Supporting Information

Experimental Section

Ag sputtering. The detailed fabrication procedure of porous carbon using interference lithography has been reported elsewhere. The carbon substrates were thoroughly rinsed with isopropyl alcohol before Ag sputtering. The films were deposited at 25°C onto the porous carbon/glass substrate surface using a 3” DC magnetron sputtering system. In order to maintain control over thin film conformality, thickness, and grain size, the Ag target was adjusted to a distance of 23.5cm from the substrate. Before initiating the deposition process, the vacuum chamber was allowed to pump to a base pressure of 1E-6 Torr. Vacuum chamber process pressure was controlled using a combination of argon mass flow control and a variable speed turbo molecular pump. After establishing the correct turbo pump conductance, argon flow into the vacuum chamber continuously adjusts to maintain the desired 3 mT operating pressure. Following pressure stabilization, DC power supplied to the magnetron was ramped at a rate 0.5 watts/second to a final set point of 55 watts. Under these operating conditions a deposition rate of 0.9 Å/s was achieved. A shutter mechanism positioned above the target provided a means for precisely controlling exposure of the sample to the sputter source. Processing time ranged from 150 to 3300 seconds depending on the desired Ag film thickness.

Molecule adsorption and desorption. Rhodamine 6G, rhodamine B, and 4-aminothiophenol were adsorbed at Ag substrates from their 0.1 mM ethanol solution for over 30 min. the substrates were thoroughly rinsed with ethanol, isopropyl alcohol, water, and dried slowly by nitrogen gas. The Raman spectrum was taken in air at room temperature. The electrochemical desorption of 4-aminothiophenol was performed using CHI 660 potentiostat. 0.1 M NaOH in 1:1 ethanol:water was used as electrolyte. Pt was used as a counter electrode and silver/silver chloride wire was used as a reference electrode.

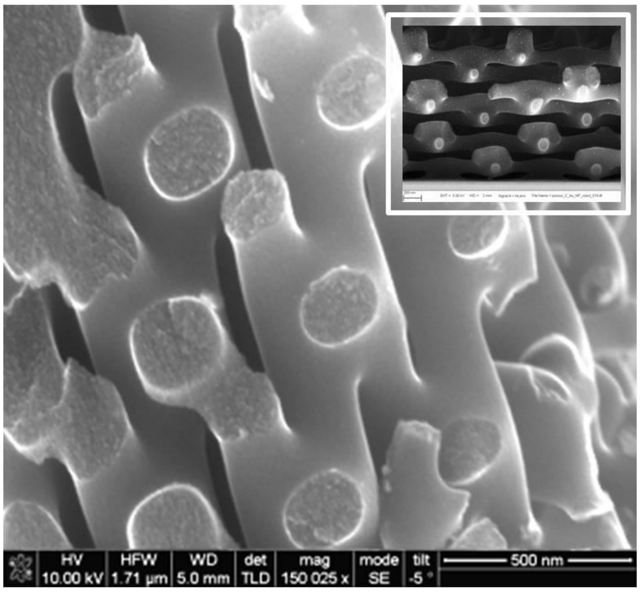

Figure S1. SEM images of side and cross view of the porous carbon substrate.

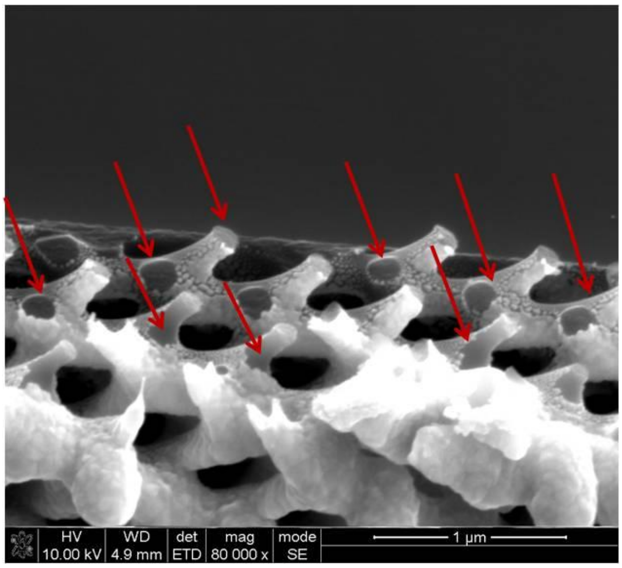

Figure S2. Cross section SEM image of Ag thin film deposited at porous carbon substrate. Ag sputtering time: 2200 s. The arrows point to the broken arms. Note: picture is inverted to emphasize underside coatings on bottom layer.

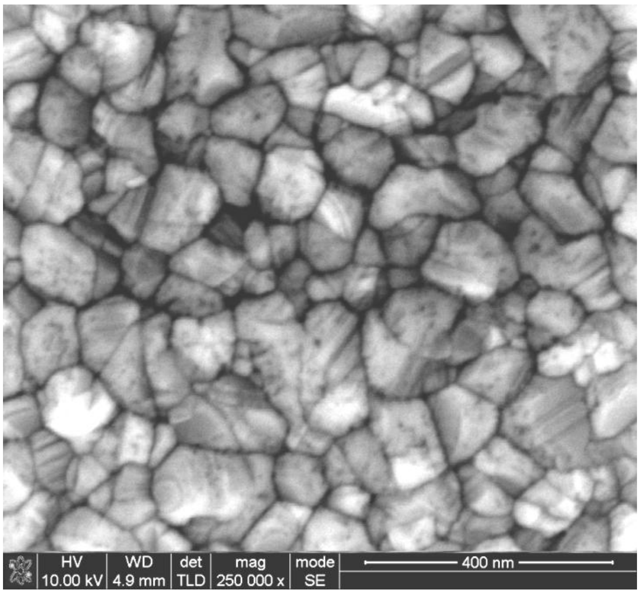

Figure S3. SEM image of typical Ag island sputtered at planar carbon substrates.

