Electronic Supplementary Information for

Photocatalytic Oxidation of Methanol Using Porous Au/WO_3 and Visible Light

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*Synthesis of acid-prepared mesoporous spheres (**SiO_2**)*

Cetyltrimethyl ammonium bromide (CTAB, 9.0 g, 24.7 mmol) was dissolved in a solution of deionized water (198 g, 11 mol), ethanol (200 proof, 55.5 g, 1.20 mol), and concentrated HCl (37 wt%, 22.0 g, 223.0 mmol) at room temperature with vigorous stirring. Tetraethoxysilane (TEOS, 20.0g, 96.0 mmol) was then added and stirring was continued for 5 min, after which a solution of NaF (0.5M, 23.8 g, 11.9 mmol) was added. The solution became turbid in about 83 s and was immediately transferred to a Teflon bottle that was sealed and placed in an oven at 373 K for 160 min. The bottle was then removed from the oven and cooled at room temperature for 60 min before filtration of the product and washing with water and ethanol. Following air drying of the product at room temperature, the material was calcined under flowing air with the following heating program: ramp from 298 K to 723 K at 2 K min^{-1}, hold at 723 K for 240 min, ramp to 823 K at 10 K min^{-1}, and hold at 823 K for 480 min before cooling to room temperature. This sample is denoted as **SiO_2**.

*Sonochemical deposition of Au NPs onto APMS (**SiO_2-Au**)*

Calcined APMS was dried at 100 °C overnight (1.0 g) before being dispersed in 150 mL H_2O in a 250 mL round-bottom flask with stir bar and then stirred for 10 min. Brief sonication of the flask (water bath-type sonicator, Branson 2510, 40 kHz, 130 W) was done to break up aggregates of SiO_2. A solution of chloroauric acid (0.0255 M $HAuCl_4{\bullet}3H_2O$, 1.366 mL, 0.0372 mmol Au) was then added and stirring continued for 30 – 40 min. Sonication of the mixture began as above, during which, concentrated aqueous ammonium hydroxide (29 wt% NH_3, 4 mL, 61.3 mmol NH_3) was added dropwise over the course of the entire sonication period (45 min). The NH_3 : Au mole ratio was 1648 : 1, and the reaction mixture pH = 10.91. The product was filtered, washed with 250 mL water, dried under vacuum air at room temperature overnight, and calcined under air flow at 773 K for 3 h (ramp rate = 0.95 K min^{-1}) yielding a red colored product. This sample is denoted as **SiO_2-Au**.

*Incipient wetness impregnation of SiO_2 with ammonium metatungstate and etching of SiO_2 to yield **WO_3***

About 3 g **SiO_2** was added to a crucible and then an aqueous solution of ammonium metatungstate (AMT, 1.5 g AMT/mL H_2O) was added dropwise to the dry powder via incipient wetness (2.992 cm^3 g^{-1} = total pore volume of **SiO_2**). The damp mixture was manually stirred for 10 min, and then the mixture was left to dry at room temperature in air for 4.5 h. The dry powder was then calcined under air flow with the following program: ramp from 298 K to 423 K, hold at 423 K for 3 h, ramp to 523 K, hold at 523 K for 3 h, ramp to 823 K, hold at 823 K for 5 h. All ramp rates were 1 K min^{-1}. The impregnation, drying, and calcination steps were repeated a second time. This yielded a yellowish-green colored SiO_2-WO_3 composite powder.

To remove the silica template, the SiO_2-WO_3 composite (1.0 g) was added to 11 mL of 10% HF in H_2O (1 mL concentrated HF with 9 mL H_2O) contained in a 15 mL plastic centrifuge tubes. *Caution: HF is extremely toxic and corrosive, wear appropriate personal protective equipment while using this acid*. The sealed tubes were placed on orbital shakers to mix gently for approximately 4 h. The solids were then centrifuged and the supernatant disposed of appropriately. The particles were washed three times with 11 mL H_2O and then once with 11 mL ethanol. The washed samples were left to dry in the centrifuge tube under air in an oven at 353 K overnight. The resulting sample is denoted as **WO_3**.

*Bulk WO_3 preparation ((**B)-WO_3**))*

Ammonium metatungstate hydrate (AMT, $(NH_4)_6H_2W_{12}O_{40} \bullet xH_2O$, 4.3 g) was ground into a fine powder and then calcined in the same way to form the SiO_2-WO_3 composite above.

