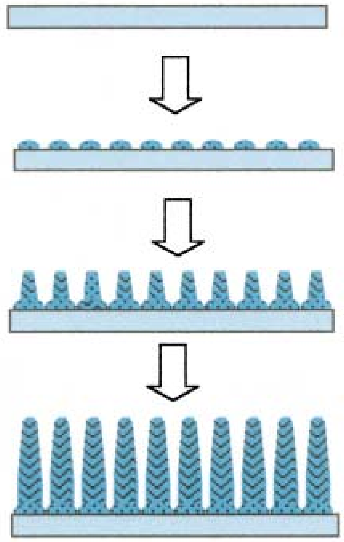
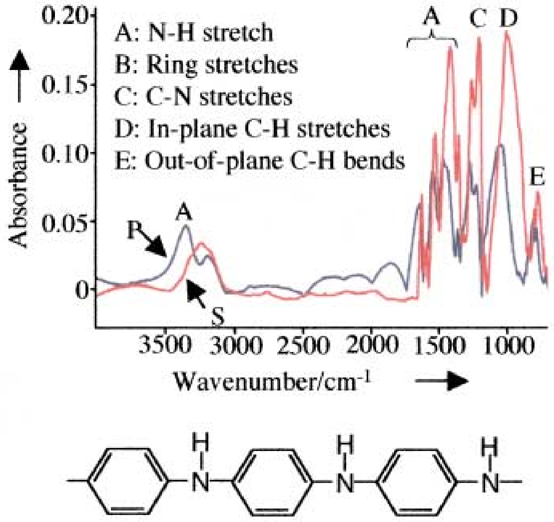
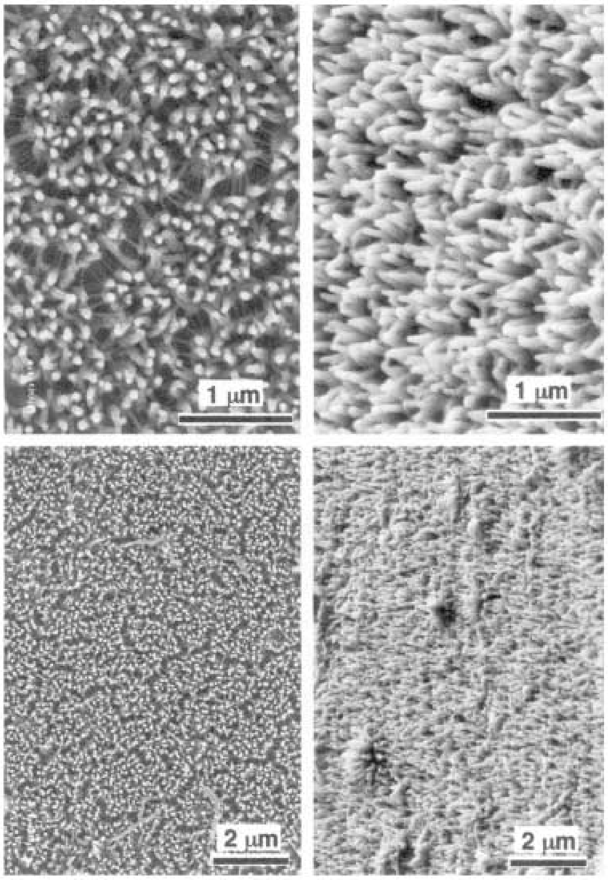
Large arrays of oriented and molecularly aligned conductive polymer nanowires and their applications



