Supporting Information

HYBRID GOLD NANOPARTICLE - POLYOXOVANADATE MATRICES: A NOVEL SERS/SEIRA SUBSTRATE

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Additional analytical methods.

TEM.

2µL of the solutions were dried on a copper mesh grid. A Jeol 1400 TEM was used to determine the size of the particles on the grid.

SEM/EDX.

The samples as prepared for the TEM measurements were also used for SEM and EDX. Images and elemental mapping were obtained using a Hitachi S-5200 Cryo-SEM.

DLS/Zeta Potential.

A Zetasizer Nano ZS (Malvern Instruments, Malvern, UK) was used to determine the hydrodynamic diameter and the corresponding zeta potential of the particles. Measurements were performed in triplicate at 25°C
UV/Vis.
A Varian Cary 50 spectrometer with a quartz cuvette (path length 10 mm) was used. Each solution was analyzed from 1100 nm to 200 nm.

XPS.
For XPS measurements, a commercial instrument of Physical Electronics (PHI 5800) was used. 5 mL of the particle solutions were lyophilized and analyzed.

PXRD.
5 mL of the particle solution was lyophilized for obtaining a powder XRD using Cu-K-alpha radiation.

Synthesis and characterization of bare AuNPs prepared by the stainless-steel assisted method.
500 µL of an aqueous 1 % NaAuCl₄ · 2H₂O solution and 4.5 mL water were added to a 250 ml flask. The stainless-steel disc (diameter of 8 mm) was added to the solution and stirred at 60°C for 50 minutes. The stainless-steel disc was placed at the bottom of the flask underneath the stirrer so that the disc did not move under stirring. The product was separated in four 1.25 mL batches and centrifuged at 10,000 g for 20 minutes. The supernatant solution was discarded, and the AuNP were dispersed in water. The pure AuNP were stored under light protection at 4 °C. The particles were characterized by UV/Vis, TEM, EDX, IR, SEM, DLS and Zeta potential.

Figure S1: UV/Vis of pure AuNP in a 1:4 AuNP to water solution. The main absorbance is at 543 nm and no sign of aggregation was observed.
Figure S2: IR absorption of pure AuNPs dried at a Si ATR waveguide surface. The broad peak at 3400 cm$^{-1}$ is associated with residual water. Two strong peaks around 2900 cm$^{-1}$ are observed from a contamination in the instrument, and less pronounced peaks at 1750 cm$^{-1}$, 1600 cm$^{-1}$ and 1300 cm$^{-1}$, which also rise from residual water.

Figure S3: SEM image of the neat AuNPs.
Figure S4: EDX analysis of the bare AuNPs. The gold peak is associated with the gold nanoparticles. The copper peak results from the copper grid. The iron peak derives from the stainless-steel disk.

**Synthesis and characterization of POM-embedded AuNPs.**

For the AuNP-POM hybrid matrix, pure AuNPs were freshly synthesized using literature methods [Ref. 18]. When the reaction mixture was turning, red indicating the presence of AuNPs, 400 µL of a 100 mM NH₄VO₃ at pH 3.8, acidified with 10 mM HCl, was added to the solution. After several seconds red flakes were evident in the solution. After 2 minutes, the solution was centrifuged in four batches at 10,000 g for 20 minutes and re-dispersed in water. The functionalized AuNP were stored protected from light at 4 °C.
Figure S5: UV/Vis spectrum of the functionalized pure AuNPs with $V_{10}$. The absorbance was slightly shifted from 543 nm for the neat AuNPs to 564 nm. The absorbance of the POM-AuNPs itself appears enhanced in the UV/Vis spectrum. The absorption onset < 400 nm is based on LMCT transitions of the decavanadate.

Figure S6: IR absorbance of dried AuNP-POM at a Si ATR waveguide surface. At 1600 cm$^{-1}$, the ammonium and at 1000 cm$^{-1}$ the broad peak of the vanadium oxide are observed.
Figure S7: SEM image of the AuNP-POM network. The bright spots indicate AuNPs embedded in the POM network.

Figure S8: EDX analysis of the AuNP-POM hybrid matrix.
Figure S9: Powder XRD data of the POM-embedded AuNPs. The peaks correspond to the Bragg reflection of (111), (200), (220) and (311) a face centered cubic (FCC) gold lattice.
Figure S10: XPS spectra of the AuNP-POM. For XPS, the atomic concentration is presented in percent of the full substance; Au: 0.64 %, Fe: 12.18 %, V: 6.81 %, O: 43.52 %, N: 0.82 %, C: 36.04 %.

**DLS and Zeta-Potential.**

Table S1: DLS and Zeta Potential measurement of bare gold nanoparticles and functionalized particles.

|                  | DLS                  | Zeta-Potential      |
|------------------|----------------------|---------------------|
| Bare AuNPs       | 84.55 nm at PDI: 0.203 | 23.63 ± 8.22 mV     |
| AuNP-POM         | 942.07 ± 66.16 nm at PDI: 0.535 | -5.73 ± 3.99 mV     |
TEM images of Gold nanoparticles produced at different conditions.

Changing Temperature at low concentrations.

Figure S11: TEM images of AuNsP produced with 0.1 % NaAuCl₄ at 40 °C. The left image illustrate that still different shape of the particle occurs. On the right image two long rods can be seen along with some particles.

Figure S12: TEM images of AuNPs produced with 0.1 % NaAuCl₄ at 60 °C. The images illustrate larger AuNPs, which have a popcorn-like appearance.
Figure S13: TEM images of AuNPs produced with 0.1 % NaAuCl₄ at 80 °C. The left image shows very large gold flakes concentrated at one place. On the right, nanoparticles with different shapes are presented.

Changing NaAuCl₄ Precursor Concentration.

Figure S14: TEM images of AuNPs produced with 1 % NaAuCl₄ at 60 °C in 1.5 mL. Both show the appearance of different shapes.
Figure S15: TEM images of AuNPs produced with 1 % NaAuCl₄ at 60 °C in 4.5 mL. Both images show all kinds of shapes.

Figure S16: TEM images of AuNPs produced with 1 % NaAuCl₄ at 60 °C in 9.5 mL. Both images again represent all kinds of shapes.
Figure S17: TEM images of AuNPs produced with 1 % NaAuCl₄ at 60 °C in 14.5 mL. The particles already started to aggregate, but different shapes are still evident.

Changing the added volume.

Figure S18: TEM images of AuNPs produced with 100 µL of 1 % NaAuCl₄ at 60 °C.
Figure S19: TEM images of AuNPs produced with 200 µL of 1 % NaAuCl₄ at 60 °C.

Figure S20: TEM images of AuNPs produced with 300 µL of 1 % NaAuCl₄ at 60 °C.
Figure S21: TEM images of AuNPs produced with 700 µL of 1 % NaAuCl₄ at 60 °C.