Supplementary information

Different nanoparticle shapes for Nanoparticle enhanced Laser Induced Breakdown Spectroscopy: nanosphere and nanorod effects

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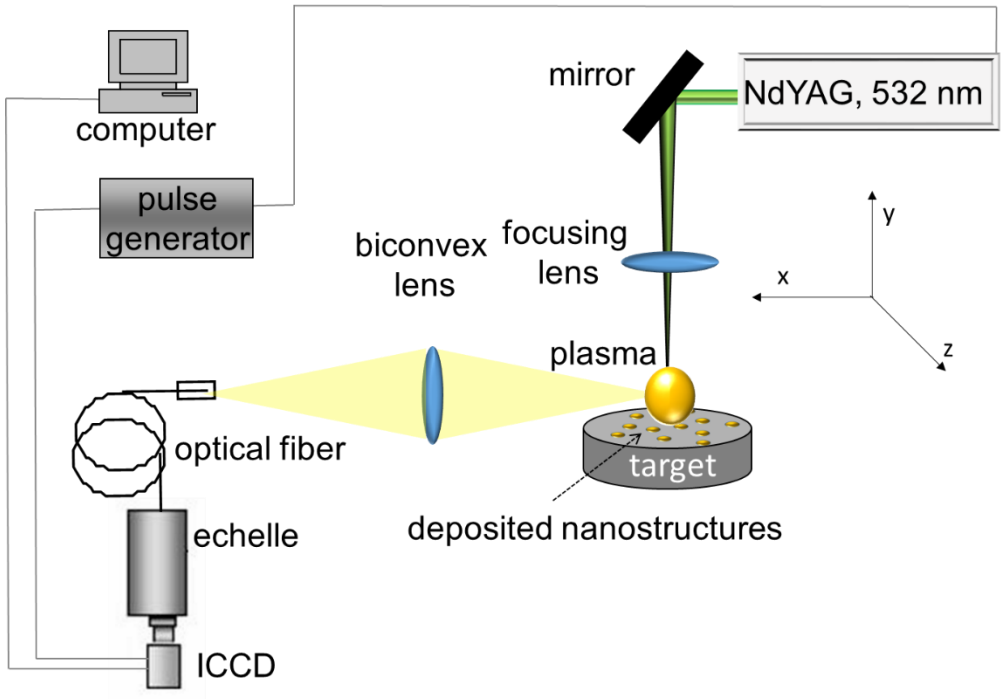

