Morphological Effects of Ni Nanostructures on Electropolymerization of Aniline

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ABSTRACT: Electrochemical polymerization of aniline on nanostructured Ni substrates was investigated. To this aim, the Ni substrate electrodes were prepared by casting various samples of Ni nanoparticles having different morphologies. The electropolymerization on these different nanostructured Ni substrates was systematically investigated by means of comparative results obtained from cyclic voltammetry and electron microscopy as representatives of electrochemical behavior and morphology, respectively. Since the Ni nanoparticles are the beginning sites for the polymer growth, polyaniline morphology is strongly controlled by the nature of the Ni nanoparticles associated with chemical properties rather than geometrical shape. In conclusions, although the substrate surfaces had a similar nanostructure, but due to the difference in their chemical properties, the morphologies electrochemical behaviors of the polyaniline films electrodeposited on these substrates are significantly different. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1579–1586, 2011

Key words: conducting polymers; morphology; nanostructure

INTRODUCTION

Fabrication of conductive polymers by means of electropolymerization is of particular interest, since it provides an opportunity for the preparation of stable solid films attached to a substrate. Since the discovery of conductive polymers,[1] electrochemical polymerization was also introduced as a powerful method for the synthesis of this class of polymer materials.[2] This method has successfully used for the preparation of different conductive polymers on noble metals such as Pt and Au. After appropriate fundamental studies of such electropolymerization processes, considerable efforts have been made to investigate possibilities of electropolymerization on different substrate electrodes for applied purposes.[2–25] This was indeed an essential requirement because noble metals are expensive and unsuitable for the practical applications. On the other hand, the interesting feature of conductive polymers, as can be understood from their name, is related to their conductivity, and thus, the main application is in microelectronic devices employing a thin film of conductive polymer attached to a specified substrate.

Most interesting candidates to be used as the substrate of conductive polymers are active metals as they are low cost and sufficiently conductive for electrodeposition process. The main problem associated with electropolymerization on active metals is obviously strong oxidation occurring in the course of electrochemical experiments. In other words, there is no stable surface for the electrodeposition of conductive polymers. However, in light of recent advancements, it is possible to design appropriate condition for the electropolymerization on various metallic substrates. In general, electropolymerization (even on noble metals) occurs just when the substrate surface is sufficiently oxidized.[19] For active metals, this oxidation process results in active dissolution of the metallic electrode instead of surface activation for the electropolymerization. This problem can be overcome by choosing the appropriate experimental conditions, e.g., appropriate electrolyte medium for a certain metallic substrate.

Among active metals, nickel has a superior position due to its vast range of applications, e.g., for metallization of silicon, magnetic materials, etc. Here, we wish to investigate electropolymerization of aniline on Ni substrate. However, a novel type of nanostructured substrate is employed, and the results will be of both fundamental and applied importance. For carbon nanotubes as the prototype of nanomaterials, electropolymerization on a paste-based substrate electrode is directly affected by the nanotubes structure,[26] as electropolymerization on carbon can be considered as a conventional case. However, for metallic paste-based electrodes, chemical activity of the metal nanoparticles also affects the electropolymerization process. In fact, we are about

to communicate a novel approach for the electropolymerization on active materials, which is of general interest and can be developed for different systems.

EXPERIMENTAL

Chemicals and apparatus

All chemicals were of analytical grade and purchased from MERCK (Darmstadt, Germany), except, graphite powder which was purchased from Fluka (St. Louis, MO). All electrochemical experiments were performed in a standard three-electrode cell using an Autolab PGSTAT30 potentiostat/galvanostat, running its standard software GPES 4.7. SEM images were taken using a Philips XL30 scanning electron microscope.

Ni nanoparticles were synthesized through a simple reaction of reduction of Ni^{2+} by sodium borohydride.[27] For this purpose, stoichiometric amounts of nickel nitrate and sodium borohydride were reacted at room temperature. In all cases, the reaction time was exactly 5 min. The resulting Ni particles were rapidly filtered to avoid further progress of the reaction. To obtain Ni nanoparticles with different morphologies, three approaches were employed to affect the morphological structure of resulting Ni nanoparticles. In the first sample, synthesis was carried out under stirring condition induced by a simple magnetic stirrer. The second sample was synthesized by putting the reactor bath in a conventional ultrasonic bath with power of 40 W.

