



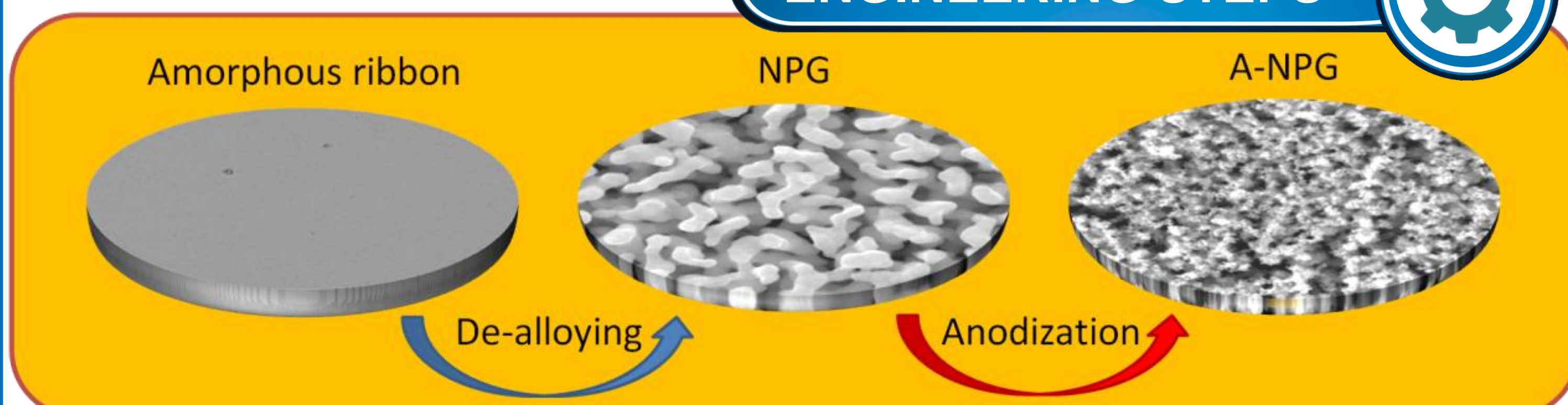
AIM OF THE WORK

SERS substrates currently on the market are assembled on a handling plate material of larger dimension respect to the active area, that limits their versatility of use. Furthermore, such devices are disposable and with a limited detection limit. The invention here described is an innovative sensor-substrate for SERS application that exhibits a higher SERS activity being able to reveal molecules in extremely low concentration. It is constituted by anodized nanoporous gold (A-NPG) prepared by de-alloying of amorphous ribbons to get nanoporous gold (NPG) followed by anodization, forming more active and tiny features on the surface.

