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Helen Reveron *, Catherine Elissalde [1], Carole Lecoutre [1], Yves Garrabos [1]

ICMCB-Bordeaux 1 University, 87 Av. Du Dr. Albert Schweitzer 33608, Pessac, France

Abstract

Here we present the synthesis of titania based microwires through an electrolytic deposition process using a scanning electrochemical microscope (SECM). The method is based on the localized hydrolysis of an aqueous precursor using the base electrogenerated on the ultramicroelectrode surface. We show that the diameter of these microwires can be controlled from the diameter of the working electrode (ultramicroelectrode of 5, 10 or 25 μm in diameter). The smallest microwire produced during this work has a mean diameter of 6.8 μm which remains uniform all along the length. Lengths of typically 880 μm were obtained after 1200 s of deposition.

Keywords: Electrochemical methods; Eletrodeposition; Microstructuring; Microwire; SECM

1. Introduction

The fabrication at the micrometer/nanometer scales of one-dimensional (1D) structures remains one of the most important technological challenges due to the wide range of applications that would be developed in the field of the micro/nanoelectronics and/or photonics [1–5]. Over the past few years, several oxide 1D structures were synthesized using sol–gel process, electrochemical deposition, laser ablation, vapour reactions or thermal evaporation methods [6,7]. Arrays of 1D elements can be obtained using templates (porous membranes) which confine and control the growth in only one direction (micro/nanochannels). Nevertheless, the order is frequently destroyed when the template is removed. Some other methods have been recently developed in order to organize 1D building blocks onto a surface (microfluidic, nano-imprinting, self or electrical-field-assisted assemblies and Langmuir–Blodgett approaches) [8,9]. However for practical applications, the organization of these 1D building blocks into functional assemblies and useful systems remains, as in the case of their synthesis, an important challenge.

The obtention of such an oxide 1D-structures seems to be very important to the development of new photonic devices. In fact, these 1D structures elaborated from oxides having high dielectric constant and large band gap values (such as TiO_2) can be organized periodically into the space to create a new kind of artificial material, called photonic crystal (PCs), where propagation of optical electromagnetic waves can be precisely controlled [10]. This possibility to control the propagation of light is expected to create a revolution on communication technologies: the photon, which can travel in a dielectric material faster than an electron in a metallic wire then carrying a larger amount of information per second, will be used in novel PCs optical devices such as high-speed switches, modulators, filters, low-threshold lasers, wave-guides, and interconnects improving their performances [11,12].

Among the techniques to synthesize 1D structures we were interested on the so-called localized electrochemical deposition (LECD) because it can allow both the synthesis and the organization without the use of templates. This method has been already employed to produce micro-columns of “metals” using conductive ultramicroelectrodes (UME or tip) and substrates [13–15]. Combining this technique with the much more classical

* Corresponding author. Present address: MATEIS UMR-CNRS 5510, Insa-Lyon, 7 Av. J. Capelle, 5ème étage, 69621 Villeurbanne, France. Tel.: +33 5 4000 6298; fax: +33 5 4000 2761.

E-mail addresses: helen.reveron@insa-lyon.fr (H. Reveron), garrabos@icmcb-bordeaux.cnrs.fr (Y. Garrabos).

[1] Tel.: +33 5 4000 6298; fax: +33 5 4000 2761.

and well-known electrolytic deposition process (EDP), here we report the synthesis of 1D oxide-based microwires using a scanning electrochemical microscope or SECM [16] and a novel "chemical-LECD approach" based on the localized hydrolysis of a precursor by the base electrogenerated on the conductive microelectrode surface. We will present the synthesis of only one kind of 1D oxide-based structure (the case of titania-based microwires) and discuss the effect of some parameters such as DC applied potential on its structure and characteristics and the possibility to control the microwire diameter by varying the diameter of the Pt-ultramicroelectrode.

