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# Synthesis of Diphenylalanine/Polyaniline Core/Shell Conducting Nanowires by Peptide Self-Assembly**

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Polyaniline (PANI) is a unique type of conducting polymer, the doping state of which is controlled by simple acid/base doping/dedoping with about a $10^9$-fold conductivity change.[1] Beside its excellent electrical properties,[1a,e] PANI has clear advantages over other conducting polymers, such as its straightforward synthesis, high environmental stability, and good processibility.[2] These features enable its application in various fields.[3–7] Potential applications of PANI include its use in gas sensors,[3] biosensors,[4] actuators/artificial muscles,[5] materials for superhydrophobic[6a,b] and anticorrosive[6c] coatings, and electronic devices.[7] The performance of nanostructured PANI, including sensitivity and response time in the detection of analytes, has been reported to be superior to that of its bulk counterpart.[3] However, there remain challenges in the synthesis of nanostructured PANI, for example, in the control of its size and morphology.[1c,8]

Herein, we report the synthesis of novel peptide/PANI core/shell conducting nanowires and hollow PANI nanotubes by peptide self-assembly. Peptide-based self-assembled nanomaterials have drawn much attention because of their unique properties, such as their molecular-recognition capability and functional flexibility.[9] In this study, we used diphenylalanine (FF) as a building block. Diphenylalanine is one of best-known self-assembling hydrophobic peptides for the fabrication of peptide nanostructures with novel mechanical, electrochemical, and optical properties.[10,11] The peptide nanowires (PNWs) were prepared by the high-temperature self-assembly of FF in the presence of aniline vapor according to our recently described procedure.[11a] We found that the PNWs were coated readily and uniformly by PANI to form PNW/PANI core/shell nanowires. The formation of a PANI shell on PNWs was confirmed by multiple analytical techniques, such as electron microscopy, Fourier transform infrared (FTIR) spectroscopy, and cyclic voltammetry. Our results show that PANI grows preferentially along the sidewall of PNWs through a specific interaction between PNWs and PANI during the polymerization process. The thickness of the PANI coating on the PNWs could be controlled by varying the reaction time and the number of coats of PANI. We could also fabricate hollow PANI nanotubes by selectively removing the PNW core from PNW/PANI nanowires.

We synthesized PNW/PANI core/shell nanowires as illustrated in Figure 1 a. An amorphous peptide thin film was prepared by placing and drying a drop of a solution of FF in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) on a solid substrate under anhydrous conditions.[11b] As a next step to induce the growth of vertically aligned PNWs from the amorphous film through a self-assembly process, the prepared amorphous peptide film was treated with aniline vapor at 100 °C for 12 h.[11a] The resulting PNW film was cooled to room temperature and then immersed in a polymerizing solution of aniline to coat the PNW structures with PANI (Figure 1 a). PANI was synthesized by using ammonium persulfate (APS, 40 mM) as an oxidant, followed by the oxidative polymerization of aniline (160 mM) in 1 M HCl solution.[2a,12] Scanning electron microscopy (SEM) images show the morphological difference between PNWs before (Figure 1 b) and after coating with PANI (Figure 1 c).

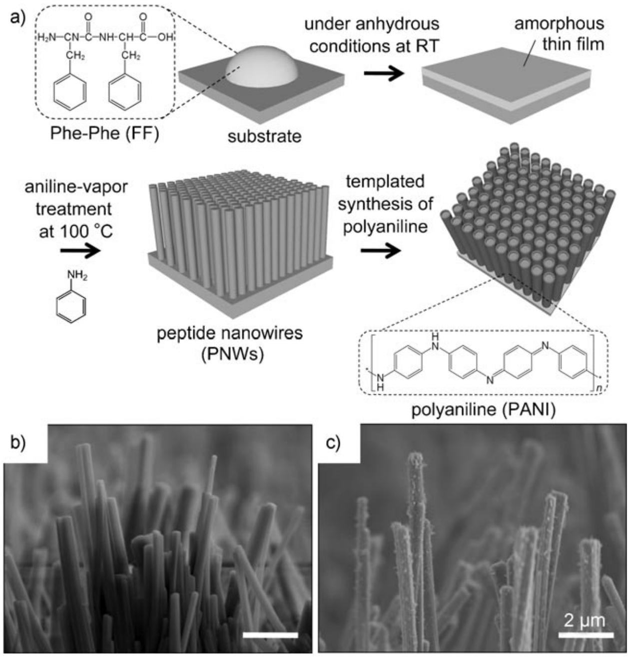

***Figure 1.*** a) Synthesis of the core/shell nanowires. b,c) Cross-sectional SEM micrographs showing vertically grown bare PNWs (b) and PNWs coated with PANI (c).

