

## Electronic supplementary information

### **Live diatoms facing Ag nanoparticles: surface enhanced Raman scattering of bulk *Cylindrotheca Closterium* pennate diatoms and of the single cells**

Simona Cinta Pinzaru\*<sup>1,2</sup> Csilla Müller<sup>1</sup>, Sanja Tomšić<sup>2</sup>, Monica M. Venter<sup>3</sup>, Ioana Brezestean<sup>1</sup>, Stijepo Ljubimir<sup>4</sup>, Branko Glamuzina\*<sup>2</sup>

<sup>1</sup>Department of Biomolecular Physics, Babes-Bolyai University, Kogalniceanu 1, RO-400084, Cluj-Napoca, Romania

<sup>2</sup>Department of Aquaculture, University of Dubrovnik, Ćira Carića 4, 20000 Dubrovnik, Croatia

<sup>3</sup>Department of Chemistry, Babes-Bolyasi University, Faculty of Chemistry and Chemical Engineering, Arany Janos 11, RO-400028, Cluj-Napoca, Romania

<sup>4</sup>Institute for Marine and Coastal Research, University of Dubrovnik, Kneza Damjana Jude 12, P.O. Box 83, HR-20000 Dubrovnik, Croatia

\* Corresponding authors. E-mail: [simona.cinta@phys.ubbcluj.ro](mailto:simona.cinta@phys.ubbcluj.ro);

[branko.glamuzina@unidu.hr](mailto:branko.glamuzina@unidu.hr)

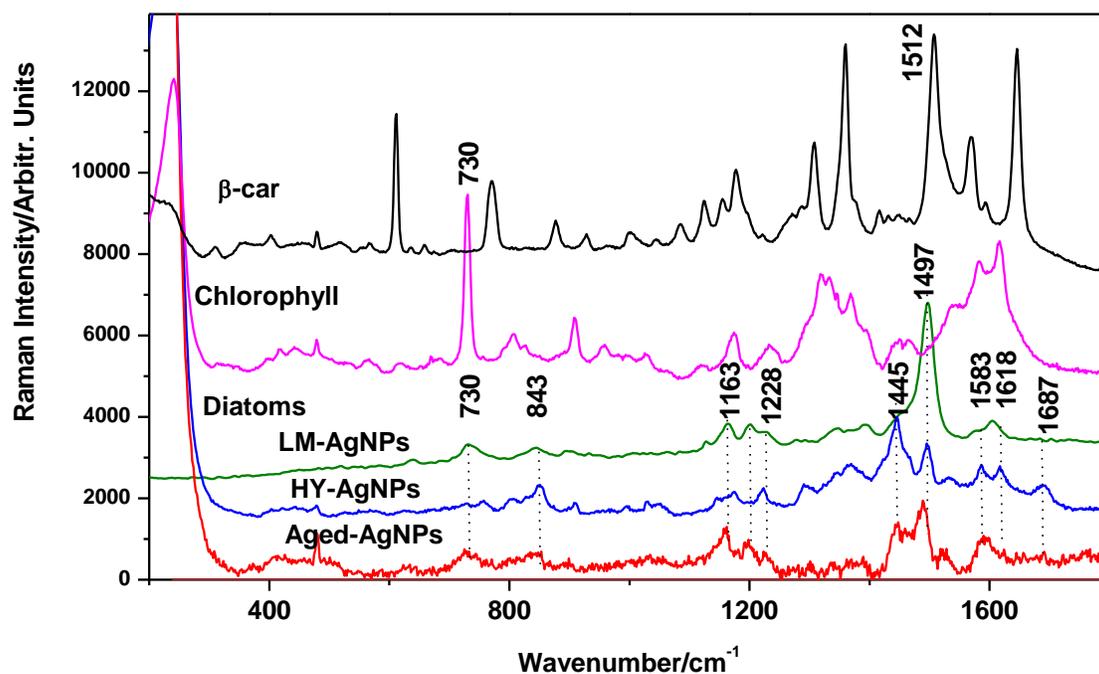


Fig. S1. SERS spectra of diatoms batch culture on the Lee-Meisel (LM-AgNPs), hydroxylamine-reduced (HY-AgNPs) and aged silver nanoparticles (AgNPs) compared with the SERS output of chlorophyll and  $\beta$ -carotene<sup>1</sup>. Excitation 523 nm.

