Precious metal catalyst recycling through photocatalytic dissolution

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1. Materials and Methods

1.1 Chemicals and materials

Titanium oxide (TiO_2, commercial sample of Degussa P-25), cerium(III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, AR, 99% trace metals basis), titanium butoxide ($C_{16}H_{36}O_4Ti$, AR, ≥99.0%), sodium citrate ($C_6H_5O_7Na_3$, AR, 98%), sodium hydroxide (NaOH, AR, 97%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \cdot 3H_2O$, AR, ≥99.9%), and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, AR, Pt ≥37.5%) were purchased from Aladdin (Shanghai, China). Ammonium hydroxide ($NH_3 \cdot H_2O$, AR, 25-28%), nitric acid (HNO_3, AR, 65-68%), acetonitrile (CH_3CN, HPLC, 99.9%), dichloromethane (CH_2Cl_2, HPLC, 99.9%), and ethanol (C_2H_5OH, HPLC, 99.8%) were purchased from Adamas-beta (Shanghai, China). Ethane (C_2H_6, 99.9%) was purchased from Youjiali Liquid Helium Co., Ltd (Shanghai, China). Hydrogen (H_2, 5% in argon) was purchased from Pujiang Special Gas Co., Ltd (Shanghai, China). Nitrogen (N_2, 99.9%), argon (Ar, 99.9%), and carbon dioxide (CO_2, 99.9%) were purchased from Dumao Ai Purification Gas Co., Ltd (Shanghai, China). All chemicals were used as received.

1.2 Catalyst characterization

The morphology of the materials was observed using a Japanese HITACHI S4800 field emission scanning electron microscope (SEM) as well as a Czech republic Tecnai G2 Spirit transmission electron microscope (TEM). The crystal structure of the samples was analyzed using an Ultima IV X-ray diffractometer (XRD) made by Science Corporation (Japan) with Cu K_α radiation as the spectral emission line (λ=1.54 Å). A Thermo Scientific K-Alpha X-ray photoelectron spectrometer (XPS) was employed for the binding energy analysis with Al K_α (1486.6 eV) as the excitation source at high voltage of 12.0 kV. The light absorption of the samples was tested on a UV-2600 UV-Vis spectrophotometer from Shimadzu, Japan, using high-purity barium sulfate as a standard reagent. Raman spectra were measured using a Jobin Yvon XploRA spectrometer from HORIBA with an excitation wavelength of 532 nm. Atom Scan 2000 inductively coupled plasma (ICP) emission spectrometer from Jarrell-Ash, Inc. was

used to perform the content testing of the catalyst samples. The amount of carbon deposition of the catalyst after the reaction was analyzed by thermogravimetric (TG) analysis on a TA TGA 550 thermal analyzer from room temperature to 900 °C under an air atmosphere.

1.3 Preparation of CeO_2 nanorods

CeO_2 nanorods were synthesized according to a typical hydrothermal method.[1] Briefly, 3.472 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 20 mL of deionized water as solution A, and 38.4 g of NaOH was dissolved in 140 mL of deionized water as solution B. Solution A was added dropwise to solution B under stirring for 30 min to form a milky suspension. The suspension was then transferred to a polytetrafluoroethylene-lined autoclave and crystallized at 100 °C for 24 h. The obtained precipitate was washed by filtration with 3 L of water, dried in an oven at 100 °C overnight and finally calcined in a muffle furnace at 450 °C for 3 h under an air atmosphere.

1.4 Preparation of TiO_2 carrier[2]

The 17 mL of *n*-butyl titanate measured in a constant pressure separatory funnel was added dropwise to 50 mL of 2 mol/L nitric acid (HNO_3) solution over 30 min with continuous stirring at room temperature for 1 h. The hydrolysis product was transferred to a PTFE lined reactor and hydrothermally treated at 140°C for 10 h. After the reactor had cooled to room temperature, it was filtered and washed with 2 L of anhydrous ethanol. The resulting white solid was dried overnight at 100°C, ground to a powder state and calcined in a muffle furnace with air at 500°C for 4 h to obtain a white powdered solid titanium dioxide (TiO_2).

