Politecnico di Torino

Doctoral Program in Material Science and Technology (31th Cycle)

Photogenerated Janus-like surface heterogeneity to design particle properties and assembly

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Heterogeneity introduces complexity: when it is compartmentalized - which means spatially-distinct within a single object - novel properties and functions can arise. This type of heterogeneity is generally indicated as Janus-like heterogeneity, named after the bi-faced roman god Janus.

The research findings, herein reported, represent the outcome of efforts in the direction of filling the research gaps in the synthesis of reliable synthetic routes of general validity to generate Janus-like heterogeneity at the micro and nanoscale. The central idea of this manuscript is developed around photochemical concepts to allow the generation of Janus-like heterogeneity by exploiting the spatial and temporal control of light-induced reactions. This enables the introduction of Janus character, to a given system, without the constrains of thermodynamically driven approaches (e.g. built upon phase segregation or heterogeneous nucleation), and thus paving the way for more complex systems with the possibility of broad material combinations. To do so, the Janus character is introduced, in all cases, in terms of Janus-like surface heterogeneity.

In this work, a tool-set of light-driven strategies to generate a variety of Janus-like surfaces at both micro and nanoscale has been developed. Thanks to their photochemical nature, the use of heat and/or metal catalysts is not required, whereas it is generally necessary to drive other available surface modification approaches. As a consequence, the photogeneration of Janus-like surfaces, while remaining efficient, can be potentially extended to systems requiring milder conditions. For each experimental contribution, a different photochemical approach has been developed and investigated. Both organic and inorganic, soft and hard surface modifications have been exploited. In parallel to the specific synthetic protocol, we explored the properties arising from the surface modifications reactions by adopting techniques allowing near-realistic-condition investigations.

In the first experimental contribution, a UV-light induced photochemical approach to generated Janus-like hybrid surfaces is reported for micrometric particles (silica cores of 500 nm in average radius). By using surface-anchored organothiols, the technique combines hard structuration with in situ photogenerated metal nanoparticles and soft structuration with polymer brushes via photografting-from methods. By playing on the hard-structuration-conditions, we demonstrated how it is possible generate Janus-like hybrid with tailorable optical properties in terms of metal nanoparticle size and, in turn, wavelength of optical absorption. In the second experimental section, we reported a long-wavelength photochemical approach to generated soft Janus-like amphiphiles from small silica cores (below 25 nm in average radius). Janus nanoparticles with hydrophilic and lipophilic hairy compartments were synthetized via two-step toposelective grafting-from reactions. This is done by taking advantage of a surface anchored Norrish I photoinitiator and a reversible electrostatic particle immobilization technique. Because of their amphiphilicity, the so-synthetized particles show precise self-assembly patterns in water. Since the self-assembly behavior is driven by hydrophobic directional forces occurring in water, we investigated the assembly process in liquid environment by employing small angle X-ray scattering and optical scattering techniques to get statistically relevant data. The assembly patters were also directly visualized in near-realistic condition by using in situ liquid phase transmission electron microscopy and confirmed by means of other direct and indirect techniques. In the last experimental section, starting from photoactive silica nanoparticles (below 20 nm in average radius), we reported a photochemical approach combining long-wavelength grafting-from and click chemistry to generate amphiphilic nanoparticles with a pH-tailorable cationic charge (from tertiary amine groups) and amphiphilic Janus-like surface properties. We investigate also the ability of these amphiphilic nanoparticles to controllably interact with cell membrane models. Since the so- synthetized hairy nanoparticles possess two distinct domains, a lipophilic cell-adhesive and a hydrophilic cell-non-adhesive, membrane-anchoring properties are likely to follow. The interaction behaviors were investigated at different pH values in order promote or depress the protonation of amine groups of the hairy corona and, in turn, to question the effect of the nanoparticle-borne surface charge on the interaction patterns. This was determined by probing the interaction from impedance measurements of the cell membrane via electrophysiology of planar lipid membrane (as cell membrane model). To further corroborate the electrophysiology findings, along with conventional techniques, in situ liquid phase transmission electron microscopy was used to unravel the interaction dynamic in near-realistic conditions.