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Review

Photocatalytic processes in spatially confined micro- and nanoreactors

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Abstract

In this review recent progress in photocatalysis on mesostructured systems, which behave as spatially confined micro- and nanoreactors, is presented. Mesoporous oxides and hybrid photocatalysts based on molecular-organized assemblies offer new possibilities of concentrating low reactant levels, controlling the reaction environment, separating photocatalyst and reaction products, and realizing host-guest catalysis of light-driven reactions. This allows one to organize the catalytic photolysis in an especially efficient way, to increase its selectivity, and to ensure another set of products as compared to photocatalysis in suspension of dispersed photocatalyst. Further increase in selectivity can be attained through functionalization of spatially confined photoreactors to impart them bio- or chemical recognition properties, to couple different photo- and redox-catalysts, and to create complicated hybrid microphotoreactors including those which mimic the natural photosynthetic centers.

Keywords: Spatial confinement; Nanoreactor; Photocatalysis; Titania; Mesoporous materials; Emulsion; Foam; Vesicle; Polyelectrolyte capsule

Contents

1. Introduction 24
2. Micro- and nanophotoreactor systems based on porous inorganic structures 24
   2.1. Micro- and mesoporous photocatalysts 24
   2.2. Structured photocatalytic membranes and films 27
   2.3. Porous beads and hollow spheres 29
3. Micro- and nanophotoreactor systems based on organized molecular assemblies 30
   3.1. Lipid vesicles modified with semiconductor nanoparticles 31
   3.2. Oil-in-water emulsions stabilized with colloidal photocatalyst 32
   3.3. Photocatalyst-loaded liquid foams 32
   3.4. Polyelectrolyte multilayered capsules 34
4. Conclusions and outlook 37
Acknowledgements 37
References 37

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1. Introduction

An organized reaction microenvironment is employed to constrain and pattern initial reagents (precursors) and to perform photoinduced heterogeneous or homogeneous synthesis (decomposition) by a controllable and pre-selected way. Advantages of the spatial confinement of the photocatalytic process are: (i) possibility of tailoring additional functionalities to the microreactor environment thus providing specific characteristics to the microreactor; (ii) large active reaction area ensuring high yield of photoiduced reactions; (iii) confined micron and submicron volume permitting one to carry out photochemical synthesis in the media possessing highly organized solvent structure, which can result in new reaction pathways and products impossible to be synthesized in media without spatial confinement; (iv) diminished overconcentration and overheating effects in the reaction system upon adding reagents; (v) possibility of modeling and mimicking photoinduced processes in Nature on the micron and submicron level. Spatially confined reaction environment can also be employed for photoinduced synthesis of complex materials (compounds) with dimensional, structural, and morphological specificity.

Several typical micron and submicron-confined environments for performing photocatalytic processes were reported to date. They are either individual (vesicles, micelles, emulsion droplets, capsules, inorganic spheres) or connected to the neighbors (micro-mesoporous bulk materials, films, liquid and inorganic foams). However, there are only few demonstrations of the idea of semiconductor-catalyzed photosynthetic (photodegradation) reactions inside spatially confined individual micro- and/or nanoreactors so far. Systematic, continuous studies of the mechanisms and reaction kinetics, influence of different parameters (size of the microreactor, solvent structure in the interior, adsorption of the reactants and intermediates, etc.) on the photosynthetic (photodegradation) processes as well as comparison of reaction products with those obtained by catalytic photolysis in nonconfined media (e.g., in the slurry of dispersed photocatalyst) were not made. Such detailed investigations can help in development of spatially confined photosynthetic approaches as well as in acquiring additional understanding of chemical and physico-chemical processes occurring in the environment providing confinement on the sub-micron scale. The effect of confined geometry alongside with controllable diffusion of the reagents could lead to results not achievable via conventional heterogeneous photocatalysis. The proposed review is an attempt to summarize the current knowledge on spatially confined photosynthesis or photodegradation and to highlight main hindrances in this new interesting area of photochemistry.

2. Micro- and nanophotoreactor systems based on porous inorganic structures

Mesoporous inorganic materials can be considered as one of the perspective microenvironments for photocatalysis due to their high porosity and specific surface area at large external size [1–5]. For example, Joy and Ramamurthy et al. [6] explored zeolites as media for achieving chiral induction of optically active organic molecules during photochemical reactions. Confined space of zeolites forces a reactant and the chiral inductor to interact intimately leading to enantiomerically enriched product with the yield as high as 90% [7–9]. Nanoengineered TiO_2 is also an effective photocatalyst for water decomposition [10], for oxidation of phenol [11], chlorophenol [12,13], mercaptoderivatives [14], aniline derivatives [15], and *n*-pentane [16,17], as a component of a photovoltaic cell [18], for photoinduced CO_2 reduction in a SiO_2 matrix [19]; for additional information also see reviews [20,21]. The combination of highly active photocatalyst with the preparative templating technique can lead to interesting photocatalytic materials with an otherwise nonaccessible combination of properties, such as excellent transport behavior, large porosity, and high specific surface area, which results in improved photocatalytic performance. Furthermore, the spatially restricted pore volume ($\sim 0.1\ \mu m^3$) can affect composition and properties of the products of the photochemical reaction performed inside pores.

2.1. Micro- and mesoporous photocatalysts

Morphological control of materials involves regulation of the outer shape and size as well as inner structure, pore size and connectivity, the colloidal dimensions, and crystal phase of the components. Novel inorganic networks with controlled morphology and properties can be fabricated using templating procedures [22–24]. Organic materials of numerous structures and forms, which can be regulated and easily removed by dissolution in appropriate solvent or by calcination, are applied as templates for formation of porous inorganic structures with pronounced catalytic and photocatalytic properties. Examples of the use of organic templates include: (i) the creation of mesoporous materials with tunable pore structures from block copolymers