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Nano-emulsion use for the synthesis of polyaniline nano-grains or nano-fibers

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We report that nano-emulsions can be creatively used as a morphology selective synthesis method to prepare not only nano-grains but also nano-fibers with high selectivity. Synthesis of the two different morphological materials was demonstrated using polyaniline synthesis as a model case. Polyaniline nano-grains were synthesized from aniline molecules in nano-size aqueous droplets as polymerization sites whose droplets were generated by inverse water-in-oil nano-emulsion use, and polyaniline nano-fibers were synthesized from aniline in aqueous nano-dimensional channels as polymerization sites whose channels were generated by direct oil-in-water nano-emulsion use containing high population of oil droplets. Using the approaches, we successfully synthesized nano-fibers of 60 nm diameter with 0.5 μm length and also nano-grains having diameter of 60–80 nm. The two different polymerization sites of nano-scale dimension were made by changing the ratio among surfactant, aqueous aniline/HCl solution, and oil, i.e. organic solvent. We found the nano-fibers synthesized from the channels formed by the direct oil-in-water nano-emulsion have higher bulk electrical conductivity than the nano-grains which were synthesized from the droplets formed by the inverse water-in-oil emulsion. We also found that the emulsion use allows us to use a room temperature synthesis unlike conventional synthesis methods which require to use ice bath temperature. Physical properties of both nano-fibers and nano-grains synthesized were characterized by Fourier transform infrared (FTIR), UV–Vis spectra, scanning electron microscopy (SEM), and four probes conductivity measurement.

Keywords: nano-emulsion polyaniline; emulsion polymerization; nano-fibers; nano-grains

INTRODUCTION

Nano-materials have become one of the main subjects in materials science and have brought together scientists and engineers in the disciplines of physics, chemistry, biology, and electrical engineering.[1] The properties and performances of these new materials are main factors of size and morphology, which in turn determine their electrical and optical properties.[2] Conductive polymers have also attracted considerable attention over the past decade. Usually, polymers are used as cheaper substitutes for metals due to their excellent mechanical properties such as flexibility and processability. However, in 1977, MacDiarmid, Heeger, and Shirakawa discovered that exposure of conjugated polymer polyacetylene—an electrically *insulating* polymer—to iodine vapor yielded an electrically conducting material.[3] Although their polyacetylene exhibits good electrical properties, its application is limited because of its poor stability in air and complicated synthesis methods.[4] Therefore, many scientists were interested in other conducting polymers such as polyaniline, polypyrrole, polythiophene, and their derivatives as alternatives. These polymers have gained significant prominence recently because of their stability in air, and optical and electrical properties. Polyaniline has attracted considerable attention due to its low cost, simple synthesis, good environmental stability,[5,6] simple nonredox doping/dedoping chemistry based in acid/base reactions,[7] and favorable optical and electrical properties.[8,9] It has found potential applications in electronic and optical devices such as batteries,[10] artificial muscles,[11] sensors,[12] capacitors,[13] hydrogen storage,[14] and fuel cells.[15] Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization. Various research groups have conducted works involving synthesis of polyaniline nano-fibers (PANI) [12,16–26] and nanoparticles.[27–33] PANI were prepared by a novel interfacial polymerization method.[26] In this method, aniline dissolved in xylene that is immiscible in water was directly added into the aqueous solution of the oxidant. Ganesan *et al*. reported the preparation of polyaniline nanoparticles with sizes of 20–40 nm by pulsed sono-electrochemical method.[27]

An emulsion is an organized heterogeneous system that provides a large interfacial area and its viscosity can be controlled easily. A typical emulsion system is made using water, oil, and surfactant, where better surfactant is used to stabilize the emulsion system.[34–36] The surfactant to be used should possess the proper solubility into both the oil and water phase. The main objective of the surfactant use is to enhance its droplets' (oil or

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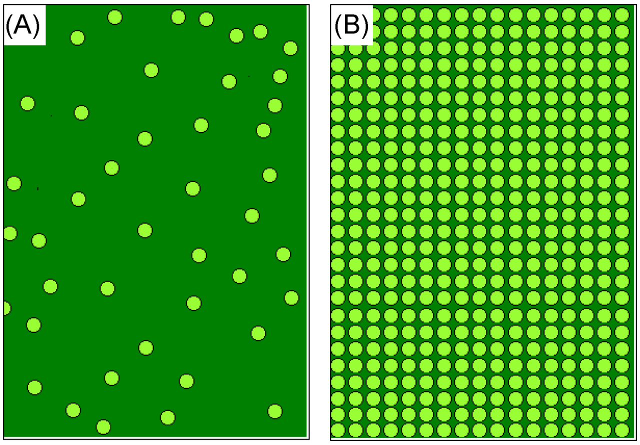

