Electronic Supporting Information (ESI)

Meniscus-Confined Capping Free 3D Printed Gold Nanoparticles for Quantitative SERS Detection of Bisphenol A

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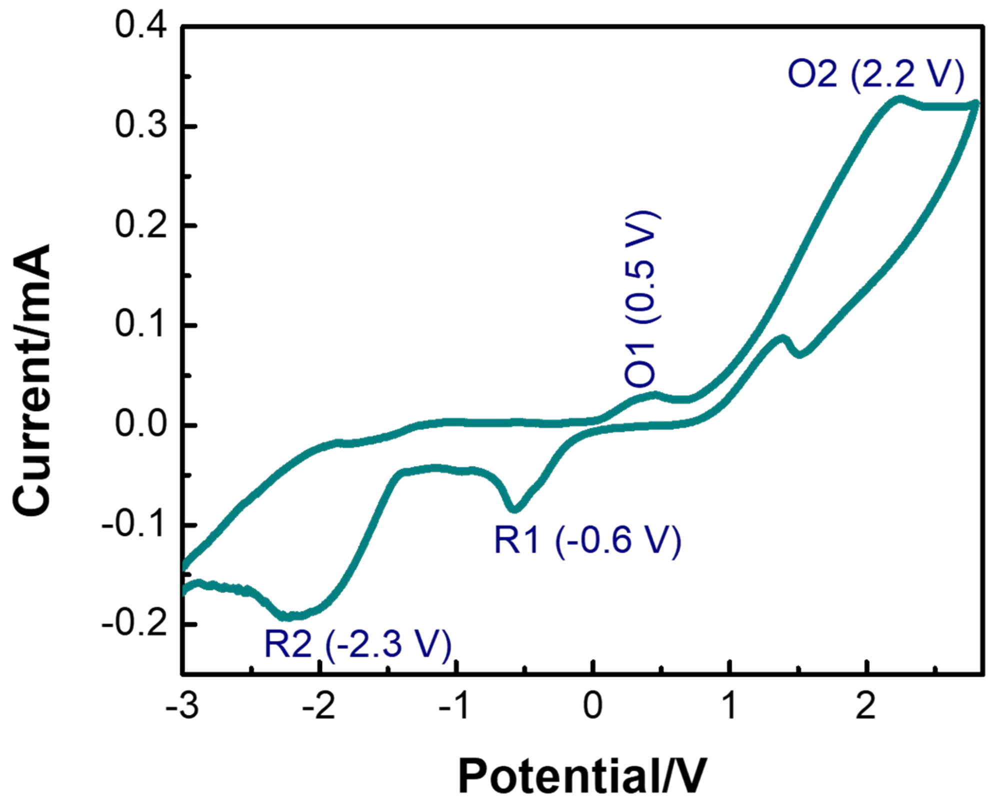

Figure SI1. CV curve of 5 mM $HAuCl_4$ electrolyte to determine the optimum deposition potential for preparing 3DPAu substrates. The scan rate was 50 mVs^{-1}.