1.5 Preparation of Au/CeO_2, Au/TiO_2 and Pt/CeO_2

Deposition-precipitation (DP) method was used to prepare PM catalysts.[3] The precious metal salt was dissolved in deionized water. An appropriate amount of CeO_2 (or TiO_2) was then added and ammonia (pH=12) was added drop by drop until the overall pH was 7.5. This suspension was then stirred for 1 h and aged for 24 h. The precipitate was washed with deionized water and dried at 100 °C before calcined in a muffle furnace at 650 °C for 6 h. The theoretical Au loading in this work is 1.0 wt%.

1.6 Recycling of PM catalysts

The deactivated Au/CeO_2 was added to 20 ml of a mixture of acetonitrile and dichloromethane.[4] The mixed solution was placed under a 365 nm LED lamp for 6 h without any other photocatalyst addition. The reaction was kept at 25°C using a thermostatic water bath. At the end of the reaction, the solid and solution were separated by centrifugation and the obtained solid were washed with ethanol and water. The precious metal salt was then precipitated from the remaining solution using a low-temperature rotary evaporator. The solvent after removal of the precious metal salts is ready for next recycling. The obtained precious metal salt and the recovered CeO_2 were further used to produce fresh Au/CeO_2 catalysts according to the deposition-precipitation method. The same preparation is for the recycling of Pt/CeO_2 and Au/TiO_2.

1.7 Catalytic testing

Ethane dehydrogenation was carried out in a fixed-bed flow microreactor at under atmospheric pressure at 650 °C. The catalyst was loaded with 200 mg whose particle size was 40-60 mesh. They were activated in N_2 flow at 650 °C for 2 h before testing. For the direct dehydrogenation, the feed gas consisted of 3 vol% C_2H_6 and the balance nitrogen; while for the dehydrogenation in the presence of CO_2, the feed gas consisted of 3 vol% C_2H_6, 15 vol% CO_2 and the balance nitrogen at a total gas flow rate of 30 mL/min.

The reaction products were detected by on-line gas chromatography and the light hydrocarbons such as CH_4, C_2H_6, and C_2H_4 were separated on a 6 m Porapak Q-packed column and detected by FID. N_2, H_2, CO, and CO_2 were separated on a 2 m 601 carbon molecular sieve packed column, and detected by TCD. The ethane conversion, ethylene selectivity, and carbon balance were calculated using the following equations:

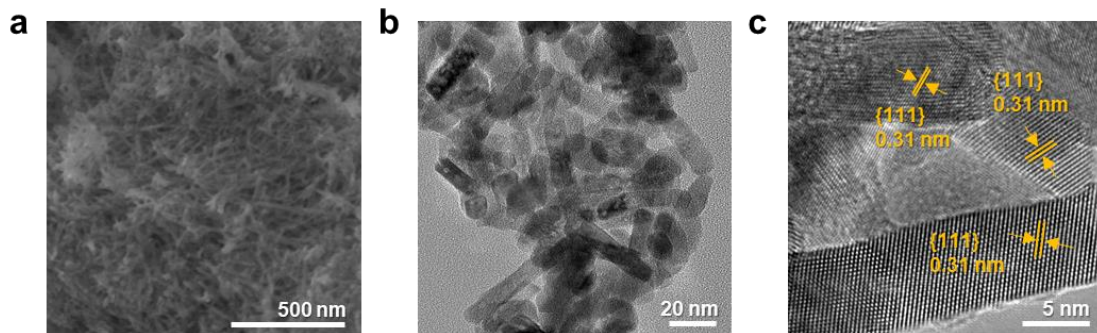$$C_2H_6 \ conversion = \frac{\sum C_xH_{y \ out} - C_2H_{6 \ out}}{\sum C_xH_{y \ out}} \times 100\%$$

$$C_2H_4 \ selectivity = \frac{C_2H_{4 \ out}}{\sum C_xH_{y \ out} - C_2H_{6 \ out}} \times 100\%$$

