Polymer Degradation and Stability 145 (2017) 120–141

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Photoactive polymeric and hybrid systems for photocatalytic degradation of water pollutants

Maria Nowakowska*, Krzysztof Szczubiałka

Faculty of Chemistry, Jagiellonian University, 30-060 Kraków, Ingardena 3, Poland

ARTICLE INFO

Article history:
Received 7 February 2017
Received in revised form
21 April 2017
Accepted 26 May 2017
Available online 29 May 2017

Keywords:
Photoactive polymers
Hybrid
Photosensitizers
Photocatalysts
Water pollutants

ABSTRACT

The review presents recent developments in the synthesis of polymeric photosensitizers and hybrid photocatalysts of various physicochemical and photochemical properties and their possible application for the degradation of water pollutants. The mechanisms of their action were presented. Photoactive amphiphilic polymers are selective and mild reagents acting as singlet oxygen generators or *via* photoinduced electron transfer. They can function independently as nano/micro heterogeneous photosensitizers or as components of the hybrid systems. The hybrid materials are usually dispersed in water and are involved in the generation of very reactive oxygen species, mostly superoxide and hydroxyl radical ions, which can oxidize organic compounds present in water. These systems are generally more photostable than photoactive polymers therefore they may function as photocatalysts. Polymeric and hybrid photocatalysts are especially well-suited for removal of chemical compounds which, although present at low concentrations in water resources, are dangerous due to their bioaccumulation in the food chain and often cannot be removed with the use of currently available technologies. Both photoactive polymeric and hybrid materials can be easily removed from the aqueous media thus the secondary contamination is avoided.

1. Introduction

Interaction of light (especially the solar light) with matter is essential for the life on our planet. The Nature is using light to carry out photosynthesis which is a photocatalytic process occurring in the green parts of plants. The solar photons are absorbed by the molecules of chlorophyll dye which are properly arranged in lipid membrane. That energy is used to split water molecules to oxygen atoms, protons, and electrons, which are utilized in the conversion of carbon dioxide molecules to carbohydrate ones. It is estimated that about 2×10^{18} kJ of photon energy is used each year in the photosynthesis process leading to the production of about 2×10^{14} tons of organic matter.

There have been many attempts to mimic this process and to carry out artificial photosynthesis using carefully designed, sophisticated and complicated systems - including the elegant arrangement known as the artificial leaf constructed by Nocera [1]. Although this system resembles the structure and function of the natural leaf (Fig. 1) it should be treated as a proof of concept rather than the system of practical importance for solar energy conversion.

There are two main approaches to practically apply solar radiation. The first one involves photovoltaics which is based on the conversion of the light energy directly into electrical energy in an electronic process that occurs in semiconductors. The second one involves photochemical reactions triggered with the light absorbed by the system. However, still very little energy of solar radiation is used by man. This is due to the lack of proper tools and methods allowing to perform the cost-effective and highly efficient photochemical reactions with the use of low energy solar radiation (from the near UV-visible-IR spectral range) which reaches the surface of Earth. That problem can be partly solved by introducing an additional component, called *photosensitizer*, to the system studied. The photosensitizer is the compound which absorbs radiation in a defined spectral region and uses the acquired energy to induce photophysical processes and/or photochemical reactions in another molecular entity present in the system which is otherwise not able to absorb the incident radiation directly. Thus, the photosensitizer makes the system photoactive (photosensitive) in a defined spectral region, e.g., sensitive to solar light. In a primary photochemical

* Corresponding author.
E-mail address: nowakows@chemia.uj.edu.pl (M. Nowakowska).

http://dx.doi.org/10.1016/j.polymdegradstab.2017.05.021
0141-3910/

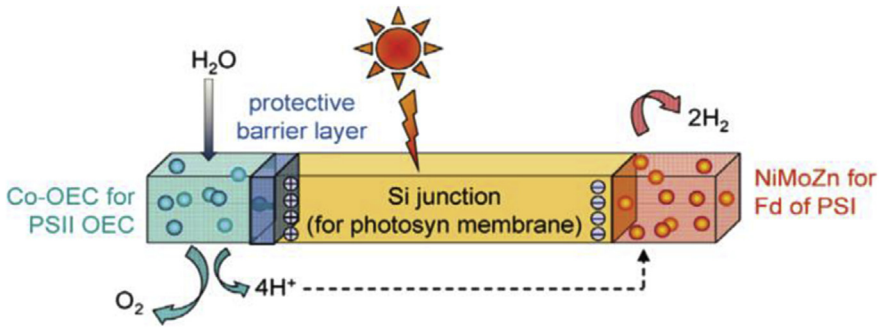

Fig. 1. Scheme of an artificial leaf [1].