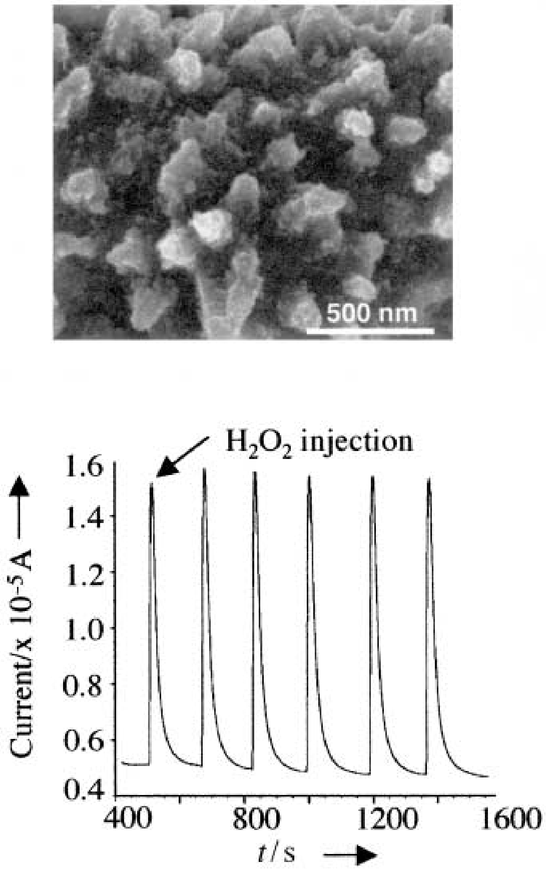
Templateless growth



Molecular alignment



Uniform and oriented nanowires



Chemical and biosensing

Templateless Assembly of Molecularly Aligned Conductive Polymer Nanowires: A New Approach for Oriented Nanostructures

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Abstract: Although oriented carbon nanotubes, oriented nanowires of metals, semiconductors and oxides have attracted wide attention, there have been few reports on oriented polymer nanostructures such as nanowires. In this paper we report the assembly of large arrays of oriented nanowires containing molecularly aligned conducting polymers (polyaniline) without using a porous membrane template to support the polymer. The uniform oriented nanowires were prepared through controlled nucleation and growth during a stepwise electrochemical deposition process in which a large number of nuclei were first deposited on the substrate using a large current density. After the initial nucleation, the current density was reduced stepwise in order to grow the oriented nanowires from the nucleation sites created in the first step. The usefulness of these new polymer structures is demonstrated with a chemical sensor device for H_2O_2, the detection of which is widely investigated for biosensors. Finally, we demonstrated that controlled nucleation and growth is a general approach and has potential for growing oriented nanostructures of other materials.

Keywords: conducting materials · nanostructures · sensors · ZnO

Introduction

Recently rational design and synthesis of extended and oriented nanostructures, such as oriented carbon nanotubes, semiconducting nanowires, oriented oxides, and metals have attracted wide attention. However, there have been few reports on oriented nanostructures of polymers such as oriented polymer nanowires. Many methods have been reported for the preparation of oriented nanostructures, but most of these methods cannot be applied to polymer materials. For example, chemical vapor deposition is a widely used method to prepare oriented carbon nanotubes,[1, 2] ZnO,[3, 4] Si,[5] silicon carbide/nitride,[6] but is not suitable for polymers. Other methods, such as hydrothermal solution synthesis used for oriented ZnO nanorods,[7, 8] have not been investigated for polymer chemistry.

In this paper we are particularly interested in the preparation of oriented conducting polymer nanostructures, a very important class of electrochemical active materials.[9, 10] Electroactive and chemically active polymers with oriented open nanostructures are highly desirable for applications ranging from chemical and biological sensing and diagnosis, microelectronic devices and interconnects, energy conversion and storage (photovoltaic cells, batteries and capacitors, and hydrogen storage devices), catalysis, optical emission, display and data storage. The high surface area and high porosity associated with the open nanostructures, as well as their favorable orientations, usually translate into high capacity and high efficiency for the devices.

Several methods, including electrospinning[11, 12] and polymer templated electrochemical synthesis,[13] have been used for preparing conducting polymer nanofibers. Highly porous conducting polymer films based on techniques like dip coating on porous supports have been widely investigated for separation and sensing,[14] but the random pore structures and misalignment of the polymers are not ideal for high efficiency and fast kinetics. The controlled orientation is more critical for other applications such as in light emitting and microelectronic devices. To date, oriented conducting polymer nanostructures, including oriented polypyrrole or polyaniline nanorods or nanotubes, were mostly obtained with a porous membrane as supporting templates.[15–20]In this approach, a substrate material with oriented nanoporosity is used as the mold (template),[21] which was filled with the desired polymer. Subsequently the substrate is partially or completely removed to leave the desired nanowires that

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replicate the size and the ordering of the template. The dimensions and the morphology of the polymer structures are defined (or limited) by the porous support. Recently Gao et al.[22] used oriented carbon nanotubes as the template to electrochemically deposit a thin polyaniline polymer coating on the surface of the carbon nanotubes.

The formation of arrays of oriented polymer rods or tubes using the membrane templating approach involves carefully etching away the membrane without disturbing the conducting polymer structure. Recent results indicate that oriented structures were only obtained for rods and tubes with a large diameter.[23] Etching away the membrane supports for nanorods or tubes with a diameter smaller than 100 nm caused the polymer to collapse into misoriented structures.[23] In addition, the necessity to use a porous support membrane limited the applicability of this approach to simple geometry or flat surfaces.

