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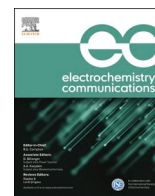
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Full Communication

Electrografting and electropolymerization of nanoarrays of PANI filaments through silica mesochannels

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ABSTRACT

Vertically aligned mesoporous silica films electrogenerated on indium-tin oxide (ITO) electrodes are used as hard templates for the electrochemical growth of polyaniline (PANI) nanofilaments. To ensure proper adhesion of PANI to the underlying ITO surface, aniline moieties are first covalently attached to the bottom of mesochannels via electrografting of aminophenyl diazonium cations, serving in a second step as precursors for PANI growth by electropolymerization of aniline through the silica mesochannels. This was achieved by cyclic voltammetry or potentiostatically at an applied potential of +0.85 V (vs. Ag/AgCl), the latter offering a better control of the nanofilaments length by tuning the electropolymerization time. PANI wires remain attached to ITO after etching of the silica membrane, confirming the importance of initial electrografting. Although PANI nanofilaments in the silica membrane remain electroactive, enhanced peak currents were observed after silica removal as PANI nanofilaments offer a larger effective surface area to the electrolyte solution.

1. Introduction

Combining organic semiconductors with low dimensionality offers advantages compared to the corresponding bulky materials in terms of improved transport properties. The resulting anisotropic nanostructures exhibit superior device performance [1–3]. 1D nanostructured conducting polymers are mainly produced by hard and soft template-based approaches or by electrospinning [4,5]. Among them, polyaniline (PANI) nanofibers are of great interest for a broad range of applications such as gas and biological sensors, printable electronics, electrochromics and photovoltaics, actuators, supercapacitors, protective applications or nanocomposites [6]. Oriented arrays with high aspect ratio, such as vertically-aligned and ordered nanowires on conductive supports [7,8], are highly demanded for various reasons: (i) 1D electronic pathways in nanowire arrays ensure fast charge transfers and efficient ion transport; (ii) each nanowire is in direct electrical contact with the electrode surface; (iii) mechanical stress during doping-dedoping processes can be avoided thanks to the space between oriented nanowires, enabling significant volume changes without damage as occurring in bulk conducting polymers. Arrays of PANI nanowires can be prepared by electrochemical growth or electroless polymerization through hard templates (e.g., membranes obtained from track-etched polymers [9,10] or anodized aluminium oxide [11,12]) or via self-assembly around soft

templates (such as surfactants of block copolymers [13,14]). The main limitation of these approaches is the achievable lowest diameters of PANI nanowires being restricted down to ca. 10 nm [8,14] whereas the template-free approaches led, as best, to diameters in the range 50–70 nm [15].

According to a pioneering work describing the possible synthesis of conducting filaments of PANI in a 3-nm-wide nanochannels of hexagonal MCM-41 mesoporous silica particles [16], and the discovery of vertically oriented mesoporous silica thin films [17,18], one can use such ordered, hexagonally-packed and vertically-aligned mesochannels as host to create ultra-thin nanoarrays of PANI filaments. Using nanoporous membranes on electrode would also enable the growth of nanofilaments by electropolymerization. This has been indeed reported in the literature, at first for polythiophene [19], and then for polypyrrole [20,21], PANI [22,23] or some other polymers [24–26]. However, the obtained polymeric wires exhibited most often diameters (i.e., 5–6 nm) larger than the mesopore apertures (i.e., 2–3 nm) [19], or they appeared in the form of bundles of wires with larger diameters (i.e., 30 nm) [21], or they were prepared from less ordered worm-like mesopores [22]. In a previous work [23], we reported the potentiostatic electropolymerization of aniline through well-ordered and oriented mesoporous silica, giving rise to PANI nanofilaments of 1–2 individual chains whose length can be adjusted up to typically 100 nm by tuning the

