Supporting Information

Nanoporous Gold Supported Ceria For The Water-Gas Shift Reaction: UHV Inspired Design For Applied Catalysis

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1. Energy dispersive x-ray (EDX) analysis of the prepared CeOx/npAu catalysts.

Figure S1: a) The sample was prepared by calcining/heating the npAu impregnated with the $Ce(NO_3)_3$ in N_2 atmosphere. The heating rate was 6 °C/min, after reaching the desired maximal temperature of 485 °C the temperature was kept for 30 minutes and subsequently cooled down to room temperature. The SEM shows the cross section of the disk sample. The ligaments and nanopore channels are uniformly distributed. The EDX data shows around 2.2 atom % Ce in the bulk area.

b) This sample was heated to 635 °C, all other preparation steps are the same as for sample a). The SEM of a freshly broken cross section of a disk shows that two different structures evolve during this treatment. In the upper section, the ligament size of npAu is at around 40 nm, as it is in the pristine samples, yet, in the lower section, the ligament size is increased to over 200 nm, indicating coarsening. The EDX data shows that the upper section contains around 7 at% Ce (yellow square), and the lower section (green square) contains no Ce (below detection limit). This suggests that the CeO_x concentration on npAu plays an important role for the stabilization of the Au ligaments.

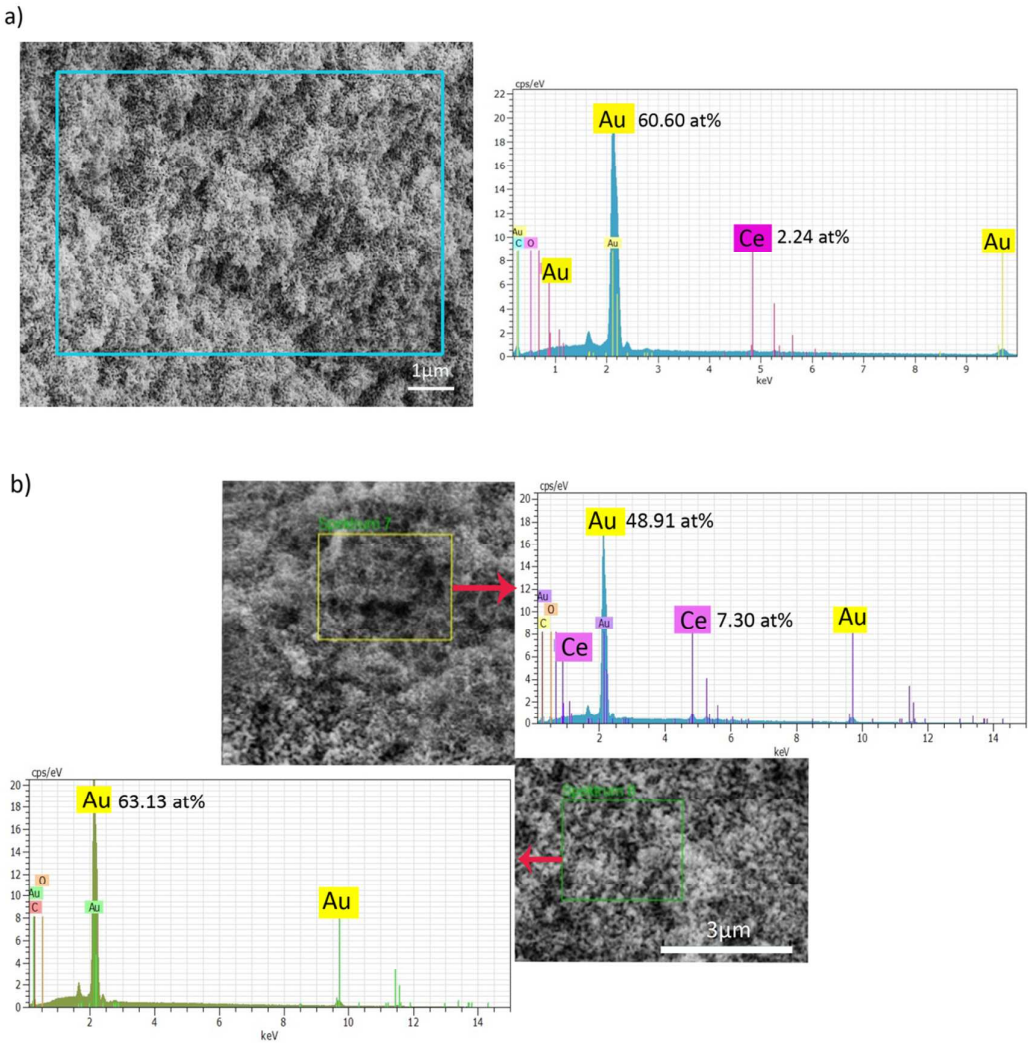

Figure S1: a, b) SEM and Energy dispersive x-ray (EDX) characterization of the prepared CeO_x/npAu catalyst.

2. Thermal stability and structural Characterization

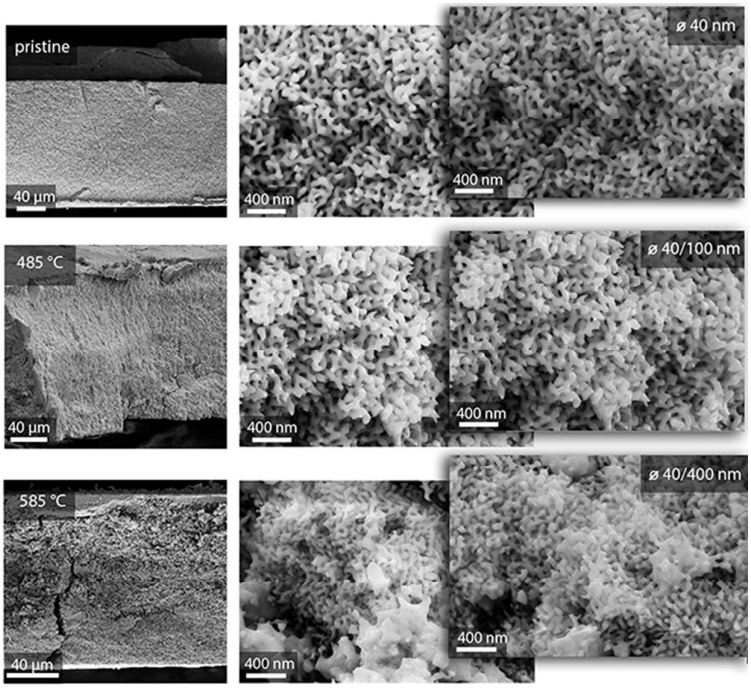

Figure S2: Cross sectional scanning electron micrographs (xSEM) of pristine npAu material and after deposition of CeO_x inside the porous structure. Micrographs on the left depict the entire cross section of the npAu disk (~200 µm thick). The higher magnification micrographs on the right depict representative sections from areas close to the outer surface (10 µm in depth, middle) and from the center of the cross section (on the right). The particular rows depict pristine as well as samples annealed in air at various temperatures (485 °C and 585 °C, see label on the upper left of each row) prior to catalytic measurements

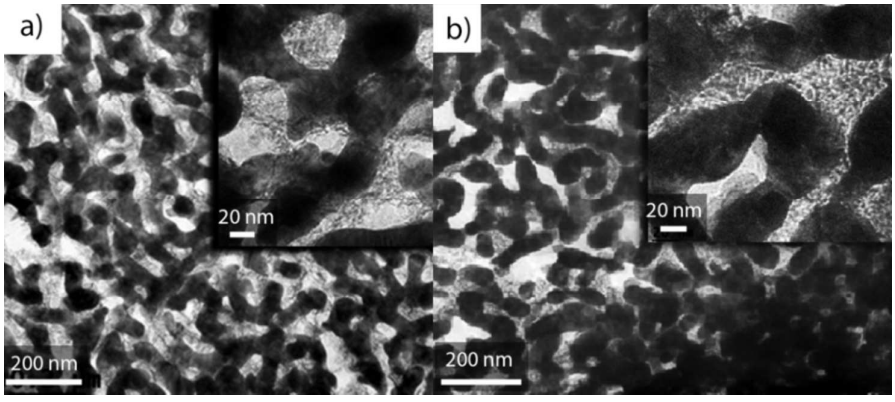

Figure S3: TEM characterization of CeO_x/npAu composites. Slices of the material (after impregnation/stabilization with a resin) with a thickness of about 30-50 nm were cut using a microtome. The dark areas represent the porous gold substrate, greyish areas indicate the cerium oxide covering the gold substrate. The upper section (A) shows the material after initial heating to 385 °C to initiate the formation of cerium oxide. The lower section (B) shows the according sample after catalytic reaction and heating up to 385 °C, accordingly.

