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1 Au-covered hollow urchin-like ZnO nanostructures for surface-2 enhanced Raman scattering sensing

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15 Abstract

16 Au-covered hollow urchin-like ZnO nanostructures were prepared with controlled size by combining 17 nanosphere lithography (NSL), atomic layer deposition (ALD), electrodeposition, and electron beam 18 (e-beam) evaporation. The optimal Au film thickness was determined by measuring the surface-19 enhanced Raman scattering (SERS) intensities of the substrates. Furthermore, the sensing 20 performances of these hybrid nanostructures have been investigated by using chemical and biological 21 molecules: thiophenol and adenine, respectively. Limits of detection (LOD) of 10-8 M and 10-6 M were 22 found for the detection of thiophenol and adenine, respectively. Additionally, the excellent uniformity 23 and batch-to-batch reproducibility of the substrates make them excellent candidates for reliable SERS 24 sensing and biosensing.

25 Highlights:

- Fabrication of Au-covered ZnO urchin-like structures for SERS sensing via high throughput
 methods
- SERS signal is homogenous throughout the substrate and reproducible by testing different
 batches
- The hybrid nanostructures offer promising prospects for the detection of adenine
- 31
- 32 Keywords: surface-enhanced Raman scattering, SERS substrates, atomic layer deposition, urchin-like
- 33 ZnO, ZnO/Au heterostructure



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38 **1. Introduction**

39 Surface-enhanced Raman scattering (SERS) has emerged as one of the most powerful analytical 40 techniques that offer single-molecule detection [1]. Its outstanding sensitivity and non-destructive 41 character have found many applications in many fields such as chemistry [2], medicine [3], biology [4], 42 and environmental sciences [5]. SERS substrates are mainly fabricated with noble metals (Ag, Au, Cu) 43 due to their strong interaction with electromagnetic waves and the excitation of the localized surface 44 plasmon resonance (LSPR) that can be tuned in the UV-Vis-NIR region [6,7]. These noble metals are 45 usually combined with nanostructures such as nanospheres [8], nanowires [9], nanogaps [10], 46 nanotrees [11], and nanorods [12] that provide roughened metal surfaces and plasmonically active "hotspots" that enhance the Raman signal by several orders of magnitude [13]. Additionally, thanks to 47 48 their inherent SERS activity [14], semiconductors have been used to fabricate metal/semiconductor 49 hybrid nanostructures that exhibit both electromagnetic enhancement and charge-transfer effects [12]. Furthermore, these highly-efficient SERS hybrids present additional properties that make them 50 51 attractive for applications such as photocatalysis [15], water splitting [16], and solar energy conversion 52 [17]. As a semiconductor material with a wide direct bandgap (3.37 eV), biocompatibility [18], and 53 promising optoelectronic properties [19,20], ZnO has been employed for the construction of highsurface-area SERS substrates with a wide range of tunable morphologies [21]. 54

55 However, the fabrication of reproducible and stable SERS substrates remains a major challenge [22]. 56 Therefore, much attention has been paid to find facile, repeatable, and high-throughput fabrication 57 methods for large-area nanostructured substrates. Among these methods, nanosphere lithography 58 (NSL) has proven to be a reproducible and inexpensive technique that offers well-ordered arrays of 59 nanostructures with wafer-scale throughput [23,24]. Thus, NSL has been used in combination with 60 other techniques to fabricate different types of SERS substrates such as silver film over nanosphere (AgFON) [25], gold semishells [26], nanoring cavities [27], nanopyramids [28], and optrodes [29]. 61 Recently, high-surface-area urchin-like structures decorated with Ag have been successfully used as 62 63 SERS substrates [30–32]. Nevertheless, even though Ag is preferred over Au due to its higher SERS 64 activity, Ag is prone to oxidation in air or water environments [33]. Consequently, decreasing its SERS 65 enhancement factor (EF) as a result of changes in its chemical and plasmonic properties [34].