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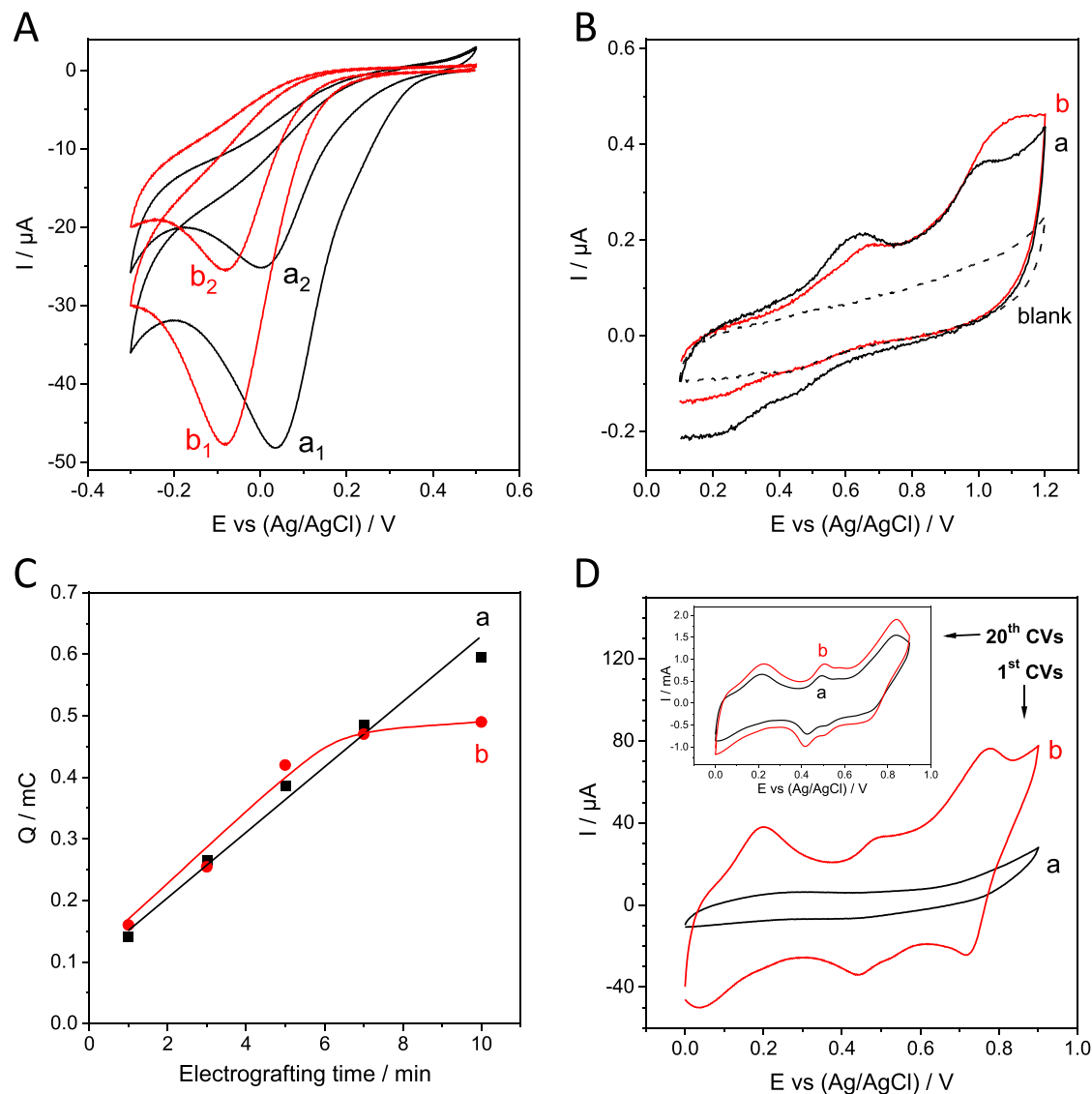