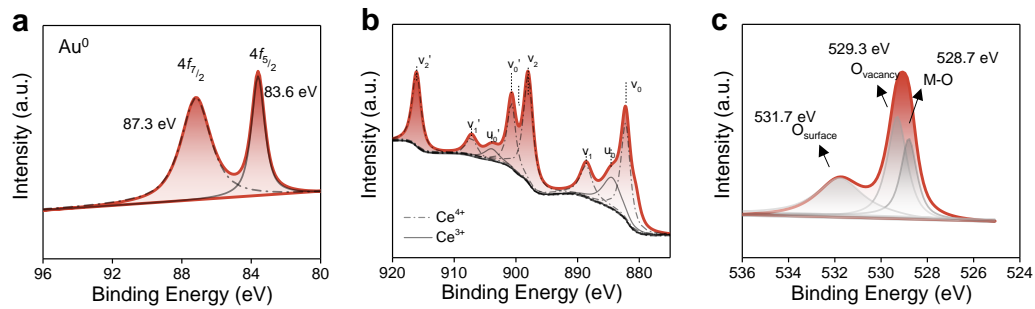$$Carbon \ balance = \frac{\sum C_xH_{y \ out}}{C_2H_{6 \ in}} \times 100\%$$

2. Supplementary Figures
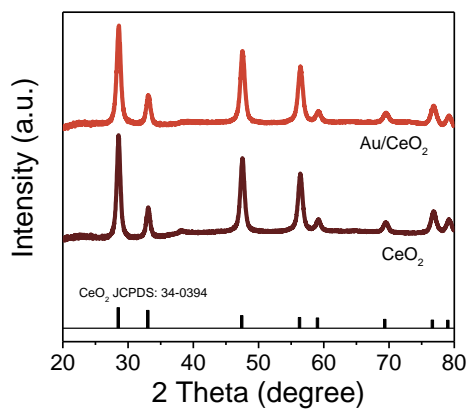
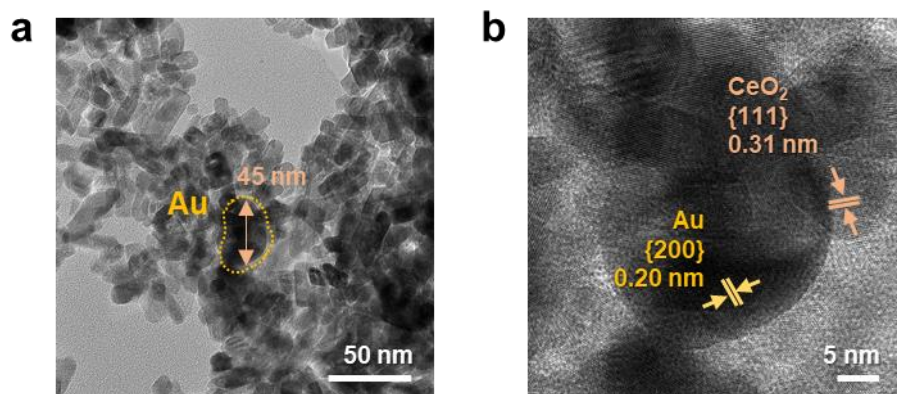**Fig. S1.** XRD pattern of CeO$_2$ nanorods and Au/CeO$_2$ catalyst.

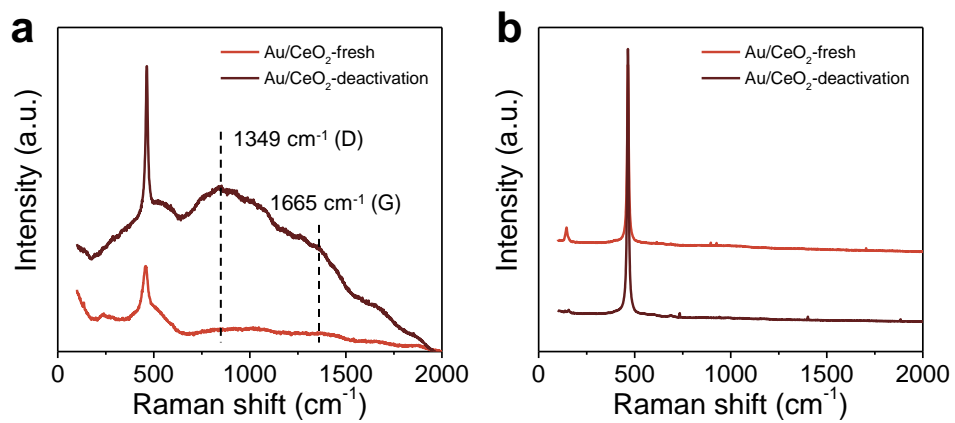**Fig. S2.** (a) SEM, (b) TEM and (c) HRTEM of CeO$_2$ nanorods.