Herein, we report on a high-surface-area reproducible SERS substrate consisting of Au-covered ZnOurchin-like hollow structures for the detection of thiophenol. This substrate was fabricated by using

scalable techniques that include NSL, atomic layer deposition (ALD) [35], electrodeposition, andelectron beam (e-beam) evaporation. NSL was used to obtain a template of well-organized spheres

70 that were later covered with a seed layer of ZnO deposited by ALD. Afterward, ZnO nanowires

71 (NWs) were grown via a hydrothermal method to obtain the urchin-like structures, which were finally

- 72 subjected to e-beam evaporation of Au. Furthermore, we investigated the SERS performances of these
- 73 hybrid nanostructures by detecting a small chemical molecule (thiophenol) and then a biomolecule
- 74 (adenine).
- 75

76 2. Material and methods

77 2.1 Materials

78 Polystyrene (PS) spheres (aqueous dispersion, 10 % w/w) with a diameter of ~500 nm and sodium

79 dodecyl sulfate (SDS, CAS: 151-21-3, purity > 99%) were purchased from Sigma-Aldrich and used as

received. Zinc chloride (CAS: 7646-85-7, purity > 98%) and potassium chloride (CAS: 7447-40-7, purity
> 99.0%) were purchased from Fluka. Thiophenol (CAS: 108-98-5, purity > 99%) was purchased from

Alfa Aesar. Diethylzinc (DEZ, CAS: 557-20-0, purity > 95%) was purchased from Strem Chemicals

83 Indium tin oxide (ITO) deposited on quartz was purchased from Präzisions Glas & Optik.

84

85 2.2 Fabrication of urchin-like ZnO structures covered by Au

86 First, ITO substrates (1 x 2 cm²) were cleaned by sonication for 15 min in acetone, ethanol, and 87 isopropanol sequentially and finally dried under air. After, the PS spheres were deposited on the ITO 88 substrates using a previously reported method with slight modifications [36]. Briefly, a 1:2 solution of 89 PS spheres and anhydrous ethanol was added dropwise with a micropipette onto the surface of a 90 tilted glass slide (previously treated with oxygen plasma) that was resting on the wall of a Petri dish filled with deionized (DI) water. Afterwards, 5 µL of an SDS solution (10 wt. %) were added to the 91 92 water surface to change the surface tension and pack together the PS spheres. The self-assembled PS 93 spheres were then transferred to the ITO substrate (previously exposed to a 4 W, 254 nm UV lamp for 94 15 min to render it hydrophilic) by carefully introducing the substrate into the Petri dish and 95 removing it from the solution at an angle of 45°. Once dry, the substrates were heated in an oven at 96 100 °C for 30 min to promote the adhesion of the PS spheres to the substrate. Next, the size of the 97 spheres was reduced to produce a non-close-packed arrangement by reactive ion etching in O₂ plasma 98 (0.6 mbar, 50W). The size of the PS spheres was controlled by adjusting the oxygen plasma exposure 99 time.

Afterward, a 20-nm thick ZnO layer was deposited on the PS spheres-covered substrates by ALD in a
home-made system. The ZnO films were grown at 80°C using diethyl zinc (DEZ) and DI water as
precursors in a typical cycle described as follows: 0.2 s pulse of DEZ, 40 s exposure, and 60 s purge
with argon, followed by 2 s pulse of H₂O, 40 s exposure, and 60 s purge with argon.

Subsequently, electrodeposition of ZnO was performed using a previously reported procedure [37]. A
three-electrode configuration was used with the ITO/PS spheres/ZnO ensemble as a working
electrode, a Pt plate as the counter electrode, and Ag/AgCl as the reference electrode. An aqueous

- 107 solution of 0.05 mM ZnCl₂ (zinc precursor) and 0.1 M KCl (supporting electrolyte) was used as the
- 108 electrolyte and was continuously bubbled with O₂ during the whole electrodeposition process. The
- 109 electrodeposition was carried out at 80°C with a constant electric potential of -1 V during 15 min in a
- VersaSTAT 3 potentiostat. Once the electrodeposition was completed, the PS spheres were burned off
 in air at 600°C for 2 h. Finally, an Au layer (10, 30 and 50 nm) was deposited by a 350 UNIVEX e-beam
- in air at 600°C for 2 h. Finally, an Au layer (10, 30 and 50 nm) was deposited by a 350 UNIVEX e-beam
 evaporation system (10 kV, 1x10⁻⁶ mbar) on top of the substrates. The deposition thickness of Au was
- $\frac{112}{112} = \frac{1}{112} + \frac{$
- 113 monitored using a quartz crystal monitor (deposition rate = 3 Å/s).
- 114