For the third sample, a certain amount of carbon nanotubes was dispersed within the reaction. In fact, it is well known that the internal channel of carbon nanotubes can be used as a 1D template for the preparation of nanostructured materials.[28–30] Similarly, the external walls of the carbon nanotubes can act as irregular templates for the formation of nanostructures. On the other hand, the circular heads can be suitable growth sites for the formation of nanoparticles. Although it is soon to judge about the exact mechanism, but existence of such nanotubes among the reaction bath has a significant influence on the formation of Ni nanoclusters. Moreover, the inclusion of such electrically conductive agent can improve the nanocluster conductivity, as the main problem in conductivity of such nanoclusters is the interfacial resistance between the individual nanoparticles. The carbon nanotubes employed here were synthesized according to the procedure developed in our lab.[31] Since detailed characteristics of this type of carbon nanotubes have been reported in our earlier paper,[31] it is excluded here. The typical amount of carbon nanotubes was 10 μg per 1 mL of the reaction bath. This amount is indeed the highest value as the carbon nanotubes can be neglected, as the ratio of carbon

nanotubes to Ni nanoparticles in the final product was less than 1 : 20. These samples are referred to as Samples 1–3 in the text, respectively.

The working electrodes were prepared by mechanical attachment of a thin layer (tens of micrometers) of metallic pastes constructed from the aforementioned Ni nanoparticles. The pastes were prepared by mixing the Ni nanoparticles with a drop of melted paraffin. To improve the paste conductivity, a powder of Ni nanoparticles and graphite fine powder (Fluka) was prepared in ratio 1 : 1, unless the case devoted to the investigation of the role of this conductive additive, as the graphite powder was absent. This typical ratio was chosen as the optimum value, as the electrode is sufficiently conductive and showing the electrochemical behavior of Ni. Note that this paste has mainly the electrochemical behavior of Ni rather than graphite (though their amounts are equal), due to the extremely higher surface area of the Ni substrate. Electropolymerization of aniline on these nanostructured Ni substrates were performed under potentiodynamic condition by cycling the potential between − 0.2 and 1.0 V versus SCE with a scan rate 100 mV/s for 20 successive cycles. The electrolyte solution was $0.1M$ aniline in $0.5M$ H_2SO_4. A saturated calomel electrode and a platinum rod were employed as counter and reference electrode, respectively.

RESULTS AND DISCUSSION

Figure 1 shows morphologies of different Ni nanoparticles prepared under various experimental conditions. As can be seen, the size of the nanoparticles and degree of agglomeration is different from case to case, but the general shapes of the Ni nanoparticles are similar. As they will be used for the fabrication of rigid substrate electrodes, the most important feature is probably charge transfer between individual nanoparticles. In other words, the effect under investigation is mainly related to the chemical properties of the clusters made from individual nanoparticles rather than physical structure of the individual nanoparticles.

To investigate the electropolymerization on such nanostructured Ni substrates, it is firstly appropriate to examine electrochemical behavior of the nanostructured Ni electrode in the acidic medium of electropolymerization electrolyte. Figure 2 indicates anodic behaviors of three nanostructured Ni electrodes in an electrolyte solution of $0.5M$ H_2SO_4. As can be seen, the current density is significantly low for anodic polarization of the nanostructured Ni electrodes, indicating existence of a protective oxide layer on the individual Ni nanoparticles avoiding strong dissolution of the metallic electrode. For a typical case of Ni nanoparticles, as can be seen in Figure
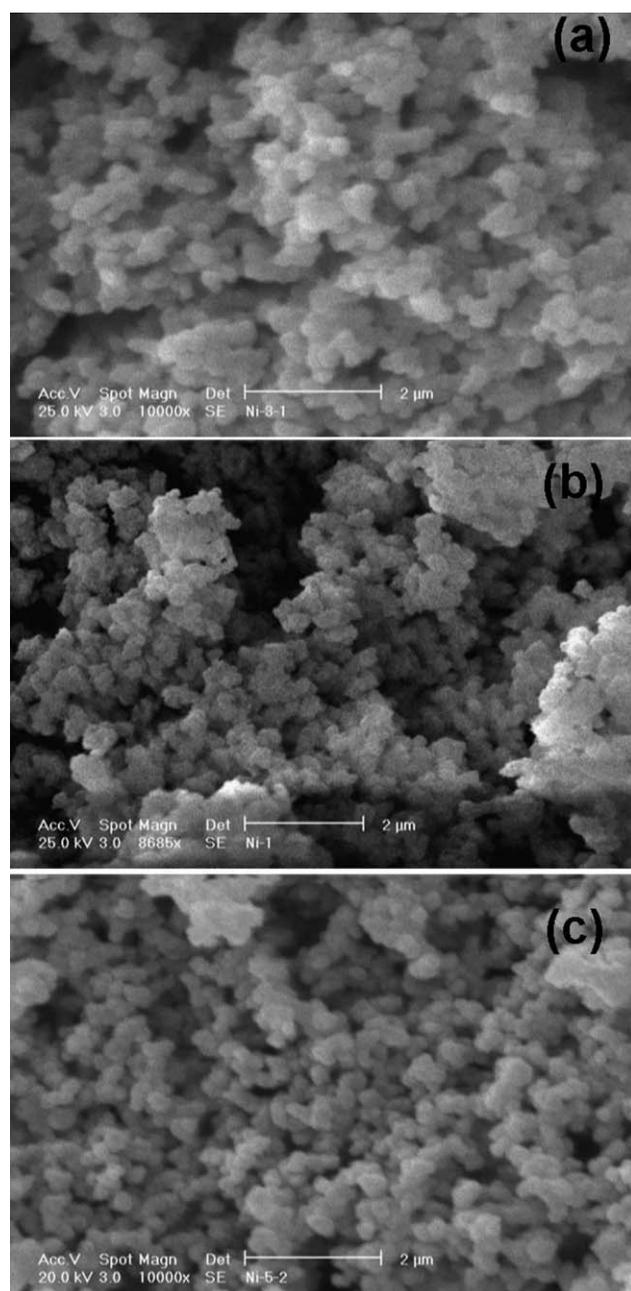
Figure 1 SEM images of Ni nanoparticles prepared by (a) stirring, (b) sonication, and (c) adding a small amount of carbon nanotubes.