Fig. 1. (A) CVs recorded in 5 mM *p*-phenylenediamine + 5 mM NaNO₂ (in 0.5 M HCl), at 50 mV s⁻¹, using (a) bare and (b) silica-modified ITO (a₁ and b₁: 1st cycle; a₂ and b₂: 2nd cycle). (B) CVs recorded in 0.5 M H₂SO₄, at 20 mV s⁻¹, using (a) bare and (b) silica-modified ITO, after potentiostatic electrografting (1 min at -0.2 V in the same medium as in (A)). (C) Variation of the charges, *Q*, as a function of electrografting time (measured from anodic signals of CVs obtained as in (B)). (D) 1st and 20th (inset) cycles obtained after multisweep CV in 0.1 M aniline (in 0.5 M H₂SO₄), at 50 mV s⁻¹, using (a) bare and (b) electrografted silica-modified ITO (same conditions as (B)).

growth time. Once confined in the mesopore channels, these individual PANI nanofilaments were electroactive, but they did not adhere strongly to the electrode surface as no covalent bond between PANI and the ITO surface was formed. A way to overcome this limitation is to deposit a layer of bulk polymer onto the electrode surface prior to silica membrane deposition and nanowires growth (as shown for polypyrrole [21], PEDOT [24] or polyquinone [26]). However, such systems constituted by both bulk polymer film and nanowires on top of it are not only individual nanofilaments directly attached to the native electrode surface (their behavior can thus be affected by the bulky part of the deposit).

Here, we provide an original method to connect PANI nanofilaments directly to ITO electrode via a covalent bond. It is based on the electropolymerization of aniline through an oriented mesoporous silica film (formed by electro-assisted self-assembly) on ITO after electrografting of aniline precursors at the bottom of the mesopores and subsequent film growth from these covalently bonded precursors under potentiostatic conditions. Each step of the process is followed by cyclic voltammetry,

including the response of the PANI nanofilaments after removal of the mesoporous silica template.

2. Experimental section

2.1. Chemicals and reagents

TEOS (tetraethoxysilane, 98%, Alfa Aesar), CTAB (cetyltrimethylammonium bromide, 99%, Acros Organics), sodium nitrate (NaNO₃, 99%, Fluka), ethanol (95–96%, Merck), sulfuric acid (H₂SO₄, 98%, Sigma) and sodium hydroxide (NaOH, VWR International) were used as received. *p*-phenylenediamine (98%, Sigma), sodium nitrite (NaNO₂, Sigma) and hydrochloric acid (HCl, 37%, Sigma) were used to generate phenylamine monodiazonium salt and subsequent electrografting experiments. Aniline (99.5%, Sigma Aldrich) was distilled under vacuum before use. High-purity water (18 MΩ cm) from a Millipore Milli-Q water purification system was used to prepare all aqueous

