Journal of Photochemistry and Photobiology A: Chemistry 314 (2016) 6–13

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Synthesis, spectral, optical and photocatalytic properties of vanadium- and carbon-doped titanium dioxide with three-dimensional architecture of aggregates

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ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form 25 June 2015
Accepted 2 August 2015
Available online 4 August 2015

Keywords:
Titanium dioxide
Vanadium
Photocatalysis
Ab initio calculations
Optical absorption

ABSTRACT

Vanadium-doped and vanadium- and carbon-doped nanostructured anatase with threedimensional architecture of aggregates has been synthesized by the developed precursor method. Glycolate $Ti_{1-x}V_x(OCH_2CH_2O)_2$ $(0.01 \le x \le 0.05)$ was used as a precursor. The obtained samples of the compositions $Ti_{1-x}V_xO_2$, $Ti_{1-x}V_xO_{2-y}C_y$ and $Ti_{1-x}V_xO_{2-y}C_y{\cdot}nC$ were characterized by X-ray diffraction, scanning electron microscopy, absorption spectroscopy in ultraviolet and visible regions and by X-ray photoelectron spectroscopy methods. It was established that the synthesized materials exhibit photocatalytic activity in the oxidation reaction in aqueous solution of hydroquinone under ultraviolet and visible light irradiation. First principle calculations of the electronic band structure and optical absorption of vanadium- and carbon-doped anatase have been performed. The calculations showed that doping gives rise to the impurity states inside the band gap, which are responsible for the appearance of absorption, and consequently, visible light photocatalytic activity.

1. Introduction

Titanium dioxide belongs to a group of advanced functional materials of great industrial importance. Possessing a unique combination of properties, low cost and availability, it finds wide application in different branches of modern engineering and technologies. One of the most important and promising directions of practical application of TiO_2 has to do with its high photocatalytic activity in the processes of deactivation of toxic organic compounds and pathogenic germs contained in domestic and industrial waste [1–4]. Recently, the investigations into the development of catalytic systems and technologies for destruction of organic pollutant molecules until complete mineralization under visible light have been intensified. However, the band gap of titanium dioxide in the form of anatase and rutile is respectively 3.2 and 3.0 eV, which restricts its spectral sensitivity only to the ultraviolet region ($\lambda < 400$ nm). According to the available literature data, the spectral sensitivity of TiO_2 can be extended into the long-wave region by doping with transition and rare-earth metals and with some nonmetals, for example, nitrogen and carbon [5–21]. The introduction of impurities forming additional energy levels in the band gap of the semiconductor makes it possible to change its band gap and to affect the concentration and mobility of free charge carriers (electrons and holes) participating in redox reactions during photocatalysis. The greatest efficiency as a dopant was exhibited by vanadium—even small additions of it into anatase structure lead to visible light photocatalytic effect [22–30]. Besides doping, the photocatalytic properties of titanium dioxide can be tuned by changing the size and morphology of its particles, as well as by modification of their bulk and surface characteristics [31–39]. It is known that transition of a substance into nanodispersed state is accompanied by the variation of existing properties and by the appearance of basically new functional properties caused by the manifestation of size effects. The nanodimensional samples of titanium dioxide are usually characterized by higher values of photocatalytic activity because of the developed particle surface, which has enhanced sorption ability with respect to substrate molecules and environment components and provides favorable conditions for the migration of photo-generated charge carriers (e^-, h^+). Generally, the photocatalytic properties of titanium dioxide are a complex function of the crystal structure, the concentration of dopants and position of their energy levels in the band gap, the

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http://dx.doi.org/10.1016/j.jphotochem.2015.08.002
1010-6030/

surface and bulk distribution, as well as imperfection, morphology, sizes and microstructure of particles, which underlines their critical dependence on the method of photocatalyst synthesis.

