Single-step synthesis of polypyrrole nanowires by cathodic electropolymerization

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Polypyrrole nanowires are successfully fabricated with a one-step process by cathodic electropolymerization from an aqueous solution without templates and chemical additives. The method utilizes electrochemically generated NO\(^+\) to oxidize the neutral pyrrole monomers, making it possible to use oxidizable metal substrates, such as Cu and Ni. The synthesized nanowires are directly deposited on the substrate in the form of a thin film consisting of fine polypyrrole nanowires with a nanoporous and interconnected network structure. The growth kinetics of the polypyrrole nanowires was investigated by analyzing the effects of the chemical composition of the electrolyte and the synthesis time on the formation of polypyrrole nanowires. It was found that the polymerization process of pyrrole is very sensitive to the reactivity of radical cations. For a radical cation with high reactivity, the polypyrrole nanospheres are synthesized near the electrode in the solution. In contrast, for a radical cation with sufficiently low reactivity, the polypyrrole nanowires are grown on the priorly deposited polypyrrole nanospheres.

1 Introduction

Since the electrical conductivity in a conjugated polymer was reported in 1977 by H. Shirakawa et al.,\(^1\) conducting polymers have been extensively investigated during the past few decades because of their novel electrical properties combined with the advantages of polymers.\(^2\) Among the conducting polymers, polypyrrole is particularly promising for its various commercial applications such as energy storage,\(^3\)-\(^7\) supercapacitors,\(^8\) sensors,\(^9\)-\(^10\) gas sensors\(^11\)-\(^12\) and corrosion protection\(^13\)-\(^14\) due to its high environmental stability, flexibility and electrical conductivity. Recently, with an increasing demand for functional organic materials in the area of nano-science and technology, a great effort has been focused on the development of one-dimensional polypyrrole nanostructures that possess novel physical and chemical properties superior to their bulky counterparts.

Nanowires and nanofibers of polypyrrole are commonly prepared via a template-based synthesis method using hard templates such as porous polymer films, anodic aluminum oxide (AAO) membrane, zeolites and highly ordered mesoporous silica thin films.\(^15\)-\(^17\) One major problem in the hard template synthesis is the difficulty in obtaining an intact final product because the fabricated nanowires are easily destroyed and can be collapsed during the removal of the hard templates. Another way to prepare the polypyrrole nanowires is by using soft templates such as surfactant molecules, liquid tubules and biomolecules, which make it possible to guide the oriented growth of polypyrrole.\(^18\)-\(^23\) During the polymerization, polypyrrole is grown along one-dimensional soft templates into polypyrrole nanowires. In contrast to the hard template synthesis, the soft template synthesis does not require the removal of the template after the synthesis. Recently, electrochemical methods using perchlorate (ClO\(_4\))-based chemical additives have also been studied as an alternative way to synthesize the polypyrrole nanowires without hard or soft templates.\(^24\)-\(^26\) These approaches provide not only a simple and facile technique for depositing polypyrrole nanowires on a substrate but also an easy way to control the structural characteristics and electrical conductivity by simply changing the electrolysis composition.

Using the electropolymerization method, polypyrrole nanowires can be easily deposited on inert electrodes such as gold, platinum and indium tin oxide (ITO) glass,\(^24\)-\(^26\) but it is quite difficult to deposit them on oxidizable metal substrates such as Cu and Ni due to their relatively low corrosion potentials in aqueous media. Indeed the polypyrrole has a relatively high oxidation potential \(E = 0.7\) V vs. SCE,\(^27\) which is more noble than the corrosion potentials of Cu and Ni, and thus the oxidizable metal substrates are predominantly dissolved before the polypyrrole monomers are oxidized by an applied anodic potential.

Herein, we suggest a new electrochemical approach for synthesis of polypyrrole nanowires on metal substrates in an aqueous medium under a cathodic potential by a cathodic electropolymerization method\(^28\) utilizing an electrochemically
generated oxidizing agent, nitrosonium ion (NO⁺). The cathodic electropolymerization method allows the direct deposition of polypyrrole nanowires on oxidizable metal substrates that are not stable under the anodic electro-polymerization conditions. Our method possesses several advantages over the conventional methods that have been used to synthesize one-dimensional polypyrrole nanostructures: it is a one-step process without a template, a fast and simple synthesis technique, a room-temperature process and it provides easy control of the structure and electrical conductivity. In addition, it would be suitable for mass production on large-area substrates due primarily to the high uniformity of nanowires deposited on the entire substrate.

