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Polypyrrole Nanowires Grown from Single Adsorbed Polyelectrolyte Molecules**

Vera Bocharova, Anton Kiriy, Hartmut Vinzelberg, Ingolf Mönch, and Manfred Stamm*

One-dimensional nanostructures of conductive polymers (CPs) have attracted a great deal of interest as building blocks for future miniaturized nanoelectronic devices[1] and highly sensitive chemical[2] or biological sensors.[3] Several "template-less" approaches to 1D superstructures of CPs based on the self-assembly of conjugated polymers, oligomers, or monomers have been reported recently.[4] Other methods for the synthesis of CP nanowires involve chemical or electrochemical oxidative polycondensation in "hard tem-

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[*] V. Bocharova, Dr. A. Kiriy, Prof. Dr. M. Stamm
Leibniz Institute of Polymer Research Dresden
01069 Dresden (Germany)
Fax: (+49) 351-4658-284
E-mail: kiriy@ipfdd.de

Dr. H. Vinzelberg, Dr. I. Mönch
Leibniz Institute for Solid State and Materials Research
01069 Dresden (Germany)

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plates" (such as zeolites, track-etched polymeric membranes, and porous alumina),[5] or "soft templates" (surfactant micelles or liquid-crystalline phases).[6] However, for various applications, CP nanowires must be properly integrated into circuits. Therefore, at least one additional step is required, such as the release of the nanowires from the templates and/or their positioning in the device.

Polymer chemistry offers a fascinating world of structures of different architecture, composition, and functionality. The use of single polymer molecules as templates constitutes a highly promising strategy to generate nanoparticles with desired size, shape, location, and with specific properties.[7] Like macroscopic objects, single molecules of polyelectrolyte (PE) can be stretched and aligned under external forces[8] (such as centrifugal or capillary forces and electric or shear fields) and can be immobilized onto surfaces by simple procedures like casting or printing.[9] Single DNA molecules have recently been used for the fabrication of metallic[10] and conductive polymer (polyaniline, PANI) nanowires.[11] In the latter case, DNA molecules were covalently attached to a Si surface and activated with aniline, which was then polymerized. However, the PANI nanowire networks produced in this way have rather low conductivity, even when doped.[11] This low conductivity is the result of a very limited quantity of PANI being formed along the template. This restriction is governed by the quantity of aniline that can be attracted by DNA during the activation step owing to electrostatic and hydrophobic interactions. The oxidative degradation of DNA templates has been proposed by some authors[11b] as a possible factor that decreases the continuity and thus the conductivity of the DNA–PANI nanowires. We therefore assumed that the use of chemically robust synthetic PE molecules might benefit the fabrication of more conductive nanowires. Herein, we report the use of single molecules of negatively charged synthetic polyelectrolyte (polystyrene sulfonic acid, PSA) to grow continuous and conductive polypyrrole (Ppy) nanowires through selective "electroless" deposition of Ppy along PSA molecules.

Spin-coating of a PSA solution onto mica or a thermally oxidized Si wafer at high rotation speed results in stretching and alignment of the PSA chains (Figure 1 a and Supporting Information). In initial experiments, mica-deposited PSA templates were incubated in pyrrole (Py) monomer solution, then rinsed with deionized water to remove unattached Py and placed in a solution of ammonium persulfate (APS) to polymerize the Py attached to the templates. The resulting product appears in AFM images as a 1D sequence of apparently separated clusters 2–4 nm in height (Figure 1 c). These structures are considerably higher than bare PSA molecules (≈ 0.5 nm),[8] which clearly reflects the formation of Ppy clusters along the PSA molecules.