115 2.3 Substrate preparation for SERS measurements

116 To evaluate the enhancing capabilities of the substrates, thiophenol was selected as the test molecule.117 The substrates were immersed in a freshly prepared ethanolic solution with different concentrations

118 $(10^{-3} \text{ M} - 10^{-8} \text{ M})$ of thiophenol for 18 h. After, the substrates were washed with copious amounts of

anhydrous ethanol and dried in air under ambient conditions. For adenine detection, the substrates

- 120 were immersed in different concentrations of adenine in DI water for 30 min. The substrates were then
- 121 removed from the adenine solution and rinsed thoroughly with DI water and dried in air under
- ambient conditions.
- 123

124 2.4 Structural, SERS and extinction characterizations

The morphology of the as-prepared Au-covered urchin-like ZnO samples was characterized by a 125 Hitachi S4800 scanning electron microscope (SEM). In addition, samples were prepared for 126 127 Transmission electron (TEM) experiments by performing angular cuts using Focus Ion Beam (FIB) 128 JEOL JIB-4000 using a gallium source working at 10 kV, with 60°, 40° and 30° incident angle 129 geometries over a large area (50 µm). In this way, several particles were cut at different axis and 130 geometry. TEM experiments were performed in an HR-TEM JEOL ARM-200F, working at 200kV, 131 equipped with an energy-dispersive X-ray (EDX) detector. Samples were cut by FIB and then were sonicated in ethanol after ion milling and drop cast on commercially available Cu grids and vacuum 132 133 dried overnight in a desiccator. X-Ray diffraction (XRD) was performed with a PANalytical X'pert-134 PRO diffractometer equipped with an X'celerator detector using Ni-filtered Cu K α radiation. The XRD 135 spectra were measured in the 20 angular region between 20° and 70° with a scan speed of 2° min⁻¹ and a step rate of roughly 0.02°/s. SERS measurements were performed with a Renishaw Invia Raman 136 microscope with laser beams at 633 nm and 785 nm. The beam was focused with a 100 × objective lens 137 138 with a N.A. = 0.9 in a backscattering geometry. The samples were irradiated with laser powers of 0.48 139 mW (633 nm) and 0.55 mW (785 nm) with acquisition times between 1 s and 10 s. For comparison, all 140 the collected spectra were normalized by laser power and acquisition time. The average SERS 141 intensities reported and relative standard deviations (RSD) were calculated with 25 SERS spectra. 142 Moreover, a LabRam spectrophotometer is employed for the Raman measurements in solution (non-SERS reference) by using the same excitation wavelength and a macro-objective with a focal length of 143 144 40 mm (N.A. = 0.18). In addition, extinction spectra of samples were recorded in normal transmission 145 mode with a Cary-5000 spectrophotometer from Agilent.



Figure 1. Scheme of the overall fabrication process

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149 3. Results and discussion

