

Supporting information for

**Surface-Enhanced Raman Scattering of Uranyl in Aqueous Samples: Implications for Nuclear Forensics
and Groundwater Testing**

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Characterization of silver nanoparticles:

1

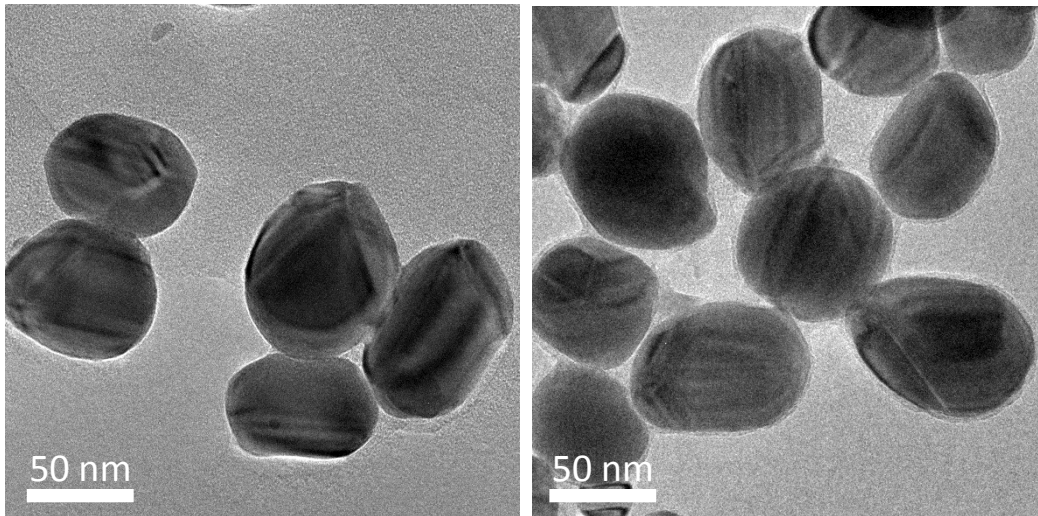


Figure S1: High-resolution transmission electron micrograph of citrate-capped silver nanoparticles before (left) and after (right) ligand exchange with glutathione. The comparison of these images indicate that the silver colloids are round and approximately 70 nm in diameter and have not changed due to ligand exchange.

2.

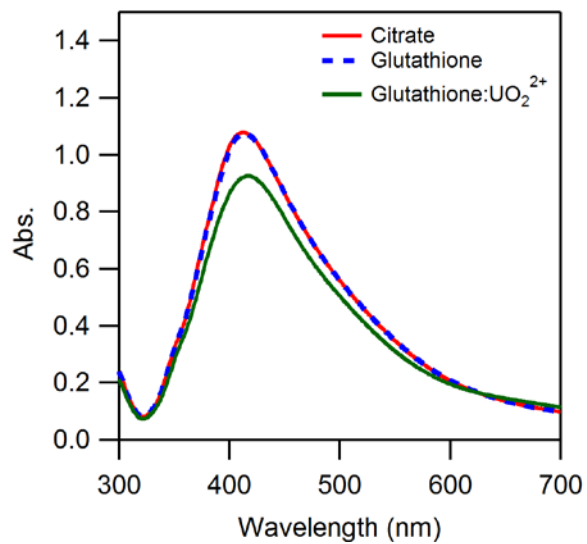


Figure S2: UV-Vis absorption spectra of the citrate capped silver colloids (red), silver colloids after ligand exchange resulting in glutathione functionalize particles (blue), and the glutathione functionalized colloids after addition of uranyl nitrate solution (green). The negligible change in the absorption spectrum after ligand exchange suggests little to no change in the size or aggregation state of the nanoparticles.

3.