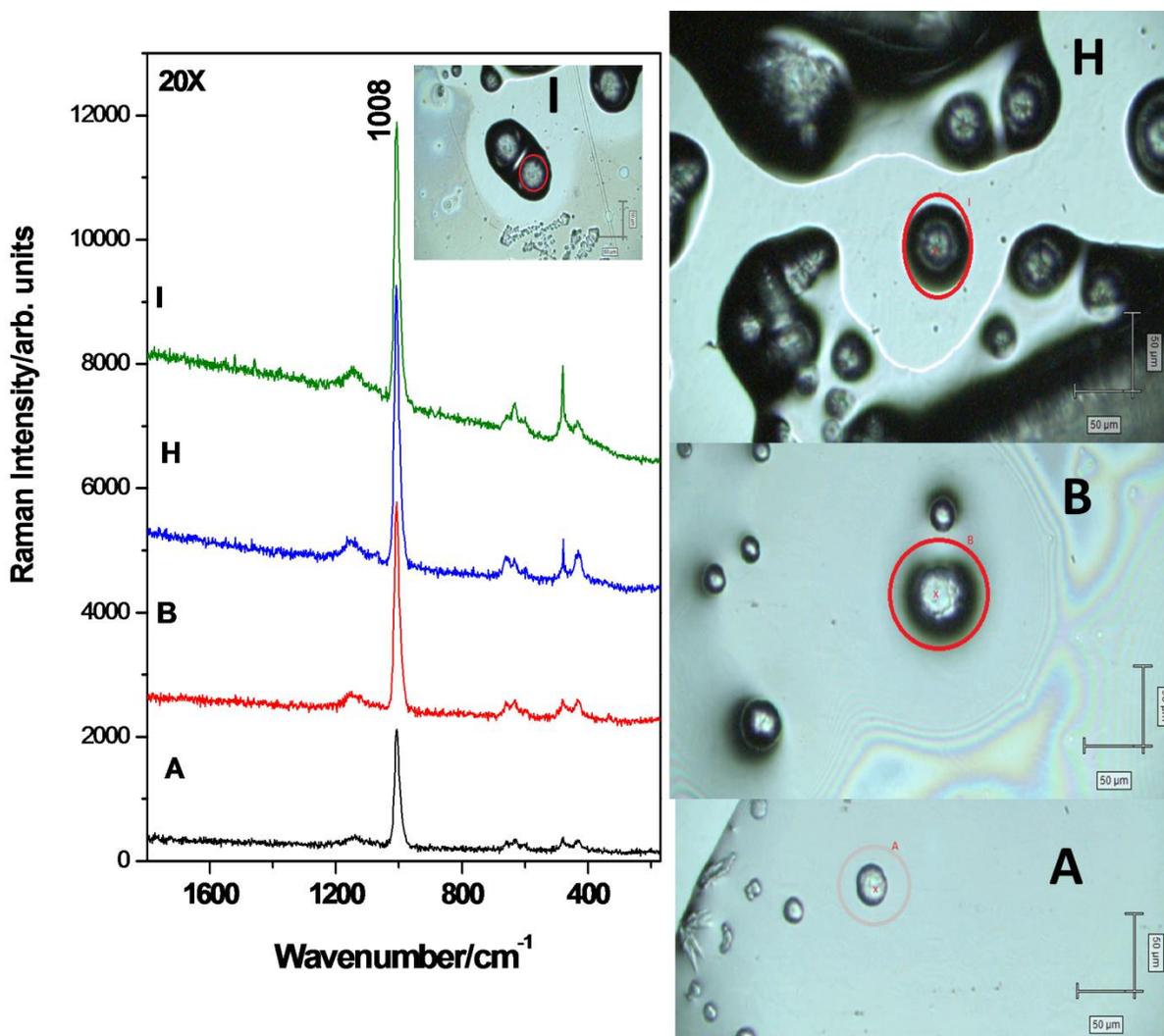


Fig. S2. Raman spectra collected from the dried black spots (denoted A,B,H. I) resulted after seawater droplet evaporation on the SpectRIM slide. The micrographs collected through the Raman microscope show the dots employed for Raman acquisition (highlighted in red circles). Scale bar: 50  $\mu\text{m}$ . The observed Raman bands are characteristic to sea salts (magnesium sulfate dominant). Excitation: 532 nm.