2(a), the protective oxide layer is still stable after 20 successive cycles and no sign of active dissolution is observable. The featureless CVs with low-current densities are indicative of the fact that such Ni nanoparticles are almost electrochemically inactive in the potential range of our experiment and act just as a conducting substrate electrode. Note that this protective layer is too thin to increase the electrode resistance.[18] Of course, it is worthy noting that the corrosion potential of Ni leading to active dissolution is located outside the potential region under investigation.[32,33] In any case, these results prove that the Ni

substrate electrodes prepared from partially oxidized Ni nanoparticles are sufficiently stable for the electropolymerization process.

Stability of the Ni nanoparticles in the electrochemical experiment indicates that they are capable
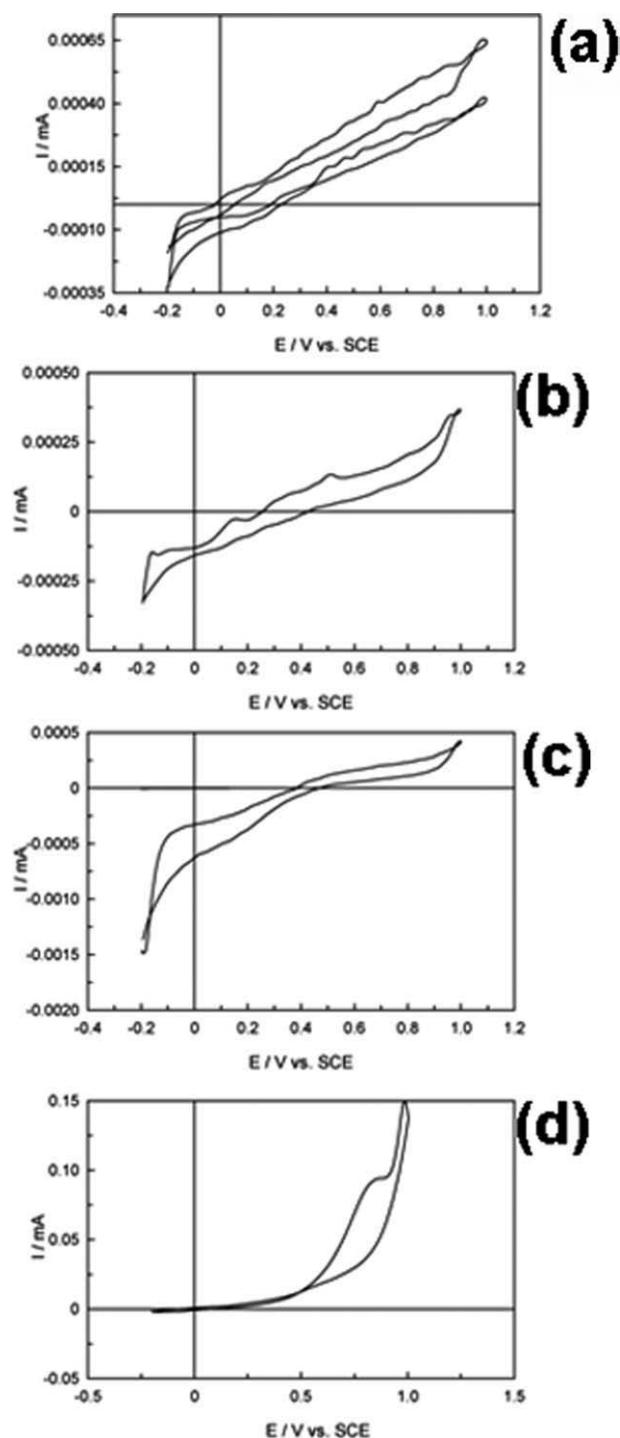

