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One Pot Synthesis of Nanoparticles of Aqueous Colloidal Polyaniline and Its Au−Nanoparticle Composite from Monomer Vapor[†]

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In this paper, we report a single pot synthesis of polyaniline nanoparticles and Au nanoparticle−polyaniline composite nanoparticles using vapor phase introduction of aniline monomer. The synthesis was carried out in a micellar medium using sodium dodecyl sulfate as the micelles. Also, H_2O_2 was used both to reduce $HAuCl_4$ to Au nanoparticles and to polymerize aniline in the same pot. The particles were synthesized in the form of aqueous dispersion with particle sizes of about 100 nm. UV−visible absorption spectra indicated the formation of emeraldine salt form in both the PANI and the composite particles. FTIR spectra showed the formation of identical polymer in both the systems. Transmission electron microscopic investigation was carried out to measure particle sizes for both the cases. X-ray diffraction measurements showed the presence of Au in the composite in addition to indicating the formation of polyaniline with low crystalline phase in both the cases. Also, the electrical conductivity of the composite nanoparticles was found to be more than 100 times than that of the polymer nanoparticles only. We also present a schematic model of the formation of nanoparticles in the micellar medium in the presence of Au nanoparticles.

Introduction

Polyaniline (PANI) is well-studied and is the preeminent electrically conducting organic polymer with the potential of a variety of applications such as in batteries,[1] microelectronics,[2] displays,[3] antistatic coatings,[4] electromagnetic shielding materials,[5] sensors,[6] and actuators.[7] Its good environmental as well as thermal stability and the electrical conductivity tunable by appropriate doping make PANI an ideal active material for several applications. Notwithstanding the immense potential, the applications remain quite below the potential due to its poor solubility in most organic solvents and insolubility in water. The industrial demand has led to the development of several strategies to overcome such problems. Quite a few numbers of protocols, such as the generation of sulfonated PANI,[8] phosphonic acid doped PANI,[9] and enzymatic synthesis of PANI/sulfonated polystyrene complex[10] have been used to make water-soluble PANI. There are several other methods that have been employed to facilitate application of PANI in various forms, such as water dispersion of PANI nanofibers,[11] self-assembled PANI nanotubes[12] formation, polymerization of aniline inside macroporous carbon,[13] rodlike inclusion complex formation of cyclodextrin and PANI,[14] and directed assembly of large arrays of PANI nanowires.[15]

The preparation of PANI in colloidal form is one of the attractive alternatives to overcome its poor processability due to its insolubility in common organic solvents and water. There have been numerous reports on the preparation of PANI dispersions with 100−300 nm sized particles. In general, they are produced with suitable polymeric stabilizers[16] such as poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), poly(vinyl methyl ether), cellulose ethers, or sophisticated tailor-made copolymer architectures. Dispersed nanometer size particles of conductive polymers, such as polypyrrole, were synthesized by controlling the rate of polymerization at low temperature.[17] PANI and polypyrrole nanotubes and nanofibers have also been synthesized through self-assembly[18] using various oxidizing agents and in the presence of camphor sulfonic acids (CSA) or β-naphthalenesulfonic acid (β-NSA), which also function as the stabilizing agents. Their use as chiral sensor has also been demonstrated.[19] Conductive polymer nanotubes[20] used for effective separation of biomolecules, have also been synthesized in various membranes, such as alumina, carbonate, or porous carbon membranes with uniform pore sizes.

Additionally, core−shell nanoparticles (NPs) consisting of metal nanoparticles as the core and polymer as the shell[21] or polymer nanoparticles as the core and metal nanoparticles deposited on the polymer surface[22] have attracted interest because of their potential applications in catalysis, controlled delivery, artificial shells, light fillers, low dielectric constant materials, acoustic insulation, and photonic crystals. Here, conducting polymer particles, with the polymer as the core or the shell, have gained considerable attention due to their associated application potentials. Synthesis of metal NP−conducting polymer composite with sizes in the nanometer domain has also been performed. Most of these methodologies used self-assembled process[23] or layer-by-layer[24] (LBL) techniques. On the other hand, synthesis of ordered PANI inverse opals, with appropriate photonic application capability have also been reported by Caruso and co-workers[25] using ordered colloidal assemblies as the template.