Fig S1. Experimental set-up

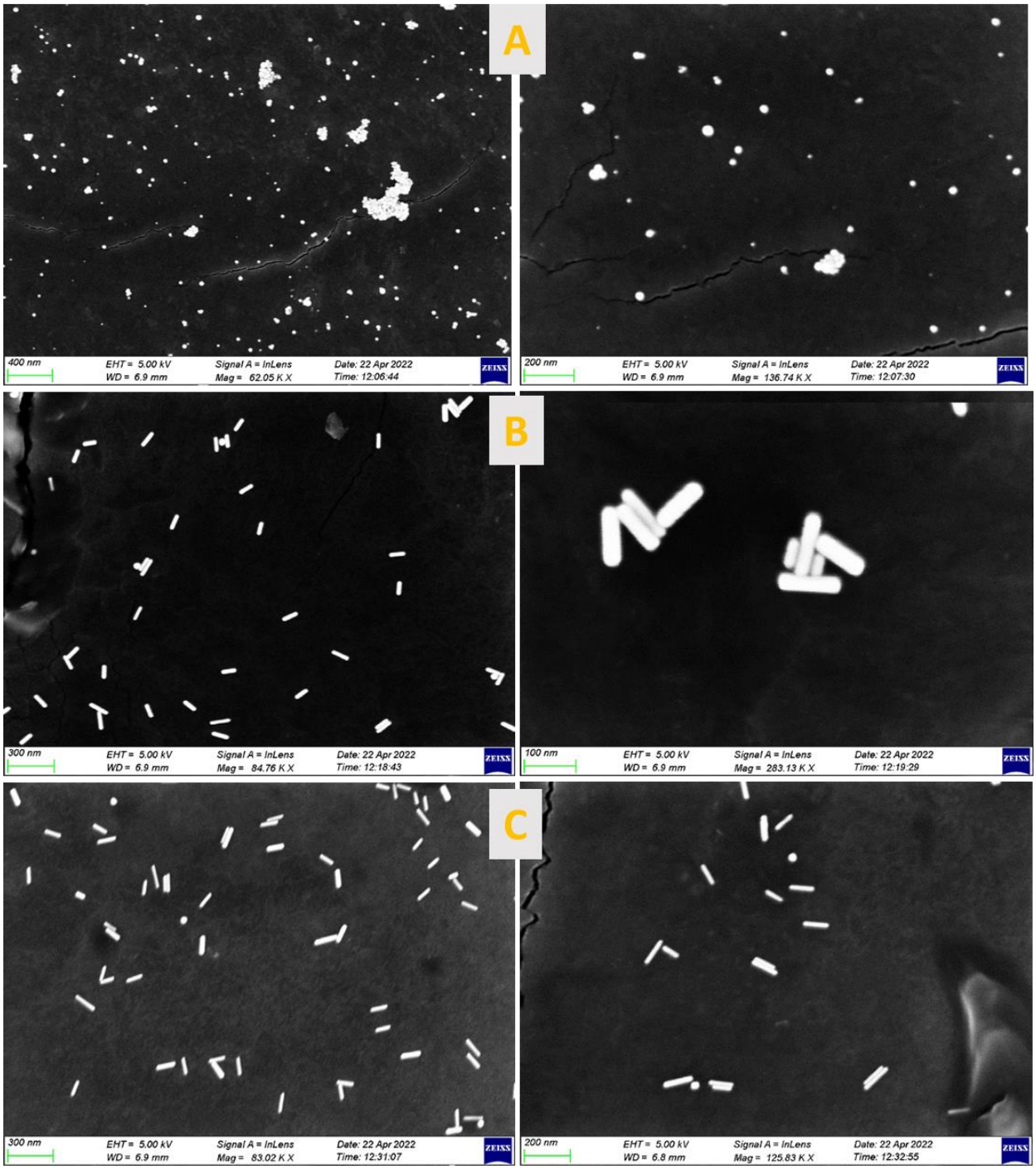

Fig S2. Representative SEM images of a) AuNSs in CTAB with surface concentration of $7x10^{13}$ AuNSs/cm^2 , b) AuNRs_50 with surface concentration of $1.3x10^{13}$ AuNRs/cm^2 and c) AuNRs_70 with surface concentration of $7.9x10^{12}$ AuNRs/cm^2 deposited on Ti target before NELIBS experiment. Left and right of the figure report different magnifications of the image.

AuNP number calculation:

The number of AuNPs (N_{AuNP}) is the ratio between the total number of Au atoms calculated from the Au concentration ($N_{total\ Au\ atoms}$), and the number of Au atoms contained in 1 AuNP ($N_{Au\ atoms\ per\ AuNP}$).

It is important to underline that the following formulae can be applied only if the known Au concentration regards a 100% yield of the reaction in terms of AuNPs. If the AuNPs are chemically synthesized, Au concentration can be the concentration of the Au reagents only if the yield of the reaction is 100%. Otherwise, it is always better to measure the concentration of Au from SPR (Surface Plasmon Resonance) spectrum (with a previous knowledge of its calibration curve).

