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# Multiphase photocatalytic microreactors

Dalia Heggo [a], Shinichi Ookawara [b,c,*]

[a] Chemical Engineering Department, National Research Centre, Egypt
[b] Chemical Science and Engineering Department, Tokyo Institute of Technology, Japan
[c] Energy Resources Engineering Department, Egypt-Japan University of Science and Technology, Egypt

## HIGHLIGHTS

- Recent microreactors with immobilized photocatalyst cannot attain high throughput.
- Photocatalyst slurry provides more reactive sites than immobilized photocatalyst.
- Mini reactor is suitable to handle photocatalyst slurry with high loading.
- Intensification of photocatalytic slurry flow reactor is of further interest.

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## ABSTRACT

Heterogenous photocatalysis has been paid much attention in the last decades since it can utilize clean and abundant sunlight energy to drive reaction systems for cleaner productions and environmental protections. Those applications are usually conducted by multiphase reactors to make immobilized or dispersed solid photocatalyst in contact with reactants involved in gas (G) or liquid (L) single phase, otherwise in GL-multiphase medium. Such GS/LS/GLS multiphase microreactors have intrinsic advantage of high specific surface area leading to high mass transport in liquid/gas bulk or through interface. This study at first provided a set of general references on fundamentals of such reactors, and subsequently review on the state of the art researches highlighting engineering efforts to intensify the merits of multiphase photocatalytic microreactors. It was also shown that one of recent trends was to use photocatalyst slurry in millimeter/centimeter scale reactors rather than in microreactors to combine advantages of high surface area, sufficient illumination and high-throughput without clogging, even by leaving the issue of catalyst recovery aside. The intensification of photocatalytic processes in such mini-size reactors was also discussed.



## 1. Introduction

For our society to be sustainable on the earth, the development of novel process is increasingly demanded for cleaner production and environmental protection. It is indispensable for those processes to be less dependent on fossil fuels as energy sources, which are depleting and emit green-house gas in use. Photocatalysis is the most promising key element to constitute such processes, since it activates reactions relying on light as energy sources, which is ultimately clean and superabundantly available from sun, such as annual irradiance of $3 \times 10^{24}$ J, i.e., 104 times as the worldwide energy consumption estimated by U.S. Energy Information Administration. Therefore, the research on the solar energy utilization has continued to be an important topic (Meng et al., 2015; Yang et al., 2016).

$TiO_2$ is the most commonly used semiconductor for photocatalytic applications, since it has preferable features such as non-toxic, inexpensive, highly-reactive leading to thorough mineralization without secondary-pollution (Meng et al., 2015). The crystal structure of $TiO_2$ such as Anatase and Rutile phases was observed to influence the photocatalytic activity (Tanaka et al., 1991). It is further noted that nano-semiconductor photocatalysts have been used due to their interesting properties over bulk materials (Chong et al., 2010; Jayamohan et al., 2016; Stephan et al., 2011). Electrons and holes, which are formed in

*Abbreviations:* AOP, advanced oxidation process; FFMR, falling film microreactor; GLS, gasliquid-solid; ID, internal diameter; LED, light emitting diode; MB, methylene blue; MPM, microchannel photocatalytic microreactor; PFA, perfluoroalkoxy alkane; PPM, planar photo catalytic microreactor; STY, space-time yield; TPA, tetraphalic acid; TPP, tetraphenyl porphyrin; UV, ultra violet; vis, visible light; WL, white light.

* Corresponding author at: Chemical Science and Engineering Department, Tokyo Institute of Technology, Japan.
*E-mail address:* sokawara@chemeng.titech.ac.jp (S. Ookawara).

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the semiconductor $TiO_2$ due to absorbed photons with sufficient energy (in UV range) and diffuse to the surface, cause oxidative–reductive reactions with reactants absorbed on the surface (Stephan et al., 2011). Much effort has been spent to modify bare photocatalysts (e.g. $TiO_2$) by doping another metal (Liu et al., 2011; Murakami et al., 2010; Ohno et al., 2003), multiple elements (Bautista et al., 2009; Meng et al., 2011; Reddy et al., 2006; Yeh et al., 2012), and non-metal elements (He et al., 2015; Mohamed et al., 2015), or to synthesize visible light responsive photocatalysts, so that higher photocatalytic activity could be obtained even under visible light (Liu et al., 2009; Qamar et al., 2011; Szilágyi et al., 2012).

The photocatalysis has been investigated to improve air quality through mineralization of pollutants without incompletely oxidized side-products, as one of the most efficient Advanced Oxidation Processes (AOPs), and hence, as one of the most important application of $TiO_2$ (Bechec et al., 2016; Cambié et al., 2016; Paz, 2010). On the other hand, in both developed and developing countries, chemical and biological contaminants are found in various water resources due to the increasing human activity. Therefore, AOPs also have been widely applied to reduce the loading of organic pollutants in water very rapidly and non-selectively by producing strong oxidants (hydroxyl radical) (Aceituno et al., 2002; Andreozzi, 1999; Meng et al., 2015; Saien and Soleymani, 2012).

## 2. General discussions on photocatalytic microreactors and microfluidics

To date, different photocatalytic reactors have been designed and examined for AOP applications as already reviewed (Lakerveld et al., 2014; McCullagh et al., 2011; Meng et al., 2015), most of which can be categorized into slurry reactors and microreactors. The former is operated with suspended photocatalyst particles while the photocatalysts are immobilized in the latter, by taking into account specific surface area of catalyst and uniform light penetration in reactor volume by different approaches (Pareek et al., 2008; Saien and Soleymani, 2012).

