

Synthesis of Nanostructured Large Particles of Polyaniline

Ali Eftekhari

Laboratory of Electrochemistry, Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

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ABSTRACT: Synthesis of larger particles of conductive polymers is usually favorable due to higher conductivity (as a result of lesser interfacial resistance). On the other hand, advantages of nanostructured materials are well known. Thus, it is desirable to fabricate large particles that have nanostructure, to gain double advantage. A simple method based on chemical polymerization under centrifugal forces is proposed to achieve this goal. It was typically employed for a well-known conductive polymer, namely, polyaniline to fabricate large particles (e.g.,

400 μm) with internal nanostructure of ~ 100 nm. This also significantly increases the electrical conductivity of the polymer. This is indeed a simple approach, which can be easily performed using a conventional centrifuge system. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 6060–6063, 2006

Key words: nanostructured polymer; polyaniline nanofibers; large particles; conductive polymers; centrifugal force; chemical synthesis

INTRODUCTION

In the realm of nanotechnology, it is favorable to fabricate nanostructured materials to gain valuable advantages of nanomaterials. Conductive polymers were not an exception in this context. Considerable efforts have been paid to synthesize nanostructured conductive polymers.^{1–7} There are various applications for this morphological structure of conductive polymers. However, it is not favorable for researchers generally studying conductive polymers. In fact, synthesis of large particles is more advantageous in comparison with nanostructured conductive polymers from general material science point of view, since material properties of conductive polymers are better when the polymer chains have been packed to form large particles.^{8–10}

Obviously, the main feature of conductive polymers is their excellent conductivity. It is known that conductivity of conductive polymers strongly depends on the particle size and increases by increasing the particle size.^{8–10} This is because of the interfacial resistance of particles which is the main obstacle in conductivity of such materials. This behavior has dismissed general studies of conductive polymers from the rapidly growing and advancing field of nanotechnology, which aims to reduce the particle sizes to gain advantages of nanostructures.

In the present article, a simple approach is proposed to synthesize large particles of conductive polymers having well-defined nanostructures. In this case,

not only the conductivity is improved because of decrease in interfacial resistance, but also advantages of nanostructure are achieved. In other words, this approach provides a double improvement and starts a new relationship between the material science of conductive polymers and nanotechnology.

For electrochemical synthesis, applying an external mechanical force induced to a system leads to the formation of electroactive materials with improved properties. Similar to the case of magnetohydrodynamics (i.e., in the presence of magnetic field), which is known for many years,^{11–13} we have recently attempted to investigate electrochemical synthesis under centrifugal forces.^{14–18} This approach has also been used for electrochemical synthesis of conductive polymers.^{18–20} Electrochemical polymerization in the presence of an applied centrifugal force leads to the formation of conductive polymers with enhanced conductivity.¹⁸ To generalize this efficient approach, we extend it to chemical synthesis.

EXPERIMENTAL

Chemical synthesis of a well-known conductive polymer was chosen as a typical example. Polyaniline was synthesized by chemical oxidation in an aqueous solution of sulfuric acid at 0°C. The oxidant (ammonium persulfate) was slowly added to an aqueous solution of aniline in sulfuric acid. The resulting green powder was rinsed first in ethanol, then in water. The solutions were 10 g water, 0.98 g H₂SO₄, 0.28 g aniline, and 0.685 g ammonium persulfate in 2 g water. The polymerization time was 15 min. This is indeed a common method for the preparation of polyaniline, as

Correspondence to: A. Eftekhari (eftekhari@merc.ac.ir).

previously described in the literature¹⁰ Scanning electron microscopy (SEM) investigations were carried out using a Cambridge electron microscope, model Steroscan 360. FTIR measurements were performed using a Bruker spectrometer. The centrifuge system employed was a conventional model for laboratory general usage. The experiments were performed at the rates of 0, 2500, and 5000 rpm corresponding to relative centrifugal forces (RCF)²¹ 0, 545, and 2180.

