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Photocatalytical properties of maze-like MoO_3 microstructures prepared by anodization of Mo plate

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ABSTRACT

In this work, we present a simple method of the formation of MoO_3 microstructures *via* an electrochemical anodization of Mo plate carried out under varied conditions. The morphology, composition and structure of samples were investigated by SEM, EDX, XRD and Raman spectroscopy. The band gap energy was estimated using the Kubelka–Munk function and was found to be 2.87 eV. Finally, the photocatalytic activities of MoO_3 samples were evaluated using the decolorisation of methylene blue (MB) as a model organic contamination. Additionally, photostability of the materials were verified and the formation of hydroxyl ions was investigated by photoluminescence (PL) spectra of terephthalic acid as a probe molecule. Various conditions of MB decolorization allow the main mechanism of dye decomposition to be identified. It was shown that the presence of F^- during anodization positively affects photocatalytic properties of tested samples. After 2 h of constant illumination, the degradation reached 34% of the initial value of MB when α-MoO_3 (prepared without F^-) was used as photocatalyst, whereas the degradation efficiency equals 57% in the case of α-MoO_3 (with F^-). Furthermore, photoluminescence intensity of the 2-hydroxyterephthalic acid formed in the presence of α-$MoO_3(F^-)$ was higher comparing to the intensity of spectra recorded in the presence of α-MoO_3.

1. Introduction

Nowadays, disposal of hazardous compounds is the one of the most important threads discussed by scientists and technologist. However, the problem of environmental pollution by organic compounds produced by industry is still not fully solved. One of the most promising method of pollutant degradation is based on conversion of electromagnetic radiation into chemical energy. Up to now, many different transitional metal oxides were tested as photocatalysts towards organic pollutant decomposition. The most often tested metal oxide as photocatalyst is TiO_2, however relatively wide energy band gap *ca.* 3.2 eV makes titania photoactive only under UV illumination [1]. Thus, great effort has been taken to research on new materials that exhibit the highest photoactivity under visible light illumination in order to use natural solar light for excitation. Among them, molybdenum trioxide which has gained interest due to its promising properties and possible applications in various processes (photocatalysis [2]), and devices (sensors [3], photochromic devices [4], supercapacitors [5], batteries [6] or photovoltaic cells [7]). Variety of applications results from rich chemistry associated with multiple valence states, photo- and electrochromic properties, electrochemical activity and relatively high chemical, electrical and thermal stability [8–10].

There are known several synthesis methods of the molybdenum trioxide, mostly based on wet chemistry approach that leads to different morphologies, such as fibers, nanoplates or nanobelts. Alizadeh *et al.* [8] synthesized MoO_3 nanometer fibers and belts structures *via* molten salt method using ammonium nitrate. MoO_3 nanoplates were fabricated through vapor-deposition method in Ar atmosphere under ambient pressure without the assistant of any catalysts by Chen et al. [11]. According to Chithambararaj et al. [2], molybdenum trioxide nanocrystals were obtained using a simple and template-free solution based chemical precipitation method. Other morphological form of Molybdenum trioxide – nanobelts were fabricated through a hydrothermal treatment of peroxomolybdic acid solution by Zhou et al. [12].

Above mentioned methods allow preparation of various MoO_3 nanostructures, but the high requirements concerning synthesis

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conditions and expensive precursors hamper their wide, commercial application. Additionally, in the case of wet chemistry synthesis methods, obtained material is in the form of powder. Thus, in order to utilize the uniform layer, immobilization process should be performed and much interest is focused on elaboration of the morphology-controllable synthesis of MoO_3 nanostructures already on the supporting material. Recently, MoO_3 layers were synthesized *via* anodization of Mo plate in glycol/water solution [13]. Lou et al. described method of Mo/MoO_3 electrosynthesis and tested it as a photoelectrode capable to store photoexcited charge. Alkali metals were intercalated into crystal structure of MoO_3 during illumination and then were released in the dark conditions resulting in current generation, simultaneously.

Herein, a simple and successful electrochemical method was utilized to prepare α-MoO_3 nanostructures directly onto the conductive substrate in accordance to Lou et al. report [13]. The investigated materials were obtained *via* anodization process of a molybdenum foil in a solution with and without fluoride ions. The presence of fluoride ions strongly affects the morphology, which has been inspected by scanning electron microscopy. EDX analysis confirmed the MoO_3 stoichiometry whereas its crystal structure was revealed by Raman spectroscopy and X-ray diffraction. The energy band gap was determined using UV–vis reflectance spectroscopy. The photoactivity of obtain samples was tested during a photocatalytic process of methylene blue decomposition with and without t-butanol. The formation efficiency of hydroxyl radicals ($^{\bullet}OH$) on the surface of illuminated samples was estimated based on photoluminescence spectra of terephtalic acid as a probe molecule.

