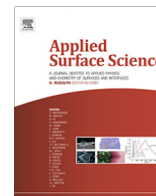




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The improvement of SiO₂ nanotubes electrochemical behavior by hydrogen atmosphere thermal treatment

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ABSTRACT

Highly defected SiO₂ nanotubes (SiO₂-NT) were obtained by a simple sol-gel procedure followed by calcination. Boron-doped diamond (BDD) polycrystalline films coated with SiO₂-NT were used as working electrodes and, unexpectedly, cyclic voltammetric experiments have shown that the concentration of both positive and negative defects at the surface is high enough to enable redox processes involving positively charged Ru(bpy)₃^{2+/3+} to occur. Conversely, no electrochemical activity was put into evidence for Fe(CN)₆^{3-/4-} species, most likely as a result of the strong electrostatic repulsion exerted by the negatively charged SiO₂ surface. The concentration of surface defects was further increased by a subsequent thermal treatment in a hydrogen atmosphere which, as EIS measurements have shown, significantly promotes Ru(bpy)₃²⁺ anodic oxidation. Digital simulation of the voltammetric responses demonstrated that this treatment does not lead to a similar increase of the number of electron-donor sites. It was also found that methanol anodic oxidation at hydrogenated SiO₂-NT-supported platinum results in Tafel slopes of 116–220 mV decade⁻¹, comparable to those reported for both conventional PtRu and Pt-oxide catalysts.

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1. Introduction

One of the fastest-growing areas of research and technology appears to be the one dedicated to nano-structured materials, primarily because of its huge number of potential applications in numerous fields, such as nanomedicine, biosensors, nanoelectronics and solar energy conversion [1]. Nano-sized silicon dioxide is among the most popular such materials as it is affordable, highly stable, and can be obtained in various structures with different morphologies and distinct properties [2]. The interest for SiO₂ sensing applications was triggered by the successful attempts to achieve electrode surface modification by encapsulating within silica matrices conventional redox probes [3,4] or active biomolecules such as glucose oxidase and hemoglobin [5]. Nevertheless, extensive use of conventional silica as electrode material is somewhat hampered by the lack of intrinsic electron conductivity of the SiO₂ network, although several ways to alleviate this drawback were devised, including the dispersion in the silica bulk of metal nanoparticles [6] or the insertion of conductive polymers [7,8]. In this context, special attention was given to ceramic-carbon elec-

trodes which are generally obtained by embedding into the SiO₂ matrix different types of carbonaceous structures such as carbon nanotubes [9–11], graphenes [12], non-graphitizable carbon [13] and conductive diamond powder [14]. These composite materials are relatively easily obtained by sol-gel procedures and, at least in principle, well suited for electrochemical applications due to their wide potential window, tunable polarity and high stability (see Ref. [15] and references therein).

A vast number of studies were devoted to investigating electronic, optic and conducting properties of a plethora of silica materials with various structures and morphologies, and a band gap higher than 8 eV was typically estimated for silicon dioxide [16–18]. As a matter of course, insulating characteristics are generally associated with SiO₂ *per se*, although supplementary intrinsic or extrinsic energy levels can be generated within its wide band gap by physical or chemical methods which are creating different specific defects [19]. Furthermore, it was found that suitable adjustment of the obtaining conditions allows controlling oxygen stoichiometry thus enabling the formation of semiconducting nanodomains on the SiO₂ particles surface [20,21]. The use of SiO₂ assemblies with cylindrical symmetry would also result in an increase of the surface conductivity of the silica network since structural deformations that such particular shape involves

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inherently lead to the formation of a non-negligible number of defects [22].

We have recently reported the synthesis by a modified sol-gel procedure of highly defected SiO_2 with tubular morphology (SiO_2 -NT) which exhibits a substantial intensification of light absorbing characteristics together with promising electrochemical features [23]. Based upon these auspicious results, the present work is aimed at studying the possibility of using SiO_2 -NT as an active material, and the extent to which its activity can be improved by a simple hydrogen thermal treatment. Such improvement, together with their inherent advantages (e.g., good cost-effectiveness, high stability and large specific surface area) could therefore make silica nanotubes well suited for being used as support material for noble metal electrocatalysts. This feature might be advantageous for methanol fuel cell applications because it was demonstrated that the use of conductive or semiconductive oxides as substrates for platinum deposition allows enhancing the active surface area of the electrocatalyst particles and, importantly, promotes to some degree alcohol anodic oxidation [24–28]. For the present study, the use of a boron-doped diamond (BDD) substrate appears to be particularly germane because it is reasonable to assume that combining two highly stable materials such as diamond and silica would allow obtaining new types of robust electrode materials. In addition, the fact that the BDD support does not interfere with the deposited oxides [29–31] could help to a certain extent in shedding some light on the effect of surface defects on the SiO_2 -NT electrochemical activity and, hopefully, in improving this activity by appropriately adjusting the obtaining conditions.

