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The Influence of Temperature and Sonication on the Preparation of Doped Polymeric Nano Particles

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Abstract : Nanomaterials such as nano particles, nanowires, nanotubes, nanorods, nanofibers and nanobelts have drawn a lot of attention because of their novel and unique properties and a wide range of applications. In particular, polymers with one dimensional nano-architecture have received an increasing interest since it provides a good material system to investigate the shape, size and dimensionality dependent electrical, optical, thermal and mechanical properties. The polyaniline is the most widely studied polymer in the group of conducting polymers and also it is important from application and academic point of view. The polyaniline is extensively studied polymer because of its high electrical conductivity, oxidative properties, environmental stability and ease of preparation etc. The conductivity of polymers can be made to vary over a very wide range, starting from insulating to semiconductor and towards metallic, by varying the concentration of the dopant. In the present study, acid doped polyaniline nanoparticles are prepared through the chemical oxidative polymerization process. Ammonium per sulfate is used as an oxidant. Sonication and low temperature effect resulted in smaller particles. The characterization by scanning electron microscope showed the formation of PANI nanoparticles and uniform distribution of the nanoparticle size. SEM results confirm the existence of nano particles with the doped acid. The molecular interactions between the solute and solvent and their binding nature are also analyzed by the FT-IR and UV-Visible spectral studies.

Keywords: Nanoparticles, Sonication, Polyaniline, SEM, Doping.

Introduction

Studies on new physical properties and applications of nanomaterials and nanostructures are possible only when nanostructured materials are made available with desired size, morphology, crystal, microstructure and chemical composition. The fabrication and processing of nanomaterials and nanostructures started long time ago, earlier than nanotechnology emerged as a new scientific field. Such research has been drastically intensified in the last decade, resulting in overwhelming literatures in many journals across different disciplines. The research on nanotechnology is evolving and expanding very rapidly.

Particularly in nanotechnology, the ultrasonication is an essential technique for the synthesisand processing purposes of nano-size materials. Since nanotechnology has gained the outstanding scientific interest, nano-sized particles are utilized in manyscientific and industrial fields. Nanomaterials are defined as particles with a dimension less than 100nm, the production and processing of nano materials require higher efforts to breakagglomerates and to overcome bonding forces. Sonochemistry is one of the simplest techniquesused to prepare nanosized materials. 10-20nm size amorphous iron nanoparticles are formed by sonicating Fe (CO) 5[1]. Single-Walled Carbon Nanotubes (SWCNTs) of high purity is produced insonochemical way[2]. The

SWCNTs can be formed by dispersing phospholipid-polyethylene glycol (PL-PEG) by sonication[3]. Sonication is one of the interesting and simple methods to prepare nanomaterials reported in literature[4].

Ultrasonication is a proven method for the production of nanoemulsions andnanodispersions. When sonicating liquids at high intensities, the sound waves that propagate into theliquid media result in alternating high-pressure (compression) and low-pressure (rarefaction)cycles, with rates depending on the frequency. Large particles aresubject to surface erosion. This leads to sharp acceleration of diffusion, mass-transfer processesand solid phase reactions due to crystallite size and structure changing.

Ultrasonication improves the mixing of the pre-cursors and increases the mass-transfer at the particle surface. This leads to smaller particle size and higher uniformity. To obtain nanoparticles with specific characteristics and functions, the surface of the particles has to be modified. Various nanosystems like polymeric nanoparticles, liposomes, dendrimers, carbon nanotubes, quantum dots etc. can be successfully functionalized for efficient applications.

Among the polymers studied, polyaniline (PANI) has received tremendous interest in the research of conducting polymers because of its wide range of electrical, electrochemical and optical properties[5-11].Polyaniline when doped with acids changes its insulating nature to conducting one. It exists in a variety of forms that differ in chemical and physical properties. The most common is green protonated emeraldine base PANI which has conductivity on a semiconductor level. PANIcan be synthesized chemically as well as electrochemically. Itis used in various applications such as textile fibers, photovoltaic devices, electrode in batteries, electrochemical devices, microwave shielding, optical switching devices, sensors, actuators, etc. Recent work deals with the synthesis of polyanilinenanomaterials.

So in the present work an attempt is made to prepare doped polymeric nanoparticles i.e. PANI perchlorate (PAPC) by sonication method with the influence of temperature. The temperature variation plays a dominant role in the nanoparticle formation. The existence of nanoparticles is confirmed by the SEM analysis. The functional groups, interactions between the molecules, binding nature, band gap energy are characterized through spectroscopic techniques.

Materials and methods

Polyaniline perchlorate (PAPC) is prepared by oxidative polymerization of aniline which is of emeraldine base, perchloric acid is used as dopant and ammonium per sulfate is used as oxidant. To a mixture of aniline and perchloric acid in deionised water, ammonium persulfate was added drop wise under constant stirring for 4 hrs. The temperature of the mixture is slowly raised, followed by cooling. Continuous stirring of the solution makes it darker and is now changed to emerald colour which indicates the polymerization reaction. The precipitate was filtered and washed thoroughly with distilled water, alcohol, acetone and ether.