*Porous TiO_2 preparation (**TiO_2**)*

In a beaker, 2.0 g **SiO_2** was mixed with 40 mL of a 50/50 (v/v) solution of ethanol and titanium isopropoxide (Ti(*i*PrO)$_4$). Brief sonication was utilized to disperse the powder, and then stirring continued for 20 h. The mixture was then centrifuged and the supernatant was removed. The product was left to dry over night at 90 °C. The dry powder was mixed with another 40 mL ethanol and was added to yield 40 mL 50/50 (v/v) solution of Ti(*i*PrO)$_4$ and ethanol, then dried at 80 °C. A 20 mL Ti(*i*PrO)$_4$/ethanol solution was mixed with the powder followed by centrifugation, decantation of the supernatant and then drying at 60 °C. Hydrolysis of the Ti(*i*PrO)$_4$ precursor loaded inside the pores of **SiO_2** was completed with a 40 mL 50/50 (v/v) solution of water and ethanol for 3 h. After evaporation of the solvent at 60 °C, the sample was calcined with the same program as used for **SiO_2**, to yield SiO_2-TiO_2.

The SiO_2-TiO_2 composite was added to 2M NaOH in a plastic centrifuge tube and shaken for about 3 h to remove the silica portion of the composite. Following centrifugation and removal of the supernatant, the material was added to a fresh solution of 2M NaOH for a second and then a third time. The final material was dried at 60 °C overnight. This sample is denoted as **TiO_2**.

*Sonochemical deposition of Au NPs onto SiO_2-WO_3 followed by SiO_2 removal (**WO_3-Au**)*

The SiO_2-WO_3 composite (1.3 g) was first dried at 100 °C overnight and then added to 195 mL H_2O in a 250 mL round-bottom flask with stir bar and then stirred for 10 min. Brief sonication was used to break up aggregates of SiO_2-WO_3. Different volumes of chloroauric acid (0.0255 M $HAuCl_4 \bullet 3H_2O$) were added to the suspension depending on the desired nominal wt% loading of Au NPs. For 1 wt% Au (based on the mass of SiO_2-WO_3), 2.521 mL (0.0687 mmol Au) were used, and for 3 wt% Au, 7.873 mL (0.215 mmol Au) were used. The suspension was stirred for 30 – 40 min. Sonication of the mixture began as above, during which, concentrated aqueous ammonium hydroxide (29 wt% NH_3, 5.2 mL, 79.7 mmol NH_3) was added dropwise over the course of the entire sonication period (45 min). The NH_3 : Au mole ratio (and pH) was 1160 : 1 (pH = 10.45) and 371 : 1 (pH = 10.76) for the 1 wt% Au sample and the 3 wt% sample, respectively. After filtration, washing, drying, and calcination as done with **SiO_2-Au** above, dark, wine purple-colored SiO_2-WO_3-Au powders were obtained. The SiO_2 portion of the SiO_2-WO_3-Au product was removed with 10% HF as described above. Some Au NPs are lost during this process as confirmed by the purple colored supernatant observed during washes. The samples are denoted as **WO_3-Au(1)** and **WO_3-Au(3)**, where the number in parentheses is the nominal Au wt% used in the synthesis.

ICP-OES sample preparation procedures

Samples were first dried at 100 °C in air for several hours. Additionally, samples that were previously etched (free of SiO_2) were calcined at 500 °C for 3 h in air to remove residual ethanol that was adsorbed during the washing step. Samples were first digested by adding 0.020 g of material to 1 mL of 2 M NaOH in a 1.5 mL Eppendorf tube followed by approximately 30 min of ultrasonication. Mixtures were left to shake vigorously for several hours to completely dissolve SiO_2 and WO_3 components. Samples containing Au NPs were allowed to settle overnight before subsequent centrifugation (15,000 rpm, 2 min) and separation. The Au pellet was washed with 1 mL H_2O then centrifuged. The supernatants were added to the initial digest solution of SiO_2 and/or WO_3. Three total H_2O washings were performed, and then the digest solution was adjusted to 0.1 M NaOH with H_2O. Diluted digest solutions of SiO_2 and WO_3 were prepared with 0.1 M NaOH in 100 mL volumetric flasks. Gold nanoparticles were quantitatively transferred via pipet from the Eppendorf tube with water to a vial and then evaporated to near dryness on a hot plate. The Au NP residue was then digested in aqua regia and then heated to evaporate solution to near dryness. To the Au/aqua regia residue, approximately 2 mL 0.5 M HCl was added, swirled, and then evaporated by heating until residue remained. This washing/evaporation step was repeated a twice before transferring the Au solution to a 25 mL volumetric flask and diluting to mark with 0.5 M HCl. Concentrations of Au, Si, and W were quantified by calibration curves using emission wavelengths of 267.599 nm, 251.611 nm, and 207.912 nm, respectively.

