

## Synergistic combination of active Pt species and light-driven photothermal catalysis for highly efficient toluene oxidation

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### Experimental sections

#### Catalysts characterization

Powder X-ray diffraction (XRD) was conducted on a X'Pert Pro diffractometer with a Cu-K $\alpha$  X-ray source at 40 kV within 5-90° and applied to analyze the crystal structure of the samples. N<sub>2</sub> adsorption-desorption measurements were carried out on a Quantachrome autosorb iQ2 instrument in liquid nitrogen (77K). Before the measurement, the samples were degassed in nitrogen at 200 °C for 4 hours to remove the purities absorbed on surface. As is known, the pore structure in P25 mainly exists in the form of mesopores, and micropores are not conducive to the adsorption and activation of toluene molecules. Therefore, here we mainly consider the mesoporous structure in the catalysts. Then Brunauer-Emmett-Teller (BET) and Barrett-Joyner Halenda (BJH) methods were applied to calculate the specific surface area, pore volume and pore diameter distribution, by applying nitrogen-relative pressure ( $P/P_0$ ) in the range of 0.05–0.35. Pt contents of the samples were measured by X-ray fluorescence (XRF) (Axios-MAX, NEP). High-resolution transmission electron microscopy (HR-TEM) images were obtained on Thermo Scientific™ Talos F200i (S)TEM at 200 kV. X-ray photoelectron spectroscopy (XPS) data were collected on an AXIS Supra by Kratos Analytical Inc. using monochromatized Al K $\alpha$  radiation source. All the spectrums have been calibrated by carbon spectra (284.8 eV). Fine spectrum of all elements were performed

by XPS peak 4.1 and iterated Shirley Background was added. The FWHM (peak-width) for principal peaks is less than 2.0 eV. The binding energy of the elements was determined according to the data from National Institute of Standards and Technology and literatures. Oxygen-temperature programmed desorption (O<sub>2</sub>-TPD) experiments were conducted on a Quantachrome Chemstar instrument. Before the programming, the samples were treated in helium at 200 °C for 1 hour to remove the adsorbed water and purities. 5% O<sub>2</sub>/helium was introduced and absorbed for 1 hour, and then temperature programmed desorption was performed in helium within 40-800 °C by a step size of 10 °C/min. The weight loss of the samples were measured by a thermal gravimetric analyzer (TGA, Netzsch TG209F3) in air with a ramp rate of 10 °C/min from 40 to 800 °C. Carbon content of the catalysts have been acquired on an elemental analyzer (EA, Elementar CHNS-O-CL). In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) were used to detect the reaction intermediates absorbed on the solid catalysts. Intermediates evolution with temperature variation were obtained on Thermo Fisher is50 instrument equipped with a smart collector and a liquid nitrogen-cooled MCT/A detector. Before the experiments, the samples were treated in nitrogen atmosphere at 200 °C for 1 hour to remove the physically absorbed purities on the catalyst surface. Then air with flow rate of 20 mL/min carried toluene stream into the reaction cell, and toluene and oxygen reactants were absorbed onto the catalyst for 30 minutes until absorption saturation. Since in situ DRIFTS is a very sensitive surface characterization, the gas inlet and outlet were then closed, and catalyst layer was heated to 158, 206 and 230 °C at a ramp rate of 10 °C/min and maintained for 40 min at every temperature points. In the meanwhile, the spectrum was collected at a scan number of 32.

**Table S1.** Light intensity and temperature under specific light source

| <b>Light source type</b> | <b>Light intensity (mW/cm<sup>2</sup>)</b> | <b>Temperature (°C)</b> |
|--------------------------|--|-------------------------|
| UV-vis-IR                | 400  | 206                     |
| UV-vis SL                | 400  | 160                     |
| UV-vis ST                | 658  | 206                     |
| IR SL                    | 400  | 176                     |
| IR ST                    | 418  | 206                     |
| 365 nm                   | 400  | 41.5                    |

