Journal of Environmental Management 212 (2018) 395–404

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Review

Investigation of amino-grafted TiO_2/reduced graphene oxide hybrids as a novel photocatalyst used for decomposition of selected organic dyes

Katarzyna Siwińska-Stefańska [a, *], Monika Fluder [a], Włodzimierz Tylus [b], Teofil Jesionowski [a]

[a] Poznan University of Technology, Faculty of Chemical Technology, Institute of Chemical Technology and Engineering, Berdychowo 4, PL-60965 Poznan, Poland

[b] Wroclaw University of Technology, Institute of Inorganic Technology, 27 Wybrzeze Wyspianskiego, 50-370 Wroclaw, Poland

ARTICLE INFO

Article history:
Received 23 February 2017
Received in revised form
28 January 2018
Accepted 7 February 2018

Keywords:
Amino-grafted titania/reduced graphene oxide hybrid
Titanium dioxide
Graphene oxide
Sol-gel method
Hydrothermal synthesis
Photocatalysis

ABSTRACT

A novel type of photocatalyst – hybrids of amino-grafted titania and reduced graphene oxide – was synthesized by a hydrothermal method. The hybrids were comprehensively analyzed, including determination of their morphology (TEM), porous structure parameters (low-temperature N_2 sorption) and crystalline structure (XRD). Additionally, to confirm the effective bonding of the amino-grafted titania and reduced graphene oxide, Raman and X-ray photoelectron spectroscopy (XPS) were used, in addition to elemental analysis. The key stage of the research was an evaluation of the photocatalytic activity of the synthesized hybrid photocatalysts with respect to the decomposition of C.I. Basic Blue 9 and C.I. Basic Red 1 dyes. It was found that the amino-grafted titania/reduced graphene oxide hybrids exhibited better photocatalytic activity in the degradation of C.I. Basic Blue 9 and C.I. Basic Red 1 than amino-grafted TiO_2 alone. The high efficiency of dye decomposition can be attributed to the higher BET surface area and good separation of photogenerated electrons and holes offered by graphene oxide.

Contents

* Corresponding author.
E-mail address: katarzyna.siwinska-stefanska@put.poznan.pl (K. Siwińska-Stefańska).