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Whereas PNWs without a PANI coating had a smooth surface and an average diameter of 200 nm, PNW/PANI had a rugged surface with a slightly greater diameter. The morphology of PANI formed on PNWs was significantly different from the typical fibrillar network structure of PANI synthesized in a bulk solution (see Figure S1 in the Supporting Information).

High-magnification SEM (Figure 2 a) and scanning transmission electron microscopy (STEM) images (Figure 2 b) also support the formation of the core/shell structure of PNW/PANI. We observed that the PANI shell grows preferentially along the sidewall of PNWs, which indicates that the PANI coating on PNWs is not formed by nonspecific adsorption of PANI during the polymerization process. Further studies are needed to unveil the molecular interaction between PANI and FF/aniline incorporated in the PNWs. A report about the enantioselective discrimination of chiral phenylalanine with a PANI film[4b] suggests a possible interaction between FF and PANI. We investigated the effect of four different dopant acids (1N)—HCl, $HClO_4$, $HNO_3$, $H_2SO_4$—on the formation of the PANI coating on the PNWs and its morphology, and found that the PANI layer was uniform along the PNWs. The morphology of the PNW/PANI nanowires was almost identical in each case, regardless of the dopant acid used (see Figure S2 in the Supporting Information).

To observe the evolution of the size of the PANI shell with time, PANI polymerization on the PNW template was carried out with a more dilute solution of the aniline monomer. The concentration of aniline was decreased by a factor of 10 (to 16 mM), and the APS concentration was maintained at 40 mM, since it is difficult to observe the morphological evolution of the PANI coating at a higher concentration of aniline as a result of the high reaction rate. We did not observe any morphological change in the initial 30 min by SEM analysis (see Figure S3 in the Supporting Information), a result attributed to the lag phase for the nucleation of PANI. The thickness of the PANI shell increased rapidly after 30 min and reached saturation (at a thickness of approximately 50 nm) after 60 min. The thickness of the PANI shell in PNW/PANI nanowires could be increased by repeating the polymerization process. Because PNW/PANI nanowires adhered well to their substrate unless scratched or sonicated, we could repeat the PANI coating process multiple times without cumbersome separation and dialysis steps. The thickness of PNW/PANI nanowires increased from 200 nm to 1 μm after four coating steps (see Figure S4 in the Supporting Information).

We characterized the PNW–PANI nanostructures by powder X-ray diffraction (XRD) and FTIR spectroscopy. Both the PNWs and the PNW/PANI film exhibited characteristic XRD peaks (Figure 3 a). The XRD patterns were almost identical to each other. We could therefore conclude that the crystal structure of the PNWs remained unchanged under the harsh processing conditions. APS is a very strong oxidant, and the reaction medium is a highly acidic aqueous solution (1M HCl). Thus, the results show that the PNW is a robust template that remains stable under highly acidic and strongly oxidizing conditions. From the FTIR spectra of the PNWs and PNW–PANI (Figure 3 b), we could confirm the chemical identity of the outer coating shell as PANI. Prior to coating with PANI, the PNW film exhibited a strong peak at 1654 $cm^{-1}$ in the amide I band region. This peak can be