RESULTS AND DISCUSSION

Figure 1(A) shows the morphology of a polyaniline sample prepared by the conventional method. This is completely similar to those reported in the literature. The particle sizes tend to increase upon performing the chemical synthesis under an applied centrifugal force [Fig. 1(B)]. This indeed suggests the usefulness of the approach proposed to improve synthesis of the conductive polymer from the material science point of view. In other words, this satisfies the requirement for the synthesis of large particles. As expected, the conductivity of the polyaniline sample with larger particles is higher. The conductivities of two similar samples prepared in the absence and presence of a typical centrifugal force of RCF 545 were 0.6 and 0.9 S/cm respectively. In addition to the largeness of the particles, which is accompanied by a lesser interfacial resistance, the mechanical force induced during the

polymer synthesis also provides another opportunity for the enhancement of the electrical conductivity. This issue has been extensively studied for the case of electropolymerization under centrifugal forces, which is a better case for fundamental investigations, as it is easier to control the electrochemical polymerization process.¹⁴

The particle sizes become larger by increasing the strength of the centrifugal force induced [Fig. 2(A)]. Interestingly, this effect is accompanied by the formation of nanostructures on these large particles. In fact, when the centrifugal force is sufficiently strong, the entanglement of the one-dimensional nanostructured conductive polymer results in the growth of extremely large particles (Fig. 2). Figure 2(B) illustrates the well-defined nanostructure of the conductive polymer synthesized. The regular nanostructure of the polyaniline consists of individual parts, which have been closely packed to form the extremely large particles shown in Figure 2(A). Although it is difficult to distinguish the lowest size of these particles, the structure quoted earlier was effectively found in the particles in the range of 20–400 μm . These microparticles are sufficiently large for easy handling. Moreover, the synthesis procedure is very simple; there is a good reproducibility for the preparation of such samples.

Since the centrifugal force induced only caused the hydrodynamical convection, it does not directly affect the chemical synthesis, and just controls the polymer

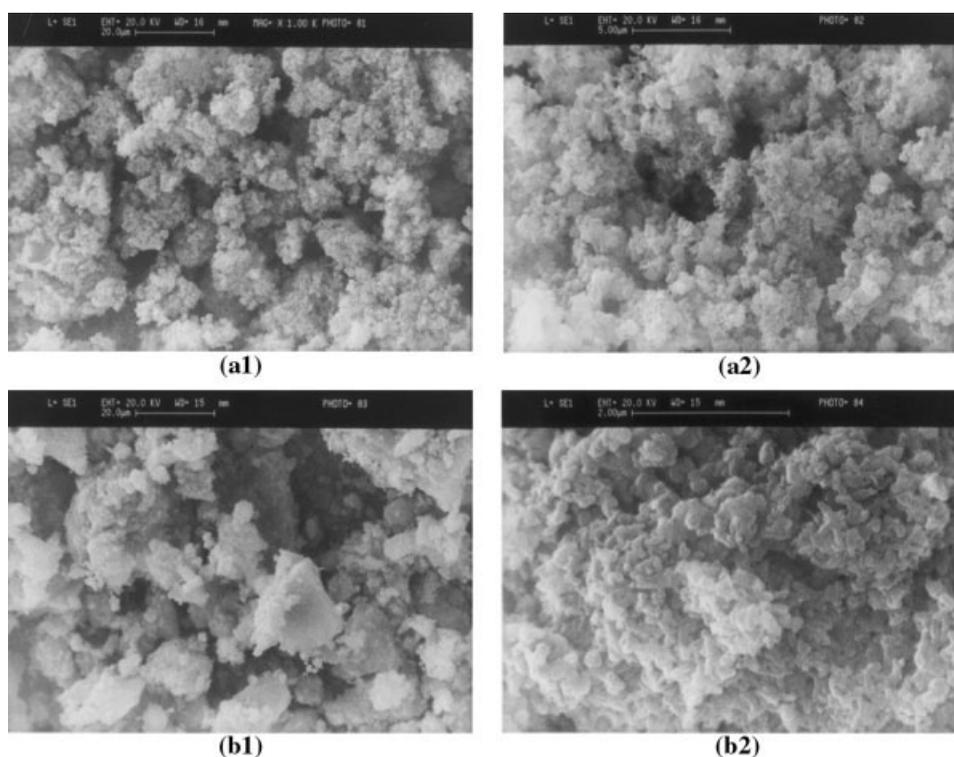


Figure 1 SEM image of the polyaniline sample prepared in (A) the absence of a centrifugal force and (B) the presence of a centrifugal force induced by rotation with speed of 2500 rpm (corresponding to RCF 545).