In the present paper, AuNPs were synthesized with PLAL, a physical method, and Au concentration was directly measured by SPR spectrum of the AuNPs colloidal solution, by employing calibration curves [13] obtained by plotting the absorbance as a function of known Au concentrations certified by Sigma Aldrich.

$$N_{total\ Au\ atoms} = \frac{[Au]\ \text{(g/l)} \cdot N_A}{PA\ \text{(g/mol)}}$$

$$N_{AuNP} = \frac{N_{total\ Au\ atoms}}{N_{Au\ atoms\ per\ AuNP}}$$

$$N_{Au\ atoms\ per\ AuNR} = \rho_{Au}\ (\text{atoms}/nm^3) \cdot V_{AuNR}\ (nm^3)$$

$$N_{Au\ atoms\ per\ AuNS} = \rho_{Au}\ (\text{atoms}/nm^3) \cdot V_{AuNS}\ (nm^3)$$

N_A= Avocadro number
PA = Atomic weight
ρ_{Au} = gold density
V_{AuNP}= AuNP volume

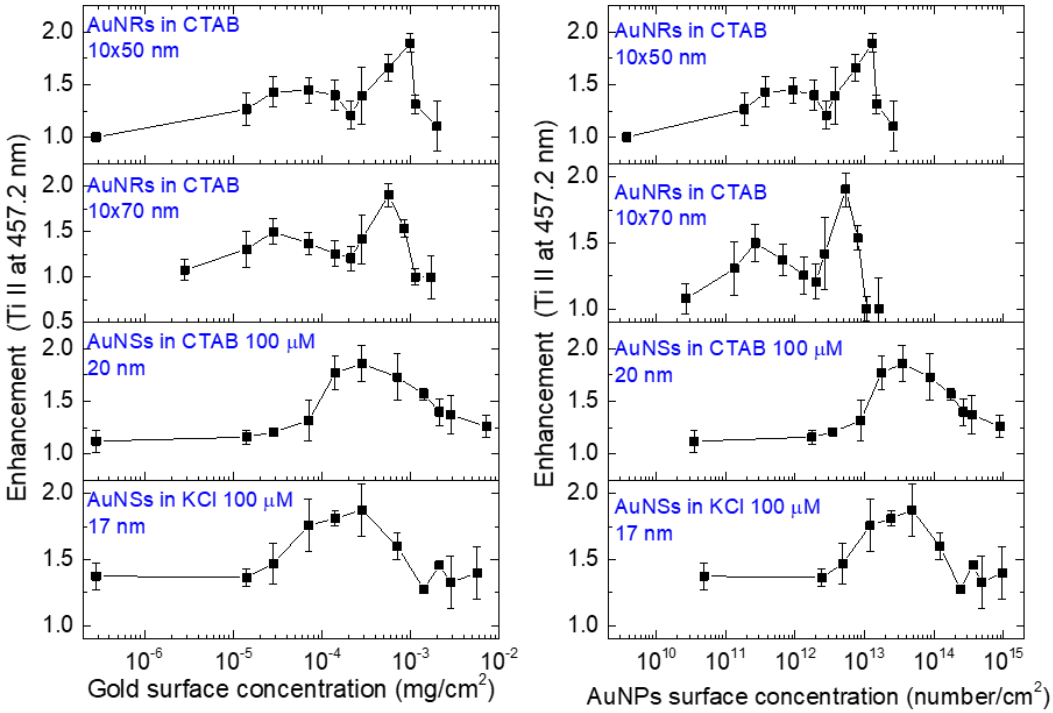

Fig S3. NELIBS enhancement of Ti II at 457.2 nm emission line as a function of the Au surface concentration as a function of the NP surface concentration (i.e the number of NPs for the surface unit) of employed AuNRs and AuNSs.