2. Experiments

The synthesis of SiO_2 nanotubes was carried out according to a modified sol-gel method from the literature [32] and was described in detail previously [23]. Briefly, gaseous ammonia was bubbled for 10 min, at room temperature, through a solution containing tartaric acid (Riedel de Häen), ultrapure water and ethanol and then TEOS (tetraorthosilicate 99% Alfa Aesar) was added dropwise to the gently stirred solution cooled at 0 °C. The gel thus obtained was allowed to stay for 5 h for aging and then filtered. Typically, calcined silica nanotubes (SiO_2 -NT) were obtained, after drying the gel for one hour at 100 °C, by thermally treating the silica mass for 3 h, at 500 °C, in air. After that, some calcined silica nanotubes were further annealed (for 1 h at 500 °C) in a hydrogen atmosphere (SiO_2 -NT-H) and also used for comparison. Both SiO_2 -NT and SiO_2 -NT-H, were analyzed by XPS technique and used in electrochemical experiments.

In order to prepare working electrodes, 20-mg samples of nanotubes to be investigated (SiO_2 -NT or SiO_2 -NT-H) were dispersed by sonication in a solution containing 10 μL Nafion (5%) and 500 μL isopropyl alcohol and appropriate amounts of the suspension were pipetted out and delivered onto 0.5 cm^2 hydrogen-terminated boron-doped diamond (BDD) polycrystalline films (deposited by microwave plasma-assisted chemical vapor deposition on Si wafers). Prior to silica nanotubes modification of the BDD, the backside of the silicon substrate was scratched, coated with conducting silver paste, electrically connected by means of conductive epoxy to a copper wire and then coated with insulating resin. Electrodes thus modified (SiO_2 -NT/BDD or SiO_2 -NT-H/BDD) were dried in air at room temperature and, for electrocatalytic methanol oxidation experiments they were further used as substrates for platinum deposition. The deposition was carried out electrochemically, from a 0.5 M H_2SO_4 + 3.25 mM H_2PtCl_6 solution, by applying consecutive potentiostatic pulses of 2-s duration each (applied potential, -0.15 V). The noble metal loading was then

calculated from the cathodic charge integrated during electrodeposition (5 mC in a typical experiment). All electrochemical measurements were performed with a PAR 273A potentiostat in a conventional three-electrode cell at room temperature and under deaerated conditions. A platinum gauze was used as counter electrode and the reference consisted in a Ag/AgCl electrode (in saturated KCl solution). A PAR-FRD 100 response detector was used for electrochemical impedance spectroscopy (EIS) experiments, carried out within the frequency range 100 kHz to 10 mHz (amplitude of the alternating signal, 10 mV). Impedance spectra were fitted with ZSimpWin 3.21 software. In some cases, a DigiSim cyclic voltammetry simulation software (version 3.03) from Bioanalytical Systems Inc. was also used in order to fit the experimental voltammetric responses.

The morphology of the SiO_2 nanotubes samples was investigated by scanning electron microscopy (SEM) by means of a Quanta 3D FEG high resolution microscope with Everhart-Thornley secondary electron detector. X-ray photoelectron spectroscopy (XPS) surface analysis was carried out by using a VG Esca 3 Mk II spectrometer and the X-ray source was Al $K\alpha$ radiation (1486.7 eV, monochromatized). The experimental spectra were fitted with Voigt functions (SDP 2.3).

3. Results and discussion

The morphology of the calcined silica was scrutinized by scanning electron microscopy and Fig. 1 shows a typical SEM micrograph. It appeared that SiO_2 hollow structures with tubular shape prevail, although fragments of SiO_2 -NT are also incorporated into the bulk of the material. The external diameter of the nanotubes ranges from ca. 300 nm to ca. 3 μm , while their wall thickness fluctuates within the range 100–200 nm. The length of the nanotubes may reach more than 100 μm , and their external surface is well-decorated with spherical SiO_2 nanoparticles. No morphological modifications for SiO_2 -NT-H were observed. It is worth pointing out that previous thorough investigations demonstrated the amorphous nature of the SiO_2 -NT obtained as above [23].

The literature dealing with electrochemical applications of undoped silica as such is rather scarce and, to the best of our knowledge, there is no detailed study concerning calcined SiO_2 nanotubes electrochemical behavior. Nevertheless, attention has been given to a certain extent to various $\text{Ru}(\text{bpy})_3^{2+}$ - SiO_2 nanoparticles systems as possible candidates for cost-effective, regenerable chemical sensors [3,4,33]. On that account we assumed that Ru

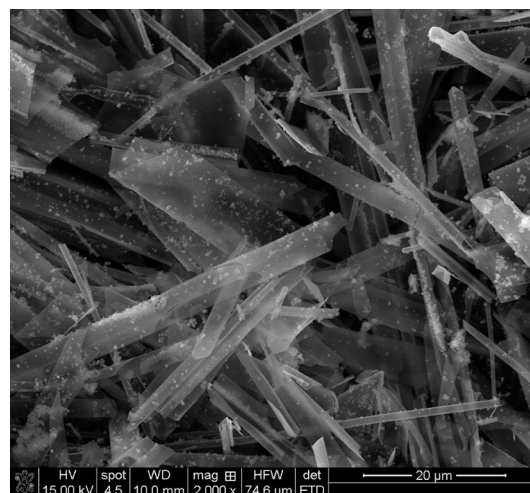


Fig. 1. SEM micrograph of calcined SiO_2 nanotubes.

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