The objective of this work is to investigate the growth kinetics of polypyrrole nanowires by cathodic electropolymerization with an emphasis on the effects of the reactivity of radical cations on the polymerization of pyrrole, and then to propose the reaction mechanism of the synthesis of polypyrrole nanowires under a cathodic potential.

2 Experimental section

The basic constituents of the aqueous electrolyte for the synthesis of polypyrrole nanowires were 0.25 M pyrrole, 0.2 M NaNO₃ and 0.8 M HNO₃. To investigate the effects of the electrolyte composition on the formation of polypyrrole nanowires, the concentrations of pyrrole and NaNO₃ were varied from 0.025 M to 0.2 M and from 0.2 M to 0.8 M, respectively. The detailed chemical composition of the baths are listed in Table 1.

The cathodic electropolymerization of pyrrole was conducted using a three-electrode cell: a nodular Cu sheet was used as a working electrode (substrate), a polypyrrole pre-coated stainless steel plate was used as a counter electrode and a saturated calomel electrode (SCE, 0.241 V vs. SHE) was used as a reference electrode. Polypyrrole nanostructures were electropolymerized for 10 min at a constant potential of −0.6 V SCE in the solution agitated with a magnetic stirrer at ~700 rpm. All the experiments were conducted at room temperature, 25 °C. The polypyrrole nanowires deposited on the Cu sheet were dried in a vacuum for 12 h after rinsing with distilled water.

The polypyrrole nanowires were observed using a scanning electron microscope (SEM) to examine the effects of the electrolyte composition and synthesis time on the morphology of the polypyrrole nanostructures. A cross-sectional SEM specimen of polypyrrole was prepared using a focused ion beam (FIB) which makes use of Ga ions to remove the material. To prepare the TEM specimens, dried polypyrrole nanowires were scraped from the Cu sheet and then dispersed in ethanol using sonication for 30 min. The chemical bonding states of the polypyrrole nanowires were investigated by X-ray photoelectron spectroscopy (XPS) and a Fourier transform infrared spectrometer (FTIR, Bruker optics) with a hyperion 3000 ATR microscopy accessory over the wavenumber range of 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹.

3 Results and discussion

3.1 Characterization of polypyrrole nanowires

Fig. 1 shows the morphology of polypyrrole nanowires synthesized by cathodic electropolymerization at −0.6 V SCE for 10 min from an aqueous solution containing 0.25 M pyrrole, 0.2 M NaNO₃ and 0.8 M HNO₃. At a low magnification, the polypyrrole deposits on a Cu sheet look like a thin black film (Fig. 1(a)), but high-magnification SEM images (Fig. 1(b) and Fig. 1(c)) reveal that the film has a nanoporous and three-dimensionally open network structure and consists of fine nanowires with a high degree of interlocking. These nanowires exhibit a high uniformity over the whole film with an apparent thickness of approximately ~100 nm and an average length of approximately 1 μm. It should be emphasized that such a unique network structure composed of dense and fine polypyrrole nanowires is quite different from the previously reported polypyrrole thin films prepared by anodic electropolymerization and spherical nanoparticles synthesized by cathodic electropolymerization. To the best of our knowledge, the synthesis method used in the present work or the direct deposition of polypyrrole nanowires on oxidizable metals via electropolymerization without chemical additives has not yet been reported.

Fig. 2 presents the FTIR spectrum of the polypyrrole nanowires synthesized on a Cu sheet by cathodic electropolymerization. The
absorption bands observed between 700 and 3500 cm\(^{-1}\) match well with those in the FTIR spectra of the electrochemically or chemically prepared polypyrrole nanowires reported previously.\(^{30-37}\) A broad band between 3300 and 3450 cm\(^{-1}\) is assigned to the N–H stretching mode,\(^{30-32}\) and the absorption band at 3100 cm\(^{-1}\) corresponds to C–H stretching vibrations.\(^{32}\) The in-plane C–H bending vibration is observed at 1300 cm\(^{-1}\) and 1040 cm\(^{-1}\).\(^{32}\) The bands at 1545 cm\(^{-1}\), 1460 cm\(^{-1}\), 1370 cm\(^{-1}\) and 1170 cm\(^{-1}\) are attributed to the C–Ca and C–N stretching vibration,\(^{32,33}\) and the bands at 1205 cm\(^{-1}\) and 929 cm\(^{-1}\) are assigned to C–H ring stretching and N–H in-plane vibrations, respectively.\(^{35}\) In addition, absorption bands associated with C–H out-of-plane deformation and C–H out-of-plane ring deformation appear near 898 cm\(^{-1}\) and 784 cm\(^{-1},^{36}\) and the N–H out-of-plane bending can be observed at 820 cm\(^{-1}\).\(^{37}\)

