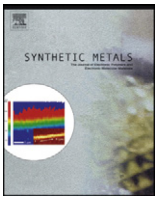
Synthetic Metals 161 (2012) 2739–2742

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

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



Synchrotron X-ray scattering reveals early-stage crystallinity during the self-assembly of polyaniline nanotubes with rectangular cross-sections

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ARTICLE INFO

Article history:
Received 21 September 2011
Accepted 18 October 2011
Available online 12 November 2011

Keywords:
Polyaniline
Nanotube
Self-assembly
Synchrotron
Diffraction

ABSTRACT

The use of synchrotron X-ray diffraction to study the crystallographic structure of nanostructure polyaniline is reported. It is shown to reveal unprecedented crystallographic information, particularly for early-stage self-assembled intermediate structures that are critical to the formation process. We discuss the new peaks, which are enabled here by specific advantages of synchrotron X-rays, including higher resolution diffraction patterns, and lower sample quantity requirements. The findings have application to the study of the structural evolution underpinning PANI nanotube formation.

The crystallographic structure of conventional polyaniline (PANI) is fairly well understood [1–3], but that of PANI nanotube self-assembly [4–12] is not [13,14]. This is despite significant research efforts over the past decade [4–12], an intractability which can be attributed to two factors: first, the fundamental complexity of the multiple-stage interactions underpinning PANI nanostructure self-assembly [13,14], and second, the tools employed by researchers [15,16]. In this proof-of-concept communication, we contribute towards the second factor, by reporting that synchrotron X-ray diffraction (XRD) can reveal unprecedented crystallographic detail for critical early-stage self-assembled PANI nanostructures. This is due to two specific advantages of a synchrotron X-ray source over a conventional laboratory X-ray source: (i) higher resolution diffraction patterns, and (ii) lowering the sample quantity requirement by orders of magnitude, thus enabling investigation of low-yield early-stage products. Herein we demonstrate these benefits by observing previously unreported XRD peaks associated with the structural evolution that leads to PANI nanotubes.

The overall motivation is that conducting polymer (CP) nanostructures – specifically, PANI nanotubes, nanofibers and nanosheets – are novel materials with a wide range of applications, including sensors, transistors and actuators, due to their unique and tunable electrical, chemical and physical properties [6,17,18]. However, synthesis pathways remain a problem, beset by complicated processes and low yields (i.e., templates, electrospinning, lithography) while others are marred by poor repeatability (i.e., self-assembly) [6,9,11,14,19]. Self-assembly may prove to be the optimal PANI nanostructure synthesis strategy (it may combine high yields with a straightforward setup), but its poor repeatability must be understood and addressed [11,13,20,21]. In particular, the early stages of self-assembly appear to be critical: very recently it was discovered that key nanosheet structural changes occur within the first minutes of aniline polymerization, affecting the course of subsequent PANI nanostructure self-assembly [20]. At this early stage conventional analysis techniques struggle, since they require relatively large amounts of sample be extracted and dried, a limitation affecting many tools typically used in PANI studies [11,20].

Among PANI nanostructures, nanotubes have received continuing attention because the mechanism of their growth is still open to discussion [8,13,14]. Polyaniline nanotubes with rectangular cross-section [22–32] represent a special sub-group. It has been proposed that crystalline aggregates produced by aniline oligomers serve as a template for the subsequent deposition of PANI that creates the nanotube walls [14,22]. The crystals formed by reaction intermediates or various insoluble salts generated in the medium may also

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doi:10.1016/j.synthmet.2011.10.012

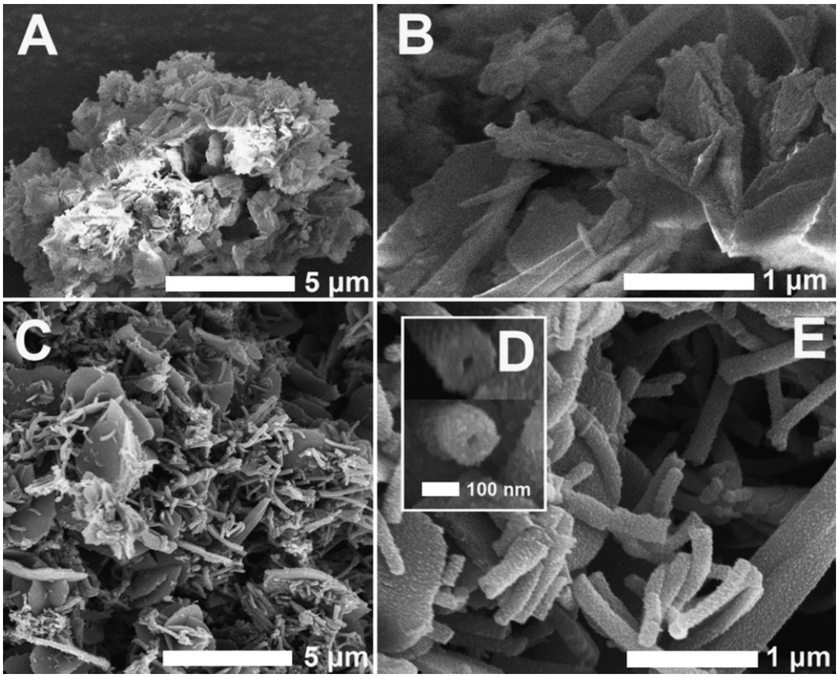

Fig. 1. SEM images of aniline chemical oxidation self-assembly products formed via "B1" synthesis conditions after (A, B) 5 min and (C–E) 8 h of reaction time. (D) Detail of square cross-section.

