J Appl Electrochem (2009) 39:747–750
DOI 10.1007/s10800-008-9701-5

SHORT COMMUNICATION

Electrochemical preparation of polyaniline microspheres incorporated with DNA

Jun Yano · Takeaki Kohno · Akira Kitani

Received: 28 June 2008 / Accepted: 22 October 2008

1 Introduction

The conductive polymer polyaniline (PANI) has various useful functions such as redox activity, color and conductivity changes depending on the oxidized state, reversible anion doping/dedoping and acid/base equilibria [1–3]. Some of the functions have already been utilized in devices such as lightweight secondary batteries, electrochromic displays, electromagnetic shielding devices and anticorrosion coatings. It has also been investigated for other practical uses [1–3]. There is no doubt that the morphology control of PANI, in particular, the control of the micro- and nanostructures, is a significant factor not only its the utilization, but also for the addition of new significant functions. For example, the nanofibrillar morphology improves the performance of PANI in most conventional applications involving polymer interactions with its environment [4]. This leads to much faster and more responsive chemical sensors, new inorganic-PANI nanocomposites and ultrafast nonvolatile memory devices [4].

Micro- and nanostructures (rods, wires, fibers and tubes) have been obtained using chemical and physical methods. Compared with the physical methods such as electrospinning [5, 6] and mechanical stretching [7], the chemical methods are attractive because there is the probability that they enable the molecular design of PANI. The chemical methods involve templated syntheses, which have been carried out both electrochemically and chemically by polymerizing aniline with the aid of various templates [8–14]. In spite of the variety of current templated syntheses, there is a need for practical synthetic methods capable of preparing pure, uniform, and template-free PANI micro- and nanostructures in bulk.

Deoxyribonucleic acids (DNAs) have been employed as one of the most attractive templates because of their helical molecular structures with negatively charged sites, and several successful examples have been reported [15–20]. In the present study, however, we attempted to employ DNA not as a template, but as an incorporating component with the PANI molecules. It can be expected that, during the oxidative polymerization of aniline, the cationic monomers and oligomers interact with the negatively charged DNA molecules, and a structurally-controlled PANI is obtained. The electrochemical polymerization of aniline in the presence of DNA was performed as a preliminary step to synthesize a structurally-controlled PANI/DNA composite material. The obtained PANI showed several novel properties versus the ordinary PANI. The PANI was microspheres having a redox activity even in a less acidic aqueous solution and a different absorption band in the visible wavelength range. The PANI microspheres were obtained by a simple electropolymerization.

2 Experimental

Reagent grade aniline (Sigma-Aldrich) was distilled under reduced pressure prior to use. Deoxyribonucleic acid (DNA) was purchased from Tokyo Chemical Industry. All other chemicals were of analytical grade and were used as

J. Yano (✉)
Department of Engineering Science, Niihama National College of Technology, Yagumocho 7-1, Niihama, Ehime 792-8580, Japan
e-mail: yano@sci.niihama-nct.ac.jp

T. Kohno · A. Kitani
Department of Industrial Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashihiroshima, Hiroshima 739-0046, Japan

received. The aqueous solutions were prepared using distilled and deionized water. The polymerizing solution for PANI was an aqueous solution containing 0.5 M (1 M = 1 mol dm^{-3}) CF_3COOH and 50 mM aniline. The reason why CF_3COOH was employed as an acid was the low growth rate of PANI. It is widely accepted that the growth rate is dependent on the type of acid in the polymerizing solution, although the reason has not yet been elucidated [21–24]. The lowest growth rate is observed for CF_3COOH [23, 24]. It is likely that the lower the growth rate becomes, the more favorably PANI molecules are rearranged for effective incorporation of DNA during the electropolymerization.

A standard three-electrode cell was employed, comprising a working electrode, a commercial Ag/AgCl electrode and a Pt plate counter electrode with an electrode area of about 8 cm^2. Three working electrodes were used for each purpose: platinum wire electrodes with an electrode area of 0.296 cm^2 for the cyclic voltammogram (CV) measurements; platinum plate electrodes for the morphology observations of the obtained PANI films; and optically transparent electrodes (ITO) for the measurements of the absorption spectra of the PANI films. Prior to use, the platinum wire and plate electrodes were treated with aqua regia for 30 s and then polarized by repeated potential cycling between −0.2 and 1.2 V vs. Ag/AgCl in 0.1 M H_2SO_4 until a voltammogram showed features associated with hydrogen adsorption/desorption and oxide formation/removal [25].

