

Supporting Information

I. EXPERIMENTAL METHOD

Gold nanoparticles were dispersed on a glass substrate using the block copolymer lithography (BCPL) method.¹ A mixture of 25.4 mg of the diblock copolymer [polystyrene_{81,000}-*block*-poly(2-vinylpyridine)_{14,200} (Polymer Source, Inc.) and 5 ml of toluene was stirred in a nitrogen purged and dark environment and stirred overnight, about 8 mg of H₂AuCl₄·H₂O were added, and this solution was stirred for 90 hours.

The glass substrates were dipped into the block copolymer solution at a constant rate of 50 $\mu\text{m}/\text{sec}$, held for 5 seconds, and then raised out of the solution at the same rate. The substrate was allowed to dry in open air and was then placed in an oxygen plasma for 10 minutes to remove the polymer, leaving only the dispersion of gold particles. The plasma was generated using an Evenson cavity in a 9 mm diameter tube. The net cavity power was between 20 and 30 W. The cavity pressure was approximately 600 mTorr and the oxygen flow was 1 sccm.

Shown in Figure 1 is an SEM image of a typical array of Au nanoparticles produced by the BCPL method. The average size of the particles is 23 ± 5 nm. The films resist light scratching indicating that the particles are chemically bonded to the substrate. A typical sample size was 5 x 12 mm, and only half of the sample was dipped in the BCP solution.

The particle density was highest near the lower edge of the sample, and all results discussed here used this high-density region. A transmission spectrum of the high-density region is shown in Figure 2, showing a strong plasmon resonance absorption peak.

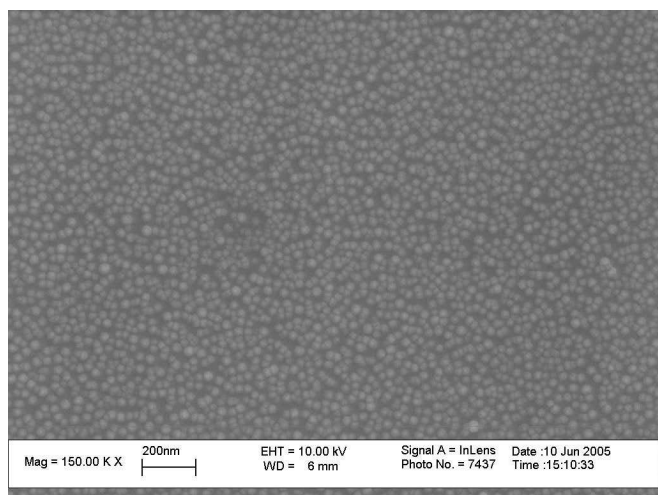


FIG. 1: Scanning electron micrograph of a monolayer array of Au nanoparticles produced by BCPL on SiO₂. The gold particles have an average diameter of ~ 23 nm.

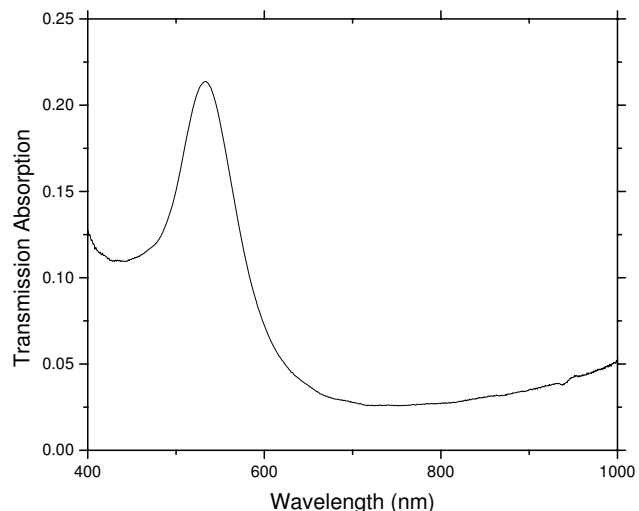


FIG. 2: A typical transmission absorption spectrum for the arrays of 23 nm Au nanoparticles on glass used in this experiment (Figure 1) The plasmon resonance is ~ 533 nm.

A. PACVD Reactor System

A schematic of the PACVD reactor system and is shown in Figure 3. The main components related to CVD are a sample cell, a pressure control system, and a precursor delivery system. The sample cell is constructed from a stainless steel vacuum flange and a mating glass viewport. The system pressure is controlled by a vacuum pump working in conjunction with a motorized control valve and a pressure gage. The precursor delivery system consists of two mass flow controllers and a bubbler which holds the CVD precursor. Since the precursors used in these experiments condense at room temperature, the sample cell and all lines from the precursor delivery system are heated. The precursor is held in a stainless steel container, a bubbler, within an oven. Argon gas flows through the bubbler, and carries sublimated precursor vapor into the sample cell.