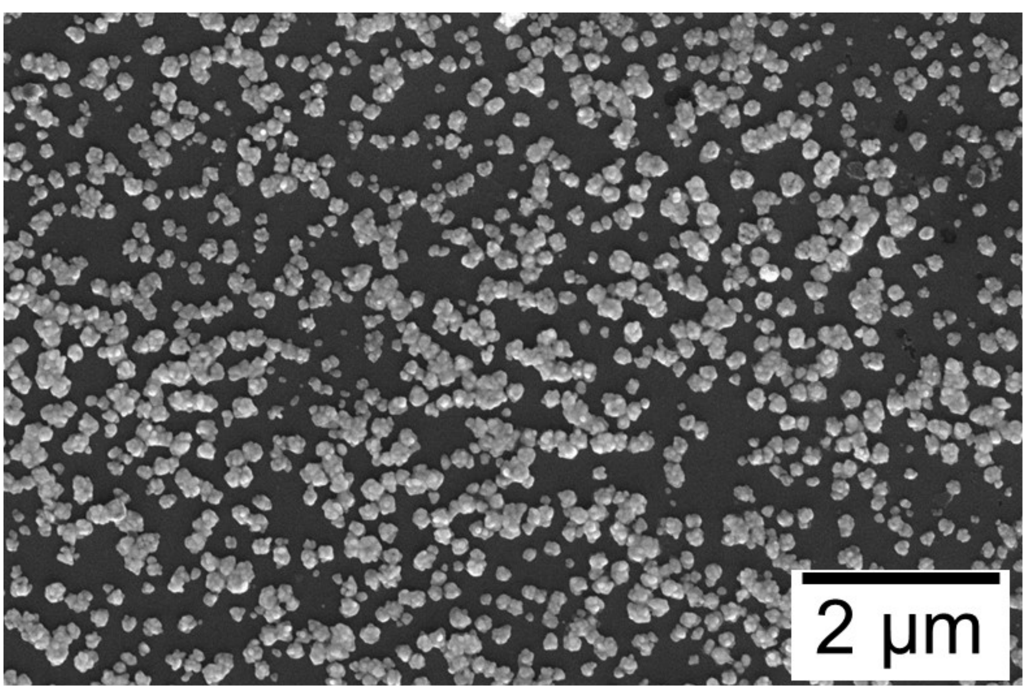

Figure SI2. Low magnification FESEM image of 3DPAu.

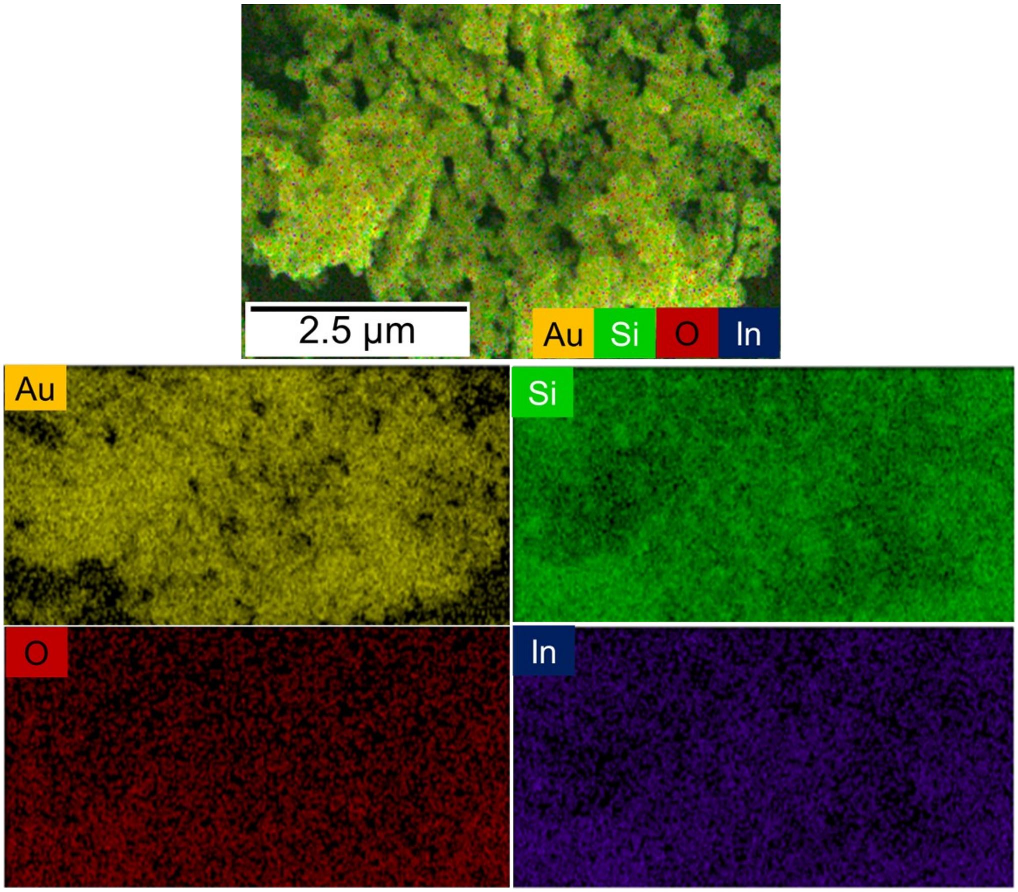

Figure SI3. EDS mapping of 3DPAu on ITO glass with separate Au, Si, O, and In mappings.