The problem of producing titanium dioxide based photocatalysts with improved functional characteristics can be solved by precursor synthesis, in which the effect of pseudomorphic transformation of precursor into oxide during heating is employed. For example, using titanium glycolate $Ti(OCH_2CH_2O)_2$ and solid solutions based thereon of the general composition $Ti_{1-x}M_x(OCH_2CH_2O)_2$ as precursors, it is possible to synthesize both pure and transition-element and carbon-doped titanium dioxide in the form of nanodispersed solid solutions $TiO_{2-y}C_y$, $Ti_{1-x}M_xO_2$, $Ti_{1-x}M_xO_{2-y}C_y$ and nanocomposites $TiO_{2-y}C_y$:nC, $Ti_{1-x}M_xO_{2-y}C_y$:nC with pre-assigned concentration of impurity elements and controlled dimensional and morphological characteristics of particles [25,26,40–46]. In most cases, the morphology and dimensions of precursor crystals depend on the method of their production. Thermal treatment of mixtures of titanium hydroxide $Ti(OH)_4$ and ethylene glycol $HOCH_2CH_2OH$ allows one to synthesize $Ti(OCH_2CH_2O)_2$ in the form of fibers, needles, extended plates and rods, which during heating in air or inert atmosphere transform into nanostructured TiO_2 aggregates and $TiO_{2-y}C_y$:nC composites inheriting the form of the precursor crystals [42]. Thermolysis of vanadium-substituted glycolate $Ti_{1-x}V_x(OCH_2CH_2O)_2$ in air was used to synthesize quasi-one-dimensional (1D) solid solutions of the composition $Ti_{1-x}V_xO_2$ with anatase structure that exhibited high photocatalytic activity in the oxidation reaction of hydroquinone in water under visible light. Thermolysis of $Ti_{1-x}V_x(OCH_2CH_2O)_2$ in inert atmosphere at 500 °C gives rise to $Ti_{1-x}V_xO_{2-y}C_y$:nC composites, whose aggregates have extended shape and are built of autonomous layers of titanium-containing phase with anatase structure and free carbon [25,26]. By varying the ratio of the reaction mixture components including titanium tetrabutoxide $Ti(C_4H_9O)_4$ and ethylene glycol, as well as the synthesis conditions, we obtained samples of titanium glycolate $Ti(OCH_2CH_2O)_2$ with three-dimensional near-spherical architecture of crystal aggregates [46]. As a result of thermolysis in air or inert atmosphere, these spherical aggregates undergo a pseudomorphic transformation into TiO_2, $TiO_{2-y}C_y$ and $TiO_{2-y}C_y$:nC particles. The photocatalysts consisting of nanostructured titanium-dioxide-based carbon-containing microspheres have high specific surface area and acceptable mechanical strength and can be easily removed from solution upon photocatalysis. The three-dimensional architecture of the nanostructured carbon-containing titanium dioxide based microspheres attracts attention of researchers owing to their pronounced photocatalytic activity under visible light [34–39]. This effect is expected to strengthen as a result of combining vanadium and carbon doping leading to the formation of dimensional, morphological and microstructural features, as well as intrinsic defect structure of photocatalyst, which are controlled by the conditions of its production. Enhancement of photocatalytic activity and its displacement into the visible region were observed for some samples of vanadium- and carbon-doped titanium dioxide synthesized by the sol-gel method, [47–51].

Therefore, the main aims of this work were to develop a method of precursor synthesis of nanocomposites $Ti_{1-x}V_xO_{2-y}C_y$:nC and nanodispersed solid solutions $Ti_{1-x}V_xO_2$ with spherical shape of aggregates and to examine their thermal, spectral, optical and photocatalytic properties as functions of the concentration of vanadium and carbon. In order to elucidate the nature of the vanadium and carbon doping effect on the optical and photocatalytic properties of anatase, we have carried out first-principle calculations of its electronic band structure and optical absorption.