serve as such templates. Similar rectangular nano/microtubes have been produced also by polypyrrole [33–36] or oxidation products of *o*-phenylenediamine [37]. The chemical nature and properties, and especially the crystallinity of the first aniline-oxidation products is thus of special interest.

To address this problem, we used synchrotron powder diffraction, which with its high flux source enabled rapid, detailed data collection from small sample quantities. This yielded X-ray diffraction patterns of products formed during the first minutes of self-assembly, an approach particularly relevant to the PANI system since there are known correlations between the crystalline properties of oligoaniline nanostructures and their resulting conductivities [20]. To the best of our knowledge, this is the first application of synchrotron X-ray diffraction to the time-resolved study of PANI nanostructure self-assembly [38–40]. The experiment involved three steps, namely (1) sample synthesis, (2) synchrotron XRD analysis and (3) scanning electron microscopy (SEM) and Fourier-transform infrared (FTIR) spectroscopy characterization. The synthesis followed standard protocols [16,20,22]: aniline, ammonium persulfate (APS) and hydrochloric acid (HCl) were mixed together in distilled water, with the ensuing chemical oxidation of aniline allowed to proceed for a set amount of time (5 minutes, 15 minutes, 4 hours and 8 hours, plotted in the figures as "**5m**", "**15m**", "**4h**" and "**8h**", respectively). Three sets of synthesis conditions were investigated, following the reports of Ding et al. [22]: "B1" had 0.2 M aniline, 0.05 M APS and 0.2 M HCl for PANI nanotubes; "B2" had 0.1 M aniline, 0.1 M APS and 0.05 M HCl for nanoflakes; and "B3" had 0.1 M aniline, 0.1 M APS and 0.1 M HCl for nanorods [22]. Synthesis was followed by (a) sample centrifugation, (b) rinsing with water, (c) drying until powdery, (d) gentle grinding into a fine powder with a pestle and mortar, and (e) loading into 0.5 mm diameter borosilicate capillaries for synchrotron XRD. This was conducted at the Australian Synchrotron on the Powder Diffraction beam line, using an X-ray wavelength of 0.61855 Å (~20 keV, calibrated using a LaB_6 NIST 660b standard). Data were collected using a Mythen detector spanning 80° (2θ) of arc, with 10 min sample exposure times and the capillary continuously spinning throughout the measurement. Part of each sample was kept for subsequent SEM imaging and FTIR characterization, with SEM results of synthesis B1 shown in Fig. 1: after 5 min the sample morphology is as shown in (A-B) and is as expected [11,16,20,22], largely consisting of nanoflakes and nanoribbons, while (C–E) after 8 h the sample morphology includes rectangular cross-section nanotubes [22].

Since PANI does not form a well-defined crystal structure as such, specific features in the diffraction patterns must be analyzed as a function of time. Here we highlight synchrotron XRD results obtained at various reaction times, and compare them with laboratory XRD results [16]. To enable this comparison, the Bragg equation was used to convert the synchrotron data to the Cu K_α wavelength typically used by laboratory instruments [16]. Laboratory XRD studies on PANI nanostructures studies typically find less than 8 peaks [5,15,16,20]; synchrotron XRD yielded significantly more, as shown in Fig. 2. These new peaks, specifically those at 5.7°, 6.0°, 17.8°, 19.0°, 26.2° and 26.5°, were found in the early stages of the reactions (Fig. 2, **5m** and **15m** patterns), times at which sample amounts may have been insufficient for detection with conventional laboratory XRD. Furthermore, peaks that we find to be distinct in synchrotron XRD patterns, such as those at 23.2° and 23.4°, were previously indistinguishable as separate peaks using laboratory XRD. However, we also found some sharp peaks corresponding to highly crystalline material, marked with asterisks in Fig. 2, that we attribute to contaminant byproducts. (Analysis of these asterisked peaks suggested at least two phases, possibly a dihydro-1,2,4-triazine [41] and (*E*)-2-phenylbenzaldehyde oxime [42], although we caution that there is a lack of support for these in the chemistry of aniline oxidation. Reference patterns for these compounds are compared with the data in the Supporting Information.) Table 1 summarizes the main peaks found, with contaminants excluded, and compares them with previous reports and assignments.

In addition to new peaks found in the **5m** and **15m** patterns of Fig. 2 for the early-stage products corresponding to oligomeric nanoflakes and nanoribbons, [11,16,20,22] we also show, in the **4h** and **8h** patterns of Fig. 2, the time-evolution leading to the square cross-section PANI nanotubes of Fig. 1C–E. Consistent