Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary information

Size, emission and surface chemistry tailoring of germanium nanoparticles via liquid-phase picosecond laser ablation

Marina Rodio[1,2,3], Alice Scarpellini[4], Alberto Diaspro[1] and Romuald Intartaglia[1]*

[1]Nanophysics, Istituto Italiano di Tecnologia, Via Morego 30, Genoa, 16163, Italy.
[2]The Hamburg Centre For Ultrafast Imaging, CUI, Luruper Chaussee 149, 22761 Hamburg, Germany
[3]Institute for Physical Chemistry, University of Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany
[4]Electron Microscopy Facility, Istituto Italiano di Tecnologia, Via Morego 30, Genoa, 16163, Italy

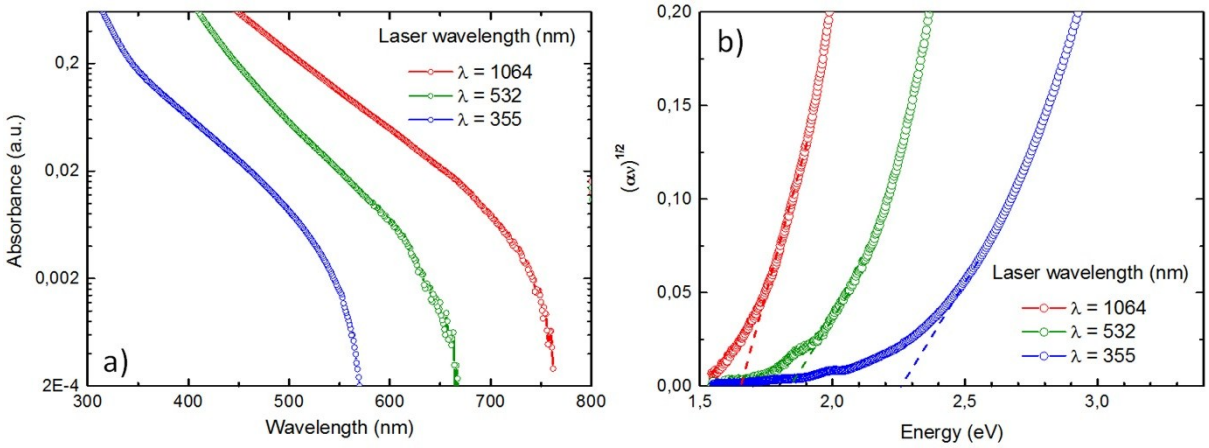

Figure S1. a) Absorption spectra in log of Ge-NPs colloidal for different laser wavelength irradiation. b) Tauc plot showing (αν)1/2 vs. Energy (eV).

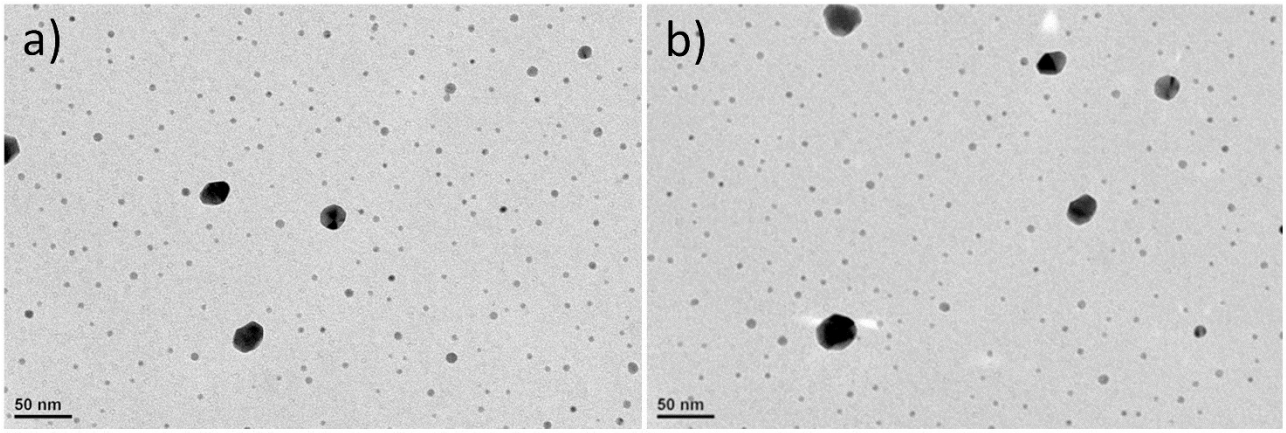

Figure S2. TEM observation of Ge-NPs in different areas. The vast majority of the produced NPs are fragmented (average size) but rarely larger NPs (not fragmented) are also observed. We can estimate that less than 10 percent of larger NPs are present. Of note, there is not a uniform distribution of nanoparticles in the liquid medium confined in the cuvette, and the subsequent diffusion of NPs in the liquid limits the fragmentation process along the laser beam path.

