Colloid Polym Sci (2009) 287:1107–1110
DOI 10.1007/s00396-009-2078-0

SHORT COMMUNICATION

Synthesis of 1-dimensional polyaniline nanofibers by reverse microemulsion

Sanjeev Kumar · Vaishali Singh · Saroj Aggarwal · Uttam Kumar Mandal

Received: 12 May 2009 / Revised: 29 June 2009 / Accepted: 29 June 2009 / Published online: 18 July 2009

Keywords Polyaniline · Nanofibre · Microemulsion

Extremely fine 1-dimensional (1D) polyaniline (PANI) nanofibers have been prepared under ambient conditions by novel reverse microemulsion route using cetyl trimethyl ammonium bromide (CTAB) as surfactant.

PANI is the most extensively studied conductive polymer due to its relatively facile processability and excellent environmental stability combined with relatively high levels of electronic conductivity as well as thermoelectric and optical properties [1–4]. Synthesis of polyaniline with reduced dimensionality having fascinating morphologies and architectures offers the possibility of enhanced performance due to fast transfer of electrons [5–11].

The fabrication of 1D polyaniline with nanometer dimensions such as nanorods, nanofibers, nanotubes, and nanobelts have attracted intensive interest because they possess the advantage of both low-dimensional system and can be envisioned for potential applications including polymeric conducting molecular wires, chemical sensors, biosensors, and light-emitting devices. Considerable efforts have been dedicated to synthesize 1D nanostructured polyaniline having fibrillar morphology by chemical routes [7, 12–19]. The use of surfactants during the polymerization has largely yielded polyaniline having particulate morphology. There are very few reports in which fibrillar morphology has been observed in surfactant-assisted polymerization of aniline [20, 21]. Microemulsion route is dynamic in nature yielding exciting morphology depending on various reaction parameters. Reverse microemulsion may be used as an effective tool to fabricate nanofibers oriented into large 1D arrays and is capable of making pure and uniform bulk nanofibers with small dimensions.

Herein, we endeavor a novel and facile approach for the synthesis of extremely fine PANI nanofibers under ambient conditions by reverse microemulsion using CTAB as the morphology directing surfactant template, along with hydrochloric acid and ammonium persulfate as dopant and oxidant, respectively.

In a typical procedure, two reverse microemulsions ME_1 containing aniline and dopant and ME_2 with initiator ammonium persulfate were prepared. Appropriate amount of CTAB was added to known volume of cyclohexane forming a murky emulsion. Aniline with dopant mixture and isoamylalcohol were then added to the emulsion under continuous magnetic stirring. The murky emulsion became transparent within seconds. The stirring was continued for 1 h at room temperature resulting in a stable reverse microemulsion (ME_1). Second reverse microemulsion (ME_2) was prepared under similar conditions with 1 M aqueous solution of the initiator ammonium persulfate in place of aniline. The homogeneous reverse microemulsion solution ME_2 was then added dropwise to reverse microemulsion ME_1 under constant magnetic stirring at room temperature. The mixture was further stirred for 24 h at room temperature 30 °C. The entire reaction was carried out under inert atmosphere. The oxidation of aniline onsets

---

S. Kumar · V. Singh · S. Aggarwal
University School of Basic and Applied Sciences, GGS Indraprastha University,
Kashmere Gate, Delhi 110403, India

U. Kumar Mandal (✉)
University School of Chemical Technology,
GGS Indraprastha University,
Kashmere Gate, Delhi 110403, India
e-mail: uttammandal@rediffmail.com

