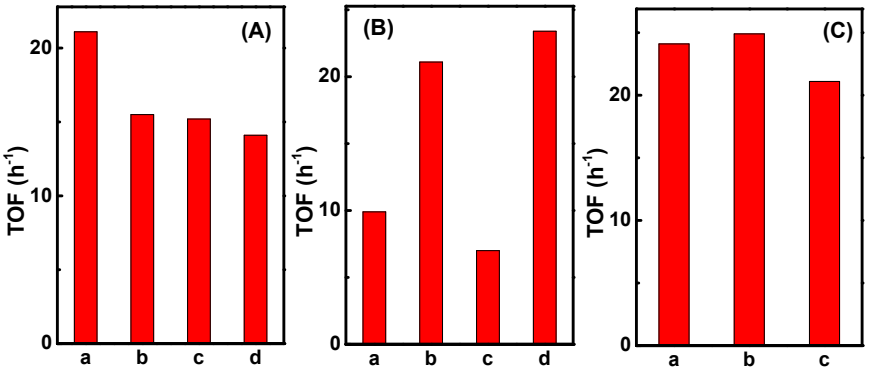


Figure S7. The TOF of (A) @CeO_2/Au nanoparticles assemblies obtained by etching @CeO_2 spheres with (a) [Bmim][BF_4], (b) NH_4BF_4, (c) $NaBF_4$, and (d) NH_4F. (B) (a) @CeO_2/Au spheres without etching treatment, (b) @CeO_2/Au nanoparticles assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4], (c) CeO_2/Au nanoparticles obtained by etching CeO_2 nanoparticles with [Bmim][BF_4] for benzyl alcohol aerobic oxidation in toluene, and (d) @CeO_2/Au nanoparticles assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4] for benzyl alcohol aerobic oxidation in trifluorotoluene. (C) The @CeO_2/Au nanoparticles assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4] with different theoretical Au loading contents at (a) 1 %, (b) 2 %, and (c) 3 % for benzyl alcohol aerobic oxidation in toluene.

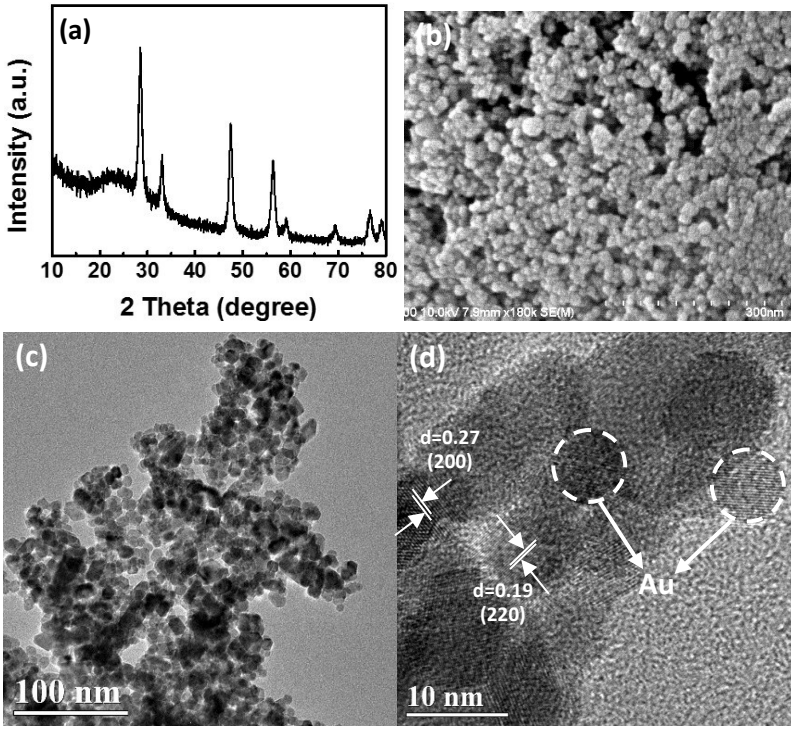


Figure S8. (a) XRD pattern, (b) SEM, (c) TEM, and (d) HRTEM images of the CeO_2/Au nanopowders.

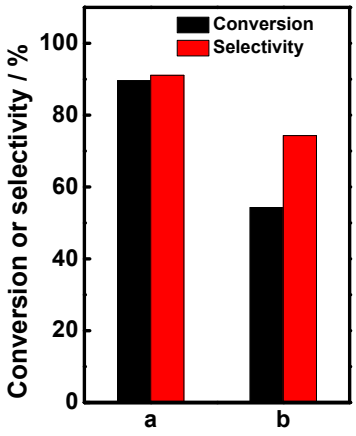


Figure S9. Catalytic performance of (a) @CeO_2/Au nanoparticle assemblies obtained by etching @CeO_2 spheres with [Bmim][BF_4]; (b) CeO_2/Au nanopowders obtained via hydrothermal method. Reaction conditions: benzylic alcohol (1 mmol), catalyst (100 mg), K_2CO_3 (1 mmol), toluene (10mL), 5 h, 80 ºC, oxygen atmosphere. The product was determined by HPLC using biphenyl as an internal standard.

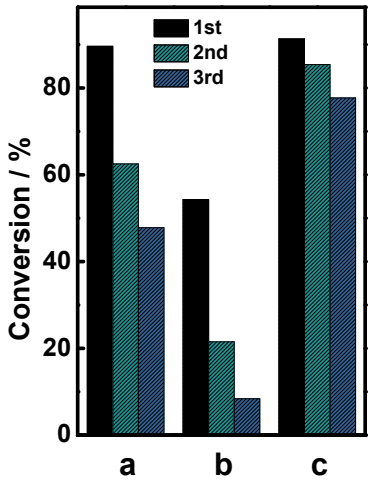


Figure S10. Recyclability of different catalysts for benzyl alcohol aerobic oxidation. (a) @CeO_2/Au nanoparticle assemblies, (b) CeO_2/Au nanopowders, and (c) @CeO_2/Au nanoparticle assemblies calcined at 300 ºC for 2 h. Reaction conditions: benzylic alcohol (1 mmol), catalyst (100 mg), K_2CO_3 (1 mmol), toluene (10 mL), 5 h, 80 °C, oxygen atmosphere. The products were determined by HPLC using biphenyl as internal standard.