

Electronic Supplementary Information for

Monolithic nanoporous gold disks with large specific surface area, tunable plasmon resonance, and high-density, internal plasmonic hot-spots

1. Experimental Section

Chemicals and materials. The alloy sputtering target Ag_{82.5}Au_{17.5} (atomic percentage) was provided by ACI Alloys, INC. Argon gas (99.999%) was used for RF-sputter etching. Fusion classic syringe pumps and microliter syringes (250 µl) were purchased from Chemyx Inc. and Hamilton Company, respectively. Silicon wafers (3") were obtained from University Wafers, and the micro coverglasses (22×40 mm, No.1) were purchased from VWR. Ethanol (200 proof) was from Decon Laboratories, Inc. Nitric acid (ACS reagent, 70%), sodium dodecyl sulfate (ACS reagent, ≥99.0%), chloroform (anhydrous, ≥99.0%), and Latex beads (polystyrene beads, 10% aqueous suspension) with mean particle sizes 0.46, 0.6, 0.8 and 1.1 µm were purchased from Sigma Aldrich.

Characterization. The NPG disks were characterized by a scanning electron microscope (PHILIPS FEI XL-30 FEG SEM). The buoyant mass of NPG disks was measured in an aqueous suspension using Archimedes particle metrology system (Affinity Biosensors, CA) to characterize further the distribution of NPG disks with single particle resolution. XPS spectra were obtained using a PHI 5700 system equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.7$ eV). IR spectra were recorded with a Nicolet iS50 FT-IR spectrometer. A zeta potential analyzer from Particle Sizing Systems, Inc. (Nicomp 380 ZLS), operating in PALS mode, was used to measure the zeta potential of different aqueous NPG disk solutions at room temperature. A Cary 50 Scan UV-visible spectrometer was used to measure the UV-vis spectra ranging from 400 to 1000 nm, and the NIR region from 915 to 3000 nm was recorded with a Bruker Tensor 27 FT-NIR spectrometer.

Calculation method. Finite difference time domain (FDTD) method was employed to simulate the E-field of NPG disks and Au disks to understand their plasmonic properties. In the simulation,

periodic boundary condition was set to perfectly matched layer (PML), and the simulation grid size was 0.002 μm . The disks were simulated in the air condition without substrates. The monitor was located right on the top-surface of the disk.

2. Non-aggregating NPG disks

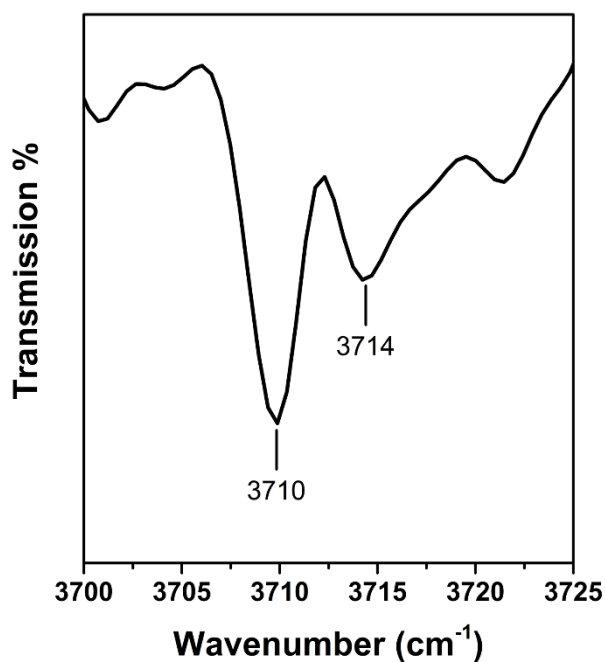


Figure S1. IR spectrum of 400 nm dried NPG disks. The aqueous NPG disk solutions were completely dried in a vacuum oven at 50 °C for 4 h before the measurement.