Figure 1. Morphology Control: synthesis using droplets or channel, (A) water-in-oil, (B) oil-in-water. This figure is available in color online at www.interscience.wiley.com/journal/pat

water) stability in emulsion and the amount of its use controls the size of droplets, thereby providing a selective place for the synthesis of either nano-grains or nano-fibers. In the first step of an emulsion-making process, small oil or water droplets are formed by mixing a system containing the organic phase, the aqueous phase, and the surfactant. In the case of inverse water-in-oil emulsion, the polymerization of aniline for the synthesis of nano-grains occurs from aniline molecules dissolved in nano-size aqueous droplets (Fig. 1A), and in the case of direct oil-in-water emulsion use, the polymerization occurs from aniline molecules in the continuous aqueous nano-dimensional channels created by high population of nano-size oil droplets (Fig. 1B). When the size of water droplets is sufficiently nano-scale, the polymer growth within the droplets will be restricted to produce nano-grains rather than nano-fibers. In the case of direct oil-in-water emulsion, a high population of oil droplets in oil-in-water emulsion will create nano-dimensional continuous aqueous channels. Thus, when the polymer growth occurs in the nano-dimensional continuous aqueous channels, fibers with nano-size diameter can be prepared. In this paper, we would like to report that the innovative use of nano-reactors (droplets) or nano-dimensional channels generated by creative use of either inverse water-in-oil or direct oil-in-water nano-emulsion, respectively, will allow scientists to have morphology selective synthesis of either nano-grains or nano-fibers of other materials. The successful synthesis of both polyaniline nano-grains having diameters ranging 60–80 nm and that of polyaniline nano-fibers having diameter 60–80 nm with 0.5 μm in length clearly supports this innovative use of nano-emulsions for the synthesis of both nano-fibers and nano-grains. We now gladly report that this innovative use of nano-emulsions can open new possibility for the synthesis of nano-size different morphological materials of metal, organic, and inorganic compound besides polymer.

EXPERIMENT

Chemicals

Aniline (99.5%), xylene, and acetone were purchased from Sigma-Aldrich. Ammonium Peroxydisulfate (APS) was purchased from Fluka Chemika. Concentrated hydrochloric acid (37%) was purchased from Mallinckrodt Inc. The nonionic surfactant sorbitan monooleate was purchased from Eastman chemical company. All the reagents were used without further purification.

Synthesis

In typical synthesis, a nonionic surfactant sorbitan monooleate (Tween 80, $C_{24}H_{44}O_6$) was dissolved in an organic solvent (xylene), while aniline was dissolved in an aqueous solution of 1 M HCl. The two solutions were then mixed together generating a milky emulsion (Fig. 2A). APS was also dissolved in aqueous solution of 1 M HCl and was added drop wise to the mixture (Tables 1 and 2). As APS oxidant gradually diffused into aqueous phase (either droplets or continuous channels), we observed a slow change of color from milky-green to dark-green over 25 min. The polymerization was performed either at room temperature or ice bath temperature, 0°C. After a 1-hr reaction, the dark-green solution was observed (Fig. 2B) and an excess amount of acetone was added to precipitate PANI powder. The obtained powder product was filtered and washed several times by acetone to remove excess surfactant and residual APS oxidant.

Apparatus

The UV–Vis spectroscopy (UV–Vis)

All the absorption spectra were recorded at room temperature on a UV–1601PC SHIMADZU spectrometer. The solutions for the absorption spectra were prepared by dissolving 0.1 mg of the samples in 5 ml of N-methylpyrrolidone (NMP).