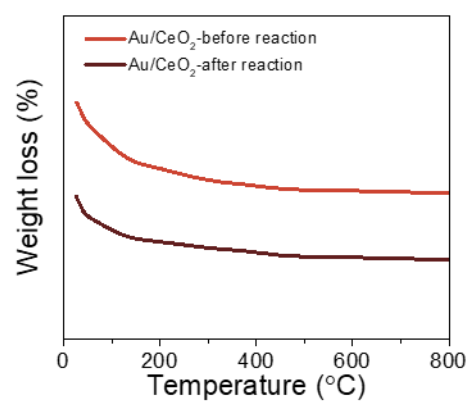**Fig. S3.** (a) Au 4*f*7, (b) Ce 3*d* and (c) O 1*s* XPS spectra of Au/CeO₂-fresh catalyst.

Fig. S4. (a) TEM image and (b) HRTEM image of deactivated Au/CeO$_2$ catalyst under N$_2$ atmosphere.
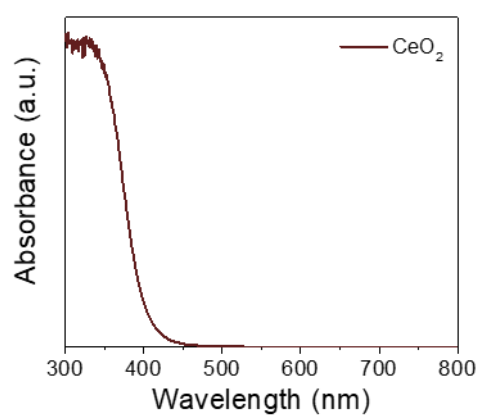
Fig. S5. Raman spectra of Au/CeO$_2$ catalyst before and after deactivation: (a) Reaction under N$_2$ atmosphere. (b) Reaction under CO$_2$ atmosphere.
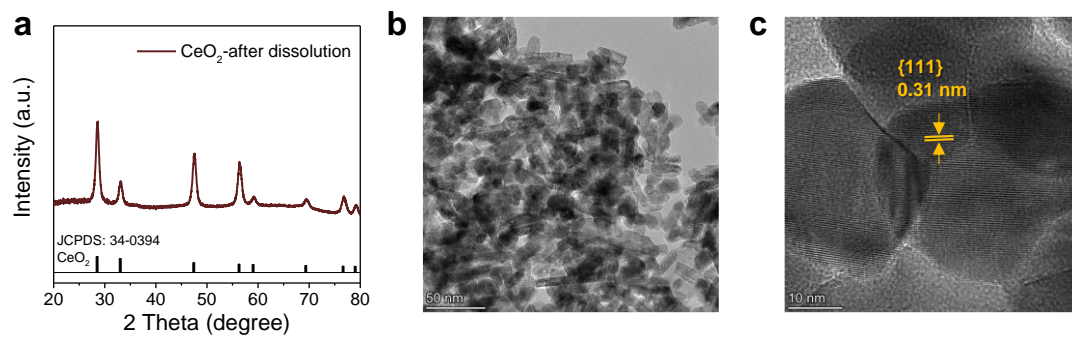
Fig. S6. TG spectra of Au/CeO$_2$ catalyst before and after reaction under CO$_2$ atmosphere.
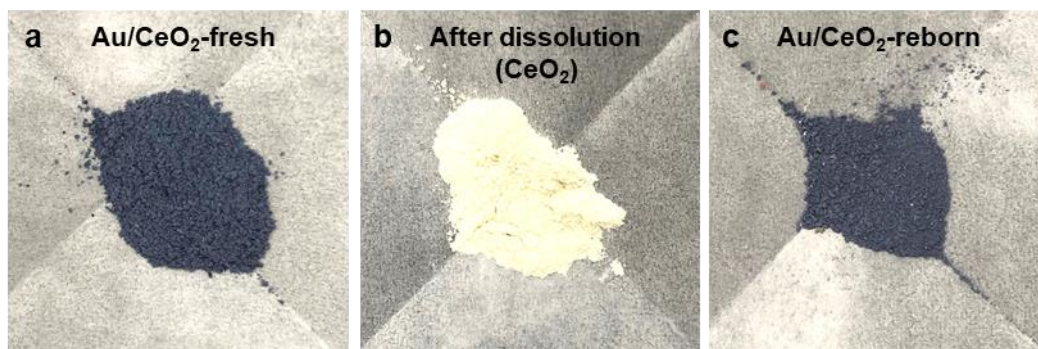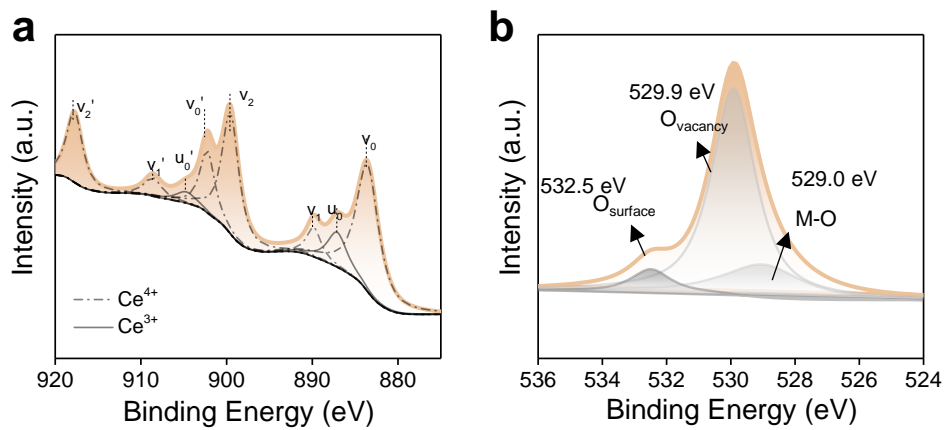
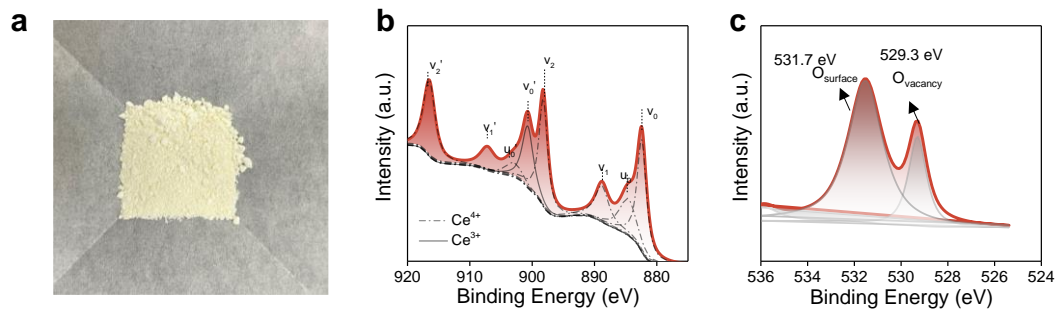**Fig. S7.** Pictures of Au/CeO$_2$ catalyst before and after recycling.

