**Supplementary Material**

**Biosilica/Polydopamine/AgNPs composites: new hybrid multifunctional heterostructures obtained by chemical modification of Thalassiosira weissflogii silica shells**

**Danilo Vona** Università degli Studi di Bari «Aldo Moro», Via Orabona 4, 70126 Bari ; **Stefania Roberta Cicco** CNR-ICCOM –Bari, Via Orabona 4, 70126 Bari ; **Roberta Ragni** Università degli Studi di Bari «Aldo Moro», Via Orabona 4, 70126 Bari ; **Gabriella Leone** Università degli Studi di Bari «Aldo Moro», Via Orabona 4, 70126 Bari ; IIT- Center for Nano Science and Technology, Via Giovanni Pascoli, 70, 20133 Milano ; **Marco Lo Presti** Università degli Studi di Bari «Aldo Moro», Via Orabona 4, 70126 Bari ; **Gianluca Maria Farinola\*** Università degli Studi di Bari «Aldo Moro», Via Orabona 4, 70126 Bari ; [gianlucamaria.farinola@uniba.it](file:///C:\Users\Downloads\gianlucamaria.farinola@uniba.it)

COLOR timing.tif

***Figure S1.*** *Images of the color turning during PDA coating of frustules samples.*

C:\Users\Stefania\Documents\mrs comm definitivo genn 2018\s1.tif

***Figure S2.*** *Contrast Phase microscopy images of amino-functionalized frustules before PDA coating (F-NH2) and after PDA coating (**F-NH2 PDA); images of bare frustules after PDA coating at pH 9.5 and 10.5 (F PDA 9.5; F PDA 10.5). Marker: 10 μm.*

**PDA nanoparticles synthesis.** For PDA nanoparticles (PDA NPs) synthesis,[1-2] 13.1 mL of bidistilled water were ultrafiltered (filters Ø of 0.2 μm) and placed in a falcon tube; then 7.3 mL of filtered ethanol and 300 μL of filtered NH4OH solution were added. Sample was strongly stirred and 4.6 mL of dopamine-hydrochloride solution (10 mg/mL) were added. Oxidative polymerization of PDA NPs was carried out for 12 h; finally, NPs were collected by centrifugation (10000 rpm) after 3 washing steps in bidistilled water. PDA NPs exhibited 181.4±34 nm diameter as DLS output result (var. 1976 nm2). PDA NPs were synthesized for UV-visible spectra characterization and comparison.

s2 1 um 200 nm.tif

***Figure S3.*** *SEM images of PDA NPs at 2 different magnifications. Markers: (a) 500 nm; (b) 200 nm.*

**

***Figure S4.*** *DLS graph of the size of PD NPs.*

**Soft biosilica extraction and PDA coating.** A volume of 1 mL of diatom culture (106 cells/mL) was treated with 2 mL of SDS (2% w/V)-EDTA (100 mM) solution in a glass tube;[3] after gently pipetting, in order to avoid foam formation, the mixture was maintained overnight at 55°C. Pellet was then washed with bidistilled water for 3 times and with TRIS buffer solution (10 mM, pH 8.5), and the extracted biosilica was stored in 0.1 mL of TRIS buffer solution. Dopamine polymerization was directly performed at pH 8.5. Reaction was carried out for 3 h at room temperature with a dopamine concentration of 2 mg/mL in the same aforementioned buffer solution. To remove the excess of PDA, a glucose gradient (a 40% w/V phase for frustules separation and a 5% w/V phase for PDA, 1+1 mL in a tube) was carried out.[4] Then PDA-coated frustules were washed three times with bidistilled water. Bare and PDA coated soft cleaned frustules are both shown in figure S4.

s3.tif

***Figure S5****. Confocal microscopy images of biosilica structures obtained via soft cleaning before (a) and after (b) PDA coating. Marker: 10 μm.*

**Architecture parameters evaluation.** Samples were morphologically evaluated by bright field optical microscopy in reflection and SEM. The number of pores / area of 50 girdles was evaluated (in areas of 500 nm x 500 nm) per sample (F-NH2, F-NH2 PDA and F-NH2 PDA Ag); also the average size of cells was investigated (100 shells per sample).[4] Image J was used for both analyses.

s4.tif

***Figure S6.*** *Architecture parameters investigations on amino-functionalized frustules before (F-NH2) PDA coating, after (F-NH2 PDA) PDA coating and after (F-NH2 PDA Ag) silver nano-precipitation.*

**References**

1. K. Y. Ju, Y. Lee, S. Lee, S. B. Park, and J. K. Lee: Bioinspired polymerization of dopamine to generate melanin-like nanoparticles having an excellent free-radical-scavenging property. *Biomacromolecules*, **12(3)**, 625-632 (2011).

2. G.M. Farinola, R. Ragni, F. Milano, S. La Gatta, R. R. Tangorra, M. Mastropasqua Talamo. M. Lo Presti, Angela Agostiano; S.R. Cicco, A. Operamolla, O.H. Omar and M. Trotta: Photoconverters with organic semiconductors and photosynthetic bacteria: positioning the bacterial Reaction Center in nanostructures. *In SPIE Organic Photonics and Electronics,* (International Society for Optics and Photonics), 994406-994406 (2016).

3. N Kröger, R. Deutzmann, C. Bergsdorf, and M. Sumper: Species-specific polyamines from diatoms control silica morphology. *Proceedings of the National Academy of Sciences.* **97(26)**, 14133-14138 (2000).

4. S.R. Cicco, D. Vona, G. Leone, M. Lo Presti, F. Palumbo, E. Altamura, R. Ragni and G.M. Farinola: From polydisperse diatomaceous earth to biosilica with specific morphologies by glucose gradient/dialysis: a natural material for cell growth. *MRS Comm.*, **7(2)**, 214-220 (2017).