**Table S2.** Summary of Pt-Ti catalysts for toluene oxidation in the literature

| Reaction condition<br>(toluene/air) | Catalysts                              | $T_{90}$ (°C) | Light intensity (mW/cm <sup>2</sup> ),      | Reference |
|-------------------------------------|--|---------------|---|-----------|
|                                     |  |               | layer temperature and<br>toluene conversion |           |
| 400 ppm, 60,000 mL/(g·h)            | Pt-P25-800N                            | -             | 282 mW/cm <sup>2</sup> , 158 °C, 89%        | This work |
| 500 ppm, 24,000 mL/(g·h)            | PtO <sub>x</sub> /TiO <sub>2</sub>     | 148           | -   | 1         |
| 500 ppm, 23,340 mL/(g·h)            | NaOH-promoted Pt/TiO <sub>2</sub>      | $T_{50}<44$   | -   | 2         |
| 200 ppm, 50,000 mL/(g·h)            | Pt/N-TiO <sub>2</sub>                  | -             | 260 mW/cm <sup>2</sup> , 126 °C, 93%        | 3         |
| 1000 ppm, 90,000 mL/(g·h)           | Pt/TiO <sub>2</sub> -C                 | -             | 300 W UV light, 74%                         | 4         |
| 1000 ppm, 160,000 mL/(g·h)          | Pt/TiO <sub>2</sub> nanotubes          | ~170          | -   | 5         |
| 1000 ppm, 30,000 mL/(g·h)           | Pt/TiO <sub>2</sub> -400               | 219           | -   | 6         |
| 1000 ppm, 120,000 mL/(g·h)          | Pt/TiO <sub>2</sub>                    | 201           | -   | 7         |
| 1000 ppm, 40,000 mL/(g·h)           | 0.2 wt% Pt/TiO <sub>2</sub>            | 183           | -   | 8         |
| 1000 ppm, 60,000 mL/(g·h)           | Pt/Ce <sub>0.15</sub> TiO <sub>x</sub> | 170           | -   | 9         |
| 200 ppm, 56,250 mL/(g·h)            | Pt/Mn-TiO <sub>2</sub>                 | -             | 625 mW/cm <sup>2</sup> , 195 °C, 90.4%      | 10        |

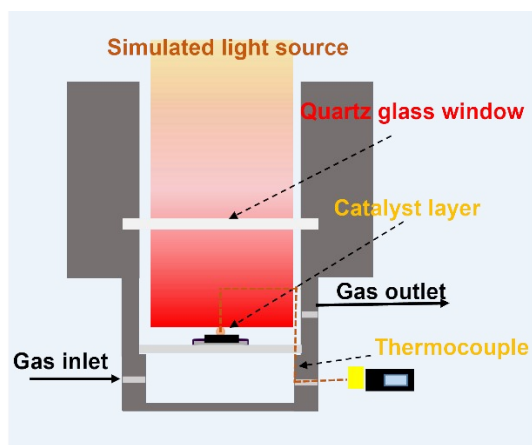


Fig. S1 Schematic diagram of experimental setup for photothermal catalytic VOCs oxidation.

