Materials Science in Semiconductor Processing ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/matsci

Decontamination and disinfection of water by solar photocatalysis: The pilot plants of the Plataforma solar de Almeria

Sixto Malato*, Manuel I. Maldonado, Pilar Fernández-Ibáñez, Isabel Oller, Inmaculada Polo, Ricardo Sánchez-Moreno

Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4, 04200 Tabernas, Almería, Spain

ARTICLE INFO

Article history:
Received 25 April 2015
Received in revised form
5 July 2015
Accepted 8 July 2015

Keywords:
Hydrogen
Solar photoreactors
Solar disinfection
Solar water treatment

ABSTRACT

This work reviews the use of sunlight to produce the HO• radicals by TiO_2 nanophotocatalysis. The reacting systems necessary for performing solar photocatalysis will be described and the factors which govern the kinetics of photocatalysis such as initial concentration of reactant, mass of catalyst, pH, temperature, radiant flux and concentration of oxygen are highlighted. Several approaches in order to improve the photocatalysis efficiency of TiO_2 will be also described. Solar reactors engineering issues for photocatalytic water treatment will be reviewed as well as the use of the solar photocatalytic processes to inactivate microorganisms present in water, placing special emphasis to the mechanisms acting during the process, mainly hydroxyl radical and singlet oxygen generation, and on experimental systems made to optimize this disinfection technique. Heterogeneous photocatalysis is also an attractive technique for obtaining hydrogen in a clean way. In the last decades different photocatalytic systems for hydrogen generation with simultaneous removal of organic pollutants have been studied at laboratory scale but, so far, little has been published about these systems at a larger scale. The present work will also show the simultaneous photocatalytic hydrogen production and organic pollutant removal under direct solar irradiation and at pilot-plant scale at the Plataforma Solar de Almería (PSA).

1. Solar photocatalysis

The main causes of surface and groundwater contamination are industrial discharges (even in small amounts), excessive use of pesticides, fertilizers (agrochemicals) and domestic waste landfills. Wastewater treatment is based on various mechanical, biological, physical and chemical processes. In fact, it is a combination of many operations, such as filtration, flocculation, sterilization or chemical oxidation of organic pollutants. After filtration and elimination of particles in suspension, the ideal process is biological treatment (natural decontamination). Unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. Advanced oxidation processes (AOPs) may be used for decontamination of water containing these compounds [28]. These methods rely on the formation of highly reactive chemical species which degrade even the most recalcitrant molecules into biodegradable compounds. Although there are different reacting systems, all of them are characterized by the same chemical feature: production of hydroxyl radicals (HO•), which are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic ions. Rate constants (k_{HO}, $r = k_{HO}$ [HO•] C) for most reactions involving hydroxyl radicals in aqueous solution are usually on the order of 10^6–10^9 M^{-1} s^{-1}. They are also characterized by their not very selective attack, which is a useful attribute for wastewater treatment and solution of pollution problems. The versatility of the AOPs is also enhanced by the fact there are different ways of producing hydroxyl radicals, facilitating compliance with the specific treatment requirements. Heterogeneous photocatalysis is based on the use of a wide-band-gap semiconductor and irradiation with UV–vis light (Fig. 1), which produces electron in the conduction band (CB) and holes [33]. This process is of special interest since sunlight can be used for it. The main disadvantage of AOPs is their high cost (expensive reactants such as H_2O_2 and UV generation). So applications could be improved through the use of catalysis and solar energy.

The heterogeneous solar photocatalytic detoxification process consists of making use of the solar irradiation (visible and near-ultraviolet) band of the solar spectrum to photoexcite a semiconductor catalyst in the presence of oxygen. Under these circumstances, oxidizing species, either bound HO• or free holes, which attack oxidizable contaminants, are generated producing a progressive break-up of molecules yielding CO_2, H_2O and diluted inorganic acids. The most commonly used catalyst is the semiconductor TiO_2, which is cheap, non-toxic and abundant. Although

* Corresponding author. Fax: +34 950365015.
E-mail address: sixto.malato@psa.es (S. Malato).

http://dx.doi.org/10.1016/j.mssp.2015.07.017
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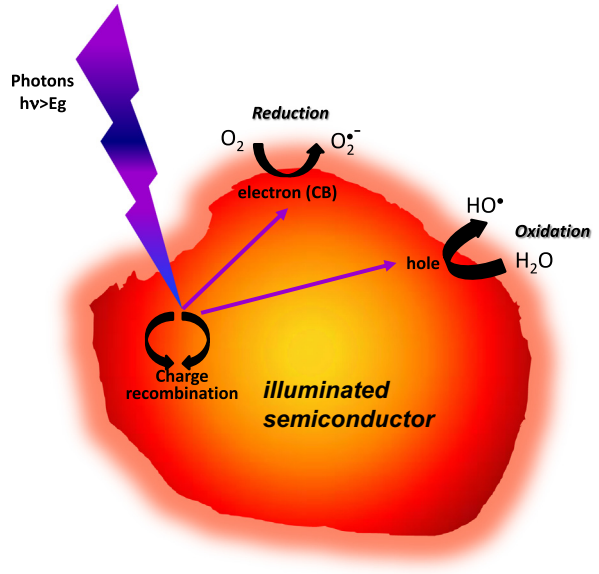

Fig. 1. Simplified scheme of production of electrons, holes and hydroxyl radicals on an illuminated particle of TiO_2.