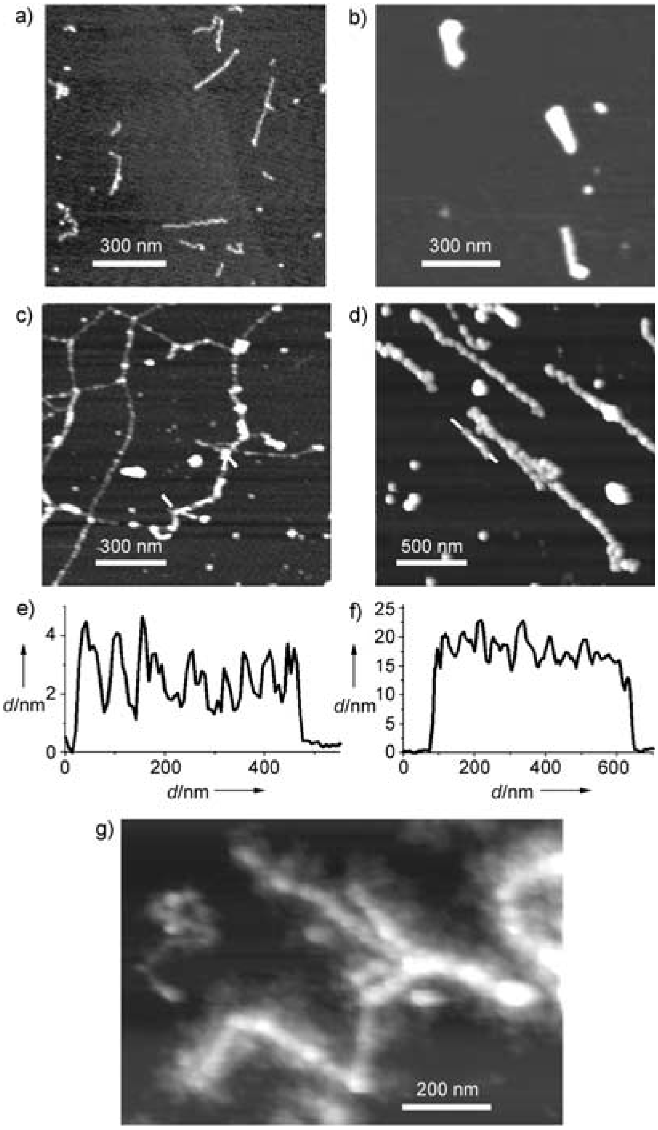

Figure 1. a) Topographic AFM image of short ($M_W = 403$ kg mol^{-1}) PSA molecules. b) AFM image of Ppy nanoparticles formed from the placement of aqueous solutions of Py and APS onto mica-immobilized PSA templates ($M_W = 403$ kg mol^{-1}) for 20 s. c) AFM image of Ppy nanoparticles formed from the incubation of mica-immobilized long ($M_W = 6940$ kg mol^{-1}) PSA molecules in Py monomer solution followed by rinsing with water and oxidation with APS. d) Surface image from the same procedure as in b), but with the use of long ($M_W = 6940$ kg mol^{-1}) PSA templates. e),f) Cross-sections along the dashed lines in c) and d), respectively. g) Surface image from the same procedure as in d), but with an APS concentration fivefold smaller.

To produce more continuous and thicker Ppy nanowires, we performed electroless deposition of Ppy.[12] PSA chains were deposited onto substrates in the stretched conformation and were then treated with aqueous solution of Py and APS for up to 60 s (for details, see Experimental Section and Supporting Information). AFM investigations revealed the successful formation of PSA–Ppy nanowires with diameters that vary from a few to hundreds of nanometers depending on the polymerization time (Figure 1 c,d). As expected for the template method, the aspect ratio of the nanowires (≈ 7 and ≈ 100 for the nanowires in Figures 1 b and d, respectively) is dependent on the contour length of the PSA molecules. The resulting nanowires, however, are somewhat shorter than the corresponding templates (usually by a factor of 1.5–3, depending on the polymerization time). The observed partial shrinkage of the nanowires is the result of attractive interactions between hydrophobic segments of Ppy, which can be avoided if the PSA templates are properly fixed to the substrate.

Close inspection of the AFM images shows that thin nanowires (∅ < 5 nm) are still sequences of isolated Ppy clusters, although the nanowires become quasi-continuous (the clusters are closely packed) if their diameter exceeds 10 nm. The clusters are localized predominantly along the PSA chains, which indicates a rather high selectivity of the deposition.

In general, growth of Ppy nanowires can be realized according to two schemes: 1) precipitation of hydrophobic Ppy nanoparticles preformed in solution onto the hydrophobic PSA–Py complex, and 2) growth of Ppy from the PSA–Py complex.[13] We performed a set of experiments to decide which scheme is realized in our case. For this, we prepared colloidal dispersions of Ppy by mixing solutions of Py and APS followed by quenching with excess sodium bisulfite (SBS) as a reducing agent. The colloids prepared in this manner were placed on a substrate with pre-adsorbed PSA template molecules. However, the formation of Ppy nanowires was never observed in these experiments regardless of the activation time, size, and concentration of Ppy colloids used. Thus, the prerequisite for nanowire growth is the presence of both Py monomer and oxidizing agent in solution. This result clearly excludes the "grafting-to" and supports the "grafting-from" scheme for Ppy nanowire formation.