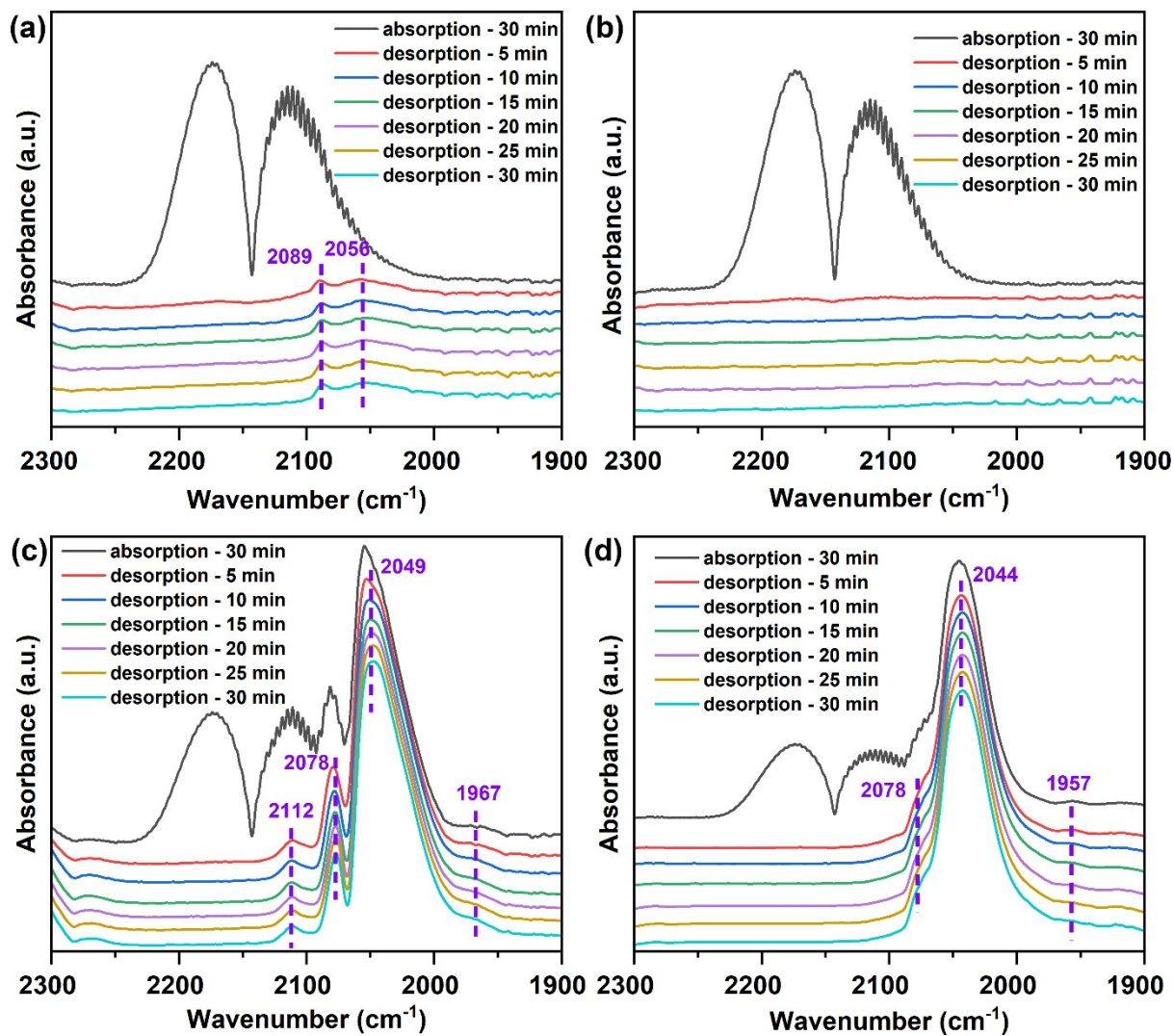


Fig. S2 CO-diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFT) of (a) Pt-P25-800N, (b) Pt-P25-800A, (c) Pt-P25-400N, (d) Pt-P25-400A.

