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Water Droplets to Nanotechnology

A Journey Through Self-Assembly

Plinio Innocenzi, Luca Malfatti and Paolo Falcaro

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Preface

THINK BIG AND...START NANO...

Within the nano-world, self-assembly is the result of a delicate balance among different chemical-physical forces, and one of the most striking properties of the nano-objects is the ability to self-organize into complex structures. Following the consideration that we are all the result of a self-organization process, we should be aware that the complexity of living structures holds the secret to self-assembly.

The self-organization depends on different variables such as composition, shape and dimension of the involved objects, as well as their different physical states.

Liquid systems have exceptional features that make them excellent candidates for self-assembly.

Firstly, liquids offer the possibility to dissolve or suspend different species such as copolymers, nanoparticles, biomolecules and biological entities. Secondly, chemical reactions occur homogenously and quickly in the liquid state. Finally, the liquid can be removed, taking advantage of the evaporation process.

Despite evaporation being a common phenomenon in everyday life, it plays a crucial role in the self-organization of systems composed of liquids and nano-objects (colloidal systems). These are either preformed solids such as nanoparticles, nanorods of sheets, or supramolecular structures formed during the self-assembly process itself. That is the case for surfactants, which are a fascinating class of molecule. Under solvent evaporation surfactants are able to generate a large variety of super-structures from basic to complex shapes.

However, there is a drawback in this business and that is the instability of the process. When evaporation is involved, most of the

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self-assembly processes are not equilibrium phenomena because they are kinetically controlled.

Achieving organization through non equilibrium sounds like an ambitious task but fortunately it works!

In this book, we have highlighted that evaporation by itself does not create organization; order is indeed driven by the forces that arise during evaporation. These forces can trigger the system to become ordered or disordered. In the latter case, the final material will not exhibit any organization at the nanoscale; only a careful control of the evaporation rate allows dancing on the tightrope of self-assembly.

This book can be treated as a small journey that reveals the secrets of self-assembly occurring during evaporation of a colloidal water droplet; little by little, the journey moves from the mysteries of a coffee stain on glassware to the formation of complex hierarchical systems for advanced multifunctional applications.

READING THIS BOOK

Nowadays, expertise in a specific field is mandatory for developing cutting edge science. However, this requirement can lead to a loss of the wider perspective, which is the basis of a multidisciplinary approach.

This book has been written with the aim of providing a general overview of self-organization processes whose complexity and potential are difficult to understand without some basic knowledge. Therefore, this book should not be considered as a comprehensive scientific treatise but rather as a journey into nanotechnology following the path of self-assembly. To keep the focus on this intriguing phenomenon, each chapter proposes a selected number of techniques and results. For example, a variety of fabrication techniques allows one to obtain specific optical devices called *photonic crystals* and Chapter **6** highlights cases involving both evaporation and self-assembly. Not all the literature in the field has been cited; to keep the story on the right path we have carefully selected the references based on our personal opinion.

The presented journey should be enjoyable to the reader and the complexity of the different topics has been simplified. Mathematical formalisms have been avoided unless strictly necessary and we have tried to explain concepts with figures and schematics where relevant.

In summary, this book is not aimed at scientists with a specific background in self-assembly, but at curious readers interested in gaining a general understanding of the topic. And finally, Professor

David Evans of the Beijing University of Chemical Technology is gratefully acknowledged for critical reading of this book and his highly appreciated comments.

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Luca Malfatti
Paolo Falcaro

Author biographies

Plinio Innocenzi is a Professor of Materials Science at the University of Sassari, Italy and Director of the Laboratory of Materials Science and Nanotechnology (LMNT). He graduated in physics from the University of Padua, Italy and was an Assistant Professor at the Department of Mechanical Engineering, Material Section at the same university. In 1994, he was awarded a Science and Technology Fellowship in Japan from the European Commission and became an associate foreign researcher at Kyoto University, Japan. He has also worked as a visiting Professor at the University Paris VI, Kyoto University, Osaka Prefecture University and Beijing University of Chemical Technology. He was one of the founders of the International Sol–Gel Society and has served on the Board of Directors. In addition, he is a Fellow of the Royal Society of Chemistry. He has authored more than 150 articles in international ISI journals, 3 books and 12 patents. His research interests are focused on self-assembly at the nanoscale, sol–gel chemistry and hybrid organic–inorganic materials.

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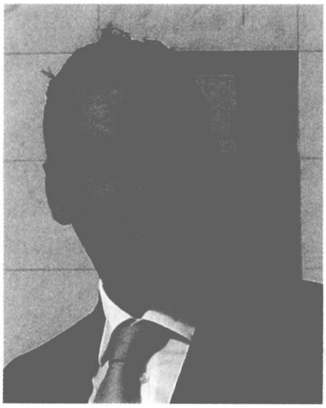
Luca Malfatti (born 1977 in Venice, Italy) is an Assistant Professor of Materials Science at the University of Sassari, Italy. He received a Master's degree in Material Science from the University of Padua in 2004 and a Ph.D. degree in "*Materials for environment and energy*" from the University of Rome Tor Vergata in 2010. He has worked as a visiting researcher at the University Paris VI, the CNEA in Buenos Aires, Osaka Prefecture University and the CSIRO Materials Science and Engineering Division in Melbourne. He has authored more than 70 articles in international ISI journals. His research deals with the synthesis of mesoporous and hierarchical porous materials obtained by supramolecular self-assembly and their application as advanced functional ceramics.