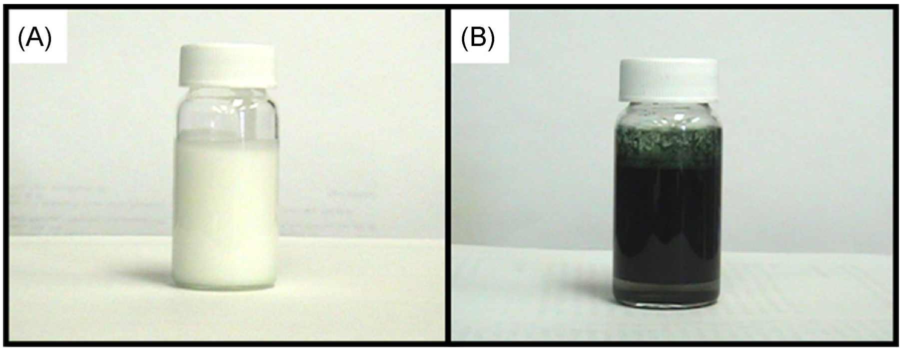

Figure 2. (A) Milky emulsion made from aniline, HCl, surfactant, and organic solvent, (B) dark green polyaniline product synthesized. This figure is available in color online at wileyonlinelibrary.com/journal/pat

Table 1. Inverse water-in-oil emulsion use for nano-grain synthesis

Exp #	SM (ml)	Xylene (ml)	Aniline (ml)	HCl (ml)	APS (g)	Morphology	Conductivity (S cm^{-1})
1	1	25	0.1	7	0.58	Grains	5.6
2	1	25	1	7	0.58	Grains	3.5
3	1	25	3	7	0.58	Grains	2.3
4	1	100	3	7	0.58	Grains	0.2
5	2.5	100	1	30	2.17	Grains	1
6	2.5	100	1	30	4.35	Grains	0.5

SM: sorbitan monooleate (Tween 80).

Table 2. Direct oil-in-water emulsion for nano-fiber synthesis

Exp #	SM (ml)	Xylene (ml)	Aniline (ml)	HCl (ml)	APS (g)	Morphology	Conductivity (S cm^{-1})
1	2.5	25	3	102	0.58	Fibers	5.2
2	2.5	25	1	102	0.58	Fibers	4.9
3	2.5	25	0.5	102	0.58	Fibers	6.2
4	2.5	25	1	102	0.58	Fibers	4.3

FTIR spectroscopy

All the infrared (IR) absorbance spectra were measured on an Nicolet Avatar FT-IR spectrophotometer (AVATAR) 360 FTIR. Pure KBr pellet was used to scan the background which is then automatically subtracted from the sampled spectrum. The samples (1% of polyaniline with 99% KBr by weight) were grounded into fine powder, pressed into pellets, and scanned for spectra. The electrical conductivity measurements were made on compressed pellets of the samples using the standard four-probe technique with a Keithley instrument.

RESULTS AND DISCUSSIONS

The optical absorption spectra of polyaniline base samples in NMP solution are shown in Fig. 3. The spectrum of nano-grain polyaniline synthesized using inverse water-in-oil nano-emulsion shows absorption bands at 333 and 634 nm. The spectrum of nano-fiber polyaniline synthesized using direct oil-in-water nano-emulsion shows absorption bands at 332 and 634 nm. The first absorption peak may be assigned to $\pi \rightarrow \pi^*$ transition and the second peak may be assigned to quinoid ring transition in the chain of polyaniline.[37] From the results, we can conclude that both samples are identical in terms of composition. The polyaniline samples synthesized from aqueous solution (control) and both inverse water-in-oil and direct oil-in water emulsions were analyzed by FTIR spectroscopy. Figure 4 shows the FTIR spectra of polyaniline salt form of each of the three samples. It is found that the FTIR spectra of these three PANI samples were essentially similar among them, which indicates that the backbone structures of the three samples are identical to each other except in morphology. The characteristic peaks are identical to the control sample (PANI–HCl) prepared through a common method. The absorption bands around 1578 and 1494 cm^{-1} are assigned to C=C stretching deformation of

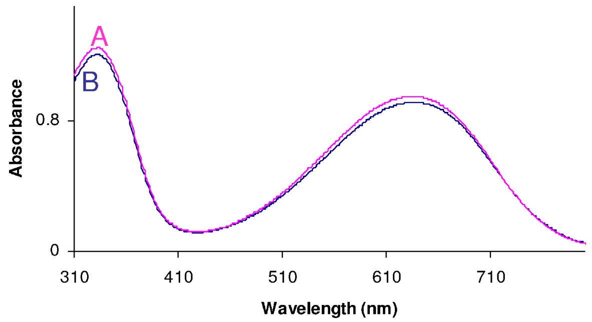

Figure 3. Absorption spectra of (A) polyaniline base synthesized by water-in-oil, (B) polyaniline base synthesized by oil-in-water. This figure is available in color online at wileyonlinelibrary.com/journal/pat

