Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS
www.re-journal.com/en/
ELSEVIER
JOURNAL OF RARE EARTHS, Vol. 32, No. 6, Jun. 2014, P. 487

Gadolinium-modified titanium oxide materials for photoenergy applications: a review

Maciej Zalas*

(Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland)

Received 28 August 2013; revised 26 February 2014

Abstract: Gadolinium doped titania materials were explored for application in photoenergy production. Incorporation of gadolinium into titania permitted improvement of photocatalytic or photovoltaic performance of the latter. This review provided a deep analysis of gadolinium applications in photoenergy processes and devices with the main focus on explanation of gadolinium doping effect on physicochemical properties of titania.

Keywords: gadolinium doped titania; Gd-TiO_2; photocatalysis; dye-sensitized solar cells; photoenergy; rare earths

---

Energy, which can be in the simplest way described as the ability to perform work, is a basic need of every living organism in the universe. The sun is the main energy source for the planet earth, the energy supplied by the sun to the earth is really huge and has been estimated as around 3×10^{24} J per year[1] (approximately 1.7×10^{17} W per year). Only a small part of this energy, about 1×10^{14} W per year[2], is used by the flora for accumulation of chemical energy, in the process of photosynthesis. The energy stored by the flora is the primary source of energy for any other organism living on the earth. Of course human civilization, from its early beginning, has been based on energy consumption, mainly as food (i.e. plants and/or animals), and fuels (firstly by burning plants, than coal, oil and finally natural gas). In the initial phase of civilization development, wood was the most important fuel, but increasing energy demand stimulated exploration of other energy carriers such as peat, lignite or hard coal. At the turn of the 18th and 19th centuries, witnessing the industrial revolution, the use of coal sharply increased. Ever-increasing energy demand caused, at the end of the 19th century, the exploitation of oil and natural gas deposits, which are still the main energy sources for our civilization. The rapid development of automotive industry, which is now the largest consumer of fuel among all sectors of global economy[3], began at that time. The use of fossil fuels generates a lot of air pollutants, especially carbon dioxide which, together with water vapour, is seen as the main cause of the greenhouse effect and probably has a great influence on global warming[4]. The global fuel crisis, in the early 1970's was the strong signal that the earth's natural wealth is not boundless and inexhaustible. The problems with the fossil fuels availability resulted in growing interest in making energy using renewable energy sources such as:

- ○ Wind power
- ○ Hydropower
- ○ Wave and tidal power
- ○ Solar energy
- ○ Biomass
- ○ Geothermal energy

Great interest has been paid to solar energy, which is, as mentioned above, the main energy source for planet earth. In 1972, when the global fuel crisis was approaching, Fujishima and Honda discovered the phenomenon of water photolysis to hydrogen and oxygen over UV-illuminated TiO_2 electrodes[5]. Since then the amount of research work on semiconductor photoenergy processes has grown exponentially. A number of devices using TiO_2 for solar energy conversion, such as solar cells[6] or photocatalytic systems[7,8] have been developed for the past four decades.

The fundamental mechanism of the photocatalytic process which occurs on TiO_2 surface, can be easily explained[9]. At the beginning, a light photon with energy greater than the bandgap of titania is absorbed, thereupon the electrons are promoted from the valence band (VB) to the conduction band (CB) creating electron-positive hole pairs. The electrons and positive holes migrate to the titania surface and react with the species adsorbed on this surface to decompose them. The photodecomposition processes, taking place on the TiO_2 surface during the photocatalytic process, usually involve one or more intermediate species or radicals such as $^{\bullet}OH$, O_2^-, H_2O_2 or O_2. These species are important substrates for processes such as photodegradation of various water pollutants, photocatalytic organic and inorganic synthesis,

---

* **Corresponding author:** Maciej Zalas (**E-mail:** maciej.zalas@amu.edu.pl; **Tel.:** 0048618296754)