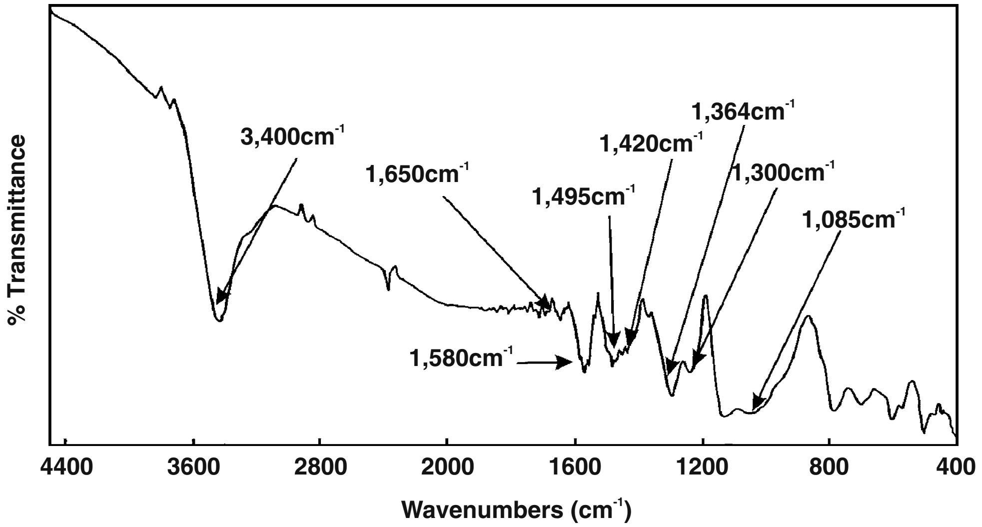

Fig. 1 FTIR spectra of polyaniline nanofibers

after 15 min was indicated by the formation of blue pernigraline at the initial stages of polymerization. This blue pernigraline form converts to a green protonated emeraldine form at the end of the polymerization. After 24 h of stirring, the resultant green color content was centrifuged at 12,000 rpm to obtain the polyaniline nanostructures followed by their washing with methanol and double-distilled water for several times. The product obtained was dried in a vacuum oven at 60°C for 48 h.

A Fourier transform infrared (FTIR) spectrum (Fig. 1) confirms the formation of PANI. Spectra are consistent with the emeraldine form of polyaniline. The absorption band around 3,400 cm^{-1} corresponds to the free N—H bond [22]. The strong absorbtion bands at 1,580 and 1,495 cm^{-1} corresponds to C═C stretching vibrations of the quinoid (N═Q═N) and benzenoid (N—B—N) rings polymer chain, respectively [23]. A shoulder band that appears around 1,650 cm^{-1} is assigned to the carbonyl group (C═O), indicating the formation of quinine during polymerization [24]. The band at 1,495 cm^{-1} can be attributed to aromatic stretching vibrations [23]. The absorption band around 1,420 cm^{-1} has been assigned previously to the symmetric stretching of phenazine rings that may be formed in small amount at the beginning of the reaction. This band is not usually observed in the spectra of "standard" polyaniline, synthesized at low pH. It has previously been suggested that the role of phenazine-like units (due to aniline coupling in ortho-position at higher pH) is to facilitate formation of nanofibers and to provide a template for growing the supramolecular nanofiber structure and ordering of oligomers [23]. Bands at 1,364 and 1,300 cm^{-1} are attributed to C—N stretching vibrations [23]. The absorption band at 1,085 cm^{-1} is associated with high electrical conductivity and a high degree of electron delocalization as reported in the literature [1, 25, 26].

The representative transmission electron microscope (TEM) micrographs of PANI nanostructures obtained via reverse microemulsion process with CTAB are composed of fibrous structures having an average diameter of 20 nm (Fig. 2). The length of the fibers ranges up to several