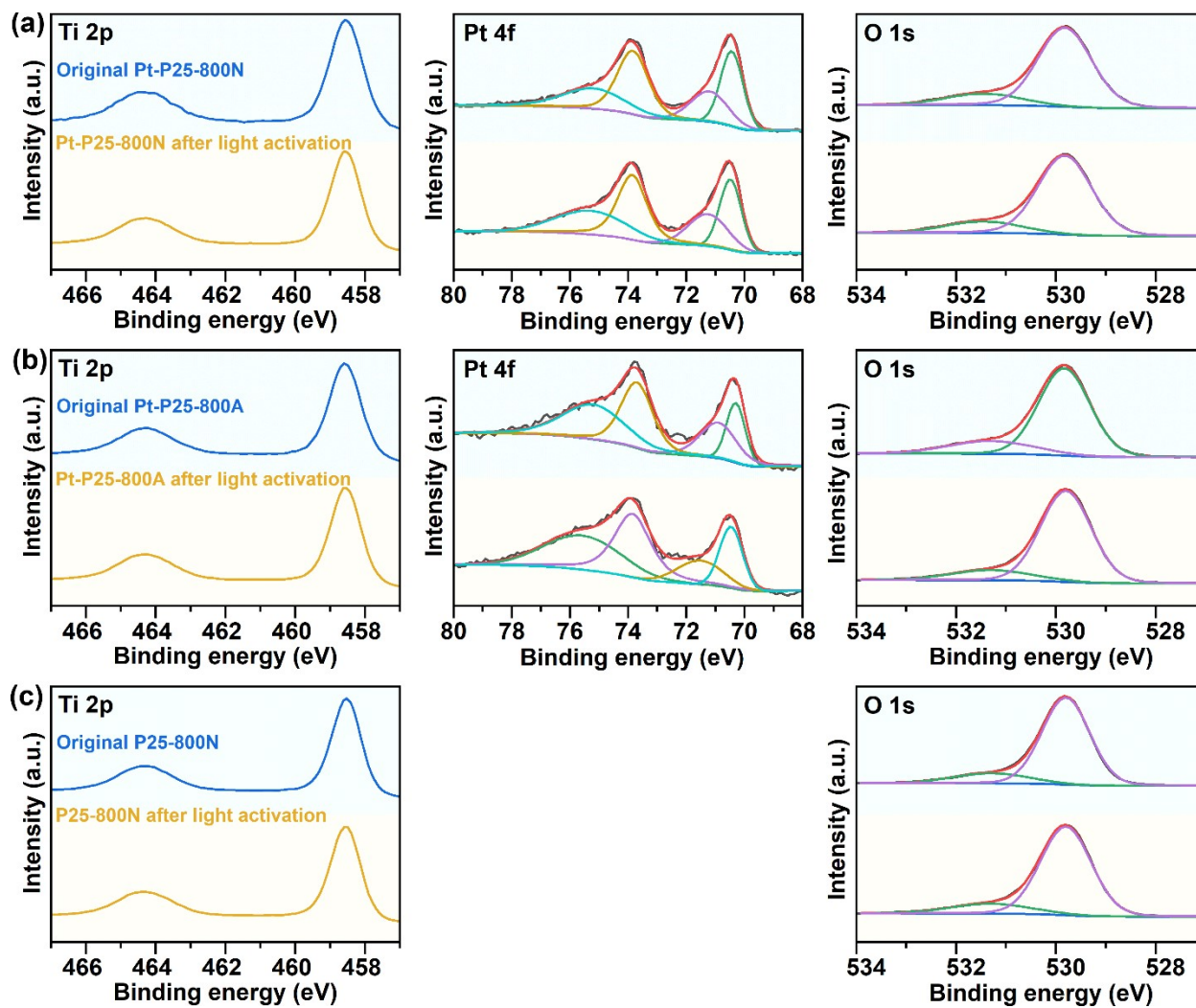


Fig. S3 XPS spectrum comparison of (a) Pt-P25-800N, (B) Pt-P25-800A and (c) P25-800N before and after light activation without toluene cutting in.