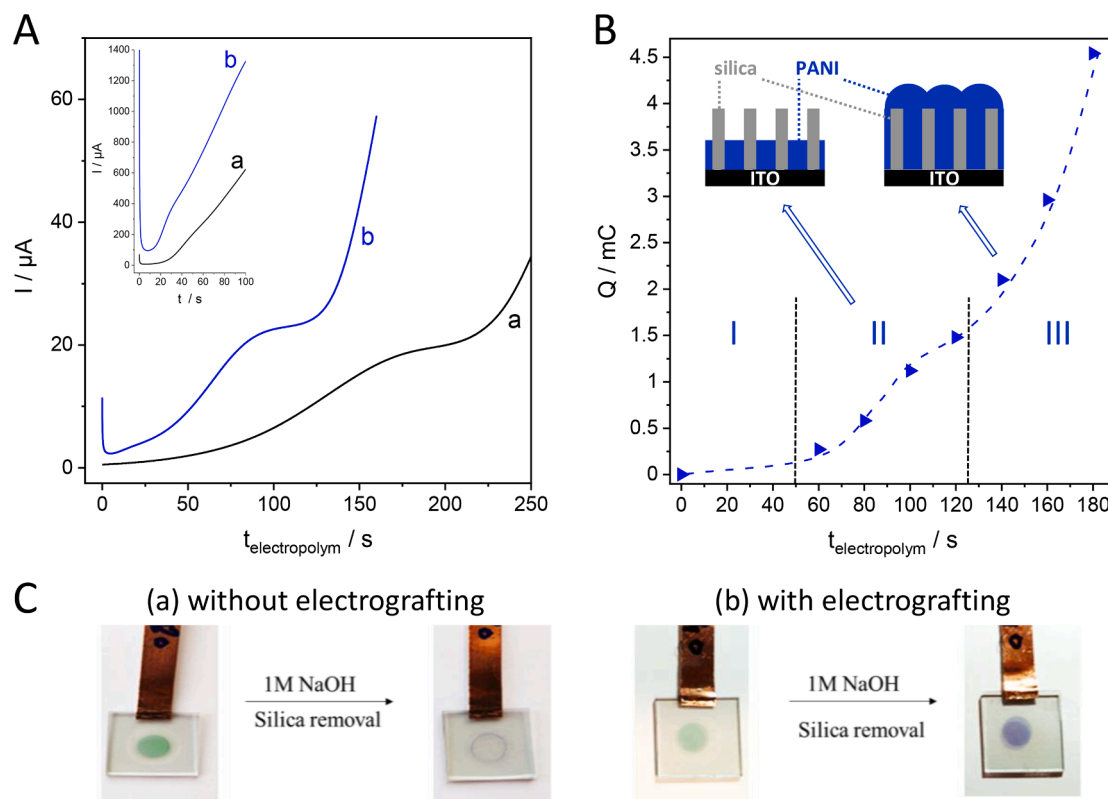


Fig. 2. (A) $I - t$ curves PANI electropolymerization (0.1 M aniline in 0.5 M H_2SO_4 , $E_{\text{app}} = +0.85$ V) at ITO electrodes covered with a mesoporous silica film without (a) and with (b) electrografting of aminophenyl groups; inset: $I - t$ curves in the absence of silica membrane on ITO. (B) Variation of charge (Q) measured as a function of electropolymerization time, integrated from $I - t$ curves obtained in the same conditions as (A); inset: schematic view of PANI growth inside and outside the mesoporous film (stages II and III of electropolymerization). (C) Photographs of PANI on ITO/mesoporous silica film, before and after etching in 1 M NaOH, for sample prepared without (a) and with (b) electrografting.

solutions.

2.2. Preparation of the oriented mesoporous silica films on ITO electrode

The Sol solution was prepared by dissolving 100 mM TEOS and 32 mM CTAB in 1:1 water:ethanol medium containing 0.1 M NaNO_3 . Its pH was adjusted to 3 by adding HCl (1 M) and the sol was hydrolyzed under constant stirring for 2.5 h. The silica membrane was generated on ITO plates (surface resistivity 8–12 Ω , Delta Technologies) by electro-assisted self-assembly (EASA [27]) from this aged solution, by applying a constant potential of -1.3 V for 20 s with a PGSTAT 101 potentiostat operated by NOVA software (Autolab), in a three-electrode cell (ITO working electrode (\varnothing : 8 mm), a silver rod as pseudo-reference electrode and a stainless steel as counter electrode). After deposition, the electrode was quickly removed from the cell, rinsed with deionized water, dried and kept overnight in oven at 130 °C. The surfactant was extracted from the silica film (by immersion in 0.1 M HCl ethanol solution for 10 min) prior to use.

2.3. Electrografting of aminophenyl groups and electropolymerization of aniline

The diazotation of *p*-phenylenediamine molecules (5 mM) with NaNO_2 (5 mM) was first performed in aqueous HCl (0.5 M) solution (for 10 min under stirring) [28]. *In situ* generated aminophenyl monodiazonium cations were then electrochemically reduced to graft aminophenyl groups onto the ITO surface using either a mesoporous silica film modified electrode or a bare ITO (for control experiments). After electrografting, the electrode was thoroughly rinsed with deionized water and sonicated for 5 min in ethanol. Electropolymerization of

aniline was then performed by applying, for selected periods of time, a constant potential of $+0.85$ V (vs. Ag/AgCl) to the working electrode (\varnothing : 5 mm) in 0.1 M aniline (in 0.5 M H_2SO_4) [23]. PANI nanowires were characterized by cyclic voltammetry, before and after etching of the silica membrane (10 min in 1 M NaOH).