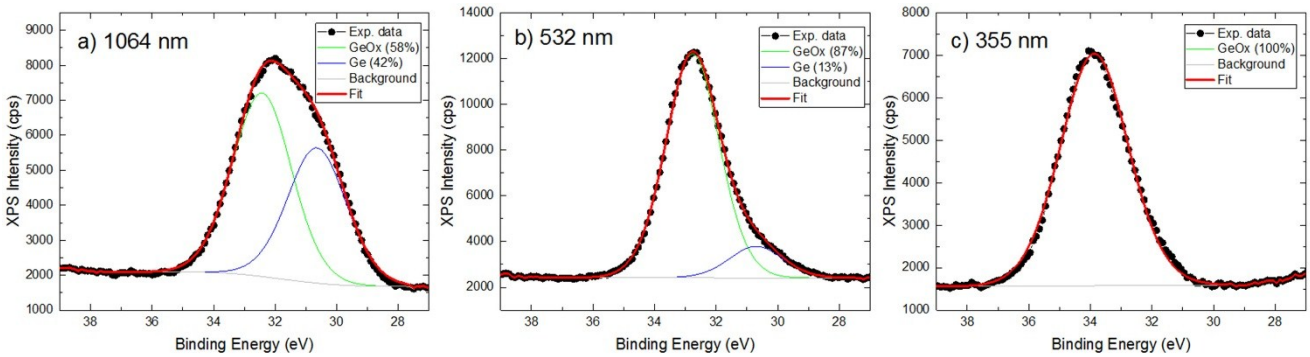

Figure S3. XPS spectra of Ge-NPs colloidal solution prepared by LP-PLA in solvent with the higher oxygen content (88.8 %) at different laser wavelengths: a) 1064 nm, b) 532 nm and c) 355 nm).

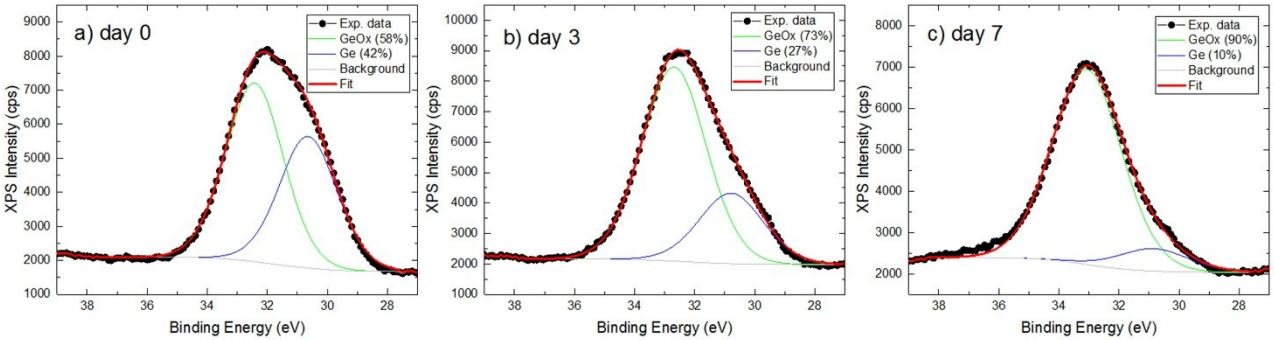

Figure S4. XPS spectra of Ge-NPs colloidal solution prepared by infrared ps laser ablation in solvent with the higher oxygen content (88.8 %) at a) day 0, b) day 3, and c) day 7.