Figure 2 Anodic behaviors of the nanostructured Ni electrode fabricated from Ni nanoparticles (a)–(c) in an electrolyte solution of $0.5M$ H_2SO_4. (d) The same voltammetric experiment on a substrate electrode made of commercial Ni particles. Scan rate 100 mV/s. In (a), the first (lower curve) and 20th cycles (upper curve) are illustrated.
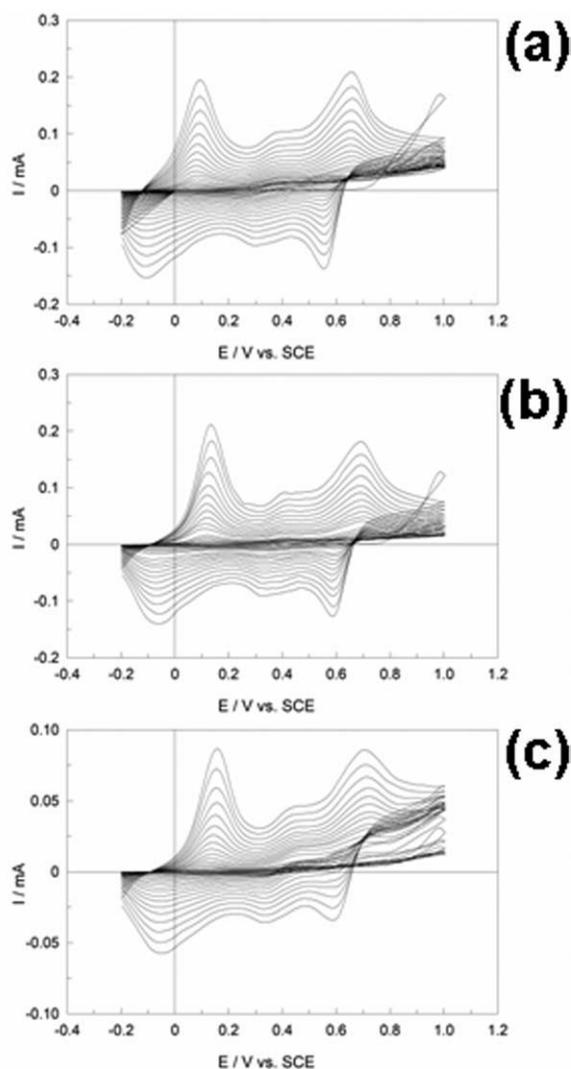
Figure 3 Electrochemical polymerization of aniline on nanostructured Ni substrates prepared from Ni nanoparticles [Samples 1–3 as illustrated in Fig. 1(a–c)] and graphite fine powder as a conducting agent. Scan rate 100 mV/s.

of fabricating required paste-based electrodes as substrates for electropolymerization, but due to the existence of the aforementioned oxide layer, graphite fine powder was added to the Ni nanoparticles to improve the electrical conductivity of the nanostructured Ni electrodes. For the sake of comparison, the voltammetric behavior of a paste-based electrode made from commercial Ni powder is also illustrated [Fig. 2(d)]. As can be seen, the metallic corrosion is very severe; the dissolution current is significantly higher than the previous cases. This is comparable with the electrochemical behavior of bulk Ni electrode in such acidic media.[32,33]

Figure 3 depicts potentiodynamic electropolymerization of aniline on the Ni substrate electrodes having different nanostructures. In general, the electropolymerization on such nanostructured Ni electrodes is similar to that on Pt substrate. In other words, these nanostructured Ni electrodes do not behave like a con-

ventional Ni electrode making severe difficulties in the electropolymerization process. For a conventional Ni electrode, anodic dissolution of the metal results in an unstable surface that is not suitable for the deposition of a solid film. This problem can be overcome just by generation of a protective passive layer on the electrode surface before electropolymerization[19] or choosing an appropriate experimental condition to form such passive layer on the substrate surface in the course of the electropolymerization process.[18] As stated earlier, due to high-specific surface area of such metallic nanoparticles, they will be immediately oxidized during the synthesis process. Thus, the nanostructured Ni electrodes prepared from the pastes of the Ni nanoparticles act as a stable substrate surface for the occurrence of electropolymerization. Of course, this stability is just needed for the first cycle.

The potentiodynamic polymerization of aniline on all nanostructured Ni electrodes shows characteristics of polyaniline electropolymerization. During the forward scan, the polyaniline is almost in semiconducting state.[34] There is a redox couple at around 0.0 V versus SCE corresponding to the transition between two semiconducting and conducting states of polyaniline due to the formation of leucoemeraldine and polaronic emeraldine forms.[34–36] A weak redox couple is also observable at potential of $\sim$ 0.4 V versus SCE, which is attributed to the formation of other structures such as the p-benzoquinoned/hydroquinone couple as a result of attack by water.[37,38] The redox couple appearing at high potentials (0.6 V versus SCE) corresponds to the formation/reduction of bipolaronic pernigraniline and its resonance form, i.e., protonated quinonediimine.[34,35,39] However, such potentials are slightly affected by the type of Ni nanoparticles employed in the substrate electrode.