3. XPS reveals composition of NPG disks

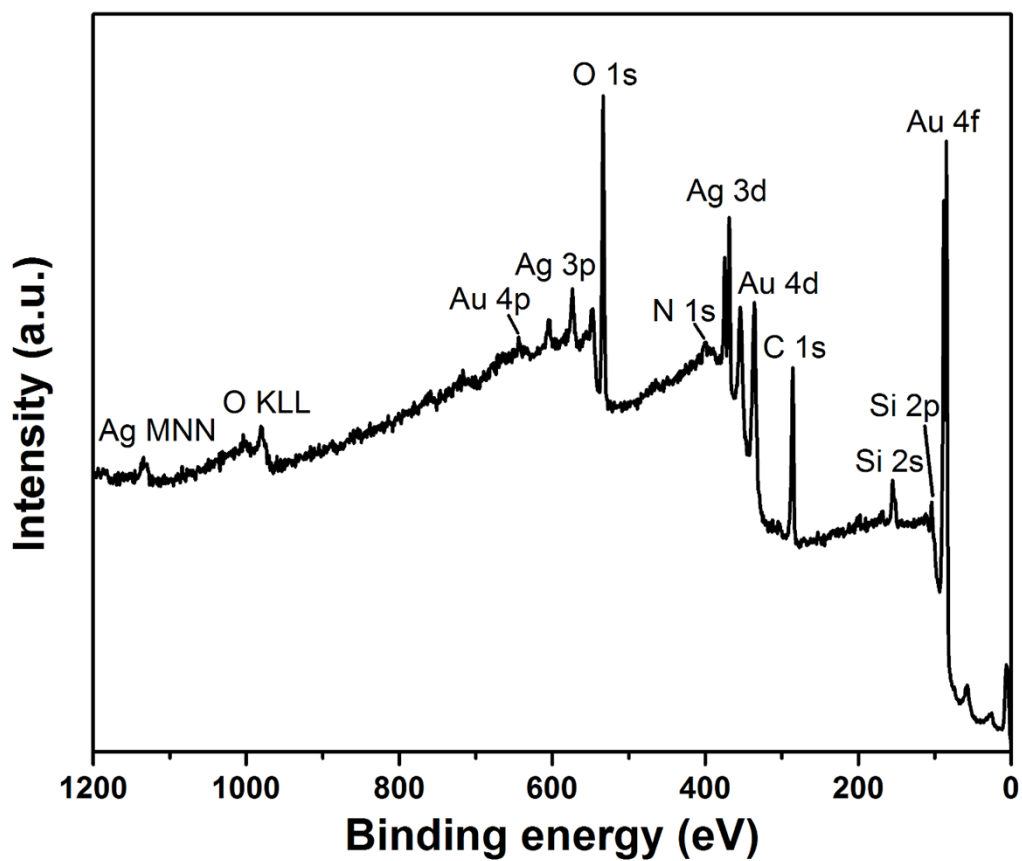


Figure S2. XPS spectrum of NPG disks. Aqueous NPG disk samples were drop-cast on a Si wafer and then dried in air prior to analysis by XPS.