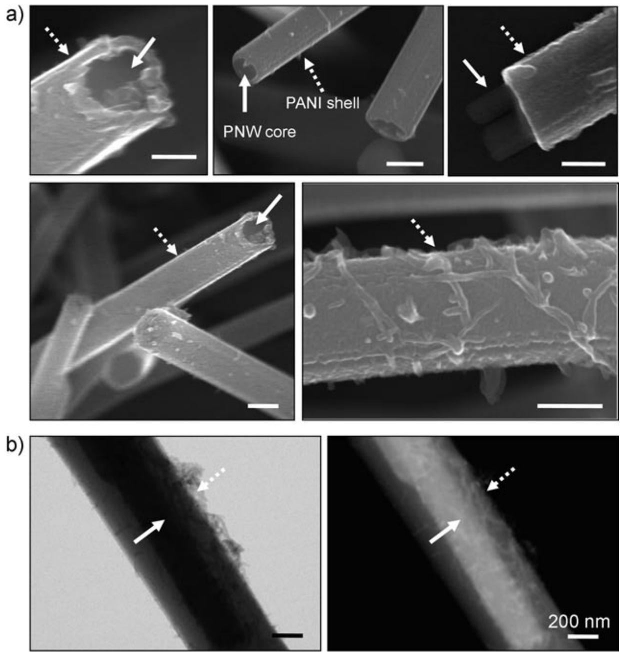

*Figure 2.* a) SEM and b) STEM images of PNW/PANI core/shell nanowires. Arrows indicate the PNW core (solid arrows) and PANI shell (dotted arrows). The core/shell structure of the PNW/PANI nanowires was clearly visible in STEM micrographs taken in a bright field imaging mode (left) and in a high angle angular dark field (HAADF) imaging mode (right).

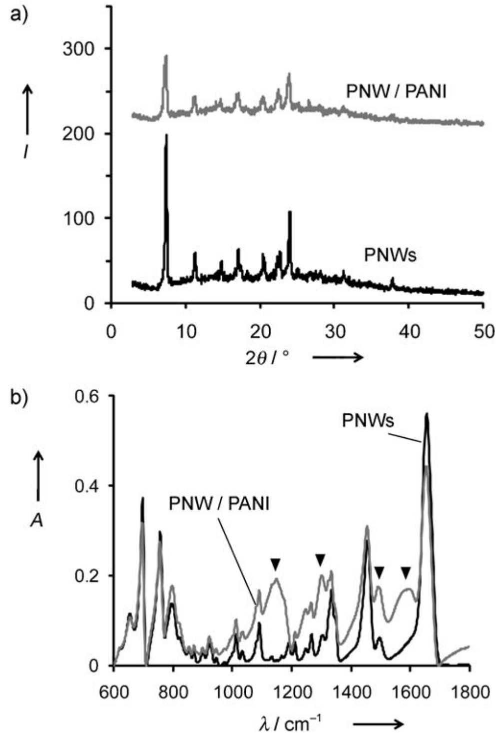

*Figure 3.* a) Powder XRD patterns and b) FTIR spectra of PNWs before and after PANI-shell formation. New peaks marked with arrows correspond to vibrations of quinoid and benzenoid moieties present in the PANI shell.

attributed to a predominant β-sheet conformation.[13] The FTIR spectrum of the PNWs did not change significantly after the formation of the PANI shell, except for the appearance of new peaks (marked with arrows in Figure 3 b), which stem from PANI molecules. FTIR peaks at 1149/1594 $cm^{-1}$ and 1303/1494 $cm^{-1}$ correspond to quinoid and benzenoid vibrations, respectively.[4c,14]

We investigated the doping/dedoping and redox activity of PNW/PANI nanowires by UV/Vis spectroscopy and cyclic voltammetry. The chemical doping and dedoping of the PNW/PANI film was achieved by exposing it to HCl and $NH_4OH$ vapor, respectively. We could clearly observe the doping and dedoping of PNW/PANI with the naked eye, since strong color changes to green and dark blue occurred upon doping and dedoping, respectively. The resulting UV/Vis spectra of the PNW/PANI film (Figure 4 a) were almost identical to those of pure PANI synthesized by the conventional method.[3a] The electroactivity of PNW/PANI nanowires was characterized by cyclic voltammetry by using a PNW/PANI-coated gold disk electrode as the working electrode. The two redox peaks observed for the PNW/PANI nanowires (Figure 4 b) correspond to the transition of PANI from fully reduced leucoemeraldine to the partially oxidized emeraldine salt and the transition from the emeraldine salt to fully oxidized pernigraniline.[4c] We also found that the anodic and cathodic peak currents of the PNW/PANI-coated electrode were proportional to the square root of the potential sweep rate (see Figure S5 in the Supporting Information). The square-root proportionality between the sweep rate and the peak currents is indicative of diffusion-limited peak currents.[4c]