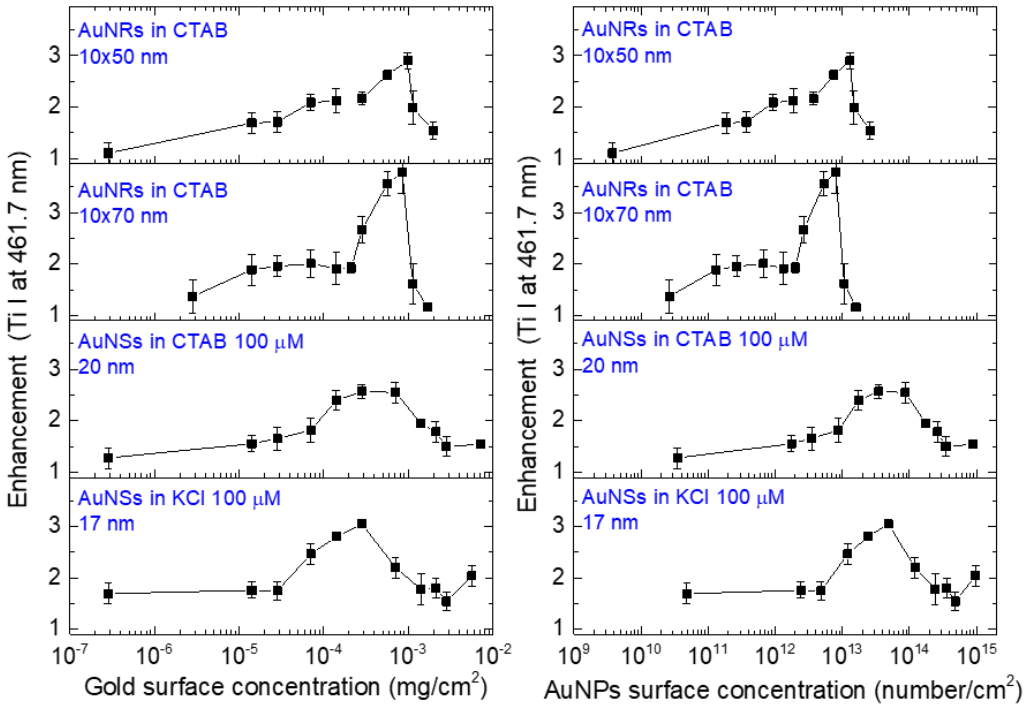

Fig S4. NELIBS enhancement of Ti I at 461.7 nm emission line as a function of the Au surface concentration as a function of the NP surface concentration (i.e the number of NPs for the surface unit) of employed AuNRs and AuNSs.