The purpose of this paper is to report a new method for direct synthesis of large arrays of uniform and oriented nanowires of conducting polymers (polyaniline) on a variety of smooth and textured substrates (Pt, Si, Au, carbon, silica, etc.) without using a supporting porous template to confine the polymers.[24] Through controlled nucleation and growth using a step-wise electrochemical deposition process, aniline molecules spontaneously assembled into desired uniform nanowires. Furthermore, the polymer molecules are also well aligned within the nanowires. The usefulness of these new polymer structures is demonstrated with a chemical sensor for H_2O_2, the detection of which is widely investigated for biosensors. Finally, we compare controlled nucleation and growth of polymers and ZnO, and point out that the new approach may have potential for oriented nanostructures of a wide range of materials.

Large Arrays of Oriented Polyaniline Nanowires

The concept of templateless growth of polymer nanowires: The main idea behind this approach is schematically illustrated in Figure 1. We speculated that we would be able to grow oriented polymer nanowires if we could separate the nucleation and growth events. In the first step, we used a high current density to generate the necessary nucleation centers on the substrate surfaces. After the completion of the first step, the current density was reduced two times for the polymers to grow from the nucleation sites.

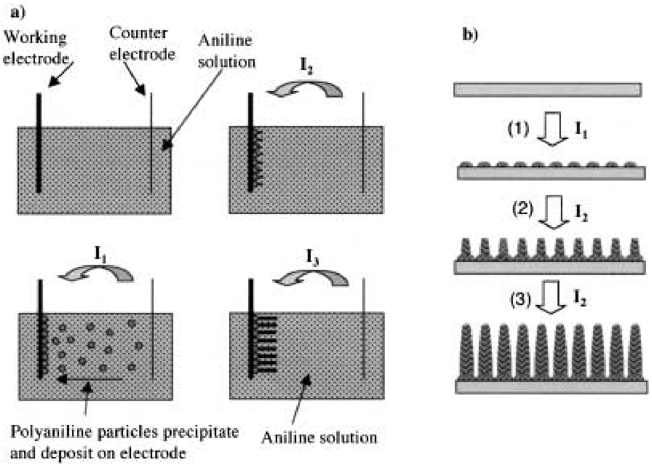

Figure 1. Schematic drawing of the steps for growing oriented polymer nanowires. a) Schematics of the reactions in the electrochemical cell. b) Schematics of the nucleation and growth.

A typical recipe involves electrochemical deposition in an aniline containing electrolyte solution (0.5 M aniline and 1.0 M perchloric acid ($HClO_4$)) using the substrate as the working electrode and contains three steps.[24] Polyaniline was grown from the surface of a platinum plate by redox polymerization of aniline, using a programmed constant-current method designed to control the nucleation and growth rate. The following procedure was used to prepare the samples reported in this paper: 0.08 mA cm^{-2} for 0.5 h, followed by 0.04 mA cm^{-2} for 3 h, which was followed by another 3 h at 0.02 mA cm^{-2}. Besides Pt, other substrates, including Ti, Au, and Si were also investigated and were found to yield similar results. Controlled experiments were also conducted to study the morphology without the step-wise control of the current density. In this case the polyaniline films were prepared by electrochemical deposition at 0.08 mA cm^{-2} for extended period of time (3 h).

The proposed mechanism for growing oriented polymer nanowires are supported by Figure 2. Figure 2a shows a micrograph obtained from a field emission electron microscope (SEM) of a sample after the first step (0.08 mA cm^{-2} for 0.5 hour). At this stage the polymer was deposited on the surface as small particles about 50 nm in diameter. If the electrochemical deposition was extended for several hours under the same current density (0.08 mA cm^{-2}), a much higher density of polymer was deposited (Figure 2b), but long oriented nanowires were not observed. In addition, thick branched polymer fibers hundreds of nanometers in diameter began to form at many locations. Only when the current density was successively reduced were uniform and oriented nanowires formed (Figure 2c).

