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Electrochemical synthesis of nanosized TiO_2 nanopowder involving choline chloride based ionic liquids

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ABSTRACT

The paper presents some experimental results regarding the electrochemical synthesis of TiO_2 nanopowders through anodic dissolution of Ti metal in choline chloride based eutectic mixtures (DES). A detailed characterization of the obtained titania has been performed, using various techniques, including XRD, Raman spectroscopy, XPS, SEM associated with EDX analysis, BET and UV–vis diffuse reflectance spectra. The anodic behavior of Ti electrode in DES has been also investigated. The photoreactivity of the synthesized materials was evaluated for the degradation of Orange II dye under UV ($\lambda = 365$ nm) and visible light irradiation. An anodic synthesis efficiency of minimum 92% has been determined. The as-synthesized TiO_2 showed amorphous structure and a calcination post-treatment at temperatures between 400 and 600 °C yielded anatase. The anodically obtained nanocrystalline oxides have crystallite sizes of 8–18 nm, a high surface area and enhanced photocatalytic effect.

1. Introduction

Nanostructured titanium dioxide (TiO_2), also known as titania, represents a highly attractive material for a large range of industrial applications including solar cells, self-cleaning, photocatalysis, chemical sensors, microelectronics or electrochemistry [1–5]. TiO_2 is a non-toxic, environmentally friendly semiconductor photocatalyst, frequently used in paints, white pigments and sun-blockers. Because of its large band gap (anatase: 3.2 eV; rutile: 3.0 eV), only a small UV fraction of solar light may be used for photocatalytic reactions. Extensive efforts have been made to develop titanium oxide photocatalysts that can efficiently utilize solar or indoor light, including various doping procedures with transition-metal ions or their corresponding oxides and/or non-metals [6–14].

Nanosized titania in its anatase phase posses higher photocatalytic performance compared to other phases and its bulk counterpart [1,14,15]. Various synthesis methods, including precipitation, microemulsion, sol–gel, as well as physical or chemical vapor deposition [16–18] have been reported, however, these routes usually involve many steps, expensive alcoxide-precursors and equipment. A potential alternative is represented by the anodic dissolution of titanium involving nonaqueous media and direct hydrolysis of the electrolyte solution to prepare nanosized TiO_2 [19,20].

A quite novel approach adequate to form anodic oxides nanopowders takes into account the use of ionic liquids [21–23], which are gaining wide recognition as potential environmentally benign solvents and widespread application in materials chemistry and electrochemistry in a green synthetic strategy [19,20,24,25]. Room temperature ionic liquids (RTILs or ILs) are organic salts, composed entirely of ions, with low melting points of below 100 °C.

Formation of ionic liquids from eutectic mixtures of quaternary ammonium salt, mostly used choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride), with hydrogen bond donor species such as amides, glycols or carboxylic acids [22–27] has recently been shown. These media, also known as “deep eutectic solvents (DES)” exhibit good air and water stability, they are potentially recyclable, biodegradable and bring no harm to human health. These kinds of ionic liquids represent a low cost alternative to classical ILs.

Thanks to these properties the ionic liquids have attracted considerable interest in the preparation of porous crystalline materials. Porous nano-titanium dioxide particles with anatase framework and crystallite sizes of approximately 15 nm were prepared

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Table 1
Ionic liquids systems involved in TiO_2 electrochemical synthesis.

System type	Electrolyte composition
ILEG-EtOH	2:1 (volume ratio) ILEG:EtOH + 1–5 mM TBAB
IL-EtOH	1:1 (volume ratio) IL:EtOH + 1–5 mM TBAB

by using *N*,*N*-bis [2-methylbutyl] imidazolium hexafluorophosphate ([PPim][PF6]) [28]. Farag et al. [29] reported the synthesis of titania in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (Py14TFSA) via sol-gel method, the nanopowder being characterized by a high thermal stability and BET surface area of $97\,m^2\,g^{-1}$. Oumahi et al. [30] reported the synthesis of Au/TiO_2 heterogeneous catalysts involving two imidazolium-based ILs (1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) and trifluoromethanesulfonate (BMIMOTf)) or a DES (eutectic of choline chloride and urea). It has been shown that using DES as synthesis medium, stronger metal–support interactions were formed compared to interactions in imidazolium ILs. Also, our group recently reported the successful electrochemical synthesis of ZnO nanopowders involving anodic dissolution of Zn metal in DES based electrolytes [31].

Despite of the growing interest in the field of “tailor-made” inorganic materials production, very few published works were devoted to the effect of DES electrolyte on the anodic behavior of valve metals and on the morphology of the obtained oxide nanostructures. Additional information in this field may significantly contribute to the extension of the practical applications of these systems. With this in view, this work presents some experimental results regarding the formation of TiO_2 nanopowder using anodic dissolution of Ti metal in some choline chloride based ionic liquids [32].

