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Alternative photocatalysts to TiO_2 for the photocatalytic reduction of CO_2

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ABSTRACT

The increased concentration of CO_2 in the atmosphere, originating from the burning of fossil fuels in stationary and mobile sources, is referred as the "Anthropogenic Greenhouse Effect" and constitutes a major environmental concern. The scientific community is highly concerned about the resulting enhancement of the mean atmospheric temperature, so a vast diversity of methods has been applied. Thermochemical, electrochemical, photocatalytic, photoelectrochemical processes, as well as combination of solar electricity generation and water splitting processes have been performed in order to lower the CO_2 atmospheric levels. Photocatalytic methods are environmental friendly and succeed in reducing the atmospheric CO_2 concentration and producing fuels or/and useful organic compounds at the same time. The most common photocatalysts for the CO_2 reduction are the inorganic, the carbon based semiconductors and the hybrids based on semiconductors, which combine stability, low cost and appropriate structure in order to accomplish redox reactions. In this review, inorganic semiconductors such as single-metal oxide, mixed-metal oxides, metal oxide composites, layered double hydroxides (LDHs), salt composites, carbon based semiconductors such as graphene based composites, CNT composites, g-C_3N_4 composites and hybrid organic-inorganic materials (ZIFs) were studied. TiO_2 and Ti based photocatalysts are extensively studied and therefore in this review they are not mentioned.

1. Introduction

1.1. Solar energy – solar fuels

The sun constitutes the major energy source in Earth, by providing in one hour all the energy needed by humanity for one year. The basic problem for the inhabitants of the Earth, is that they are not able to exploit these huge amounts of energy [1]. The total emitted solar radiation reaching the Earth's surface is composed of infrared radiation (52%, >700 nm), visible radiation (43%, 400–700 nm) and ultraviolet radiation (5%, <400 nm). There are several types of solar energy collectors, some of them have flat surface and collect the solar irradiation without concentrating it, so its intensity is rather low. There are also solar energy collectors that concentrate the solar irradiation (such as reflectors and luminescent solar collectors) but they are not commercially available because they are not stable and they exhibit inadequate collection efficiency [2]. For over 50 years, serious attempts have also been performed in order to produce useful compounds-fuels by utilizing solar energy.

The solar fuels are compounds produced via a biomimetic approach that have captured and stored solar energy in their chemical bonds (chemical energy) [3]. The production of solar fuels is a great challenge for the scientific community. Solar fuels constitute a broad group of chemicals that can be used for electricity generation, transport and industrial purposes. The two main categories of solar fuels are (a) hydrogen and (b) carbon based fuels such as methanol (CH_3OH), carbon monoxide (CO) and methane (CH_4). Another significant goal for the scientists is the large scale production of the solar fuels, their transportation, their storage and the opportunity to be commercially available [1].

Abbreviations: AC, activated carbon; ATP, adenosine-tri-phosphate; CB, conduction band; CCS, carbon capture and storage; CNTs, carbon nano-tubes; CTA, cetyl-trimethyl-ammonium; DAC, direct air capture; DHF, di-hydro-furan; DMF, di-methyl-formamide; LDHs, layered double hydroxides; NADPH, nicotinamide adenine dinucleotide phosp-hate; OFMR, optical fiber monolith reactors; PEC, photo-electrochemical reduction; RGO, reduced graphene oxide; SSR, solid state reaction; THF, tetra-hydro-furan; VB, valence band; ZIFs, zeolitic imidazolate frameworks.

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1.2. Production of solar fuels

1.2.1. Hydrogen-water splitting

Hydrogen (H_2) is a very useful solar fuel with serious advantages and disadvantages. As major advantages are considered, its abundance in water and biomass, its convenient storage as hydride, the absence of pollutants after its combustion and the high amount of energy released when it is used as a fuel. On the other hand, hydrogen must be highly compressed during its transportation and this is an expensive process or it must be stored as a metal hydride which is an expensive and rather dangerous process too [4]. It is a transport fuel but it is also used in many industries. In nature, hydrogen is produced from water splitting via various molecular reactions involving PSII (photobiological water splitting). The water splitting mechanism includes the formation of a large number of reaction intermediates which finally produce dioxygen, electrons and protons. Advanced techniques have shown an interaction between the metal center which acts as a catalyst and its protein environment that induce the oxidation of the water molecules. The mechanism of the biological formation of hydrogen by the reaction of electrons and protons, formed from photosynthesis (PSI or PSII), is not fully understood, but it is clear that enzymes such as hydrogenases and nitrogenases play a crucial role, as they produce hydrogen from protons and electrons formed via water splitting [5]. By mimicking the nature, scientists tried to use to advantage the most abundant material in Earth, water, in order to produce hydrogen. Steam reforming, constitutes a process which involves the generation of hydrogen from CH_4 and steam (H_2O) via the production of CO, is mainly used for hydrogen production. Besides, hydrogen is generated by coal gasification, a process that involves the reaction of coal with O_2 and steam at high temperature and pressure and produces mainly a mixture of hydrogen, methane, CO_2 and CO. Biological, pyrolysis and thermochemical processes that use the biomass are also used for the production of H_2. All these conventional methods followed for the formation of H_2 require enhanced amounts of energy. Besides, the formation of pollutants such as CO_2, as byproducts, is not avoided. It is also widely known that hydrogen is produced via electrolytic or thermochemical or photobiological or photocatalytic water splitting. The thermochemical water splitting uses the heat from the sun, whereas the photocatalytic water splitting uses the sunlight irradiation and photocatalysts i.e. materials that accelerate the reaction, they are found in tiny amounts in the reaction mixture and they are not consumed at the end of the reaction. The general principle is that the energy of the absorbed photons must be higher than the band-gap energy of the photocatalyst, in order to achieve the photogeneration of electrons and holes participating in the redox reactions which produce hydrogen and oxygen. Specifically, photoinduced electrons, transported from the valence band (VB) of the photocatalyst to the conduction band (CB), reduce H+ to form H_2, on its surface. Photogenerated holes oxidize H_2O to H+ and O_2 in VB. Photocatalysts such as the TiO_2 analogues and other metal oxides and salt composites have been widely used [4,6].

