

## Supporting Information

# In-Situ Synthesis of Hydrogen Peroxide for Highly Selective Oxidation of Methane to Methanol over Noble-Metal-Free Catalyst

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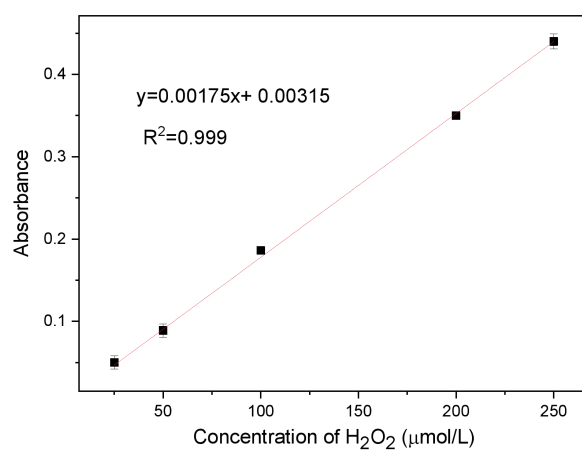
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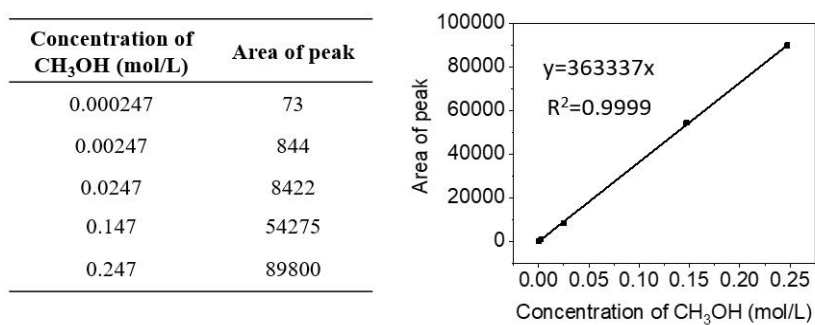
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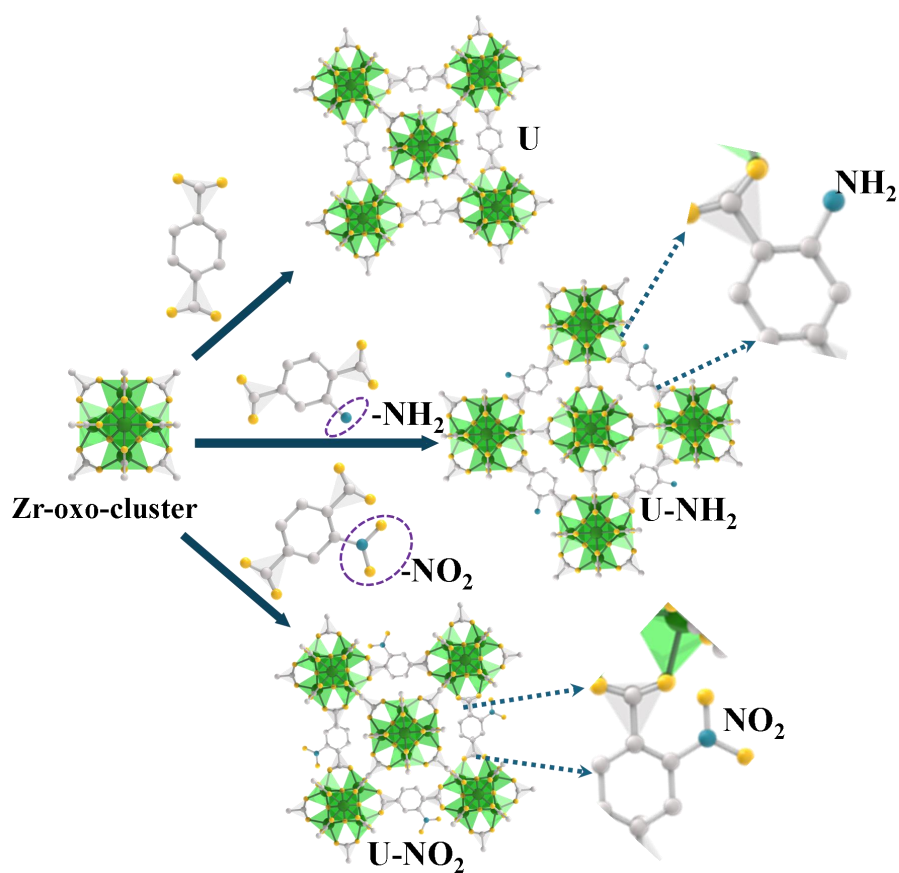
<sup>5</sup> *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China;*



