

Editorial

Photocatalysis—A Special Issue on a Unique Hybrid Area of Catalysis

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Received: 7 June 2012; in revised form: 26 July 2012 / Accepted: 30 July 2012 /

Published: 9 August 2012

Where is photocatalysis situated in the broad field of catalysis? Photocatalysis is a term that combines the basic notion of a catalyst as a material that enhances the rate as a reaction approaches equilibrium without being consumed with the notion that the reaction is accelerated by photons, which of course are consumed. Thus, it is a hybrid concept. As with other areas of catalysis, it has its heterogeneous and its homogeneous dimensions with the former dominating the research literature. Nevertheless, the homogeneous opportunities should not be overlooked. A typical example of a homogeneous case can be found with a dye photocatalyst having two oxidation states where one state can achieve an electron transfer after excitation by light, where that reaction is not feasible from the ground state. If the resulting oxidation state is thermally or photochemically unstable, a catalytic cycle can be completed. Some non-dye examples of homogeneous photocatalysts include soluble ions with multiple oxidation states, including at least one readily excitable by light, such as the polyoxometallates of tungsten or Fenton's reagent. Although photochemists prefer the term "sensitizer", excited states that transfer energy to a molecule that then reacts can be viewed as photocatalysts.

Heterogeneous photocatalysis owes its present prominence to the excitement generated by the report in *Nature* in 1972 by Fujishima and Honda [1] describing the photo-assisted electrolysis of water on irradiation of TiO₂ with photons of energy greater than the band gap of TiO₂, regarding TiO₂ as a semiconductor. This stimulated a theme that continues intensely on approaches to solar energy storage for fuel formation mimicking photosynthesis in plants. This is not catalysis since the reaction in question is not thermodynamically feasible without the photons. It is an energy storage reaction that can be termed photogalvanic. However, in 1976 Carey *et al.* [2] reported photodechlorination of polychlorinated biphenyls (PCBs) and the wave of papers on photocatalysis for environmental remediation was underway. As Rajeshwar reports in his excellent historical essay [3], the number of papers grew exponentially from 249 in 1975–1980 to 16,757 in 2000–2010. TiO₂ continues to dominate the literature because it is non-toxic (it is often included in pharmaceuticals), photo-stable,

and inexpensive. Few other semiconductors can compete in terms of these three aspects. The obvious drawback of TiO₂ is that the photons required must be equal to or greater than the energy of near UV photons (wavelength < 385 nm). Only a small fraction (3%–5%) of the solar radiation reaching the earth can achieve this band gap excitation. A similar small fraction of the output of the common “clear white” fluorescent lamps can also excite TiO₂. Consequently, a substantial photocatalytic industry has grown, especially in Japan [4]. It is based primarily on passive processes that utilize the limited UV light from the sun or fluorescents already installed for other purposes. Most successful applications need not accomplish large scale chemistry in short periods of time and can be effective with the small UV photon flux. These applications include among others [5]: self-cleaning tiles, window glass and wallpaper; air treatment for volatile organic compounds (VOCs); sterilization of medical venues and equipment; deodorization and decolorization; and prevention of mirror fogging using surprising superhydrophilic properties. At present the three leading areas of application are to external construction materials, followed by cleaning equipment, then internal construction materials [5].

As the latest paper counts indicate, photocatalysis is an area of intense research activity globally. Papers on the subject are well represented in journals focused on catalysis, but perhaps they are even more prominent in the literature of environmental remediation of air, water and soil. The interested researchers form a continuum from chemists to materials scientists, to environmental scientists to engineers with the occasional solid state physicist contributing insight into fundamental processes important to the field. The evolution of knowledge of photocatalytic materials can be described, as Rajeshwar [3] suggests, in terms of three “generations”.

The first generation (1975–1985) focused primarily on the studies that provided the understanding of the semiconductor/solution interface under illumination from studies of single crystal semiconductor surfaces and the exploration of a wide variety of semiconductors. At the time it was already recognized that polycrystalline materials would be more suitable in most applications and the first generation of photocatalysis work did focus on suspensions of finely divided material. The second generation, the first important one for photocatalysis with exponential growth of the literature well underway, spans approximately 1986 through 2000. This phase featured work on polycrystalline thin films, efforts to dope semiconductors to exploit visible light, dye sensitization, and widespread use of suspensions to explore the scope of photocatalysis. It was in this period that the industry emerged. Dye sensitized photocatalysts have been extensively evaluated for destruction of dyes in waste streams. Unfortunately many of these papers use UV sources and do not distinguish dye sensitization from band gap excitation.

In the third generation period since 2000, photocatalysis research has continued to expand so that in the 2006–2010 period, publications on photocatalysis exceeded those aimed at energy conversion, 16,757 to 12,811 [3]. This period has seen recognition of two fundamental principles, the special properties of the nanoscale and the power of self-organization, which converge to provide a new conceptual platform on which to construct photocatalysts. Key examples emerge as nanostructured semiconductors and composites, size dependent quantization or “quantum dots”, and nanowires or nanofibers.

Independently of these developments, there has been continuing research on the design of photocatalytic reactors to achieve treatment of water and air at high flow rates competitive with such established technology as UV disinfection. This continues to be limited by the separation problems

faced if slurries are used. Yet slurries offer the best way to achieve uniform distribution of photons over catalytic particles in a well stirred reactor that reduces the mass transport problem for delivering substrates to the active surface to crossing the diffusion layer. If the separation problem is overcome by design of fixed beds, the problems of uniform exposure of substrate to active sites and uniform illumination of photocatalyst must be addressed. Also, oxygen or other electron acceptors must be delivered in conjunction with the contaminants to be oxidized. So far, success in design of reactors that outperform slurries has remained a challenge.

This Special Issue aims to continue the conversation among researchers interested in the still fruitful approach to practical application inherent in the second generation approaches and researchers presenting third generation advances. The reactor designers can make a major contribution and this issue may lead to generating interest among some catalysis researchers, not now in this field, to consider its attractions and challenges.

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