Patent Application number: 10202000024382

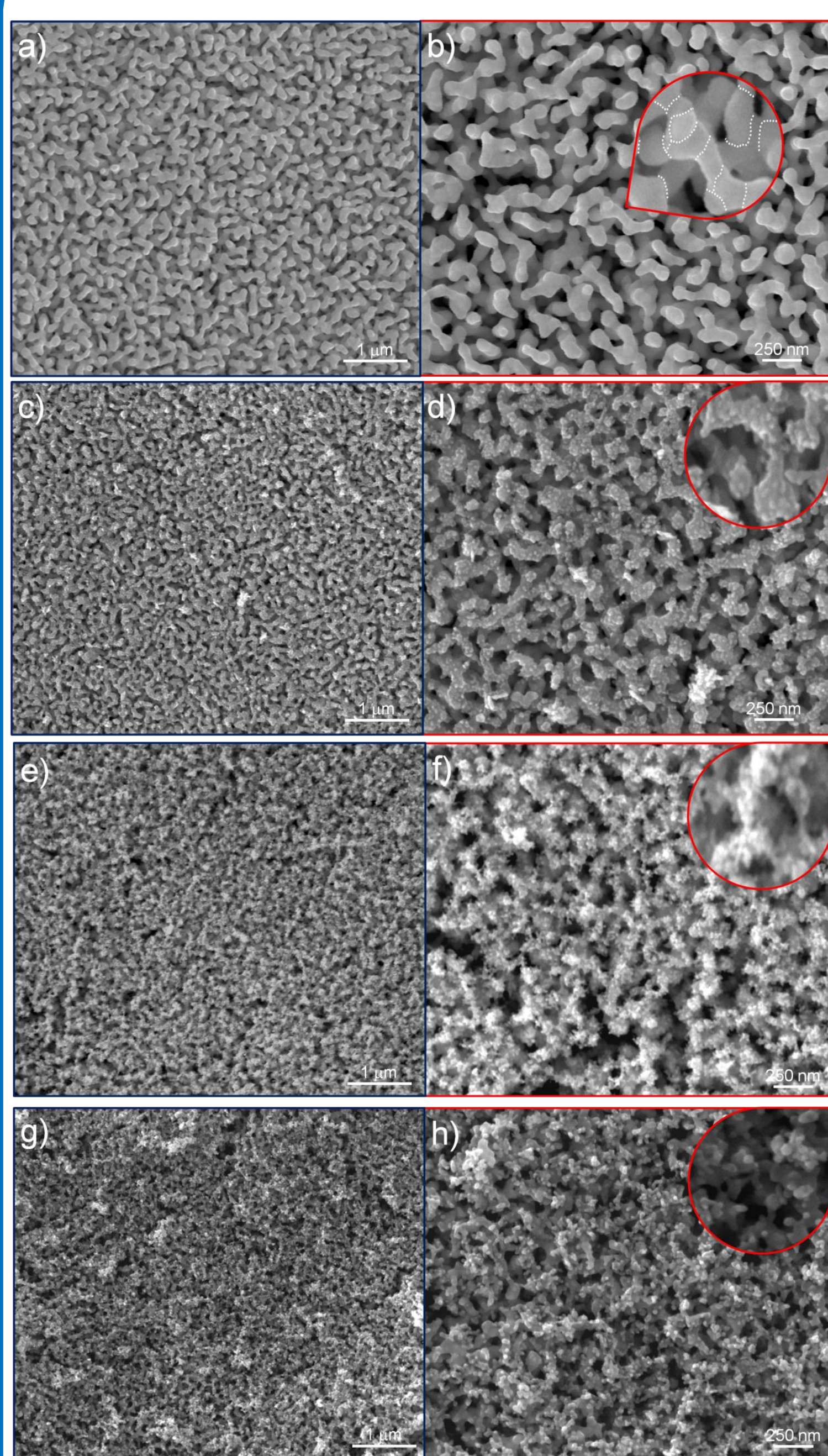
<https://en.unito.it/research/knowledge-transfer/patents/laboratory-and-processes/anodized-nanoporous-gold-ultra>

ENGINEERING STEPS



Engineering step procedure for A-NPG: the amorphous ribbon is dealloyed to obtain NPG. Then, anodization of NPG in 0.3 M oxalic acid solution leads to anodized NPG.