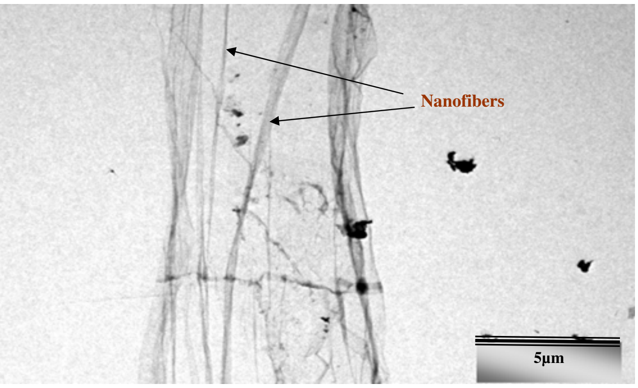

Fig. 2 TEM image of polyaniline nanofibers

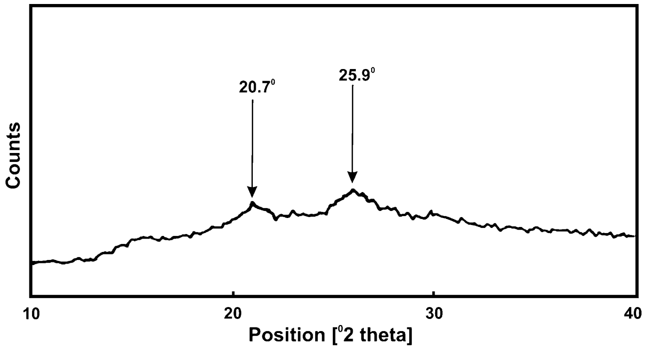

Fig. 3 XRD patterns of polyaniline nanofibers

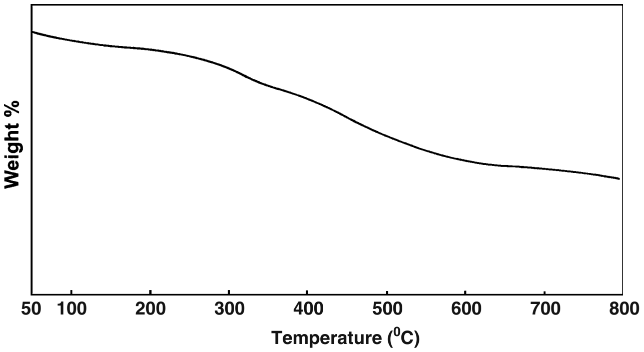

Fig. 4 TGA diagram of polyaniline nanofibers

micrometers. TEM analysis reveals that nanofibers obtained are extremely fine as shown in Fig. 2. The samples were sonicated before TEM analysis, which results in segregated fibers (Fig. 2).

To further confirm the crystal structure of the polyaniline nanostructures, the samples have been subjected to X-ray diffraction (XRD) analysis at 30 °C. Figure 3 shows the XRD patterns of the resultant polyaniline nanostructures. The broad diffraction peaks centered at $2\theta=20.7°$ and 25.9° (d-spacing=4.3 and 3.5 Å, respectively) are observed in the samples obtained from the reverse micelles based on CTAB. This indicates that the resulting polymer is in the form of highly doped emeraldine salt and has good crystallinity [27, 28]. The latter diffraction peaks at $2\theta=25.9°$ (d-spacing=3.5 Å) implies that the phenyl rings are densely packed giving rise to a planar conformation and, thus, to an extensive interchain $\pi\rightarrow\pi^*$ orbitals overlap [27, 28]. Furthermore, the increased crystallinity indicates a high doping level [28].

The electrical conductivity of a pressed pellet of polyaniline nanofibers is 4.68×10^{-1} S cm^{-1} at room temperature. The measured room temperature direct current conductivity of our samples was found to be at par than those reported by other researchers [29–31].

Figure 4 presents the thermograms for polyaniline nanofibers used to find the decomposition temperature. This decomposition temperature sets an upper limit for the temperature at which polyaniline nanostructures can be heated for subsequent works. The acid doped polyaniline showed three steps of decomposition process as proposed by previous workers [32]. It is suggested that the initial stages of weight loss are due to volatilization of water molecule and oligomers as well as unreacted monomer elimination. Then, at higher temperature, the protonated emeraldine form of polymer is lost, and at more extreme temperature, the polymer chain breaks, leading to the production of gases such as acetylene and ammonia [32, 33]. Thermogravimetric analysis reveals that nanofibers have high thermal stability with decomposition beginning above 400 °C.

In conclusion, we demonstrate a novel route to synthesize fine and uniform polyaniline nanofibers at room temperature. The synthesis is easily scalable and reproducible. In reverse microemulsion, the structure-determining materials direct the nanostructures to specific crystallite size and shape. The room temperature direct current conductivity value is at par as compared to the conductivity reported for polyaniline nanofibers synthesized using surfactants via reverse microemulsion. These highly conducting and thermally more stable polyaniline nanofibers may provide potential applications such as nanodevices, neuron devices, chemical sensors or actuators, and many more.