Varying the reaction conditions influences the morphology of the Ppy nanowires. With excess oxidant, the resulting nanowires display a relatively smooth morphology (Figure 1 c,d). In contrast, a lack of oxidant leads to the formation of "hairy nanowires" that resemble "molecular brushes"[14] (Figure 1 g). These observations are consistent with the "grafting-from" scheme of Ppy growth.[15]

Electrical characterization was performed for the larger Ppy nanowires (Figure 2). For this, Ppy nanowires 50–60 nm thick were grown onto devices with gold micro-electrodes (the distance between the electrodes was 1 μm). The amount of PSA–Ppy nanowires produced was adjusted to allow only a few Ppy nanowires to bridge the electrodes; the other nanowires remained disconnected. This allowed us to measure the dc conductivity of individual nanowires. After deposition, the device was carefully investigated by AFM, and the amount, location, and size of all nanowires was noted. These electrical measurements revealed the resistance of a single nanowire to be ≈0.6–1.5 MΩ, which corresponds to a conductivity of ≈1–3 S cm^{-1}. This rather high conductivity approaches the conductivity of Ppy in bulk.[16] The nanowires display a linear current–voltage dependence (Figure 2 h, inset), which reflects good contacts between the nanowires and the electrodes and good connectivity of the Ppy clusters along the PSA molecule. To break a certain nanowire, we slowly increased the potential between the electrodes until an abrupt increase in resistance was observed. The significant resistance increase after this procedure (from 1.1 to 21 MΩ for the nanowire in Figure 2 b) proves that the measured conductance is indeed caused by this particular nanowire. On the other hand, AFM inspection of the broken nanowires reveals the formation of gaps (usually one or two per broken wire, Figure 2 b–g). An even more pronounced decrease of the conductance (the resistance increased from a few MΩ to a