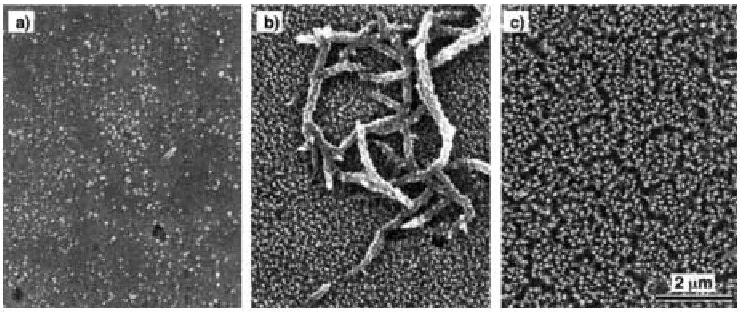

Figure 2. Growth stages of polyaniline on Pt. a) Polyaniline particles after 0.5 h at 0.08 mA cm^{-2}. b) Polyaniline particles and fibers after 3 h at 0.08 mA cm^{-2}. c) Oriented polymer wires after step-wise growth.

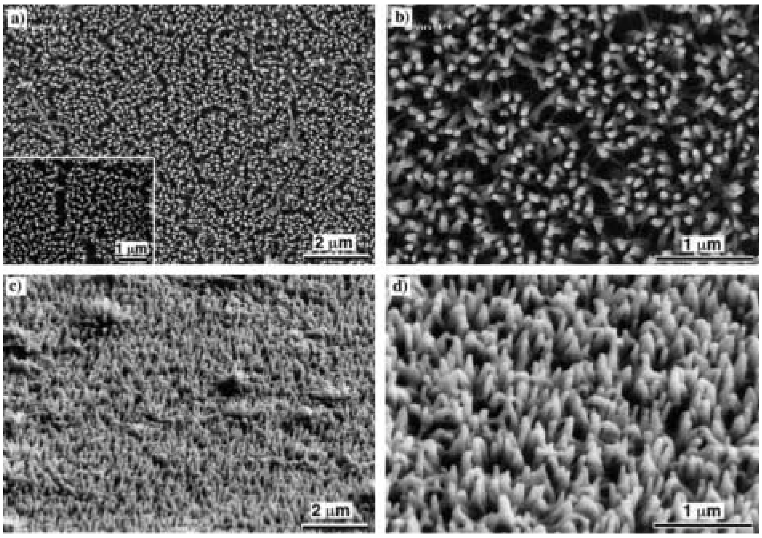

Figure 3. SEM micrographs of oriented polyaniline on Pt. a) Low magnification face-on. b) High magnification face-on. c) Tilted view, low magnification. d) Tilted view, high magnification. The insert in Figure 3a is the image of the oriented nanowires on Si substrate.

The morphology of the film by step-wise growth was examined under SEM. When viewed from an angle perpendicular to the surface at a low magnification (top view, Figure 3a), the film appears to contain uniform white spots all across the surface. At a higher magnification (Figure 3b), it is revealed that the white spots are actually the tips of uniform nanowires, mostly oriented perpendicular with respect to the substrate. The diameters of the tips range from 50 to 70 nm. Some thin filament structures, 20 or so nanometers in diameter, can also be observed at the base of the oriented nanowires. When the sample is tilted, the morphology and the orientation of the nanowires are clearly revealed (Figure 3c and d). The oriented nanowires are fairly uniform in length and diameter, but the diameter is slightly smaller at the tip position than at the base position. Judging from the tilt angle (about 40°), the nanowires are about 0.8 µm in length. We have also prepared similar oriented conducting polymer nanowires on other substrates, such as silicon, glass, gold. The insert in Figure 3a shows typical oriented nanowire structures grown on Si wafers.

Hierarchical structures: Since the method reported in this paper does not involve porous membranes to support the polymer, it is applicable to surfaces of complex geometry. The oriented polymer nanowires will conform to the surface topologies of the substrate, and thus allow us to build hierarchical structures. Here we show two examples (Figure 4a): the first one is oriented polymer nanowires grown on monolayers of colloidal silica spheres, and the second one is oriented polymer nanowires on a textured surface.

We first deposited a monolayer of closely packed silica spheres on the substrate and expected that the polymer nanowires would grow with an orientation perpendicular to the particle surfaces (not the substrate surface). In order to illustrate how the polymer grows from the silica particles, we first show the results in an area where the particles were not closely packed. Figure 4b shows the surface roughness induced by the presence of silica particles, which follow the contours of the individual particles. The radial growth of the polymer wires around the particles is clearly illustrated. Figure 4c shows the morphology of the polymers across the edge of the silica monolayer. Close to the front where there are no silica particles, the polymers are oriented vertically, but on top of the silica particles the polymer orientation is disrupted and randomly connected. In the area occupied by a monolayer of densely packed silica spheres, the radial growth of polymer nanowires overlap and form three-dimensionally interconnected polymer networks (Figure 4d to e).