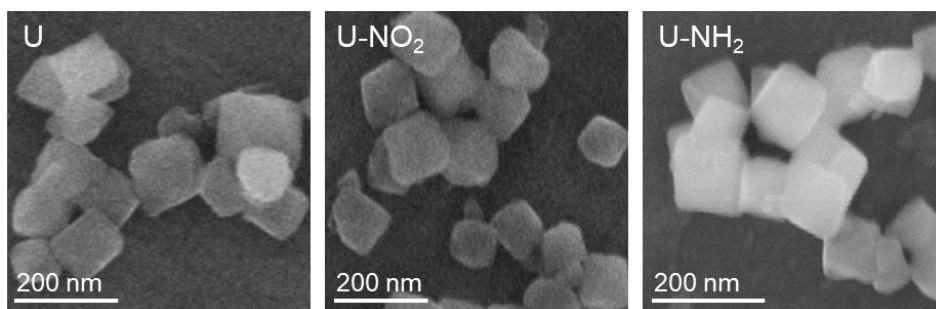
**Figure S1.** The quantitative calibration curve of H<sub>2</sub>O<sub>2</sub> based on the concentration and UV-vis absorbance at 551 nm.



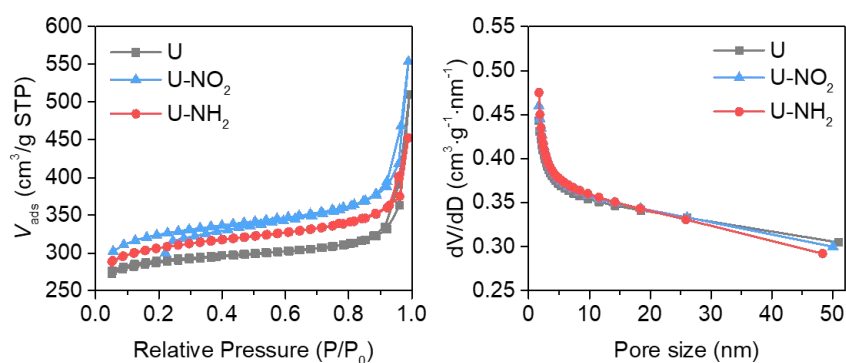
**Figure S2.** The quantitative calibration curve of CH<sub>3</sub>OH product based on the concentration and area of peak.



**Figure S3.** Schematic synthesis of U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> samples.

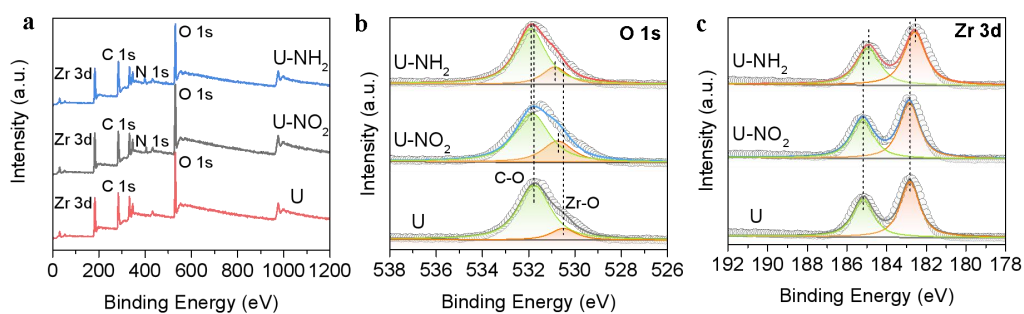


**Figure S4.** SEM images of U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> materials.

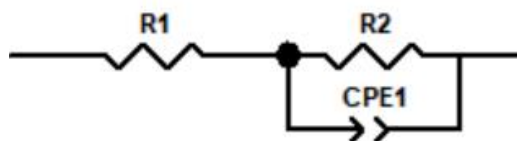


| Samples           | $S_{BET}$ (m <sup>2</sup> ·g <sup>-1</sup> ) | $P_v$ (cm <sup>3</sup> ·g <sup>-1</sup> ) | $D_p$ (nm) |
|-------------------|----------------------------------------------|-------------------------------------------|------------|
| U                 | 667                                          | 0.56                                      | 3.3        |
| U-NO <sub>2</sub> | 729                                          | 0.62                                      | 3.8        |
| U-NH <sub>2</sub> | 697                                          | 0.66                                      | 3.3        |

