ISSN 2555-1061 Volume **4**, Number **2/2019**

PHOTOCATALYTIC ACTIVITY OF DOPPEDTIO$_2$ OVER ORGANIC COMPOUNDS DEGRADATION

Amalia-Maria SESCU[1], Maria HARJA[2],DoinaLUTIC[3], Lidia FAVIER[4], Gabriela CIOBANU[5]

Abstract. *Nanomaterials have attracted a great interest among the researchers due to their special proprieties and wide applicability in different fields, with special emphasis on wastewater treatment processes. Heterogeneous photocatalysis is a process in which a semiconductor material is irradiated and generate hydroxyl radical, which are able to degrade and mineralize organic compounds. In order to improve some drawbacks of semiconductors, researchers focused their attention on improving synthesis methods and changing the surface structure of the photocatalyst. Some of the most used synthesis methods are: sol-gel method, hydrothermal method and doping the photocatalyst with different metallic or non-metallic ions. The aim of this paper is to show the influence of synthesis methods on the photocatalytic activity of nanomaterials.*

Keywords: nanomaterials, synthesis methods, water treatment

1. Introduction

Over the last decades, nanotechnology has become one of the most interesting research areas, being an advanced technology, whose main exertions are the synthesis, characterization and exploration of nanomaterials. Due to their small dimensions, nanomaterials have unique structure and properties compared to bulk materials [1, 2].

Nanomaterials are extensively used in different fields, such as: cancer treatment [3, 4], cardiovascular diseases treatment [5], supercapacitor [6], solar cells [7], gas sensors [8], UV protection [9], environmental applications [10-13] etc.

1PhD, "CristoforSimionescu" Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, "Gheorghe Asachi" Technical University of Iasi, Romania (amalia.sescu@ch.tuiasi.ro)
2Assoc.Prof., "CristoforSimionescu" Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, "Gheorghe Asachi" Technical University of Iasi, Romania (mharja@tuiasi.ro).
3Assoc. Prof.,"AlexandruIoanCuza" University of Iasi, Faculty of Chemistry, Iasi, Romania
4Assoc. Prof, Ecole Nationale Supérieure de Chimie de Rennes, Univ Rennes, France (lidia.favier@ensc-rennes.fr).
[5]Prof., "CristoforSimionescu" Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, "Gheorghe Asachi" Technical University of Iasi, Romania (gciobanu@tuiasi.ro).

Out of all these applications, the subject of cleaning the environment attracted a great interest due to the impact of various contaminants on flora, fauna and human health, water contamination being a special issue [14]. Conventional wastewater treatment can be expensive and have also other drawbacks. In this respect, the research in this area led to development of advanced oxidation processes (AOPs), that are based on the generation of reactive oxygen species, such as hydroxyl radicals which are capable of degrading and mineralize organic pollutants [14, 15].

Among AOPs, heterogeneous photocatalysis seems to be very effective in the elimination of organic pollutants from water and wastewater. It is a technology that uses a semiconductor material, being irradiated with UV light [16]. The semiconductor absorbs photons and some electrons in the valence band (VB) pass in the conduction band (CB), leaving holes in the VB and generate electron-hole pair. The electrons in the CB reacts with the oxygen from water to produce hydroxyl radicals, which attack organic molecules and eventually mineralize them into water and CO_2 [17, 18].

Various photocatalysts were used in this process, such as TiO_2, ZnO, WO_3, CdSe, SnO_2 for wastewater treatment [19-22]. TiO_2 remains the most studied photocatalyst, due to its chemical stability, abundance, low toxicity, high stability and low cost.

However, despite its advantages, TiO_2 has some drawbacks, such as limited adsorption capacity and high electron-hole recombination rate. To overcome these drawbacks, researches have been conducted on improving semiconductors synthesis in order to achieve a better performance [23].

2. Synthesis methods

The synthesis method is a key factor in determining the efficiency of the materials and represents a challenge for researchers to achieve the desired properties to control the shape, dimensions and surface structure of the synthesized materials.

Nanoparticles are usually obtained by two main approaches: top-down (fragmentation of bulk materials into nanomaterials) and bottom-up (the nanomaterials are produced from molecular precursors) [2].

Bottom up approaches seem to be very effective methods to obtain well defined nanoparticles and more homogeneous chemical composition. Usually, the reaction is conducted in a solvent, the diffusion and the transport of reagents and heat occur, taking place the assembly of nanoparticles [24].

2.1. Sol-gel synthesis

Sol-gel is currently the most investigated synthesis method due to the fact that it can be applied to a wide range of materials. It is a versatile process, which allows the possibility to control the shape, texture and dimension of nanoparticles.

Hydrolysis and condensation are two typical steps of the sol-gel method. Briefly, in the hydrolysis process, water is used to disintegrate the precursor bonds. This process is followed by condensation, which leads to gel formation and after the excess water is removed to form particles and determine the final structure of the material [26].