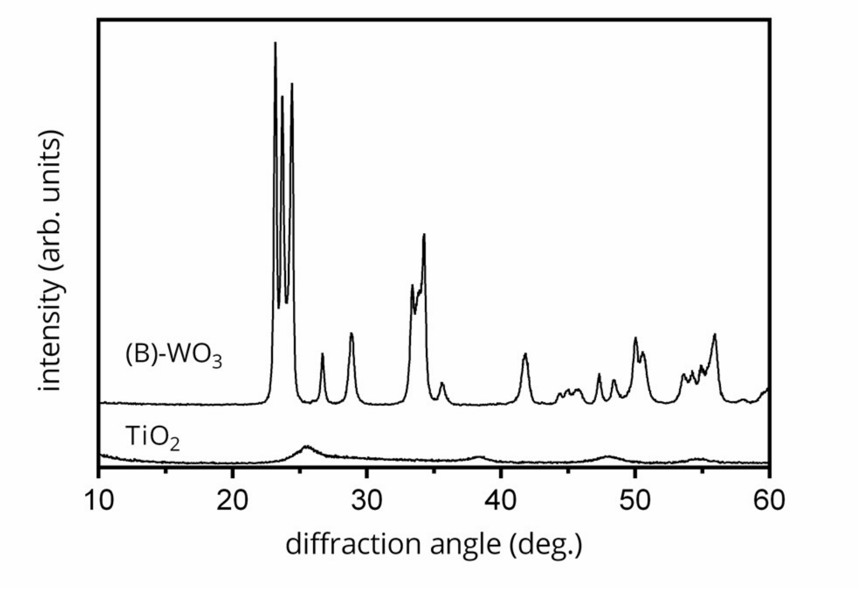

Figure S1. XRD patterns of (B)-WO_3 and porous TiO_2. Monoclinic WO_3 and anatase TiO_2 are the only observed crystalline phases for these samples.

