VIDEO ARTICLE

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Gel Networks as Nanoconfined Reaction Media

David Díaz Díaz[1,2]

[1]Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany
[2]Departamento de Química Orgánica e Instituto de Bio-Orgánica Antonio González, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez 3, 38206 La Laguna, Tenerife, Spain

Corresponding author: E-mail: ddiazdiaz@ull.edu.es
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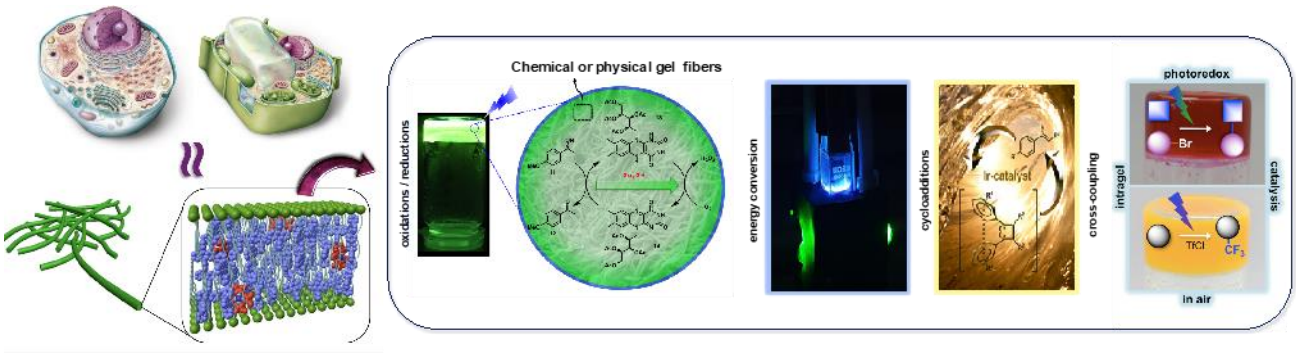
Graphical Abstract

Gel networks have been demonstrated to serve as versatile reaction vessels and nanoreactors to facilitate chemical transformations by mimicking nature's nanoconfinements.



Abstract

Through millions of years of evolution, nature have refined its ability to control kinetics, conversion, and selectivity of biochemical processes by means of confined reaction environments such as enzyme pockets, bilayer membranes, micelles, vesicles, cells, or bioorganic frameworks. The main reason for such advancement is the optimal molecular alignment and restricted motion of reactant molecules compared to those found in bulk solution. Inspired by this fact, numerous synthetic photonanoreactors based on supramolecular self-assembled systems have been developed during the last decades, including mesoporous inorganic materials, microemulsions, micelles, vesicles, lipid bilayer foams, etc. In general, nanoreactors modify the key properties of the molecules within them, thus affecting their chemical reactivity. For instance, confinement may improve photochemical processes by influencing critical aspects such as light absorption and the lifetime of redox intermediates. Among the nanoreactor-like systems described in the literature to facilitate photochemical processes, the more recent use of viscoelastic supramolecular gels, [**1**] typically made of low-molecular-weight compounds self-assembled through noncovalent interactions, as compartmentalized reaction media is particularly appealing due to the versatility of these materials in terms of fabrication, properties, and processability. Furthermore, the high specific surface areas found in supramolecular gels, their stimuli-responsive reversibility, good diffusion properties enhancing the interactions between reactants and the 3D porous network, functional tunability, and blocking effect of external oxygen are some of the

most important features that can benefit photoinduced processes carried out in confined gel media. From a practical point of view, the incorporation of reactants in the gel media can be done by mixing reactants, solvent and gelator molecules before starting the gelation process. Not surprisingly, the efficiency of photochemical processes inside gel media is largely dependent on the type of reaction, characteristics of the gel network, solvent nature, reactant properties, and reaction conditions. In some reactions the synergistic integration of donor-acceptor pairs in the gel nanofibers is reminiscent of the biological photon-harvesting apparatuses in which excitation light energy is effectively harvested and converted in the array of photosynthetic pigments embedded in biomembranes. Thus, the main focus of this lecture is to provide a concise overview of the most relevant examples reported by our group in order to illustrate the main advantages associated with the emerging use of gel-based materials as nonconventional reaction media to facilitate and control photochemical reactions. Although other non-photochemical reactions will be mentioned, we will focus herein on light-induced processes. In particular, photodimerization, triplet−triplet annihilation upconversion coupled to single electron transfer, photooxidation, photoreduction, cross-coupling and trifluoromethylation reactions, among others, will be illustrated during the lecture [**2-5**]. The use of physical or chemical gels as reaction systems may also accelerate high-throughput screening of photocatalysts. Overall, a judicious choice of gelators, reactants, solvent, and reaction conditions for the assembly of these gelators is crucial for controlling conversion, kinetics, and selectivity of intragel photoinduced processes. In conclusion, nonconventional gel media may provide a versatile platform for the discovery of new reaction pathways and facilitate the way that photochemical reactions are traditionally carried out in academia and industry regarding reaction conditions and required infrastructure.

Keywords: Gels; confined spaces; catalysis.

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Biography of Presenting Author

David Díaz Díaz received his BSc (1997) and PhD (2002) in Chemistry from the University of La Laguna, Spain. Then, he joined Prof. M.G. Finn's group as postdoc at The Scripps Research Institute (CA, USA), where he also worked in close collaboration with Prof. Barry Sharpless on the first applications of click chemistry on Materials Science. Since 2006, he has held various positions in academia and industry (Ramón y Cajal researcher, Autonomous University of Madrid, Spain, 2006; Sr. Chemist, Dow Chemical, Switzerland, 2007; Tenured Scientist, The Spanish National Research Council, Spain, 2009; Alexander von Humboldt Experienced Researcher, University of Regensburg, Germany, 2010; DFG Heisenberg Professor (being the first Spanish scientist holding this distinction), University of Regensburg, Germany, 2013. Since 2018, he is Priv.-Doz. at the University of Regensburg, and in 2020 he was appointed as Distinguished Researcher (Beatriz Galindo, Senior) at the University of La Laguna, Spain. Among several international recognitions, he has received the Young Investigator Award from the Polymer Network Group (Japan), Honorary Adjunct Professorships from Jiangsu University (China) and University of Nigeria Nsukka (Nigeria). In 2021, he received the accreditation as Full Professor by the ANECA agency from the Spanish Ministry of Education and the Research Excellence Award by the Spanish Royal Society of Chemistry (RSEQ). He is the Editor-in-Chief of the journal Gels and has published more than 200 scientific articles as well as numerous book chapters, outreach publications, and editorials. His main research interest focuses on the development of soft multifunctional materials for applications in biomedicine (e.g., drug delivery, neuroregeneration, tissue engineering), catalysis, molecular sensing, actuators, polymeric coatings, adhesives, environmental remediation and energy.

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