3. Results and discussion

Fig. 1A shows typical cyclic voltammograms (CVs) of ITO electrodes (bare or covered with mesoporous silica) recorded in a 0.5 M HCl solution containing 5 mM *p*-phenylenediamine and 5 mM NaNO_2 (expected to be in the form of monodiazonium salt, $\text{H}_2\text{N}-\Phi-\text{N}_2^+\text{Cl}^-$ [28]). They exhibit well-defined reduction peaks associated with the formation of aryl radicals likely to attach to the ITO surface, consistent with previous observations for the electrografting of aminophenyl moieties to gold [28] or carbon electrodes [29]. A cathodic shift of ca. 120 mV is observed in the presence of the mesoporous silica film, suggesting slower electron transfer kinetics, but peak currents remain of the same intensity, confirming fast mass transport through the film (as common for such oriented and closely-packed nanochannels operating under total overlap diffusion regime [27]). The lower peak currents observed on the second CV cycles (see curves “2” in Fig. 1A) are consistent with the passivation of ITO surface due to the formation of a grafted layer onto the electrode. This is less marked than for gold electrodes electrografted with the same aminophenyl groups [28], suggesting slower processes on ITO (as observed for the electrochemical reduction of other diazonium salts [30]). Successful electrografting of the aminophenyl moieties is also demonstrated by X-ray photoelectron spectroscopy, via the characteristic N_{1s} peak located at 399.1 eV (NH_2) and a carbon component at 285.9 eV (C-NH₂) on the C_{1s} core level spectrum [31]