Herein we report a new microemulsion based method to form dispersed aqueous PANI as well as Au−NP−PANI composite NPs by introducing the aniline monomer from the vapor phase while the reaction was performed in aqueous solution. Microemulsion based synthesis has previously been used to obtain metal and polymer nanoparticles[26] wherein the particle sizes were determined by the microemulsion "reactor" sizes. On the other hand, in our work, the introduction of aniline from the vapor phase to an aqueous acidic micellar solution containing

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the oxidizing agent resulted in the formation of nanometer size PANI particles. If the solution contained Au−NPs and the oxidizing agent then Au−NP−PANI composite NP formation was observed. Room temperature vapor phase introduction not only releases monomer in controlled concentration but also supplies the monomer in rather pure form in a process that is akin to immediate low-temperature distillation. In a previous work,[27] we reported the synthesis of Au−NP−PANI bulk composite using H_2O_2 both as oxidizing and as reducing agent in aqueous medium and introducing anilinium chloride directly into the reaction medium. Ability to synthesize nanoparticle and polymer using the same reagent in aqueous solution for generating nanoparticles and polymer in the form of a composite is considered to be important as it reduces the number of steps otherwise required in a complex set of sequential reactions leading to the formation of a composite. In addition, a more uniform and molecularly defined composite material could be obtained in a single-pot synthesis. However, the composite reported in our earlier work suffered from the same processing disadvantages as those of the bulk polymer, namely insolubility in common solvents, and therefore was not suitable for versatile applications. In the present report, a different experimental approach has been used where aniline was introduced into the reaction mixture from the vapor phase with slow release from a separate container kept under ambient condition. In this way we could obtain stable nanoparticles of PANI and Au−NP−PANI composite dispersed in aqueous solution. For the formation of composite H_2O_2 has been used both for the reduction of $HAuCl_4$ as well as polymerization of aniline in acidic pH thereby producing emeraldine salt of PANI in the composite.

The formation of the PANI was confirmed by UV−visible and FTIR spectroscopy. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) studies indicated the formation of NPs for both the PANI and the composite in addition to confirmation of incorporation of Au NPs in the composite. Our observations suggest that nanoparticles of PANI and Au−NP−PANI composite could be obtained using the present method where particle sizes were below 100 nm diameter. The electrical conductivity of the composite NPs was more than 100 times than that of the PANI particles. Finally, TEM micrographs showed the evidence of formation of a Au−core−PANI−shell nanocomposite with a thin layer of PANI over the Au NP cores.

Experimental Section

Materials: Aniline (Merck) was distilled under vacuum prior to use. Sodium dodecyl sulfate (SDS) and 30% H_2O_2 solution were from Merck. $HAuCl_4$ (17% w/w in HCl solution) was obtained from Aldrich and used without further purification. For all the experiments Milli-Q (18.2 MΩ) grade water was used.

Preparation of Dispersed PANI Particles. Here, 0.17 g of SDS was dissolved in 45 mL of water in a 250 mL stoppered conical flask to obtain 1.2×10^{-2} M (~1.5 cmc) SDS solution. To the solution was added concentrated HCl (11.2 M), so that the total concentration of acid in the solution was 0.1 M. Then 600 μL of H_2O_2 was added to the acidic surfactant solution. After this, 2 mL of distilled aniline was taken separately in a 3 mL sample vial, and the vial was kept hanging from the top of the conical flask so that only the aniline vapor could go into to the solution and no liquid aniline came in contact with the solution. The experimental setup is shown schematically in Figure 1.

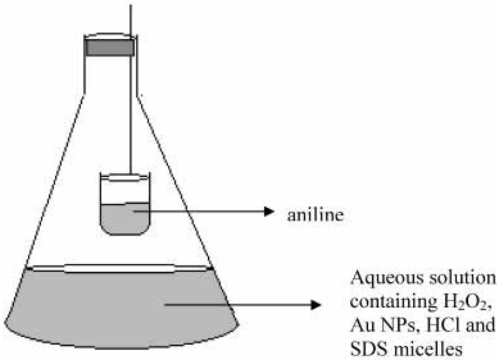

Figure 1. Schematic representation for the experimental setup for the formation of conducting PANI NPs and Au−NP−PANI composite particles. The monomer was introduced from the vapor phase, whereas the Au NPs were formed in the aqueous solution containing SDS micelles.

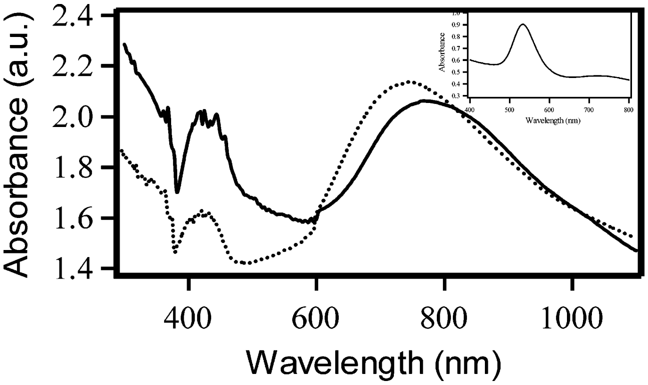

Figure 2. UV−visible spectra of colloidal PANI (dotted) and Au NP−PANI composite (solid) in aqueous SDS solution prepared by the present method using H_2O_2 both as oxidizing and reducing agent. Inset shows the UV−visible spectrum of Au NPs synthesized in aqueous SDS solution using H_2O_2 as the reducing agent.