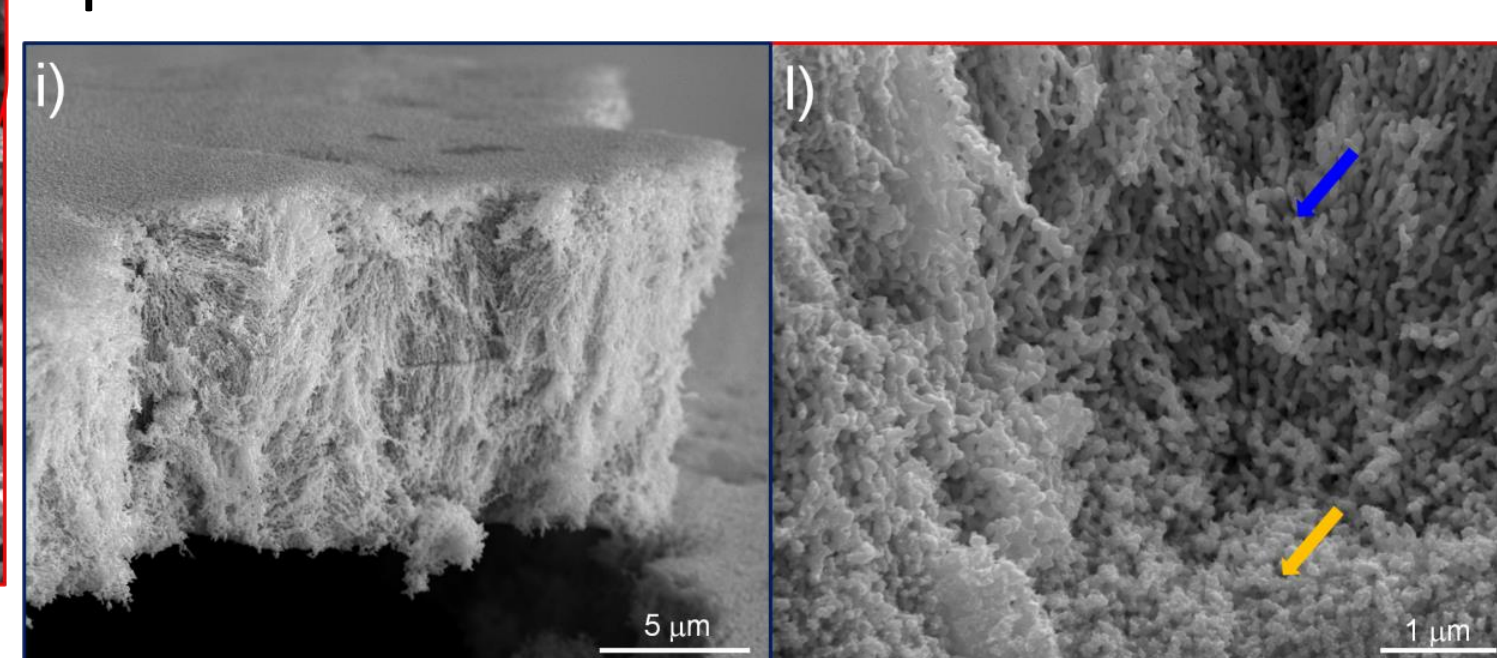
NPG AND A-NPG



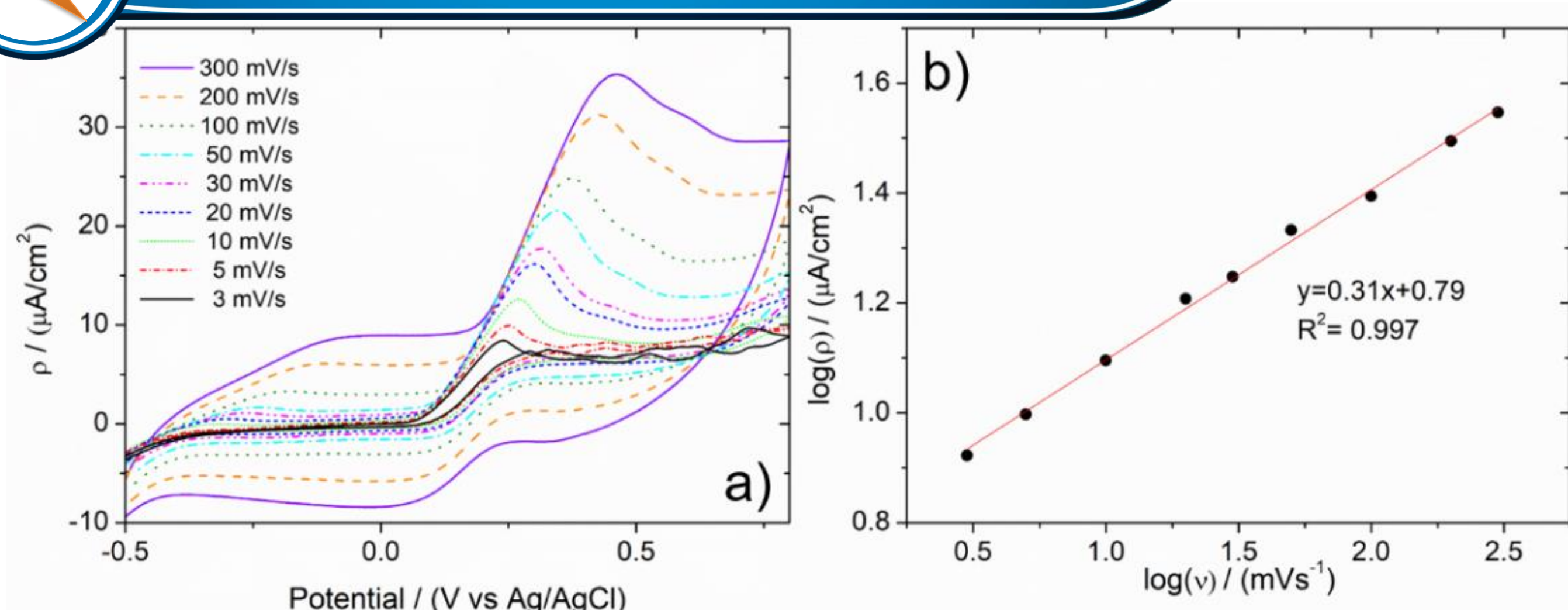
SEM images of the surface of samples: (a,b) NPG; (c,d) 3 min A-NPG; (e,f) 5 min A-NPG; (g,h) 7 min A-NPG. In these insets, an increased level of detail of ligaments is shown; (i) cross-sectional view of NPG; (l) cross-sectional view of the 5 min A-NPG.