Oriented polyaniline nanowires were also prepared on textured surfaces as shown in Figure 4 f and g. The polyaniline nanowires on complex geometry may be useful for applications such as active filtration membranes and high surface area supports for sensors.

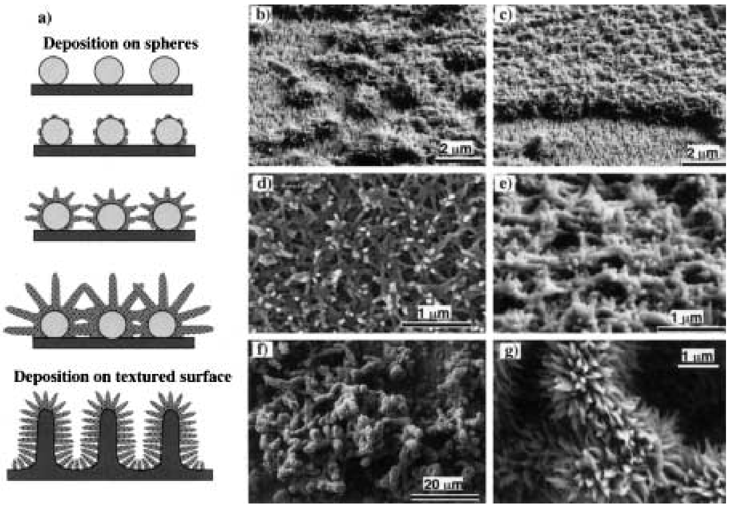

Figure 4. Hierarchical nanostructures from oriented nanowires. a) Growth of nanowires on silica spheres (top four figures) and on textured surfaces (bottom figure). b) Radial growth of the nanowires from single silica particles. c) The morphology of nanofibers on the edge of the colloidal silica monolayer. d) Top view of the interconnected nanofibers. e) Tilted view of the oriented nanofibers. f) Low magnification of nanowires on textured surfaces. g) High magnification of nanowires on textured surfaces.

Molecular alignment: Polarized infrared spectroscopy suggested an aniostropic molecular structure for the nanowires, indicating that not only are the polymer nanowires well oriented, the polymer molecules within the nanowires are also aligned. Here the polarized infrared spectra of the light reflected from the surface were collected in both the p- and s-polarizations, which allowed for the determination of the orientation of the polyaniline molecules by separately detecting bonds whose polarization vectors are perpendicular to the surface, rather than those that are parallel.

Although there are five major features of the polyaniline spectra shown in Figure 5a, three of them prove to be particularly useful in determining the orientation of the polymer chains. Peak A, at 3347 cm^{-1}, is assigned to the N-H stretch.[25, 26] This peak is strong in the p-polarized spectrum, but almost completely missing in the s-polarized spectrum, implying that the N-H bonds are nearly perpendicular to the surface. The only structure that would allow all N-H bonds to be perpendicular to the surface is one where the polymer backbone is parallel to the surface, with the phenyl rings standing on-edge (Figure 5b). This hypothesis is supported by the fact that nearly all of the other absorptions are stronger in the s-polarized sample, particularly C and D, which are assigned to the C-N stretch and in-plane C-H bends, respectively. In the proposed orientation, both of these peaks would be non-zero in both polarizations, but would be considerably stronger in the s-polarization. The N-H stretch has a second component at 3185 cm^{-1} that can be attributed to the hydrogen bonded amine groups. We believe that the hydrogen bonding between the polyaniline molecules disturbed the in-plane alignment of N-H stretch, and therefore this mode is allowed in both the p- and s-polarized modes.

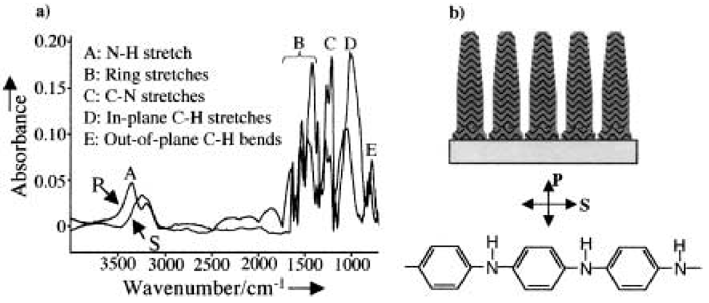

Figure 5. Polarized IR spectra of the oriented nanowires and schematic illustration of the growth process. a) IR spectra. b) Schematics of the polymer alignment.