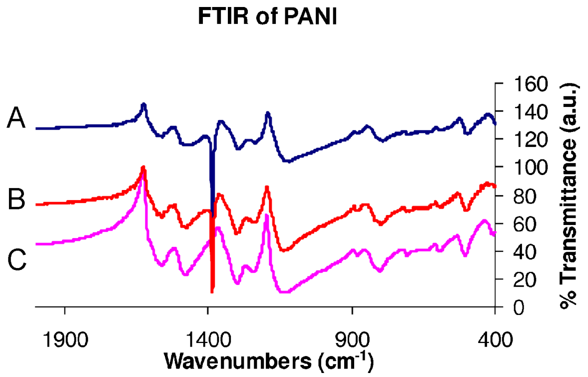

Figure 4. Infrared spectra of (A) polyaniline synthesized in aqueous solution, (B) polyaniline base synthesized by water-in-oil, (C) polyaniline base synthesized by oil-in-water. This figure is available in color online at wileyonlinelibrary.com/journal/pat

quinoid and benzoid ring, respectively, 1304 cm^{-1} C–N stretching of secondary aromatic amine, and the out-of-plane deformation of C–H around 1143 and 817 cm^{-1} are also observed.[38]

Bulk electrical conductivity of the samples synthesized from both approaches was compared (Tables 1 and 2). We found the nano-fibers synthesized from the use of the channels give higher bulk conductivity than the nano-grains synthesized from the use of the droplets. The measurement was made with pelletized sample of each sample. The higher bulk electrical conductivity with nano-fibers will be most likely due to the better connectivity with nano-fibers compared with nano-grains in the same unit volume.

Inverse water-in-oil nano-emulsion use for nano-grain synthesis

Figure 5A indicates that a typical product synthesized from the use of aqueous nano-droplets generated from the inverse water-in-oil nano-emulsion shows nano-grains shaped products with an average diameter of 60–80 nm. However, the control sample, Fig. 5C, synthesized by aqueous solution polymerization shows no uniform morphological products— poor selectivity. The nano-grain samples synthesized under various conditions at room temperature are shown in Table 1. When the synthesis was done using a water-in-oil (excess of oil) system, the polymerization of aniline occurred in nano-droplets (nano-reactors) such that polymer growth was confined within each nano-reactor that produced nano-grains.[39] To synthesize nano-grains with good reproducibility, we recommend using approximate ratio of 1:7–10:25, 1:10:100, or 1:12:40 among surfactant: water (HCl solution plus aniline solution): oil by volume (examples 1–3, 4, 5, 6, respectively, as shown in Table 1). Furthermore, we would like to report that an increased concentration of surfactant with decreased concentration of water contributes to easy synthesis of smaller nano-grains resulted from the synthesis occurred within the smaller size of aqueous nano-droplets (reactors).

Direct oil-in-water nano-emulsion use for nano-fiber synthesis

Figure 5B indicates that the product synthesized from the use of aqueous channels generated from oil-in-water emulsion shows a nano-fibers shaped products with a diameter of approximately 60–80 nm and a length of 0.5 μm. When the synthesis was done using the aqueous nano-dimensional channels formed from direct oil-in-water emulsion system with high population of oil droplets, the polymerization of aniline in the channels occurs in the continuous channels such that polymer faces restriction in growth in diameter but no restriction in growth in length to grow fibers unlike polymerization in the nano-reactors, so it was able to produce nano-fibers in channels (the sample as shown in Fig. 5B). In order to synthesize nano-fibers with good reproducibility, we recommend using approximate ratio of 1:40–42:10 among surfactant: water/oil by volume (examples 1–4 as shown in Table 2).

Tables 1 and 2 show electrical conductivity of polyaniline samples prepared by both polymerization pathways. It was found that the conductivity of nano-fibers is higher than that of the nano-grains. This might be due to the better connectivity among nano-fibers than among nano-grains in unit volume basis. In

