1-8-4. Photochemical Reactions in Organic and Inorganic Composites

Overview

Organic molecules can exhibit photochemical behavior that differs significantly from that observed in homogeneous solutions when they form composites with inorganic materials. For instance, the adsorption of organic molecules onto inorganic surfaces can induce changes in i) monomolecular photochemical properties and ii) intermolecular photochemical processes. Representative inorganic materials that are combined with organic molecules include zeolites, layered compounds such as clay minerals (Fig. 1), and titanium dioxide. Although controlling the assembly structure of organic molecules within organic/inorganic composites is not straightforward, recent advances in techniques for controlling the assembly structure of organic molecules have led to the development of fascinating research on the monomolecular photochemical properties and intermolecular processes of organic molecules.

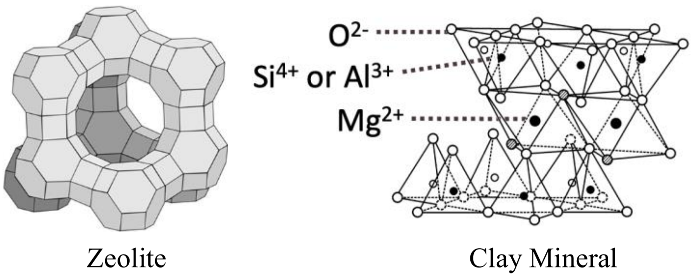

Figure 1. Typical inorganic materials that form composites with organic compounds.

Current Status and Frontiers

With the aim of modifying the photochemical properties of organic molecules and manipulating photochemical processes through their organization, a great number of researchers in Japan have pioneered this field since the 1970s. For an overview up to the mid-2000s, readers are referred to Section "1-8-4. Photoreactions in Organic/Inorganic Composites" in the Photochemistry Div report described in Japanese.

URL: https://division.csj.jp/div-report/02/0210804.pdf

Organic molecules and inorganic materials can form composites through electrostatic interactions, hydrophobic interactions, and other mechanisms. Organic molecules are incorporated into the pores of zeolites, while in clay minerals they are adsorbed onto the surface or are incorporated into the interlayer spaces. Organic molecules incorporated into zeolites undergo fluorescence-phosphorescence switching and selective control of photochemical reaction products through heavy atom effects and light atom effects. While classical zeolites have limitations on the types of organic molecules that can be incorporated due to pore size constraints, recent years have seen progress in the development of zeolites with larger pore sizes. In organic molecule/clay mineral composites, organic molecules often undergo molecular aggregation due to their concentration on surfaces or in interlayer spaces. While this can lead to unique intermolecular photochemical reactions, aggregation can also result in shortened excited-state lifetimes of organic molecules, leading to unfavorable photochemical properties. In clay minerals, techniques to suppress aggregation while maintaining high-density complexation of organic molecules have been developed based on the size-matching rule, resulting in significant advances in understanding the photochemical properties of organic molecules complexed with clay minerals. In typical clay minerals, cationic dye molecules are readily complexed due to the presence of negative charges within their framework structures. Reflecting the atomically smooth surfaces of clay minerals, planarization of complexed organic molecules and suppression of molecular skeletal motion occur. As a result, changes in molecular orbital energies and potential energy surfaces of organic molecules take place, leading to the discovery of fascinating photochemical phenomena such as surface-fixation-induced emission enhancement. By applying the size-matching rule, photocatalytic reaction systems with light-harvesting functions on clay mineral surfaces have been constructed (Fig. 2).

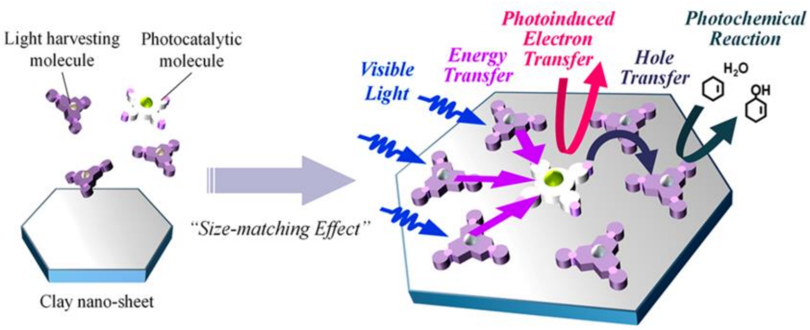

Figure 2. Construction of photocatalytic systems with light-harvesting functionality on clay surfaces. Reproduced with permission from [5]. Copyright 2018 American Chemical Society.

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Future Perspectives and Directions

Challenges to be addressed and achieved within the next 10 years: More active control of molecular assembly structures and photochemical properties in composites. Application development through organic-inorganic semiconductor composites and related systems.

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