The electropolymerization processes on the Ni nanoparticles prepared under stirring (Sample 1) and sonication (Sample 2) are similar is accompanied by a strong oxidation peak appearing only in the first scan at potentials more than 0.8 V versus SCE. This is due to the active oxidation of the monomer at the bare substrate surface, but formation of first layers of polyaniline films avoids this process leading to continuous growth of the polymer chain. This is indeed a characteristic behavior in the electropolymerization of aniline even on Pt substrate.[40] The strange behavior is that this phenomenon is absent in the case of the Ni nanoparticles prepared by adding carbon nanotubes (Sample 3). This suggests that electropolymerization occurs via an autocatalytic mechanism as there is no need to the monomer oxidation for the occurrence of the electropolymerization.[41]

Although the amount of carbon nanotubes is very small, and it is not normally detected in SEM images of corresponding Ni nanoparticles [Fig. 1(c)], it seems that they play an important role in charge transfer

across the nanoparticles as such oxidation process does not occur even in the first cycle of the electropolymerization [Fig. 3(c)]. Instead, such oxidation process is transformed to a slight oxidation peak occurring not only in the first cycles but also in the subsequent cycles. It seems that carbon nanotubes can induce an oxidation process at high potentials as it occurs even when a thin polyaniline film formed (during the first cycles) on the Ni substrate surface. A possible mechanism can be attributed to the electrocatalytic activity of the carbon nanotubes, which makes the initial monomer oxidation easier during the first cycle. However, this electrocatalytic activity will affect the electrochemical system even in subsequent cycles. Similar behavior was also detected for simultaneous chemical and electrochemical polymerization of aniline, where the chemical reaction assists the initial polymer growth without needing the initial monomer oxidation on the substrate electrode.[42] Note that Ni nanostructures have been partially formed on the carbon nanotube added, and its role is different from graphite powder as a conductive agent, as this issue will be discussed.

The most mysterious influence of the Ni nanostructures on the electropolymerization process can be found in morphologies of the polyaniline films synthesized. Although the general shapes of Ni nanoparticles (Fig. 1) and the electropolymerization processes on these nanostructured Ni electrodes (Fig. 3) are similar, morphologies of the resulting polyaniline films are totally different (Fig. 4). The polyaniline film electrodeposited onto the Ni nanoparticles prepared under stirring condition has a uniform and concrete structure with smoothness in nanoscale [Fig. 4(a,b)], whereas polyaniline formed on the Ni nanoparticles prepared by sonication has separated islands protruded from the main film attached to the substrate surface [Fig. 4(c)]. The summits in the form of microparticles are indeed smooth spheres, but for larger ones, tiny wrinkling is also detectable [Fig. 4(d)]. As expected from the data obtained for electropolymerization on different Ni substrates, the morphological structure of the polyaniline film electrodeposited onto the Ni nanoparticles prepared in the presence of carbon nanotubes is significantly different from two previous cases. In the latter case, concrete sheets are formed which are subject to strong cracks, probably due to their largeness [Fig. 4(e)]. In spite of this different structure, the tinier structure as inspected from the edges of such huge sheets is somehow similar to that of the polyaniline formed on the Sample 2. Once again, islands growth on the main polymer film with smooth summits and wrinkled alpines are observable [Fig. 4(f)].

Electrochemical behaviors of the polyaniline films electrodeposited on three nanostructured Ni electrodes (Fig. 5) are in agreement with the results indicating significant differences in the morphology (Fig. 4). Although cyclic voltammetric polymerizations of aniline in all three cases suggest a similar polymer formation (Fig. 3), the cyclic voltammetric behaviors of the polyaniline films synthesized in the supporting electrolytes are quite different (Fig. 5). The first CV [Fig. 5(a)] shows a voltammetric behavior similar to that appeared during electropolymerization [Fig. 3(a)], and a significant difference is observable for the second one [Fig. 3(b)] having a high background current. However, an extraordinary cyclic voltammetric behavior [Fig. 5(c)] is detected for the polyaniline film electrodeposited onto the Ni nanoparticles prepared in the presence of carbon nanotubes. Similar to electrochemical synthesis of this polyaniline film [Fig. 3(c)], its corresponding CV [Fig. 5(c)] displays an elevated cape at high potentials. Consequently, a deeper cathodic peak is appeared during the reverse scan. The most obvious feature of this CV is the appearance of higher capacitive behavior, which is long known for polyaniline.[43] Since the carbon nanotubes were not detected in the surface imaging of the Ni nanoparticles and it is thought that they are interred within the agglomeration of the clusters of Ni nanoparticles, they cannot be responsible for this capacitive behavior (note that only a small amount of carbon nanotubes is available beneath the polymer film which has been swallowed by the substrate). This suggests that Ni nanostructures employed as substrate electrode not only controls the polymer morphology but also its electrochemical properties.