Fig. S8. UV-vis absorption spectra of CeO$_2$ nanorods.

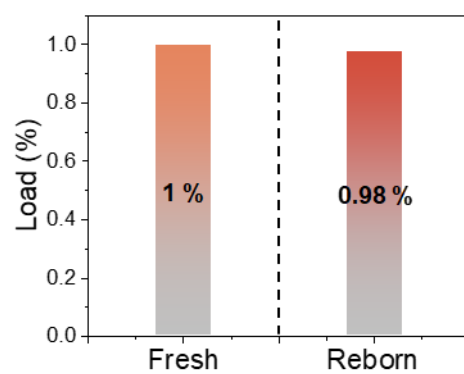**Fig. S9.** (a) XRD pattern, (b) TEM and (c) HRTEM image of recovered CeO₂ nanorods.

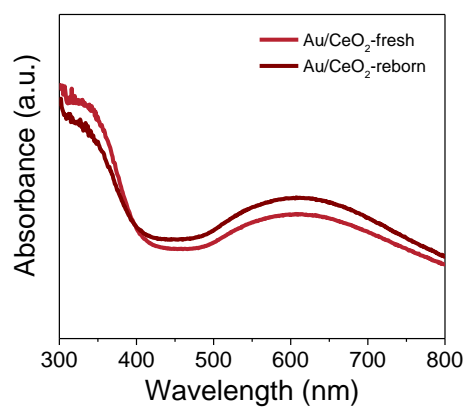**Fig. S10.** (a) Ce $3d$ and (b) O $1s$ XPS spectra of recovered CeO_2.

