- SUPPORTING INFORMATION -

Nanoporous Gold Assemblies of Calixarene-Phosphine-Capped Colloids

Christian Schöttle,^a Ezra L. Clark,^{ab} Audrey Harker, Andrew Solovyov,^a Alexis T. Bell,^{ab} Alexander Katz^{*a}

- ^a Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, California 94720, USA.
- ^b Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.
- * Email: <u>askatz@berkeley.edu</u>

1. Analytical tools

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM): High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted with a modified, double aberration-corrected FEI Titan³ 80-300 microscope operating at 300 kV and a FEI Tecnai F20 microscope operated at 200 kV. HAADF-STEM samples were prepared by evaporating suspensions in dichloromethane on amorphous carbon (Lacey-)film suspended on copper grids. Average particle diameters were calculated by statistical evaluation of at least 100 particles (ImageJ 1.47v software).

Scanning electron microscopy (SEM): Scanning electron microscopy (SEM) was performed on a FEI Quanta 3D FEG operated at 15 – 30 kV. Samples were prepared as described for HAADF-STEM.

UV-Vis spectroscopy: UV–Vis spectroscopy of gold nanoparticles in dichloromethane solutions was performed with a Varian Cary-400.

Electrochemical Characterization: All electrochemical measurements were conducted in a custom gastight electrochemical cell machined from PEEK.¹ The cell was sonicated in 20 wt. % nitric acid and thoroughly rinsed with DI water prior to all experimentation. The working and counter electrodes were parallel and separated by an anion-conducting membrane (Selemion AMV AGC Inc.). Gas dispersion frits were incorporated into both electrode chambers in order to provide ample electrolyte mixing. The exposed geometric surface area of each electrode was 1 cm² and the electrolyte volume of each electrode chamber was 1.8 mL. The counter electrode was a glassy carbon plate (Type 2 Alfa Aesar) that was also sonicated in 20 wt. % nitric acid prior to all experimentation. Platinum was not used as the anode electrocatalyst due to the possibility of contaminating the cathode with Pt.² The working electrode potential was referenced against a Ag/AgCl electrode (Innovative Instruments Inc.) that was calibrated against a homemade standard hydrogen electrode (SHE). A 0.05 M Cs₂CO₃ (99.995% Sigma Aldrich) solution prepared using 18.2 MΩ DI water was used as the electrolyte. Metallic impurities in the asprepared electrolyte were removed before electrolysis by chelating the solution with Chelex 100 (Na form Sigma Aldrich).³ Both electrode chambers were sparged with CO₂ (99.999% Praxair Inc.) at a rate of 5 sccm for 30 min prior to and throughout the duration of all electrochemical measurements. Upon saturation with CO₂ the pH of the electrolyte was 6.8, which was maintained throughout the duration of chronoamperometry.

Electrochemistry was performed using a Biologic VSP-300 potentiostat. All electrochemical measurements were recorded versus the reference electrode and converted to the RHE scale. Potentiostatic electrochemical impedance spectroscopy (PEIS) was used to determine the uncompensated resistance (R_u) of the electrochemical cell by applying voltage waveforms about the open circuit potential (OCP) with an amplitude of 20 mV and frequencies ranging from 50 Hz to 500 kHz. The potentiostat compensated for 85% of R_u *in-situ* and the last 15% was post-corrected to arrive at accurate potentials. The electrocatalytic activity of each electrode and surface alloy was assessed by conducting chronoamperometry at -1.5 V vs RHE for 40-50 min.

Product Analysis: The effluent from the electrochemical cell was introduced directly into the sampling loop (250 μ L) of an Agilent 7890B gas chromatograph (GC) equipped with a pulsed-discharge helium ionization detector (PDHID). The constituents of the gaseous sample were separated in He (99.9999% Praxair Inc.) using a Hayesep-Q capillary column (Agilent) in series with a packed ShinCarbon ST column (Restek Co.). After sampling the reaction effluent, the column oven was maintained at 50 °C for 1 min followed by a temperature ramp to 250 °C at 30 °C/min, which was maintained for the duration of the analysis. The signal response of the PDHID was calibrated by analyzing a series of NIST-traceable standard gas mixtures (Airgas Inc.).

Electrochemical Surface Area (ECSA): The relative electrochemically active surface areas of the nanoporous gold assemblies studied herein were determined by measuring the capacitance of the electrode-electrolyte interface. This was accomplished by measuring the scan rate dependence of the capacitive charging current during cyclic voltammetry in a potential window where no Faradaic processes occurred (\pm 50 mV vs OCP). The capacitive charging was measured at scan rates of 100, 200, 300, 400, and 500 mV/s, with the slope of the corresponding line being equivalent to the capacitance of the electrode-electrolyte interface. The relative magnitudes of the capacitance of the electrochemical double layer were assumed to be equivalent to the relative surface areas of the nanoporous gold assemblies. In order for this assumption to be valid the specific capacity of the electrode-electrolyte interface must not change based on the slight variations in the calixarene ligands between samples, which are utilized to prevent nanoparticle agglomeration.

2. Experimental Details

General: The synthesis of **1a**, **2a**, **3a**, **1b**, **2b** and **3b** were described elsewhere.¹

Electrode preparation: Glassy carbon plates (Alfa Aesar, type 2, 2 mm thick) were cut in sqares with 2.2 cm length. They were pretreated with 1N Nitric acid (Sigma-Aldrich, \geq 99.999% trace metals basis) for 2 hours. Followed by rinsing with water (Millipore), *n*-hexane and 2-propanol. After polishing with 1 µm and 50 nm alumina the electrodes were rinsed and sonicated in water.

The calixarene-functionalized Au nanoparticles were drop casted from 0.3 ml ethanol solution to yield a loading of 2.12 mg gold per cm⁻².

3. Calixarene-stabilized gold cluster building blocks. (1b, 2b and 3b)



Figure S1: HAADF-STEM images of the as-prepared phosphine calixarene capped Au nanoparticles: a) detail image of **1b** with a mean-size diameter of 0.9 ± 0.1 nm, b) overview image of **2b** with a mean-size diameter of 1.1 ± 0.2 nm,⁴ c) detail image of **3b** with a mean size diameter of 1.0 ± 0.2 nm.



Figure S2: HAADF-STEM overview images of 1b.



Figure S3: Size distribution of **1b** by statistical evaluation of at least 100 nanoparticles on HAADF-STEM images $(0.9 \pm 0.1 \text{ nm})$.



Figure S4: HAADF-STEM images of 3b.



Figure S5: Size distribution of **3b** by statistical evaluation of at least 100 nanoparticles on HAADF-STEM images $(1.0 \pm 0.2 \text{ nm})$.

4. Nanoporous gold assemblies (1, 2 and 3)



Figure S6: UV-Vis spectra of 1b (black – labeled as-prepared) and 1 (red – labeled after constant potential).

Table S1: Electrochemically active surface areas of 1 - 3.

Compound:	Relative specific surface area
1	2.91
2	3.31
3	1.00



Figure S7: HAADF-STEM images of 1.



Figure S8: HAADF-STEM images of 2.



Figure S9: HAADF-STEM images of 3.



Figure S10: HAADF-STEM image of **3** showing beam damage after electron beam irradiation, due to the decomposition of the organic calixarene ligand.



Figure S11: SEM images of 2.



Figure S12: SEM images of 3.

5. Dodecanethiol-capped Au nanoparticles



Figure S13: HAADF-STEM of as-prepared dodecanthiol-capped Au nanoparticles.

6. References:

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