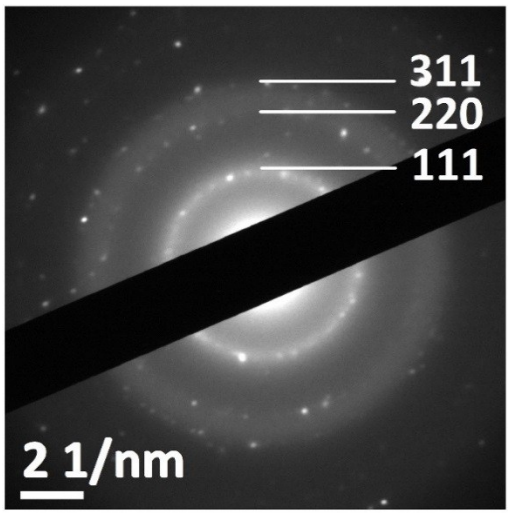

Figure S5. SAED pattern of Ge-NPs colloidal solution prepared by infrared ps laser ablation in aqueous solution displays diffraction rings that can be assigned to (111), (220) and (311) of a face-centered cubic Ge (JCPDS Card. No. 04-0545).

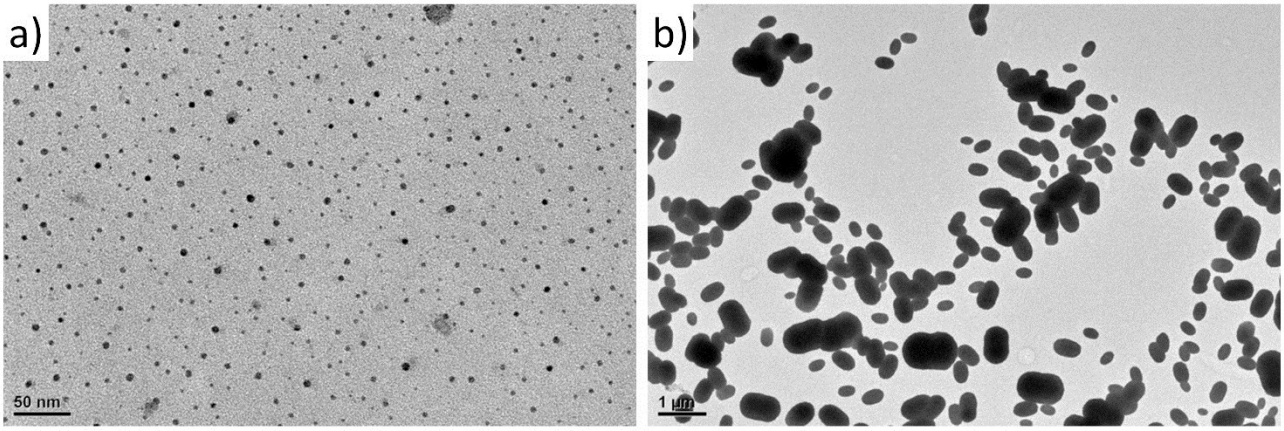

Figure S6. TEM observation of (a) fresh Ge-NPs prepared by green LP-PLA of Ge target placed in aqueous solution, and (b) after 1 week. Similar to other works [3], Ge-NPs are in a metastable state.

Solvent	Water	Acetone	Chloroform
Oxygen atom ratio (%)	88.8	15.99	≈ 0
Carbon atom ratio (%)	≈ 0	12.01	10.06

Table S1. Oxygen and carbon atom ratios of molecules used as organic solvents in LP-LPA.