**Figure S5.** N<sub>2</sub> adsorption-desorption isotherms and pore diameter distribution of U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> materials.



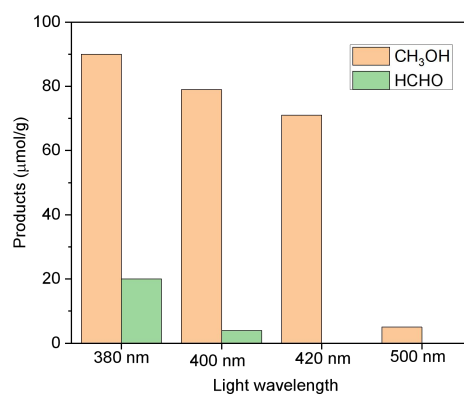
**Figure S6.** (a) X-ray Photoelectron Spectroscopy (XPS) spectra, (b) and (c) High-resolution XPS spectra of O 1s and Zr 3d of U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> materials.



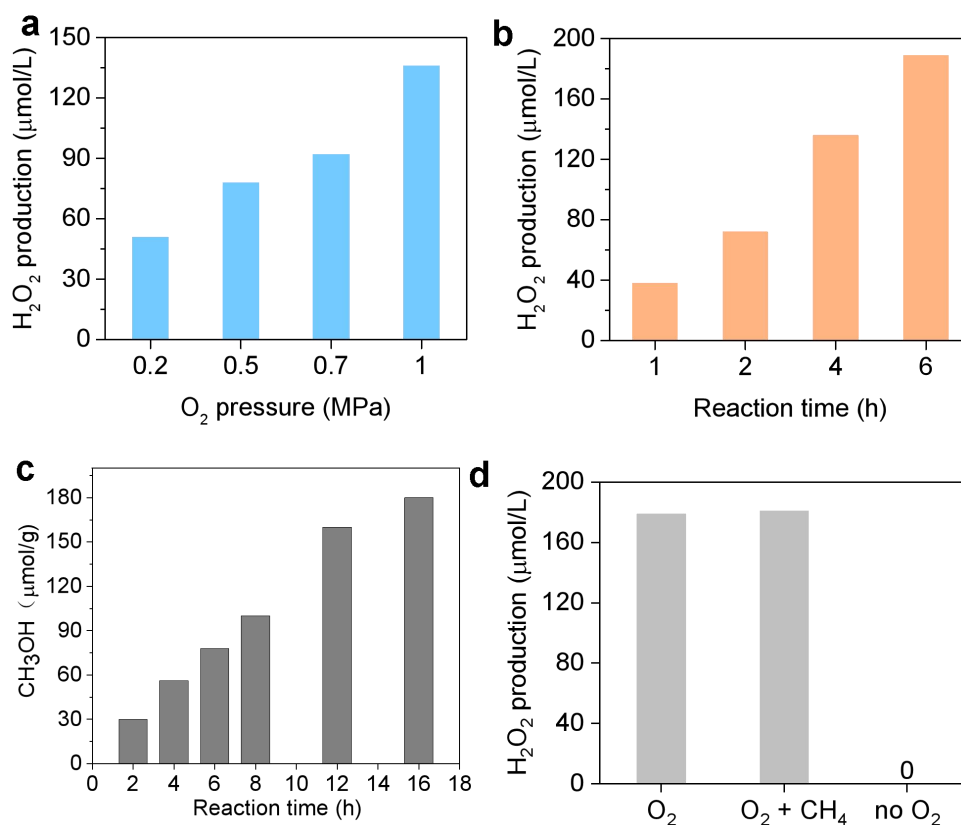
**Scheme S1.** The fitting equivalent circuit diagram for U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> samples.