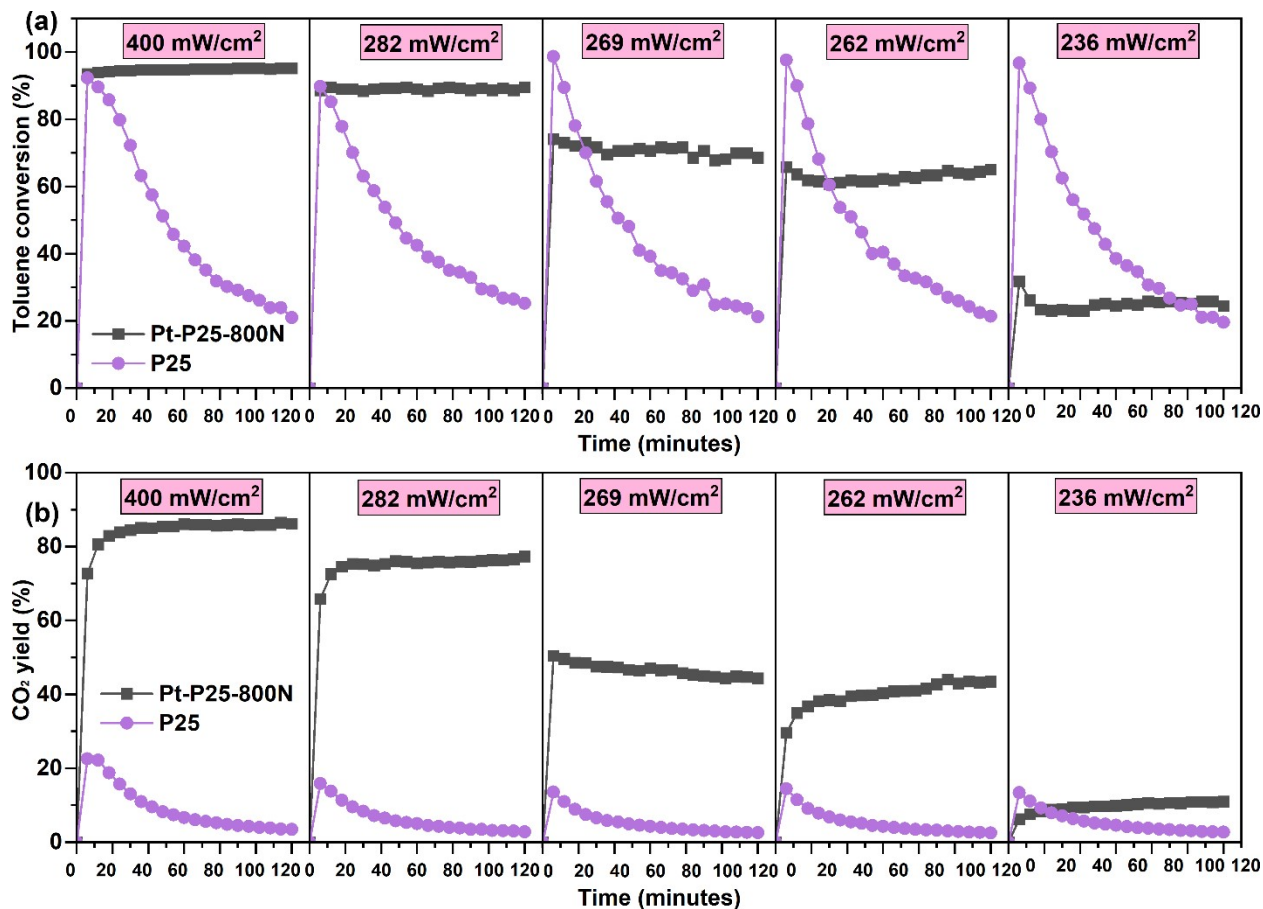


Fig. S4 (a) Toluene conversion and (b) CO<sub>2</sub> yield under light irradiation with intensity of 400, 282, 269, 262 and 236 mW/cm<sup>2</sup>.

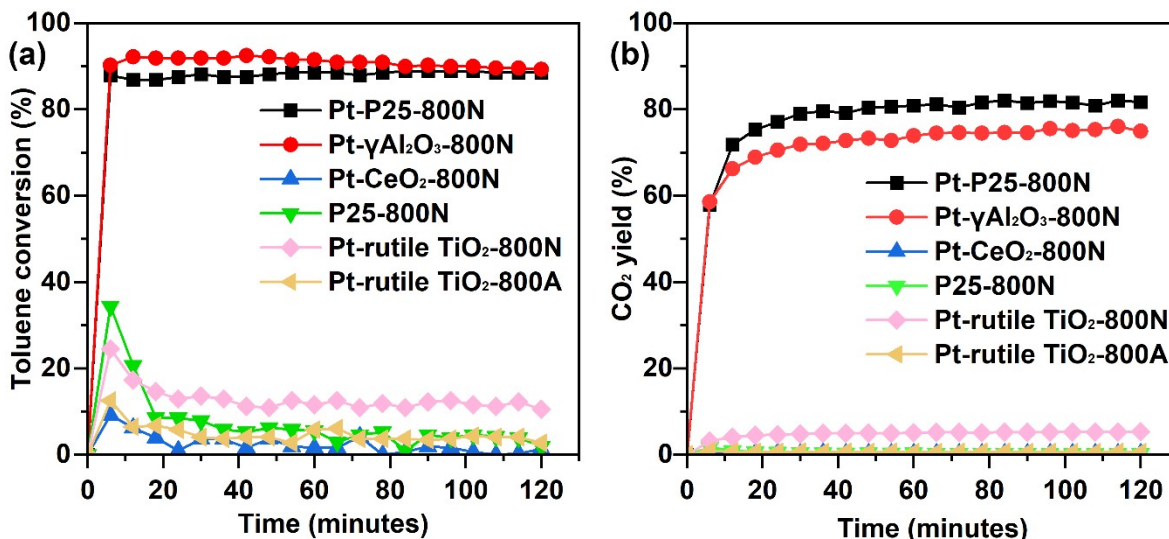


Fig. S5 (a) Toluene conversion and (b) CO<sub>2</sub> yield under irradiation with intensity of 282 mW/cm<sup>2</sup>.