150 The overall process for the fabrication of the Au-covered hollow urchin-like ZnO structures is 151 depicted schematically in Fig. 1. Among the different approaches to fabricate ordered arrays of PS spheres, the direct assembly at the air-water interface has been demonstrated to be a simple and low-152 153 cost method that offers high-quality monolayers over large areas. Fig. 2a shows a SEM micrograph of a large area monolayer of PS spheres with a high degree of order. In order to produce a non-closed-154 155 packed monolayer, the PS spheres are exposed to oxygen plasma (Fig. 2b). This treatment allows 156 controlling the size of the urchins and space between them. After reducing the size of the PS spheres, a 157 thin 20-nm ZnO layer was deposited by ALD as a seed layer to promote the growth of ZnO NWs (Fig 158 2b). Owing to its high conformality and homogeneity, the ALD method promotes the uniform generation of ZnO NWs on the surface of the PS spheres, unlike pure hydrothermal methods or 159 sputtering were the thickness control of the seed layer becomes a challenge [38]. In addition, the ALD 160 layer anchors the PS spheres to the ITO substrate and renders their surface electrically conductive for 161 the electrodeposition process. Fig. 2c shows the morphology of the urchin-like ZnO structures. Thanks 162 to the homogenous ALD seed layer, the electrodeposited ZnO NWs are evenly distributed on the 163 164 surface of the PS spheres. The size and length of the ZnO NWs of the urchin-like structures deposited 165 by electrodeposition can be tuned by changing the electrochemical conditions (i.e., zinc precursor concentration and charge density) [39]. Finally, the urchins are homogenously covered by an Au film 166 deposited via e-beam evaporation with thicknesses of 10, 30, and 50 nm, respectively. Fig. 2d shows 167 the as-synthesized Au-covered urchin-like structures with a gold layer thickness of 30 nm (10 nm and 168 169 50 nm are shown on Fig. S1).



171 Figure 2. SEM micrographs of (a) an array of well-organized PS spheres, (b) PS spheres 172 after been subjected to an oxygen plasma treatment, (c) ordered hollow urchin-like ZnO 173 structures, and (d) urchin-like ZnO structures covered by a 30 nm-thick Au layer deposited by e-gun evaporation (scale bar = 1 μ m). The insets show higher magnifications of the corresponding SEM images (scale bar = 500 nm).

The morphology and crystallinity of the urchin-like structures were studied by TEM. Fig. 3a clearly 176 177 shows the Au film that covers the top of the urchin-like structures and the 20 nm ZnO seed film deposited by ALD. Notably, the TEM images display a cavity with a reduced contrast and a shell with 178 a uniform dark gray color (Fig. S2), clearly showing the hollow character of the structures. The high-179 resolution (HR) TEM image from Fig. 3b shows the lattice fringes that correspond to ZnO and Au. 180 181 Likewise, the FFT of the HRTEM image shows the (002) plane of ZnO. Additionally, to further confirm 182 that the PS core of the urchin structures is removed after annealing, an EDX mapping was performed. 183 Fig. 3c shows a scanning TEM (STEM) image of a single urchin structure and Fig. 3d shows the 184 corresponding EDX elemental mapping of Fig. 3c. Fig. 3d shows that Zn and O are located in the core 185 of the urchin, while Au is covering the outer shell of the structure.

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Figure 3. a) TEM image of an Au-covered ZnO urchin-like structure and b) high-resolution
image of the selected area in image a). The inset in b) shows the FFT operation of the image.
c) STEM and (d-g) EDX elemental mapping images of an Au-covered hollow ZnO urchinlike structure. Blue, red, and green illustrate Zn, O, and Au, respectively.

193 XRD measurements were carried out to study the crystallinity of the samples. The XRD patterns of 194 ITO, urchin-like ZnO, and Au-covered urchin-like ZnO structures are displayed in Fig. S3. The 195 diffraction peaks at 31.8°, 34.4°, and 36.4° can be assigned to the hexagonal würtzite planes of (100), 196 (002), and (101) of ZnO [40,41], while the peaks at 38.2°, 44.5°, and 64.6° can be assigned to the face-197 centered-cubic (fcc) planes of (111), (200), and (220) of Au [42,43]. These results show the crystalline 198 nature of the samples and the successful fabrication of a ZnO/Au composite. The remaining peaks 199 correspond to the ITO film deposited on quartz that is used as a substrate [44].