As shown in Fig. 3, the XPS analysis also indentifies the synthesized nanowires on the Cu sheet as polypyrrole in accordance with the result of the FTIR analysis. The C1s main peak is fitted with five components at 284.1, 285.1, 286.2, 287.8 and 290.4 eV. The peaks at 284.1 and 285.1 eV are assigned to the β-carbons and α-carbons of the pyrrole ring, respectively.\(^{38}\) The peak at 286.2 eV may correspond to the C=–N, C=–OH and ≡C–NH\(_{+}\) (polaron) bonds.\(^{39}\) The binding energy centered at 287.8 eV is attributed to –C=–N\(^+\) (bipolaron)\(^{40}\) or C=–O bonds\(^{41}\) formed with oxygenated carbon atoms of pyrrole rings. The π–π\(^*\) satellite in aromatic polypyrrole is observed at 290.4 eV which is higher than that of the main C peak.\(^{39}\) The N1s peak is decomposed into three peaks at 398.1, 399.75 and 401.7 eV (Fig. 3(b)). The lowest peak at 398.1 eV is attributed to –N– (imine-like nitrogen), and the peak centered at 399.75 eV corresponds to the neutral amine nitrogen in the pyrrole ring (–NH\(_{3}\)).\(^{42}\) The peak at 401.7 eV is related to positively charged amine nitrogen in polypyrrole.\(^{43}\) Therefore, the results of FTIR and XPS analyses clearly demonstrated that the polypyrrole nanowires were successfully deposited on the Cu sheet by the cathodic polymerization method.

To examine the structure of the polypyrrole film consisting of fine nanowires, a cross-section of the film was observed after cutting by a focused ion beam (FIB). Interestingly, the polypyrrole film is composed of two different layers: an outer “nanowire layer” and an inner “nanosphere layer”. As shown in Fig. 4, while the outer layer consists of highly dense polypyrrole nanowires that were grown horizontally, the inner layer is constructed of less dense spherical nanoparticles with sizes of 200–300 nm that were stacked on the nodular Cu sheet. This double-layered structure implies that the spherical nanoparticles were priorly deposited on the substrate before the growth of polypyrrole nanowires.

Fig. 5 shows the growth kinetics of the polypyrrole film on the Cu sheet via cathodic electropolymerization as a function of
synthesis time. As described in the Experimental section, in this study, a nodular Cu sheet was used as a substrate instead of a typical smooth Cu sheet because nodules on the Cu substrate can significantly improve the adhesion between the deposited layer and the substrate due primarily to the mechanical interlocking effects of the nodules.44 Thus, the deposits with 1 µm size observed in Fig. 5(a) are Cu nodules and the aggregated smaller nanoparticles deposited on the nodules are the synthesized polypyrrole. At a deposition time of 1 min, a small quantity of polypyrrole nanospheres was sparsely deposited on the nodular Cu, as shown in Fig. 5(a). As the deposition time increased, the nanowires grew from the initial deposits laterally spread over the substrate surface, and the density and length of the nanowires dramatically increased (Fig. 5(b)). Consequently, the substrate is gradually covered with the polypyrrole nanowires. At a deposition time of 5 min, the Cu substrate was almost fully covered with the polypyrrole nanowires (Fig. 5(c)). Further increase in the deposition time does not show the dramatic growth of the polypyrrole nanowires that was seen at the initial growth stage from 1 min to 5 min, but the nanowires become slightly thinner and longer at the stage from 5 min to 10 min (Fig. 5(d)).