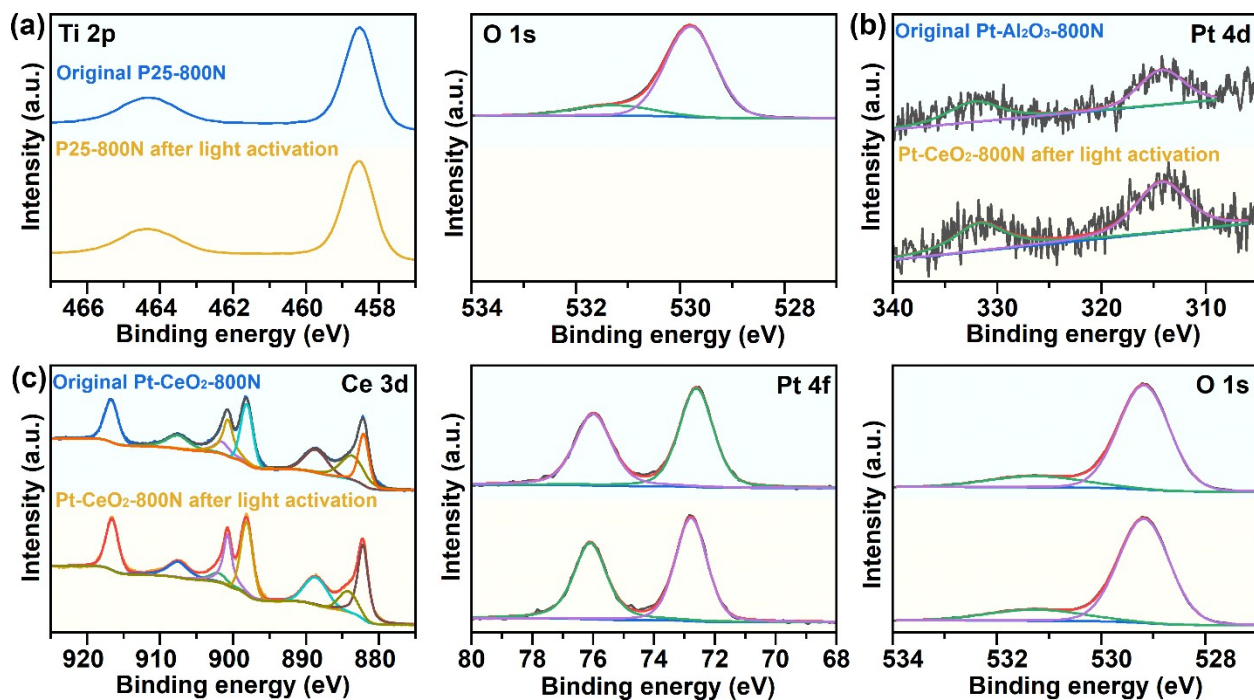


Fig. S6 XPS spectrum comparison of (a) P25-800N, (B) Pt-Al<sub>2</sub>O<sub>3</sub>-800N and (c) Pt-CeO<sub>2</sub>-800N before and after light activation without toluene cutting in.

