

## **Heterogeneous Catalytic Oxidation of Glycerol Over a UiO-66- Derived ZrO<sub>2</sub>@C Supported Au Catalyst at Room Temperature**

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# 1. Experimental

## 1.1 Synthesis of catalysts

**ZrO<sub>2</sub>@C:** The UiO-66 material was synthesized hydrothermally under autogenous pressure according to a reported method with slight modifications. In a typical synthesis, 12 mmol (2.8 g) ZrCl<sub>4</sub>, 12 mmol (1.99 g) terephthalic acid (H<sub>2</sub>BDC), 40 mL glacial acetic acid and 400 mL N,N-dimethylformamide (DMF) were mixed and subjected to ultrasonication for 0.5 h; the mixture was then introduced into a Teflon-lined stainless-steel autoclave and kept at 120 °C. After 24 h, the oven was naturally cooled to room temperature. The resulting white crystalline powder was filtered and washed three times with DMF and ethanol. Subsequently, the solid sample was dried at 80 °C for 12 h and calcined at 600 °C for 5 h under a flow of argon gas at a heating rate of 5 °C/min. Finally, a black powder was obtained and denoted ZrO<sub>2</sub>@C (Scheme 1).

**ZrO<sub>2</sub>:** ZrO<sub>2</sub> was synthesized according to a literature method. Typically, 1.5 g PEG (polyethylene glycol), 0.9 g NaOH and 3.22 g ZrOCl<sub>2</sub>·8H<sub>2</sub>O were dissolved in 80 mL deionized water. The mixture was stirred for 4 h and then transferred into a 100 mL Teflon-lined stainless-steel autoclave. Next, the autoclave was placed in an oven at 110 °C for 24 h. A white powder was isolated by filtration and washing with deionized water. The filtered sample was dried at 120 °C overnight and calcined at 600 °C in static air for 5 h at a heating rate of 5 °C/min.

**Activated charcoal (C):** Activated charcoal was purchased from Aladdin Industrial Inc. and was used without further purification.

**ZrO<sub>2</sub>-C:** ZrO<sub>2</sub>-C was prepared by mixing activated charcoal and ZrO<sub>2</sub> with a ball mill for 30 minutes.

**Supported Au catalysts:** The supported catalysts were fabricated via a colloidal deposition method and have been extensively described elsewhere. The preparation of Au/ZrO<sub>2</sub>@C is described as an example. First, 6.27 mL HAuCl<sub>4</sub> solution (0.0324 M) was dispersed in 50 mL distilled water, and then a certain amount of protective agent PVA was introduced (the quality ratio of PVA/Au was 0.5). After stirring for 30 min, 5 mL freshly prepared NaBH<sub>4</sub> solution (0.1 M) was added rapidly, and the mixture was stirred for another 30 min, which led to the formation of colloidal gold solution. Afterwards, Au particles were immobilized on the supports at room temperature by adding the supports to the abovementioned colloidal gold solution under stirring, and the suspension solution was kept for 5 h to ensure that total adsorption (3 wt% gold on the support) occurred. Finally, the solids were collected by filtration and washing with excess deionized water. The filtered catalyst was dried at 60 °C overnight under vacuum (Scheme 1). The same procedure was used to prepare the other supported catalysts to minimize the size discrepancies of Au nanoparticles.

## 1.2 Characterization of catalysts

XRD was performed on a Rigaku Smart Lab X-ray diffractometer equipped with a CuK $\alpha$  radiation source ( $\lambda = 0.15432$  nm, operating at 40 kV and 40 mA). The N<sub>2</sub> adsorption-desorption isotherm was measured at liquid N<sub>2</sub> temperature (77 K) using a

Micromeritics ASAP 2460 specific surface area and porosity analyser. Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) of the catalysts was performed by using an Auto Chem II 2920 instrument with a thermal conductivity detector. The microstructures and crystalline sizes were determined, and energy-dispersive spectroscopy (EDS) element mapping images were obtained by using an FEI Tecnai G2 F20 electron microscope at an accelerating voltage of 200 kV. The sizes and distributions of the Au NPs were obtained from transmission electron microscopy (TEM) images by averaging the values for a minimum of 200 particles. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Scientific ESCALAB Xi<sup>+</sup> electron spectrometer with an Al K $\alpha$  X-ray source. The binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp<sup>2</sup> hybridized (C=C) carbon in the sample.