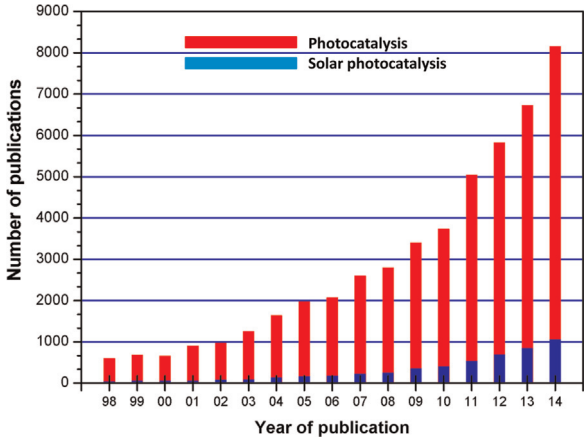

Fig. 2. Publications treating photocatalysis and the share treating solar-driven photocatalysis (source: www.scopus.com, 2015).

these processes have been studied for at least three decades, industrial/commercial applications, engineering systems and engineering design methodologies have only been developed recently [45,16]. The publications regarding the photocatalytic process rose continuously over the last years surpassing meanwhile a total number of more than 8000 peer-reviewed publications per year in 2014. Fig. 2 shows the evolution of these publication activities. Fig. 2 also illustrates that much of the literature takes into account the possibility of driving the process with solar radiation. In this work we highlight some of the science and technology being developed to improve the solar photocatalytic disinfection and decontamination of water, as well as first efforts to photocatalytic hydrogen production.

2. Photocatalytic water treatment: solar reactors engineering issues

Most solar photochemical processes use UV or visible sunlight. Sunlight at wavelengths over 600 nm is normally not useful in any photochemical process. Nevertheless, the specific hardware needed for solar photochemical applications has much in common with those used for thermal applications. As a result, both photochemical systems and reactors had followed conventional solar thermal collector designs during the 90s', such as parabolic troughs and non-concentrating collectors [4,61]. At this point, their design begins to diverge, since photocatalytic reactors: (i) should not be expensive, (ii) should make use of both direct and diffuse solar radiation, (iii) water should not heat up significantly, (iv) should have both high optical efficiency and high quantum efficiency with low photonic density permitting low recombination of e^-/h^+, (v) should guarantee weather resistance, chemical inertness and ultraviolet transmission and (vi) should permit turbulent flow (favors mass transfer).

The original solar photoreactor designs for photochemical applications were based on line-focus parabolic-trough concentrators (PTCs). In part, this was a logical extension of the historical emphasis on trough units for solar thermal applications. Furthermore, PTC technology was relatively mature and existing hardware could be easily modified for photochemical processes. The first outdoor engineering-scale reactor developed (in USA) was a converted solar thermal parabolic-trough collector in which the absorber/glazing-tube combination had been replaced by a simple Pyrex glass tube through which contaminated water could flow. Immediately afterwards, in 1990, a similar facility was designed and built at the Plataforma Solar de Almería. Both these facilities, which were followed by others, were based on parabolic-trough collectors with hundreds of square meters of collector surface, and can be considered the starting point of solar photocatalytic technology development [3]. One-sun (non-concentrating) collectors are, in principle, cheaper than PTCs, as they have no moving parts or solar tracking devices [73]. They do not concentrate radiation, so efficiency is not reduced by factors associated with concentration and solar tracking. An extensive effort (Fig. 3) in the design of small non-tracking collectors had resulted in the testing of several different non-concentrating solar reactors [23,72,27,29,30]. But all of them were abandoned as they did not fulfill the main criteria stated above and necessary for photocatalytic reactors.

There is a category of low concentration collectors, called Compound Parabolic Concentrators (CPCs), that are a good option for solar photochemical applications. CPCs were invented in the 60s to achieve solar concentration with static devices [18], since they were able to concentrate on the receiver all the radiation that arrives within the collector "angle of acceptance". They do so illuminating the complete perimeter of the receiver, rather than just the "front" of it. These concentrating devices have ideal optics, thus maintaining both the advantages of the PTC and static systems. All solar radiation that reaches the aperture area of the CPC (direct and diffuse) can be collected and redirected to the reactor [17]. The light reflected by the CPC is distributed all around the tubular receiver (Fig. 4) so that almost the entire circumference of the receiver tube is illuminated. The CPCs fulfill the main i–vi criteria stated above [8]. The CPCs have the advantages of both technologies (PTCs and non-concentrating collectors) and none of their disadvantages so they seem to be the best option for photocatalytic processes based on the use of solar radiation [2]. All materials used must be inert to degradation by solar light. With regard to the reflecting/concentrating materials, aluminum is the best option due to its low cost and high reflectivity in the solar UV spectrum on earth surface. The photocatalytic reactor must contain the catalyst and be transparent to solar UV radiation providing good mass transfer of the contaminant from the fluid stream to an illuminated photocatalyst surface with minimal pressure drop across the system. The reflectivity (reflected radiation/incident radiation) between 300 and 400 nm of traditional silver-coated mirrors is very low and aluminum-coated mirrors is the best option in this case. Reflectivities range from 92.3% at 280 nm to 92.5% at 385 nm. Photocatalytic reactors must transmit solar UV light.

Please cite this article as: S. Malato, et al., Materials Science in Semiconductor Processing (2015), http://dx.doi.org/10.1016/j.mssp.2015.07.017