2. Experimental

In this work, a titanium aqueous–peroxo solution consisting of 0.005 M $TiCl_4$ and 0.010 M H_2O_2 in methyl alcohol–water solvent (3:1 vol.%) was used as precursor. In a typical procedure, metal salt was added first to the half of the solvent volume, then the hydrogen peroxide and finally the another half of solvent. Solvents were cooled before the dissolution process which was performed in an ice water bath in order to avoid the formation of orthotitanic acid $Ti(OH)_4$. During H_2O_2 addition, the color of the solution changed from transparent to orange, indicating the formation of the titanium peroxo-complex $[Ti(O_2)(OH)_{n\ 2}]^{(4\ n)+}$. The sequence of reactions for the peroxo-complex formation is expected to be as follows [17,18]:

$$\text{Dissociation of the salt: } TiCl_4 \rightarrow Ti^{4+} + 4Cl \quad (1)$$

$$\text{Complex: } Ti^{4+} + H_2O_2 + (n-2)H_2O \rightarrow [Ti(O_2)(OH)_{n\ 2}]^{(4\ n)+} \quad (2)$$

Right after the mixing process, the peroxoprecursor solution was stored in a fridge at 4 °C. For preparing titania-based microwires, the cooled peroxoprecursor solution was filled in the electrochemical cell of the SECM microscope (SECM 900A, CH Instruments) which was also surrounded by an ice water bath. A conventional three-electrode setup consisting of a Pt-UME working electrode (25, 10 or 5 μm in diameter), a Pt counter electrode (Pt-wire) and an Ag/AgCl reference electrode, was mounted in the electrochemical cell. For all experiments, the UME was positioned at a distance of 1500 μm from the bottom of the cell and a constant DC potential (voltage range from −1.6 to −3.2 V) were applied across electrodes during 1200 s. The positive terminal was connected to the Pt-wire counter electrode and the negative terminal to the Pt-UME working electrode (cathode) where the localized hydrolysis of precursor took place. The obtained microwires were recovered on a microscope glass slide fixed at the bottom of the cell. The morphology and microstructure analysis were conducted using an inverted optical microscope (Axiovert 200M, Zeiss) and by scanning electron microscopy (SEM: JSM 6360A, JEOL). For SEM observations, the microwires were directly mounted on carbon films and coated with Au. The microwire growing process was observed and recorded in-situ (see Supporting Information) by mounting the electrochemical cell on the inverted microscope support.

3. Results and discussion

The "chemical" mechanism for the electrolytic synthesis of these titania based microwires does not differ a lot from the most probable mechanism already reported in the literature in the case of electrolytic coating of metals [17]:

To form the microwire, the titanium peroxoprecursor is hydrolyzed (reaction (3)) by the base electrogenerated at the cathode during the reduction of water (reaction (4)).

Hydrolysis by the electrogenerated base:

$$[Ti(O_2)(OH)_{n\ 2}]^{(4\ n)+} + mOH\ + kH_2O \rightarrow TiO_3(H_2O)_x \quad (3)$$

The cathodic reaction that generates the base:

$$2H_2O + 2e\ \rightarrow H_2 + 2OH \quad (4)$$

The deposition step in the mechanism described above is "chemical" rather than electrochemical because the electron transfer is necessary only to increase the pH (reduction of water) very close to

