Interfacial Polymerization of Polyaniline Nanofibers Grafted to Au Surfaces

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Organic nanowires, particularly those made from polyaniline (PANI), have recently received considerable attention because of their unique chemical sensing and electrical properties. Interest has been directed toward fine-tuning the synthesis of tubular morphologies by controlling reaction conditions. The method frequently employed to construct such morphologies has typically involved template-free chemical synthesis, in which the aniline monomer polymerizes in the presence of large bulky acids. For instance, Huang et al.[1] recently developed a simple, practical method using biphasic or "interfacial" polymerization for making uniform, template-free[2] nanofibers. Furthermore, Wan et al.[3−6] and others[7,8] have developed a template-free solution method in which the diameter of the tube can be controlled by the dopant functionality and amount. Aside from the many challenges in polymerizing these chains into nanosized tubes, the next greatest hurdle is arranging these nanosized fibers onto a substrate in an ordered fashion for the purpose of fabricating useful nanoscale devices such as chemiresistive vapor sensors. The ability to polymerize nanostructures directly on metallic substrates has been previously achieved by MacDiarmid,[9] Hayes et al.,[10] and Porter et al.,[11] using electrochemical and Langmuir−Blodgett methods to grow and organize nanometer-sized polyaniline tubes on modified Au electrodes. Current methods for synthesizing nanostructured PANI covalently bound to metal surfaces require templates and utilize electrochemical or time-consuming lithography methods that produce low yields.

In this communication, we report a simple, two-step process for the synthesis of conductive nanosized PANI fibers bound directly to the surface of an Au substrate. The process uses an interfacial polymerization technique to form a two-dimensional mesh of PANI fibers that are grafted to the Au surface using self-assembled monolayer of 4-aminothiolphenol (4-ATP). The two-step process is as follows: (1) A self-assembled monolayer (SAM) of 4-ATP is created on a Au surface, and (2) then PANI nanofibers are directly synthesized onto the Au surface by placing the substrate at the interface of a biphasic solution of dopant and aniline monomer. The use of exact molar ratios of reactants facilitates the formation of the nanofibers.

The objective of the SAM formation step is to functionalize the Au surface with an amine that will promote covalent attachment of PANI. A SAM of 4-ATP was created using a standard monolayer formation technique[12] and was confirmed by X-ray photoelectron spectroscopy (XPS) and grazing-angle IR absorption measurements. During the polymerization, the 4-ATP-treated substrate sits at the interface of the organic/aqueous biphasic system (Figure 1) used to synthesize PANI nanofibers.[1] If a a high mole ratio of 1*R*-(−)-10-camphorsulfonic acid (dopant) to aniline monomer is used,[1] the polymerization is autocatalyzed by the presence of the doping acid and proceeds at a high rate. During the reaction, aniline monomer diffuses from the organic layer (bottom) to the interface, is protonated by the acidic aqueous layer to form an anilinum cation (stabilized by the phenyl group), and then connects to the "tail" end of an oligomer. Nanofibers form in or near the interface, which suggests that species or conditions at the interface influence polymer morphology. In this template-free synthesis, the driving force(s) involved in forming nanofibers is (are) unclear, but it is hypothesized that preferential electrostatic interactions[13] between the aniline monomer and the growing PANI chains that favor nanosized fiber formation might occur.

The growth of these nanofibers on Au was monitored with a scanning electron microscope (SEM)[14] by recording micrographs of chips that were submerged in the interfacial reaction mixture for 1, 3, and 5 min (Parts b-d, respectively of Figure 2) and after 24 h (Figure 3). As shown in Figure 2b, the growth of the polyaniline nanofibers begins with the formation of submicron fingerlike projections emanating on the patterned Au surface. After 3 min, the Au surface is covered with two-dimensional interconnecting ribbon structures that span the Au strips. The growth of these submicron PANI structures, as seen in Figure 2c, appears to be guided by the preabsorbed monolayer of 4-ATP. With increased polymerization time, these ribbonlike structures form rods (Figure 2d) that are surrounded by amorphous aggregates. The rods serve as a new polymerization initiation site from which aniline nucleates and grows into nanosized fibers. After 24 h, both the Au and glass are covered by a thick mat of nanofibers (Figure 3) and,

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(14) To prevent charging, a low accelerating voltage of 2 kV was used to image the structures. At such a low accelerating voltage, it was not necessary to coat PANI with a conducting layer. A tip current of less than 6×10^{-12} A allowed images of up to 30 000 times magnification at 2 kV without charging.

