STUDIES OF PHOTOCATALYTIC PROPERTIES AND BIOACTIVITY OF TITANIUM-OXO CLUSTERS

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Introduction

The unique physicochemical and biological properties of titanium dioxide favour its wide application in various fields of our life. Especially, the photocatalytic properties and bioactivity of materials based on TiO_2 are intensively studied in recent time [1,2]. Titania photoactivity is utilized in water splitting, air and water purification, environmental pollutants reduction, and in antimicrobial applications. However recently, considerable attention is devoting to the use of titanium(IV) oxo-complexes (TOCs) as systems exhibiting similar properties to TiO_2. The results of previous studies revealed significant importance of TOCs in the synthesis of inorganic-organic composite materials, which are produced through introduction of metal oxo-clusters into the polymer matrix [3]. The possible interactions between inorganic and organic components may result in an improvement of structural properties of the polymer, as well as of its thermal and mechanical ones due to crosslinking and filling. The unique properties of oxo-clusters, e.g. photochromicity, photocatalytic/biological activity can give completely new properties to the composite material in comparison to the base polymer [3]. Therefore, the studies on TOCs synthesis of the titanium-oxide core of the desirable architecture, size, physicochemical properties and their bioactivity, are important [4-6]. Especially, the studies on the structural conversion of Ti(IV) multinuclear oxo-complexes containing $\{Ti_a\text{-}(\mu_i\text{-}O)_b\}$ cores are relevant for their controlled synthesis [7-9]. The purpose of our research works is to optimize synthesis conditions of Ti(IV) oxo-complexes containing functionalized carboxylate groups and their structure determination. The estimate the photocatalytic properties and bioactivity of composites produced by dispersion of TOCs in polymeric matrixes is an important part of our works.

Materials and Methods

Multinuclear oxo-complexes were synthesized in the direct reaction of the titanium(IV) alkoxides and organic acids in different molar ratios and solvents using standard Schlenk techniques under Ar atmosphere and in room temperature. The slow evaporation of the reaction liquors under the inert gas (3-5 days), led to the isolation of crystalline products. Single crystal X-ray diffraction studies allowed to solve the structure of crystals, which quality was suitable. The structure of the remaining produced oxo-complexes was determined basing the analysis of spectroscopic data (IR, Raman, MS, NMR). Photocatalytic activity studies were carried out basis on the studies of the UV-Vis induced degradation processes of organic dyes, stearic acid and acetone. In order to evaluate of antimicrobial activity, LIVE/DEAD, Alamar Blue staining and CFU method were used.

Results and Discussion

The direct reaction of the titanium(IV) alkoxides $(Ti(OR)_4$, R = ^iPr, ^iBu) and functionalized organic acids (4:1 alkoxide/acid molar ratio, standard Schlenk techniques, inert atmosphere, room temperature) led to the formation of $[Ti_3O(O^iPr)_8(O_2CR')_2]$ and $[Ti_4O_2(O^iBu)_{10}(O_2CR')_2]$ (R' = $PhNH_2$, PhCl, $PhNO_2$, $C_{13}H_9$, C_4H_7) complexes [9,10]. The molecular structure of $\{Ti_aO_b\}$ cores, which were found in the structure above mentioned compounds, determined using single crystal X-ray diffractions, are presented in FIG. 1.

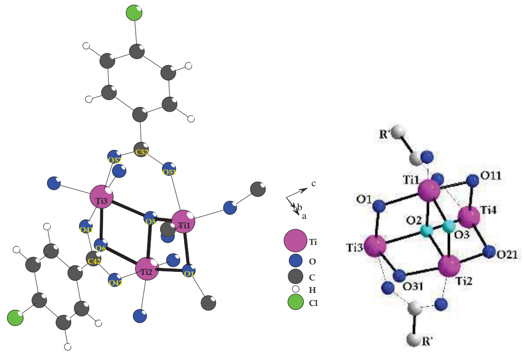

FIG. 1. The structures of $\{Ti_aO_b\}$ (a = 3, 4, b = 1, 2) cores, which was found in $[Ti_3O(O^iPr)_8(O_2CR')_2]$ and $[Ti_4O_2(O^iBu)_{10}(O_2CR')_2]$ (R' = $PhNH_2$, PhCl, $PhNO_2$, $C_{13}H_9$, C_4H_7) complexes (crystallographic ball-stick scheme). For clarity, the terminal alkoxide groups are omitted.

The type of the $\{Ti_aO_b\}$ core and the carboxylate group allows to modulate the band-gap of synthesized compounds in the range of 3.6 – 2.0 eV. The Ti(IV) oxo-complexes were applied in fabrication of poly(methyl methacrylate)/TOCs composite materials (the oxo-complex content - 20%). The highest photocatalytic activity was evidenced for these composites, which contain fluorene $(\text{-OOCC}_{13}H_9)$ and -OOCPhNH_2 groups in the TOCs structure. Simultaneously, the results of microbiological tests revealed that the best biocidal activity (*S. aureus*, *E. coli*, and mixtures of mold spores) was noticed for polymer/TOCs composite coatings, which contain the $\text{-OOCC}_{13}H_9$ and -OOCPhNH_2 ligands.

Conclusions

The results our works allowed to optimize the synthesis conditions of three- and tetranuclear Ti(IV) oxo-complexes $([Ti_aO_b(OR)_c(OOCR')_2]$ (a = 3, 4, b = 1,2, c = 8,10; R = ^iPr, ^iBu, R' = $PhNH_2$, PhCl, $PhNO_2$, $C_{13}H_9$, C_4H_7)). The dispersion of the produced TOCs in the polymer solutions made it possible to the formation of polymer/TOCs composite coatings. The use of TOCs, which contain fluorene and -OOCPhNH2 ligands, in synthesis of polymer/TOCs systems allows to receive the coating materials with suitable photocatalytic properties and microbicidal activity.

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