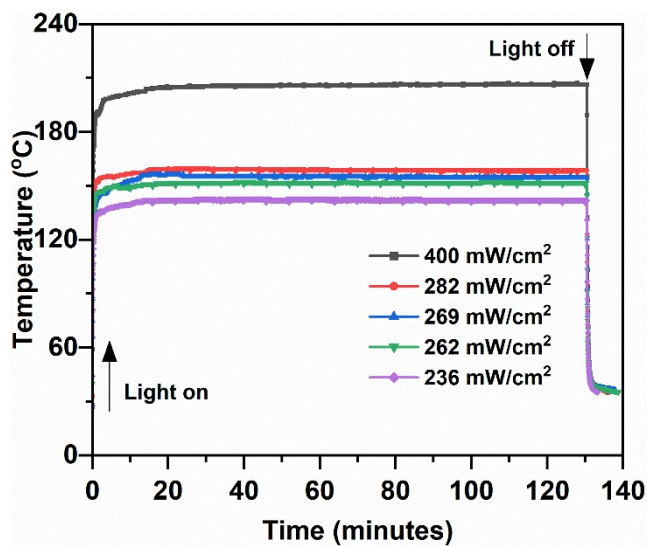


Fig S7. Temperature evolution under light irradiation with intensity of 400, 282, 269, 262 and 236 mW/cm<sup>2</sup>.

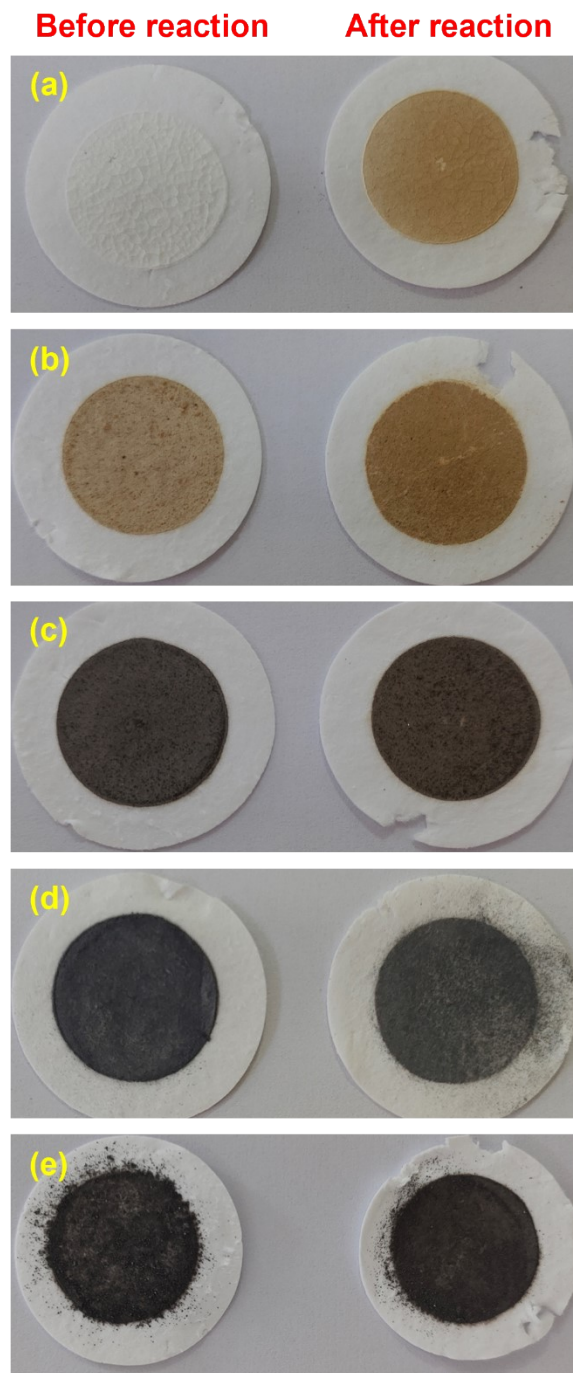


Fig. S8 Catalyst bed layer variation of (a) Pt-P25-800N, (b) Pt-P25-800A, (c) Pt-P25-400N, (d) Pt-P25-400A before and after photothermal catalytic oxidation reaction.