The electrochemical experiments were carried out using a Hokuto Denko HSV-100 potentiostat connected to a personal computer. The morphology of the obtained PANI was measured using a JEOL JSM-6320F field-emission scanning electron microscope (SEM). The PANI samples were dried under vacuum for 24 h at room temperature after adequate rinsing with water. A 5 nm Pt layer was sputtered on the samples prior to the SEM measurements.

3 Results and discussion

Figure 1 shows typical CVs measured during the oxidative electropolymerization of aniline. In the first and second positive potential scans, the anodic current at about 0.97 V was assigned to the oxidation of aniline to its cation radical. The two-redox current peaks are due to the redox reactions of the PANI film growing on the electrode surface. The yield of the growing PANI film is reflected in the increased current peaks, and the first anodic peak (i_{pa}) at about 0.2 V was taken as the criterion of the growth rate of the PANI film. As can be seen in the inset in Fig. 1, i_{pa} increases with the potential scan (N). The increase was suppressed by the presence of DNA in the polymerizing solutions (Fig. 2), suggesting that DNA interacts with the growing PANI molecules during the polymerization.

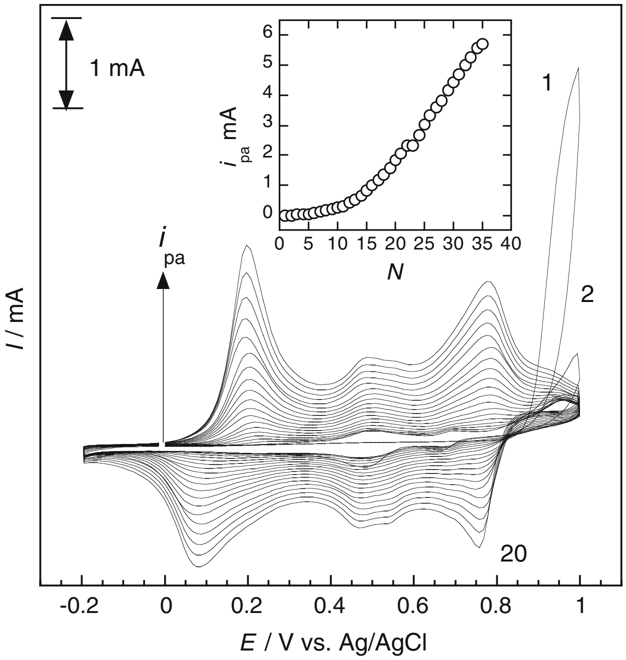

Fig. 1 Cyclic voltammograms at 100 mV s^{-1} during the electropolymerization of aniline in 0.5 M H_2SO_4 solution containing 0.5 M aniline (Inset) dependence of the first anodic current (i_{pa}) on the repeated potential scan number (*N*)

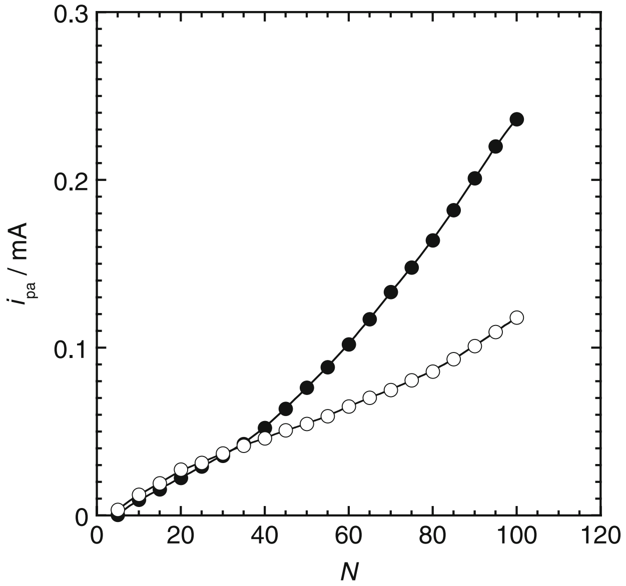

Fig. 2 Effect of the presence of DNA in the CF_3COOH polymerizing solution on i_{pa}: added amount of DNA = 0.1 (*filled circle*) and 5.0 g L^{-1} (*open circle*)