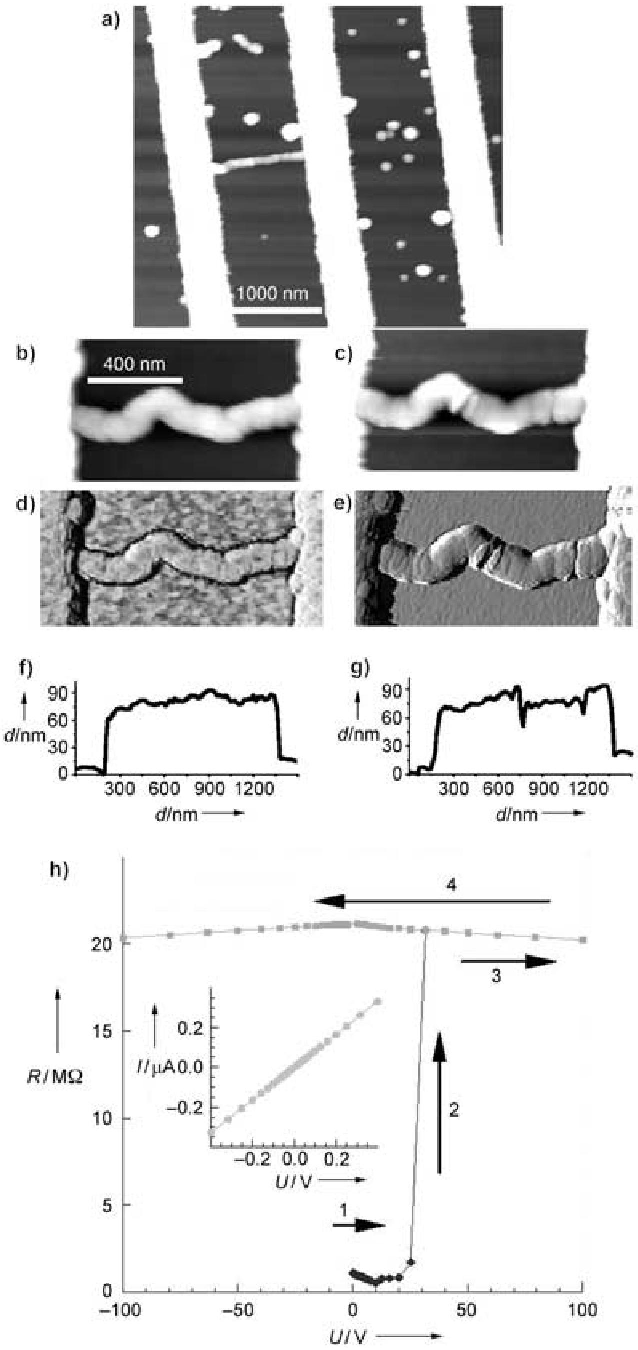

Figure 2. a) AFM topography image of a representative Ppy nanowire with a resistance of ≈1 MΩ. b),c) High-magnification topography and d),e) phase AFM images of the pristine Ppy nanowire bridging two microelectrodes. The intact nanowire shown in b) and d) was broken by applying a high voltage (25 V; c) and e), respectively). f),g) Cross section profiles of the nanowires in images b) and c), respectively. h) Room-temperature resistance–current characteristics of the pristine nanowire with a resistance of 1.1 MΩ; numbered arrows indicate the sequence of increasing (1–3, ◆) and subsequent decreasing (4, ■) voltage. The same nanowire after breakage with high voltage displays a resistance of ≈21 MΩ. (Inset: demonstration of the linear I–U dependence of the pristine nanowire at low voltage.)

few GΩ) was observed when the nanowires were mechanically broken by movement of the AFM tip operating in contact mode (Supporting Information).

Finally, we evaluated the possibility of using Ppy nanowires as active elements in sensors. In general, the conductivity of Ppy can be modulated by changing the doping level: the conductivity is high in an oxidized (doped) state and low in a reduced (de-doped) form. Alternatively, Ppy in the reduced form can be doped by acids and de-doped by bases. As expected, the Ppy nanowires synthesized by oxidative polycondensation display a rather high conductivity that changes only slightly upon further exposure to acidic (HCl) or basic (NH_3) vapors. To make the conductivity of the Ppy nanowires sensitive to acids and bases, they were reduced by rinsing with an aqueous solution of $NaBH_4$ ($1\,g\,L^{-1}$), which resulted in an increase in resistance from 1–5 MΩ for doped nanowires to more than 1 GΩ for the de-doped wires. In the reduced state, the nanowires reversibly change their resistance upon exposure to HCl and NH_3 vapors from several MΩ to a few GΩ.[17]

In conclusion, we have developed a simple chemical route to conductive Ppy nanowires by the grafting of Ppy from isolated synthetic polyelectrolyte molecules. The location and length of the synthesized Ppy nanowires are defined by the location and length of adsorbed single-molecule templates. The diameter of the nanowires can be varied from a few nanometers to hundreds of nanometers by adjusting the polycondensation time and concentration of the reagents. The dc conductivity of individual Ppy nanowires approaches the conductivity of Ppy in bulk. This result opens up broad opportunities for the fabrication of electronic devices and sensors at a molecular level.

Experimental Section

Polystyrene sulfonic acid (PSA; $M_W = 6940\,kg\,mol^{-1}$, PDI = 1.3; $M_W = 403\,kg\,mol^{-1}$, PDI = 1.3) was purchased from the Polymer Standards Service, Mainz, Germany. Ammonium persulfate (APS), pyrrole (Py), and all other chemicals were purchased from Aldrich.

Ppy nanowires: Stretched PSA molecules were deposited from aqueous solution $(0.01\,g\,L)^{-1}$ onto clean Si wafers or freshly cleaved mica by spin-coating at high speed (10000 rpm). Py ($3\,g\,L^{-1}$, 50 μL) and APS ($30\,g\,L^{-1}$, 50 μL) in deionized water were placed for a limited time (10–60 s) onto the substrates with predeposited PSA molecules. Afterwards, the samples were rinsed with water, dried, and examined by AFM (NanoScope IV-D3100, Digital Instruments, Santa Barbara, USA) in tapping mode. The diameter of the Ppy nanowires was dependent on the polymerization time and was found to be < 10, 10–30, and 30–60 nm for polymerization times of 15, 30, and 60 s, respectively. "Hairy nanowires" were produced with a similar procedure in which the only difference was a lower concentration of APS ($6\,g\,L^{-1}$).

For electrical measurements (Keithley 236 Source-Measure Unit), 18-finger gold micro-electrodes (step height: 50 nm; width: 500 nm; separation: 1 μm) were fabricated by photolithography on a Si wafer with an insulating SiO_2 layer (300 nm).

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