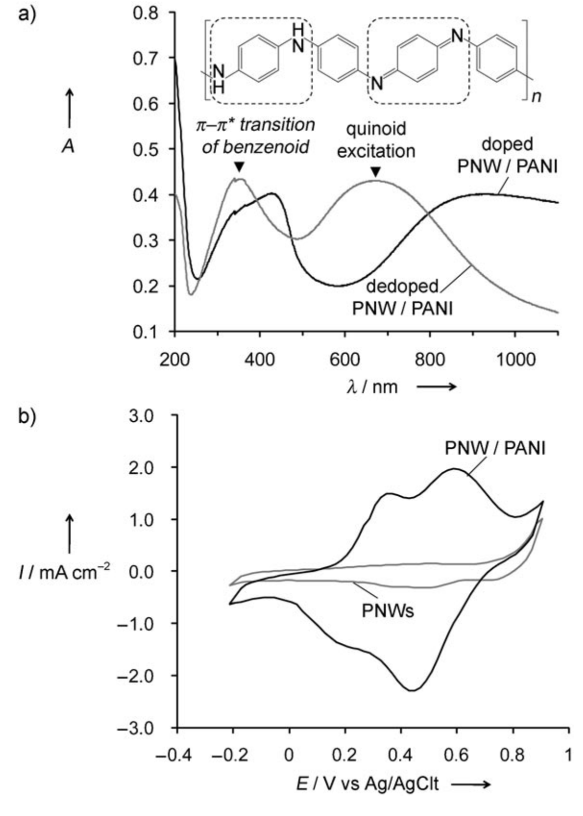

*Figure 4.* Characterization of the redox properties of PNW/PANI nanowires by a) UV/Vis spectroscopy and b) cyclic voltammetry. Cyclic voltammograms of the PNW/PANI- or PANI-coated gold disk electrodes were measured in 1 M HCl solution in the range −0.2–0.9 V (versus Ag/AgCl) at a scan rate of 200 $mV s^{-1}$

Next, we attempted to fabricate hollow PANI nanotubes by selectively removing the PNW core from the PNW/PANI nanowires. In the case of FF nanotubes self-assembled in aqueous solution,[10a] we could selectively dissociate or remove peptide nanostructures by enzymatic hydrolysis. In the present study, however, we could not utilize selective enzymatic degradation of the peptide-nanostructure template because of the resistance of the PNWs to enzymatic proteolysis. The PNWs remained unchanged even after treatment with a solution of proteinase K (20 units $mL^{-1}$; 50 mM 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), pH 8.0) for 12 h at 60 °C, under which conditions the enzyme exhibits maximum activity (data not shown). Instead, we removed the PNW core with the solvent HFIP, which can dissolve peptide aggregates into monomeric states.[10a,15] Since, like PNW, PANI is also soluble in HFIP, we cross-linked PANI to decrease its solubility, either by incubating PNW/PANI nanowires at 200 °C for 1 h (thermal cross-linking[16]) or by exposing them to a strong camera flash (photothermal cross-linking or flash welding[2b]; Figure 5 a). High-temperature or flash-welding treatment did not affect the structure or morphology of PNW/PANI nanowires. We could obtain PANI nanotubes by treating thermally or photothermally cross-linked PNW/PANI nanowires with HFIP (Figure 5 b,c). From the diffraction patterns of the PNW/PANI nanowires before and after treatment with HFIP, we could confirm that the PNW core was removed completely (see Figure S6 in the Supporting Information). The thickness of the PANI-nanotube wall could be increased by carrying out multiple PANI coating steps (Figure 5 c).

In summary, we have shown that self-assembled peptides can be used as a robust and useful template for the synthesis of conducting PANI nanostructures. The templated polymerization of PANI on PNWs resulted in the formation of PNW/PANI core/shell nanostructures, and the thickness of the PANI shell could be controlled readily either by varying the reaction time or by applying multiple PANI coatings. We confirmed through doping/dedoping tests and electrochemical characterization that the PNW/PANI nanowires were active both chemically and electrochemically. Whereas template removal is often a problem in the conventional templated synthesis of PANI nanostructures, we could fabricate hollow PANI nanotubes without difficulty by the selective removal of the PNW from PANI-coated PNWs. This study demonstrates that self-assembled peptide nanostructures can be used as a versatile template for the synthesis of functional nanomaterials.