If PANI microspheres were obtained without any additions of a steric stabilizer, they would be important materials for practical use in various fields, for example,

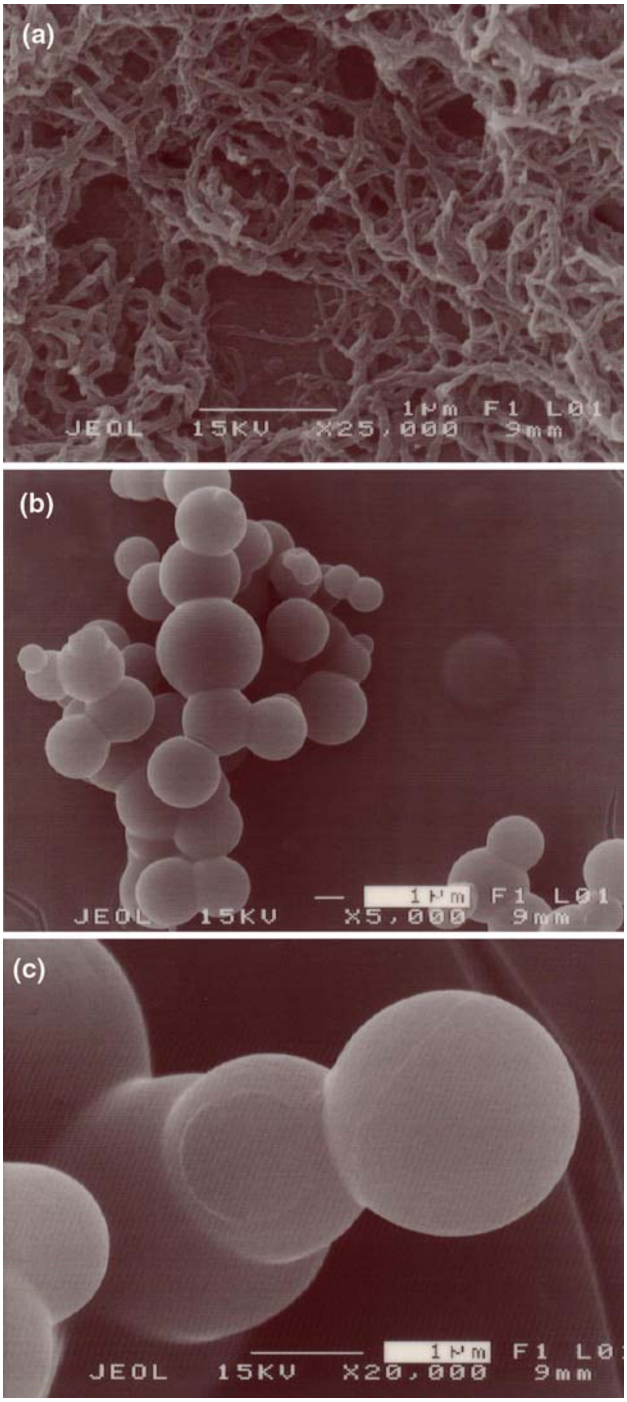

Fig. 3 SEM images of the PANI microspheres obtained from the CF_3COOH polymerizing solution **a** without and **b**, **c** with DNA (added amount of DNA = 16 g L^{-1}, $N = 400$)

conductive paints, antistatic agents and conductive fillers in transparent conductive thin films. The microspheres with a smooth surface have not yet been prepared although a variety of PANI morphologies have been reported for various dopant anions [26–29]. However, the microspheres were successfully obtained for the PANI electrodeposited from the CF_3COOH polymerizing solution containing DNA (Fig. 3). No microspheres are formed and the morphology is a fibril structure when the polymerizing solution does not contain DNA (Fig. 3a). The presence of DNA in the polymerizing solution produces a drastic morphological change. The fibril structure is transformed into a microsphere structure (Fig. 3b, c). The microspheres started to appear on the compact underlayer of PANI when the number (N) of repeated potential cycles exceeded about 50. In addition, the microspheres formation was observed when the amount of DNA was more than 4.0 g L^{-1}.