2. Materials and methods

2.1. Synthesis

The samples were synthesized by the precursor method with the use of glycolate of the composition $Ti_{1-x}V_x(OCH_2CH_2O)_2$ ($0 \le x \le 0.05$) as a precursor taking into account that the crystals of this compound are able to undergo a pseudomorphous transformation into aggregates $Ti_{1-x}V_xO_2$, $Ti_{1-x}V_xO_{2-y}C_y$ and $Ti_{1-x}V_xO_{2-y}C_y$:nC during heating under pre-assigned conditions [25,26,42–45]. To produce a precursor with spherical shape of crystal aggregates, we have developed a technique allowing for the following reactions:

$$Ti(C_4H_9O) + 2HOCH_2CH_2OH = Ti(OCH_2CH_2O)_2 + 4C_4H_9OH \quad (1)$$

$$2NH_4VO_3 + 3HOCH_2CH_2OH = 2VO(OCH_2CH_2O) + HOCH_2CHO + 3H_2O + 2NH_3, \quad (2)$$

$$VO(OCH_2CH_2O) + HOCH_2CH_2OH = V(OCH_2CH_2O)_2 + H_2O \quad (3)$$

$$(1-x)Ti(OCH_2CH_2O)_2 + xV(OCH_2CH_2O)_2 = Ti_{1-x}V_x(OCH_2CH_2O)_2 \quad (4)$$

The solid products of reactions (1, 2, 4) were obtained as individual chemical compounds, and reaction (3) is hypothetical. The reagents – titanium tetrabutoxide $Ti(C_4H_9O)_4$ and ethylene glycol $HOCH_2CH_2OH$ taken in the volumetric ratio 1/2:1/5 – were heated jointly in a glass vessel at 150 °C until glycolate was formed in the form of a white precipitate. Upon cooling the vessel with the contents to room temperature, the unreacted ethylene glycol was separated from the solid precipitate by vacuum filtration and by washing with acetone. On completion of this operation, the precipitate was dried at 50 °C in air for 1 h and was placed into airtight reservoirs to be stored in conditions excluding the contact with air moisture. To produce carbon-containing composites $TiO_{2-y}C_y$:nC and $Ti_{1-x}V_xO_{2-y}C_y$:nC, the powders $Ti(OCH_2CH_2O)_2$ and $Ti_{1-x}V_x(OCH_2CH_2O)_2$ were heated in helium atmosphere at 500 °C for 2 h. Then, to reduce the concentration of carbon and to obtain the solid solutions $Ti_{1-x}V_xO_{2-y}C_y$, the synthesized sample of $Ti_{1-x}V_xO_{2-y}C_y$:nC was annealed in air at 300, 325, 350, 375, 400, 450 and 500 °C with sampling after each stage of annealing during 2 h. The powders of $Ti_{1-x}V_x(OCH_2CH_2O)_2$ have a pale yellow color, which intensifies with the growth of the concentration of vanadium.

2.2. Method of experiment

The phase analysis of the precursors and the products of their thermolysis was performed by means of a POLAM S-112 polarizing microscope in transmitted light and a STADI-P X-ray powder diffractometer (STOE, Germany) in $CuK\alpha_1$ radiation. The size and shape of the particles of the precursors and their thermolysis products were determined by scanning electron microscopy on a JSM5900LV device and by transmission electron microscopy on a JEM-200CX electron microscope. The IR absorption spectra were registered on a Vertex 80 IR Fourier spectrometer (Bruker) in the range 4000–400 cm^{-1} from powder-like samples (pellets in CsI). The Raman spectra were obtained at room temperature on a module attachment RAMII compatible with an IR Fourier spectrometer Vertex 80 (λ = 1064 nm, Nd:YAG, P = 450 mW) and on a RENISHAW-1000 spectrometer (λ = 514.5 nm, P = 25 mW). The UV–vis spectra were recorded in the interval 190–800 nm on a UV–3600 (Shimadzu, λ = 310 nm) spectrometer using $BaSO_4$ as standard. The valence state of vanadium and the nature of carbon were established by X-ray photoelectron spectroscopy (XPS) methods. The measurements were carried out using an ESCALAB MK spectrometer with the use of nonmonochromatic radiation $MgK\alpha$ radiation (1253.6 eV). The concentration of structurally