



# Toward a simple method for the fabrication of 1D or 3D nanostructures of polyaniline

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## ABSTRACT

We present a one-step chemical method for the fabrication and isolation of conjugated polymer nanostructures, in particular, polyanilines (PANIs), either in the pernigraniline or emeraldine oxidation state. The polymerization is initiated by the addition of a solid oxidant into an unstirred anilinium hydrochloride solution. This step allows a slow release of the oxidant, via its solubilization and diffusion into the undisturbed solution. The formation of visible macroscopic heterogeneous seeds promotes the homogeneous polymerization and growth of bulk nanostructures in solution. The shape of the first formed heterogeneous seeds was found to be dependent on the solubility/diffusion of the oxidant, allowing the prediction and control of the nanomorphology (1D vs. 3D or granular) of the bulk polyanilines. X-ray analyses of the as-prepared nanostructured PANIs showed that, compared to the literature data, the crystallite growth in the present study is significantly enhanced, with the 1D fibrillar morphology exhibiting a higher crystallinity per volume of nanostructure than that of a 3D granular counterpart. The electrical conductivity ( $\sigma$ ) of pelletized HCl doped PANIs or emeraldine salts (ES) showed significant differences depending on the fibrillar or granular morphology, but a close relationship among number of unit cells, crystallite size and electrical conductivity is evidenced.

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## 1. Introduction

Owing to their unique physical and chemical properties, the syntheses and potential widespread applications of nanostructures (e.g., nano-rods, tubes, fibers, helices and spheres) of intrinsic conducting polymers (ICP), e.g. polyanilines (PANIs), have received much attention in recent years [1,2]. The three commonly cited oxidation states of PANIs can be summarized with the structure shown in Fig. 1, where  $x$ ,  $y$  and  $1 - y$  indicate the degree of polymerization, the reduced and oxidized repeat units, respectively. The completely reduced state of PANIs, leucoemeraldine base (LEB), is obtained when  $1 - y = 0$ . While the completely oxidized state ( $1 - y = 1$ ) is pernigraniline base (PB), that of emeraldine base (EB) is obtained when  $1 - y = 0.5$ .

The typical electrochemical or chemical syntheses leading to 1D nanofibers of the most investigated ICP, polyaniline (PANI), may require the use of (a) hard templates (e.g., zeolite channels [3], truck-etched polycarbonates [4], and anodized alumina [5]), (b) soft templates (e.g., surfactants [6], micelles [7], liquid crystals [8] and polyacids [9]), (c) a biocatalyst (e.g., coprinus cinereus per-

oxidase) as oxidant [10], and (d) a crown ether derivative [11] or complex/bulky surfactants as dopants [12].

More recent strategies for the fabrication of nanofibers of PANIs include methods such as rapid stirring of the polymerizing solution [13] or a careful slow addition of a solution of oxidizing agent into the monomer containing (unstirred or briefly stirred) solution [14], DNA templated synthesis [15], biphasic interfacial polymerization [16], electrospinning [17], seeding with (HipCo single-walled carbon nanotubes, nanofibers of hexapeptide and  $V_2O_5$ ) [18] or aniline oligomers [19].

The chemical synthetic procedures reported thus far, invariably, require the dissolving of an inorganic oxidant, e.g., ammonium peroxy disulfate, (APS) in water prior to its addition into the monomer containing solution. Such a conventional protocol is presumably aimed at improving chemical kinetics via homogeneous phase polymerization which is also often aided by stirring.

Despite the diversity of the reported synthetic efforts, there is still a need to search for an expeditious synthetic route that can, reproducibly and controllably, fabricate PANI nanofibers/nanostructures.

Here, we report on an extremely simple chemical polymerization procedure, which involves neither the stirring of the polymerizing bath nor the addition of foreign seeds or the use of hard/exotic/soft (detergents) template(s) or bio oxidizing

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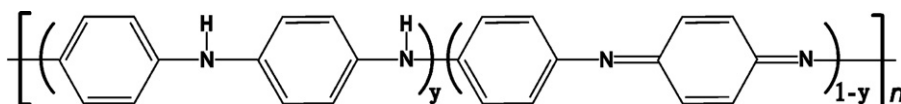


Fig. 1. Chemical structure of PANIs of various oxidation states: emeraldine base (EB)  $y=0.5$ ; pernigraniline base (PB)  $y=0$ , and leucoemeraldine base (LEB)  $y=1$ .

agent(s), thereby circumventing post-synthetic removal of templates, tedious pre-fabrication of seeds or their isolation from natural/bio-sources. Our synthetic approach merely involves the addition of a solid oxidizing agent into an unstirred solution of aniline at ambient temperature, a key step that reveals to be successful to, in-situ, induce growth of heterogeneous seeds which precedes and promotes bulk (homogeneous) polymerization in the liquid supernatant. The as-prepared PANIs are investigated by optical microscopy, SEM, AFM, conductivity, UV-vis, IR spectroscopy, and X-ray diffraction; their physical characteristics are discussed in regard of the 1D or 3D morphology and the polymerization process.

## 2. Experimental

### 2.1. Materials

Ammonium peroxy disulfate (APS), vanadium oxide ( $V_2O_5$ ), and potassium persulfate (KPS) were used as received from Aldrich without further purification. Aniline (Aldrich) was vacuum distilled before use.