Paolo Falcaro is a materials scientist who received his Ph.D. in Material Engineering in 2006 from Bologna University. From 2005 to 2008, he worked as a research scientist in the Nanofabrication Facility (Civen/Nanofab, Venice, Italy) for industrial applications using sol–gel technologies. In 2009, he joined CSIRO (Material Science and Engineering Division, CMSE in Melbourne, Australia) as a Postdoctoral Fellow. He is currently a research scientist at CSIRO and an ARC Discovery Early Career Research Fellow. He is the recipient of several national and international awards, including the Ulrich Award, the Japan–Australia Emerging Leader Award and the CSIRO Julius Award. He investigates self-assembled porous materials preparation and patterning and fabrication techniques to control the formation of functional materials. He also works on functional nanoparticles for sensing applications and biolabelling.

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CHAPTER 1

The Coffee Stain: Using a Water Droplet for Self-assembly

This first chapter is dedicated to showing how a simple phenomenon, such as the evaporation of a droplet of a colloidal solution, can become a sophisticated tool for self-assembly and the fabrication of nanodevices. The chapter will be also be used to explain what the coffee-stain effect is and how it is generally understood and applied for designing patterns that self-organize upon droplet evaporation.

1.1 THE COFFEE-STAIN EFFECT

Drinking a cup of coffee, especially a good Italian espresso, is one of those little pleasures of everyday life. It can be difficult to imagine, therefore, a small droplet of our coffee as the starting point of a journey into self-assembly and nanotechnology as we try to enjoy our moments of relaxation. However, there is so much interesting and unexpected physics and chemistry behind the evaporation of a coffee droplet that it is worth observing the details of this phenomenon. The coffee-stain effect is intriguing because after the evaporation, what is left behind is not a homogeneous halo. It is a ring (**Figure 1.1**). This is a general effect as it does not matter what kind of solution is used as the coffee stain seems to be an ubiquitous phenomenon. The effect can be reproduced using different solvent−solute combinations, which comprise single molecules[1], nanoparticles[2], polymers[3], salts[4] and even bacteria; it is also observed at different length scales, from micron-sized particles to nano-objects as well as on the molecular level. It can also be observed on different types of substrates, such as silicon, glass, metal, mica and concrete. The coffee stain effect may represent an issue if homogeneous

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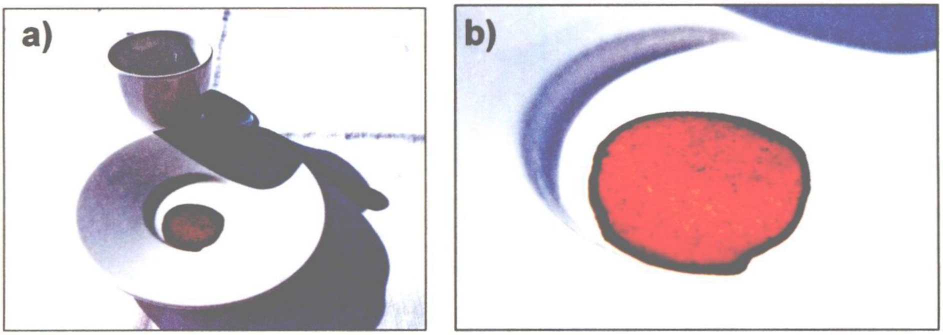

Figure 1.1 Dropping a coffee droplet on a solid substrate leaves upon evaporation a typical stain with a ring b) Enlarged image of the coffee stain presenting the typical ring shape (pictures by Laura Villanova).

spots are required. For instance, without preventing such an effect, the ink-jet technology would produce dishomogeneous plots[5,6]. A detailed understanding of the formation mechanism is necessary either to prevent the formation of the coffee-stain effect, or to take advantage of it in the development of new applications.

The first comprehensive explanation was reported by Deegan and co-workers in an article published in *Nature* (1997) and it is based on the observation that a mechanical constraint of an evaporating droplet causes a capillary flow towards the contact line[7]. When we pour a liquid droplet and observe how its evaporation occurs two different scenarios can be envisaged: in the first case the droplet is free to move on the substrate and in the second case the surface irregularities cause a blockage of the contact line that remains pinned until the evaporation process has gone almost to completion.

In the first case, therefore, the contact line is not pinned and the droplet shrinks; the profile of the droplet will not change while its radius, R, decreases (**Figure 1.2**). In contrast if the contact line is pinned[8] the droplet will flatten modifying its profile while the liquid evaporating from the edge is replenished by the liquid from the interior (**Figure 1.3**). If the liquid contains dispersed particles they will be carried out to the edge of the droplet by capillary flow that is induced by the pinning. The mass accumulation at the contact line then forms a ring-like structure around the droplet.

We can have a closer look at the evaporation process as described by Deegan[9] for an ideal case of a small, thin, dilute and circular drop with a fixed radius, R. The contact line is pinned and at every point of the droplet, r, and there is an evaporative flux, $J(r)$, which reduces the height, $h(r)$, of the droplet. The evaporation rate, however, is not