**Table S1.** The fitting equivalent circuit parameters of Scheme R1 for the U, U-NO<sub>2</sub>, and U-NH<sub>2</sub> samples.

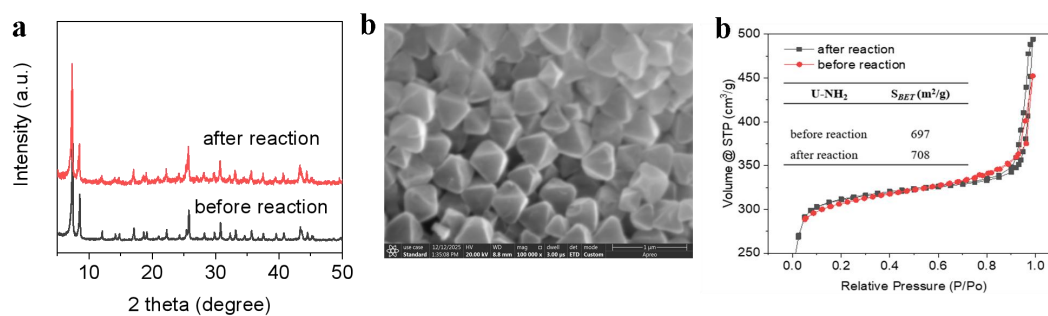
|                   |                |                |
|-------------------|----------------|----------------|
| U                 | R <sub>1</sub> | 14.94 $\Omega$ |
|                   | R <sub>2</sub> | 8565 $\Omega$  |
|                   | CPE1           | 0.796 $\Omega$ |
| U-NO <sub>2</sub> | R <sub>1</sub> | 15.26 $\Omega$ |
|                   | R <sub>2</sub> | 4526 $\Omega$  |
|                   | CPE1           | 0.825 $\Omega$ |
| U-NH <sub>2</sub> | R <sub>1</sub> | 15.08 $\Omega$ |
|                   | R <sub>2</sub> | 3688 $\Omega$  |
|                   | CPE1           | 0.823 $\Omega$ |



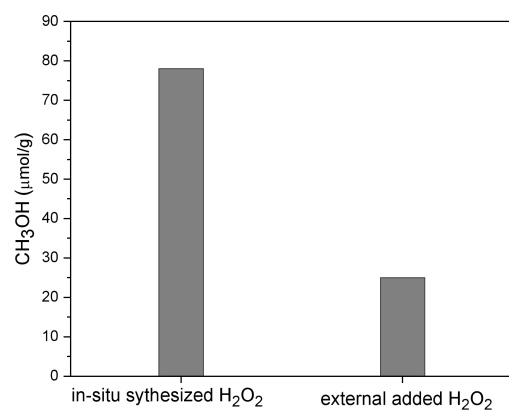
**Figure S7.** Different wavelength-response catalytic yield of methane oxidation.



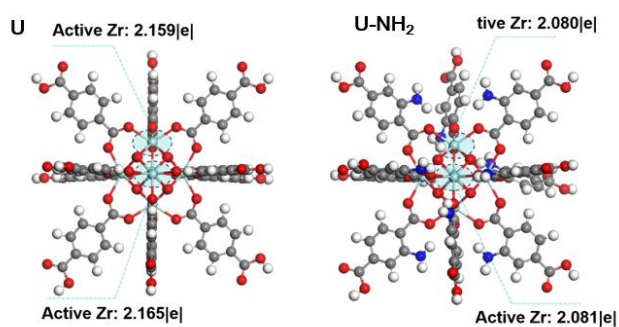
**Figure S8.** Reaction over U-NH<sub>2</sub> catalyst: (a) Generation yields of hydrogen peroxide under different oxygen pressures. (b) Time-dependent production of hydrogen peroxide at 1.0 MPa oxygen pressure. (c) Time-dependent production of methanol generation. (d) Control experiments of H<sub>2</sub>O<sub>2</sub> generation.