Acknowledgements We acknowledge technical support from Mr. Sandeep Arya for assistance in TEM measurements (Sophisticated Analytical Instrumentation Facility, Department of Anatomy, AIIMS, Delhi). We also thank Mr. Amarjeet Singh for his help in X-ray diffraction measurements (Textile Department, IIT, Delhi).

References

1. Kang ET, Neoh KG, Tan KL (1998) Prog Polym Sci 23:277
2. Huang WS, Humphrey BD, MacDiarmid AG (1986) J Chem Soc Faraday Trans 82:2385
3. Chiang JC, MacDiarmid AG (1986) Synth Met 13:193
4. Majidi MR, Kane-Maguire LAP, Wallace GG (1994) Polymer 35:3113
5. Stejshal J, Kratochvil P, Armes SP, Lascelles SF, Riede A, Helmstedt M, Prokes J, Kivka I (1996) Macromolecules 29:6814
6. Kim B-J, Oh S-G, Han M-G, Im S-S (2000) Langmuir 16:5841
7. Huang J, Kaner RB (2004) Angew Chem Int Ed 43:5817
8. Li D, Kaner RB (2006) J Am Chem Soc 128:968
9. Martin CR (1995) Acc Chem Res 28:61
10. Pan L, Pu L, Shi Y, Sun T, Zhang R, Zheng Y (2006) Adv Funct Mater 16:1279
11. Zhong W, Deng J, Yang Y, Yang W (2005) Macromol Rapid Commun 26:395
12. Haung J, Kaner RB (2006) Chem Commun 4:367
13. Sawall DD, Villahermosa RM, Lipeles RA, Hopkins AR (2004) Chem Mater 16:1606
14. Wang J, Bunimovich LY, Sui G, Savvas S, Wang J, Guo Y, Heath JR, Tseng HR (2006) Chem Commun 29:3075
15. Chiou NR, Epstein AJ (2005) Adv Mater 17:1679
16. Antonietti M, Basten R, Lohmann S (1995) Macromol Chem Phys 196:441
17. Candau F (1997) Microemulsion polymerization. In: Asua JM (ed) Polymeric dispersions: principles and applications. Kluwer, Dordrecht, pp 127–140
18. Kuramoto N, Genies EM (1995) Synth Met 68:191
19. Armes SP (1993) US Patent 5256730
20. Yu L, Lee JI, Shin KW, Park CE, Holze R (2003) J Appl Polym Sci 88:1550

21. Osterhalm JE, Cao Y, Klavetter F, Smith P (1994) Polymer 35:2902
22. Roa PS, Sathyanarayana DN, Palaniappan S (2002) Macromolecules 35:4988
23. Trchova M, Sedenkova I, Konyushenko EN, Stejskal J, Holler P, Gric-Marjanovic G (2006) J Phys Chem B 110:9461
24. Venancio EC, Wang PC, Mac Diarmid AG (2006) Synth Met 159:357
25. Meng L, Lu Y, Wang X, Zhang J, Duan Y, Li C (2007) Macromolecules 40:2981
26. Cao Y, Li S, Xue Z, Guo D (1986) Synth Met 16:305
27. Stejskal J, Riede A, Hlavata D, Prokes J, Helmstedt M, Holler P (1998) Synth Met 96:55
28. Pouget JP, Josefowicz ME, Epstein AJ, Tang X, MacDiarmid AG (1991) Macromolecules 24:779
29. Zhang L, Wan M (2002) Nanotechnology 13:750
30. Wei Z, Zhang L, Yu M, Wan M (2003) Adv Mater 15:1382
31. Chiou NR, Lee LJ, Epstein AJ (2007) Chem Mater 19:3589
32. Ansari R, Price WE, Wallace GG (1996) Polymer 37(6):917
33. Konyushenko EN, Stejskal J, Trchova M, Hradil J, Kovarova J, Prokes J et al (2006) Polymer 47:5715