There is no doubt that the presence of DNA is crucial for the microsphere formation because no morphology, but fibril structures are observable for the PANI prepared from the CF_3COOH polymerizing solution without DNA. Although little is known about the mechanism of the microsphere formation, we have a suggested postulation. The chemical polymerization of aniline proceeds by the oxidation of aniline followed by a coupling of the resulting intermediate species with aniline. Successive couplings of the oligomeric species occur, and a polymer chain reaches a critical length required for precipitation. During this polymerization, we believe that two factors are strongly related to the microsphere formation: (1) low solubility of polymer-acid complexes, and (2) uniformity of the polymer chains. These factors are considered to contribute to one another. Due to the oxidative polymerization in the acidic polymerizing solution, the polymer chain possesses cationic sites at the amine or imine groups. The cationic polymer forms a polymer-acid (PANI-acid) complex. As pointed out by Tang and coworkers [30], the PANI-acid complex has the most stable form when the anion is the most lyophilic. As a result, because of the most lyophilic CF_3COO^- ion, the PANI-CF_3COOH complex is the most difficult to dissociate, and their solubility is the lowest. For this reason, the PANI-CF_3COOH and PANI-$HClO_4$ complexes precipitate in the stable precipitation form. On the other hand, there is obviously a tendency that the microspheres are formed when the polymerization rate is low. This low polymerization rate enables the polymer chains to rearrange and assemble in the most favorable and stable precipitation form. The polymerization rate is also low enough for the PANI molecules to effectively incorporate bulky DNA molecules. This incorporation results in the uniformity of the polymer chains as the precipitation form and this uniformity significantly contributes to the microspheres formation.

The fact that the PANI microspheres incorporate DNA molecules was strongly supported by two experimental results; new absorption band at 620 nm and redox activity in a neutral aqueous solution. The PANI film with the microspheres had a different color from the ordinary PANI films. This is reflected by the absorption spectra (Fig. 4). A broad absorption was evident at around 800 nm for the PANI film without DNA, while a broad absorption at around 620 nm

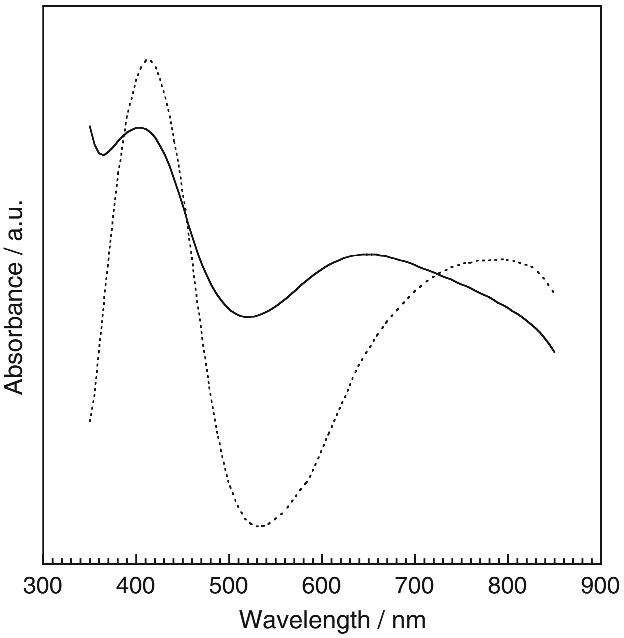

Fig. 4 Absorption spectra of the PANI film prepared from the CF_3COOH polymerizing solution without DNA (*dotted line*) and with DNA (*continous line*)

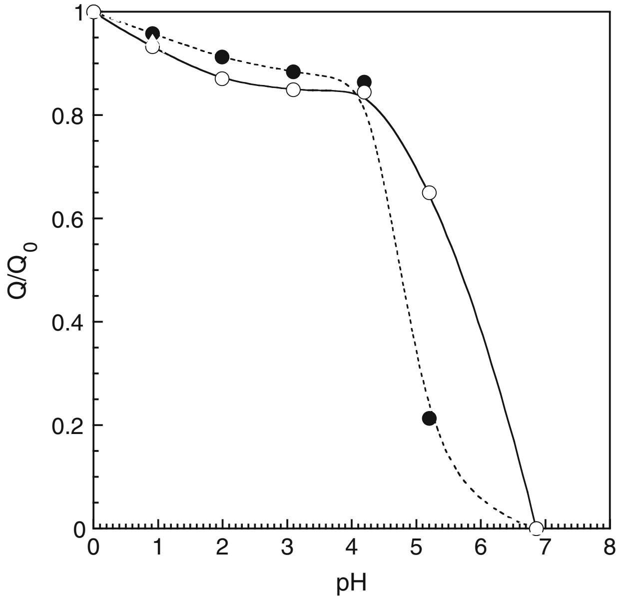

Fig. 5 Relationship between the solution pH and the redox charge (*Q*) of the PANI obtained from the CF_3COOH polymerizing solution with DNA (*open circle*) and without DNA (*filled circle*)