https://doi.org/10.1016/j.jenvman.2018.02.030

1. Introduction

Recent years have seen increasing interest in many aspects of environmental protection. These relate in particular to the high quantities of pollutants present both in the air and in water systems, which are a result of continuing industrial progress. Among the many technological methods used for their removal, the phenomenon of photocatalysis plays a crucial role (Hoffmann et al., 1995; Huang et al., 2014; Rajeshwara et al., 2008). Photocatalytic decomposition of pollutants does not require the use of conventional non-renewable sources of energy, whose acquisition involves degradation of the environment. The idea is to mineralize the impurities present in the environment (chiefly organic pollutants) completely into simple inorganic compounds, utilizing UV radiation and active photocatalysts. There are many oxide materials that can be used in the photocatalytic decomposition of various compounds, but the most important are titania and zinc oxide (Habisreutinger et al., 2013; Xing et al., 2012; Liu et al., 2010; Chen et al., 2010). These semiconductor materials are photocatalytically stable, effectively activated by UV light, chemically and biologically inert, cheap and easy to synthesize, and do not cause harmful effects either to humans or to the environment. The crystalline structure and the energy band gap are of great importance for their photocatalytic behavior (Stoyanova et al., 2013; Wu et al., 2011). These parameters are determined by the selection of an appropriate method of synthesis of oxide materials, and can be modified by changing the process conditions. Many scientific centers worldwide are working on the improvement of titania and other related catalysts. The aim is to enhance their activity by increasing the energy band gap or by altering their crystalline structure formation. This can be achieved by the incorporation of other active species into the photocatalyst structure via the well-known doping method (Rajeshwara et al., 2008; Liu and Chen, 2014). Among the many reported dopants, Cr, Zr, Mn and Mo may be mentioned (Lam et al., 2007; Venkatachalam et al., 2007; Di Paola et al., 2002; Hagfeldt and Grätzel, 1995). Another strategy is to synthesize hybrid materials composed of two or even more active components, such as TiO_2-SiO_2, ZnO-SiO_2, TiO_2-ZnO and TiO_2-ZrO_2 (Tobaldi et al., 2010; Hirano et al., 2004; Lathasree et al., 2004; Lizama et al., 2002; Akyol et al., 2004; Yu et al., 2003; Hameed et al., 2009). The incorporation of a second component during the synthesis of the semiconductor leads to a qualitatively different, novel material with enhanced structural properties such as surface area, porosity and crystalline structure. More importantly, combining semiconductor photocatalysts with different materials improves their photocatalytic activity and/or expands their spectral sensitivity range (Lam et al., 2007; Venkatachalam et al., 2007; Di Paola et al., 2002; Hagfeldt and Grätzel, 1995; Tobaldi et al., 2010; Hirano et al., 2004; Lathasree et al., 2004; Lizama et al., 2002; Akyol et al., 2004; Yu et al., 2003; Hameed et al., 2009). Excellent mechanical properties, large surface area and flexible structure are regarded as very important factors in the selection of such a component. Reports to date contain information about various dyes, metal complexes, nanocrystals (NCs) of metals or other semiconductors, conjugated polymers, and various forms of carbon, used for example as promoters of the photocatalytic activity of TiO_2 (Natalya and Stroyuk, 2014; Ni et al., 2014). The unique properties exhibited by carbon-based materials make them the most favored component for this purpose. For this reason, topics related to the production of advanced functional hybrid materials composed of synthetic oxides (such as TiO_2, SiO_2, ZrO_2, etc.) and carbon materials, such as graphene oxide or its derivatives, are of increasing interest worldwide (Tang et al., 2012; Yang et al., 2012). In environmental applications, graphene oxide or its derivatives can be used both as supports and as catalysts. The advantage of combining graphene-based materials with well known photocatalysts such as TiO_2 is that they do not cause defect states in the energy band gap of titania. As a result of the production of titania/graphene-based hybrids, materials are obtained with improved light absorption and separation of photogenerated electrons and holes, due to the excellent conductivity and intense light absorption of the graphene-based component (Qiu et al., 2012; Di Lupo et al., 2014). Recently, numerous attempts have been made to combine TiO_2 with graphene oxide in order to improve its photodegradation efficiency (Kusiak-Nejman et al., 2017; Perera et al., 2012; Najafi et al., 2017; Hu et al., 2017; Thomas et al., 2014; Jiang et al., 2011; Štengl et al., 2013; Siwińska-Stefańska and Kurc, 2015; Kurc et al., 2016; Kruk and Jaroniec, 2001; Jaroniec and Solovyov, 2006). In the last few years, various methods for obtaining TiO_2/graphene oxide composites have been proposed, including hydrothermal synthesis, electrochemical deposition, the sol-gel method and self-assemble approaches (Kruk et al., 1997). The best-known approach is the hydrothermal method. Kusiak-Nejman et al. (2017), who prepared hybrid nanocomposites containing crystalline TiO_2 and graphene-related materials using the hydrothermal method, showed that the presence of graphitic carbon depends not only on temperature, but also on the type of modification applied and the conditions of preparation (Kusiak-Nejman et al., 2017). Perera et al. (2012) used an alkaline hydrothermal process to prepare TiO_2 nanotube (TNT)/reduced graphene oxide (hGO) composites. They found that the ratio of hGO to TNT in the hybrid material significantly affected its photocatalytic activity. TiO_2/GO nanocomposites with different TiO_2 morphologies were successfully synthesized via a hydrothermal method by Najafi et al. (2017). The obtained TiO_2/GO nanocomposite demonstrated good photocatalytic activity in the degradation of Methylene Blue (MB). Hu et al. (2017) synthesized TiO_2/graphene (TiO_2/GR) composites by a hydrothermal reaction. These composites exhibited better photocatalytic properties than other nanocomposites.

The present research is concerned with the hydrothermal synthesis, physicochemical characterization and application of hybrids of amino-grafted titania with reduced graphene oxide (TA/rGO). Since such a material had previously been tested as an electrode material in Li-ion batteries and found to exhibit excellent electrochemical behavior (Siwińska-Stefańska and Kurc, 2015; Kurc et al., 2016), an investigation was made of its photocatalytic activity. Photocatalytic tests were performed to verify the possibility of using TA/rGO hybrid materials for the photocatalytic decomposition of two model organic impurities (C.I. Basic Blue 9 and C.I. Basic Red 1). The preliminary results are very promising, and provide direct justification for the proposed line of research.

2. Experimental section

2.1. Materials

All chemical reagents used in the experiments, including titanium(IV) isopropoxide (TTIP, 97%, Sigma-Aldrich), propan-2-ol