Fig. S11. (a) Photographs of CeO$_2$ nanorods before reaction. (b) Ce 3d and (c) O 1s XPS spectra of CeO$_2$ nanorods.
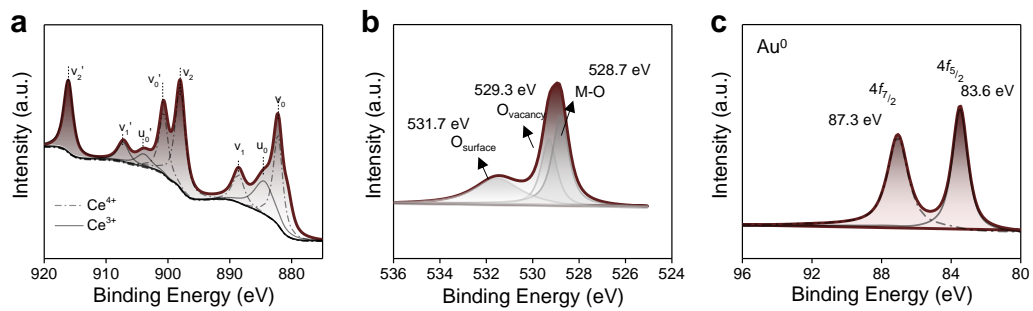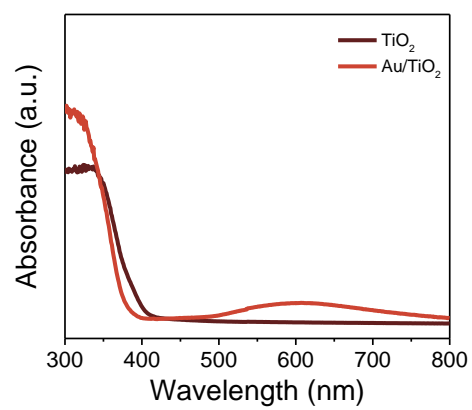
Fig. S12. Loading of Au on Au/CeO$_2$ before and after recycling.
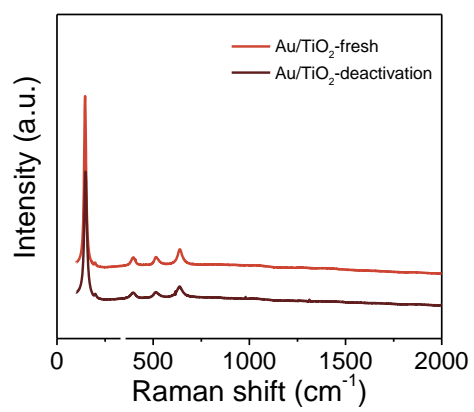
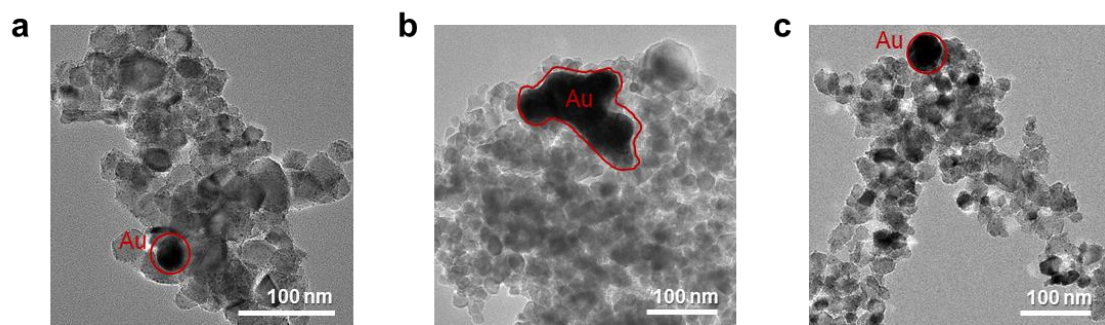**Fig. S13.** UV-vis absorption spectra of Au/CeO2-fresh and Au/CeO2-reborn catalyst.