As stated earlier, the pastes for the fabrication of substrate electrodes were prepared by mixing different Ni nanoparticles with graphite fine powder to increase the paste conductivity. In fact, the metal oxide formed on the surfaces of the Ni nanoparticles decreases the electrical conductivity of Ni nanostructure and this problem may be noticeable when attaching such thick pastes to the working electrode. In this case, the graphite-included pastes have sufficient conductivity and electropolymerization on such conducting substrates proceeds successfully as well as conventional ones. Thus, charge transfer across the paste occurs via the conductive agent and simultaneously Ni nanostructures affect the electropolymerization. In other words, graphite provides a conventional conducting substrate electrode but with a specified morphology provided by the Ni nanoparticles. This provides an opportunity for study of electropolymerization of such different Ni nanostructures in the absence of problems associated with the cell circuit (inside the working electrode).

However, we also examine the electropolymerization on pure Ni nanoparticles without using the conducting agent (Fig. 6). The general patterns for all three cases are the same displaying three characteristic redox couples of aniline electropolymerization, and similar to those obtained for graphite-included pastes (Fig. 3). Even, the occurrence of strong oxidation peak at high potential quoted earlier is similar to
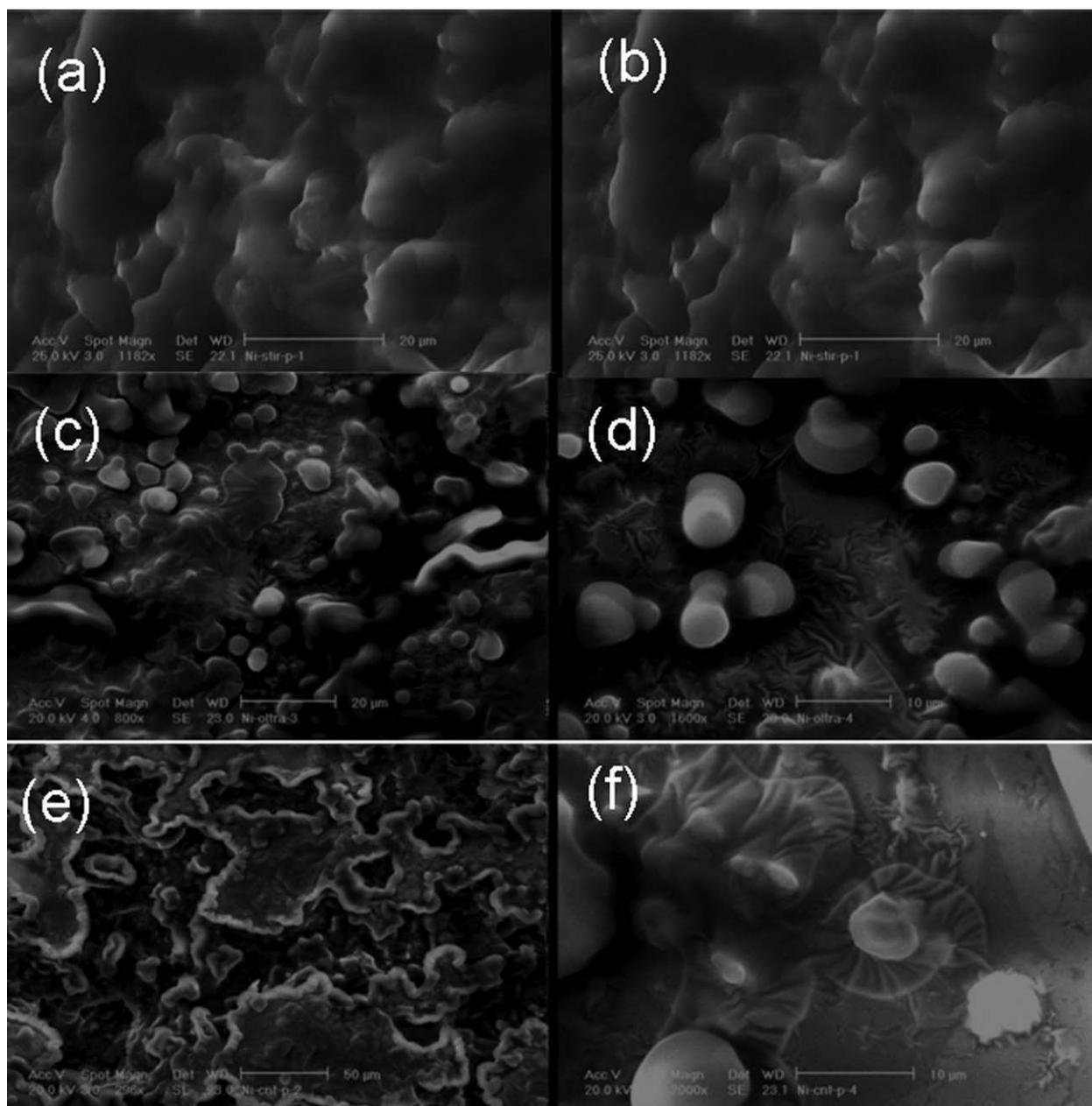
Figure 4 SEM images of the polyaniline films electrodeposited onto Ni nanoparticles prepared by (a and b) stirring, (c and d) sonication, and (e and f) adding a small amount of carbon nanotubes.