To clearly investigate the growth of polypyrrole nanowires, we focused on the morphological changes in polypyrrole nanostructures inside of the film, the inner “nanosphere layer”. Fig. 6 exhibits the high-magnification SEM images of polypyrrole nanostructures prepared with different synthesis times. In agreement with Fig. 5(a), polypyrrole nanospheres 100–200 nm in size were deposited on the nodular Cu sheet at a deposition time of 1 min (Fig. 6(a)), but the polypyrrole nanospheres were changed to a sea urchin-like structure as the time increased to 2 min. (Fig. 6(b)). Interestingly, further increase in the synthesis time changed the sea urchin-like structure to a wire-like structure (Fig. 6(c)), and finally to the nanowires (Fig. 6(d)). This observation demonstrates that polypyrrole nanowires grew along specific directions from the priorly deposited nanospheres which acted as seeds. However, this specific form of growth kinetics of polypyrrole nanowires in the absence of chemical additives and soft templates has not yet been reported for cathodic electropolymerization. Therefore the detailed formation mechanism will be investigated and discussed in the following section.

3.2 Formation mechanism of polypyrrole nanowires by cathodic electropolymerization

The two redox reactions associated with the electrochemically generated NO\(^+\) (nitrosonium ion) and pyrrole monomer are involved in the synthesis process of polypyrrole nanowires by cathodic electropolymerization. The first reaction is an electrochemical reaction in which NO\(^+\) is generated by the reduction of NO\(_3^-\) (nitrate ion) from HNO\(_3\) (nitric acid) and NaNO\(_3\) (sodium nitrate) under a cathodic potential. Since HNO\(_3\) is thermodynamically unstable at high concentration, small quantities of NO, NO\(_2\) and HNO\(_2\) (10\(^{-6}\) to 10\(^{-3}\) mol l\(^{-1}\)) are spontaneously formed under sufficiently strong acidic conditions\(^{45}\) and this initiates the generation of NO\(^+\) according to reaction (2). Under these conditions, more NO\(^+\) can be produced from the electrochemically reduced HNO\(_3\) (reaction (1)) and from the spontaneously generated HNO\(_2\). Accordingly an increase in not only the acidity but also the applied cathodic potential results in a higher concentration of generated NO\(^+\).

\[
\text{HNO}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HNO}_2 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{HNO}_2 + \text{H}^+ \rightarrow \text{NO}^+ + \text{H}_2\text{O} \quad (2)
\]

The second reaction involves the chemical oxidation of pyrrole monomer by NO\(^+\). It is well known that NO\(^-\) is a superior electron transfer agent that can act as a strong oxidant and electrophile (reduction potential, \(E_{\text{red}}^0 = 1.50\) V vs. SCE).45 When NO\(^-\) and neutral pyrrole monomers coexist in an aqueous solution, the pyrrole monomers are strongly oxidized by NO\(^+\) according to the charge transfer reaction (reaction (3)), leading to the formation of a pyrrole radical cation. The pyrrole radical

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**Fig. 5** SEM images of the polypyrrole nanowires synthesized by cathodic electropolymerization at –0.6 \(V_{\text{ SCE}}\) from an aqueous solution containing 0.25 M pyrrole, 0.2 M NaNO\(_3\), and 0.8 M HNO\(_3\) with different synthesis times: (a) 1 min, (b) 3 min, (c) 5 min and (d) 10 min.

**Fig. 6** High-magnification SEM images of the polypyrrole nanostructures synthesized by cathodic electropolymerization at –0.6 \(V_{\text{ SCE}}\) from an aqueous solution containing 0.2 M NaNO\(_3\), 0.8 M HNO\(_3\), and 0.25 M pyrrole with different synthesis times: (a) 1 min, (b) 2 min, (c) 3 min and (d) 4 min.
cation is thermodynamically unstable, and hence it dimerizes with another radical cation to reduce its energy. As a result, dimer (reaction (4)), trimer (reaction (6)) and oligomeric products (reaction (7)) are sequentially formed following the typical polymerization mechanism.\(^4\)

\[
\begin{align*}
\text{Py} + \text{NO}^+ &\rightarrow \text{Py}^+ + \text{NO} \quad (3) \\
\text{Py}^+ + \text{Py}^+ &\rightarrow \text{Py–Py} \quad (4) \\
\text{Py–Py} + \text{NO}^+ &\rightarrow \text{Py–Py}^+ + \text{NO} \quad (5) \\
\text{Py}^+ + \text{Py–Py}^+ &\rightarrow \text{Py–Py–Py} \quad (6) \\
\text{Py}^+ + (\text{Py})_n^+ &\rightarrow \text{PPy} \quad (7)
\end{align*}
\]