3. Catalytic Experiments

Figure S4 shows the measured CO_2 signal (IR gas analyzers, URAS 3G, Hartmann und Braun) from the WGSR as a function of the reactor temperature between 185℃ to 535℃ with 50℃ intervals. The temperature was kept constant for over 25 minutes at every interval (catalyst: 150 µm disk CeO_x/npAu, total mass 5.1mg).

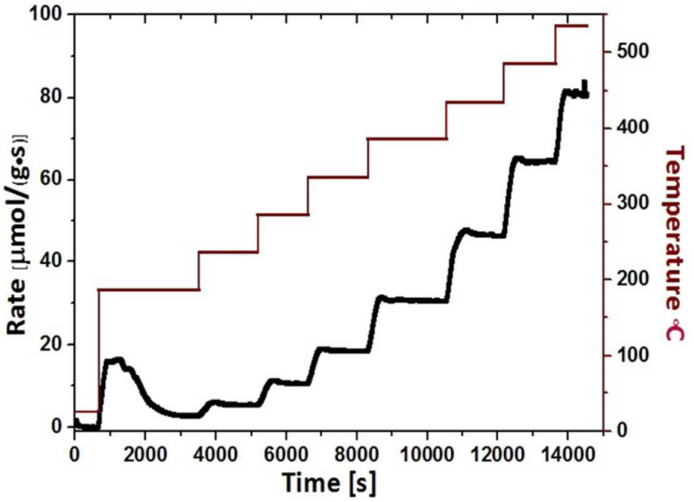

Figure S4: Temperature dependency of WGSR from 185-535 ℃ (4.2% CO, H_2O 16.0% in N_2, total gas flow 43.8 ml/min M_{catal}= 5.1mg). The "bump" in the rate at about 1500 sec is caused by the initial adjustment of the flow meters which led to a temporarily higher concentration of educts.

Figure S5 shows the measured CO_2 signal (from WGSR) for a membrane CeO_x/npAu material coated on a Si substrate (the initial "bump" was again caused by initially adjusting the flow meters). The temperature was increased from 235 °C to 535 °C with 50 °C intervals. The mass of catalyst was estimated based on the density and geometry of the material: For Gold bulk the density is around 20 g/cm^3, the (relative) density of the material (70% porous) is 0.3 and ~ 7 g/cm^3, respectively. The 100 nm thick film has accordingly a mass of 0.07 mg per cm^2. The area of the Si support is around 6 × 6 mm^2 (the film covering the entire surface), so that the estimated mass of the catalyst is around 0.0252 mg.

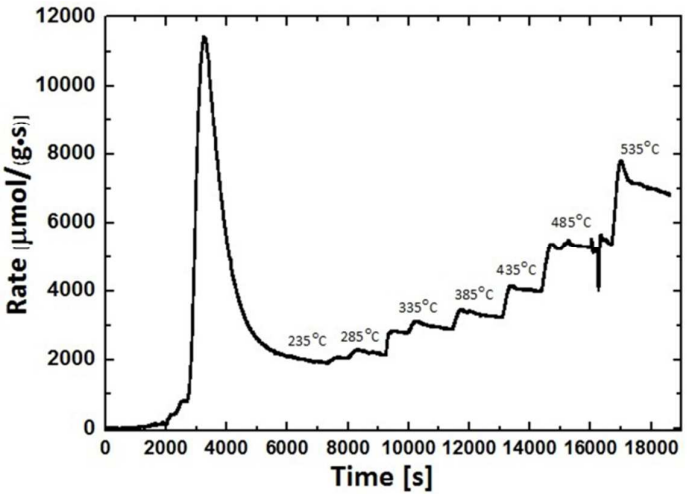

Figure S5: Temperature dependency for the WGSR from 235-535 °C (CO 5.23% 1.835 ml/min, N_2, H_2O 8.52 vol%. Total flow rate was 35.37 ml/min, M_{catal} = 0.0252mg).