The reaction was allowed to continue for about 12 h, while the solution was being continuously stirred. The reaction was stopped as soon as the color of the solution turned green, which is indicative of the formation of emeraldine salt form of polyaniline. This was achieved by removing the vial containing aniline from the flask and quickly stoppering the same. Further, the solution was allowed to stand for 1 h more at room temperature whereupon the color of the solution turned from light green to dark green. The solution was observed to have remained in the dispersed state for months without any observable precipitation. To obtain the polymer, the dispersed solution was mixed with methanol and then centrifuged, and the process was repeated several times. The addition of methanol helped remove the SDS from the polymer. The precipitate was then dried under vacuum prior to analytical measurements. The reaction was carried out at room temperature, which varied between 20 and 30 °C.

Preparation of Dispersed Au—NP—PANI Composite. In a conical flask 45 mL of 1.2×10^{-2} M SDS solution was prepared in water. From a stock solution of $HAuCl_4$, 600 μL of was added to the micellar solution so that the total concentration of $HAuCl_4$ in the solution became 4.5×10^{-4} M. To the solution 600 μL of H_2O_2 was then added and magnetically stirred for 5 min whereupon Au NPs were generated with the characteristic purple-red color. The UV−visible spectra of the Au NPs thus synthesized had a characteristic plasmon resonance band at 530 nm (inset of Figure 2). To the solution concentrated HCl was added so that the final concentration of HCl was adjusted to 0.1 M. The purple color of the Au NPs faded away upon addition of HCl to the solution. Aniline was then introduced from the vapor phase in a separate vial, and the conical flask was sealed. The reaction was allowed to take place with magnetic stirring for about 10 h until the color of the solution turned light green. Then the aniline-containing vial was removed from the conical flask. After about an hour, the color of the solution had turned from light to dark green. To obtain the composite in solid form, the dispersed solution was first mixed with methanol and then centrifuged; the cycle was repeated for several times and then the precipitate thus obtained was dried under vacuum on a glass plate prior to further studies. Again the reaction was carried out at room temperature, which varied between 20 and 30 °C.

Analytical Studies. UV−visible spectra of the dispersed particles as synthesized were recorded in a Hitachi UV−visible spectrophotometer (model U2001). FTIR spectra of the cleaned and dried precipitates were recorded in KBr pellets, using a Perkin-Elmer FTIR (Spectrum one) spectrometer. X-ray diffraction studies were performed by depositing the colloidal particles on a glass slide (after solvent evaporation) followed by drying in a vacuum. A Seifert powder X-ray diffractometer (XRD 3003 TT) with Cu Kα source (wavelength 1.54 Å) was used for recording the data at room temperature. The transmission electron microscopic studies of the samples were performed, by depositing the colloidal particles on a copper grid and then air-drying. A JEOL electron microscope (JEM 100 CX II) operated at 80 kV accelerating voltage was used for these measurements.

Results and Discussion

Recently, we have found a new method of generation of Au NPs from $HAuCl_4$ using H_2O_2 as the reducing agent in acidic condition. We could use the same reaction condition to generate Au−NP−PANI bulk composite having higher electrical conductivity than the corresponding polymer (PANI) only. However, as mentioned earlier, the composite suffered from the same processing disadvantages as those of the bulk polymer, namely insolubility in common solvents, and therefore it was not suitable for versatile applications such as biocompatibility. We were interested in finding an easier way of dispersion polymerization where the particle size growth could be controlled by slow release of the monomer. As aniline has sufficient vapor pressure at room temperature, an easy way out is to introduce aniline into the reaction mixture from the vapor phase and stir the reaction mixture vigorously. This would ensure slow and controlled release of the monomer as one could place the vial of aniline to initiate the reaction and take it out to stop the reaction. We have done exactly the same and have obtained both PANI and Au−NP−PANI composite in the form of NP dispersion in water. In both cases the dispersed solutions were stable for months without observable precipitation.