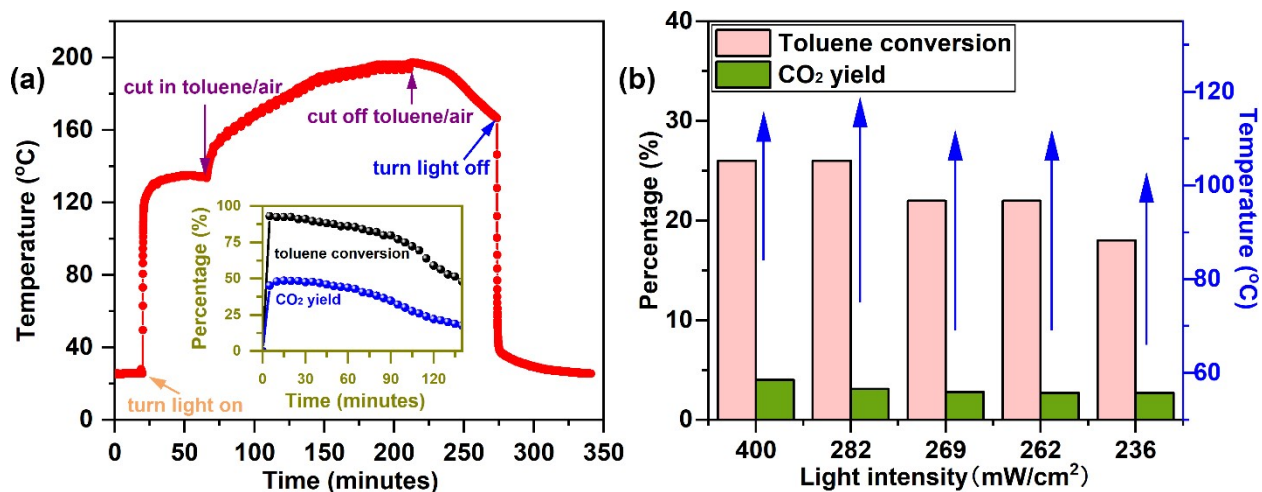


Fig. S9 (a) Temperature variation with toluene cutting in/off and turning light on/off (light intensity: 650 mW/cm<sup>2</sup>), and catalytic performance of P25. (b) Photothermal catalytic performance and temperature evolution over P25 before and after toluene cutting in under light irradiation with intensities of 400, 282, 269, 262 and 236 mW/cm<sup>2</sup>.

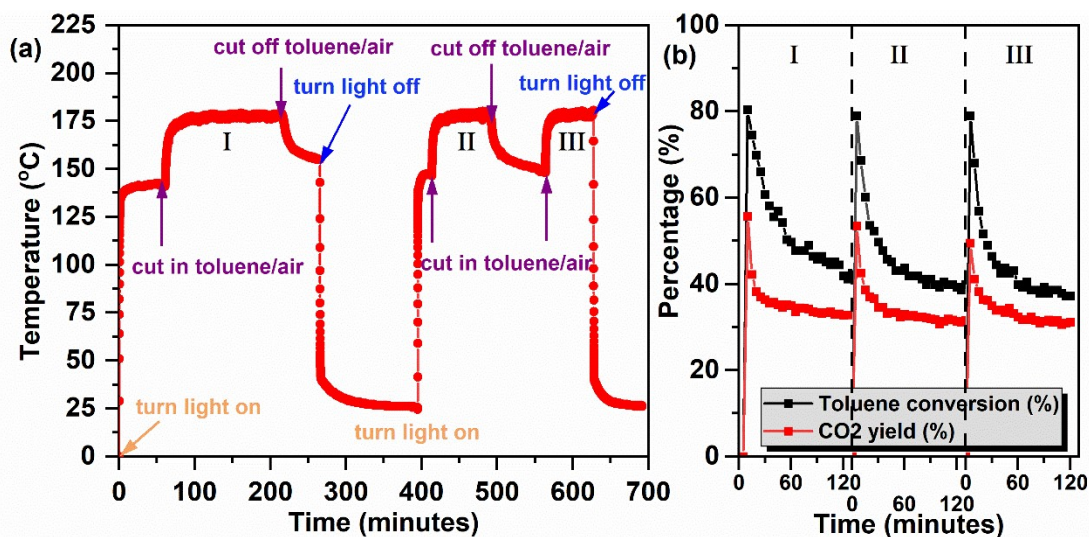


Fig. S10 (a) Temperature variation with toluene cutting in/off and turning light on/off under light intensity of 650 mW/cm<sup>2</sup>, and (b) catalytic performance of CeO<sub>2</sub>.

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