2. Experimental

2.1. Chemicals and materials

Choline chloride-based ionic liquids were synthesized as shown in Table 1. Choline chloride (denoted as ChCl, 99%), ethylene glycol (EG, 99.5%), urea (99.5%), tetrabutylammonium bromide (TBAB, ≥98%), ethanol (EtOH), were purchased from Aldrich and used as received. TiO_2 nanopowder of 99.5% purity was supplied by TitanPE Technologies, Inc., China (particle size of maximum 20 nm, surface area of $115\,m^2\,g^{-1}$ and average pore size of 130 Å). The eutectic mixtures have been prepared by mixing and heating with gentle stirring ChCl with EG (symbolized ILEG) and ChCl with urea (symbolized IL) in 1:2 molar ratio at a temperature in the range 80–100 °C, until a homogeneous, clear liquid was formed. EtOH as well as TBAB were then introduced to prepare the electrolytes.

2.2. Electrochemical synthesis of TiO_2

The electrochemical synthesis experiments were performed in stationary conditions and in an open system, using a DC power supply (0–5 A, 0–60 V). The cell has a two-electrode configuration and contains 400 mL ionic liquid as electrolyte. Pure titanium discs (4 mm thickness) of $38.46\,cm^2$ exposed surface area have been used as sacrificial anode and Ni strips (0.3 mm thickness) as cathode. The ratio of anodic to cathodic area was 1:1. Current densities between 20 and $70\,mA\,cm^{-2}$ were applied at temperatures in the range of 30–60 °C for durations between 2 and 6 h. After Ti anode dissolution, 10 mL of water has been added to the electrolyte in the cell. Thus, a direct hydrolysis occurred with the formation of a white gel. The gel was washed with ethanol and then subjected to centrifugation at 4000 rpm for 15 min. This sequence was repeated for 4 times, followed by drying at 110 °C for 1 h and calcination at temperatures between 400 °C and 600 °C for 1 h. Faradaic anodic efficiency has been calculated by the mass ratio between the practically to theoretically obtained titania powder.

In another series of experiments, anodic behavior of Ti electrode in choline chloride based ionic liquids has been investigated by cyclic voltammetry, using a three electrode glass cell with a Ti working electrode ($1\,cm^2$), a platinum counterelectrode and a silver wire as quasi-reference electrode. The reference and counterelectrode were immersed in the solutions without using a separate compartment. The working electrode was polished with 0.3 μm alumina paste, rinsed and dried prior to all measurements. The voltammetric studies were performed using an Autolab PGSTAT 12 potentiostat controlled with GPES software.

2.3. Characterization

The composition and structure of the prepared nanosized TiO_2 have been investigated using an X-ray diffractometer Rigaku Ultima IV instrument with graphite diffracted beam monochromator for CuK_α radiation. The UV–vis absorption spectra were recorded from 200 to 700 nm on dry nanopowder samples using a JASCO 570 UV–VIS spectrophotometer with an integrating sphere. Raman spectroscopy was conducted at room temperature using a Horiba LabRam HR 800 equipment, in which excitation was made by 633 nm wavelength laser light (He–Ne laser). The nanopowder morphology was analyzed by scanning electron microscopy (SEM) associated with energy-dispersive X-ray (EDX) analysis (Zeiss EVO50 equipment provided with Bruker–EDX probe, SEM accelerating voltage of 2 kV, EDX accelerating voltage of 21 kV). X-ray photoelectron spectroscopy (XPS) was carried out on a Quantera SXM equipment, with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was Al K_α radiation (1486.6 eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the Au $4f_{7/2}$ line. In order to take into account the charging effect on the measured binding energies (BEs), the spectra were calibrated using the C 1s line (BE = 284.8 eV, C—C (CH)n bondings) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e^- and Ar^+ ion beams) has been used to compensate the charging effect in insulating samples. Nitrogen adsorption–desorption isotherms were recorded at liquid nitrogen temperature (77 K) on a Quantachrome Instrument (NOVA 2000 Series) and the specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method. The Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distributions derived from the BJH desorption isotherms.

2.4. Photocatalytic experiments

The photoreactivity of the synthesized materials was evaluated for the degradation of Orange II dye under UV irradiation ($\lambda = 365$ nm), using a VL 204 UV lamp and under visible light illumination using a 150 W Hg lamp. For these experiments, 0.025 g of the electrochemically synthesized nano-titania anatase powder was added into 25 mL Orange II solution having a concentration of 20 ppm. For comparison, the photodegradation experiment has been performed in the presence of commercial TiO_2 nanopowder (TitanPE Technologies, Inc., China), too. The reactant aqueous suspension was irradiated by the UV or visible lamp under continuous and constant stirring. Prior to UV–vis illumination, the suspension was subjected to stirring in the dark for 30 min to reach the equilibrium sorption of the compound. The absorbance of the dye solution was periodically measured at $\lambda = 484$ nm to determine the photodegradation efficiency. The liquid aliquots were passed through