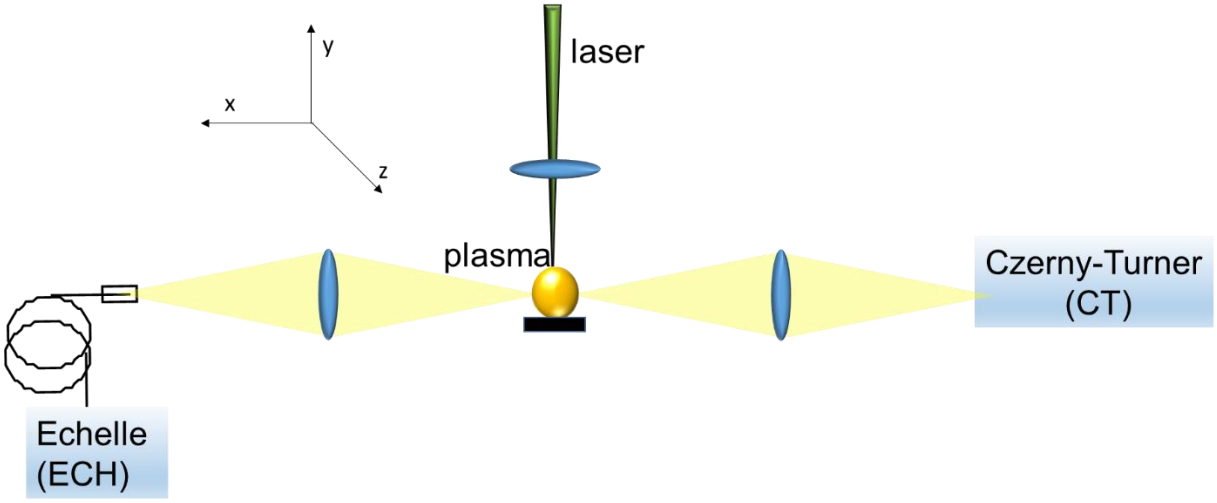

Fig.S5 Sketch of the simultaneous acquisition of laser induced plasma by employing two spectrometers, Echelle (ECH) and Czerny-Turner (CT), respectively. y: laser and plasma expansion axes, x: detection axis.

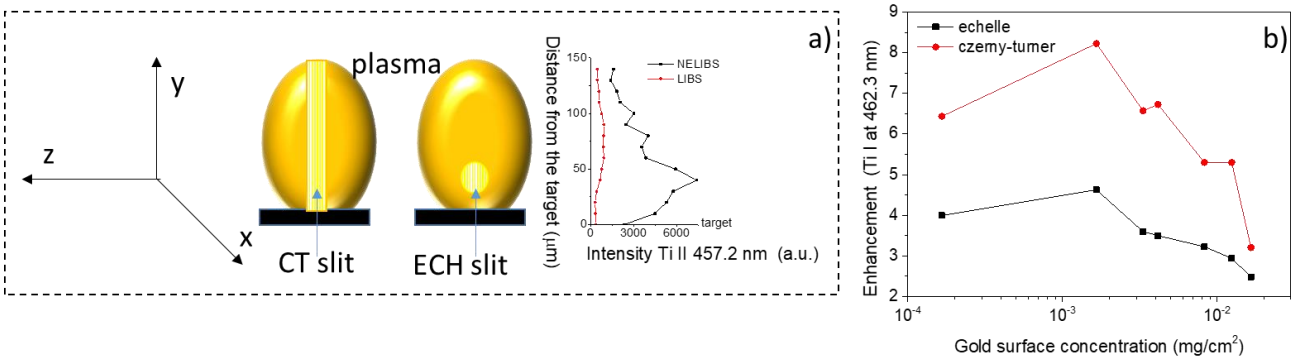

Fig.S6 a) sketch of the plasma emission portion acquired with the two spectrometers as described in Fig.S5. (y: laser direction and plasma expansion axes; x: detection axis). The amount of acquired plasma emission is determined by both slit aperture and plasma image dimension focused on the optical fiber in the case of ECH and directly on the slit in the case of CT. The right part of a) shows the spatially resolved plasma emission along the plasma expansion axis. It was acquired along y axis with the Echelle spectrometer by positioning the optical fiber on a micrometric stage.

b) concentration curves of the enhancement of Ti I emission line at 462.3 nm simultaneously acquired with ECH and CT spectrometers (NELIBS with AuNSs in CTAB) as shown in the experimental set-up of Fig. S5. The aperture of echelle is a spherical slit with a diameter of 40 μm, the Czerny-Turner slit was imposed at 30 μm. Plasma image and slit representations are not reported in true scale.

Table S1 Spectroscopic data of Ti I emission lines used for the Boltzmann plot. (A_{ki} Einstein coefficient, E_k upper level energy, g_k upper level degeneracy)

Emission lines	**Wavelength (nm)**	**A_{ki} (s^{-1})**	**E_k (cm^{-1})**	**g_k**
Ti I	462.3	5.74E7	35652	7
Ti I	464.5	8.57E7	35503	1
Ti I	465.005	2.6E7	35527	3
Ti I	466.75	2.51E6	21588	9
Ti I	467.51	1.85E6	29986	7
Ti I	468.19	2.71E6	21739	11
Ti I	474.27	5.3E7	39115	9
Ti I	475.81	7.13E7	39152	11
Ti I	475.92	7.4E7	39198	13