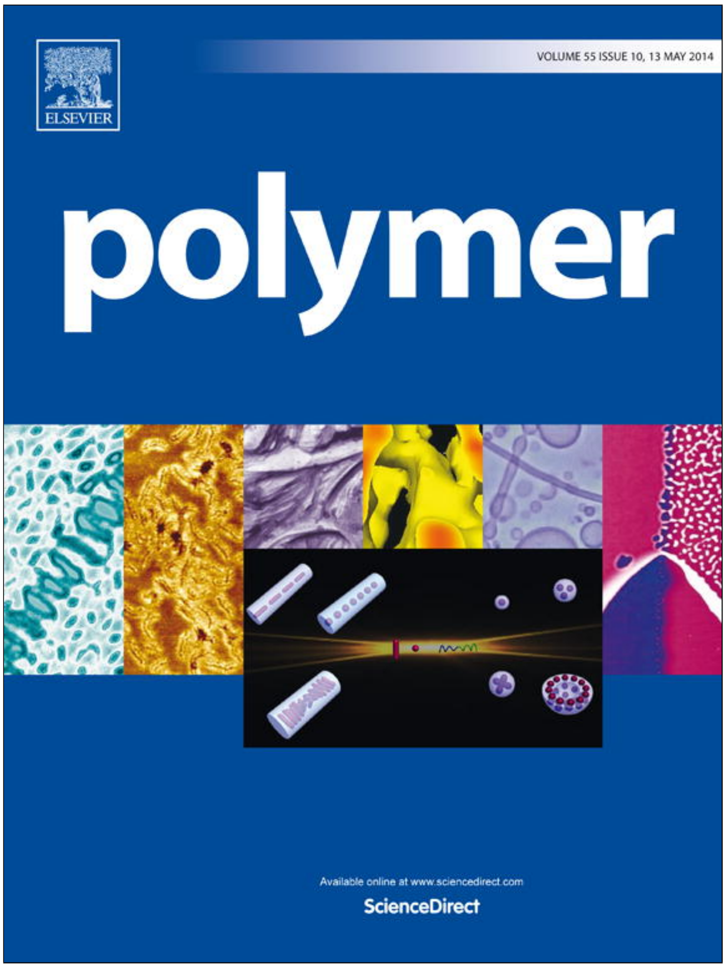
VOLUME 55 ISSUE 10, 13 MAY 2014
ELSEVIER
polymer
Available online at www.sciencedirect.com
ScienceDirect

Polymer 55 (2014) 2440–2444

Contents lists available at ScienceDirect

Polymer

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

Fast electrochromic response of ultraporous polyaniline nanofibers

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A R T I C L E I N F O

Article history:
Received 7 February 2014
Received in revised form
13 March 2014
Accepted 24 March 2014
Available online 29 March 2014

Keywords:
Polyaniline
Nanofibers
Switching time

A B S T R A C T

Polyaniline (PAni) nanofibers were prepared by a one-step electrosynthetic method. A gold sputtered electrode was used as the substrate for the nanofiber growth at a constant current density value of 100 μA cm^{-2}. Substrate morphology induces fiber growing and allows having a remarkable quantity of fibers in a short period of time. Tandem chronoabsorptometric and chronocoulometric data of the electro-synthesis process were collected and analyzed. Several electrochromic parameters were characterized and a short response time (T_{90}) of 20 ms was obtained for a contrast (ΔT %) of 10%. The main reason for this fast response is the ultraporous nature of the prepared nanofibers. This approach represents a straightforward, easy and low cost method to obtain a fast color switching film with potential application in the deployment of an electrochromic device.

1. Introduction

Electrochromism is a phenomenon observed in some materials that involves reversible and significant visible change in color depending on the redox state [1]. A wide variety of electroactive inorganic and organic materials show this property, including transition metal oxides like CuO_2 and metal coordination complexes like prussian blue [2], monomers and conducting polymers (CP) [3–9] and the combination of both inorganic and organic materials [10].