During such an electropolymerization, a monomeric radical cation may undergo a different coupling reaction, depending on its reactivity.\(^4\) A highly reactive radical cation rapidly polymerizes with a neighboring radical cation, but a relatively less reactive radical cation can diffuse a short distance to polymerize with more reactive species. Since extended conjugation in the polymer is more easily oxidized than the monomer (reaction (5)), the polypyrrole nanospheres deposited on the substrate (Fig. 5(a)) are readily oxidized by NO\(^+\). Therefore, when the radical polypyrrole cation preferentially reacts with the oxidized polypyrrole nanospheres rather than neighboring radical cations, polypyrrole nanowires grow on the deposited nanospheres. In other words, the “reactivity” of the radical cation determines the morphology of polypyrrole nanostructures.

In cathodic electropolimerization of pyrrole, the reactivity of radical cations is greatly dependent on the concentrations of the produced NO\(^+\) and neutral pyrrole monomer. As the ratio of NO\(^+\) to neutral pyrrole become higher, the generation of radical cations will be promoted, and the radical cations will be forced to polymerize each other, i.e., the reactivity of the radical cations is increased. In contrast, with lower ratio of NO\(^+\) to neutral pyrrole, the radical cations can afford to diffuse to more reactive species, such as deposited nanospheres. Therefore, the reactivity of radical cations is decreased.

To elucidate the effects of the reactivity of radical cations on the formation of polypyrrole nanowires, the ratio of neutral pyrrole to NO\(^+\) was varied as listed in Table 1. In the first set of experiments, the concentration of NaNO\(_3\) was varied from 0.2 M to 0.8 M at fixed concentrations of 0.25 M pyrrole and 0.8 M HNO\(_3\) (bath 1 ~ bath 4). Since a sufficiently strong acidic condition is essential to generate the NO\(^+\) from HNO\(_2\), the concentration of NaNO\(_3\) was only varied with a fixed concentration of HNO\(_3\) of 0.8 M to maintain a constant pH in the solution.

Fig. 7(a) displays the current–time curve recorded during cathodic electropolymerization at a constant potential of −0.6 V\(_{SCE}\) for 10 min from bath 1, bath 2, bath 3 and bath 4, as listed in Table 1. As the concentration of NO\(_3^-\) increased, the cathodic current density significantly increased due to the promoted reduction of NO\(_3^-\) to HNO\(_2\) (reaction [1]), thereby leading to an increase in the concentration of NO\(^+\) generated via reaction [2]. As predicted, the morphology of the deposited polypyrrole nanostructures changed from nanowires to nanospheres as the concentration of NO\(_3^-\) increased (Fig. 8). The result proves that the higher reactivity of radical cations, i.e., the increase in the concentration ratio of NO\(^+\) to neutral pyrrole,

\[\text{NO}^+ + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{H}^+ + \text{e}^- \]

Fig. 8 SEM images of the polypyrrole nanowires synthesized by cathodic electropolymerization at −0.6 V\(_{SCE}\) for 10 min from an aqueous solution containing 0.25 M pyrrole and 0.8 M HNO\(_3\) with different concentrations of NaNO\(_3\): (a) 0.2 M, (b) 0.4 M, (c) 0.6 M and (d) 0.8 M.
results in the formation of polypyrrole nanospheres. In other words, the growth of nanowires is thoroughly inhibited when radical cations are highly reactive.

In the second set of experiments, the concentration of pyrrole was varied from 0.025 M to 0.2 M at fixed concentrations of 0.2 M NaNO₃ and 0.8 M HNO₃ (bath 5 ~ bath 8) to decrease the reactivity of the radical cations. Fig. 7(b) shows that the cathodic current density decreased as the concentration of pyrrole increased. In fact, according to reaction (1) and reaction (2), a change in the pyrrole concentration cannot affect the electrochemical reactions because the pyrrole monomer and polymeric products are not involved in any charge transfer reactions occurring on the cathode. Consequently, the cathodic current would be constant regardless of the change in the pyrrole concentration. Although the process is not yet fully understood, we believe that the reduced cathodic current density with the increase in pyrrole concentration is due to an increase in the thickness of the polypyrrole layer which impedes the charge transfer reaction.