Potential for Chemical and Bio-Sensing

Oriented arrays of conductive polymers provide an ideal platform for a range of sensing applications. In this paper we demonstrate a chemical sensor for hydrogen peroxide (H_2O_2). The reliable and sensitive detection of hydrogen peroxide, in particular amperometric determination, is of great importance for biosensing based on oxidase type enzymes.[27, 28] Hydrogen peroxide determination is also important to ensure the safety and quality of pharmaceutical and cosmetic formulations.[29]

In our approach, we used the conductive polymer arrays to support highly dispersed hexacyanometallates, iron(III) hexacyanoferrate (FeHCF), which functions as the active ingredient for H_2O_2 detection. Polynuclear transition metal hexacyanometallates have attracted wide attention because of their electronic, electrochemical, and spectrochemical properties,[30, 31] but their stability remains central to practical usage.[33, 34] Previous work suggested that the presence of organic conducting polymers in a composite film increases the stability of FeHCF.[35–38]

In this paper the H_2O_2 sensor is based on fine FeHCF nanoparticles supported on polyaniline nanowires. The polyaniline/FeHCF sensor was prepared electrochemically by several steps. In the first step, oriented polyaniline nanowires were deposited on the glassy electrode surface as discussed earlier. In the second step, FeHCF was electrodeposited on the polymer covered glassy electrode in an aqueous solution containing $FeCl_3$ and $K_3Fe(CN)_6$. The potential was cycled between -0.50 and $+0.80$ V at 50 mV s^{-1}. The oriented microstructure and the high surface area will favor high FeHCF loading, and has potential for high sensitivity detection. Besides, the amount of FeHCF loaded onto the organic polymer film can be easily controlled by following the cyclic voltammograms of the film as a function of time.

The surface of the polyaniline/FeHCF covered electrode was characterized by SEM. Figure 6a shows the oriented polyaniline nanowires on the glass electrode. A high magnification SEM picture indicates that FeHCF was deposited on the polymer surface as dispersed nanoparticles (20 nm) (Figure 6b). The existence of iron containing particles was confirmed by X-ray photoelectron spectrometry (XPS) spectrum (Figure 6c) and other techniques.

The chemical sensor was evaluated by catalytic reduction of H_2O_2 in a flow injection analysis (FIA) system (Figure 7)

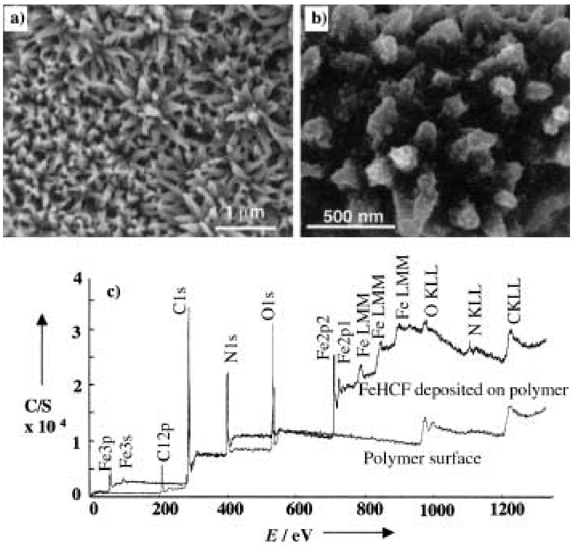

Figure 6. H_2O_2 sensor based on FeHCF and polyaniline nanowires. a) SEM image of the polyaniline nanowires on the glassy electrode. b) SEM image of FeHCF particles on polyaniline. c) XPS results supporting the deposition of FeHCF.

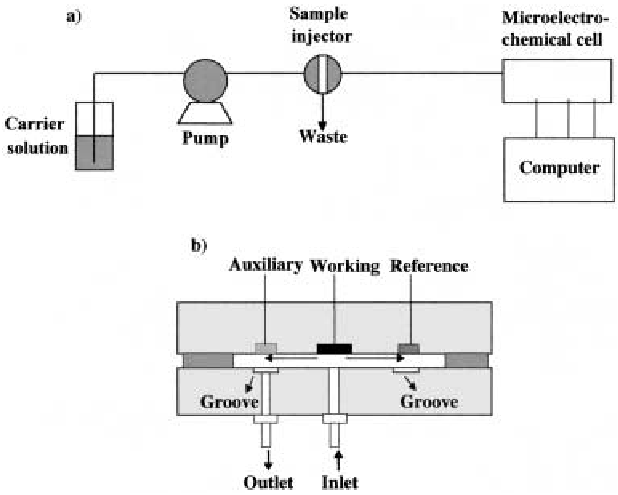

Figure 7. Experimental setup for sensing test. a) Flow diagram of the flow injection/amperometric detection system. b) Micro-electrochemical cell based on flow- configuration design.