A huge number of conducting polymers have been synthesized and characterized, many of them based on basic structures like poly(3,4 ethylenedioxythiophene) (PEDOT) [11], polypyrrole [12], polythiophene [13], polyaniline (PAni) [14], poly(3,4-propyldioxythiophene) (PProDOT) [2], among others. As these materials in general exhibit rapid optical response, high color contrast, low optical switching potential and high coloration efficiency there is a grown interest in CP research considering the great potential for important applications. In addition to the optical behavior, flexibility and thickness, low power consumption, fast switching times, long term cycling stability are desirable attributes for electrochromic devices [1,2,15–17].

In spite of the huge amount of information in the literature to improve color switching rates and contrast ratios there are few examples of their use in displays with moving images; this is mainly due to the response times reported, always around several hundreds of milliseconds for this kind of materials [2,7,17–20]. The response time is normally controlled by the transport rate of counterions into the film during the redox process [16]; this time can be reduced by decreasing the film thickness, but concomitantly the coloration of the film becomes very poor.

This phenomenon is one of the greatest drawbacks of the film based electrochromic devices using CP. Clearly the solution points to decrease the diffusion length for the counterions in the polymer. In this sense, nanotubes and nanowires show a fast switching between redox states because these structures provide short pathways for counterion diffusion.

One of the possible approaches to achieve these nanostructures is performing an electrochemical template synthesis controlling parameters like the applied potential, monomer concentration and base electrode shape to determine the morphology [11,16,23]. Using this approach, Cho and Lee synthesized nanotubular structures of PEDOT achieving fast, less than 10 ms, electrochromic response for a reflectivity change of 30% [11].

Polymer nanostructures, without using templates, have also been electrochemically developed on different surfaces [12–14], including gold films on silicon wafers [12]. Alternative methods for the preparation of conducting polymer nanofibers without using templates involve the interfacial polymerization at the interphase between two immiscible solutions [19,20].

Polyaniline is one of the most studied CP for electrochromical applications and can be easily prepared [14,17–22]. The synthesis of PAni can be done in a chemical or electrochemical way with a wide spectrum of parameters to control the growing process [3,4,21].