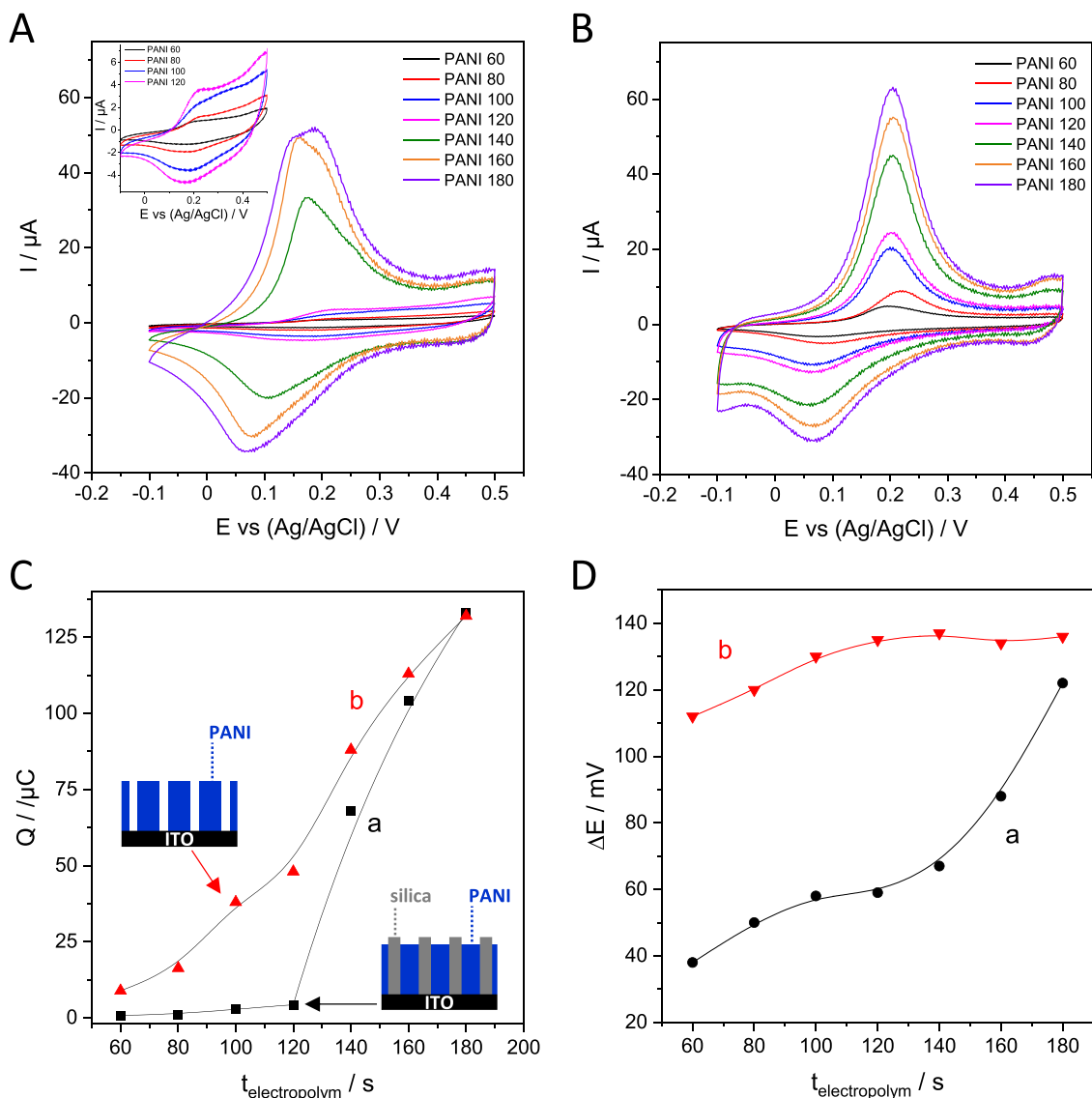


Fig. 3. (A,B) CVs of PANI electropolymerized for increasing times (from 60 to 180 s) before (A) and after (B) removal of the silica template (20 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$). Electrodes were prepared in the conditions of Fig. 2; inset in (A): enlargement of the curves obtained for 60–120 s electropolymerization. (C,D) Charge (Q) variation calculated by integration of the anodic peaks (C) and of the anodic-to-cathodic peak separation (ΔE) (D), as a function of the electropolymerization time.

(Fig. S1). The above CVs are used to select an appropriate potential for electrografting in potentiostatic mode. A value of -0.2 V appears to be suitable for functionalization of both ITO electrodes (bare and covered with the silica membrane). The grafted groups are electroactive, as revealed by CVs recorded in $0.5 \text{ M H}_2\text{SO}_4$ (see Fig. 1B for ITO electrodes electrografted for 1 min at -0.2 V), resulting in a signal at $+1.0 \text{ V}$ consistent with the irreversible oxidation of the grafted aminophenyl groups [28]. The presence of an additional signal at lower potential ($+0.6 \text{ V}$), yet less intense, indicates that one cannot rule out the formation of PANI oligomers [29,32]. Integrated charges (Fig. 1C), consistent with the formation of multilayers commonly observed for electrode surface modification by reduction of diazonium salts [33,34]. This tends to level off in the presence of the silica membrane (see curve b in Fig. 1C), possibly due to less radical recombination or pore blocking effects in the mesopore channels. From here on, electrodes were treated at -0.2 V for 1 min in 5 mM aminophenyldiazonium salt solution to produce thin aryl-amine layers. PANI electropolymerization in aniline medium is possible on so grafted ITO electrodes, more efficiently than on

bare ITO (compare curves “a” and “b” on Fig. 1D), for which several successive CV scans are needed to see PANI growth (Fig. 1D, inset). These experiments demonstrate the aminophenyl attachment to ITO by electrografting and subsequent PANI electropolymerization.