The UV−visible absorption spectra, of the PANI and Au−PANI composite dispersed in aqueous medium are shown in Figure 2. The UV−visible spectrum of dispersed PANI particles synthesized in absence of Au NPs showed peaks at 760 and 435 nm, characteristic of the emeraldine form of PANI. Also, shown in the inset of Figure 2 is the characteristic visible spectrum of Au NPs synthesized by the reduction of $HAuCl_4$ with H_2O_2 in aqueous SDS solution (1.2×10^{-2} M) recorded in the wavelength range 800−400 nm. The surface plasmon resonance peak appeared at 530 nm. This was the first step in the synthesis of Au−NP−PANI composite. When concentrated HCl was added to the Au NP solution, the intensity of the plasmon resonance band had diminished. The solution had turned colorless. It is well-known that surface plasmon resonance band of metal nanoparticles are sensitive to the environment.[28] If the dielectric constant of the medium is changed the absorption peak as well as intensity can change drastically. For example, Shin et al. have observed a significant change in absorption intensity as well a shift of maximum peak position of the plasmon resonance of Au NPs in Au−polypyrrole encapsulated NPs.[21b] In the present case, the change in pH reduced the oscillator strength such that no plasmon resonance absorption could be observed. It may also be mentioned that after the formation of Au−NP−PANI composite NPs the Au−NP plasmon resonance band was still obscured. This could also be due to reduction of absorption change in the presence of PANI surroundings (acid doped form). In addition, the strong absorption of PANI in the same region could also result in the lack of observation of a peak in the same region. Further, Selvan et al. conjectured that the diminishing of Au NP peak in the Au−polypyrrole nanocomposite could be due to strong absorption of the polymer in the same region.[29] Upon introduction of aniline from the vapor phase, the color of the solution changed from colorless to light green to dark green. The solution absorption spectrum exhibited peaks at 790 and 435 nm, characteristic of the formation of emeraldine PANI. The plasmon resonance band of the Au NPs was not observed in the composite spectrum probably due to reduction of absorption intensity by the surrounding polymer. The longitudinal band due to PANI in the case of the composite appeared red-shifted by about 30 nm compared to that of only PANI prepared in absence of Au NPs. The longitudinal band shift could be due to formation of PANI of a different molecular weight or could also be a signature of the level of protonation of PANI in the composite.

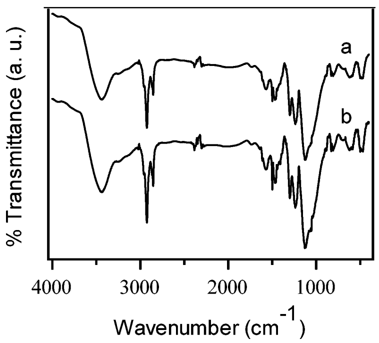

Figure 3. FTIR spectra of (a) PANI and (b) Au NP−PANI composite recorded in KBr pellets.

FTIR spectra of PANI and Au−NP−PANI composite shown in Figure 3 are identical. This observation suggests that there is no structural difference between PANI alone and PANI in the Au NP−PANI composite. The peaks at 1590 and 1500 cm^{-1} are due to the usual quinoid and benzoid deformations of the emeraldine form of polyaniline. In both the cases the quinoid band at 1590 cm^{-1} is less intense than that of the benzoid band at 1500 cm^{-1}. The weak and broad band at around 3400 cm^{-1} is assigned to the N−H stretching mode. The strong band at 1150 cm^{-1} was described by MacDiarmid and co-workers[30] as the "electronic like band" and is considered to be a measure of degree of delocalization of electrons and thus a characteristic peak of conductive PANI. The absorbance band observed at 688 cm^{-1} is due to N−H bending vibrations of the emeraldine salt.

We further pursued transmission electron microscopic (TEM) investigation to learn about the particle sizes of PANI and Au−NP−PANI composite as formed in the aqueous solution in the present method. We recorded TEM pictures of the samples dried on a copper grid. The micrographs are shown in Figure 4. The