the case reported in Figure 3. Electropolymerization on first two Ni nanoparticles (Samples 1 and 2) is accompanied by the occurrence of strong oxidation peak only at the first scan, but weaker one not disappearing in the course of first cycles is detected for the case of Sample 3. One may think that such oxide-coated Ni nanoparticles with lower electrical conductivity are indeed absent in the electropolymerization process and the graphite powder is responsible for the electropolymerization processes detected in Figure 3 and electropolymerization merely occurs on graphite particles. The similarity of the general shape of CVs in Figure 3 and Figure 6 indicates that this hypothesis is wrong and electropolymerization proc-

esses at different cases (whether in Fig. 3 or Fig. 6) are strongly affected by the Ni nanostructures.

In spite of aforementioned similarities, some significant differences are observable in comparison with the case of conducting agent-included pastes (Fig. 3). First of all, the charge transfer across the substrate electrode is not uniform and consequently the polymer growth is not uniform (due to the existence of local inhomogeneities affecting electrochemical systems[44]). In other words, significant instability is detected in the series of CVs (Fig. 6). This failure can be attributed to weak electrical charge transfer inside the paste-based electrodes (without conducting agent), and in better sentence, the system has encountered an electrical failure. On the
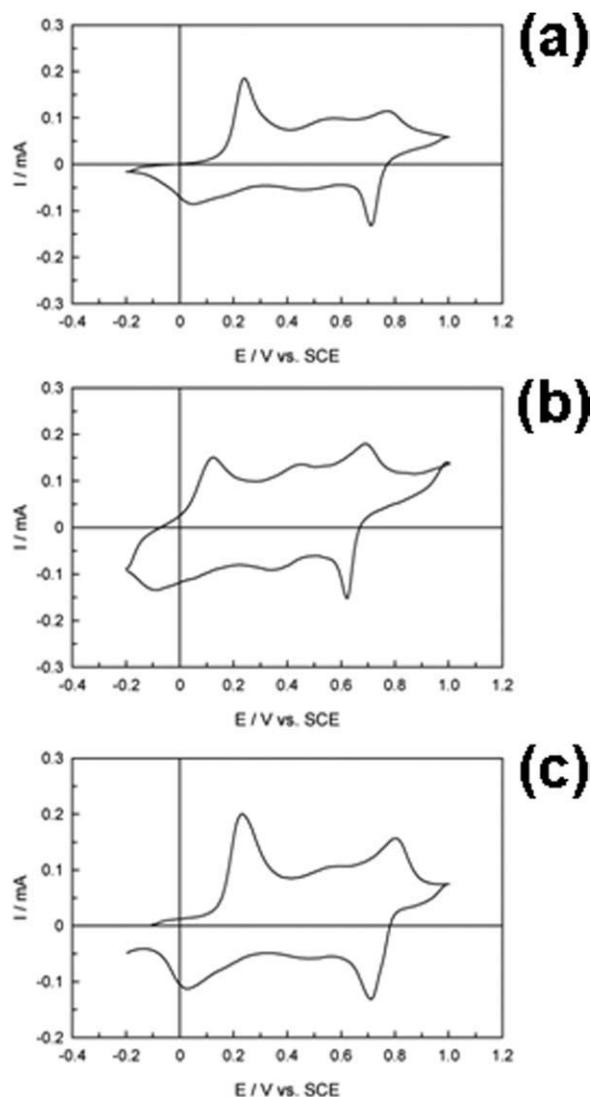
Figure 5 Voltammetric characteristics of the polyaniline films formed on Ni substrates (a–c) in the supporting electrolyte of 0.5*M* H₂SO₄. Scan rate 100 mV/s.

other hand, the current density for electropolymerization is one order of magnitude lower than that for the case of pastes with the conductive agent of graphite powder. This can be attributed to weaker charge transfer across the oxide-coated Ni nanoparticles. These are strong evidence for the discussion made earlier for the requirement of graphite powder as a conducting agent.