step the energy is absorbed by the molecule of photosensitizer inducing its excitation and transition to one of the upper electronic states. The excess of the energy can be then transferred to the substrate molecule thus inducing the photochemical reaction. In this process the photosensitizer plays a role of an energy donor (D), while the substrate is an energy acceptor (A):

$$D \rightarrow D^* \quad (1)$$

$$D^* + A \rightarrow S + A^* \quad (2)$$

$$A^* \rightarrow \text{reaction} \quad (3)$$

The efficiency of the process is controlled by the difference in energy levels of a D-A pair and is strongly dependent on the distance between the A and D molecules. There are two main mechanisms of the energy transfer (ET) process. One of them is a long range resonance dipole-dipole coupling, known also as the Förster mechanism (or resonance mechanism) [2,3], while the other is a short-range one and involves exchange of electron between molecules, known also as the Dexter mechanism (exchange mechanism) [4]. Thus, the energy transfer occurring according to the Förster mechanism does not require physical contact between the donor and acceptor molecules and can occur when the separation between the donor and acceptor molecules is several times greater than the sum of their van der Waals radii. However, the process is effective only, first, if it is exothermic, which means that the energy level of excited donor must be higher than that of acceptor (i.e., $E_{D^*} > E_{A^*}$) and, second, if there is an overlap between donor emission spectrum and the acceptor absorption spectrum.

The electronically excited molecules of photosensitizer (donor molecule) can be deactivated in bimolecular process involving not only energy transfer but also in photoinduced electron transfer (PET):

$$\boldsymbol{D^* + A \rightarrow D\cdot^+ + A\cdot^-} \quad (4)$$

The photoinduced electron transfer is thermodynamically possible if ΔG of that process is negative. The change of free energy for electron transfer can be calculated using Rehm-Weller equation [5]:

$$\boldsymbol{\Delta G_{ET} = E_D^{ox} - E_A^{red} - E_s^* + C} \quad (5)$$

where $E_D^{ox}{}_D$ and E_A^{red} are the oxidation potential of the donor and the reduction potential of the acceptor, respectively, E_s^* is the energy of the excited singlet state of the donor, and C is an electrostatic correction term.

The electron transfer process results in the formation of ion-radical pair surrounded by the solvent molecules. The process is reversible and the back reaction occurs with the diffusion controlled rate. Thus, the solvent polarity and viscosity play an essential role in the stabilization of the radical pair *via* so called solvent cage effect and in the formation of separated photoreduced-photooxidized species which can initiate further photochemical reactions.

Thus, by applying the properly chosen photosensitizer, the light energy can be used to produce chemically active species such as electronically excited states of the substrate molecules (S*, T*), singlet oxygen ($^1O_2{}^*$), radical cations ($R^+\cdot$) and radical anions ($R^-\cdot$). These can initiate secondary photochemical reactions in the system studied. Low-molecular-weight photosensitizers are easy to be used, but they create some problems. The relatively high photosensitizer concentration required to ensure the efficiency of the process may be beyond its solubility, inducing aggregation processes and may lead to the toxicity. Also, the chemical interactions of the photosensitizer molecules with the reaction substrates or products are possible. Moreover, the separation of the photosensitizer when the reaction is completed is a serious issue. Some of these problems can be eliminated by replacing low-molecular-weight photosensitizers with photoactive polymeric or hybrid systems.

2. Polymeric photosensitizers

Polymeric photosensitizers can be obtained by covalent attachment of chromophores to the polymer chain, their entrapment in the polymer matrix or inside the polymeric micro/nanospheres, complexation with polymer or covalent attachment/adsorption at the surface of polymeric micro/nanospheres. These photosensitizers have various advantages over the low-molecular-weight ones. Among them the enhancement of the photosensitizing effect due to energy migration among the chromophores and high efficiency of energy transfer combined with the easy separation of the photosensitizer from the reaction mixture are the most important. Such systems have been demonstrated to act as efficient and selective photosensitizers in wide variety of photochemical processes including these important in photovoltaics [6], synthesis of fine chemicals [7–12], initiation of polymerization [13–21], so called photodynamic therapy (PDT) [22–34], and in controlled degradation of water pollutants [35–45]. In the current review we will concentrate on the last option.

2.1. Polymeric photosensitizers for degradation of water pollutants

The amphiphilic (co)polymeric photosensitizers have been demonstrated to be particularly useful for degradation of water pollutants. The chromophores can be covalently attached to the monomer and introduced to the polymer *via* (controlled) radical