Anodization involved only a few microns on the nanoporous structure inside the thickness of the ribbon (yellow arrow); the inner part of the ribbon was indeed untouched by the treatment (blue arrow).

EDS analyses of ligaments: almost pure gold (96.9 at. %), with impurities of copper (0.3 at. %), silver (1.2 at. %), silicon (1.5 at. %), and palladium (0.1 at. %) as remains of the dealloying process.



ELECTROCATALYTIC PROPERTIES



(a) CV scans of 0.02 M ascorbic acid in 0.1 M KH_2PO_4 solution at 3 min A-NPG electrode as a function of scan speed; (b) plot $\log(p)$ vs. $\log(v)$ showing linearity trend and diffusive control process.

✓NPG and A-NPG samples result in an **easy-to-handle, self-standing material, well suited** as an **electrode for electrocatalysis** and **substrate for SERS**. SERS activity shows a **LOD of 10^{-16} M**; for **3 min A-NPG** sample the intensity is **11 times higher** compared with that of the NPG and ascribed to the localized enhanced electromagnetic fields at nanosized ligaments and features obtained after anodization. **A-NPG can be successfully applied as an ultrasensitive sensor-substrate platform for SERS and as an electrode for catalysis or chemical and biological analyses.**



APPLICATIONS

- ✓ **Ultra-sensitive sensor-substrate** for Surface Enhanced Raman Spectroscopy.
- ✓ Possible **integration** as a part of sensor or sensor itself.
- ✓ **Electrode** for electro-catalysis.



KEY ADVANTAGES

- ✓ **Strongly enhanced SERS signal.**
- ✓ **Detection limit of 10^{-16} M.**
- ✓ **Self-standing, mechanically stable and flexible.**
- ✓ **No need of a handling plate.**
- ✓ **Different operative conditions: in solution, at air, in cuvette.**
- ✓ **It can be re-used several times keeping its sensitivity unchanged after washing procedure.**