### 2.2. Instrumentation

Spectroscopic properties of products were investigated using a FTIR 380 Thermo Electron and a UV-vis Beckman DU 520; morphological characteristics were carried out on optical microscopy (Olympus BH2), SEM (JEOL JSM 880 operating at 15 kV), and AFM (Veeco Multimode Nanoscope IIIa). A collinear four-probe technique using a LakeShore 120 CS DC microcurrent source and a Keithley 2100 digital multimeter were employed to determine the electrical conductivity of pelletized polyaniline samples. X-ray diffraction experiments were performed on a PANalytical X'Pert Pro operating at  $\lambda = 1.5416 \text{ \AA}$  (Cu-K $\alpha$  radiation). Structure refinements were done using the Check Cell software. Elemental analyses were performed by the Service Central d'Analyse at the Centre National de la Recherche Scientifique (Solaize, France).

### 2.3. Preparation of polyaniline nanostructures

Typical procedures for polymerization and isolation of PANI nanostructures are provided below.

- A mixture of 0.148 g (1.59 mmol) aniline and 140 mL 1 M HCl (dopant) are magnetically stirred for 1 h (25 °C) in a 400-mL Pyrex beaker. The magnetic stir bar is removed and 0.64 mmol of crystalline solid oxidizing agent APS or KPS is added. The polymerization is allowed to proceed undisturbed for 18–24 h; when  $V_2O_5$  is used as the oxidant, the reaction is allowed to proceed for a longer period of time (48–72 h due to slower kinetics). At the end of the reaction, about one-third of the top (less colored) liquid supernatant is discarded. An aliquot (~10 mL) of the remaining deep green colored (emeraldine salt) mixture is dialyzed in de-ionized water (dialysis tube from Fisher Scientific, 12,000–14,000 MW cut off) until the water pH reaches ca. 4.5. A drop of the suspension is placed on a silicon wafer, air-dried, then coated with a thin layer of gold/palladium under vacuum, and analyzed via SEM.
- Alternatively, the reaction mixture (after removal of the top, less colored liquid supernatant as mentioned above) is

quenched into 0.1 M aq.  $NH_3$  (until a pH of 8.5–9.0 is obtained) and centrifuged. The isolated PANIs is placed in a test tube, washed with copious amounts of de-ionized water until a neutral pH is obtained. The mixture is centrifuged, and the product is rewashed with acetone in order to remove soluble organic by-products/oligomers until colorless washings are obtained after which time, a sample of the mixture is dialyzed against de-ionized water. A portion of the isolated solid product (emeraldine base) is re-suspended in water by brief shakings and the resulting suspension is placed on a silicon wafer, air-dried, and then analyzed via SEM. A sample of the above dialyzed material (emeraldine base) is vacuum-dried (overnight) and analyzed via FTIR (KBr pellet) or UV-vis. (NMP solvent). This blue solution in NMP is then treated with a few drops of 1.0 M HCl (aq.) to provide a green solution (emeraldine salt) whose UV-vis spectrum is also recorded. Another portion of the above dialyzed solid product is doped with 1 M HCl (overnight), centrifuged and vacuum-dried overnight (80 °C). Electrical conductivity of the resulting deep green solid (emeraldine salt) is obtained via the conventional four-probe technique.

- Isolation of PANIs in the pernigraniline oxidation state.

The procedure described in part (a) above was repeated in a Pyrex Glass Petri dish (10 cm in diameter and 2 cm in height) with all amounts of reactants cut to down to 1/3. The entire reaction deep blue mixture is poured into ~400 mL cold (0 °C) 0.5 M NaOH (aq.) after 30–40 min from the onset of formation of colored seeds (pH of liquid supernatant after treatment with base is ~11). The cold mixture is rapidly suction filtered (Millipore membrane; GSWP; 0.22  $\mu\text{m}$ ), washed with copious amounts of cold water until a colorless filtrate is obtained. The product was placed in a test tube and washed with small amounts of acetone until a colorless liquid supernatant is obtained. It was then centrifuged. The dark purple product is vacuum-dried (overnight). A portion of this dried product is suspended in de-ionized water by brief shakings and a drop of the resulting suspension is subjected to SEM. Another portion of the dried product was analyzed by FTIR (KBr pellet), UV-vis (NMP, deep purple solution). It is worth mentioning that all fibrillar products isolated (emeraldine base, the corresponding salt or pernigraniline base) can be easily suspended in water by brief shakings or sonication. The resulting suspensions remain stable (i.e., no obvious precipitation was observed) for several weeks.

- Isolation of comets and/or nanostructures (fibers, beads, string of beads)

The experiment in (c) above is repeated in a Petri dish, except that the reaction is allowed to proceed for 18–24 h after which time the mixture was quenched with aq.  $NH_3$  (0.1 M) until a basic pH ~9 is obtained. The reaction mixture is then poured into a separate container. The comets anchored on the Petri dish are sequentially washed with de-ionized water, acetone and ether and then dried in air before analyses via optical microscopy and/or AFM. Alternatively, the comets and/or nanostructures (fibers, beads, string of beads) can also be isolated onto cover (glass) microscope slides initially immersed into the reaction mixture prior to the addition of APS. The reaction is allowed to proceed for 2.5–3 h. It was quenched with aq. 0.1 M  $NH_3$  and then poured into a separate container. The deep purple nanostructures anchored on the glass slides are

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