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http://dx.doi.org/10.1016/j.polymer.2014.03.050
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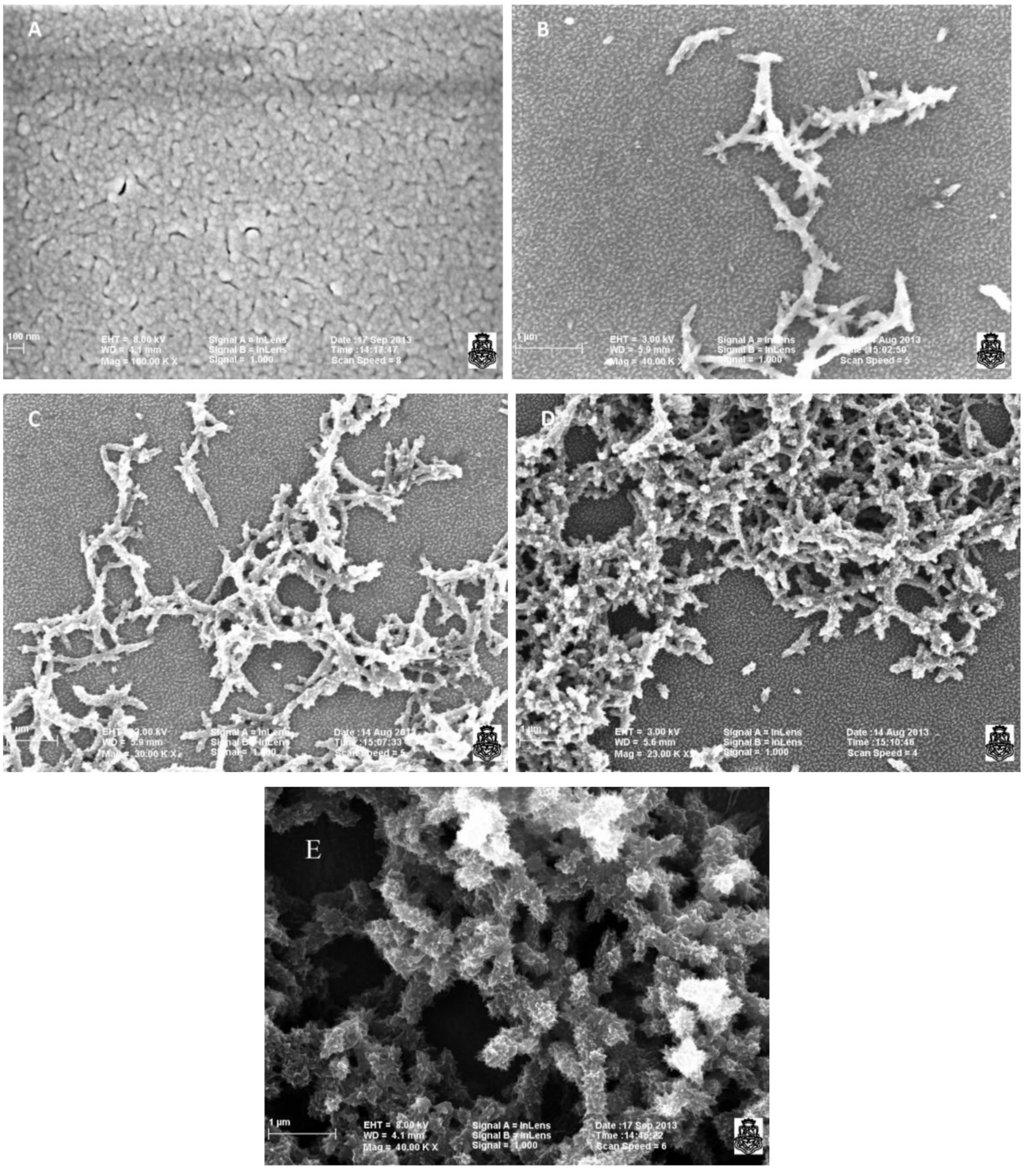

Fig. 1. SEM images of nanostructured PAni synthesized over gold sputtered electrodes for different growing time intervals (τ). (A) bare gold sputtered electrode; (B) $\tau = 5$ min; (C) $\tau = 10$ min; (D) $\tau = 20$ min and (E) $\tau = 40$ min.

PAni nanotubes, nanowires and nanofibers under different experimental conditions, including or not the use of templates, have been widely investigated and characterized [11,22–26].

In this work, we propose a simple one step galvanostatic method to fabricate PAni nanofibers over a gold sputtered glass substrate without using any kind of template. The electrochromic properties of the synthesized polyaniline nanofibers were evaluated.

2. Experimental

Aniline (Tetrahedron) and hydrochloric acid (Cicarelli) were used as received, without further purification. Ultrapure water (18 MΩ.cm) was obtained using a Milli-Q water purification system (Millipore). Glass microscopy slides were cleaned for 30 min in sulphonitric solution (70:30, H_2SO_4:HNO_3) and then rinsed with ultrapure water and dried. These glass slides were used for the preparation of working electrodes by two sputtering steps involving the deposition of a thin adhesion chromium layer (~5 nm) subsequently covered by a gold film (~100 nm). Electric contact of the working electrodes was made by a copper wire glued to the upper extreme of the electrodes with silver paint and later fixed with epoxy resin.

PAni films were prepared by a single galvanostatic step of 100 μA.cm^{-2}. Using a 1 M hydrochloric acid solution as base electrolyte.