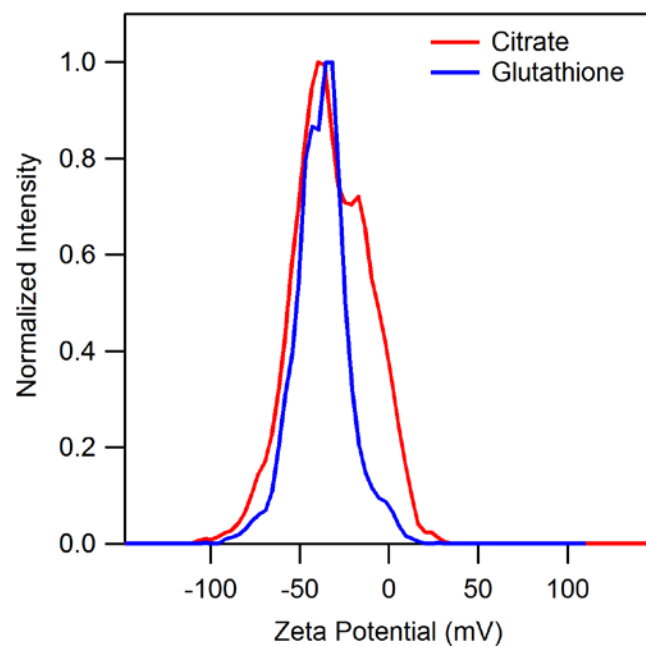


Figure S3: Zeta potential measurements of citrate-capped nanoparticles (red) and glutathione functionalized nanoparticles (blue). Both samples zeta potentials are approximately -35 mV, indicating that the ligand exchange reaction does not have a significant effect on the colloids stability in suspension.

4.

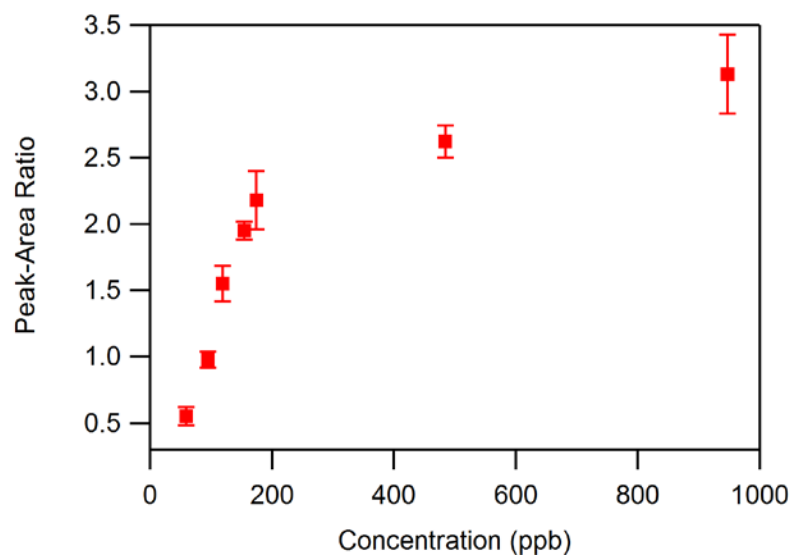


Figure S4: Left: Ratio of the uranyl symmetric stretch band area (834 cm^{-1}) to area of a ligand band (670 cm^{-1}) plotted as a function of concentration up to 1 ppm. This data demonstrates a leveling at higher uranyl concentrations indicating saturation of the nanoparticle surface.

5.