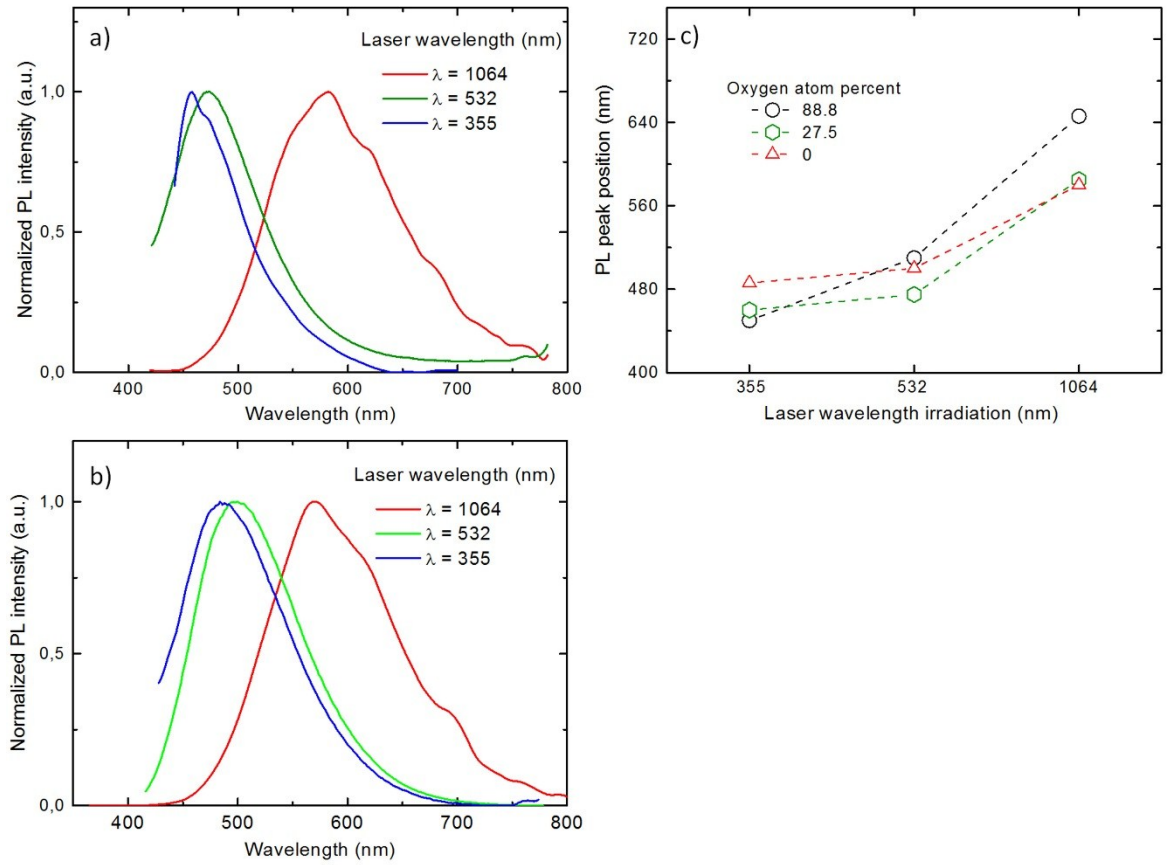

Figure S7. Photoluminescence spectra of Ge-NPs prepared by LP-PLA of Ge target placed in solvent with a) ≈27,5 and b) ≈ 0 oxygen atom percent, at different irradiation wavelength (355 nm, 532 nm and 1064 nm. c) Maximum PL peak position of Ge-NPs in solvents with different percent of oxygen atom. Oxygen contamination and solubility parameters are not take in consideration.

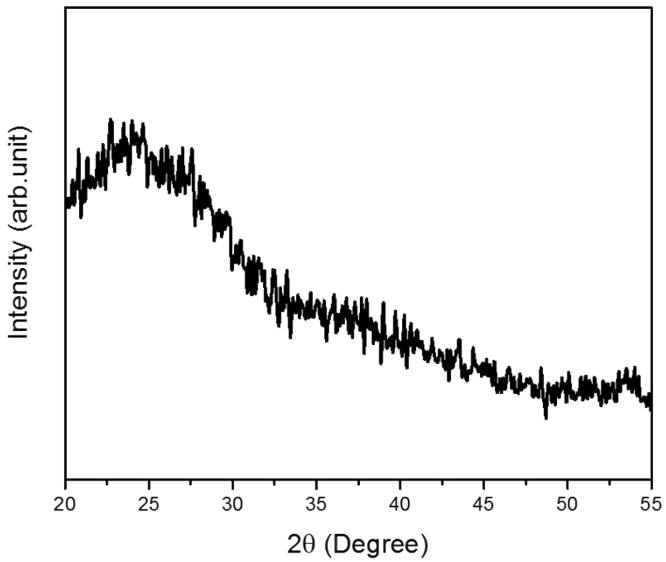

Figure S8. X-ray diffraction pattern of (3,0 ± 1,7 nm) Ge-NPs.