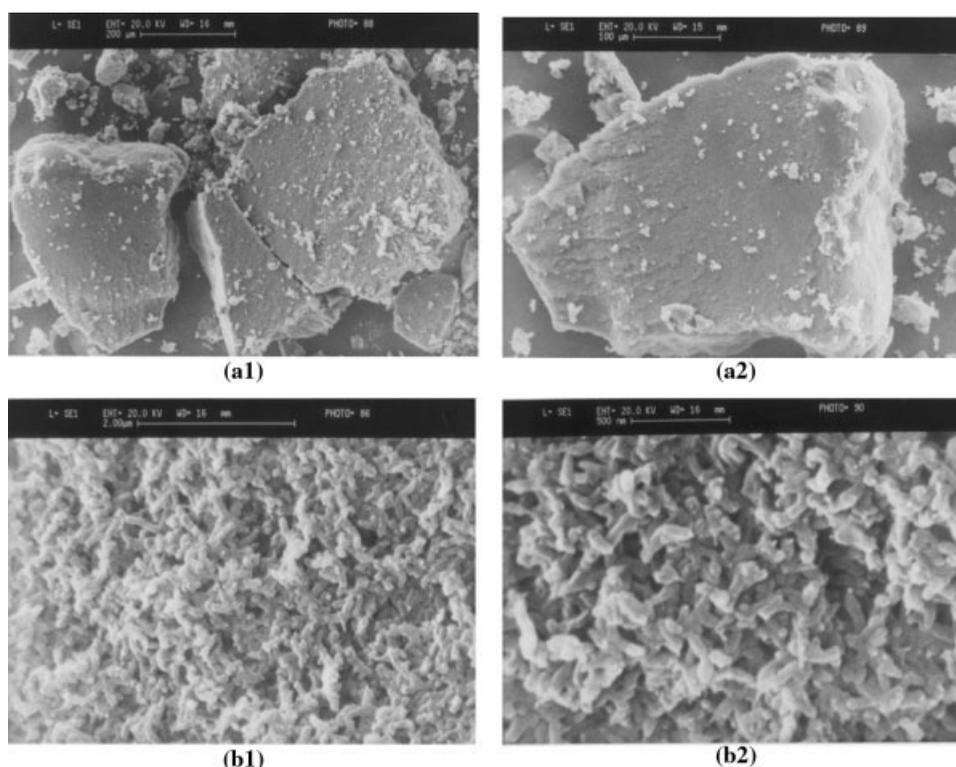


Figure 2 SEM images of the polyaniline sample prepared in the presence of a sufficiently strong centrifugal force, i.e., RCF 2180 corresponding to the rotation speed of 5000 rpm.

growth and its corresponding morphology. FTIR spectrum of the polyaniline large particles having nanostructure is presented in Figure 3. This spectrum is similar to the characteristics of polyaniline FTIR spectrum as has been widely discussed in the literature. The characteristic bands of the emeraldine salt of polyaniline,²² e.g., the C=C stretching of quinoid and benzenoid ring bands centered at 1567 and 1487 cm^{-1} , the C—N stretching mode at 1300 cm^{-1} , the absorption peaks of N—Q—N (Q is the quinoid ring) at 1140 cm^{-1} , and the N—H stretching vibration at 3400 cm^{-1} are observable (Fig. 3). Indeed, inducing a centrifugal force has no significant influence on chemical structure of the conductive polymer, as the FTIR spectra of all samples prepared in the absence or presence of centrifugal forces with different strengths are approximately the same (not shown).

The significant influence of the applied centrifugal force on the chemical synthesis of the conductive polymer is to change its morphology. It is worth noting that the uniform nanostructure of such large particles provides a great opportunity for better (ionic) diffusion through the polymer matrix,²³ which is an essential process in the practical performances of conductive polymers (e.g., applications associated with electrochemical processes such as batteries, sensors, etc.).