DOI: 10.1016/S1002-0721(14)60097-1

photocatalytic water decomposition, photocatalytic killing of bacteria or even tumor cells killing in light-induced TiO_2 supported cancer treatment[8,9]. The efficiency of TiO_2 photocatalytic activity depends on the catalyst surface area and crystallinity. The larger the surface area, the higher the photocatalytic activity of the material, but large surface area increases surface defects concentration, which increases the probability of electron-hole recombination process and this, in consequence, decreases the photocatalytic process rate. To decrease the surface and bulk defects concentration, a higher crystallinity of TiO_2 material is needed. It is usually obtained upon high temperature treatment, which leads to aggregation of small nanoparticles and to a decrease in the surface area, so the synthesis of the photocatalysts must be a compromise between these conditions. Development of highly efficient photocatalytic devices based on TiO_2 is often limited by the wide bandgap, which is 3.0 eV and 3.2 eV for rutile and anatase phases, respectively[8]. Such a large bandgap forces the use of UV region of solar spectra to promote electrons from VB to CB of titania. The UV region is less than 10% of the overall solar intensity, so the most part of energy carried by sunlight to the devices based on pure titania is wasted[7]. A possibility of extension of the TiO_2 photocatalysts response to the visible light region has been intensively studied. The typical ways to obtain titania photocatalysts operating under visible light include coupling with narrow bandgap semiconductors (CdS, CdSe[10,11]), doping with non-metals (N, C, S[12–14]) or transition metal ions (Cu^{2+}, Cr^{3+}, Fe^{3+}, V^{5+}, Mo^{5+}, lanthanides and many more[15–21]), incorporation of noble metals on the titania surface[7,8,21] or surface sensitization with organic dyes[22–24].

The most spectacular career of the dye sensitization of TiO_2 surface has been launched when almost two decades after the Fujishima's and Honda's discovery of photocatalytic water splitting over the titania electrodes, O'Regan and Grätzel have presented the first highly efficient dye sensitized solar cell (DSSC)[25]. The device made by O'Regan and Grätzel is based on a mesoporous titania electrode sensitized with a ruthenium dye and is able to convert the energy of incident light to electricity with efficiencies around 7%–8%. A typical DSSC is built with two sheets of tin conducting oxide (TCO) coated glass, one of which, the so-called working electrode, is covered by the mesoporous electrode, mostly made of nanocrystalline TiO_2, sensitized with an organic dye (mostly ruthenium complexes). The second TCO glass sheet, the so-called counter electrode, is covered by a thin layer of platinum. These two electrodes are arranged in a sandwich cell and the space between them is filled with a liquid electrolyte containing I^-/I_3^- redox pair solution in organic solvent(s)[6]. The principle mechanism of the DSSC working cycle is straightforward and may be described with five steps of electron movement. The first step is the excitation of an electron from the ground to the excited state of the dye molecule by a photon of incident light. Next, the excited electron is injected from the dye molecule into the conducting band of the mesoporous semiconducting electrode, afterwards the electron is transported across the mesoporous electrode and external circuit into the counter electrode. Now electron reduces the oxidized form of the redox couple in the electrolyte and as the last step, the reaction between the reduced form of the redox mediator and the oxidized dye molecule occurs thereupon the ground state of the dye molecule and oxidized form of the redox couple are restored and DSSC working cycle is closed[1,6,26]. In the ideal system the whole process takes place without consumption or permanent transformation of any chemical species and theoretically it can occur until illumination is present. For improvement of electron injection efficiency or electron lifetime in the electrode, some post-synthesis-treatment methods have been proposed. The most common method is deposition of a thin layer of TiO_2 on the electrode external surface using $TiCl_4$ aqueous solution treatment or $TiCl_3$ electrodeposition[6]. Modification of TiO_2 electrodes by covering them with a thin layer of another semiconductor or an insulator can generate an energetic barrier for the electron back-transfer and improve the photoelectrical properties of DSSC[27–30]. The alkaline metal, transition metal or lanthanides ions doping of porous TiO_2 electrode have been recently proposed to increase the DSSC efficiency[31–35].

A number of reports on the application of lanthanide elements (the so-called rare earths (RE)) as dopants to the TiO_2 materials have been published for the last 15 years. The photocatalytic activities of RE doped TiO_2, in contrast to the transition metal modified TiO_2, are in general (especially in low concentrations) higher than those of unmodified titania[21]. The main feature of RE elements, giving them significantly different properties those of transition metals, is the nature of 4f electrons. The shielding of 4f orbitals by fully filled 5p and 6s orbitals is responsible for the very interesting spectroscopic properties of lanthanides and has an significant influence on the properties of RE modified titania applied in photoenergy processes. The gadolinium, which has a half filled f electrons configuration, when used as a TiO_2 dopant, shows mostly positive influence on the electronic properties of TiO_2 and leads to an increase in its photocatalytic and photovoltaic activity. Although it is easy to check if the Gd-modified titania is more active in photocatalytic or photoelectric process than the unmodified establishment of the fundamental reasons for this phenomenon may be difficult. In this short review we focus on studies of the influence of Gd-modification on the activity of titania materials applied in photoenergy processes.