

Supporting Information

O₂ Plasma-activated CuO-ZnO Inverse Opals as High-performance Methanol Microreformer

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EXPERIMENTAL SECTION

For synthesis of CuO-ZnO catalysts with non-inverse opal nanostructure, the starting solution of copper-zinc was prepared by mixing 0.5 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5%, Aldrich) and 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich) in ethanol. This solution was then applied dropwise to the inner surface of the microchannels. Infiltrated samples were then placed in air at room temperature for 2-4 h. Finally, the resulting CuZnO composites were heated in air to 300 °C to obtain the CuO-ZnO catalysts with random microstructure.

For synthesis of O_2 -plasma CuO-ZnO inverse opals, 10 wt % of polystyrene (PS) colloidal suspension (Microparticles GmbH, 500 nm) was introduced into the microchannels. After room temperature evaporation of water from the suspension, PS opals with well-defined structures were formed inside the microchannels. These PS particle-packed microchannels were heated at 90 °C for 3-6 h in order to improve the connectivity between the neighboring particles. The copper-zinc precursor solution containing 0.5 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5%, Aldrich) and 0.5 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich) in ethanol was then applied dropwise over the surface of the PS layer. These infiltrated samples were then placed in air at room temperature for 2-4 h. Finally, the resulting CuZnO/PS composites were heated in air to 300 °C to obtain the CuO-ZnO inverse opals. These pristine CuO-ZnO inverse opals were then exposed to O_2 plasma for a short duration of 3-15 min to obtain O_2 -plasma treated CuO-ZnO inverse opals. The process of plasma-chemical surface modification was performed in a parallel-plate reactor with a DC flowing discharge (PCD-150; ALL

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REAL TECHNOLOGY CO., Ltd.; Taiwan). The distance between ground electrode and powered electrode was about 6 cm. The plasma chamber was 250 mm in diameter and 140 mm in height. The electrode was in the form of disk with around 6 inch in size. For the O₂ plasma treatment, the substrate temperature, total gas pressure and DC power were maintained at room temperature, 200 mTorr and 50 W, respectively.

For microstructural investigations, XRD analyses were performed using a Bruker D8 Advance diffractometer with Cu (40 kV, 40 mA) radiation. SEM images were obtained on a JEOL 6700 filed-emission SEM. XPS analyses were carried out using a Microlab 350 system. For TEM (JEOL JEM-2100) observation, the products formed on the CuO-ZnO inverse opal/microchannel substrate were scratched and dispersed on a carbon-coated Cu grid. Micro-Raman analyses were performed on a Jobin Yvon Labram HR800 spectrometer. BET measurements were carried out using a Micrometry Tristar instrument. The catalytic performance tests were conducted using an integrated microchannel-reactor under atmospheric pressure. The Al-alloy (6061) chip of the microreactor was fabricated in-house with laser machining. Ten microchannels per Al-alloy chip were separated by 800 μm fins; with width, depth and length of 500 μm , 200 μm and 4.3 cm, respectively. For the calculation of the catalyst weight for MRR, we measure the total weight including CuO-ZnO inverse opal by precision electronic balance (± 0.1 mg; Sartorius). The commercial CuO-ZnO-Al₂O₃ catalysts (Sud-Chemie; MDC-3) were used as reference sample, which were deposited on the inner surface of microchannels using the wash-coated method. After reduction of

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CuO-ZnO inverse opals in a H₂/N₂ (5/95), flown at the rate of 50 mL min⁻¹ at 200 °C for 1 hr, premixed water, oxygen and methanol with a H₂O/O₂/MeOH molar ratio of 1/0.125/1 were fed into the preheater maintained at 200 °C by means of microfeeder. The feed and product gas streams were analyzed inline using a thermal-conductivity-detector gas chromatograph (TCD-GC; China Chromatography CO., LTD.) and CO detector (Gastech CO., Ltd.; GTF200).

