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Theories of polyaniline nanostructure self-assembly: Towards an expanded, comprehensive Multi-Layer Theory (MLT)

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ABSTRACT

Nanostructured conducting polymeric materials are of exceptional interest due to their potential applications in sensors, actuators, transistors and displays. Arguably the most promising method for synthesizing polyaniline nanostructures is self-assembly, which is very advantageous in its simplicity and volume. However, this self-assembly remains only partly understood, with a number of already established models (a "micelle theory" and a "phenazine theory") at odds with more recent discoveries (nanosheet curling and nanoparticle agglomeration), leading to a fragmented understanding of this important topic. In this paper we address this problem in two ways. First, we review the aforementioned older models and recent discoveries. Second, we propose an expanded polyaniline nanostructure self-assembly model – "Multi-Layer Theory" – that goes beyond the scope of existing theories, thereby accommodating the more recent discoveries. The expanded synthesis framework we present is based on a multi-layered approach incorporating intrinsic morphologies. The three proposed intrinsic morphologies underpinning our model are nanofibrils, nanosheets and nanoparticles; the forces driving their subsequent self-assembly interactions are mainly π–π stacking, hydrogen bonding and charge–charge repulsion from protonation. These interactions between the three intrinsic morphologies give rise to observed growth, agglomeration and curling behaviours that ultimately generate complex multi-layered nanostructures such as double-walled conducting polymer nanotubes.

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1. Introduction to conducting polymers (CPs)

Unlike traditional polymers, which are electrical insulators, conducting polymers (CPs) are semiconducting and can be doped into regions of metallic conductivity [1–7]. This novel finding, at odds with what had been previously expected of polymers, yielded the 2000 Nobel Prize in Chemistry for Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for the discovery and subsequent development of this new class of materials. Thanks to intense research efforts, there are now a large variety of CPs, with polyacetylene, polythiophene, polypyrrole and polyaniline (PANI) being four of the most studied and promising types. PANI exhibits high conductivity, excellent environmental stability, and is low-cost and straightforward to synthesize [8]. It is also unique among CPs in that it has a reversible and relatively simple acid–base doping–dedoping pathway, useful for tuning its electrical and optical properties [9]. By offering metal-like electrical and optical properties in addition to the inherent ease of processing and mechanical flexibility of polymers, innovative new devices and applications have been made possible by CPs. Moreover, the morphology of such materials can be tuned at the nanoscale. This nanostructuring of materials, by designing their dimensions to be on the order of hundreds of nanometres or lower, often yields novel properties [10]. Examples are improved strength and conductivity [11], usually due to an increase in molecular ordering, as well as improved reactivity [12], typically due to higher surface area.

Combining these two sources of innovation – CPs and nanostructuring – has been an area of intense study in recent years [6,13–17], yielding innovative applications [18,19]. The challenges that motivate much of this research have to do with understanding and ultimately controlling the morphology and underlying structure of nanostructured CPs, which this review will focus on. Specifically, we address the questions that ask: under what conditions and through which mechanism do CP nanostructures self-assemble? Furthermore, can an improved understanding of this self-assembly allow us to design new types of nanostructures?

2. Polyaniline (PANI) structure, synthesis and properties

Fundamentally, PANI is composed of two types of segments: benzenoid diamine units, which are reduced, and quinonoid diimine units, which are oxidized. Different forms of PANI are based on which constituent units repeat, with the *leucoemeraldine* form being fully reduced, the *pernigraniline* form fully oxidized, and the *emeraldine* form half-oxidized, half-reduced. This latter form is the most interesting, since emeraldine can transport electrons well when doped [20]: the non-conductive $\sigma < 10^{-10}\,\mathrm{S\,cm^{-1}}$ emeraldine base treated with aqueous acids (pH < 1) yields the conductive $\sigma > 10^{1}\,\mathrm{S\,cm^{-1}}$ emeraldine salt form of PANI [21]. This occurs through proton induced spin unpairing [22], and is a reversible process, with deprotonation transforming the conductive emeraldine salt of PANI into an insulating emeraldine base. Thus, the resulting conductivity can vary based on both the extent of oxidation and the extent of protonation, which makes PANI unique among CPs [9].

PANI can be synthesized in various sizes and morphologies, with a useful distinction to be drawn between bulk and nanostructured PANI. The bulk, granular PANI can be easily obtained through conventional processing methods, namely by dissolving the aniline monomer in a strong acid such as 1 M HCl, and then polymerizing it through the addition of an oxidant [23]. For nanotubular PANI the options are more varied, with a number of synthesis methods under active research and development [13,24–27]. Using an external template to form PANI nanostructures is the most conceptually straightforward synthesis method of all—this is known as template synthesis. For example, having aniline polymerize within a tubular channel will yield a PANI nanotube, repeatedly and reliably: using an aluminosilicate template featuring 3 nm wide hexagonal channels can mold conducting PANI nanofiber growth [28]. However, template removal presents one of the major obstacles for this synthesis strategy, since structural damage to PANI can occur, leading to degraded properties such as poor conductivity [29]. An alternate template-based technique that addresses some of these issues is nanofiber seeding [30], where the templating involves the addition of small amounts (<1%) of biological, inorganic or organic nanofibers to the conventional chemical oxidative polymerization of aniline. This results in a change of product morphology, from granular particulates to high yields of nanofibers. A related approach is that of template synthesis on polymer acids, which, unlike external templates, are designed to remain an integral part of the PANI nanostructure, acting as dopant and solubility enhancing agents. Yoo et al. have shown that by varying the molecular characteristics of these polymer acid templates one can tune the resulting PANI composites [31], yielding well-conducting and water-dispersible structures that are of controllable crystallinity and conjugation length. Control