occurred for the PANI film with the microspheres, which has never been seen for ordinary PANI films, showing that there is some electronic interaction between the incorporated DNA and the PANI molecules. On the other hand, the PANI film with the microspheres was also different in redox activity in the less acidic media. It is widely accepted that PANI gradually loses its redox charge as the solution pH becomes higher. The charge suddenly drops at around pH 4 and PANI has only a small redox charge at pH > 5. Although the PANI without DNA had the same tendency, the PANI with DNA still had an adequate redox charge at pH 5, about 62% of the redox charge measured in the solution of pH 1 (Fig. 5). This adequate redox activity in the less acidic solution is probably due to the enrichment of H^+ in the PANI that originated from the anionic sites (the phosphate part) of the incorporated DNA.

Acknowledgement The authors gratefully acknowledge support for this research by a grant from the Kato Foundation for the Promotion of Science.

References

1. Salaneck WR, Lundström I, Rånby B (1993) Conjugated polymers and related. Oxford Science Publications, Oxford
2. Skotheim TA, Elsenbaumer RL, Reynolds JR (1998) Handbook of conducting polymers. Marcel Dekker, New York
3. Chandrasekhar P (1999) Conducting polymers, fundamentals and applications. Kluwer Academic, London
4. Skotheim TA, Reynolds JR (2007) Handbook of conducting polymers, 3rd edn, vol 7, Marcel Dekker, New York, p 1
5. Reneker DH, Chun I (1996) Nanotechnology 7:216
6. MacDiarmid AG, Jones WE, Norris ID, Gao J, Johnson AT, Pinto NJ, Hone J, Han B, Ko FK, Okuzaki H, Llaguno M (2001) Synth Met 119:27
7. He HX, Li CZ, Tao NJ (2001) Appl Phys Lett 78:811
8. Huang LM, Wang ZB, Wang HT, Cheng XL, Mitra A, Yan YX (2002) J Mater Chem 12:388
9. Wei ZX, Zhang ZM, Wan MX (2002) Langmuir 18:917
10. Wang CW, Wang Z, Li MK, Li HL (2001) Chem Phys Lett 341:431
11. Choi SJ, Park SM (2000) Adv Mater 12:1547
12. Martin CR (1996) Chem Mater 8:1739
13. Wu CG, Bein T (1994) Science 264:1757
14. Michaelson JC, McEvoy AJ (1994) Chem Commun 79
15. Ma Y, Ali SR, Dodoo AS, He H (2006) J Phys Chem B 110:16359
16. Shi L, Xiao Y, Willner I (2004) Electrochem Commun 6:1057
17. Ma Y, Zhang J, Zhang G, He H (2004) J Am Chem Soc 126:7097
18. Sergeev VG, Lokshin NA, Golubev VB, Zezin AB, Levon K, Kabanov AVA (2003) Phys Chem 390:118
19. Shao Y, Jin Y, Dong S (2002) Electrochem Commun 4:773
20. Nagarajan R, Liu W, Kumar J, Tripathy SK, Bruno FF, Samuelson LA (2001) Macromolecules 34:3921
21. Zotti G, Catterin S, Comisso N (1988) J Electroanal Chem 239:387
22. Nunziante P, Pistoia G (1989) Electrochim Acta 34:223
23. Duic L, Mandic Z, Kovacicek F (1994) J Polym Sci Polym Chem 32:105
24. Desilvestro J, Scheifele W (1993) J Mater Chem 3:263
25. Breiter M, Böld W (1961) Electrochim Acta 5:145
26. Yoshikawa K, Yoshioka K, Kitani A, Sasaki K (1989) J Electroanal Chem 270:421
27. Kitani A, Kaya M, Tsujioka S, Sasaki K (1988) J Polym Sci Polym Chem 26:1531
28. Huang W, Humphrey BD, MacDiarmid AG (1986) J Chem Soc Faraday Trans 182:2385
29. Choi S, Park S (2002) J Electrochem Soc 149:E26
30. Tang H, Kitani A, Shiotani M (1996) Electrochim Acta 41:1561