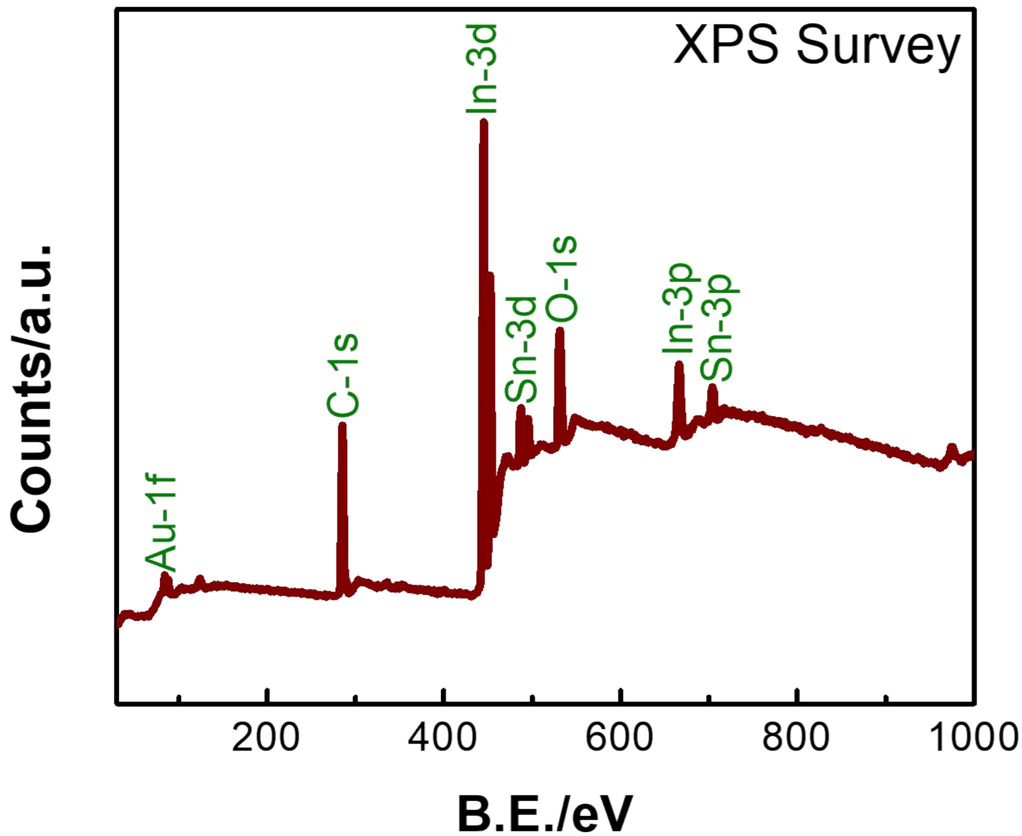

Figure SI4. Complete XPS survey of 3DPAu on ITO glass.

S1. Enhancement factor calculation

The average SERS analytical enhancement factors (AEFs) for the 3DPAu substrates were calculated using the following equation:

$AEF = (I_{SERS}/ I_{NR}) \times (C_{NR}/C_{SERS})$ (1),

I_{SERS} and I_{NR} are the integrated intensities in arbitrary units (a.u.) observed from SERS and normal Raman spectra. While C_{SERS} and C_{NR} stand for concentrations used during SERS and normal Raman measurements, respectively. The equation took into consideration the fact that all other experimental conditions, such as laser wavelength, laser power, microscope objective lenses, spectrometer, etc., are identical both in SERS and normal Raman measurements.[1,2]

The concentrations of BPA for SERS and normal Raman measurements were 10^3 and 2.3×10^5 ppm, respectively. The characteristics band at 1616 cm^{-1} of BPA was chosen for the AEF calculation. The detailed AEF calculation is as follows:

We have, I_{SERS} = 31457, I_{NR} = 526, $C_{NR} = 2.3\times10^5$ ppm, $C_{SERS} = 10^3$ ppm

Putting all the values in equation-1 provides:

AEF = 1.4×10^4.

AEF for corresponding to other characteristics peaks are provided in **Table SI1**.

Table SI1. AEF for 3DPAu substrate at different Raman bands of BPA.