### **1.3 Catalyst testing**

A stainless-steel autoclave reactor equipped with a mechanical stirrer and a temperature-control system was used to evaluate the catalytic performance of the catalysts. In a typical experiment, 30 mL glycerol aqueous solution (0.1 mol L<sup>-1</sup>), 0.026 g catalyst (glycerol/Au = 750 mol/mol) and 0.16 g NaOH (NaOH/glycerol = 4 mol/mol) were placed in the autoclave reactor. After the mixture was purged with pure O<sub>2</sub> three times, the pressure was maintained at 10 bar, and then the temperature was raised to 25 °C under stirring at 600 rpm. After 6 h, the mixture was separated by filtration with an organic microfilter (0.45  $\mu$ m). The filtrate was analyzed by high-performance liquid chromatography (HPLC, Sykam S-501) with both refractive index (S3590-RI, temperature of 40 °C) and UV (S6852-UV/Vis, wavelength of 210 nm) detectors. An

Aminex HPX-87H ion exclusion column (Bio-Rad) was applied to analyze the reaction mixture, and the mobile phase was an aqueous solution of formic acid (0.005 M) that flowed at 0.4 mL/min at 40 °C. The quantification of the reactants and the product was analyzed by an external standard method.

## 2. Results and discussion

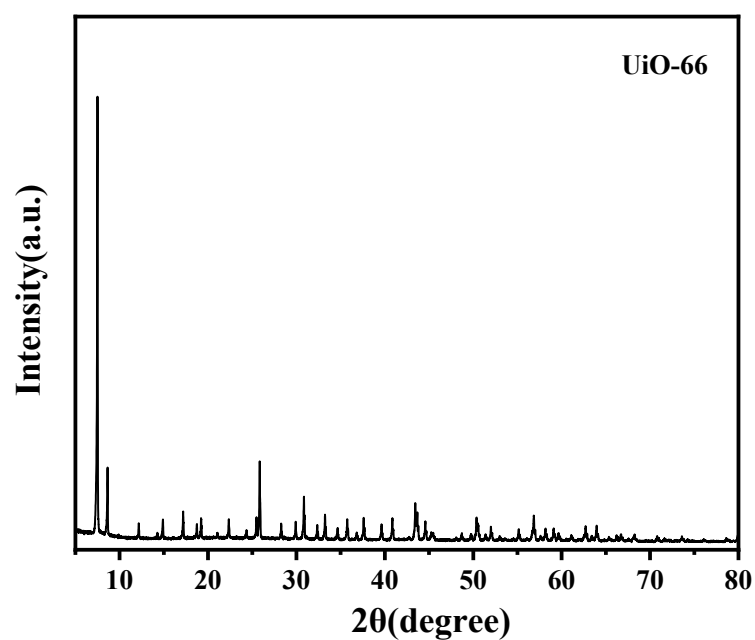


Fig. S1 The XRD patterns of UiO-66

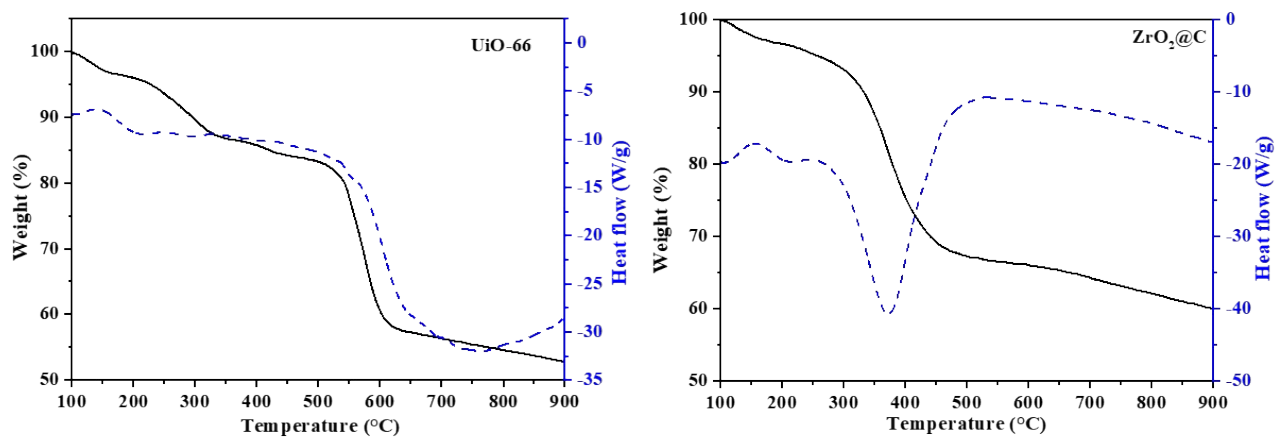
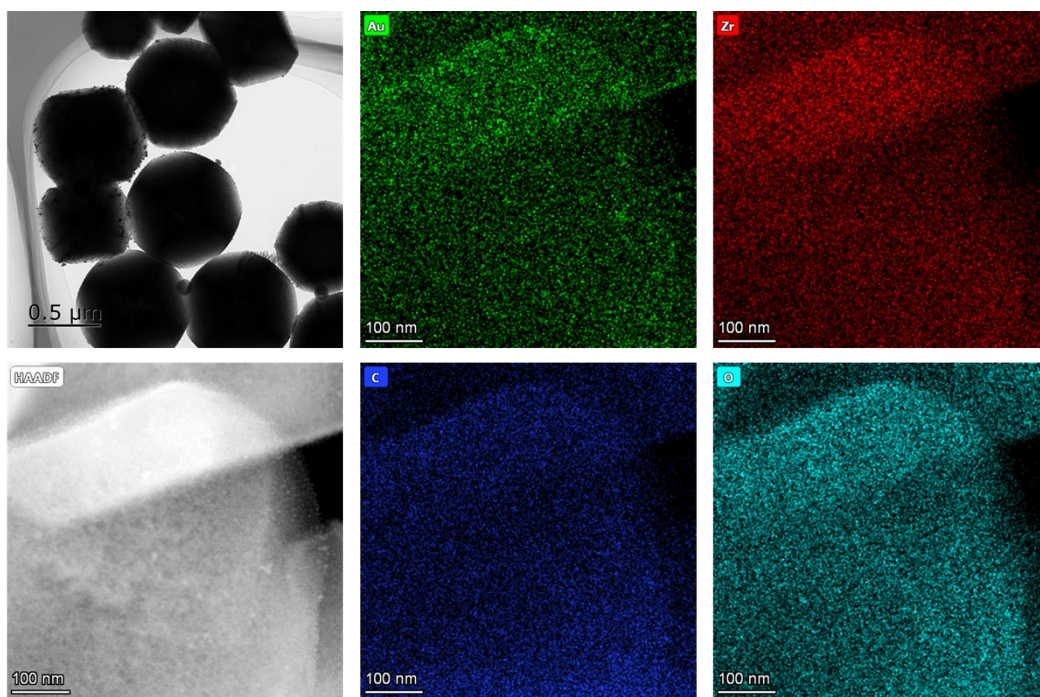


Figure S2 The TG-DSC of UiO-66 and ZrO<sub>2</sub>@C material.



**Fig. S3** TEM images and corresponding EDX-mapping analysis of the Au/ZrO<sub>2</sub>@C catalyst.

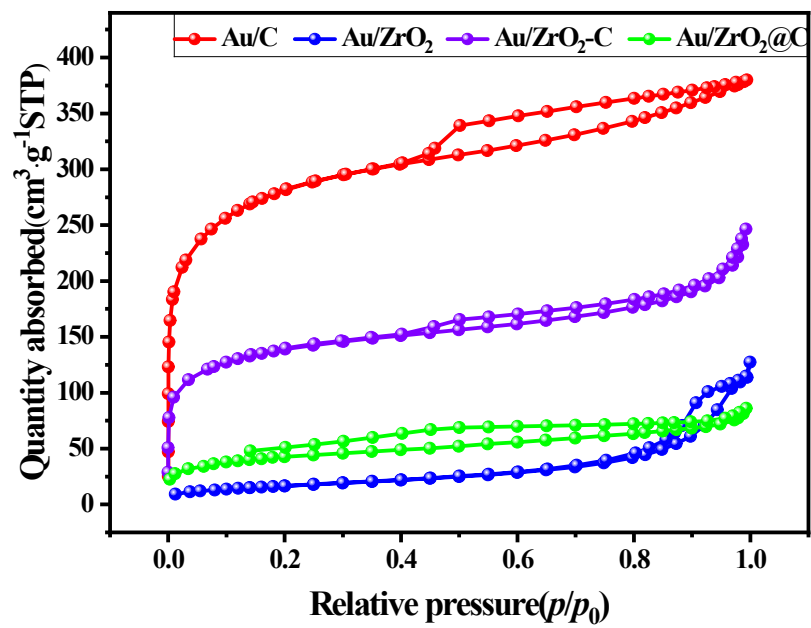


Fig. S4 The Nitrogen adsorption-desorption isotherms of supported Au catalysts



Table S1. The loss of Au and Zr in during recycling

Recycling times	Au loss (wt%)	Zr loss (wt%)
1	1.71	7.60
2	0.69	4.27
3	0.72	3.58