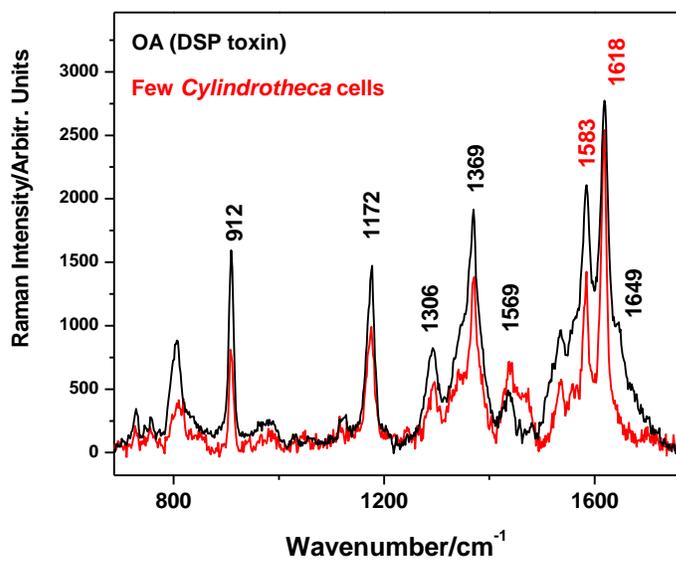
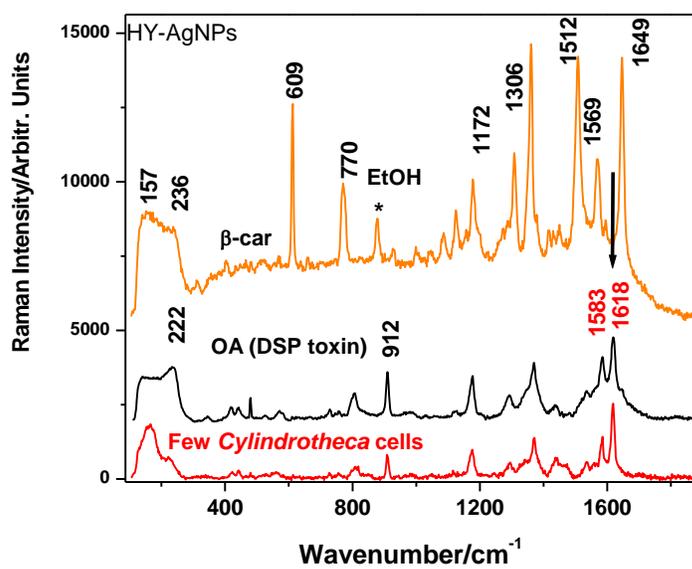


Fig. S3. Upper: SERS spectra collected from few *Cylinthrotheca* diatom cells with HY-AgNPs compared to the SERS signal of a DSP toxin (okadaic acid)<sup>2</sup>. Lower: Detail of the 700-1800 cm<sup>-1</sup> range.