Peak Number	**BPA Peak position (cm^{-1})**	**I_{SERS} (a.u.)**	**I_{NR} (a.u.)**	**AEF**
1	1116	33876	616	1.3×10^4
2	1183	36314	772	1.1×10^4
3	1235	30476	548	1.3×10^4
4	1264	27227	403	1.6×10^4
5	1616	31457	526	1.4×10^4
6	3067	51379	1570	0.8×10^4

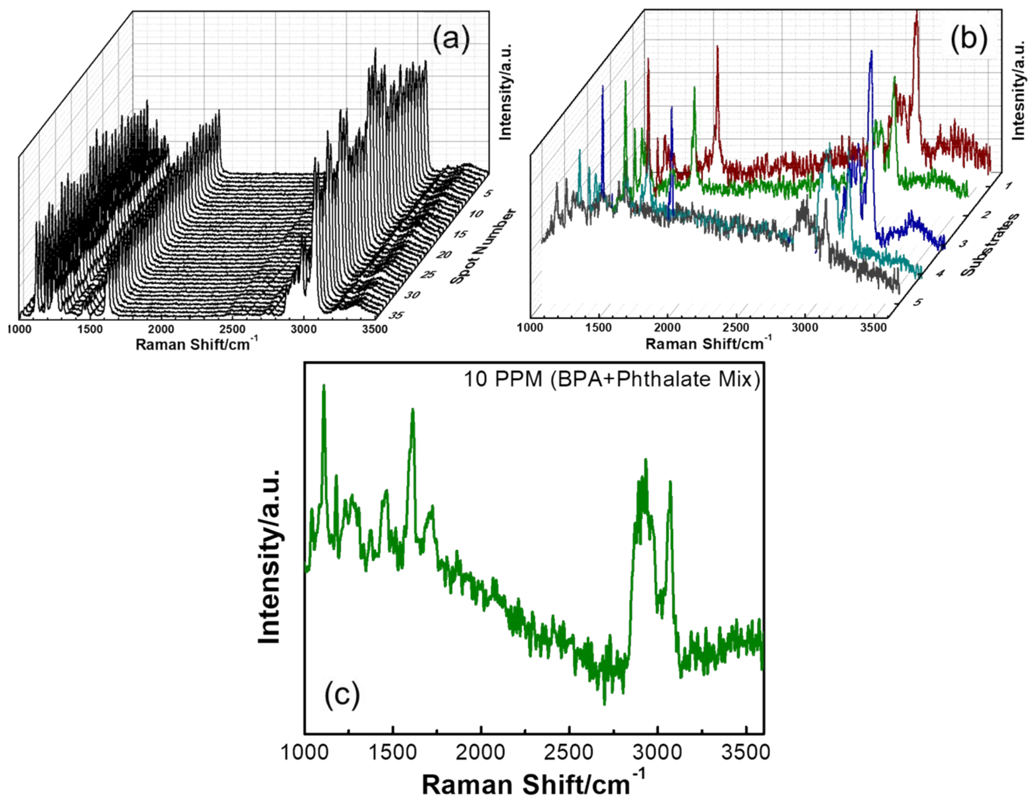

Figure SI5. SERS spectra of 100 PPM BPA@3DPAu corresponding to (a) 36 random spots of 3DPAu substrates indicating repeatability, (b) 5 different substrates showing reproducibility, and (c) SERS spectra of a mixture of 10 PPM BPA and phthalate ester mix of same concentration to show the selectivity of 3DPAu towards BPA detection.