200 3.1 SERS performances for chemical sensing

201 The SERS activity of the substrates was optimized by depositing different Au thicknesses. Fig. 4 shows202 the SERS spectra of thiophenol molecules grafted on the ZnO urchin-like structures covered with 10,

30, and 50 nm of gold for the two excitation wavelengths used here. Thiophenol was selected due to 203 its ability to form self-assembled monolayers (SAMs) via S-Au bonds [45] and the absence of 204 205 molecular vibrational activity near the selected excitation wavelengths (633 nm and 785 nm). The characteristic vibrational modes of thiophenol molecules (10-3 M) are well-observed (see refs [46-48]) 206 207 like those at 999 cm⁻¹ corresponding to the ring out-of-plane deformation and the C-H out-of-plane 208 bending (noted, respectively: r-o-d and γ (CH)), 1022 cm⁻¹ corresponding to the C-C symmetric 209 stretching and the ring in-plane deformation (noted, respectively: v(CC) and r-i-d), 1072 cm⁻¹ 210 corresponding to the C-C symmetric stretching and C-S stretching (noted, respectively: v(CC) and v(CS)), and at 1572 cm⁻¹ the C-C symmetric stretching (noted: v(CC)). For comparison, we studied the 211 peak intensity at 999 cm⁻¹. It is noticeable that the Raman peaks intensities become larger as we 212 213 increase the Au layer thickness for the two excitation wavelengths. This is in accordance with 214 literature reports where it is shown that the thickness of the metallic layer plays an important role on 215 the overall SERS enhancement [49–51]. For our complete study, we chose the 30-nm thickness with the 216 excitation wavelength of 785 nm in order to obtain a good compromise between the SERS signal 217 enhancement and a low overall cost of production of these SERS substrates. Fig. 5a shows the 218 thiophenol spectra obtained from different structures for the purpose of comparison. When ZnO 219 nanowires covered with Au (30 nm) of a size comparable from those on the ZnO urchin-like structures are used, the characteristic Raman peaks of thiophenol can barely be distinguished. Similarly, for the 220 bare Au film (30 nm), the thiophenol peaks can be hardly identified. This result shows that the urchin-221 like structures present the highest SERS activity from these three types of substrate configurations. 222



Figure 4. SERS spectra of thiophenol (10⁻³ M) from different Au film thicknesses (10, 30, and 50 nm) for the two
 excitation wavelengths used in our experiments: (a) 633 nm and (b) 785 nm.



Figure 5. (a) SERS spectra of thiophenol (10⁻³ M) from a 30-nm Au film, a 30-nm Au ZnO NWs, and a 30-nm Au covered urchin-like ZnO, which present an offset to improve the data visualization. (b) SERS
 spectra of the 30 nm Au-covered ZnO urchins with different thiophenol concentrations. The spectra are not background-corrected, and recorded at the excitation wavelength of 785 nm.

Given the complex 3D morphology of the urchins, it is difficult to know the exact number of 232 233 molecules that are excited in the SERS measurements [52,53]. For this reason, the EF for the 30 nm Aucovered ZnO urchins SERS substrates was calculated by using the formula: EF $\approx I_{SERS}/I_{ref}$ [10] were I_{ref} 234 235 represents the Raman intensity of a thiophenol solution in ethanol (1 M; see fig. S4 in SI) and ISERS 236 represents the Raman intensity of the SERS measurements. Thus, the highest EF value for the Raman peak at 1572 cm⁻¹ was 5.3×10^2 (Table 1). From the extinction spectra (see figure 6), we observed that 237 the excitation wavelengths of 633 nm and 785 nm are, respectively, more and more close to maximum 238 239 of one resonance when the gold thickness increases that can significantly improve the enhancement 240 factor. Moreover, it is known that EF is proportional to the extinction intensities (Q_e) [50,54], i.e. $EF \sim Q_e(\lambda_{exc}) \times Q_e(\lambda_{Raman})$. We observed that the EF values (see Table 1) follow qualitatively the same 241 242 trend than those observed from the extinction spectra. These EF values can be attributed to the 243 combination of different effects such as efficient light trapping [31] and the generation of hotspots from almost-touching NWs from adjacent urchins [55]. Additionally, the size of the gaps between the 244 245 Au-covered urchin-like structures is in the same range as the excitation wavelength, which could contribute to the enhancement of localized electromagnetic fields and effective absorption of light by 246 247 the LSPR [10,32]. SERS measurements with a range of molecular concentrations from 10^{-5} M – 10^{-8} M were performed in order to assess the limit of detection (LOD) of the substrates. Fig. 5b shows the 248 249 Raman spectra of the substrates grafted with different thiophenol concentrations. The intensities of the 250 Raman peaks remain strong up to a concentration of 10-7 M and then fall considerably for the 251 concentration of 10-8 M where only the peak at 999 cm⁻¹ remains visible. This LOD is comparable with 252 values reported in the literature for thiophenol and similar Au-based structures [47,50].