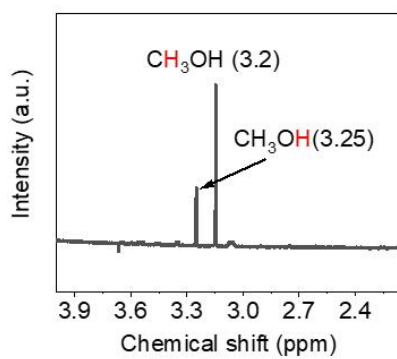
**Figure S9.** Comparison of XRD patterns (a), (b) SEM image of U-NH<sub>2</sub> after reaction, and N<sub>2</sub> adsorption-desorption isotherms (c) of U-NH<sub>2</sub> catalyst before and after reaction.



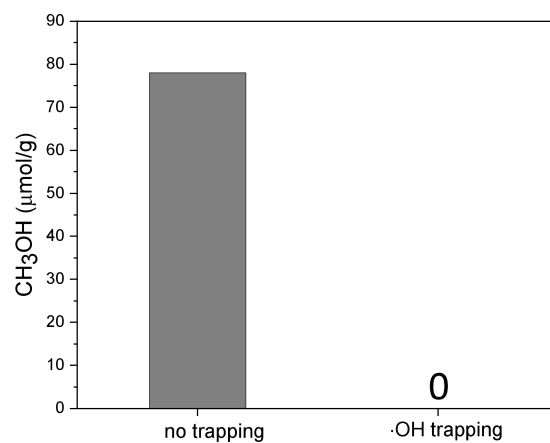
**Figure S10.** Comparison of methanol generation with same concentration (189 μM) of in-situ synthesized H<sub>2</sub>O<sub>2</sub> and external added H<sub>2</sub>O<sub>2</sub>.



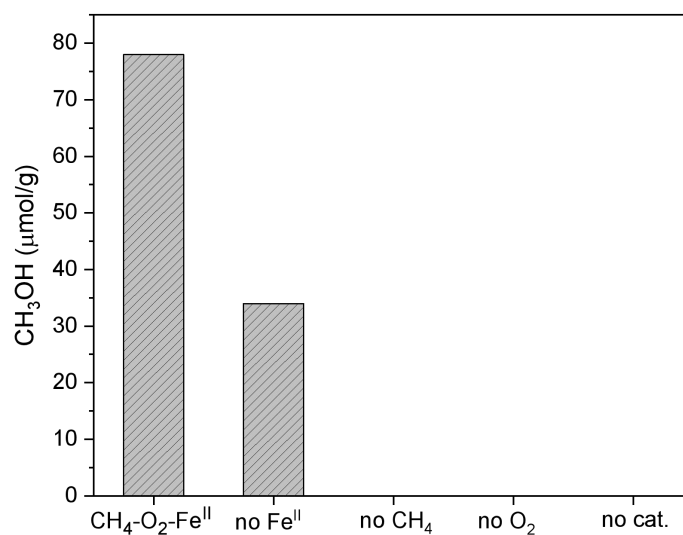
**Figure S11.** Mulliken charge analysis of the active Zr sites in defective U and U-NH<sub>2</sub> models.



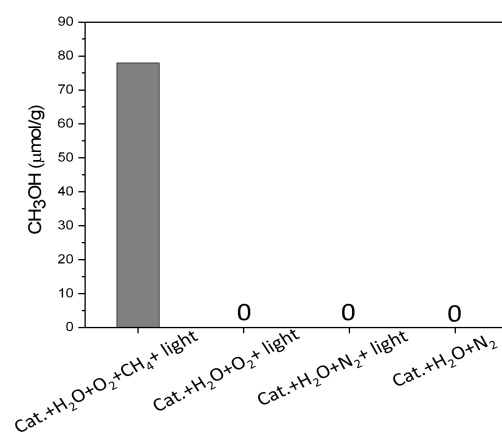
**Figure S12.** <sup>1</sup>H NMR spectra of the products generated during reactions.



**Figure S13.** Trapping experiment of  $\cdot\text{OH}$  radicals by using scavenger.



**Figure S14.** Controlling experiments of CH<sub>4</sub> conversion under different conditions with or without O<sub>2</sub>, Fe<sup>II</sup> and catalyst.



**Figure S15.** Control experiment and comparison: Cat.+H<sub>2</sub>O+O<sub>2</sub>+CH<sub>4</sub>+light, Cat.+H<sub>2</sub>O+O<sub>2</sub>+light, Cat.+H<sub>2</sub>O+N<sub>2</sub>+light, and Cat.+H<sub>2</sub>O+N<sub>2</sub>.