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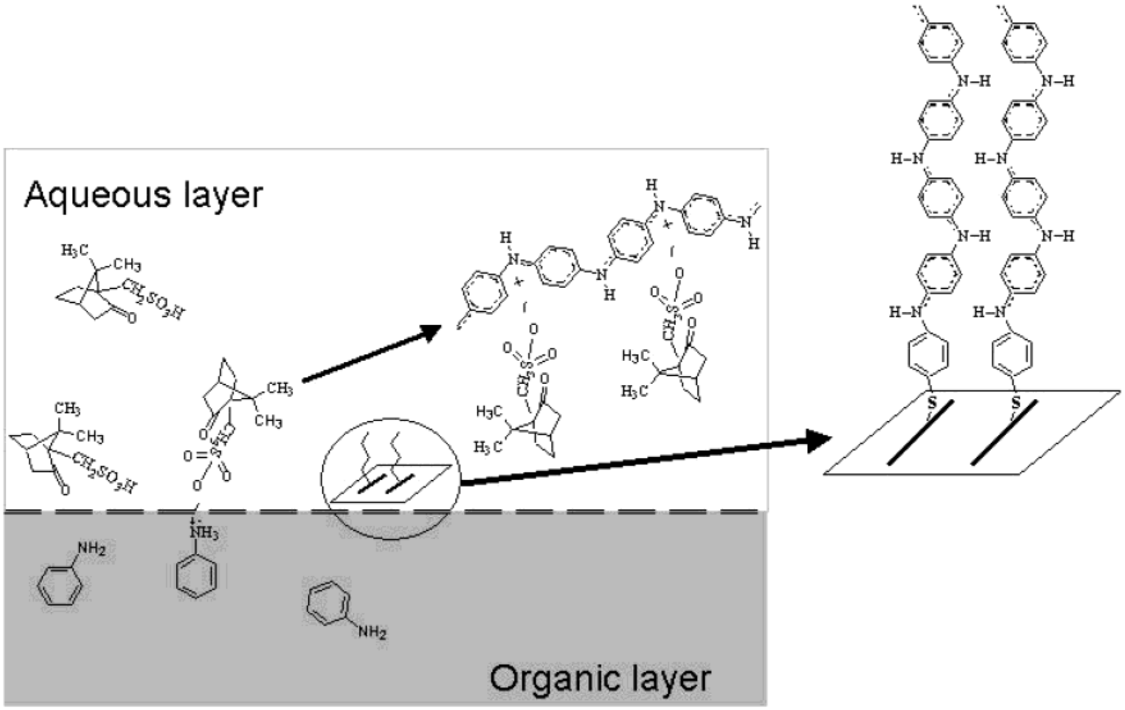

Figure 1. Schematic of the interfacial synthesis of polyaniline (PANI) nanofibers grafted onto a Au substrate using a self-assembled monolayer of 4-aminothiophenol (4-ATP). It is not clear whether the PANI grows directly off the 4-ATP-modified gold surface or the PANI is synthesized in solution at the interface and then diffuses to the gold surface where it "links" with the self-assembled monolayer of gold.