Figure S6 shows the double-logarithmic plots of CO and H_2O which were used to determine the reaction order.

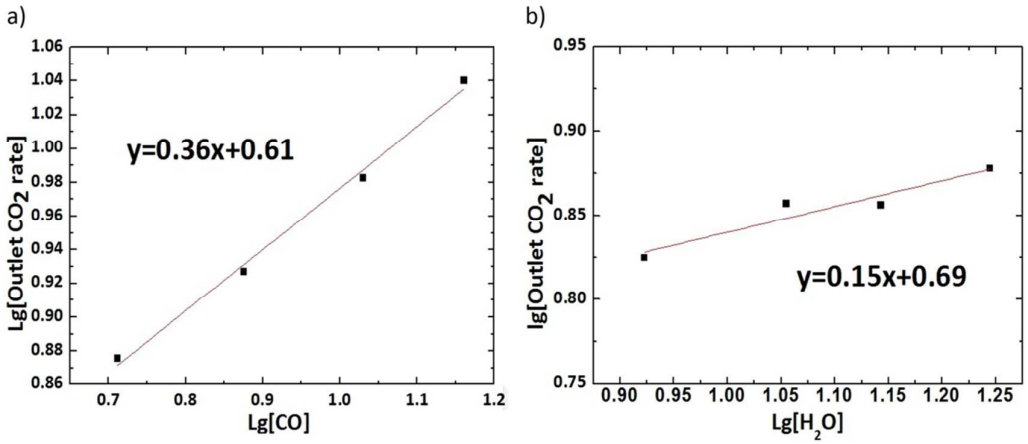

Figure S6: Double-logarithmic plots of a) CO and b) H_2O for determination of reaction orders

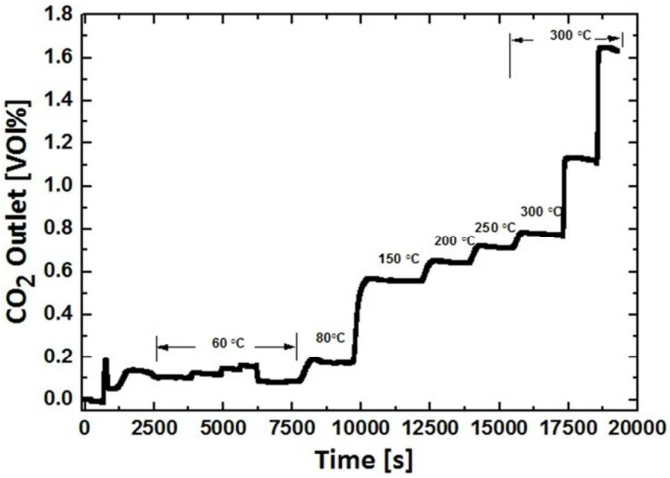

Figure S7: The CO_2 signal detected at the reactor outlet during CO oxidation catalyzed by a 150 µm thick disk of CeO_x/npAu (M_{catal} 4.4 mg). The CO_2 signal was measured by IR gas analyzers (URAS 3G, Hartmann und Braun). The gas composition was 46 vol% O_2, 2.9 vol% CO at a total flow of 62.8 ml/min, except at 60 °C and 300 °C (see details below).

In order to further assess the catalytic activity, the turn-over frequencies (TOF) were calculated. The equation and detailed calculation can be found in a former publication from our group in reference [1]. In this experiment, the total flow of gases was set to 43.8 ml/min, the specific surface area was assumed to be 4 m^2/g, the mass of the material is 5.1 mg. The density of surface atoms for the energetically most stable Au(111) surface is $1.4 \cdot 10^{19}$ atoms/m^2.

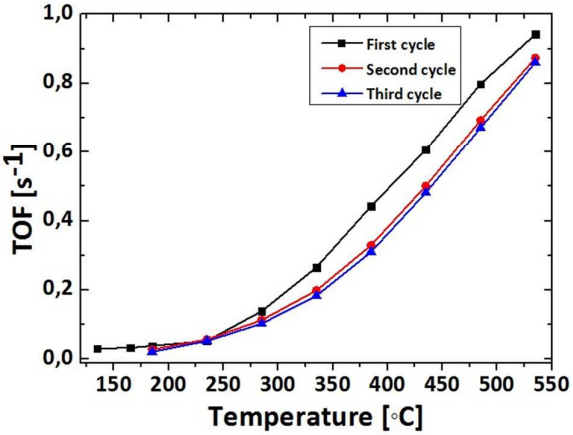

Figure S8: The TOF of WGSR using a 150 µm thick free standing membrane of npAu/CeO_x (4.2 vol% CO, 16.0 vol% H_2O in N_2, total gas flow 43.8 ml/min, M_{catal}= 5.1mg).