The solution thus prepared was kept in a constant temperature bath at 5°C. The sonicator is set for 15 minutes, making sure that the temperature doesn’t rise above 10°C. This can be done by sonicating in 5 minutes intervals, then pausing and letting the solution cool to 5°C before the next sonication period. The resulting solution is clear indicating that the particles are evenly dispersed. The same procedure is repeated for the room temperature preparation also. Now the final product is centrifuged for 15 min. The final product is collected and dried in an oven in 50°C for three days. By use of this procedure, the particles sizes are found to be identical between different preparations so that the reproducibility is quite good for colloidal synthesis.

The prepared doped PANI is hard and brittle and insoluble in common organic solvents. Since the insolubility/infusibility of PANI is related to its π-π^* conjugation system.Several strategies are employed to overcome both PANI organic and inorganic insolubility. Introduction of substituent[12-14] on the aromatic ring or imine nitrogen, copolymerization with aliphatic monomers[15] have led to more solubility. So the prepared PAPC is dispersed in a non-aqueous medium in the presence of sonicator at different temperature. Thefinalproduct is taken for further analysis. The influence of temperature is analyzed by various characterization techniques.

Results and discussion

a. SEM analysis

SEM results showed that the acid dopant modulated the resultant PANI into nanoparticles. These nano particles exhibited diameter sizes around 70nm. Use of mild sonication resulted in smaller particles than without the sonication treatment. The temperature also influences sonication effect on reducing the particles size. The two images (Figs1, 2) of SEM show the temperature effect with 5°C and the other at room temperature which shows that the size of the nanoparticles at 5°C is quiet smaller compared to the particles at room temperature.

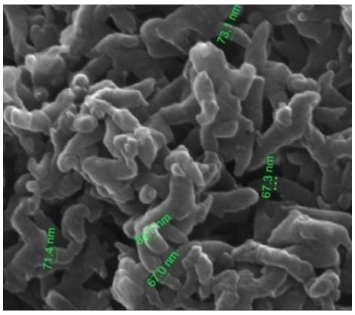

Fig.1: SEM image of PAPC - 5°C

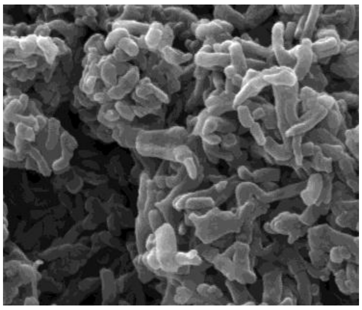

Fig.2: SEM image of PAPC - 35°C

Further the SEM results indicate that after 10 min of intermittent sonication and subsequent filtration, the sample consists almost of nanoparticles. When the period of sonication increases, large micrometer sized aggregates reappear. These particles are typically larger, with a very broad size distribution when compared with the reduced sonicating duration. At the nanoscale it appears to prevent the formation of very large particles, possibly through thesmall-scale turbulence in the solution. Similar experiments have been carried out in our lab on sonication for polymer samples which showed little effect on particles size. So the success of this method will likely depend on the nature of the molecule used.

It is expected that sonication can lead to non- equilibrium structures that might act as defects in these particles. And also this result indicates that the particle tends to agglomerate when the sonicating time is increased.

b. FT-IR analysis

In the infra red spectrum of formamide exhibits a broad absorption at 3600 -3000cm^{-1} (Fig.3). This indicates the presence of stretching vibration due to O-H, N-H groups. The frequency at 3404 cm^{-1} arises due to intra molecular associations between formamide molecules. The stretching frequency at 2886 cm^{-1} is assigned to the C-H group of formamide.

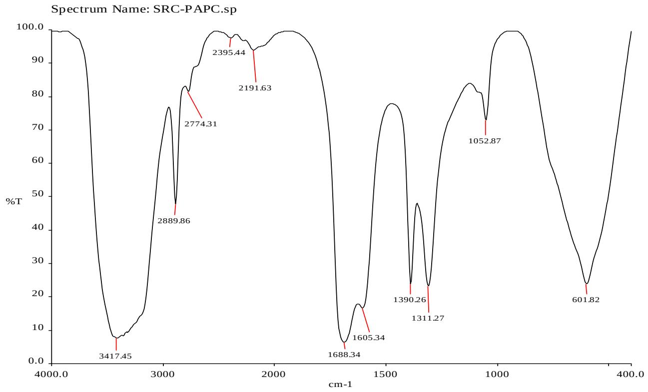

Fig.3: FT-IR spectrum- solvent

Table: 1 FT-IR observed spectral frequencies

Sample	**Vibrational frequencies in cm^{-1}**							
	N-H	***C-H***	***NH+***	***C=O***	***C=N***	***C-N***	***C-O***	***δ***
Formamide	3600 - 3000	2886, 2770 2687	2196	1684	1390	1309	1053	603
PAPC solution	3939, 3417	2886, 2771, 2689	2396, 2227, 2194	1688, 1605	1390	1311	1052	601

Frequencies at 2770 cm^{-1} and 2687 cm^{-1}(Table.1) may be due to the enolic form (Fig.4a) of formamide which may contribute a smaller extent compare to the dimer form (Fig.4b).