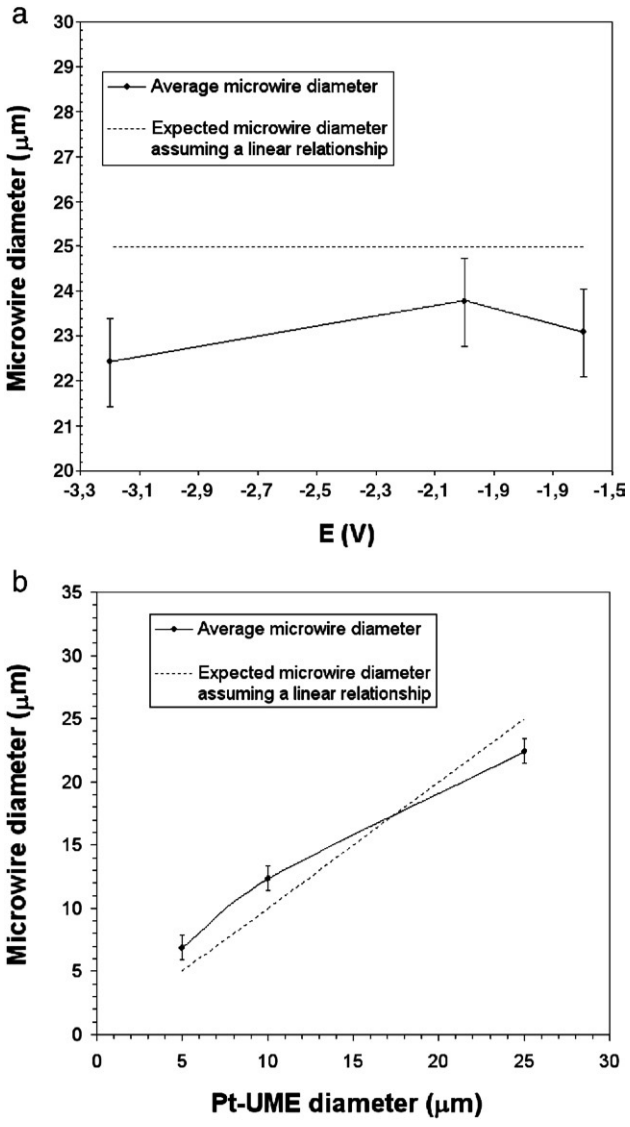

Fig. 1. Microwire diameter as a function of (a) the DC potential using 25 μm Pt-UME and (b) the Pt-UME diameter at −3.2 V.

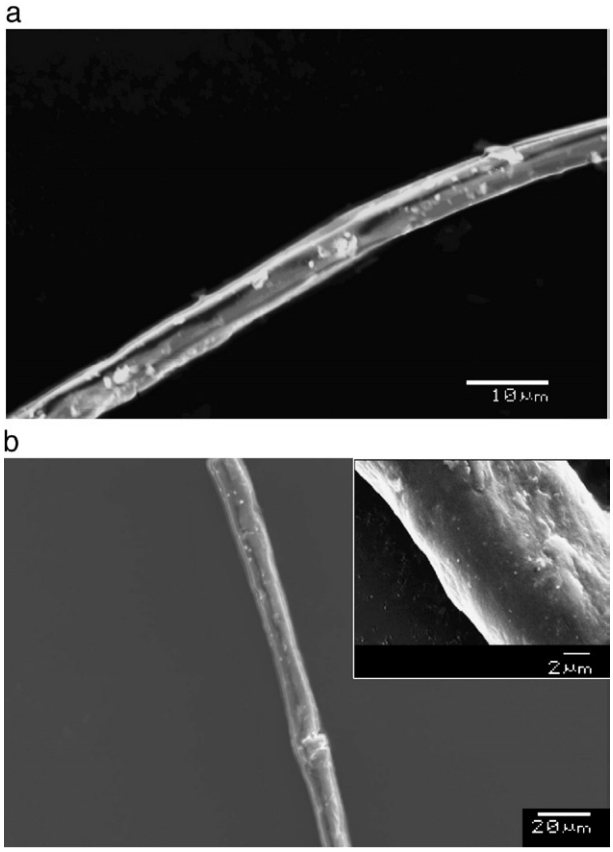

Fig. 2. SEM images of microwires obtained at −3.2 V from (a) 5 µm Pt-UME and (b) 15 µm Pt-UME.

the UME surface; the electrogenerated base hydrolyses the precursor forming a gel which is structured in only one dimension along the deposition process. In our experimental setup as the ultramicroelectrode is mounted vertically into the electrochemical cell, the growth direction of microwires is also vertical. The growth begins at the UME surface and the structured gel (microwire) extends into the precursor solution throughout the time of deposition. This is the reason why our novel approach is called "chemical LECD". To prepare TiO_2 microwires, the as synthesized microwire has to be thermally treated in order to decompose the peroxotitanium hydrate [17]:

$$TiO_3(H_2O)_x \rightarrow 2TiO_2 + O_2 + 2xH_20 \quad (5)$$

The microwire growing process was observed and recorded in situ. An example of film is attached electronically to this work (see Electronic Annex in the online version of this article). During the synthesis, the base produced on the cathode (Pt UME) hydrolyses "locally" the precursor forming a gel which grows in only one direction. At the same time, the dihydrogen gas produced according to the reaction (4) leaves the peroxoprecursor solution through the as synthesized wire surface.