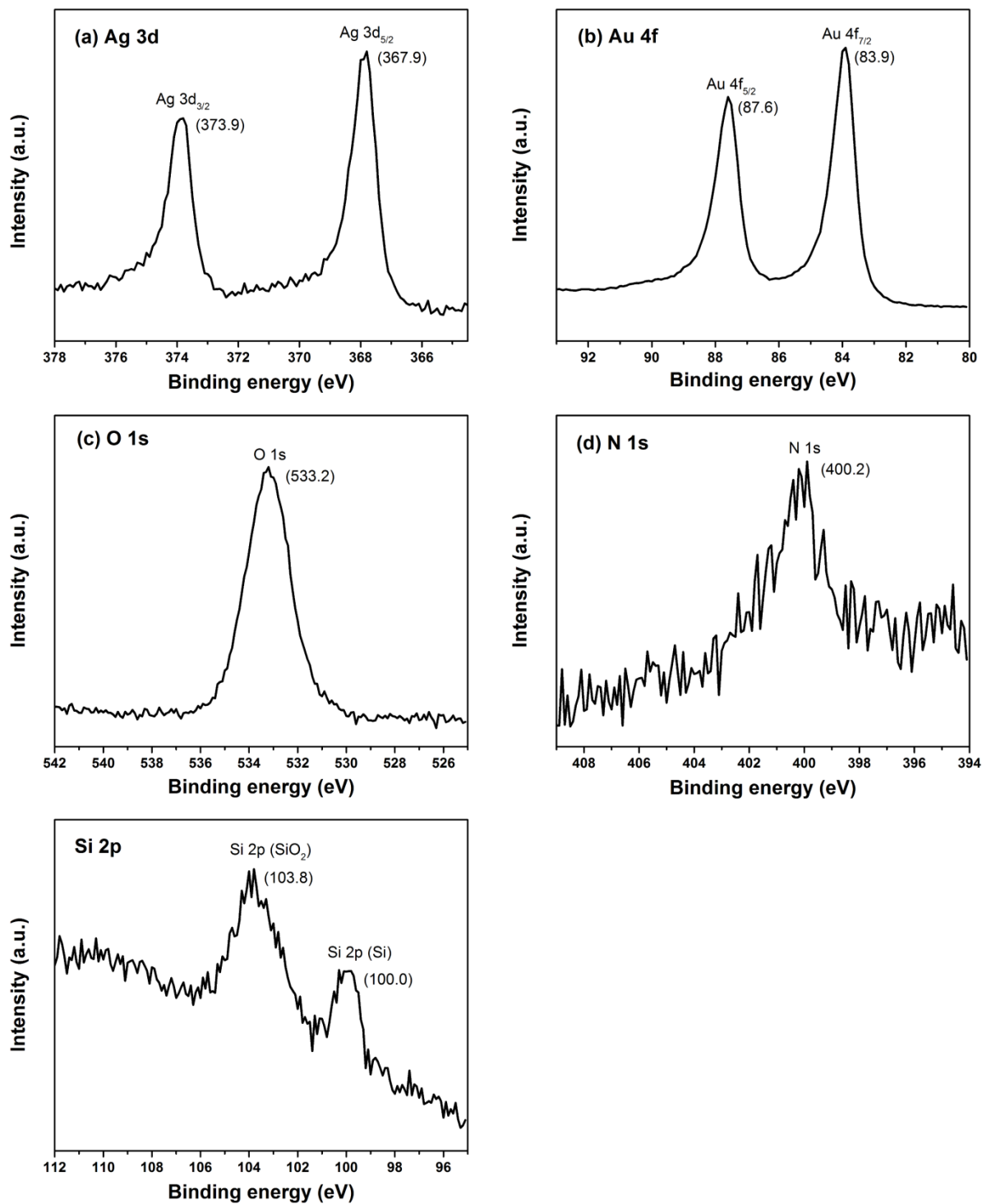


Figure S3. XPS spectra of the following regions: (a) Ag 3d, (b) Au 4f, (c) O 1s, (d) N 1s, and (e) Si 2p.