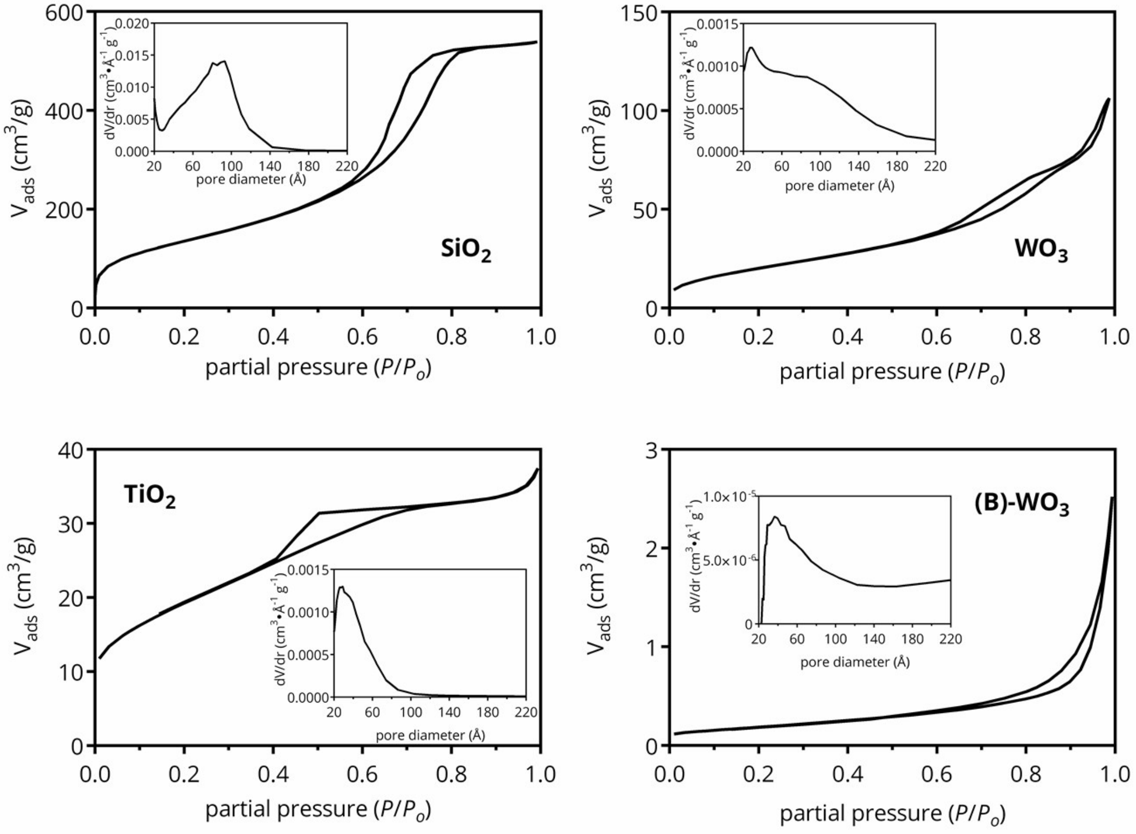

Figure S2. N_2 physisorption isotherms and pore size distributions (insets) for catalysts not modified with Au NPs.