made of a peristaltic pump, an injector with a 50 µL sample loop, interconnecting PTFE tubing, and a thin-layer amperometric detector. H_2O_2 can be oxidized on the electrode at sufficiently high anodic potential (exceeding 0.6 V vs. Ag/AgCl reference electrode).[39] However, many other substances present in biological samples can also discharge on the electrode at such a high anodic potential, and thus interfere with the results. FeHCH deposited on the polymer surface acts as an electron transfer mediator between the electrode and hydrogen peroxide.[40] This lowers the over-potential of H_2O_2 electro-oxidation to an appropriate level and prevents the interference from other species when the potential is applied.

When held at a negative potential the oxidized form of FeHCF, Prussian Blue, was converted to reduced form, Prussian White. At the same time, the polyaniline/FeHCF modified electrode showed a characteristic cathodic response. This cathodic response (current) was directly related to the H_2O_2 concentration. Figure 8a shows catalytic reduction currents at a constant potential of 0.10 V as a function of H_2O_2 concentration. Curve i) is from the polyaniline/FeHCF modified electrode, and Curve ii) is from the electrode without FeHCF. The almost linear response over a wide concentration range suggests that the polyaniline/FeHCF electrode is a useful configuration for H_2O_2 sensors. Without FeHCF, the polyaniline glassy carbon electrode has a very low response. The stability and reliability of the sensor were also tested. Figure 8b shows the flow injection response of six repetitive injections of 50 µL H_2O_2 solutions. Well-defined, reproducible peaks are observed at a low operation potential (0.10 V).

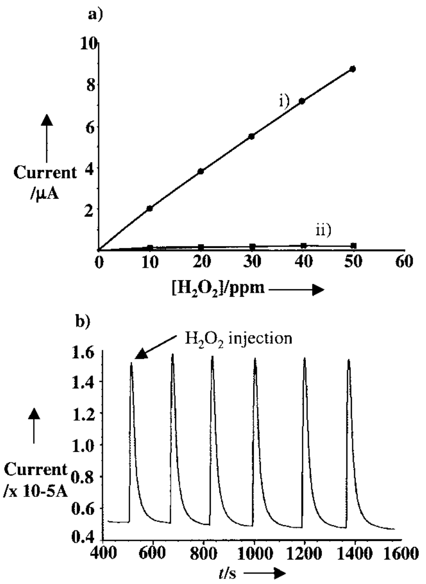

Figure 8. Catalytic reduction currents of hydrogen peroxide at polyaniline/FeHCF modified electrodes in a flow injection system. a) Response of the sensor to H_2O_2 concentration change. i) PANI/FeHCF modified glassy carbon electrode. ii) PANI modified glassy carbon electrode. Flow rate, 0.5 mL min^{-1}; operating potential, +0.10 V; carrier solution, 0.1 M KCl + 0.05 M acetate buffer, pH 6.0. b) Flow injection responses for repetitive injections of 50 ppm H_2O_2 at PANI/FeHCF modified electrode.

Outlook: Potential for Other Oriented Nanostructures

Although electrochemical deposition of conductive polymers seems to be drastically different from solution synthesis of other materials such as oxides, the general principle of controlled nucleation and growth should be similar. The method discussed in this paper has implications for preparing oriented nanostructures for a wide range of materials. According to the classic theory of nucleation and growth,[41] the free energy of forming stable nuclei on a substrate is determined by four factors: the degree of supersaturation S, the interfacial energy between the particle (c) and the liquid (l) σ_{cl}, the interfacial energy between the particle and the substrate (s) σ_{cs}, and the interfacial energy between the substrate and the liquid σ_{sl}:

$$\Delta G = -RT\ln S + \sigma_{cl} + (\sigma_{cs} - \sigma_{sl})\,A_{cs} \tag{1}$$

where A is the surface area of the particle.

Figure 9 is a schematic plot of the number of nuclei (N) as a function of degree of supersaturation (S),[41] which indicates that there is a narrow window where nucleation is favored for oriented nanostructures. Unfortunately most solution synthesis is carried out at too high a concentration so that undesirable precipitation dominates. As a result, oriented nanostructures were difficult to achieve.