All electrochemical experiments were performed in a lab-made three electrode cell using a platinum wire as auxiliary electrode and Ag|AgCl$_{(s)}$|KCl,3M reference electrode. Electrochemical techniques were performed with a potentiostat-galvanostat (PGSTAT-101, AUTOLAB) interfaced to a computer. Simultaneous spectroscopic characterizations were carried out with a high resolution spectrometer (HR2000. Ocean Optics Inc.) coupled to a 1 cm-cuvette holder using optical fibers and a tungsten light source (LS-1. Ocean Optics Inc.). Due to the short optical-switching time of PAni nanofibers the T_{90} response time was quantified by a silicon photodiode connected to an oscilloscope.

Morphological characterization of PAni films was made by field-emission scanning electron microscopy FEG-SEM (CARL ZEISS,

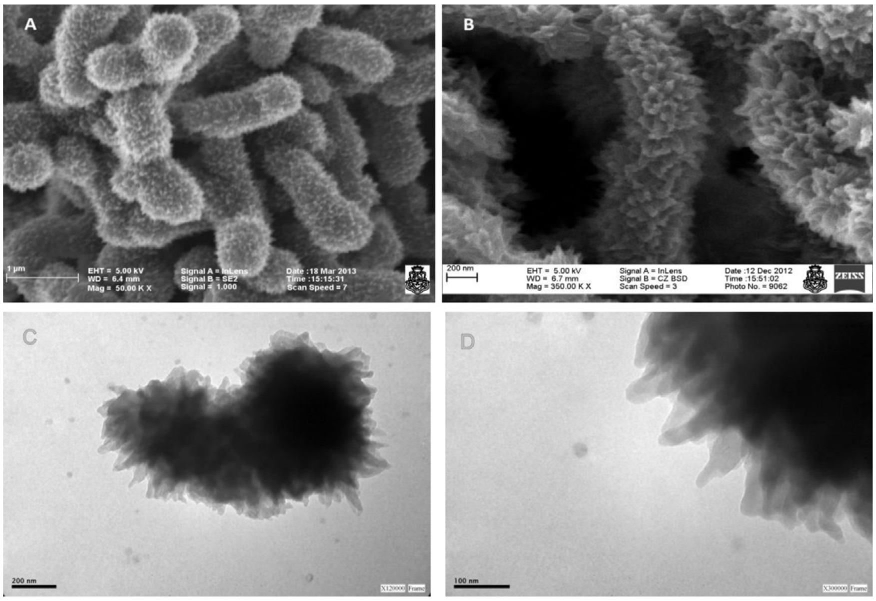

Fig. 2. Magnified SEM (A and B) and TEM (C and D) images of ultraporous PAni microfibers.

∑igma) and transmission electron microscopy TEM (Jeol 1200 – EXII). Samples were not metalized for SEM observation.

3. Results and discussion

Fig. 1 shows electron microscopy images of PAni films synthesized over gold sputtered glass slides by a galvanostatic step, with different growing time intervals (τ). By comparison of Fig. 1B, C and D two different domains can be recognized in this material: a homogeneous film of PAni fibers with small diameter mimicking a grass-like carpet (PAni nanofibers) and a ramified structure of fibers that became more evident at longer τ values (PAni microfibers). The grass-like structure remain uniform over the entire substrate and its thickness did not change with longer τ values; opposite, the ramified structure increasingly covers the substrate surface with longer τ values. Even so, this later structure keeps its high surface area and mesoporous structure.

It should be noted that each individual PAni microfiber has an intrinsically high porosity. Fig. 2 shows images of the ultraporous structure obtained. Fig. 2A and B shows a higher resolution electron microscopy image where the individual PAni microfiber morphology can be analyzed. It can be observed that each PAni microfiber is composed of small nanoplates that apparently extend from a central (axial) thin fiber. These nanoplates, with diameters smaller than 50 nm, are flat in shape. Transmission electron microscopy images, shown in Fig. 2C and D, also indicate the same fiber geometry perhaps evidencing that the fiber porosity extends to the center of the fiber, not only at its surface. This particular geometry improves the counterion (dopant) transport, i.e. the mean free diffusion path for anion transport is small due to the high fiber porosity; in consequence the oxidation–reduction cycle of the polymer is faster than in flat films of globular polyaniline.