PANI electropolymerization through the mesoporous silica membrane is then performed by applying a potential $E_{\text{app}} = +0.85 \text{ V}$ for increasing times, to control better its growth [23]. Typical $I - t$ curves are depicted on Fig. 2A, showing the characteristic three-step mechanism involving a first nucleation period where currents are rather low, then an increase of intensity with a plateau current corresponding to the 1D growth of PANI filaments in the mesopore channels, and finally a sharp current increase due to the 3D deposition of bulk PANI outside the mesoporous silica membrane. The main differences observed between the electrodes prepared without (Fig. 2A, curve “a”) and with electrografting of aminophenyl groups at the bottom of pores (Fig. 2A, curve “b”) are: (i) a faster electropolymerization in the latter case (i.e., time to reach a current value equal to half of the plateau current, $t_{1/2} = 57 \text{ s}$ with grafted aminophenyl and $t_{1/2} = 120 \text{ s}$ without electrografting), consistent with Fig. 1D, and (ii) noticeable anodic currents in the early

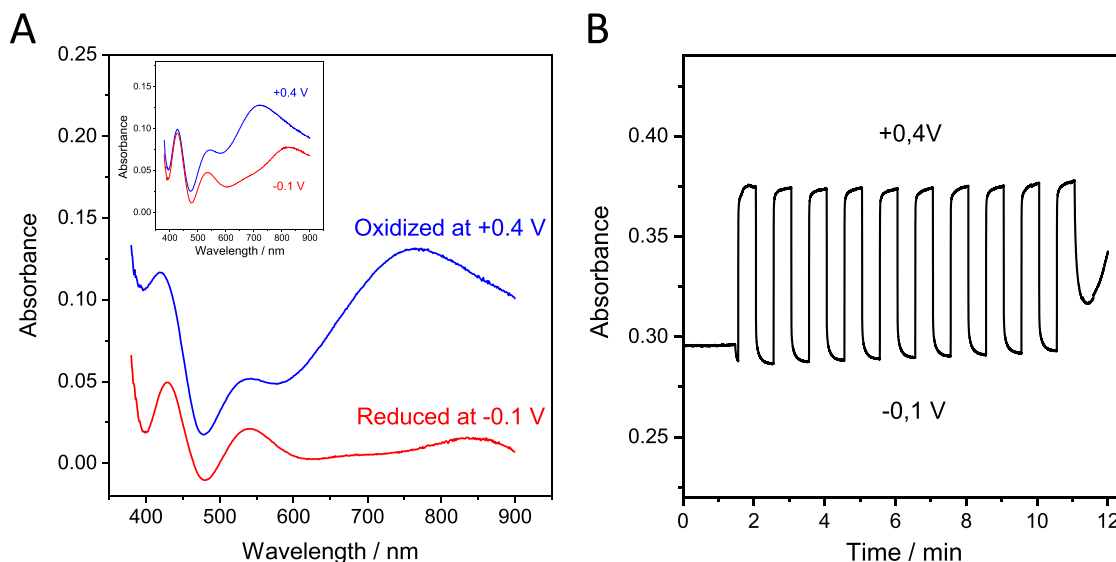


Fig. 4. (A) UV-vis spectra of the oxidized (blue curve) and reduced (red curve) forms of PANI electropolymerized for 140 s on electrografted ITO electrode covered with mesoporous silica, before (inset) or after dissolution of the silica template. (B) Transient profiles of transmittance changes at 760 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

beginning of the experiment (corresponding to the oxidation of aminophenyl moieties). For ITO electrodes without mesoporous silica film, one observes only the nucleation and 3D growth steps (i.e., no plateau currents, see inset in Fig. 2A), yet with faster processes in the presence of grafted aminophenyl groups (compare curves “a” and “b” in the inset). The three-step mechanism for PANI growth can be also shown by plotting the charges calculated from electropolymerization $I-t$ curves stopped at various times (Fig. 2B), illustrating the progressive filling of mesopore channels (stage II) followed by PANI growth outside the membrane (stage III) when nanofilaments reach the film surface. PANI nanofilaments deposited on electrografted ITO through the silica membrane (see green spots on Fig. 2C) remain attached to the substrate after dissolution of the silica material in alkaline medium. Without electrografting, PANI nanofilaments are lost in solution during treatment in NaOH (Fig. 2C, picture “a”), whereas those prepared on electrografted ITO remain on the electrode after removal of the silica membrane (Fig. 2C, picture “b”). The color change from green to blue is due to deprotonation of PANI in alkaline medium [35]. This confirms the importance of grafting aminophenyl groups prior to electropolymerization to ensure effective binding of PANI wires to the ITO.

