

Powering Fuel Cells with CO via Aqueous Polyoxometalates and Gold Catalysts

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Supporting Online Material

Synthesis of gold nanotube membranes

Poretics[®] track-etched polycarbonate membranes (Osmonics, Inc. K02CP14220) were used for all studies, and these materials were 10 μm -thick and contained pores of 220 nm-diameter with a pore density of ca. $3 \times 10^8 \text{ cm}^{-2}$. All chemicals were used as received: anhydrous SnCl_2 (Alfa Aesar 41960), CF_3COOH (Mallinckrodt 1942-57), AgNO_3 (Sigma-Aldrich 209139), anhydrous Na_2SO_3 (Mallinckrodt 8064), HCHO (Fisher F79), and a gold solution 'Oromerse SO Part B' (Technic Inc. 180227PB). Milli-Q water and methanol (Fisher A452) were used to prepare all solutions and to rinse the membranes.

Two polycarbonate membrane sheets ($8 \times 12 \text{ cm}$ in size) were placed in polycarbonate holders and immersed for 50 min in 500 ml of a solution consisting of 0.026 M SnCl_2 and 0.070 M CF_3COOH with a 50/50 water/methanol as the solvent. The membranes were next immersed in methanol for 2.5 min two consecutive times, followed by immersion in 300 ml of an aqueous ammoniacal AgNO_3 solution (0.029 M) for 5 min and subsequent immersion in methanol for 5 min. The ammoniacal silver solution was prepared freshly by addition of a 0.88 M NH_4OH solution drop by drop to the AgNO_3 solution until the color of the solution became completely clear. Electroless deposition of gold commenced when the Ag-treated membranes were placed in a bath containing 1500 ml of a plating solution at a temperature of 276 K. The aqueous plating solution consisted of 0.127 M Na_2SO_3 , 7.9×10^{-3} M gold in chemical form of $\text{Na}_3\text{Au}(\text{SO}_3)_2$, and 0.693 M HCHO . After 15 min to 2 h of electroless gold deposition, the membranes were rinsed in water and wiped gently with a methanol-soaked Kimwipes[®] EX-L tissue (Kimberly-Clark 34256) to remove gold from the outer surfaces. The membranes were then rinsed with water three times and cleaned by immersion in 25 % nitric acid for 15 h, followed by rinsing in water three times. Membranes were dried and stored in a vacuum desiccator.

Reactive ion etching

Reactive ion etching (RIE) was used to expose gold nanotubes grown within the pores of track-etched polycarbonate. The gold membranes were mounted on a cover slip and placed on a plasma electrode inside the RIE system (Plasma Therm 1441 RIE at the Wisconsin Center for Applied Microelectronics). The frequency of the RF generator was 13.56 MHz with a power of 100 W. After the RIE chamber was evacuated, dioxygen gas was introduced at a flow rate of $15 \text{ cm}^3 \text{ min}^{-1}$ and the chamber pressure was maintained at 5×10^{-6} bar. The etch rate was 156 nm min^{-1} , and the etching time was varied to achieve the desired length of gold nanotubes to be exposed.

Reaction kinetics studies

Reaction kinetics studies of CO oxidation with polyoxometalate compounds over gold nanotube membranes were conducted using an apparatus consisting of three main sections: i) the feed section, where the gas and liquid inlet compositions are fixed, ii) the membrane reactor, where the reaction takes place, and iii) the analysis section, where the products are quantified.

In a typical experiment, the feed to the membrane reactor consisted of a gaseous stream on one side of the membrane and a liquid stream on the other side. The composition of the gas stream was fixed by mixing the appropriate flow rates of carbon monoxide (AGA, commercial grade, 99.9%) and dinitrogen (Praxair, 99 % purity) at a total pressure of 1 bar. These gases were purified using Alltech molecular sieve traps to remove traces of hydrocarbons and water. Further purification of carbon monoxide (i.e., elimination of iron carbonyls) was achieved by flowing this gas through a glass U-tube heated to 473 K. The total flow rate of gas feed to the membrane reactor was $50 \text{ cm}^3 \text{ min}^{-1}$. All flow rates were fixed using mass flow controllers from Hasting Instruments. The liquid feed consisted of pure water or an aqueous solution of a polyoxometalate compound. Millipore water was used for the liquid feed and also for the preparation of all solutions. All liquids were continuously degassed by sparging with N_2 at $100 \text{ cm}^3 \text{ min}^{-1}$. A typical flow rate of liquid to the membrane reactor was $1 \text{ cm}^3 \text{ min}^{-1}$, as delivered using a PEEK digital pump from LabAlliance.