Several bibliographic reports emphasize on different and complicate electrochemical schemes necessary to obtain PAni fibers [27–29]; these preparation protocols emphasize on the need of a thin layer of small polymer seeds prepared in a first electrochemical step followed by additional electrochemical steps for growing and elongation of polymer nanofibers. We have obtained ultraporous polyaniline fibers using different electrochemical conditions (sweeping techniques, potentiostatic/galvanostatic pulses, etc) with almost identical morphology. It seems that in our experimental system the most important aspect, responsible of the fiber development, is the starting morphology of the substrate. Fig. 1A shows an image of the bare sputtered electrode. Several defects are evident on this substrate, but more important, the gold layer is formed by the agglomeration of small nanoparticles acting as seeds for the later growth of PAni fibers. When a mirror polished gold electrode is used as the substrate, non-structured PAni

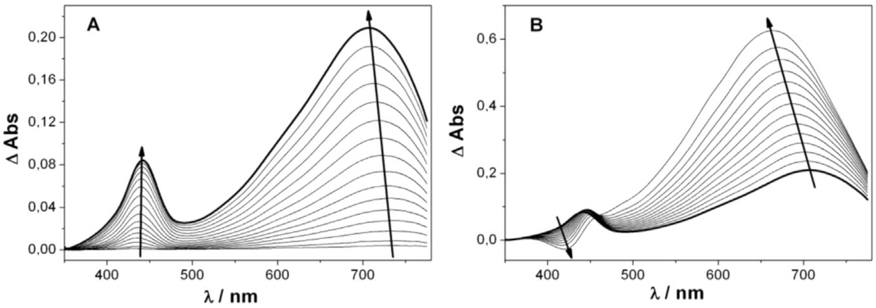

Fig. 3. Absorbance change spectra obtained for nanostructured PAni during a positive potential sweep performed at a scan rate of 10 mV.s^{-1}. Reference spectrum taken at 0.00 V. Spectra were recorded every 20 mV in the following ranges: (A) 0.00 V–0.32 V; (B) 0.32 V–0.70 V. Bold spectra in each plot correspond to the same spectrum (i.e. 0.32 V). Arrows indicate the direction of change of absorbance.

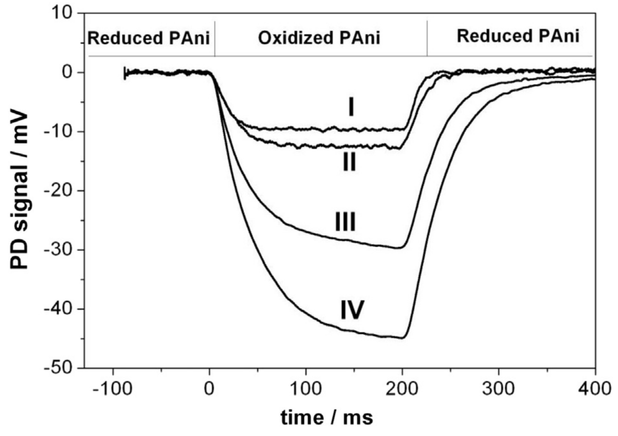

Fig. 4. Optical switching of nanostructured PAni. Negative photodiode signal corresponds to higher optical absorbance. I, II, III and IV correspond to PAni fibers prepared with different τ values: 5, 10, 20 and 40 min respectively.

was obtained under all the electrochemical conditions used in this work.

