

Synthesis of anisotropic defective polyaniline/silver nanocomposites

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Abstract. The chemical synthesis of anisotropic defective polyaniline/Ag composite (PANI/Ag) is explored using silver nitrate (AgNO_3) as the precursor material. This study provides a simple method for the formation of PANI/Ag nanocomposites at two different aniline concentrations 5 μl (PANC5) and 10 μl (PANC10). The composite PANC5 exhibits UV-Visible absorption peaks at 436 nm and 670 nm whereas, PANC10 exhibits absorption peaks at 446 nm and 697 nm. This shift is caused by the strong interaction between polyaniline and silver. The characterized FTIR peaks observed at around 3410 cm^{-1} (PANC5) and 3420 cm^{-1} (PANC10) was due to the N-H stretching vibrations. The appearance of a broad band instead of a sharp peak can be attributed due to the presence of a high concentration of N-H groups in the nanocomposite. The TEM images show that the sample contains defective spherical, truncated triangular and rod shaped particles. The results showed that the PANI/Ag nanocomposites are composed of nano-sized particles of 43-53 nm that contain Ag domains of 33-37 nm with polymer thickness 5.7-11.2 nm at two different aniline concentrations.

Keywords: silver nanoparticles; polyaniline; polyaniline-silver nanocomposites; trisodium citrate; polymer

1. Introduction

Materials with unusual combination of properties are required for enhancing technologies continuously. In order to obtain nanomaterials with determined functionality numerous efforts have been made in the last decades using novel nanotechnology and nanoscience knowledge. One such class of nanomaterial is the polymer nanocomposite which includes polymer matrices reinforced with nano-scale fillers, has revealed enhanced optical, electrical and dielectric properties. The incorporation of inorganic nanoparticles into a polymer matrix permits properties from inorganic nanoparticles and polymer to be enhanced and accordingly an advanced new function can be generated to the polymer-inorganic nanocomposites (PINCs) (Tamboli *et al.* 2012).

Conducting polymer exhibits tunable electrical, optical and magnetic properties. In comparison

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with other conducting polymers, polyaniline is considered as one of the most studied material because of its easy preparation method, chemical and thermal stabilities and relatively high electrical conductivity (Correa *et al.* 2012). Polyaniline has been extensively studied as a novel material for potential use in batteries (Karami *et al.* 2003), chemical sensors, antistatic coating (Gangopadhyay *et al.* 2001), electromagnetic shielding (Wang *et al.* 2004), and corrosion protective coating (Wessling 1994). Silver exhibits very high conductivity and high thermal stability because of which it is considered as an important metal to produce nanoparticles (Greenwood and Earnshaw 1997). Silver nanoparticles have potential applications in catalysis, conductive inks, thick film pastes and adhesives for various electronic components, photonics and photography industry (Wang *et al.* 1997, Lin *et al.* 1996, Gould *et al.* 2000, Wang *et al.* 2001).

In order to enhance sensing and catalytic capabilities and to change electrical and optical features of PANI, the incorporation of metallic material in PANI, mainly at nanoscale is considered as an important approach. There are two general methods to produce nanocomposites of conducting polymers and metals. In the first one, metal nanoparticles are added directly to the polymeric matrix, but with the major inconvenience of promoting the agglomeration of the inorganic phase (Choudhury 2009, Leroux *et al.* 2007). In the second, nanoparticles are generated during the polymerization step in order to obtain a more homogeneous material having uniform distribution of the nanoparticles (Lee *et al.* 2003, Khanna *et al.* 2005). Incorporation of metal nanoparticles into different polymer matrix results into enhancement of the electrical, optical and dielectric properties of the polyaniline composites. Among all the metals, since silver exhibits highest electrical and thermal conductivities (Sun and Xia 2002), the combination of PANI with silver could yield functional materials possessing enhanced electrical properties (Choudhury 2009).