While many AOPs applications of photocatalysis can be found in the literature of wastewater treatment, those corresponding reactors found in the patents were often applied to air treatment (Leblebici et al., 2015; Paz, 2010). Due to the suboptimal designs available, photocatalytic reactors are still not commonly implemented in industrial processes (Li Puma and Yue, 2003; Sagawe et al., 2004; Stephan et al., 2011; Lakerveld et al., 2014; Leblebici et al., 2015; Mul et al., 2010).

The slurry reactors operating with dispersed nanoparticles assure a number of active sites per unit volume of the reaction medium (Saien and Soleymani, 2012). However, the use of powdered photocatalysts necessitates their downstream recovery leading to higher operational and capital costs (Li et al., 2013). Further, it limits the depth of light penetration due to its absorption and scattering (Kar et al., 2009), as expressed by Bouguer-Lambert-Beer law (Cassano et al., 1995; Colina-Márquez et al., 2010). The insufficient light penetration over the larger reactors is a main reason why the scale-up of photocatalytic slurry reactor is difficult. It should be further noted that safety issues should be paid attention to operate even photochemical reactors for bio-applications (Lévesque and Seeberger, 2011), and with toxic/hazardous compounds (Wang et al., 2013; Bremus-Köbberling et al., 2012; Su and Hessel, 2015).

Saien and Soleymani (2012) claimed that slurry photocatalytic microreactor dispersing $TiO_2$ particles is a very promising technique. Generally, the photocatalytic microreactor provides large surface to volume ratio (>10,000 $m^2\ m^{-3}$) and consequently, attain high heat and mass transfer rate, uniform illumination without light attenuation, and resultant satisfactory catalytic effect (Lindstrom et al., 2007). In addition, their small size enables safe operations, minimum footprint and waste (Aran et al., 2011). The slurry photocatalytic microreactor can be thus regarded as an instrument by which highly fast, exothermic/endothermic, complex and multiphase chemical reactions achieve their maximum selectivity, which were previously inaccessible (Wörz et al., 2001). In case of three phase microreactor with dispersing catalyst nanopowder, higher absorptivity and adsorption rate were found in the organic wastewater treatment. However, it should be noted that the photocatalytic activity decreases with particle size. The aggregated particles also make recycle difficult after the photocatalytic process, which can be mitigated by stabilizing particles with surfactants (Das and Srivastava, 2016). The control of size and shape of (multiple elements co-doped) nanoparticles is a still big challenge, especially to be used in a complicated GLS multiphase process (He et al., 2015; Wörner, 2012).

In conventional slurry reactors, immobilization of catalyst onto inert carrier particles to make catalyst recovery easier, could reduce effective active sites of catalyst, and bring about limitations of mass transfer (Saien and Soleymani, 2012). Microreactor with photocatalytic thin film deposited on its inner spaces is an interesting alternative to the slurry photocatalytic reactors, which are mostly in flat or annular shape (Banić et al., 2016; Li Puma and Yue, 2003; Saien and Soleymani, 2012).

The GLS three-phase microreactor is an attractive and promising option for GLS catalytic reactions (Protasova et al., 2010; Zhao and Middelberg, 2011). The thin catalytic layer immobilized onto its inner surfaces can be effectively in contact with reactants in gas or liquid phase (Aran et al., 2011). The typical flow regimes found in it are bubbly flow (De Loos et al., 2010), slug flow (Serizawa et al., 2002) or annular flow (Chung and Kawaji, 2004) depending on the operating conditions (Liu et al., 2016).

The design and operation of microreactor with immobilized thin-film catalyst can be justified by an advantage that it does not require a separation operation to remove photocatalyst after reaction, while it has large illumination surface area per volume. Such high surface area also enhances in-bulk and inter-phase mass transfer of gaseous species, for example Oxygen that accepts electron and resultantly prevents electron–hole pair recombination in the photocatalysis leading to high reaction efficiency, unless its solubility is significantly low (Furman et al., 2007; Brosillon et al., 2008; Stephan et al., 2011). Compared to suspended catalyst particles, however, still smaller interfacial surface area per catalyst mass can be the main disadvantage of photocatalytic thin film immobilized on the inner surface of microreactors (Chen and Dionysiou, 2006). It should be further noted that both of illumination area and throughput of the single microchannel reactor is significantly low, such as often in the range of micro-liters/min for the latter (Yang et al., 2016). The coupled effects of aforementioned photocatalytic reaction and mass transfer limitation has been identified in the previous works (Charles et al., 2011; Corbel et al., 2014). Therefore, the intensification of mass transport in the GLS three-phase microreactor should be regarded a foremost challenge (Liu et al., 2016).

In order to improve the reaction efficiency, recently, different microreactors have been developed (Liu et al., 2016; Oelgemöller and Shvydkiv, 2011), such as: micro-capillary reactors (Elvira et al., 2013; Ramos et al., 2014b), single-microchannel reactors (Eskandarloo et al., 2015; Padoin et al., 2016), multi-microchannel reactors (Knust et al., 2013), and planar reactors (Lei et al., 2010; Liao et al., 2016; Wang et al., 2014), although its photocatalytic and energy efficiency as well as throughput still need to be improved (Liao et al., 2016; Yang et al., 2016).

Krivec et al. (2015) and Oelgemöller et al. (2014) simply increased the length or the number of microchannels to attain