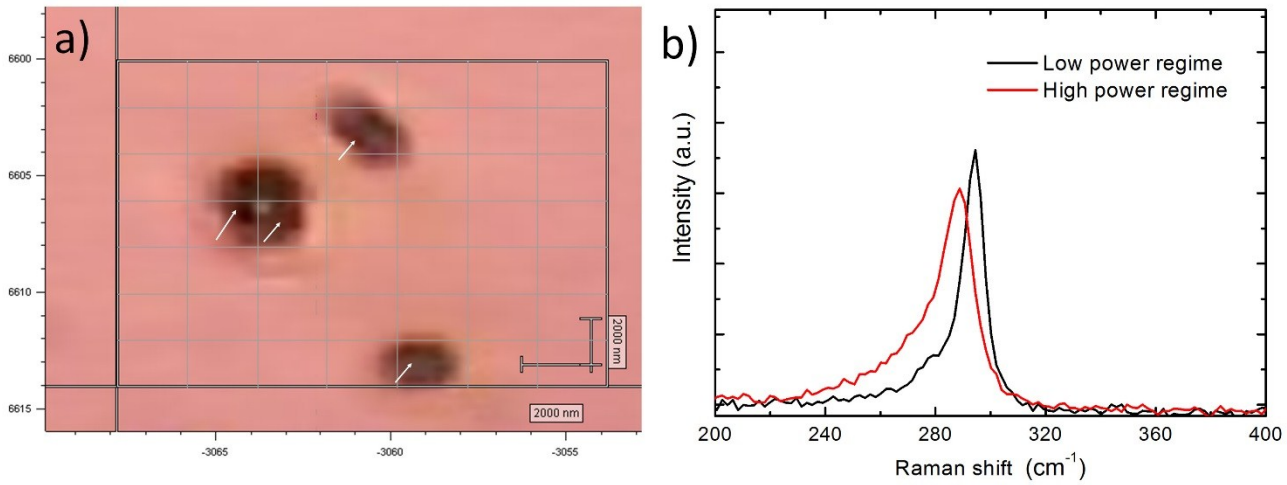

Figure S9. (a) Optical image of mapping area of Ge-NPs samples prepared by blue LP-PLA of Ge target deposited on glass surface. (b) Micro Raman analysis of Ge-NPs samples prepared by blue LP-PLA of Ge target placed in aqueous solution, in the low and high power regime. All analysis were performed in the low power regime in order to avoid thermal destruction of nanoparticles, typically characterized by a redshift and broadening of Raman transition as shown in b) redline. [1,2]

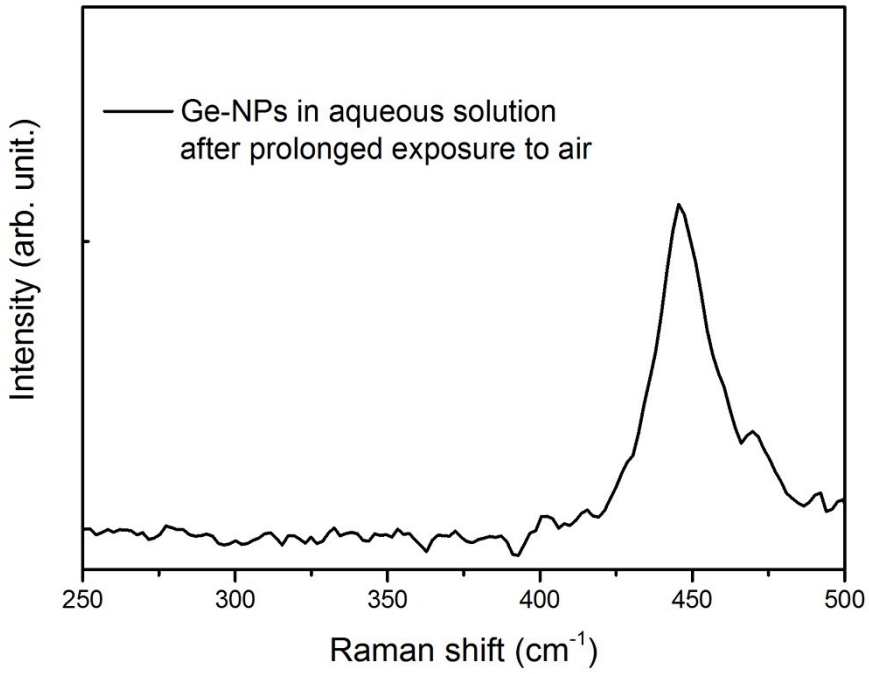

Figure S10. Micro Raman analysis in the low power regime of Ge-NPs prepared by infrared LP-PLA of Ge target placed in aqueous solution after prolonged exposure to air (1 day).

References

[1] Alim, K. A., Fonoberov, V. A., Shamsa, M., & Balandin, A. A. (2005). Micro-Raman investigation of optical phonons in ZnO nanocrystals. *Journal of Applied Physics*, *97*(12), 124313.

[2] Ou, H., Ou, Y., Liu, C., Berg, R. W., & Rottwitt, K. (2011). Formation and characterization of varied size germanium nanocrystals by electron microscopy, Raman spectroscopy, and photoluminescence. *Optical Materials Express*, *1*(4), 643-651.

[3] Liu, J., Liang, C., Tian, Z., Zhang, S., & Shao, G. (2013). Spontaneous growth and chemical reduction ability of Ge nanoparticles. *Scientific reports*, *3*.