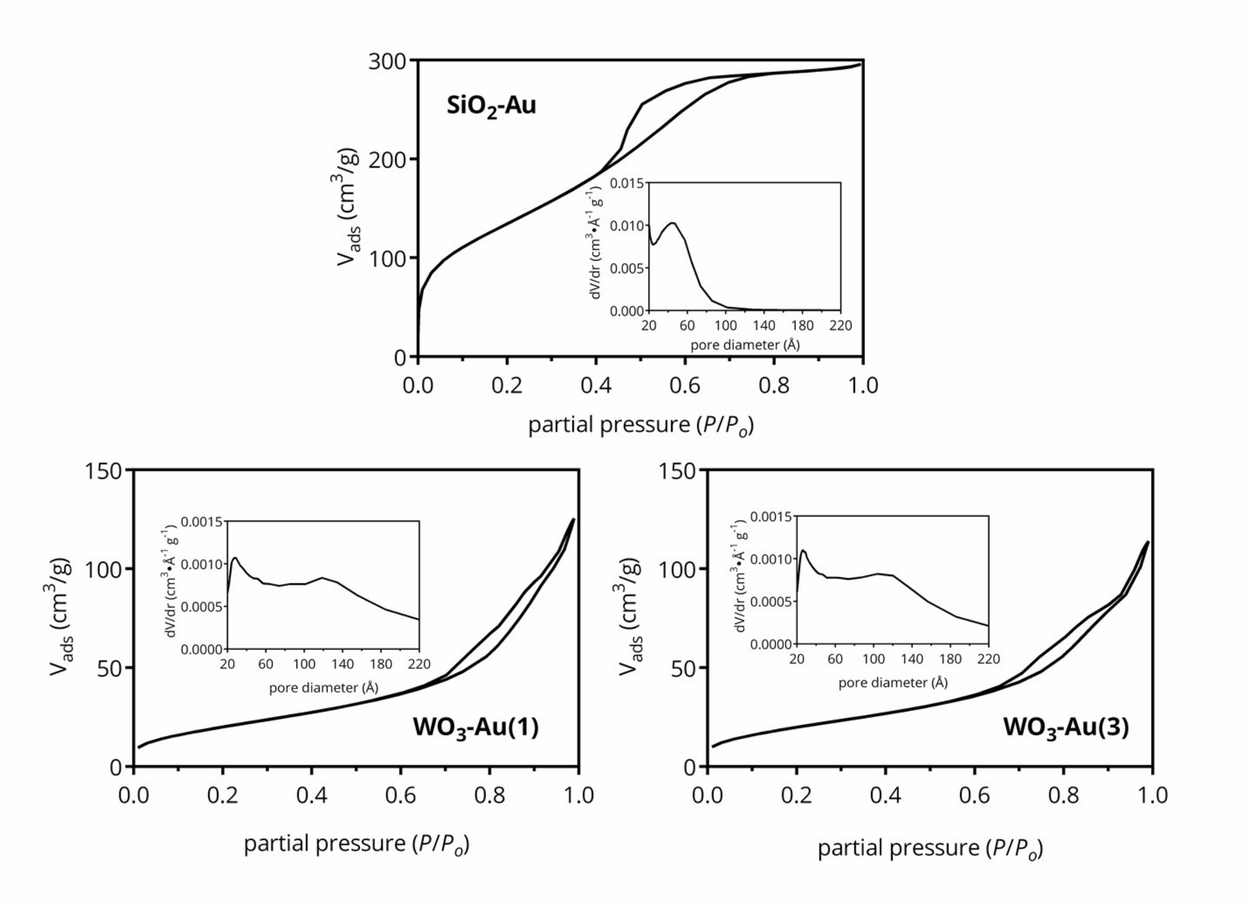

Figure S3. N_2 physisorption isotherms and pore size distributions (insets) for Au-modified catalysts.

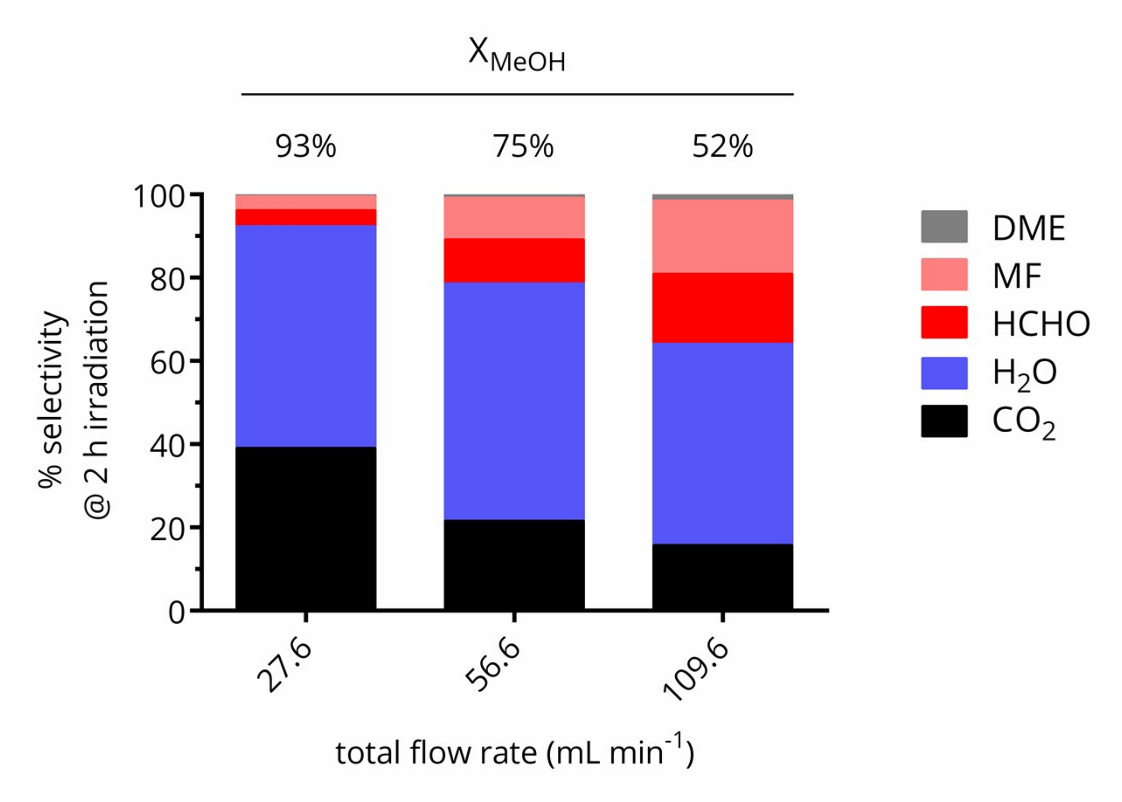

Figure S4. Product distributions for the WO_3-Au(3) catalyst at 2 h of irradiation with varying total flow rates. Methanol conversions (%) at 2 h of irradiation are shown above each distribution.