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Interfacial Novel Phenomena on Heterogeneous Photocatalysis

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ABSTRACT: Heterogeneous photocatalysis is a photon driven reaction process with multiple elementar steps or phenomena at the interphase interface, involving the generation and transport of electrons, radicals, atoms and/or molecules [1]. It has found various applications, particularly in the field of environmental remediation; however, further activation of photocatalysis and/or its application in the energy field is a challenging task towards a sustainable future society. In this talk, particular focus is placed on interfaces of heterogeneous photocatalytic systems, where various novel phenomena are exhibited as special interfacial behaviors. Two particular topics are selected to exemplify such phenomena. Novel cocatalytic effects of new-type lanthanide oxychloride LnOCI (Ln=Sm,Nd) photocatalysis mechanically-grafted on BiOCI, is evaluated by photoremoval of nitric oxide (NO) gas, is first introduced [2], with special emphasis on microstructural analysis on the interface. A significant cocatalytic effect is only exhibited in highly humid air, where, at the (assumed) steady-state, the maximal NO photoremoval rate is ~5 times more than pure BiOCI, or, 20 times if BiOCI would be the only active photocatalyst of the powder composite. There is a characteristic incubation period prior to activation of the novel behavior. Further, when LnOCI is grafted on TiO2 powder, the NO removal rate in humid air is almost completely eliminated. This is opposite to the case on BiOCI. Since, in dry air condition, there is not a large difference between TiO₂ and BiOCI will be discussed.

Secondly, activation challenge of light harvesting by magnetic field will be discussed. If a key (rate-determining) step of photocatalysis is controlled by a magnetic field, wider environmental applications, as well as energy harvesting, would become possible. The magnetic field effect (MFE) on homogeneous reaction systems has been relatively well-established, however, MFE research on heterogeneous systems, photocatalysis in particular, is limited, and the mechanism is not agreed-upon. Although several MFE parameters have been found responsible for photocatalytic dye degradation, significant roles of oxygen at/near interface are here emphasized. Molecular oxygen is paramagnetic, and typically involved with photocatalysis through ROSs (reactive oxygen species) generation and reactions. In the volume in close proximate to photocatalyst, electrostatic potential and the corresponding magnetic flux would be perturbed, resulting in net Lorentz force acting on dissolved oxygen (DO), which is responsible for MFE phenomena (OANS model [3]). Short-range-order (SRO) diffusion in the Helmholtz layer just outside photocatalyst would be a key step, and correlated to magnetic adsorption/desorption. Through kinetic forces of friction and form drags, DO would cause fluid convection, as ³magnetic² diffusion. Representative MFE features on heterogeneous photocatalysis, directly or indirectly associated with interfacial reaction mechanisms, will be discussed, including the significant roles of oxygen and water, in terms of molecular perspectives and surface conditions of photocatalyst.

[1] Okumura, H., Int. J. Magnetics Electromagnetism, (2016) 2:004.

[2] H. Okumura, et al., Chem. Commun., (2017) 53, 8854-8857.

[3] H. Okumura, et al., Catalysis Today, 258 (2015) 634-647.

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