1.2.2. Carbon based fuels – natural/artificial photosynthesis

The natural photosynthesis is the way of the biological world to produce organic fuels, such as sugars, using mainly two abundant compounds, H_2O and CO_2, via the harvest and exploitation of solar energy. The natural photosynthetic process exhibits low overall efficiency, still it constitutes an inspiration for scientists in order to produce useful fuels from CO_2, H_2O and sunlight. The natural photosynthesis involves the utilization of compounds that can be oxidized producing electrons, compounds that can be reduced from these electrons producing fuels and of course solar irradiation. Green plants, algae and cyanobacteria absorb the solar energy in order to oxidize water to O_2, protons and electrons. The photogenerated electrons possess adequate negative redox potential, thus they are able to reduce photogenerated protons and CO_2 in order to form hydrogen gas, carbohydrates and lipids. Plants consist of a number of subsystems combined together, so that to perform the photosynthetic process. Antenna systems are responsible for targeting the appropriate wavelengths of light and transporting that energy to the reaction centers, where the transfer of photoinduced electrons takes place and charge separated states are formed. Water oxidation and O_2 formation is accomplished at the reaction center in PSII after the absorption of four photons whilst H^+ and CO_2 reduction is carried out by the biological molecule NADPH (nicotinamide adenine dinucleotide phosphate). The formation of ATP (adenosine triphosphate), which has a key role in the transportation of energy by several enzymes and the generation of transmembrane proton gradients is also realized by reduction mechanisms. In conclusion natural photosynthesis is a very complicated exergonic process, consisting of a large number of redox reactions which lead to the production of carbon based fuels [7,8]. On the other hand, by the term "artificial photosynthesis" is meant the utilization of CO_2, renewable (solar) energy, synthetic catalysts and water in order to produce a large range of fuels/chemicals such as hydrogen and carbon based compounds [9]. Water is used as reductant that is the electron source. In artificial photosynthesis the first step is the absorption of the ultraviolet or visible radiation. The second step is the charge generation and separation and the last step is the catalytic reaction [10]. Inspired by the natural photosynthesis, where chlorophyll molecules diffuse sunlight, artificial photosynthetic reactions also need the presence of light harvesting complexes, such as dye sensitizers. The photon capture is followed by the electron-transfer reactions that lead to charge separation. This means that electrons and positive holes move apart in order to avoid charge recombination, leading to the formation of potent oxidizing or reducing species. These species drive the desirable redox reactions such as CO_2 reduction. A major difference between natural and artificial photosynthesis is the capability of biological systems to induce self repair. Unfortunately, until now there is no man-made photocatalyst with the ability to retrieve the loss of reactivity during operation [11,12]. The artificial photosynthesis products are used as synthetic fuels for transportation and storage or as useful industrial materials (plastics, fertilizers, pharmaceuticals, chemicals etc.) [1]. The greatest benefit is obtained in case that a direct conversion of solar energy into fuels is achieved. The use of water as a raw material is an important perspective too. The catalysts for the artificial photosynthesis may be either nanomaterials with nature guided design, or molecular compounds or solid state components, or combinations of them. Their common feature is the way that they participate in the multielectron redox reactions during the artificial photosynthesis process. Abundant or less abundant materials can be used as homogeneous or heterogeneous catalysts. The most common molecular catalysts are based on ruthenium and constitute model systems for the study of artificial photosynthesis [13,14]. In Fig. 1 a comparison of natural photosynthesis and artificial photosynthesis is shown [14]. One principal scientific goal currently is the enhancement of the photocatalytic efficiency in the CO_2 reduction by using technical means. Methanol and methane are the most important solar fuels resulting from the photocatalytic CO_2 fixation as they can store a lot of hydrogen. Other possible products are CO, HCOOH, HCHO and H_2 [15].

1.3. Why the reduction of CO_2 in the atmosphere is so important? Greenhouse effect and mitigation of CO_2

The burning of fossil fuels, apart from their depleting them, has raised serious environmental issues, such as the anthropogenic Greenhouse effect which is considered as one of the most seri-