The reactor consists of gas and liquid chambers. The gold membrane is placed between these chambers using a pair of membrane holders containing arrays of 1/4-inch holes. The chambers and the holders are made of polycarbonate. Each chamber has a volume of 40 cm³, and the gas or liquid streams are distributed at the bottom of the corresponding chamber using a channel with a row of evenly spaced holes. Each chamber has an o-ring in a groove to ensure that no leaks occur between the chambers and the membrane holders. For studies of membranes that had been subjected to reactive ion etching, the etched side was positioned to face the gas stream. The area of a single membrane directly exposed to each reaction chamber is 96 cm². Prior to collecting reaction kinetics data, both chambers were purged with N₂ at 100 cm³ min⁻¹ at least 1 h. The liquid chamber was then closed and N₂ was kept flowing through the gas chamber. Subsequently, the liquid feed was pumped into the corresponding chamber, and the outlet valve was opened when the chamber was full with liquid. At this point, CO was fed to the reactor. All reactions in this study were conducted at room temperature (approximately 298 K). The gas and liquid streams flow out from the reactor at the tops of the corresponding chambers through channels with evenly spaced holes. The transport of gas to the liquid chamber or the transport of liquid to the gas chamber can be controlled using back-pressure regulators (Tescom Corporation) at the effluent of each stream. Under the reaction conditions used in this study, the pressure gradient was kept below 0.35 bar to avoid the transport of gas to the liquid chamber, and the pressure gradient was maintained above 0.04 bar to prevent the flow of liquid to the gas chamber.

The feed and the products in the effluent gas streams were analyzed with a gas chromatograph (Hewlett Packard 5890) equipped with a TCD, a 30-foot Alltech column packed with 120/100-mesh Hayesep DB, and using nitrogen as a carrier. The column was initially kept at 313 K for 10 min, and the temperature was then ramped at 20 K min⁻¹ to 513 K, where it was kept for 10 min. The temperature program allows the analysis of non-condensable gases and water vapor. For gaseous streams with low concentrations of non-condensable gases, further analyses were conducted with a Shimadzu GC-8A, which was equipped with a TCD and a 30-foot Alltech column packed with 120/100-mesh Hayesep DB. This GC was operated isothermally at 323 K, and had a cold trap (at 193 K) at the inlet to condense water vapor, thus allowing faster and

cleaner analyses of the gas stream. Both gas chromatographs were calibrated using customized mixtures of H₂ in N₂, CO in N₂, and CO₂ in N₂ from AGA.

Energy storage

Two different reactor systems were employed to chemically reduce solutions of polyoxometalate compounds at 298 K: a semi-batch type reactor and a pressurized batch reactor. The semi-batch reactor was first purged with 50 cm³ min⁻¹ of N₂ for at least 1 h, and then 50 cm³ min⁻¹ of CO was fed continuously at 1 bar through a fritted gas cylinder wrapped with a sheet of gold nanotube membrane, which was immersed in 250 cm³ of polyoxometalate solution. The reactor was a three-neck glass vessel (500 cm³ volume) with a magnetic stirrer and a water-cooler condenser at the gas outlet. The gaseous product stream was analyzed using the on-line GC employed in reaction kinetics studies until no further CO₂ was produced. The pressurized batch reactor was purged three times with CO and then filled with CO at a pressure of 15 bar. The reactor was a stainless steel vessel (approximately 350 cm³ volume), and it was filled with 100 cm³ of the polyoxometalate solution placed in a glass liner with a magnetic stirrer in the presence of turnings of 1 sheet of gold nanotube membrane. The gas phase products were analyzed using the same GC for kinetics studies every 3 hours by releasing pressure, followed by pressurizing with CO at 15 bar again. This release of gas phase and pressurization of CO was repeated until no further CO₂ was produced.

Fuel cell studies

Various types of fuel cells were employed to investigate the generation of electrical energy from reduced polyoxometalate solutions produced by oxidation of CO on gold nanotubes, having the following combinations of (anode)/(cathode): 1) (gold nanotubes)/(Pt/C), 2) (gold nanotubes)/(gold nanotubes), 3) (graphite on carbon paper)/(Pt/C), and 4) (graphite on carbon paper)/(graphite on carbon paper). The gold anode and cathode (4 × 4 cm size) were fashioned from gold nanotube membranes (gold deposited for 2 h without removing the surface gold to improve electric conductivity), and the Nafion[®] membrane and Pt/C cathode were purchased from Aldrich (Nafion[®] 117, 27467-4) and h-tec (Item 1996E), respectively. Carbon paper (E-TEK, B-3/2050A-2050)

was used to make electrodes loaded with graphite (Carbone of America, Ultra F purity). A slurry of above powder with an aqueous solution of polyvinyl alcohol (Aldrich, 34840-6) was pasted on one side of the carbon paper, and the electrode was then heat-treated in a helium atmosphere at 573 K for 4 h.