Fig. S14. (a) Ce 3*d*, (b) O 1*s* and (c) Au 4*f*7 XPS spectra of Au/CeO$_2$-reborn catalyst.

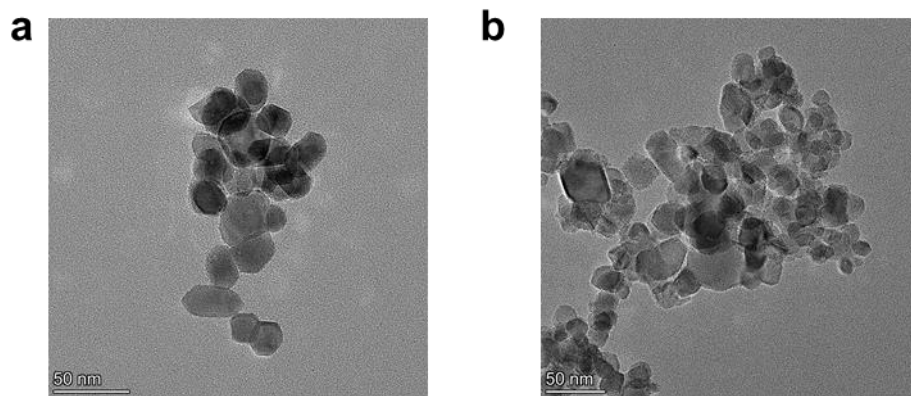**Fig. S15.** UV-vis absorption spectra of TiO_2 and Au/TiO_2.

Fig. S16. Raman spectra of Au/TiO₂ catalyst before and after reaction.

Fig. S17. TEM image of (a) Au/TiO$_2$-fresh, (b) deactivated Au/TiO$_2$ and (c) Au/TiO$_2$-reborn.

Fig. S18. TEM image of TiO_2 nanoparticle (a) before and (b) after regeneration.
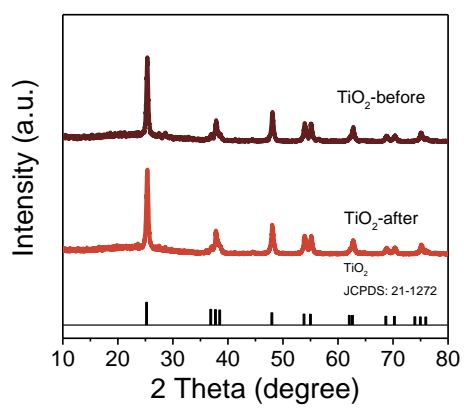
Fig. S19. XRD pattern of TiO$_2$ before and after regeneration.
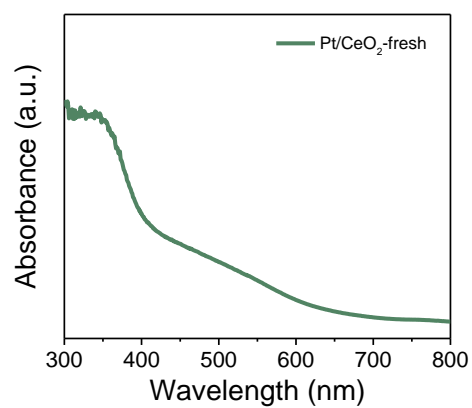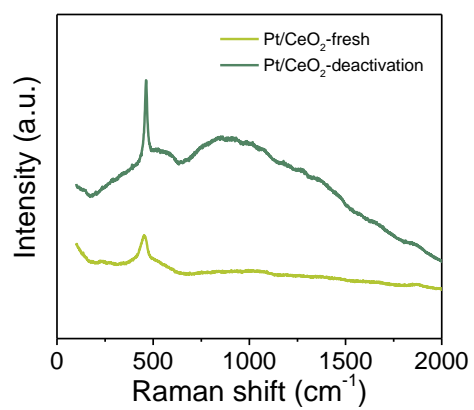
Fig. S20. UV-vis absorption spectra of Pt/CeO₂-fresh catalyst.