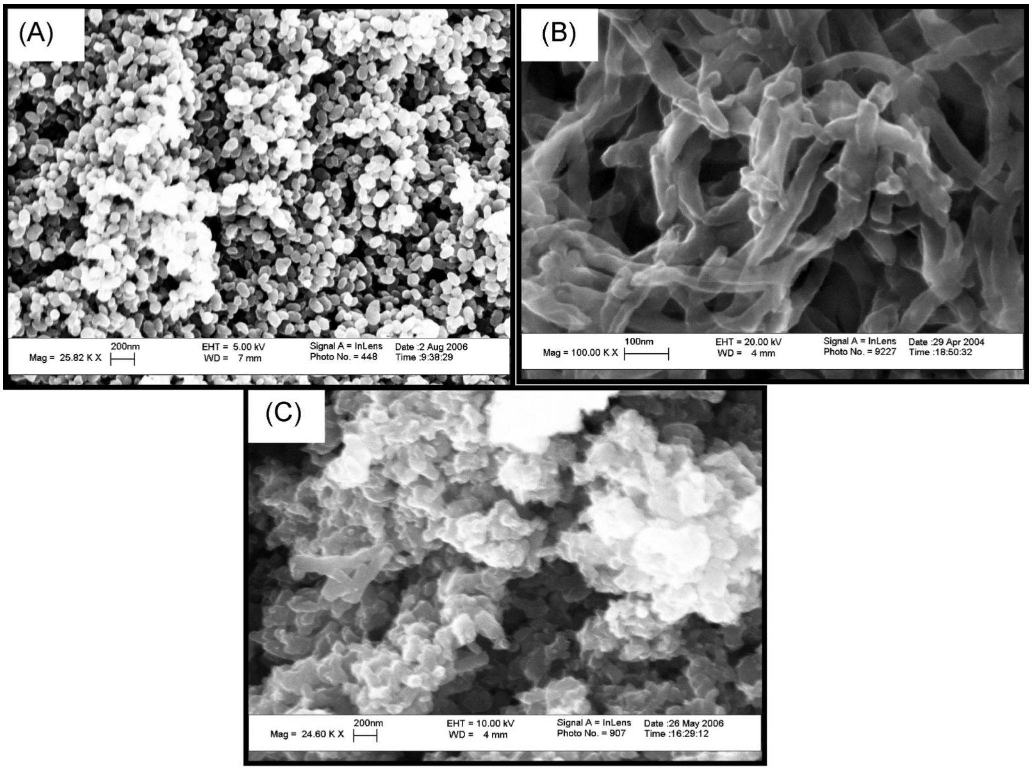

Figure 5. SEM picture of polyaniline, (A) nano-grains synthesized using water-in-oil, (B) nano-fibers synthesized using oil-in-water, (C) irregular shapes from aqueous synthesis.

addition, we observed that the polyaniline products synthesized by both pathways are somewhat soluble in water. The best results, so far, were obtained by dissolving up to 50 mg in 30 ml of deionized water (DI) water which resulted in a dark-green solution with no aggregation (or sedimentation) for several days. It may be due to molecular level thickness coating of surfactant on the surface of both polyaniline nano-grains and fibers. We are investigating the reason why the samples from the pathways have better solubility than the samples synthesized using common aqueous polymerization. This new property can simplify overall process to prepare polyaniline ink or solution from polyaniline nano powders.

In summary, our results, as shown in Tables 1 and 2, indicate that an innovative use of emulsion polymerization can provide us with highly selective and robust nano-size polyaniline synthesis methods of either nano-grains or nano-fibers with good reproducibility using room temperature synthesis.

CONCLUSION

Nano-emulsions can be creatively used as a morphology selective synthesis method to prepare not only nano-grains but also nano-fibers with high selectivity. Synthesis of the two different morphological materials was demonstrated using polyaniline synthesis as a model case. Polyaniline nano-grains were synthesized from aniline molecules in nano-size aqueous droplets as polymerization sites whose droplets were generated by inverse water-in-oil nano-emulsion use, and polyaniline nano-fibers were synthesized from aniline in aqueous nano-dimensional channels as polymerization sites whose channels were generated by direct oil-in-water nano-emulsion use containing high population of oil droplets. Using the approaches, we successfully synthesized nano-fibers of 60 nm diameter with 0.5 μm length and also nano-grains having diameter of 60–80 nm. The two different polymerization sites of nano-scale dimension were made by changing the ratio among surfactant, aqueous aniline/HCl solution and oil, i.e. organic solvent. We found the nano-fibers synthesized from the channels formed by the direct oil-in-water nano-emulsion have higher bulk electrical conductivity than the nano-grains which were synthesized from the droplets formed by the inverse water-in-oil emulsion. We also found that the emulsion allows us to use a room temperature synthesis unlike conventional synthesis methods which require to use ice bath temperature.

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