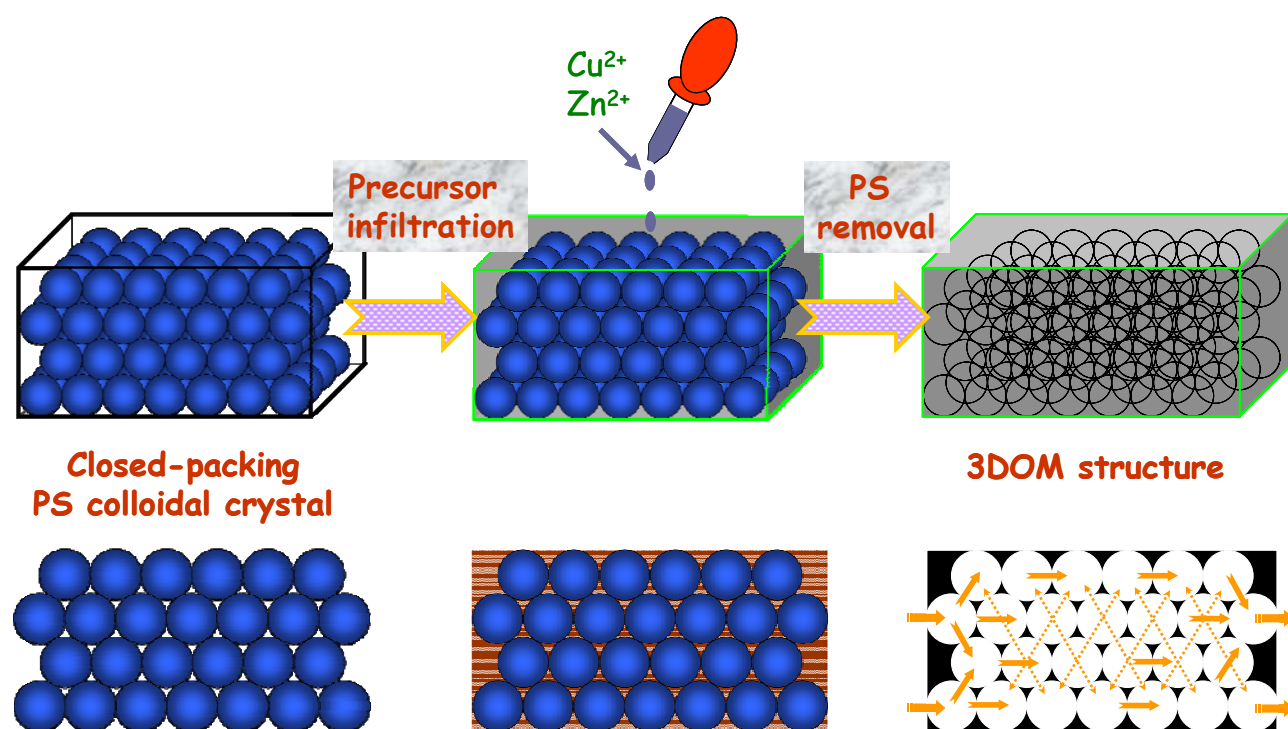


Fig. S1 Procedure for the preparation of CuO-ZnO inverse opals using polystyrene colloidal crystal templates.