The most important feature of electropolymerization on the paste electrodes without conductive agent is significant shift of the CVs toward more negative potentials (Fig. 6). Since detailed discussion of this feature falls out of the aim of the present manuscript, it is almost disregarded here, but it is emphasized that occurrence of such behavior is due to the oxide-based structure of the substrate electrode.[45–47] Since formation of diradical dications (bipolarons) on the polymer chain guarantees further polyaniline growth,[41] it can be concluded that bipo-

larons, which are normally formed at high potentials during potentiodynamic polymerization of aniline, can be generated at lesser positive potential in the case of pure Ni nanoparticles. Interestingly, the third redox couple attributed to the formation/reduction of bipolaronic pernigraniline and its resonance form, i.e., protonated quinonediimine[34,35,39] is highly strengthened in the latter case. In general, the electropolymerization potential is highly dependent on the experimental condition, e.g., the electrolyte solution.[48–51] It is well known that the substrate electrode should be sufficiently oxidized before the occurrence of electropolymerization.[19] By choosing appropriate condition, it is possible to lower the electropolymerization potential.[18,19] This is also valid for passivated substrate surfaces as the substrate electrode is not needed to be oxidized.
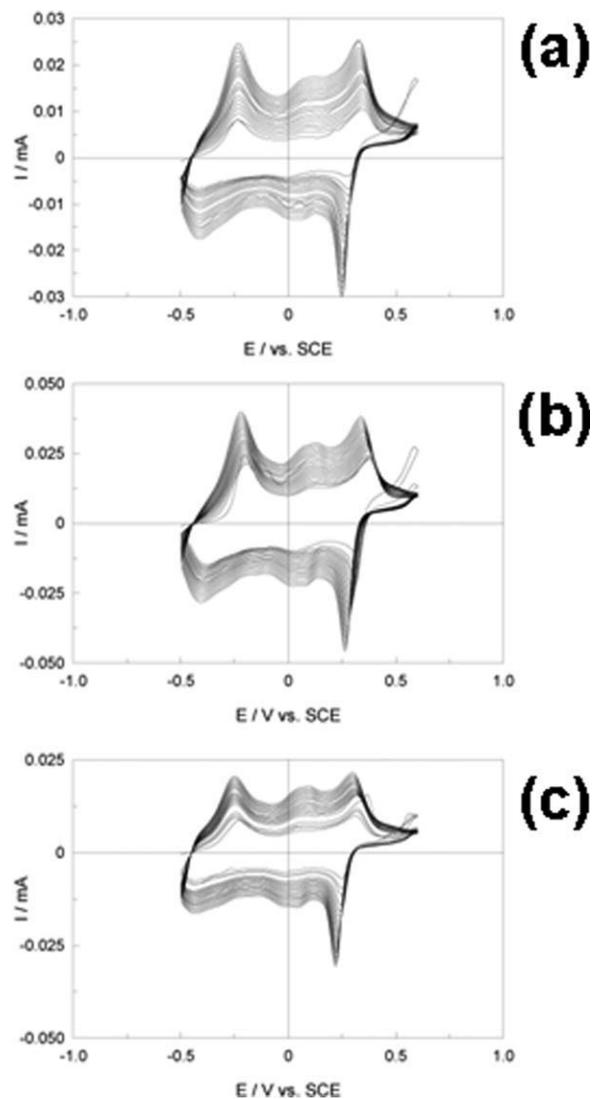

Figure 6 Electrochemical polymerization of aniline on paste-based substrate electrodes made from pure Ni nanoparticles in the absence of the graphite additive. The electrolyte solution was 0.5*M* H₂SO₄ and scan rate 100 mV/s.

CONCLUSIONS

Extensive studies of electropolymerization of aniline on nanostructured Ni substrate electrodes indicated that the electropolymerization, and consequently, the morphological structure of the conductive polymer are highly affected by the Ni nanostructures. Since the Ni nanoparticles are slightly covered with a protective oxide layer, such nanostructured Ni electrodes are sufficiently stable in acidic media for the purpose of electropolymerization. However, as such oxide materials weaken the electrical conductivity of the working electrode, a conducting agent is added to the paste utilized for the fabrication of nanostructured Ni electrodes. In any case, the polyaniline films prepared are directly affected by the chemical properties of Ni nanoparticles rather than their morphologies (as they are apparently similar as judged by electron microscopy). Similar effects were also found for electropolymerization on a conventional Pt substrate but in the presence of Ni nanoparticles dispersed into the electrolyte. In addition to the fundamental aspect of this study, it also is of applied interest, as it proposes a practical approach to control the morphological structure of conductive polymers electrodeposited onto conventional substrates or nanostructured ones.

As the final remarks, it is emphasized in the light of the experimental results obtained that although the influence of apparently similar Ni nanostructures is not normally observed on the electrochemical polymerization of aniline, it is very significant on the morphology of the polyaniline films formed. Surprisingly, the cyclic voltammetric behaviors of such polyaniline films in the supporting electrolyte are significantly different from their corresponding potentiodynamic syntheses.

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