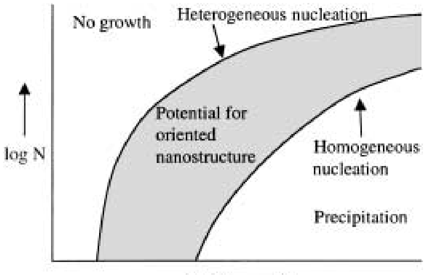

Figure 9. Idealized diagram for nucleation and growth.

From Equation (1) and Figure 9, we can use the following rules to design a generalized solution synthesis method for oriented nanostructures:

1) Controlling the solubility of the precursors and the degree of supersaturation so that massive precipitation is not the dominating reaction. Experimentally this is accomplished by reducing the reaction temperature, and by reducing the precursor concentrations (reducing the current density in case of electrochemical deposition), while at the same time ensuring nucleation and growth can still take place. The formation of the new materials is characterized by the increase in cloudiness of the solution, which can be monitored by light scattering or turbidity measurement. A rapid increase in cloudiness is an indication of rapid precipitation and should be avoided.
2) Reducing the interfacial energy between the substrate and the particle. In the literature surface functionalization is widely used to ensure that nucleation is favored on the substrate rather than in the solution. A more practical approach is to generate large number of nuclei (seeds) of the same material that need to be prepared on the surface first to minimize energy barrier for the subsequent growth of the nanostructures.
3) Ensuring the kinetic growth of oriented nanostructures is more favored over non-oriented structures. Kinetically, we believe that initially the nanowires may not be well aligned, as evidenced by some horizontally oriented fibers near the substrate surface (Figure 3b). However, the growth of randomly oriented polymer wires becomes kinetically retarded when these polymers begin to overlap with one another. Only the polymers perpendicular to the substrate surface are allowed to grow freely. This kinetically controlled nucleation and growth produces the uniform oriented nanowires.

The preparation of oriented polymer nanowires follows the above guidelines. We used similar procedures to prepare other oriented oxide nanowires and nanorods. Figure 10 compares oriented oxides with oriented polymers. The oriented ZnO nanowires from seeded growth (Figure 10a: on a smooth substrate; Figure 10b: on a rough surface) are remarkably similar to the oriented polymer nanowires (Figure 10c and d), implying a similar growth mechanism. The ZnO nanorods were prepared by first depositing a layer of ZnO nanoparticles on a glass substrate. The glass substrate containing the ZnO nanoparticles was then placed in a dilute $Zn(NO_3)_2$ solution in a sealed container and reacted at 60 °C for up to three days.[42] Using the same method, oriented FeOOH nanostructures (columns) have also been prepared (Figure 10e). The results for growing oriented ZnO will be published in the near future, but we hope to expand this approach to prepare other oriented nanostructures, including oxides, hydroxides, semiconductors.

Conclusion

In this paper we have demonstrated the preparation of large arrays of oriented conducting polymer nanowires without using porous templates to support the polymer structures. This approach is applicable to a wide range of substrates and is not limited by the substrate geometry. The unique conductive polymer nanowires have potential for chemical and biosensing. From the preliminary results of oriented ZnO nanowires, we also believe that this approach can be extended to other systems.

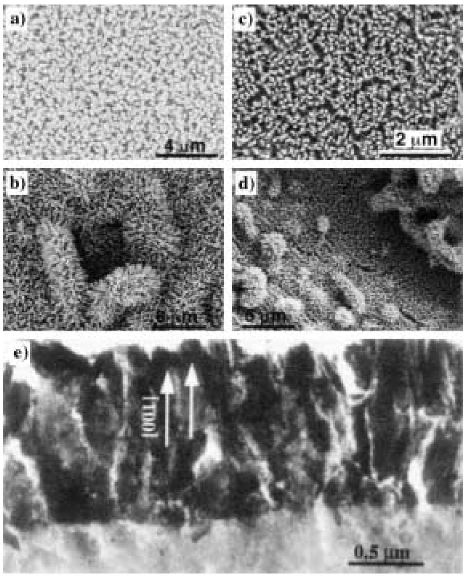

Figure 10. Generalized approach for controlled nucleation and growth of oriented nanostructures. a) Seeded growth of ZnO on smooth surafces. b) Seeded growth of ZnO on rough surfaces. c) Polyaniline on smooth surfaces. d) Polyaniline on rough surface. e) Oriented FeOOH.

Acknowledgements

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