The voltammetric response of PANI nanofilaments generated for increasing times through the mesoporous membrane on ITO (grafted with aminophenyl groups) is then characterized, before and after removal of the silica host (Fig. 3), in a potential window corresponding to the oxidation of leucoemeraldine to emeraldine [22]. Comparing parts A and B of the figure shows a distinct behavior of PANI nanofilaments when they are confined in the mesoporous silica membrane (Fig. 3A) or free of silica template (Fig. 3B). In the latter, CV peaks increase regularly with the electropolymerization time. Charge variation (Fig. 3C) follows well the electrodeposition process (Fig. 2), suggesting that the entire PANI material is electrochemically accessible to be fully and reversibly transformed between its undoped (leucoemeraldine) and doped (emeraldine) states (CVs remain identical after 100 cycles (Fig. S2), indicating long-term stability). Before silica dissolution, hosted PANI nanofilaments are electroactive (Fig. 3A, inset) but the intensity of voltammetric peaks is much smaller, probably due to restricted mass transport of electrolyte ions counterbalancing charges generated in the doping process. Only PANI deposits formed outside the silica membrane at longer electropolymerization times (≥ 140 s) are likely to undergo intense doping-dedoping processes, with charges

reaching almost those before silica template removal (Fig. 3C). The anodic-to-cathodic peak-to-peak separation is close to a Nernstian behavior ($\Delta E = 60$ mV) for PANI nanofilaments confined in the silica nanochannels (i.e., physically separated from each other), or even lower, e.g., 38 mV for the sample prepared from 60 s electropolymerization (see beginning of curve “a” in Fig. 3D), similarly as other types of nanowires in mesoporous silica [36]. It becomes larger for PANI grown outside the membrane and for all samples analyzed after removal of the silica host (see end of curve “a” and whole curve “b” in Fig. 3D), reaching values in the 100–140 mV range, i.e., not so far from those reported for bulk PANI prepared via electrochemical polymerization [37].

It appears that such free (i.e., after dissolution of the silica membrane) PANI nanofilaments covalently attached to the ITO electrode surface can be quantitatively and reversibly oxidized and reduced, as demonstrated by the total vanishing of the UV-vis band at 760 nm upon reduction at -0.1 V and its restoring after oxidation at $+0.4$ V (Fig. 4A), as expected in case of complete interconversion between oxidized and reduced states of PANI [38], which cannot be achieved with bulk PANI films and only partially for composite nanostructures containing PANI in mesoporous silica hosts (Fig. 4A, inset) [22,23]. The good operational stability (Fig. 4B) highlights promising applications of these ‘brush electrodes’ made of PANI filaments in the field of electrochromism.

4. Conclusion

We have demonstrated the formation of adherent PANI nanofilaments on ITO via the electrochemical polymerization of aniline through a mesoporous silica membrane electrodeposited as a solid template on the electrode surface. The adhesion is ensured by a preceding electrografting of aminophenyl moieties onto the ITO surface, which then serves as covalently bonded precursors for the vertical growth of PANI nanofilaments, these latter remaining attached to the electrode after removal of the silica host. The PANI wires can be electrochemically converted from their oxidized and reduced in a quantitative and reversible way. The concept of combining electrografting and electropolymerization at electrodes modified with an oriented silica film opens the door to the generation of other types of electroactive polymer nanofilaments.

CRediT authorship contribution statement

Wahid Ullah: Methodology, Investigation, Writing - original draft. **Grégoire Herzog:** Conceptualization, Validation, Resources. **Neus Vilà:** Conceptualization, Formal analysis, Validation, Visualization. **Alain Walcarius:** Conceptualization, Funding acquisition, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2020.106896>.

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