A series of experiments were performed in order to investigate the effect of the applied potential and the diameter of the Pt UME upon microwire microstructure. Taking into account that during the deposition process dihydrogen gas is produced (water reduction; see reaction (4)), the formation of non homogeneous wires is expected by increasing the applied potential. On the contrary, only small variations in the mean microwire diameter were observed (Fig. 1a). Moreover, as the production of base increases with the applied potential, an increase in the microwire growth rate was also observed. Working at 3.2 V and using 25 µm Pt UME, the mean microwire growth rate was estimated to 0.80 ± 0.08 µm/s. The effect of the UME diameter was studied at 3.2 V (maximum potential at which the SECM 900A instrument is capable to work). The diameter of the as synthesized microwires closely matched with that of the ultramicroelectrode (Fig. 1b). In Fig. 1a and b, the expected microwire diameter was also presented assuming that if reduction of water is carried out on the whole Pt UME electrode surface, precursor must be hydrolyzed as well close to this surface producing a wire having the same UME diameter.

Fig. 2 displays the representative morphology of microwires prepared from 10 and 5 µm Pt UME at 3.2 V. The surface of the as synthesized structures appears homogeneous and dense all along the wire length. Further characterization was conducted using the inverted microscope in reflection and transmission (phase contrast) modes (Fig. 3).

As shown in Fig. 3a, the surface and diameter all along the wire length appear homogeneous as previously discussed from SEM micrographs. Nevertheless, Fig. 3b shows a contrast difference between the surface and the core of wire that could be related to some variations in phase composition or refractive index across the wire.

The smallest microwire produced during this work has a mean diameter of 6.8 µm which remains uniform all along the length. Lengths of typically 880 micrometers were obtained after 1200 s of deposition (0.72 ± 0.08 µm/s using a 5 µm Pt UME) indicating that the microwire growth rate is not strongly dependent on the Pt UME diameter.

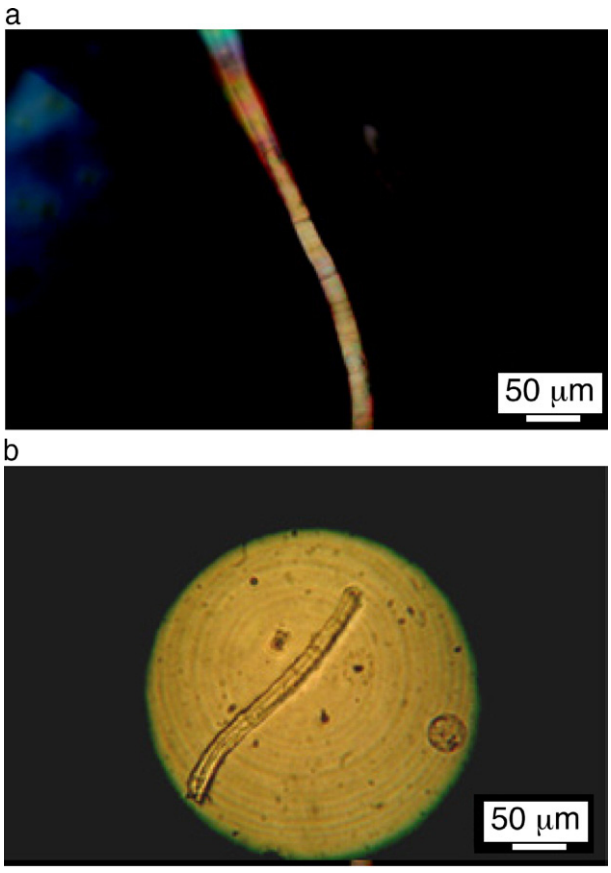

Fig. 3. Optical microwire image of a microwire obtained from 25 µm Pt-UME at −3.2 V and using (a) reflection and (b) transmission mode.

4. Conclusions

In summary, we have demonstrated that the synthesis of oxide-based microwires is possible using a novel "chemical-LED" approach which is based on the "localized hydrolysis" of aqueous precursors. We show that the diameter of these microwires can be controlled from the diameter of the working electrode (ultramicroelectrode) and the microwire growth rate from the applied potential. At the experimental conditions here employed, the as-synthesized wire surfaces appear homogeneous and dense all along their length. These results and the progress recently reached on microelectrodes miniaturization [19] considerably increase the potentiality of this technique in the synthesis of oxide-based wires or 1D structures at the nanometer scale. Moreover, in order to organize micro/nanowires onto a surface, an array of some micro/nanoelectrodes operating in a parallel manner can be developed.

Acknowledgement

Authors gratefully acknowledge financial support from the CNRS, the European Network of Excellence FAME, the CNES, the "Région Aquitaine" and ArcoFluid 33.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2007.07.049.

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