Fig. 9 shows the morphological changes in the polypyrrole nanostructures from nanospheres to nanowires as the concentration of pyrrole monomer increases at a fixed concentration of NO₃⁻. At the pyrrole concentrations of 0.025 M and 0.1 M, spherical nanostructures and sea urchin-like nanostructures were deposited on the Cu substrate, respectively. A notable feature in Fig. 9 is that the polypyrrole nanowires were only synthesized in the solution with pyrrole concentration over 0.1 M at a fixed concentration of 0.2 M NaNO₃ and 0.8 M HNO₃. In fact, it is difficult to define the critical concentration ratio of pyrrole to NO₃⁻ for the formation of polypyrrole nanowires, but the result demonstrates that a certain degree of reactivity of radical cations is required for the growth of nanowires. In agreement with the first set of experiments, the second set of experiments clearly demonstrates that the reactivity of the radical cation is the crucial parameter determining the polymerization kinetics of polypyrrole nanowires in the cathodic polymerization process.

From the results and discussion in this study, a novel growth mechanism of polypyrrole nanowires is proposed based on the reactivity of radical cations. As illustrated in Scheme 1, the initial deposition kinetics of polypyrrole nanospheres is not different from the previous cathodic deposition.²⁸ Since NO⁺ is predominantly generated on the cathode according to reaction (2), polypyrrole nanospheres that are formed near the cathode by the cathodic polymerization process are easily adsorbed on the substrate (Scheme 1(a)). When the radical cation has a high reactivity, such polymerization and deposition processes repeatedly occur, and consequently polypyrrole nanospheres were progressively deposited (Scheme 1(b) → Scheme 1(c)). In contrast, at a sufficiently low radical cation reactivity, the stable radical cation preferentially reacts with priorly deposited nanospheres (Scheme 1(d)) instead of radical cations in the solution. In other words, a step-growth polymerization of pyrrole in the bulk solution changed to a chain-growth polymerization on the surface of the substrate with a decrease in the reactivity of radical cations. As a result, the polypyrrole nanowires are grown on the polypyrrole nanospheres (Scheme 1(e)).

According to the proposed mechanism, only a part of the synthesized polypyrrole nanospheres are deposited on the substrate, whereas the rest of the nanospheres near the electrode are diffused into the solution and then become colloid nanoparticles (Scheme 1(b) and (d)). The colloids are black owing to their conductive state, and hence the color of the solution changes to an opaque color (almost black) with cathodic electropolymerization. Fig. 10 shows such a change in electrolyte color before and after cathodic electropolymerization. The degree of color change in the electrolyte was quite different depending on its composition: bath 5 used for the preparation of polypyrrole nanospheres (Fig. 10(a)) became much darker after 10 min electropolymerization than bath 8 used for the synthesis of polypyrrole nanowires (Fig. 10(b)). The result demonstrates that the amount of colloid nanoparticles is much lower in the solution (bath 8) prepared for the synthesis of polypyrrole nanowires than that (bath 5) prepared for the synthesis of polypyrrole nanospheres. This agrees well with our proposed mechanism as shown in Scheme 1.
4 Conclusions

In the present work, polypyrrole nanowires were successfully synthesized by a cathodic electropolymerization process from an aqueous solution without templates and chemical additives. The method utilizes electrochemically generated NO+ to oxidize neutral pyrrole monomers, making it possible to use oxidizable metal substrates such as Cu and Ni. The synthesized nanowires are directly deposited on the Cu substrate as a thin film that has a nanoporous and interconnected network structure consisting of fine polypyrrole nanowires. The examination of morphological changes in polypyrrole nanostructures with synthesis time showed that polypyrrole nanospheres initially deposited on the Cu substrate gradually changed to nanowire structures in the form of a thin film. The polymerization kinetics of pyrrole in cathodic electropolymerization is greatly affected by the reactivity of radical cations. When the reactivity of the radical cations is high, they rapidly polymerize with neighboring radical cations, thereby forming the polypyrrole nanospheres in the solution near the cathode, which are then deposited on the substrate. In contrast, when the reactivity of the radical cations is sufficiently low, the stable radical cations preferentially react with priorly deposited nanospheres instead of other radical cations, resulting in the growth of polypyrrole nanowires on the polypyrrole nanospheres.

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Notes and references