In addition, this is associated with an excellent conductivity for the nanostructured large particles of

polyaniline, which was 1.7 S/cm. Since these particles are extremely large, the common difficulties in handling the nanomaterials are absent. In other words, there is no need to pack this nanostructured material for the applied purposes. This *in situ* packing also provides a great opportunity for the enhancement of the conductivity (in comparison with nanomaterials mechanically packed). This will be an invaluable advantage for the systems utilizing ionic conductivity of conductive polymers, as the electroactive species can

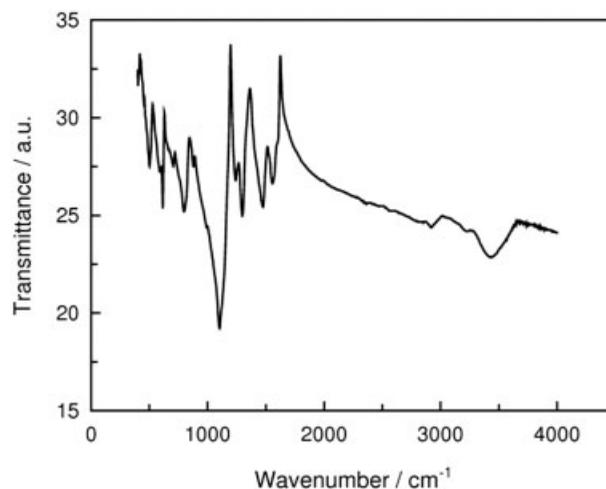


Figure 3 FTIR spectrum of the polyaniline sample illustrated in Figure 2.

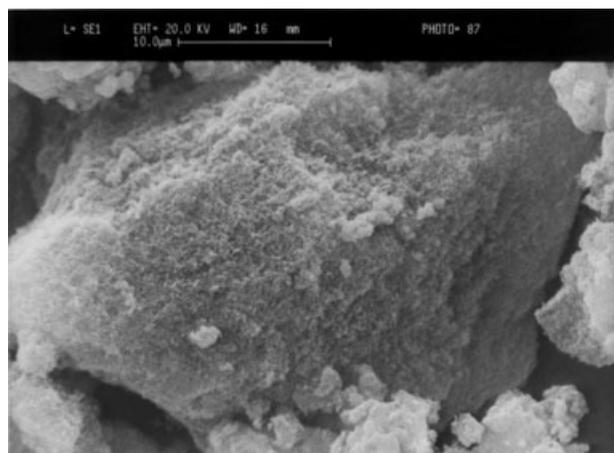


Figure 4 The complete view of a smaller particle with opportunity to distinguish nanostructures at this scale.

easily diffuse inside the bulk material through the nanostructured polymer. The uniform porous nanostructure of the polymer spread across a large particle is illustrated in Figure 4 for a smaller particle to observe nanostructures. According to the model proposed in Ref. 23, it is obvious that diffusion process is more effective in this case.

Inducing a centrifugal force may have two effects on the chemical bath, like the case of magnetohydrodynamics: (i) the mechanical force induced to the floating species with respect to their specific weight, and (ii) the hydrodynamical convection induced as a result of concentration gradient. The latter one is similar to stirring. This is a significant effect on the uniformity of nanostructure formed, as it avoids the possible increase in local concentration leading to local growth of the polymer. However, the main factor in the formation of the above-mentioned morphology is induction of mechanical force to the reactive species. Since the rate of synthetic reaction is higher in the presence of an applied centrifugal force (due to both effects), nanostructure is formed instead of gradual growth of the polymer chain. Formation of smaller particles in the presence of centrifugal force has also been reported for the case of electrodeposition under centrifugal forces, which involves an additional rate-limiting process, viz. electron transfer.^{17,19} On the other hand, the mechanical force induced persuades the forming particle to be closely packed to create extremely large particles [as illustrated in Fig. 2(A)]. It should be emphasized that this naive hypothesis is just a speculation based on experimental observation, and there is no claim that it is really followed in the chemical synthesis of polyaniline. This is indeed a possible mechanism for the formation of such morphology, and this issue will be out of the aim of the

present article, which aims to report this interesting phenomenon for applied purposes.

CONCLUSIONS

The present report is just the beginning for the synthesis of nanostructured large particles. This is a rough case typically showing this possibility. It is well known that the chemical synthesis of conductive polymers results in the formation of uniform structures upon using dilute oxidant concentration, slow addition of reactants, and long polymerization duration (c.f. Ref. 10). However, because of the technological limitations we used the worst case for this typical study. Gradual addition of reactant in a rotating device requires additional apparatus, which is not appropriate for the typical study aiming to report the original phenomenon without other experimental errors. Using dilute solutions needs huge rotating device. However, such difficulties are not very important in the future development of this approach. In other words, significantly better results will be obtained upon further investigations of the approach proposed for different cases.

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