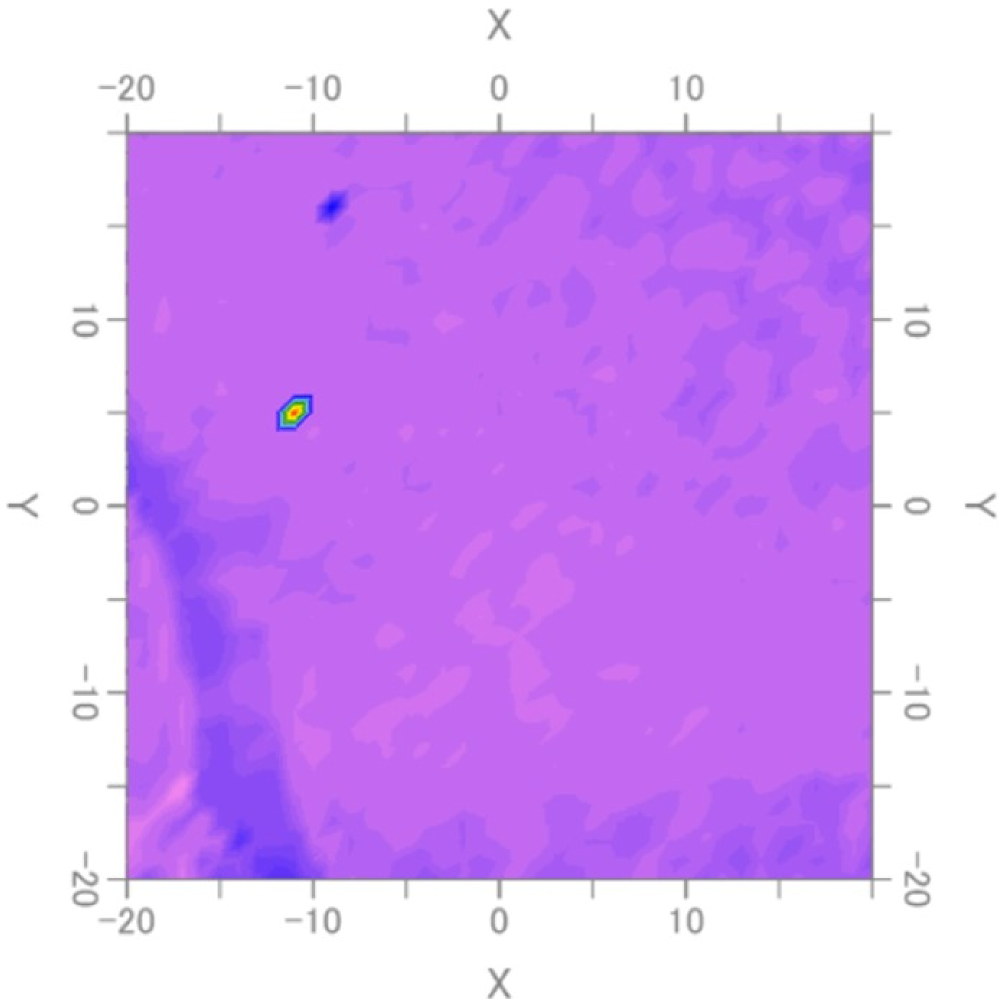

Figure SI6. SERS map data of 100 PPM BPA@3DPAu corresponding to an area of 40 * 40 μm^2.

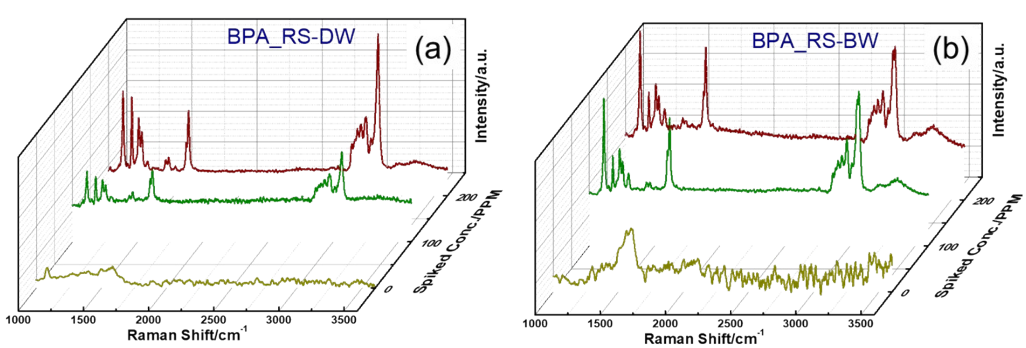

Figure SI7. SERS spectra correspond to different spiked concentrations of BPA in real samples. (a) for drinking mineral water packaged in plastic bottles (BPA_RS-DW) and (b) water samples (BPA_RS-BW) obtained by boiling polycarbonate baby milk bottles.

References

1 Y. Liu, S. Xu, H. Li, X. Jian and W. Xu, *Chem. Comm.*, 2011, **47**, 3784–3786.

2 E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoint, *J. Phys. Chem. C*, 2007, **111**, 13794–13803.