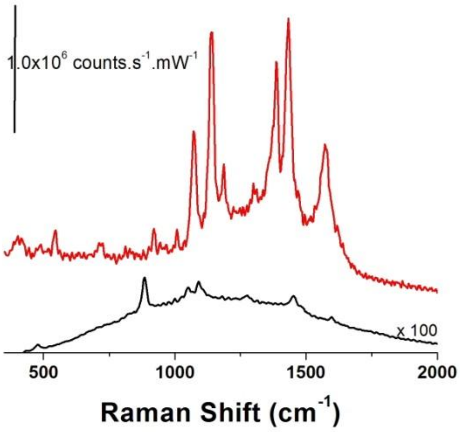

Figure S4.Comparison of Raman spectrum between adsorbed 4-aminothiophenol (ATP) for 2200 sec of sputtered silver onto porous carbon (red) and 0.1 X 10^3 M solution (black). Each spectrum was acquired with a WiTec Raman system with an excitation wavelength of 532 nm and 3.7 mW of incident laser power. For the porous structure a 0.001 s acquisition time was utilized whereas the solution necessitated a collection time of 0.3s. The ATP surface concentration was 2.2 x 10^{-8} mol/cm^2.

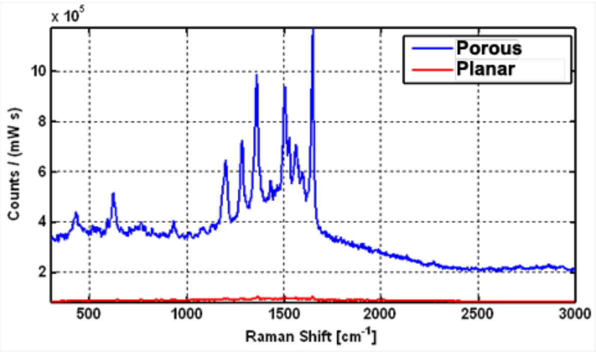

Figure S5. Comparison of adsorbed Rhodamine 6G for 1100 sec of sputtered silver onto porous (blue) and planar (red) carbon using an WiTec Raman system with an excitation wavelength of 532 nm, 0.01 s acquisition time, and 0.75 mW of incident laser power

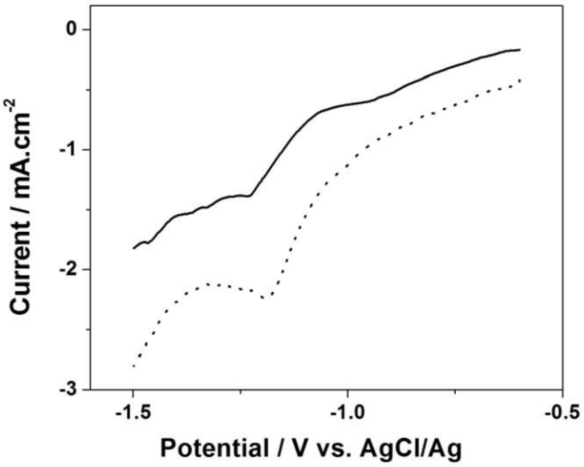

Figure S6. Typical cyclic voltammogram of electrochemical desorption of 4-aminothiophenol at porous (dotted) and Ag island substrates (solid). Electrolyte: 0.1 M NaOH in 1:1 ethanol:water. Scan rate: 50 mV/s.

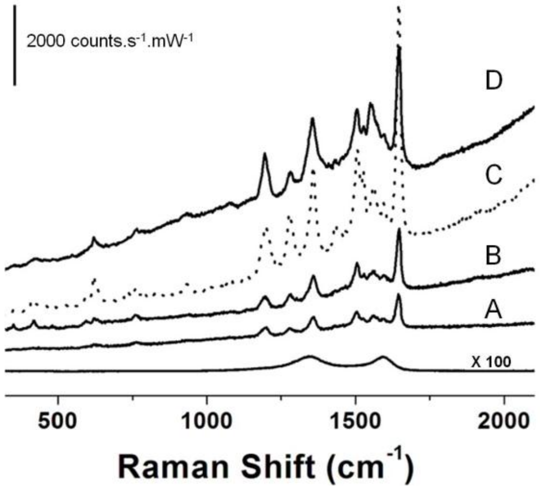

Figure S7. Raman scattering of rhodamine B at porous Ag substrates with increased film thickness from A to D. Ag was sputtered for 150 (A), 1100 (B), 2200 (C), and 3300 s (D), respectively. The spectrum of porous carbon itself was obtained at 50 mW, showing glassy and graphitic structural nature of the porous carbon template.