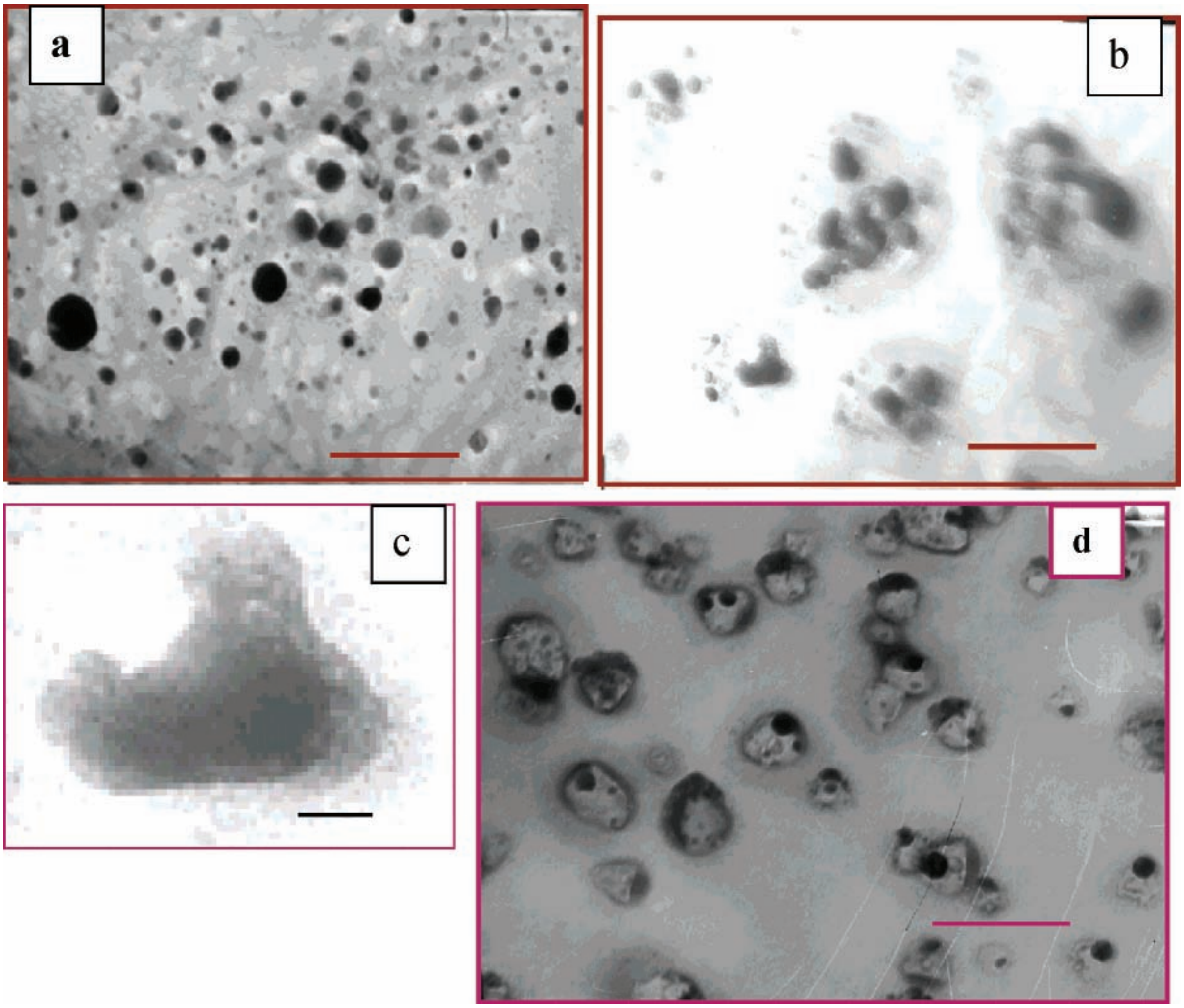

Figure 4. (a) Transmission electron micrograph of colloidal PANI particles prepared by the present method. Scale bar is 200 nm. (b) TEM of Au−NP−PANI composite with scale bar at 200 nm. (c) Au NP/PANI core shell nanoparticle. Scale bar is 20 nm. (d) Au NPs in the conducting PANI shells. Scale bar is 200 nm.

micrograph in Figure 4a indicates that PANI was generated in the form of largely spherical particles having a wide distribution of particle sizes with average particle diameters below 100 nm. On the other hand, the TEM studies of Au−NP−PANI composite (Figure 4b) revealed the formation of aggregated particles, with PANI layer formation surrounding a cluster of aggregated Au−NPs, resulting in greater than 100 nm diameter clusters of well-separated composite particles. A closer look into the TEM micrograph indicates the formation of Au−NP−PANI core−shell nanocomposites with assembled Au−NP distinguishable by dark cores surrounded by grayish shells of PANI (Figure 4c). In another similar run of experiment we have observed that a single Au NP could also be encapsulated inside a shell of PANI although there were some composite particles containing more than one Au−NP encapsulated by the same polymer shell. This is shown in Figure 4d. In this run, it was observed that Au NPs of average dimension of 20 ± 5 nm were surrounded by a shell of PANI, the dimension of the composite particles had wide distribution with average diameter of 80 ± 40 nm. In brief, TEM micrographs showed that individual Au−NP−PANI composite nanoparticles were formed in the present set of experiments.

The presence of Au NPs in the dispersed composite was further confirmed by powder X-ray diffraction studies. The results are shown in Figure 5. In the case of PANI (only) particles, two broad bands appeared at 2Θ values of 22 and 26° indicating the formation of low level of crystalline phase in the polymer.[31] In the Au−NP−PANI composite, the peak appearing at 23° is sharper and stronger, implying that the molecular chains of the PANI prepared in the micellar medium are in a much more ordered state in the presence of Au NPs and the crystallinity of the PANI in the composite was higher than that in PANI only. Further, three strong bands appeared with maximum intensity at 38.5, 43.4, and 65.1° representing Bragg's reflections from (111), (200), and (220) planes of Au. This means that the Au NPs had growth in all the three planes.