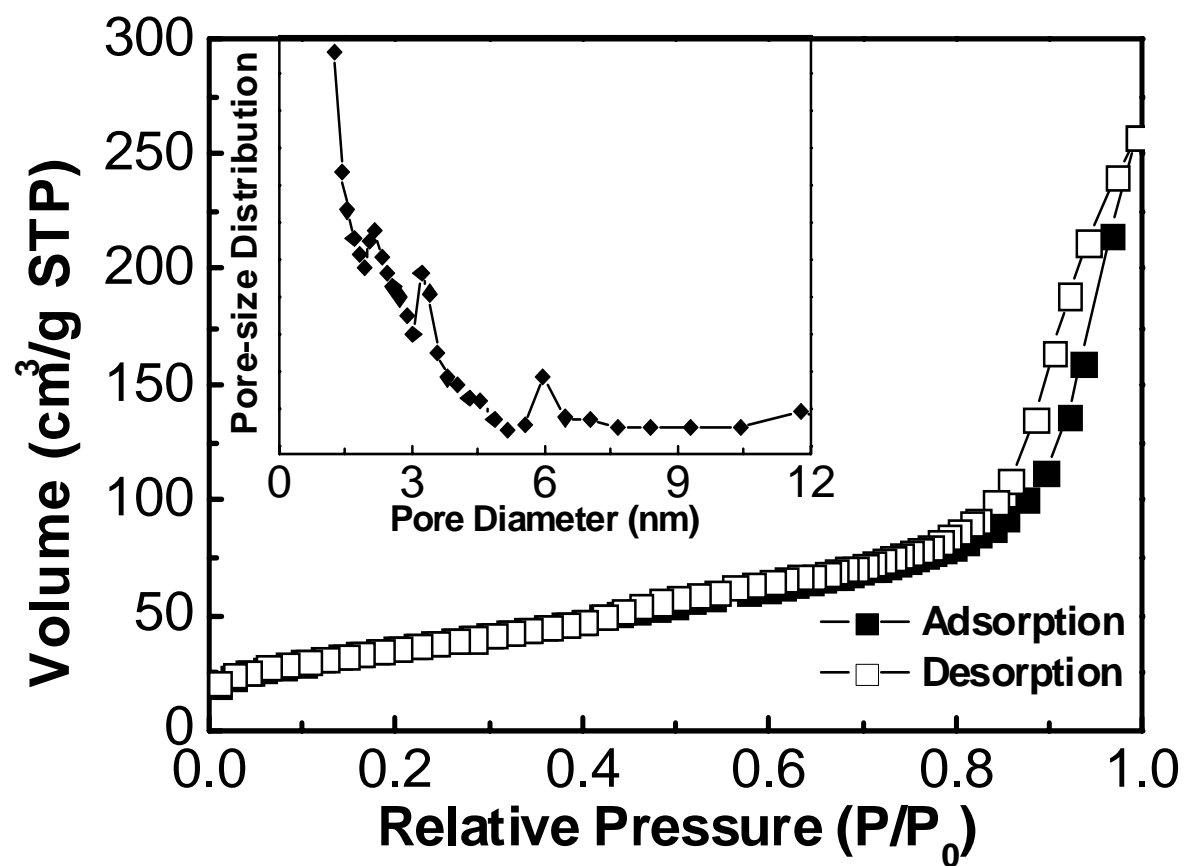


Fig. S2 N₂ adsorption-desorption isotherm and pore-size distribution (inset) of CuO-ZnO inverse opals without O₂-plasma treatment.

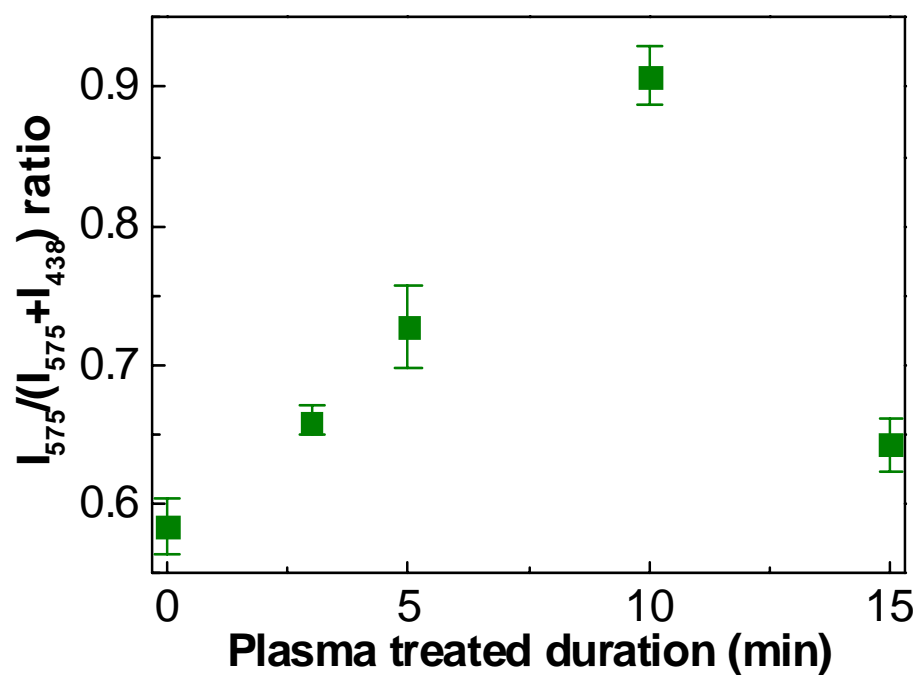


Fig. S3 Relative ratio of the integrated 575 cm⁻¹ peak intensity to the sum of the 438 and 575 cm⁻¹ peaks as a function of O₂-plasma exposure time for CuO-ZnO inverse opals.