Electrochromism of the PAni substrate originates from three different (multicomponent) absorption bands appearing at different polarization potentials. Fig. 3 shows the change of absorbance as the potential of the working electrode is swept between the reduced PAni state (0.00 V) and 0.32 V (Fig. 3A) and from this last state up to 0.70 V (Fig. 3B). It can be observed that up to 0.32 V there is a clear development of an absorption band centered at 438 nm and a multicomponent band located around 710 nm. These bands have being respectively assigned to the cation-radical absorption [30], and a convolution of different bands including: localized polarons [31,32], non-localized polarons [31,33], and dimer interchain cation-radical absorption [31,33]. When the polarization potential increases up to 0.70 V the multicomponent band continuously increases in amplitude and shifts toward lower wavelength values. At this high potential values there is another absorption band, centered at 425 nm that decreases as the polarization potential increases. It is not the purpose of this report to perform a detailed analysis of band contributions to the absorption spectra; however it should be noted that the absorption spectra of the PAni fiber samples are simpler than those previously published for PAni films [32,34], perhaps due to the relatively ordered structure of the PAni fibers.

The most remarkable property of the PAni fibers is its short optical-switching time. This fast response precludes the use of a spectrometer to record the full spectrum during the color switching of the film; instead of, a fast response photodiode was used to quantify the above mentioned optical change. Fig. 4 shows the response of a silicon photodiode (PD) located just behind the substrate when the PAni fibers are illuminated with white light from a light emitting diode (light transmission mode). Initially the substrate was polarized at 0.0 V vs Ag|AgCl|KCl$_{(sat)}$ (reduced polymer). At a given time ($t = 0.0$ s) the substrate is polarized at a constant positive potential (0.40 V) where the polymer is oxidized and gains color (PD signal decreases). The time necessary to reach 90% of the full PD signal change is defined as the optical-switching time (T_{90}). T_{90}, for the coloration of the polymer, is in the range of 20 ms for a low optical contrast ($\%\Delta T = 10\%$ – low PAni fiber coverage) up to 100 ms for a higher optical contrast ($\%\Delta T = 50\%$ – high PAni fiber coverage). Bleaching of the polymer, when the polarization of the substrate is reverted to the initial value (at $t = 0.2$ s), occurs approximately in the same timescale.

Table 1
Electrochromic parameters for coloration (C) and bleaching (B) processes.

T [min]	Coloration				Bleaching	
	T_{90} [ms]	H^a [cm^2.C^{-1}]	ΔT [%]	ΔAbs	T_{90} [ms]	H [cm^2.C^{-1}]
5	18	171	9.6	0.35	22	–168
10	53	132	9.9	0.63	39	–146
20	85	90	54.1	1.07	62	–98
40	92	78	49.6	1.45	70	–86

[a] Electrochromic efficiency was evaluated as the ratio of optical absorbance change over electric charge density needed to reach a steady change of color.

Table 1 summarizes several electrochromic parameters of the prepared PAni fibers. It should be noted that the optical-switching time is comparable to the response of ultra fast electrochromic nanostructured NiO films, recently reported by Cai et al. [35].

Electrochromic efficiency (H, see Table 1) strongly depends on the amount of polymer synthesized; longer and more ramified fibers increase the probability of extinction of polarons due to the longer diffusion pathlength. This last effect is evidenced by smaller electrochromic efficiency at longer optical-switching time values. In fact, these two parameters are linearly related (see Fig. S1, Supp. Info.).

4. Conclusions

We have presented a simple method to obtain polyaniline fibers with high porosity and short response time values, compatible with moving-image display technology. This simple method implies only a constant current anodization of the monomer without using templates or complicated electrochemical schemes for the anodization. The porosity of the electrode is the main factor influencing the formation of the polyaniline nanofibers. The high porosity of the synthesized fibers increases the area to volume ratio, improving the doping efficiency of the polymer. This approach represents a straightforward, easy and low cost method to obtain a fast color switching film with potential application in the deployment of an electrochromic device.

Acknowledgments

E.M. Erro thanks CONICET by the posdoc fellowship granted. Authors want to acknowledge the following supporting agencies: SeCYT – UNC, FONCYT and CONICET. Thanks are given to LAMARX laboratory and INTA for technical support with FE-SEM and TEM microscopy.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.03.050.

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