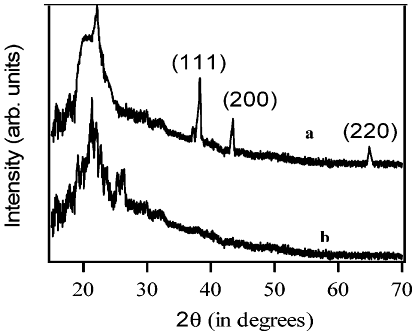

Figure 5. Powder X-ray diffraction patterns of (a) Au NP−PANI composite particles and (b) PANI particles. The spectra were recorded by depositing the colloidal solutions on a glass plate. The principal Bragg's reflections are identified for the Au nanoparticles.

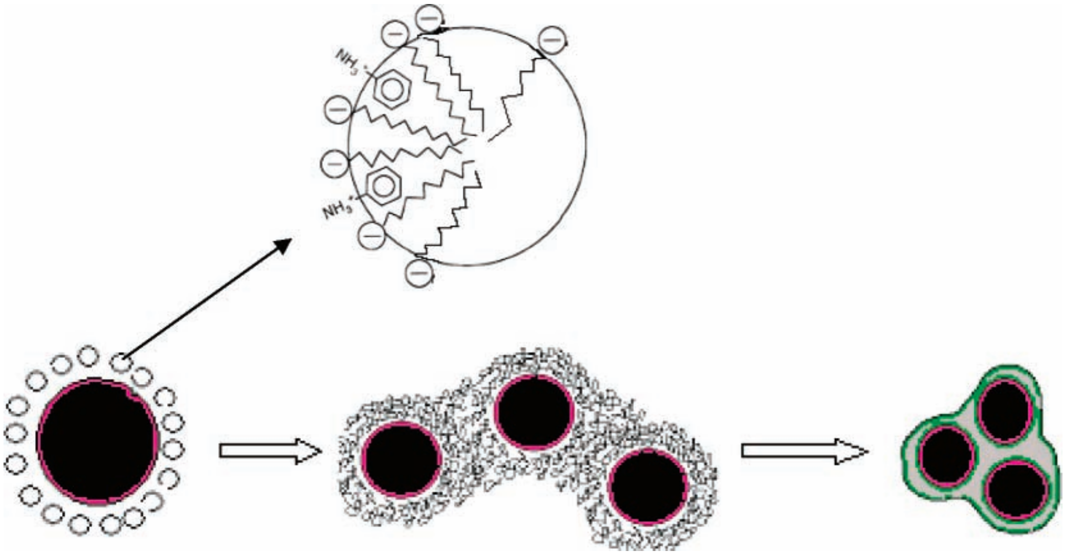

Figure 6. Pictorial representation for the dissolution of anilinium ions at the micelle−water interface (top). Schematic representation for the formation of Au NP−PANI composite particles at the nanometer dimension (bottom). Each circle surrounding the Au−NP (bottom) corresponds to the diagram in the top section.

We also measured the electrical conductivities of both the PANI and the composite NPs using a four-probe method. For the electrical conductivity measurements thin films of dispersed PANI and Au−NPs-PANI composite particles, with micelles removed by treatment with methanol, were deposited on clean mica surfaces. It was observed that there was an increase in electrical conductivity by 2 orders of magnitude for the composite NPs compared to the polymer particles alone. The typical value of the electrical conductivity for the Au NP−PANI composite particles synthesized by our method was 1.08 S cm^{-1} whereas that for the PANI particles in absence of Au NPs was 8.89×10^{-3} S cm^{-1}.

Finally, using the method of vapor phase introduction of aniline, we have been able obtain PANI and Au−NP−PANI composite in the form of a nanometer sized particle dispersion in aqueous medium. In this regard, we have taken advantage of two key factors that might have been responsible for the particle size. First is the vapor phase introduction of aniline, which means a slow release of a reagent and also termination of the reaction is controllable by removing the vial containing aniline. The second factor, which is equally important, is the use of SDS micelles in the reaction medium. It is well-known that hydrophobic molecules are dissolved in the hydrophobic core of micelles, whereas the polar molecules are solubilized at the micelle−water interface. In the case of anilinium ion, it has been reported that anilinium cations are adsorbed at the micellar surface by electrostatic interaction with anionic parts of SDS molecules fully exposed to the aqueous phase.[32] Thus, we assume that the aniline monomers were solubilized at the micelle−water interface, which is schematically shown in Figure 6. It is fortuitous that SDS micelles are also known stabilizers of Au NPs. In the present scenario the micelles with the anilinium ions might surround Au NPs as shown in Figure 6.

Subsequent polymerization might lead to the composite formation where one or a few Au NPs would be encapsulated by PANI. The large size and their variation in the polymer particles generated indicate a large number of such micelles with dissolved anilinium ions might have come together at the time of formation. Also, the number of such micelles varied widely leading to the variation of sizes of the polymer particles generated in the medium. The whole process of composite formation is described schematically in Figure 6. In absence of Au NPs, a large collection of SDS micelles with dissolved anilinium ions might come together leading to the formation of nano size PANI particles. The presence of large concentration of SDS and low concentration of anilinium ions might prevent the formation of larger particles, thereby producing nanometer size particles only.