The frequency at 2196 cm^{-1} is thus due to the NH^{+} frequency of the enolic form.

The stretching frequency at 1684 cm^{-1} confirms the existence of intra molecularly bound carbonyl group [16].Two similar stretching vibrations 1390 cm^{-1} and 1309 cm^{-1} can be assigned to the C-N, C=N groups. At 1053cm^{-1}C-O stretching vibration is found. The broad absorption at 603 cm^{-1}is due to the bending vibration of C-H as well as C-N groups.

When PAPC is dispersed in formamide the NH stretching absorption is shifted to 3417 cm^{-1} i.e. towards higher frequency side by1 cm^{-1}. C=O stretching is shifted to 1688 cm^{-1} i.e. towards higher frequency side by 1.99 cm^{-1}. These slight deviations in the absorption peaks are due to the tightening of H-bonds in the caged structure (Fig.4). No shift is observed in NH out of plane bending.

a.Enol form b. Dimer form

Fig.4: structure of formamide

From the FT-IR study the solute –solvent interaction is found to be higher. It is already confirmed that, when PANI is dissolved in polar non aqueous solvent, it promotes thermodynamically a more stable chain. Amine (NH_2) group can be recognized by absorption due to NH stretching in the region 3000-3500 cm^{-1}. The band at 3415 cm^{-1} is due to NH stretching (Table.1)[17, 18].

The C-Cl stretching peak arises at 601 cm^{-1}. This confirms the Cl^{-} doping of the synthesized polyaniline[19]. The C=C stretching absorption of aromatic compounds generally occur in the range of 1475 - 1625 cm^{-1}. In the present study this peak was obtained at 1605 cm^{-1}. The peaks at 1040 and 505 cm^{-1} correspond to the stretching and bending vibrations [20]. The occurrence of these peaks in the PAPC spectrum (Fig.5) indicates that polyaniline is successfully doped.

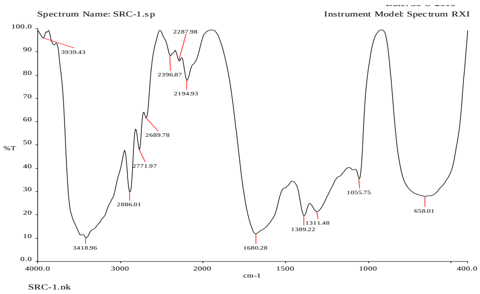

Fig.5: FT-IR spectrum-PAPC solution

c. UV-Visible analysis

The absorption band at 375 nm corresponds to n-π* transition in the benzenoid units (Fig.6). The broad band at 600-620 nm is due to n-π* transitions of quinine-imine groups (Table.2)[21].

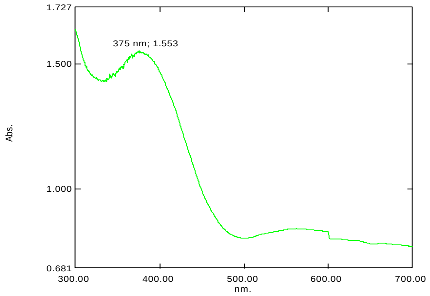

Fig. 6: UV-Vis spectrum – PAPC solution

Table: 2 UV-Visible Spectral Frequencies

Formamide λ (nm)	PAPC	
	λ(nm)	Band gap energy (ev)
210	375	3.07
213	500-600	

This broad band is ascribed to the exciton like transition in quinoidimino units. The band gap energy is found to be 3.07ev.

The presence of two very close peaks at 213 nm and 210nm in the visible spectrum of the solvent (Fig.7) are attributed to the enolic (Fig.4a) and the dimer form (Fig.4b).

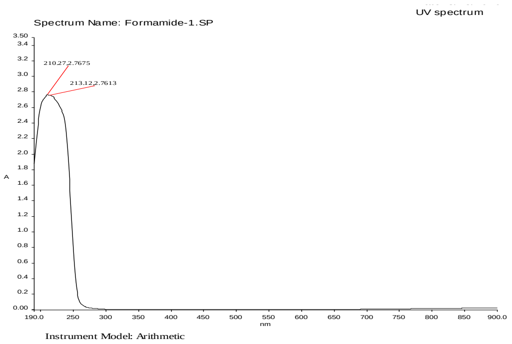

Fig. 7: UV-Vis spectrum – Formamide

Conclusion

The present study shows that sonication provides an efficient way to synthesize polymeric nano particles. Both the size distribution and crystallinity of the particles can be controlled by controlling the duration of sonication and the temperature effects. The temperature influences the size of the nano particles, improved the synthesis condition and reduced the single particle size. The spectral results show that solute solvent interaction is higher and polymer is successfully doped.

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