## Experimental Section

Synthesis of coated nanowires: Diphenylalanine (FF; Bachem AG, Switzerland) was dissolved in HFIP at a concentration of 50 mg $mL^{-1}$. An amorphous peptide thin film was prepared by drying a drop of the resulting solution on a solid substrate (e.g., Si), and was then treated with aniline vapor at 100 °C for 12 h to promote the growth of

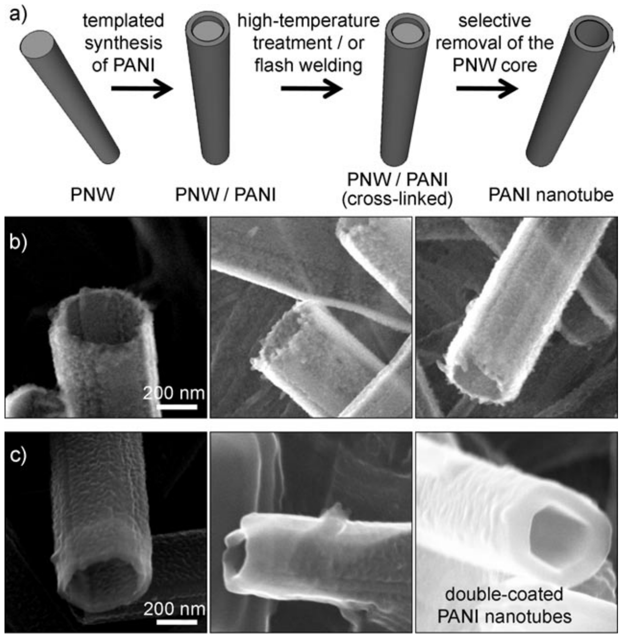

***Figure 5.*** a) Fabrication of PANI nanotubes by selective removal of the PNW core from PNW/PANI core/shell nanostructures. b,c) Electron micrographs showing the PANI nanotubes fabricated by the b) thermal or c) photothermal cross-linking of PNW/PANI nanowires and treatment with HFIP. Double-coated PANI nanotubes are shown in the right-hand image in (c).

vertically aligned PNWs from the film.[11] The PNW film was cooled to room temperature and then immersed in a polymerizing solution of aniline (prepared by rapidly mixing a solution of aniline (320 mM) in 1M HCl with a solution of ammonium persulfate (APS, 80 mM) in 1M HCl) for the desired length of time without stirring. After the completion of polymerization, the nanowire film was washed with 1M HCl and dried in a stream of $N_2$ gas.

Fabrication of polyaniline nanotubes: Before selective removal of the FF core, the PANI shell was cross-linked either by heating the PNW/PANI nanowires at 200 °C for 1 h or by exposing the nanowires several times to a strong camera flash.[2] The core/shell nanowire film was then treated with HFIP to selectively remove the peptide core. The resulting film of hollow PANI nanotubes was washed with HFIP and dried with $N_2$ gas.

Characterization: The synthesized PNW/PANI core/shell nanowires were imaged with an S-4800 SEM instrument and an HD-2300 A STEM instrument (Hitachi High-technologies Co., Japan). For STEM imaging, the nanowire film was sonicated in deionized water to detach the nanowires from the substrate, and a formvar-coated Cu TEM grid was treated with a drop of the nanowire dispersion. For the measurement of UV/Vis absorption, the PNW film with or without a PANI coating was grown on a quartz plate. The film was kept as thin as possible (less than 100 nm) to prevent absorption saturation in the UV spectral region. Absorption spectra of the PNW/PANI nanowires were measured before and after exposure to HCl or $NH_4OH$ vapor with a BioSpec-Mini spectrophotometer (Shimadzu Co., Japan). FTIR spectra were obtained in an attenuated total reflection (ATR) mode with a Hyperion 3000 spectrometer (Bruker Optics Inc., Germany) at a resolution of 4 cm$^{-1}$. For the electrochemical characterization of PNW/PANI nanowires, PNWs were grown on a gold disk electrode (working electrode, 0.1 cm$^2$) and then coated with PANI. Cyclic voltammograms of the PNW/PANI nanowires were measured in 1M HCl solution with a WMPG 1000 potentiostat/galvanostat (WonATech Co. Ltd., Korea) by using a platinum counter electrode and an Ag/AgCl (3M NaCl) reference electrode. The structure of the PNWs before and after coating with PANI was analyzed with a D/MAX-IIIC powder X-ray diffractometer (Rigaku Co., Japan) under the following conditions: scan speed, 3° min$^{-1}$; Cu$_{K\alpha}$ radiation, $\lambda = 1.5418$ Å; scan range, 2–50°.

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