Versatile Bionanostructured Materials via Direct Reaction of Functionalized Catechols

Beatriz García[a], Javier Saiz-Poseu[a], Josep Sedó[b], Jordi Hernando,[c] Felix Busqué[c] and Daniel Ruiz-Molina[b]

[a] *Fundación Privada ASCAMM, Unidad de Nanotecnología (NANOMM), ParcTecnològic del Vallès, Av. UniversitatAutònoma, 23 - 08290 Cerdanyola del Vallès, Spain*

[b] *Centro de Investigación en Nanociencia y Nanotecnología, Campus UAB, 08193, Cerdanyola del Valles,Spain.*

[c] *Chemistry Department, Universitat Autònoma de Barcelona, Campus UAB 08193, Cerdanyola del Vallès, Spain*

e-mail: bgarcia@ascamm.com

Wettability is a fundamental property of solid surfaces governed by both the chemical composition and the surface topographic microstructure. Thus, to obtain highly hydrophobic surfaces, many methodologies based on, for instance, fluorinated materials, and control of surface microstructure have been developed. However, most of these methodologies involve thermal treatments, surface patterning, or the use of sophisticated deposition techniques, such as chemical vapor deposition, enhanced plasma vapor deposition, self-assembly and spin coating. Regarding practicality, cost-effectiveness and scalability, such elaborate treatments are often inadequate. In order to obtain both water and oil repellent properties, there still exists the challenge to develop methodologies for fabricating materials relying on operationally simple procedures.

Nature can be a good source of ideas to design and develop such novel functional materials. This is the case of coatings bio-inspired on mussel adhesion proteins containing catecholic (L-DOPA) residues, shown to adhere very strongly to virtually any surface. Inspired by this natural system, in this work catecholic polymers with one or two unsubstituted (fluoro) alkyl chains in the aromatic ring have been used to generate surface-coating materials under alkaline conditions. These materials convey oleo-/hydrophobic properties to different kinds of surfaces by means of robust coatings of nanometric thickness that are effective over a large range of surfaces and materials -nanostructured or otherwise-.

Herein we report a new approach for the preparation of catechol-based materials based on a simple polymerization process in the presence of ammonia in a way reminiscent of melanization reactions. This strategy represents a significant advance in combining many advantages: ease of preparation, solubility in appropriate solvents and a high ratio of adhesive (catecholic)-to-functional moieties.

When the material resulting from the reaction of functionalized catechol with ammonia is dissolved in non-polar solvents such as hexane, robust coatings on a representative variety of substrates, both at the nano-/macroscale are obtained, by means of a quick and *ex situ* approach without any pretreatment or modification. Whereas catechol monomers bearing a long alkyl chain afford coatings with a persistent hydrophobic character, it was shown that this methodology can be extended to several other catechols with different ring pendant groups, providing varied surface functionalities such as oleophobic/hydrophilic, anti-fouling, anti-bacterial activities and water remediation.

On the other side this material is shown to spontaneously structure in the form of nanoparticles a few hundred nanometers in diameter in water, which easily stick to polyester fibers affording stable NP coatings.

References

[1] J. Sedó, J. Saiz-Poseu, F.Busqué, D. Ruiz-Molina, Adv. Mater., **25** (2013), 653-701.

[2] J. Saiz-Poseu, J. Sedó, B. García, C. Benaiges, T. Parella, R. Alibés, J. Hernando, F. Busqué, D. Ruiz-Molina, Adv. Mater., 2013, DOI: 10.1002/adma.201204383.

Figures

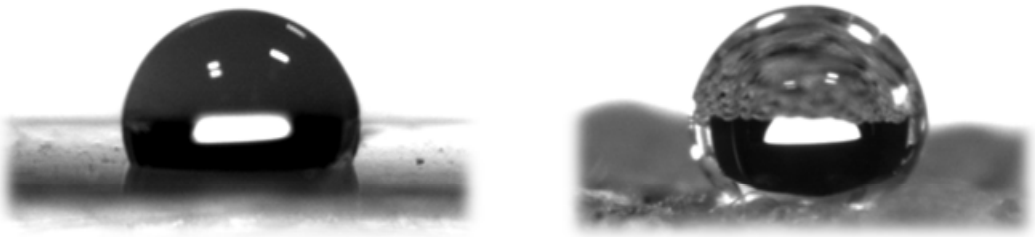

Figure 1. Water droplets on polymer- coated glass (left) and polyester (right).

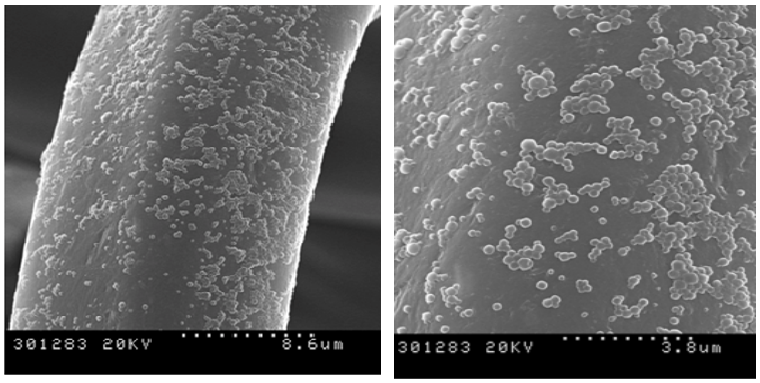

Figure 2. Catechol nanoparticles attached to a fiber.