4. **Photoelectron spectroscopic characterization**

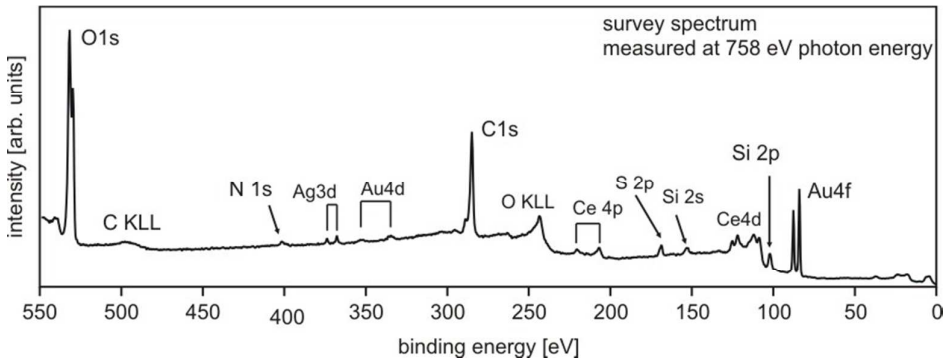

Figure S9: PES survey of a npAu-CeO_x sample (thin coating on Si wafer) after WGS catalysis at 285 °C. Besides the Au support and the CeO_x deposits contributions from ubiquitous contaminants (e.g. S, N, C) are visible (Si stems from the sample substrate). Also, Ag residues stemming from the leaching of the Au-Ag alloy is visible. Even though its bulk concentration is well below 1 atom% it can enrich at the surface and, thus, becomes detectable by surface sensitive PES.[2, 3]

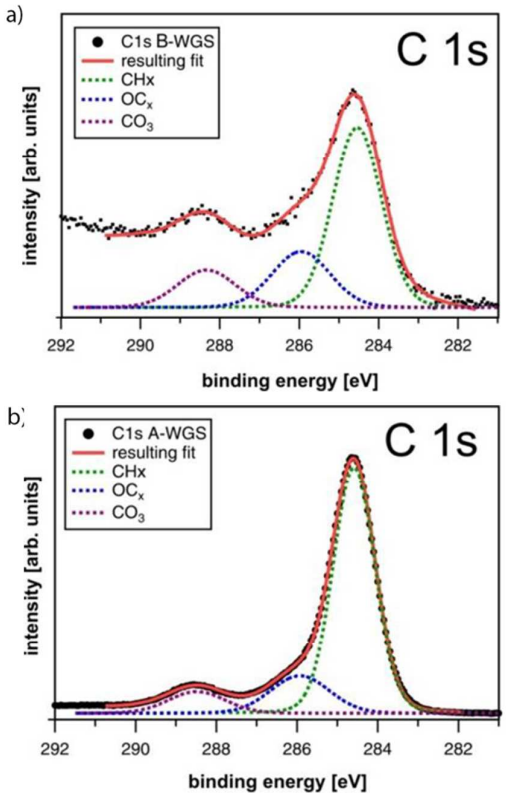

Figure S10: The Photoemission features of carbonates on the CeOx/npAu film catalysts before(A) and after WGSR(B)

References

1. A. Wittstock, V. Zielasek, J. Biener, C. M. Friend and M. Bäumer, Science **327** (5963), 319-322 (2010).
2. A. Schaefer, D. Ragazzon, A. Wittstock, L. E. Walle, A. Borg, M. Baumer and A. Sandell, J. Phys. Chem. C **116** (7), 4564-4571 (2012).
3. A. Wittstock, B. Neumann, A. Schaefer, K. Dumbuya, C. Kübel, M. M. Biener, V. Zielasek, H.-P. Steinrück, J. M. Gottfried, J. Biener, A. Hamza and M. Bäumer, J. Phys. Chem. C **113** (14), 5593-5600 (2009).