2. Experimental

2.1. Synthesis

Molybdenum trioxide nanostructures were prepared *via* an electrochemical anodization of a Mo plate (Sigma Aldrich, 99.7%) in the solutions with and without source of fluorine ions. Prior to anodization, molybdenum sheets were ultrasonically cleaned in acetone, ethanol and water (for 10 min in each solvent) and dried under a stream of cold air. The anodization process was performed in a two electrode configuration, where a Mo plate served as an anode and a platinum rectangular mesh as a cathode. The distance between the electrodes was kept constant at 2.5 cm. Anodization process took place in the electrolyte containing 0.5 M H_3PO_4 in 5%/95% v/v water–ethylene glycol solution with and without 0.1 M NH_4F. According to the electrolyte composition, samples were coded as α-MoO_3 (F^-) and α-MoO_3. After optimization of the anodization procedure, the voltage of 40 V was applied for 0.5 h and then 20 V for 1.5 h. The whole anodization process took place in a cell with the cooling jacket that kept constant temperature at 23 °C (±1 °C) using a thermostat (Julabo F-12). The anodization progress was automatically registered as the current changes over time (Keithley 2400). Fig. 1 shows the transient currents registered when Mo plate were anodized in solutions with and without the source of fluoride ions. The shapes of both j–t curves are similar, but significant difference in the value of anodization current is observed. About 9 times higher current was recorded in the case of fluoride containing electrolyte. The presence of F^- ions enables proceeding of the dissolution reaction of the molybdenum trioxide on the surface of the electrode. Since the current is related to Mo oxidation, higher current density is observed due to a smaller surface area of metallic molybdenum covered by molybdenum oxide. Probably, simultaneous formation and dissolution of molybdenum trioxide affects the formation of the unique structures of MoO_3.

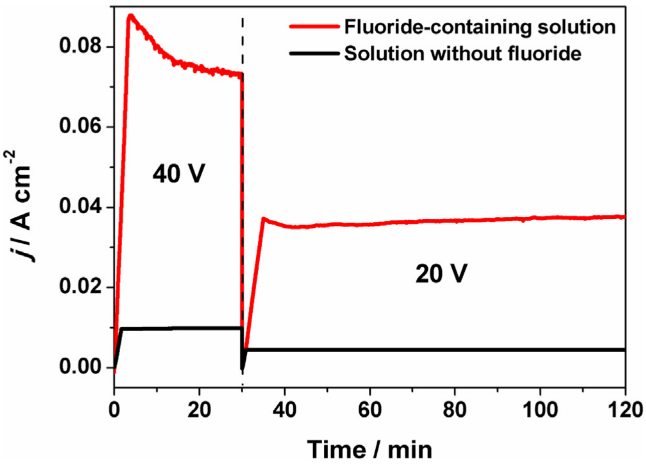

Fig. 1. The transient current recorded during anodization of Mo foil in electrolyte with and without fluoride ions.

Finally, the prepared samples were cleaned by sonication in water and then thermally annealed at 450 °C in air atmosphere for 2 hours, with a heating rate of 2 °C min^{-1}. Calcination was performed in order to convert the amorphous MoO_3 layer into the crystalline α-phase.

2.2. Apparatus

The morphology and cross-section of the samples were investigated by the Schottky field emission scanning electron microscopy (FEI Quanta FEG 250) with ET secondary electron detector. Beam accelerating voltage was kept at 10 kV. For elemental analysis, the Energy Dispersive X-ray Spectroscopy was performed by EDAX Genesis APEX 2i with ApolloX SDD spectrometer in a particular area of each sample. The crystalline phase of materials were determined by Raman spectroscopy (micro-Raman spectrometer Renishaw InVia) using 514 nm laser as the light source. The UV–vis reflectance spectra of MoO_3 nanostructures were measured with a dual beam UV–vis spectrophotometer (Lambda 35, Perkin-Elmer) equipped with a diffuse reflectance accessory. Spectra were registered in a range of 350–900 nm, with a scanning speed of 120 nm min^{-1}. Bandgap energy (E_{bg}) values were determined as the intercept of the tangent of the plot of transformation of the Kubelka–Munk function: $f(KM) = \frac{(1-R)^2}{2R}$, where R is reflectance. Crystal structure of the obtained materials were also determined from X-Ray diffraction patterns (XRD), using X-ray diffractometer (Xpert PRO-MPD, Philips) with copper K_α radiation ($\lambda = 1.5404$ Å).

2.3. Photocatalytic measurement

The photocatalytic activity of samples with a geometric area of 2.5 cm^2 was evaluated *via* degradation of methylene blue (MB) aqueous solution (50 mL) with an initial concentration of 10 μM. Measurements were also performed in a presence of hydroxyl radicals scavenger tert-butyl alcohol (TBA, 1 mM). The concentration of remaining MB was controlled using the Lambda 35 UV–vis spectrophotometer (Perkin Elmer). The formation efficiency of hydroxyl radicals at the illuminated samples/water interface was verified by the fluorescence method using the terephthalic acid (TA) as a probe molecule. The experimental procedure is similar to the MB photodegradaton experiment except replacing the MB solution with the 50 mM aqueous solution of terephthalic acid in 50 mM NaOH. Photoluminescence arises from 2-hydroxyterephthalic acid excited by 315 nm light formed *via* reaction between TA