

Dipartimento di Scienze fisiche, della Terra e dell'ambiente

**Dottorato in Scienze e tecnologie ambientali,
geologiche e polari**

38° Ciclo

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Structural and mechanistic insight into the biomolecular corona
formation of engineered nanomaterials and nanoparticles to unravel
their impact on marine biodiversity

Settore scientifico disciplinare: BIO/07

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Thesis structure

The general introduction of this PhD thesis aims at providing an overview on engineered nanoparticles (NPs) in the marine environment and on the molecular and cellular mechanisms that govern their interactions with marine organisms. In the first sections, some general aspects related to what nano-bio interactions are, how they have been studied in (eco)toxicology, and the main transformations NPs undergo in seawater are provided. A further section is dedicated to explaining how marine biomolecules form interfacial layers on NP surfaces and how this “acquired” biological identity can modulate recognition, uptake, and biological effects. In order to unravel the mechanisms underlying these responses, the potential involvement of immune-relevant proteins and pathways is presented, with a particular focus on the coelomic fluid and immune cells (coelomocytes) of the sea urchin *Paracentrotus lividus* as a suitable model.

The thesis is divided into four chapters. Each chapter is provided with a graphical and a written abstract summarizing concisely the key contents as rationale, hypothesis and main findings. An introduction presents the topic addressed in the chapter and provides a background on the existing research. Then, a methodology section describes how the research was conducted. The critical parts of the research are expressed in the results and discussion sections, where the obtained data are shown and interpreted. Finally, a conclusion part restates the main arguments of the work and summarizes main findings. Each chapter ends with a list of references. Here below a summary of the content of each chapter.

Chapter 1 examines the formation of the bio-corona in the coelomic fluid of *P. lividus* and correlates its composition with *in vitro* immune cell (coelomocytes) responses. The integration of physicochemical characterization, proteomic analysis, and coelomocyte bioassays clarifies how NP surface properties and the selective adsorption of proteins influence recognition, internalization, and immune cell responses.

Chapter 2 extends the analysis to the *in vivo* scale, evaluating how NPs transform in natural seawater (NSW) and how these transformations shape whole-organism responses under environmentally realistic exposure conditions. The combined use of cellular and enzymatic biomarkers links eco-corona formation to physiological and immune responses.

Chapter 3 focuses on the protein side of the interface, investigating whether adsorption onto the NP surface induces modifications in the secondary structure of bound proteins and whether such changes affect their biological function. In particular, structural alterations of the toposome, a key protein in echinoderm immune responses, are examined as a mechanistic case study.

Chapter 4 addresses the methodological challenge of corona traceability by developing and validating a fluorescent labeling strategy capable of preserving corona organization at the single-particle level. This approach enables more reliable tracking of coronated NPs without altering their interfacial identity.

Taken together, these four chapters reconstruct the progressive acquisition of biological identity by NPs in the marine environment, demonstrating how the corona acts as a central element in modulating nano-bio interactions across multiple organizational scales, from the molecular to the biological level.