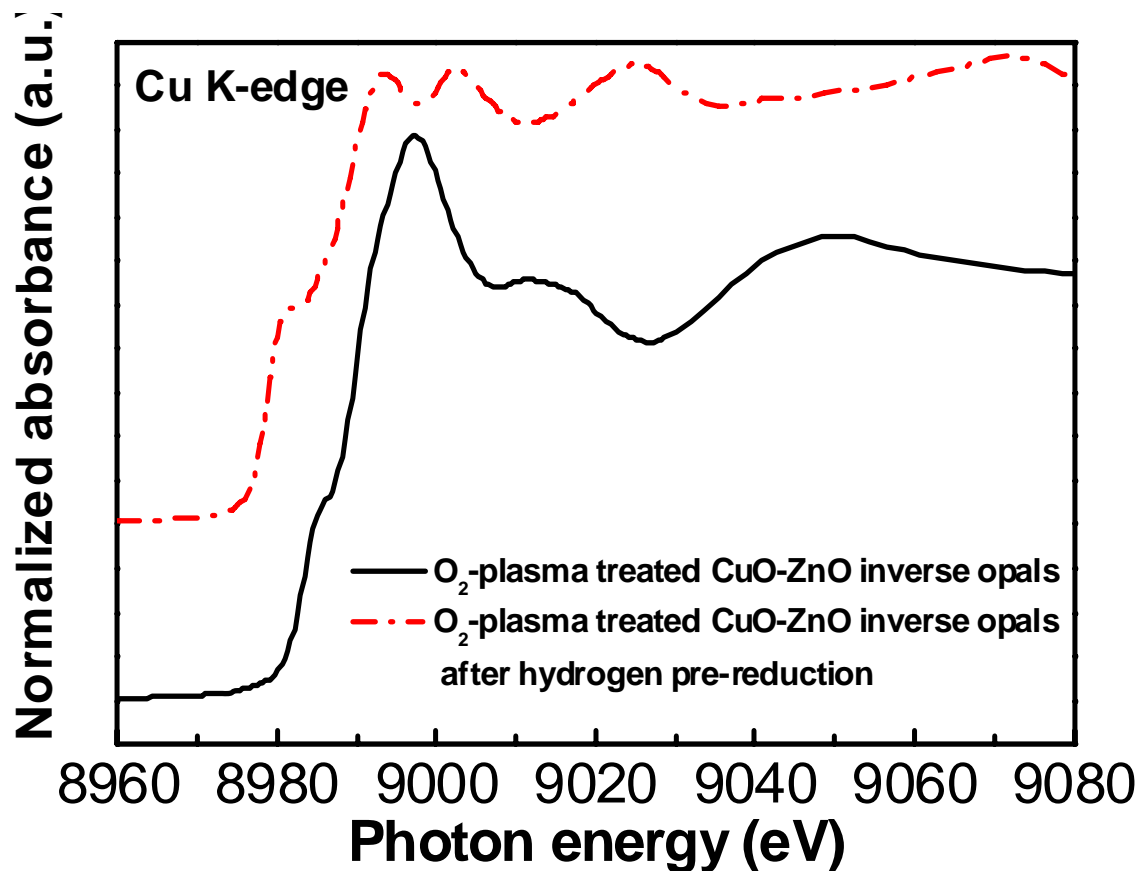


Fig. S4 Cu K-edge X-ray absorption near-edge spectroscopy (XANES) of O₂-plasma treated CuO-ZnO inverse opals and O₂-plasma treated CuO-ZnO inverse opals after H₂ reduction. From XANES analysis, after H₂ reduction of O₂-plasma treated CuO-ZnO inverse opals, all the CuO will turn to metallic Cu.

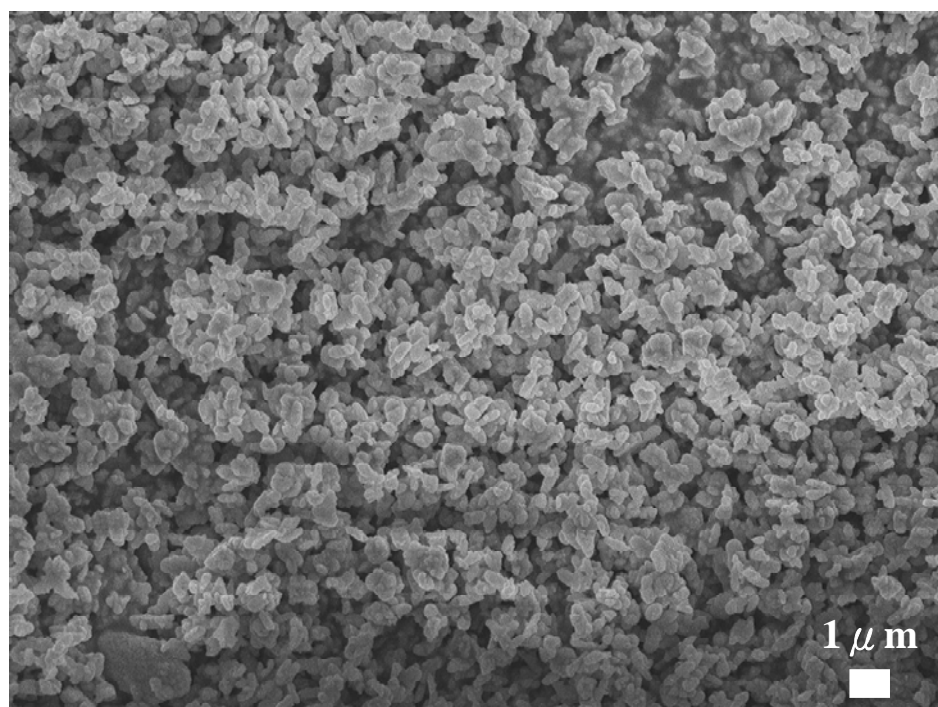


Fig. S5 SEM image of Cu-ZnO catalysts with non-inverse opal nanostructure.