The Nafion[®] membrane was sandwiched between the anode and cathode electrodes, and this assembly was placed between a pair of stainless steel current collector screens. The volumes of the anode and cathode chambers were equal to approximately 2 cm³. The reduced polyoxometalate solution (blue color) was fed through anode chamber at a flow rate 1 cm³ min⁻¹. The cathode chamber was supplied with 10 cm³ min⁻¹ of O₂ for the Pt/C cathode, or it was supplied with oxidized polyoxometalate solution (yellow color) at a flow rate 1 cm³ min⁻¹ when a gold nanotube membrane or carbon was employed as the cathode. As illustrated in Figure 1, the color of polyoxometalate solution changed reversibly between blue and yellow, depending on the electron transfer. The current density was determined by measuring voltages generated by the fuel cell when it was loaded with a variable resistance from 9000 to 0.01 Ω (1433-W Decade Resistor, General Radio USA).

Supplementary Table and Figures

Table S1.

Figures S1 and S2.

Table S1. Storage of energy by oxidation of CO with polyoxometalates on gold nanotubes and generation of electrical energy from fuel cell at 298 K

Polyoxometalate	CO oxidation			Hydrogen-storage solution		
	Molarity (M)	P _{CO} (bar)	Reactor	Total CO ₂ (μmol) ^a	e ⁻ /Keggin ^b	e ⁻ /Keggin ^c
H ₃ PMo ₁₂ O ₄₀	0.01	1	semi-batch	4400	3.52	
	0.05	1	semi-batch	21000	3.36	3.00
	0.1	15	batch	16300	3.26	4.95
	0.5	15	batch	122000	4.89	4.25
	1.0 ^d	15	batch	122300	4.45	4.10
H ₃ PW ₁₂ O ₄₀	0.01	1	semi-batch	250	0.20	

^a Total amount of CO₂ produced in gas phase and measured by GC. ^b Number of electrons stored per Keggin unit, measured by the amount of CO₂ production. ^c Number of electrons stored per Keggin unit, calculated by integrating the electric current (in amperes). ^d CO-pressurized batch reaction with liquid amount of 55 cm³.