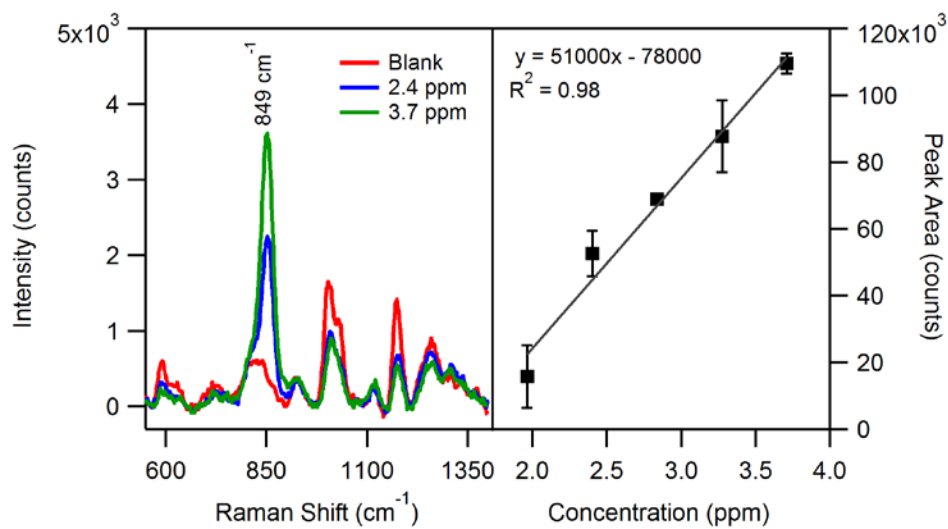


Figure S5: Left: Surface-enhanced Raman spectra of aminomethylphosphonic acid (APA) functionalized colloids (red) as well as in the presence of uranyl at 2.4 ppm (blue) and 3.7 ppm (green). Identical sample preparation was performed using gold colloids functionalized with aminomethylphosphonic acid (APA), a ligand previously used for the detection of uranium. The decreased shift of the uranyl symmetric stretch to 849 cm⁻¹ in the presence of APA from 867 cm⁻¹ in solution indicates weaker uranyl binding to APA than glutathione which shifts to 834 cm⁻¹.

Right: The area of the uranyl band after background subtraction of the spectrum is plotted as a function of concentration which is linear from approximately 1.5-3.7 ppm and yields a limit of detection of 0.404 ppm, which is significantly higher than our detection limit of 0.024 ppm. Error bars indicate the standard deviation of peak area from separately prepared replicate samples.

6.

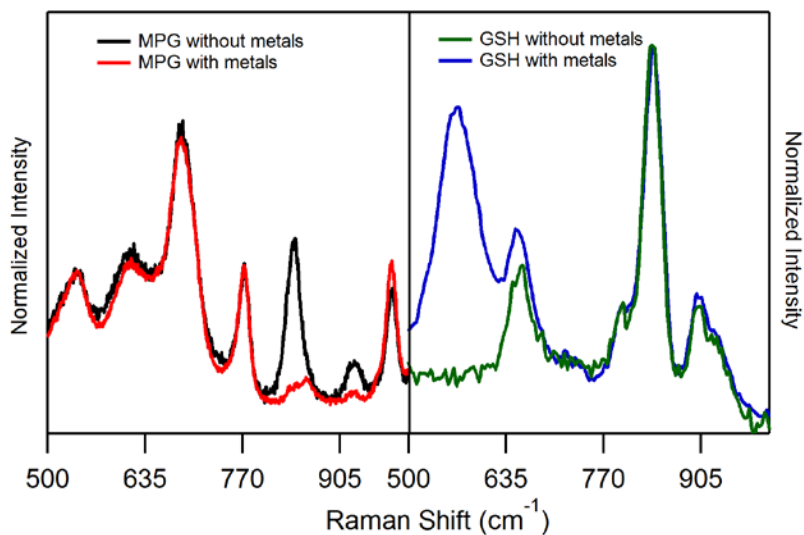


Figure S6: Left: Normalized SERS spectra of N-(2-mercapto-propionyl)glycine (MPG) functionalized particles in the presence of 175 ppb uranyl solution both without and with metal interferences likely to be present in groundwater (black and red respectively). Right: Normalized SERS spectra of glutathione-functionalized particles in the presence of 175 ppb uranyl solution both without and with metal interferences likely to be found in groundwater (green and blue respectively). Almost zero recovery of the uranyl symmetric stretch band (834 cm^{-1}) is seen for the MPG system while excellent recovery (84%) is seen for the GSH system. These results demonstrate that our method has potential for uranyl analysis of water with metal ion interferences present.