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Integrative chemistry: Positioning chemical reactors within the geometric space as a tool for the design of advanced functional materials

Chimie intégrative: Positionner les réacteurs chimiques dans l'espace géométrique comme outil pour le design de matériaux fonctionnels avancés

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ABSTRACT

Chemical sciences are on continuous evolution offering more and more complex synthetic strategies that rely on emerging inter- and trans-disciplinary vocation. In this tutorial review, we demonstrate how integrative chemistry, through combining soft matter and soft chemistry, allows positioning chemical reactors within the geometric space. Therefore, we focus the examples on biliquid foam oil/water interfaces and sol–gel chemistry. In this view we distinguish between diluted and concentrated emulsions, acting respectively as discrete chemical reactors and percolated ones. Along the manuscript, non-exhaustive morphosyntheses of advanced functional materials are proposed when dedicated either to heterogeneous biocatalysts, energy conversion systems and thermo-stimulated delivery of encapsulated substances.

RÉSUMÉ

Les sciences chimiques sont en constante évolution, ce qui se traduit par des modes opératoires de plus en plus complexes à vocation inter- et transdisciplinaire. Dans cette revue, nous démontrons comment la chimie intégrative, en combinant matière molle et chimie douce, parvient à positionner les réacteurs chimiques dans l'espace géométrique. Ainsi, nous focalisons le propos sur les interfaces huile/eau d'émulsions et la chimie sol–gel. Dans cette optique, nous distinguons les émulsions diluées et concentrées, intervenant respectivement comme réacteurs chimiques discrétisés ou percolés. Dans cet article, nous donnons des exemples non exhaustifs de morphosynthèses de matériaux fonctionnels dédiés, par exemple, à la biocatalyse hétérogène, à la conversion d'énergie ou à la délivrance thermo-stimulée de substances encapsulées.

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1. Introduction

Chemical shapes and functionalities are certainly the two most important tools employed toward the reaction schemes of living organisms. Historically, chemical science first addressed and was interested in the composition of matter rather than its shape. Indeed, it is only in the middle of the XIX century that the notion of “isomers” has emerged when the chemical structure formulae replaced the global one. The notion of shape is becoming more and more important in chemical science. For instance the notion of key/host when addressing dynamic combinatorial chemistry is extensively employed when dealing with supramolecular chemistry [1a]. Another good example relies on the carbon case where fullerenes, graphenes and nanotubes bear divergent properties when compared with the basic graphite or diamond allotropic forms.

Today, society high standard specific needs are pleading for chemists to conceive entities more and more complex, multi-scales, multifunctional and capable of developing a certain degree of autonomy, taking inspiration from *Mother Nature*. The chemical paths employed to generate such complex architectures are becoming more and more complex and certainly interdisciplinary, bio-inspired or not. When considering the field of bio-inspired materials “integrative synthesis” has been first proposed by S. Mann [2] while coupling transcriptive, synergistic and spatially restricted syntheses. This approach was further refined by C. Sanchez [3] who summarized perfectly the outstanding revolution in modern materials chemistry. This concept was finally fully theorized when enouncing the concept of “Integrative Chemistry” [4] as “*the integration of the sol–gel process, inorganic chemistry, lyotropic mesophases, supramolecular architectures, air-liquid foams, biliquid foams, external fields, organic polymers, nanofunctionalization and nanotexturation, (...) [, which] offers the possibility of achieving new architectures at various length scales and with enhanced properties*.” Hence, *Integrative Chemistry* can be understood as a method for material design where the initial bricks, relevant from several domains of chemical sciences, are connected and assembled with the help of different driving forces occurring *via* multiscale reactions and structuring mechanisms. In this regard and conceptually speaking, *Integrative Chemistry* [3] is certainly the link between the notions of “complexity in chemistry” [5] and the bio-inspired integrative synthesis [1,2]

The goal here is certainly not of being exhaustive considering the design of advanced functional materials, but more importantly to depict how *Integrative Chemistry* allows positioning chemical reactors within the geometric space. For this purpose we will drive the discussion with material morphosyntheses when using only emulsions, either direct or reverse, diluted or concentrated, as tools to shape final material shapes, sizes and morphologies.

2. General background

2.1. Emulsions and their oil/water interfaces employed as chemical reactors at a glance

Emulsions are thermodynamically meta-stable: over time, the dispersed and continuous phases will macroscopically segregate. They are typically classified into two categories: water-in-oil (W/O) also called reverse emulsions and oil-in-water (O/W) also called direct emulsions (Scheme 1) [6].

To enhance their thermodynamic stability, surfactants are traditionally employed to stabilize the interfaces. As shown in Scheme 1 those surfactant molecules made of a polar head group and a hydrophobic chain will take position at the oil/water interface to minimize the interfacial energy. The choice of the surfactant is important: the Bancroft rule states that a surfactant bearing the higher affinity with one phase will promote this phase as the continuous one [7]. Most of the time the micelles will be swollen with a small amount of the disperse phase, creating a micro-emulsion (nanometer length scale) which is thermodynamically stable contrary to a macro-emulsion (micrometer length scale). Considering their use as soft templates, these concentrated micro-emulsions will promote a second porosity, called mesoporosity, within the final monolithic materials when calcinated. If the wall skeleton is amorphous as it is the case for silica or polymers, final materials will bear intrinsic microporosity, leading overall to a hierarchical porosity. As depicted in Scheme 2, the oil/water interface is crucial when addressing chemical reactions within the continuous phase.

From a chemistry point of view, we can distinguish concentrated and diluted emulsions. Indeed everything relies on the repartition of the oil/water interfaces that will act preferentially as chemical reactors. When promoting nucleation and growth within the continuous phase, the nucleation will always start preferentially at these interfaces, because they represent defects at which the associated heterogeneous nucleation enthalpy is strongly minimized when compared with the bulk homogeneous one. Still from a thermodynamic point of view, the interfaces (Scheme 1) bear high charge density that will favor the under growing nuclei electroneutrality, thereby optimizing both the nucleation and growth steps. Considering the oil/water interfaces as chemical reactors, when concentrated through the use of concentrated emulsion, the chemical reactors will percolate within the geometric space (Scheme 2a) promoting the generation of porous monolith-type materials, while when spread through the use of diluted emulsions, these chemical reactors cannot percolate anymore, leading this time to the generation of discrete capsules (Scheme 2b). It is this aptitude of positioning chemical reactors into the geometric space that will be illustrated hereafter when addressing the design of advanced functional materials.

2.2. Concentrated emulsion-based foams: polymer and ceramic at a glance

Foams are materials containing gaseous voids surrounded by a denser matrix, usually a liquid or a solid. The cells can be closed or open: in closed cell foams, the voids are isolated from each other and cavities are surrounded by complete cell walls whereas in open cell foams the structure consists mainly of ribs and struts. Polymer foams are the most common but their applications are limited by their inferior mechanical strength, poor surface quality and

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