The optical components for the PACVD are also shown in Figure 3. The laser is a 532 nm, 40 mW (CW), air-cooled, diode-pumped, solid-state laser (Lasermate, Inc.). It is focused with an optical microscope using a 50X, long working-distance objective and three external lenses. The beam diameter was measured using the knife-edge method² to be 1.5 ± 0.1 μm . The maximum laser power measured at the sample is 21 mW and can be controlled by crossed polarizers. Mounted on one of the eyepieces of the microscope is a video camera to allow viewing during deposition, and on the other, is an optical power meter for measuring *in situ* the reflected power from the sample during deposition. An electro-

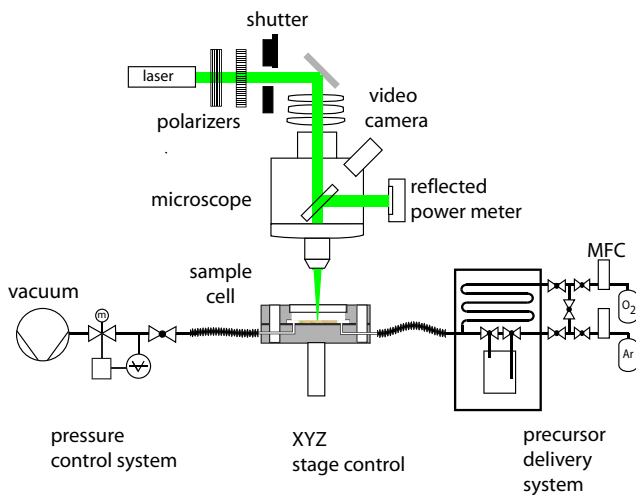


FIG. 3: Schematic of the PACVD experiment.

mechanical shutter is also placed in the beam path to control the exposure. The sample cell is mounted on a XYZ translation stage, which is under computer control.

B. Deposition Experiments

The first set of experiments were done using the met-alorganic Pb precursor $\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ (Epichem, Inc.).³ For these experiments, the bubbler was held at a temperature between 75 and 85 °C to insure adequate vapor pressure, and the sample cell was heated to 100 °C to avoid precursor condensation on the cell walls and window. No deposition was observed under these conditions in the absence of laser illumination. Importantly, this temperature is well below the temperature at which gold and lead form a eutectic or at which the precursors decompose.

The gas lines were kept above 100 °C to prevent the precursor from condensing. The Ar flow to the bubbler ranged from 2-50 sccm, and oxygen flow ranged from 0-2 sccm. Experiments were conducted with sample cell pressures in the range of 2–100 Torr.

The gas flow was first established and stabilized, and then the laser was focused onto the top surface of the sample, keeping the power low enough that no deposition resulted. Once the laser was focused, the power was increased to a level between 5 mW and the maximum laser

power of 21 mW. To form dots, the laser remained at the same spot for several minutes until measured laser reflectance began to decrease substantially, indicating the onset of deposition. The shutter was then closed, and the sample cell was translated so that a fresh area on the substrate would be exposed to the laser when the shutter was opened. To form lines, the beam was translated along the surface at a constant rate.

For the experiments depositing titania, the Ti precursor $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_2[\text{C}_{11}\text{H}_{19}\text{O}_2]_2$ (Epichem, Inc.) was

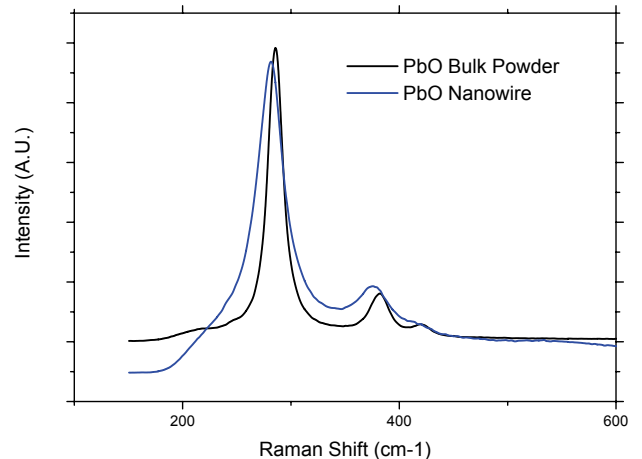


FIG. 4: Raman spectra of a commercial PbO powder and PbO nanowires grown by PACVD. The nanowire features are red-shifted and broadened compared to the bulk powder.

used.⁴ The run conditions were similar to those of the PbO experiments. The reactor pressure was kept constant at 5 Torr. The flow rates were 18 and 1 sccm of Ar and O_2 , respectively. Only full laser power was used in these experiments.

C. Micro-Raman analysis

The micro-Raman spectrometer used in the characterization of the PACVD deposits and the material standards was a Renishaw M1000. The laser wavelength was 514.5 nm. Shown in Figure 4 is a comparison of Raman spectra of a commercial PbO powder and PbO nanowires grown by PACVD. The features of the nanowires are red-shifted and broadened compared to the bulk powder.

¹ Jaramillo, T. F., Baeck, S.-H., Cuenya, B. R., and McFarland, E. W. *J. Am. Chem. Soc.* **125**, 7148–7149 (2003).

² Cohen, D. K., Little, B., and Luecke, F. S. *Appl Optics* **3**(4), 637–640 (1984).

³ Malik, M. A., OBrien, P., Motevalli, M., Jones, A. C., and Leedham, T. *Polyhedron* **18**(1641) (1999).

⁴ Jones, A. C. *J Mater Chem* **12**, 2576 (2002).