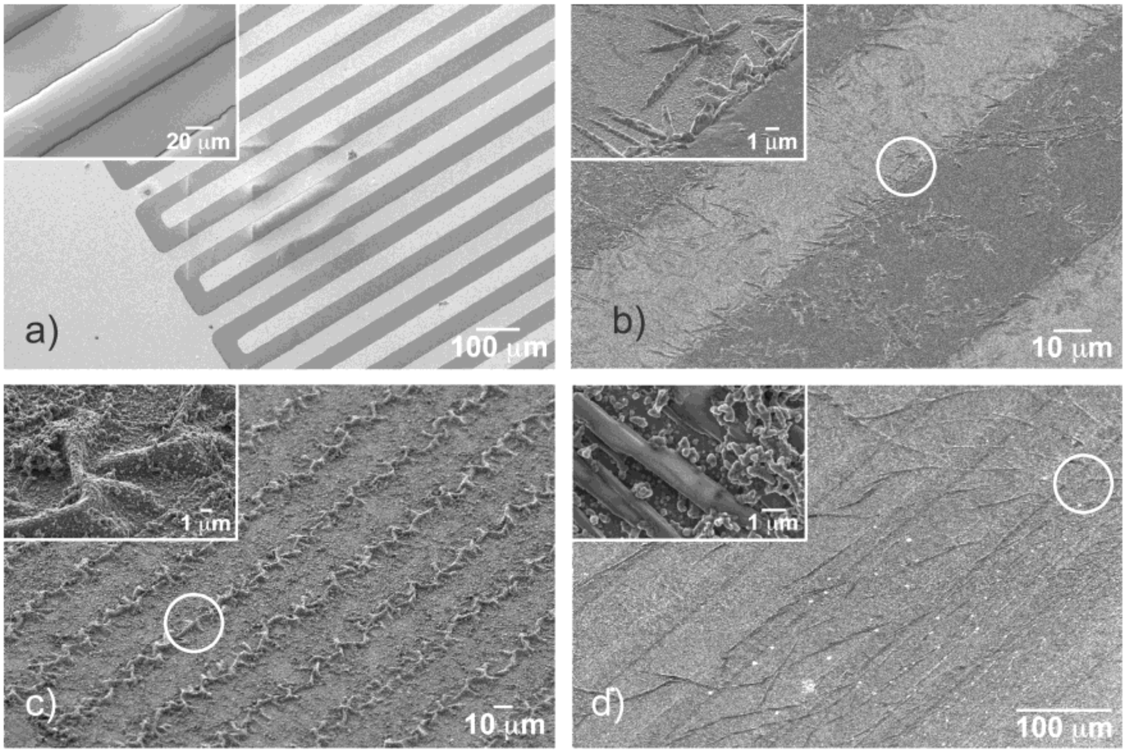

Figure 2. (a) SEM image of a bare, interdigitated gold electrode pretreated with a self-assembled monolayer of 4-aminothiophenol (light area). (b−d) SEM images following the growth of submicron-sized PANI on a 4-aminothiophenol-treated gold electrode using an interfacial polymerization technique. The chips were removed from the reaction mixture and imaged after (b) 1, (c) 3, and (d) 5 min. Insets show magnification of the circled areas.

to the eye, has the appearance of a uniform green film. The fibers within this dense mat had nearly uniform diameters of 40−50 nm, which is consistent with interfacially grown fibers first observed by Huang et al.[1] The low resistance of the PANI nanofibers in Figure 3 across the interdigitated electrodes suggests a minimal amount of contact resistance at the interface between the PANI fibers and the Au.

To ensure that the PANI nanofibers are not merely physisorbed, the 4-ATP monolayer was substituted with

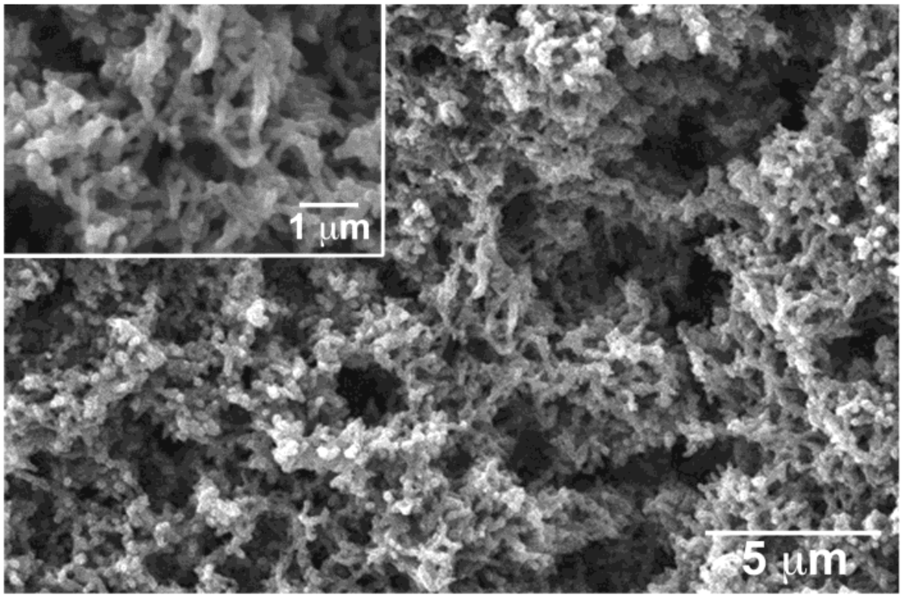

Figure 3. SEM image of the chip from Figure 2 after a reaction time of 24 h shows a dense mat of nanofibers, completely obscuring the underlying gold interdigitated electrode.

a benzenethiol (BT). Using the same polymerization conditions as yielded the PANI nanofiber morphology in Figure 2, the same morphology was not observed with the BT-treated chip. This supports the notion that the 4-ATP directs the growth of the PANI on the surface of the substrate.

Although it has been clearly established in the literature[15] and in our laboratory that PANI films grow on untreated substrates, the resulting adhesion is noncovalent and mechanically weak. The most important aspect of this novel procedure is the remarkable durability of the covalently bonded nanofibers to the Au interface. For instance, samples prepared without a 4-ATP SAM do not exhibit the same improved adhesion, nor do samples of neat PANI nanofibers drop cast onto Au substrate preadsorbed with a monolayer of 4-ATP. Repeated finger abrasion and Scotch tape tests indicated improved adhesion of the covalently bonded PANI fibers compared to physisorbed samples. In addition to these simple abrasion tests, a series of acid/base exposures (doping/dedoping) showed little influence on the durability or conductivity of the PANI nanofibers. These two important physical and chemical durability experiments distinguish this method from other nanopatterning techniques for polyaniline on Au surfaces.

This communication is a preliminary report of a novel and easy method for chemically synthesizing template-free polyaniline nanofibers directly onto a functionalized Au substrate. The 4-ATP SAM acts as an template, directing the growth of the PANI nanofibers into structured morphologies. The mechanism for this process is not well understood, but the covalent attachment of the PANI nanofibers to the Au leads to improved durability over current nanofiber fabrication techniques.

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