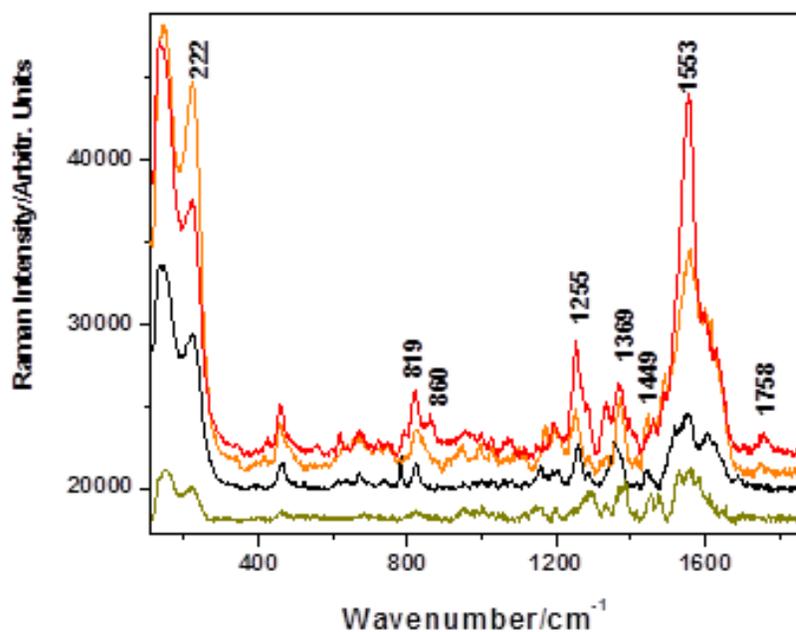
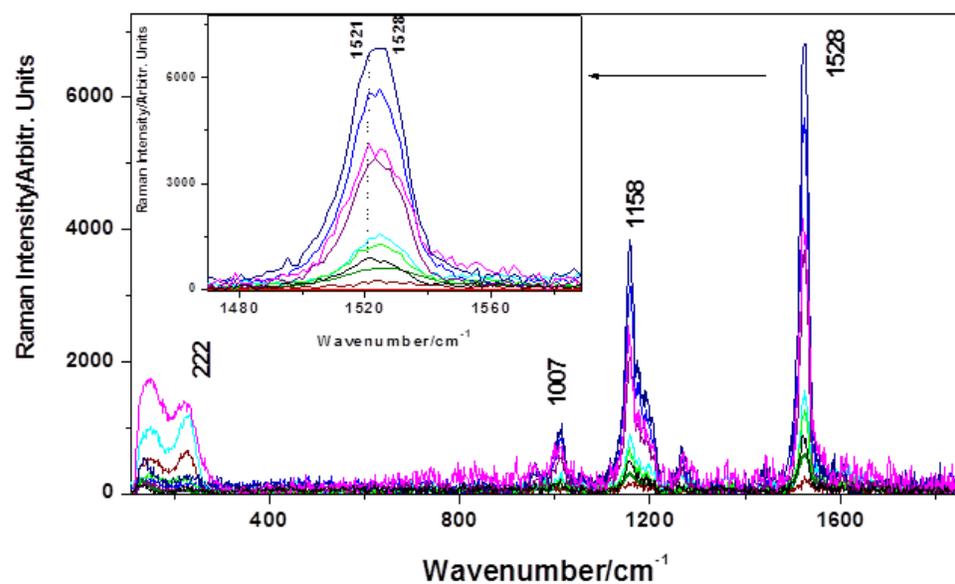


Fig. S4. Top. Background subtracted SERS spectra collected from the immobilised diatoms green body after coating with colloidal LM-AgNPs. Bottom: Spectra collected from the extracellular substances (spectra 9-12 from Fig. 8, after normalization and background subtraction).

## References

1. S. Cintă Pinzaru, Cs. Müller, S. Tomšić, M. M. Venter, B. I. Cozar, B. Glamuzina, (2015), New SERS feature of  $\beta$ -carotene: consequences for quantitative SERS analysis. *J. Raman Spectrosc.*, 46:597–604. doi: [10.1002/jrs.4713](https://doi.org/10.1002/jrs.4713).
2. S. Cinta Pinzaru, Cs. Müller, S. Tomšić, I. Ujević, A. Bratoš Cetinić, B. I. Cozar, R. Stiufiuc, M. M. Venter, B. Glamuzina, Noble Metal Nanoparticles in Seawater: Nano Risk Towards Aquatic Organisms Assessed by SERS, *Proc. of the ICAVS 8*, (Eds)B. Lendl, C. Koch, M. Kraft, J. Ofner, G. Ramer, Vienna, 2015, p. 106-107.  
[http://www.icavs.org/icavs8/images/program/program\\_web.pdf](http://www.icavs.org/icavs8/images/program/program_web.pdf)