EXPERIMENTAL METHODS

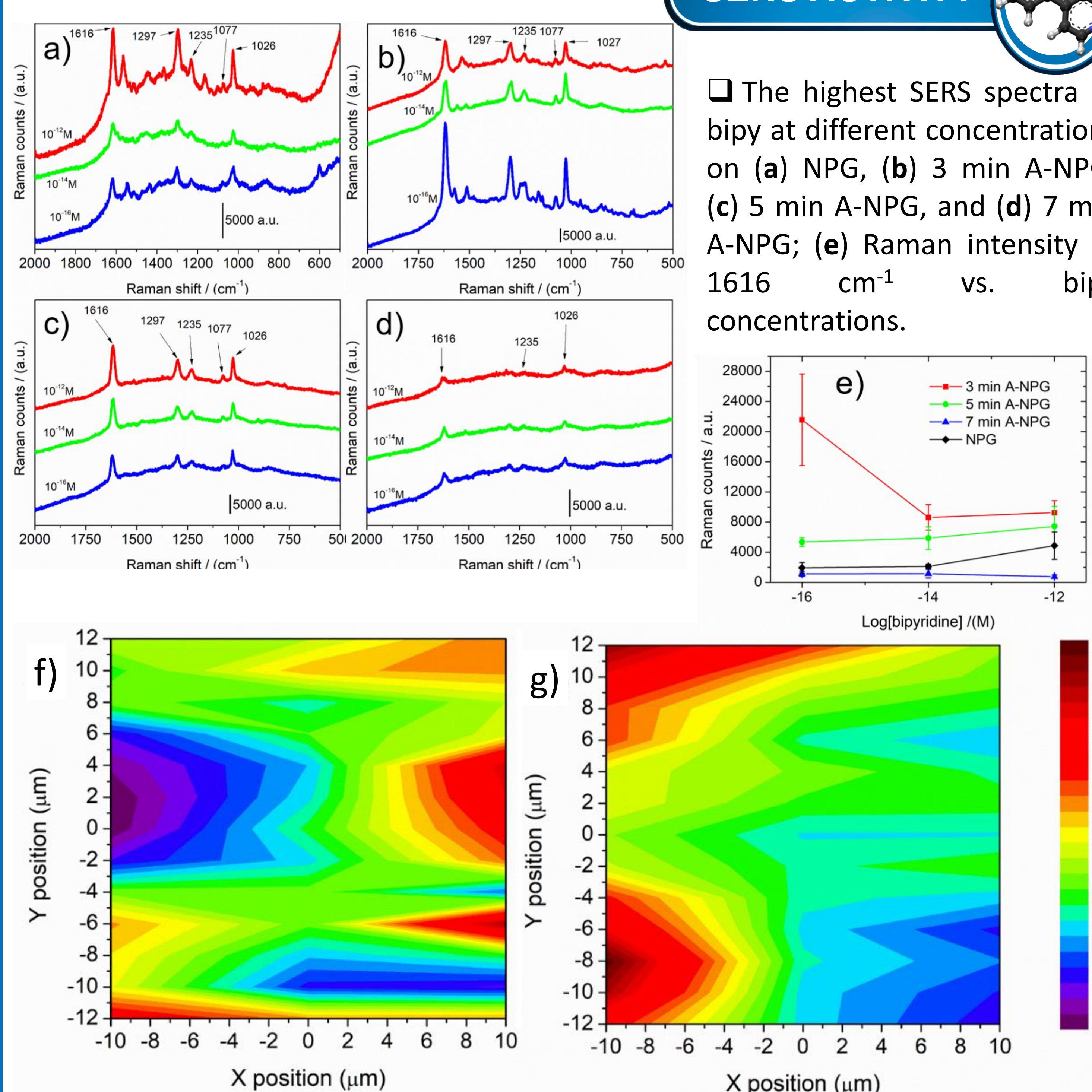


- Ingots of $\text{Au}_{20}\text{Cu}_{48}\text{Ag}_7\text{Pd}_5\text{Si}_{20}$ by arc-melting pure elements under Ar atm.
- Ribbons (20-25 μm thick and 2 mm wide) obtained by **melt-spinning process**.
- **NPG** by **chemical de-alloying** in 10 M HNO_3 + 0.5 M HF at 70 °C for 4 h.
- **Anodization** of NPG in 0.3 M oxalic acid solution at 8 V for 3, 5, and 7 min: samples used as WE in a cell composed of an Ag/AgCl RE and a Pt-grid CE.
- **SERS** measurements setup: with a Renishaw inVia Raman Microscope with **785 nm** laser line, acquisition time of 20 s, accumulation of 10 spectra, 50 \times ULWD objective, 0.05 % power. **4,4'-bipyridine (bipy) in ethanol** was chosen as probe molecules for SERS experiments [**10^{-12} M, 10^{-14} M and 10^{-16} M**].
- Prior to SERS experiments, NPG and A-NPG samples were rinsed several times in de-ionized water and then immersed in the probe molecule solution overnight, enabling the probe molecules to be adsorbed on the surface. Measurements were performed on the sample after drying in air, acquiring random spots on the surface or maps in contiguous areas.
- SERS intensity mapping image of a 20 \times 24 μm^2 area with a step length of 2 μm was collected using bipy 10^{-12} M through monitoring the characteristic peak of the probe molecule at 1619 cm^{-1} .
- **Electrocatalytic properties** toward **oxidation of ascorbic acid** were studied using the same experimental setup as that applied for anodization. A buffer solution of 0.1 M KH_2PO_4 with 0.02 M ascorbic acid was used as the electrolyte.

SERS ACTIVITY



□ The highest SERS spectra of bipy at different concentrations on (a) NPG, (b) 3 min A-NPG, (c) 5 min A-NPG, and (d) 7 min A-NPG; (e) Raman intensity at 1616 cm^{-1} vs. bipy concentrations.



□ SERS intensity map image of 20 \times 24 μm^2 by lateral step of 2 μm with 4-4' bipy concentration of 10^{-12} M based on characteristic peak at 1616 cm^{-1} on (f) NPG and (g) 3 min A-NPG.

CONCLUSIONS