The common pathway of sol-gel method for preparing TiO_2 is by the hydrolysis of alkoxides (usually, titanium tetraisopropoxide or titanium n-butoxide) which are mixed with an organic solvent. The hydrolysis process is performed by adding water dropwise in the titanium solution. After, the condensation process occurs with the gel formation. Further, the obtained gel is dried and calcined. The photocatalytic activity of TiO_2 is strongly depended on parameters conditions, type of precursor and the organic solvent [27].

Rodríguez-Reyes and Dorantes-Rosales [28] obtained TiO_2 nanowires using titanium tetraisopropoxide, isopropanol and acetic acid. To obtain the gel, the sol was dried at 100°C for 24h. Finally, the gel was calcined in a conventional oven at 400, 500 and 600°C for crystallization of TiO_2 nanowires.

2.2. Hydrothermal synthesis

The hydrothermal method is a simple method, in which a solvent (generally water) is used, at a moderate temperature and high pressure to obtain TiO_2 nanoparticles. In hydrothermal processing, the reaction in aqueous solution takes place in a stainless-steel Teflon autoclave, where the temperature can be raised above the boiling point of the water, reaching the saturation pressure of the vapors [24]. Typically, the raw materials in form of nitrate or acetate are mixed with a solution of titanium in an organic solvent to obtain a sol, which is dried to produce the gel. Further, the gel is introduced in autoclave for the hydrothermal process at a moderate temperature and auto-generated pressure. The obtained product is filtered and washed [28].

2.3. Doping TiO_2 with noble metals

To enhance the photocatalytic activity of TiO_2, the semiconductor can be simply doped with different metals. One of the greatest advantages of metal doping is the inhibition of electron-hole recombination due to the Schottky barrier formed at the metal-TiO_2 junction, improving the photocatalytic activity [29].

3. Synthesis and activity of obtained photocatalysts

Incipient wetness impregnation is one the most commonly used method for the preparation of doped catalyst. In a typical procedure, over dehydrated TiO_2, a dopant solution containing Au and Pd precursors, respectively is rapidly poured in an adequate amount to completely wet the powder. Further, the product is dried and calcined at 600°C to obtain the catalyst.

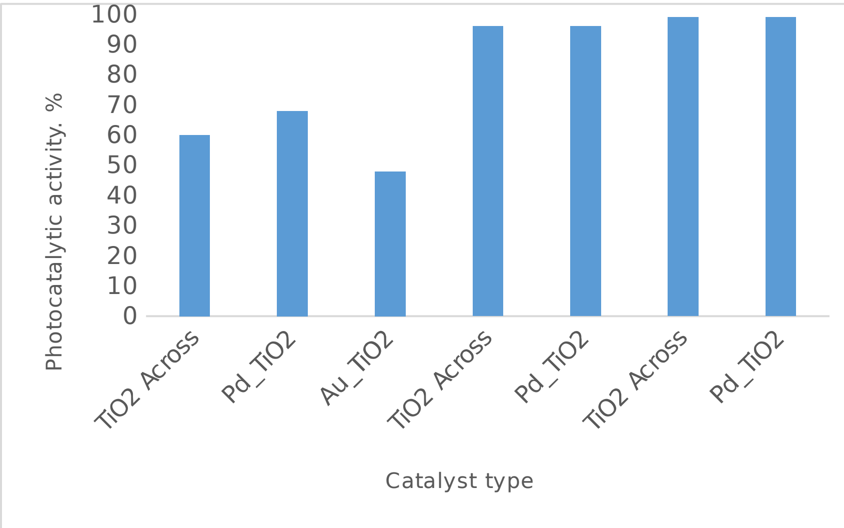

Fig. 1 Degradation of some organic compounds in presence of different catalysts

In Fig. 1 there are presented some results obtained by catalysts obtained by different synthesis method in the photocatalytic degradation of 2,4dinitrophenol, rhodamine 6G and clofibric acid. As can be seen, Pd ions improve the photocatalytic activity of TiO_2. This can be due to the fact that Pd ions can act as electron trapping sites, slowing electron-hole recombination rate and therefore increasing the photocatalytic activity.

On the other hand, in the case of Au doped TiO_2, a lower activity is observed in the degradation of 2,4dinitrophenol. This can be due to the fact that Au ions block TiO_2 active sites.

Conclusions

(1) The field of nanotechnology has grown intensively in the last years and has a great impact in developing new materials, with a large surface-to-volume ratio and special properties.

(2) Oxidicnanomaterials have attracted a great interest due to their wide applicability in different fields, from electronics to medicine.

(3) Nowadays, TiO_2 is one of the most investigated semiconductors, especially in the photocatalytic degradation of organic compounds from water and wastewater.

(4) Due to some drawback of TiO_2, efforts are still dedicated in order to improve its photocatalytic activity by adjusting and optimizing synthesis parameters or by doping bare TiO_2 with different ions.

(5) Studies shown that the synthesis method is a key factor in controlling the shape, dimension and the structure of nanomaterial.

(6) Results shown that doping TiO_2 can have a favorable effect or can inhibit the photocatalytic activity of the catalyst.

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