Conclusion

Herein we have reported the generation of conducting PANI and Au−NP−PANI composite nanometer size particles dispersed in aqueous medium. The controlled polymerization had been achieved using sodium dodecyl sulfate surfactants as the micellar medium and controlling the monomer concentration by introducing aniline from the vapor phase. Polymerization of aniline using H_2O_2 as the oxidizing agent in acidic solution resulted in the formation of nanometer size spherical particles well separated from each other. In the case of the composite, H_2O_2 was used both as the oxidizing and as the reducing agent. The result was the formation of aggregated particles, with the PANI shell formed around aggregated or individual Au NPs. Both the colloidal PANI and the composite particles were formed in their emeraldine salt form. The electrical conductivity of the Au−NP−PANI composite particles was more than 2 orders of magnitude higher than the PANI NPs prepared in absence of Au NPs. The PANI particles produced were on the order of 100 nm sizes whereas those of the composite had average size greater than 100 nm. In a separate run formation of a composite with core Au NPs surrounded by PANI shells could also be observed.

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References and Notes

(1) Kaneko, M.; Nakamura, H. *J. Chem. Soc., Chem. Commun.* **1985**, 346.

(2) (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741. (b) Burroughes, J. H. *Nature* **1990**, *347*, 539. (c) Wohlgenannt, M.;

Tandon, K.; Mazumdar, S.; Ramsesha, S.; Vardeny, Z. V. *Nature* **2001**, *409*, 494. (d) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (e) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 1441.

(3) (a) Pages, H.; Topart, P.; Lemordant, D. *Electrochim. Acta* **2001**, *46*, 2137. (b) Kitani, A.; Yano, J.; Sasaki, K. J. *Electroanal. Chem.* **1986**, *209*, 227.

(4) Duke, C. B.; Gibson, H. W. *Encyclopedia of Chemical Technology*; Kirk-Othmer: John Wiley: New York, 1982, Vol. 18, p 755.

(5) (a) Koul, S.; Chandra, R.; Dhawan, S. K. *Polymer* **2000**, *41*, 9305. (b) Joo, J.; Lee, C. Y. *J. Appl. Phys.* **2000**, *88*, 513.

(6) (a) Sukeerthi, S.; Contractor, A. Q. *Anal. Chem.* **1999**, *71*, 2231. (b) Xue, H.; Shen, Z.; Li, Y. *Synth. Met.* **2001**, *124*, 345. (c) Xie, D.; Jiang, Y.; Pan, W.; Li, D.; Wu, Z.; Li, Y. *Sens. Actuators B* **2002**, *81*, 158.

(7) Wang, H.-L.; Gao, J.; Sansinena, J.-M.; McCarthy, P. *Chem. Mater.* **2002**, *14*, 2546.

(8) (a) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665. (b) Wei, X. L.; Wang, Z. H.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 2545. (c) Chan, H. S. O.; Neuendorf, A. J.; Ng, S. C.; Wong, P. M. L.; Young, D. J. *Chem. Commun.* **1998**, 1327. (d) Chen, S.-A.; Hwang, G.-W. *J. Am. Chem. Soc.* **1995**, *117*, 10055.

(9) Chan, H. S. O.; Ho, P. K. H.; Ng, S. C.; Tan, B. T. G.; Tan, K. L. *J. Am. Chem. Soc.* **1995**, *117*, 8517.

(10) (a) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 71. (b) Liu, W.; Cholli, A. L.; Nagarajan, R.; Kumar, J.; Tripathy, S.; Bruno, F. F.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 11345.

(11) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314.

(12) Wei, Z.; Zhang, Z.; Wan, M. *Langmuir* **2002**, *18*, 917.

(13) Lei, Z.; Zhang, H.; Ma, S.; Ke, Y.; Li, J.; Li, F. *Chem. Commun.* **2002**, 676.

(14) Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. *Langmuir* **1999**, *15*, 910.

(15) Liang, L.; Liu, J.; Windisch, C. F., Jr.; Exarhos, G. J.; Lin, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3665.

(16) (a) Armes, S. P.; Vincent, B. *J. Chem. Soc., Chem. Commun.* **1987**, 288. (b) Armes, S. P.; Aldissi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 88. (c) Cawdery, N.; Obey, T. M.; Vincent, B. *J. Chem. Soc., Chem. Commun.* **1988**, 1198. (d) Vincent, B.; Waterson, J. *J. Chem. Soc., Chem. Commun.* **1990**, 683. (e) Stejskal, J.; Kratochvil, P. *Langmuir* **1996**, *12*, 3389. (f) Armes, S. P.; Aldissi, M.; Agnew, S. F.; Gottesfeld, S. *Langmuir* **1990**, *6*, 1745. (g) Banerjee, P.; Bhattacharyya, S. N.; Mandal, B. M. *Langmuir* **1995**, *11*, 2414. (h) Chattopadhyay, D.; Banerjee, S.; Chakravorty, D.; Mandal, B. M. *Langmuir* **1998**, *14*, 1544.