4. The buoyant mass

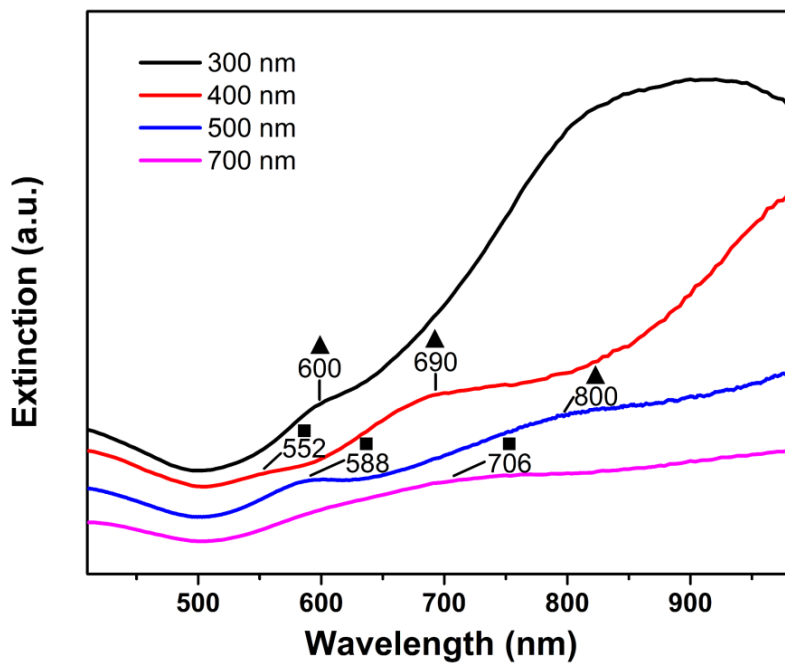
The histogram of 400 nm NPG disk buoyant mass distribution, with an average of $6.04 \times 10^{-14} \pm 7.6 \times 10^{-15}$ g, is shown in Fig. 2d. A *Hi-Q* sensor purchased from Affinity Biosensors, CA, was calibrated using NIST standard 335 nm polystyrene particles (Bangs Labs) to obtain a sensitivity (S) of mHz/fg. The buoyant mass (m_b) is calculated using the equation $m_b = \Delta f S$, where Δf is the change in resonant frequency of the sensor.

The buoyant mass of Au nanodisk was calculated using the equation:

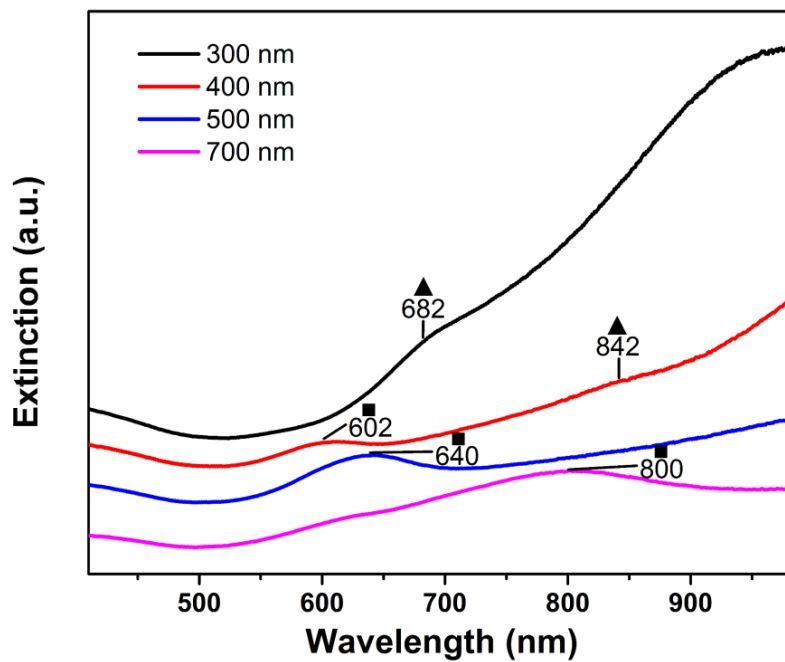
$$m_b = m_o \left(1 - \frac{\rho_f}{\rho_o}\right) \quad (1)$$

where m_b is the buoyant mass, and m_o is the dry mass of the sample. The parameters ρ_f and ρ_o are the densities of the sample and the fluid, respectively. The calculated buoyant mass of a single Au nanodisk was 17.2×10^{-14} g. Thus, the mass ratio of a NPG disk to an Au nanodisk is ~ 0.35 .

5. Zoom-in of Figure 3a and 4a between 410-980 nm



(a)



(b)

Figure S4. Extinction spectra of NPG disks having different diameters over the region from 410 to 980 nm: (a) in air and (b) in water.