Fig. S21. Raman spectra of Pt/CeO$_2$ catalyst before and after reaction.
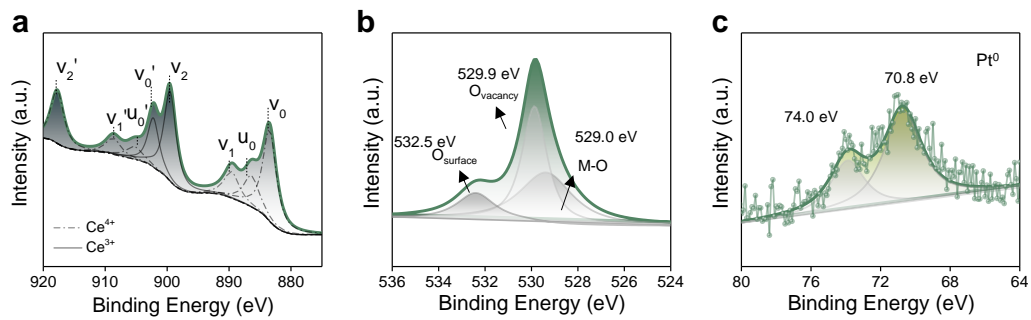
Fig. S22. (a) Ce $3d$, (b) O $1s$ and (c) Pt $4f$ XPS spectra of Pt/CeO$_2$-fresh.

3. Supplementary Tables

Table S1. Reaction data for different Au/CeO$_2$ in ethane dehydrogenation under N$_2$ atmosphere.

Catalysts	Conversion (%)[a]	Selectivity (%)[a]		C$_2$H$_4$ yield (%)[a]	Carbon balance	Coke (%)
		CH$_4$	C$_2$H$_4$			
Au/CeO$_2$-fresh	17.3 (2.5)	0.5 (5.7)	99.5 (94.3)	17.2 (2.3)	95.0	n.d.
Au/CeO$_2$-reborn	21.9 (3.4)	0.5 (5.6)	99.5 (94.4)	21.8 (3.2)	95.3	n.d.

[a] The values out and in the brackets are obtained at 10 min and 6 h, respectively.

Table S2. Actual loadings of precious metal in the samples

Sample	Precious metal content (wt%)
Au/CeO$_2$-fresh	1
Au/CeO$_2$-reborn	0.98
Au/TiO$_2$-fresh	1
Au/TiO$_2$-reborn	0.97
Pt/CeO$_2$-fresh	1
Pt/CeO$_2$-reborn	0.95

Table S3. Activity of ethane dehydrogenation in different Au/CeO_2 samples under CO_2 atmosphere.

Catalysts	Conversion (%)[a]	Selectivity (%)[a]		C_2H_4 yield (%)[a]	Carbon balance	Coke (%)
		CH_4	C_2H_4			
Au/CeO_2-fresh	17.0 (17.4)	2.1 (1.7)	97.9 (98.3)	16.7 (17.1)	96.6	n.d.
Au/CeO_2-reborn	16.7 (17.4)	1.8 (1.5)	98.2 (98.5)	16.4 (17.1)	97.5	n.d.

[a] The values out and in the brackets are obtained at 10 min and 6 h, respectively.

Table S4. Activity of ethane dehydrogenation in different Au/TiO$_2$ samples under N$_2$ atmosphere.

Catalysts	Conversion (%)[a]	Selectivity (%)[a]		C$_2$H$_4$ yield (%)[a]	Carbon balance	Coke (%)
		CH$_4$	C$_2$H$_4$			
Au/TiO$_2$-fresh	9.7 (6.5)	4.0 (5.6)	96.0 (94.4)	9.3 (6.1)	95.4	n.d.
Au/TiO$_2$-reborn	9.3 (6.8)	3.4 (5.0)	96.6 (95.0)	9.0 (6.5)	96.6	n.d.

[a] The values out and in the brackets are obtained at 10 min and 6 h, respectively.

Table S5. Activity of ethane dehydrogenation in different Pt/CeO$_2$ samples under N$_2$ atmosphere.

Catalysts	Conversion (%)[a]	Selectivity (%)[a]		C$_2$H$_4$ yield (%)[a]	Carbon balance	Coke (%)
		CH$_4$	C$_2$H$_4$			
Pt/CeO$_2$-fresh	28.7 (1.0)	9.5 (3.7)	90.5 (96.3)	26.0	92.3	n.d.
Pt/CeO$_2$-reborn	26.9 (1.3)	0.5 (4.4)	99.5 (95.6)	26.8	93.4	n.d.

[a] The values out and in the brackets are obtained at 10 min and 6 h, respectively.

4. Reference

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