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Raman shift (cm ⁻¹)	999	1022	1072	1572
Isers	15066	12199	16926	9539
IRaman	79	32	55	18
EF	1.9×10^{2}	3.8×10^{2}	3.1×10^{2}	5.3×10^{2}



Figure 6. Extinction spectra of Au/ZnO-urchins with different thicknesses of gold: (a) Au = 10 nm, (b) Au = 30 nm,
and (c) Au = 50 nm. On each extinction spectrum, the excitation wavelengths of 633 nm (dark red line) and 785
nm (red dashed line) are displayed, and also the region of the corresponding Raman scattering wavelengths (999
to 1572 cm⁻¹; dark red/yellow rectangle associated to the excitation wavelength of 633 nm, and dashed red/yellow
rectangle those associated to the excitation wavelength of 785 nm).

271 3.2 Uniformity and substrate-to-substrate reproducibility of SERS signal

To demonstrate the large-area uniformity of the Au-covered hollow urchin-like structures, we constructed a Raman intensity map of the 999 cm⁻¹ peak over a $20 \times 20 \ \mu\text{m}^2$ area with a step size of 1 μ m (Fig. 7a). The 400-point map shows an almost continuous bright-colored area with a few darker

275 spots where the intensity is lower, which demonstrates the reasonable uniformity of the substrate.





277Figure 7. (a) Raman map image of the 999 cm⁻¹ peak from a randomly selected area ($20 \times 20 \ \mu m^2$) on278the Au-covered hollow urchin-like structures at the 785-nm excitation wavelength. (b) Intensity279distribution of the 999 cm⁻¹ peak of three different samples with an average RSD value < 10%.</td>

Additionally, the substrate-to-substrate reproducibility was investigated by measuring the intensity of the 999 cm⁻¹ peak from three different batches. Fig. 7b shows the intensity distribution for three different samples. The average RSD value was found to be < 10%, which indicates a good reproducibility of the SERS substrates and shows their excellent performance.

284 3.2 SERS performances for biological sensing

Finally, to demonstrate the biosensing capability of these substrates, we chose the biomolecule adenine which can be used in the detection of DNA or RNA analytes [10,27]. Fig. 8 shows SERS spectra of Adenine at three different concentrations using the urchin-like ZnO structures covered with 30 nm of Au, and recorded at the excitation wavelength of 785 nm. The characteristic purine stretch at 736 cm⁻¹ is noticeable up to a concentration of 1 μ M and the spectra show a low signal-to-noise ratio, which is beneficial for future biosensing applications and is comparable to results published in the literature [10,27].



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Figure 8. SERS spectra for different concentrations of adenine with a LOD of $1\,\mu\text{M}.$

295 **4. Conclusion**

296 In summary, high-surface-area Au-covered hollow ZnO urchin-like structures were prepared by 297 combining NSL, ALD, electrodeposition, and e-beam evaporation. These high-throughput methods 298 are readily scalable and allow the precise control of the size of the urchins and the interparticle 299 distance. The amplification of the SERS signal for thiophenol was investigated by depositing different thicknesses of Au, and the 30-nm thickness was selected for its good compromise between the 300 301 enhancement of the SERS intensity and the low cost of production. The LOD of the selected substrates was tested by detecting thiophenol down to 10-8 M. Additionally, the batch-to-batch repeatability was 302 303 demonstrated and an average RSD < 10% was obtained. Finally, adenine was detected up to a 304 concentration of 10-6 M in order to demonstrate the biosensing capability of our substrate. These 305 results suggest that the Au-covered hollow urchin-like ZnO structures are viable candidates for 306 ultrasensitive and reproducible SERS sensing and biosensing.

307

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