(17) (a) Jang, J.; Oh, J. H.; Stucky, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4016. (b) Jang, J.; Oh, J. H. *Chem. Commun.* **2002**, 2200.

(18) (a) Huang, L. M.; Wang, Z. B.; Wang, H. T.; Cheng, X. L.; Mitra, A.; Yan, Y. X. *J. Mater. Chem.* **2002**, *12*, 388. (b) Huang, K.; Wan, M. *Chem. Mater.* **2002**, *14*, 3486. (c) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314.

(19) Huang, J.; Egan, V. M.; Guo, H.; Yoon, J.-Y.; Briseno, A. L.; Rauda, I. E.; Garrell, R. L.; Knobler, C. M.; Zhou, F.; Kaner, R. B. *Adv. Mater.* **2003**, *15*, 1158.

(20) (a) Wu, C. G.; Bein, T. *Science* **1994**, *264*, 1757. (b) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739. (c) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61. (d) Parthasarathy, R.; Martin, C. R. *Nature (London)* **1994**, *369*, 298. (d) Lei, Z.; Zhang, H.; Ma, S.; Ke, Y.; Li, J.; Li, F. *Chem. Commun.* **2002**, 676.

(21) (a) Liu, Y. C.; Chuang, T. C. *J. Phys. Chem. B* **2003**, *107*, 12383. (b) Shin, H. J.; Hwang, I. W.; Hwang, Y. N.; Kim, D.; Han, S. H.; Lee, J. S.; Cho, G. *J. Phys. Chem. B* **2003**, *107*, 4699. (c) Choi, S. J.; Park, S. M. *Adv. Mater.* **2000**, *12*, 1547. (d) Marinakos, S. M.; Anderson, M. F.; Ryan, J. A.; Martin, L. D.; Feldheim, D. L. *J. Phys. Chem. B* **2001**, *105*, 8872. (e) Cao, H.; Xu, Z.; Sang, H.; Sheng, D.; Tie, C. *Adv. Mater.* **2001**, *13*, 121.

(22) (a) Brown, K. R.; Natan, M. J. *Langmuir* **1998**, *14*, 726. (b) Jackson, J. B.; Halas, N. J. *J. Phys. Chem. B* **2001**, *105*, 2743. (c) Ji, T.; Lirtsman, V. G.; Avny, Y.; Davidov, D. *Adv. Mater.* **2001**, *13*, 1253. (d) Kaltenpoth, G.; Himmelhaus, M.; Slansky, L.; Caruso, F.; Grunze, M. *Adv. Mater.* **2003**, *15*, 1113. (e) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davies, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(23) (a) Zhang, L.; Wan, M. *J. Phys. Chem. B* **2003**, *107*, 6748. (b) Watson, K. J.; Zhu, J.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 462.

(24) Oldenburg, S. J.; Averitt, R. D.; Westcott, S. L.; Halas, N. J. *Chem. Phys. Lett.* **1998**, *288*, 143.

(25) Wang, D.; Caruso, F. *Adv. Mater.* **2001**, *13*, 350.

(26) (a) Kuramoto, N.; Genies, E. M. *Synth. Met.* **1995**, *68*, 191. (b) Kinlen, P. J.; Liu, J.; Ding, Y.; Graham, C. R.; Remsen, E. E. *Macromolecules* **1998**, *31*, 1735. (c) Riede, A.; Helmstedt, M.; Riede, V.; Stejskal, J. *Langmuir* **1998**, *14*, 6767. (d) Premachandran, R.; Banerjee, S.; John, V. T.; McPherson, G. L.; Akkara, J. A.; Kaplan, D. L. *Chem. Mater.* **1997**, *9*, 1342. (e) Cason, J. P.; Miller, M. E.; Thompson, J. B.; Roberts, C. B. *J. Phys. Chem. B* **2001**, *105*, 2297.

(27) Sarma, T. K.; Chowdhury, D.; Paul, A.; Chattopadhyay, A. *Chem. Commun.* **2002**, 1048.

(28) Mirkin, C. A. *Inorg. Chem.* **2000**, *39*, 2258.

(29) Selvan, S. T.; Hayakawa, T.; Nogami, M.; Moeller, M. *J. Phys. Chem. B* **1999**, *103*, 7441.

(30) Sun, Y.; MacDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 529.

(31) Yan, F.; Xue, G. *J. Mater. Chem.* **1999**, *9*, 3035.

(32) Kuramoto, N.; Tomita, A. *Polymer* **1997**, *38*, 3055.