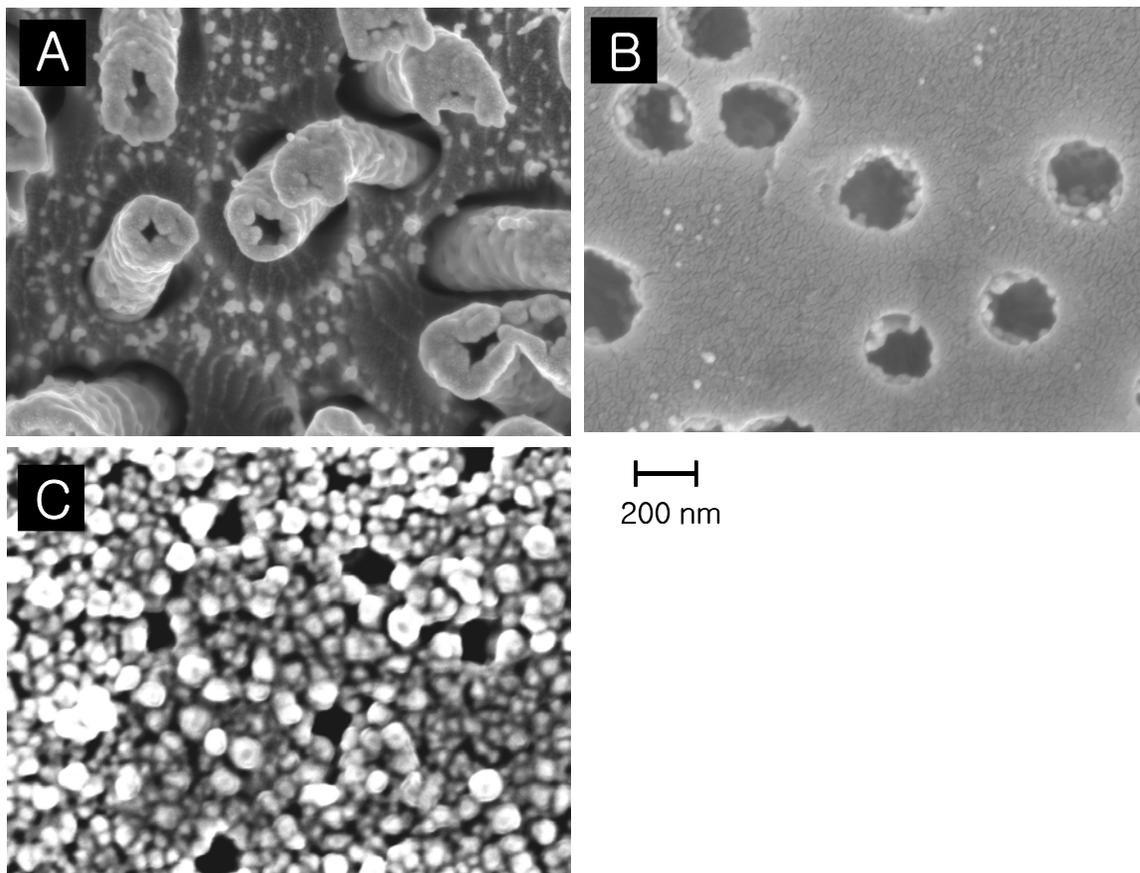


Figure S1 Field-emission scanning electron microscopy images of gold nanotubes used as membrane catalysts for CO oxidation and electrodes for fuel cell with a scale bar of 200 nm. Gold nanotubes formed by electroless deposition for 2 h after RIE (A), 0.25 h without surface gold (B), and 2 h with surface gold (C).

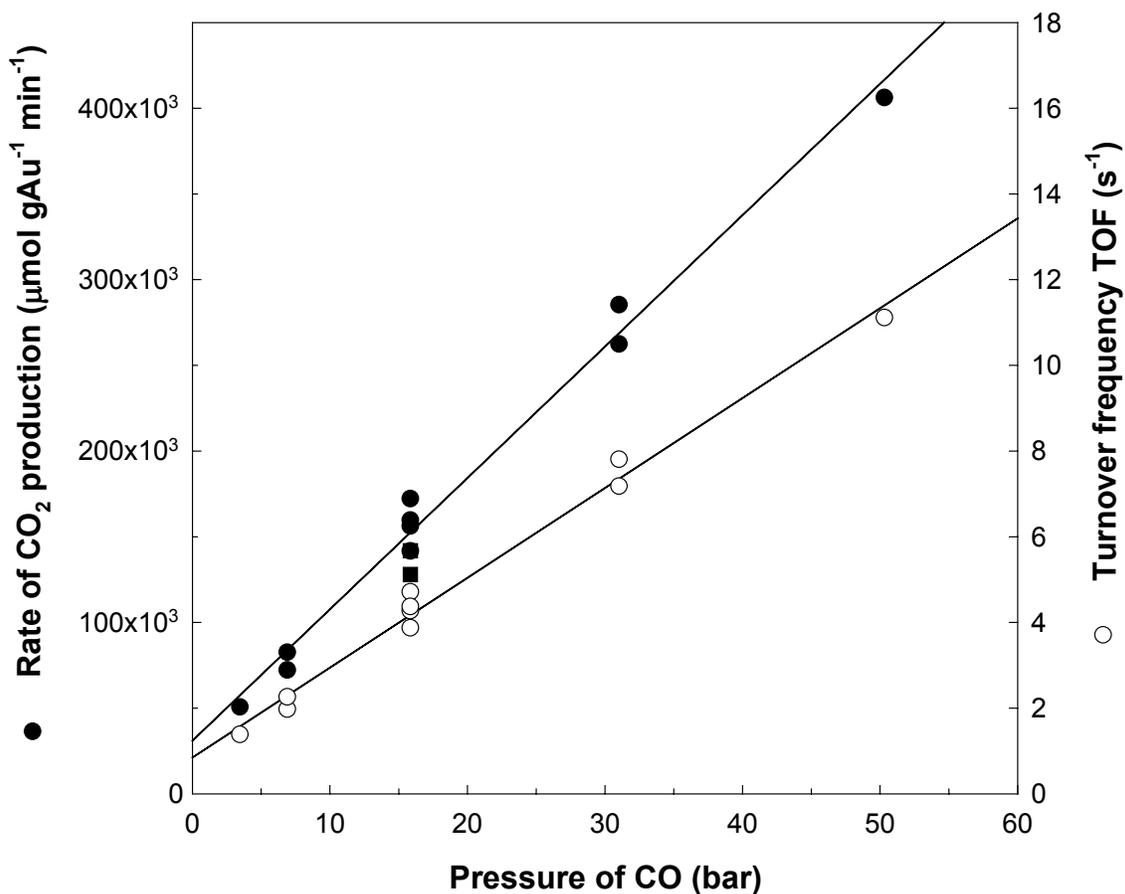


Figure S2 Rate of CO oxidation with polyoxometalate (POM, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) on gold nanoparticles supported on carbon (filled circles for rate and empty circles for TOF) and on titania (filled squares for rate). Amount of POM = 20 cm³; concentration of POM = 0.05 M; amount of 0.8 wt% Au/C (World Gold Council, Sample 4D with water content of 40 wt%) = 30 mg; amount of 1.5 wt% Au/TiO₂ (World Gold Council, Sample 18A) = 50 mg. Rates were measured at reaction time of 10 min.