Until now, several approaches have been reported for the synthesis of PANI/Ag composites nanostructures in different systems. For instance, Bertino and co-workers has described the synthesis of PANI composite nanofibers decorated with noble-metal (Ag or Au) nanoparticles by γ radiolysis (Pillalamarri *et al.* 2005). Chemically deposited metal particles (Ag, Au, and Pt) and clusters with various sizes and morphologies on top of the PANI thin films and porous asymmetry membranes have been reported by Wang and co-workers (Wang *et al.* 2007). Karim *et al.* has reported the synthesis of Sulfonated polyaniline-silver (SPANI-Ag) hybrid nanocomposites at different silver nitrate concentrations by the in situ reduction using a UV radiation-induced polymerization method without using any reducing or binding agent (Karim *et al.* 2009). Whereas polyaniline/CoFe₂O₄ nanocomposites exhibited the promising photocatalytic activity for the photo-decoloration of the methyl orange dye under UV light irradiation (Khan *et al.* 2013). It has been reported that the use of dopant material enhances the conductivity of composite materials. The PANI/Ag nanocomposites are considered to have potential applications in sensors, catalysis, batteries and electronic devices. Variation in the synthesis technique and by using certain dopants such conducting nanocomposites are considered as the promising candidates for coatings with improved anticorrosion performance, sensors and catalysts compared to pure aniline. (Choudhury 2009, Tamboli *et al.* 2012, Gupta *et al.* 2010). Recently, Stejskal outlined the potential applications of hybrid composites (Stejskal 2013),

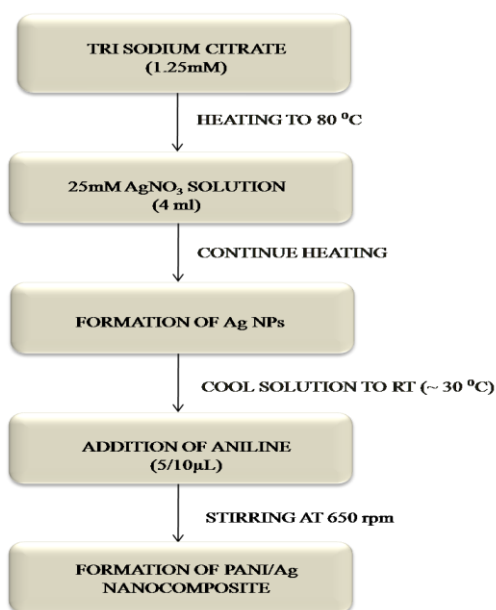
In the present investigation, a simple chemical route has been adopted for the synthesis of PANI/Ag nanocomposites with two different aniline concentrations.

2. Experimental

Silver nitrate (AgNO_3 , 99.9% MERCK), Aniline ($\text{C}_6\text{H}_5\text{NH}_2$, $\geq 99\%$, MERCK), Trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$, MERCK) and Ammonia solution (NH_3 , RANKEM) were used. All chemicals were used as such without further purification. All the solutions were prepared using milli-Q water during the synthesis. Each apparatus were washed by aqua regia, rinsed, dried in hot air oven and then used.

The synthesis of PANI/Ag nanocomposite was carried out as mentioned. In a typical synthesis, 0.051 g trisodium citrate was dissolved in 140 ml milli-Q water to obtain 1.25mM solution. The solution was kept at heating to attain 80°C and then 4 ml 25mM AgNO_3 solution with 2 drops of 1:40 aqueous NH_3 was added. The heating was continued till pale yellow color of solution was obtained indicating the formation of silver nanoparticles. Then after the solution was allowed to cool down to room temperature RT ($\sim 30^\circ\text{C}$) using a water bath. Then $5\mu\text{L}$ aniline was added under continuous stirring at the rate of 650 rpm and allowed the solution to stir for 4 hrs. The color of the solution changed from pale yellow to brownish black solution. The resultant solution was then centrifuged immediately at 12,000 rpm to avoid further polymerization. The obtained precipitates were named as PANC5 and then were analyzed. The same procedure was repeated with $10\mu\text{L}$ of aniline and the resultant precipitates were named as PANC10.

UV-Vis spectra of PANI/Ag nanocomposites (PANC5 & PANC10), Ag nanoparticles (SNP) and pure polyaniline (Polyaniline salt form (PES) & polyaniline base form (PEB)) were recorded in optical quartz cuvettes using Shimadzu UV-1800 spectrophotometer in the range of 200-1100 nm. The measurements were made at room temperature. The samples for FTIR analysis were dried at room temperature and then mixed with KBr, crushed and prepared in the form of a pellet. Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a SHIMADZU 8400 FTIR spectrometer. Transmission electron microscope (TEM) images were recorded on a TECHNAI G^2 -20 TWIN model at an acceleration voltage of 200 kV. The samples were deposited from suspensions of the products onto 3 mm copper grids before examination.



Scheme 1 Schematic for the synthesis procedure

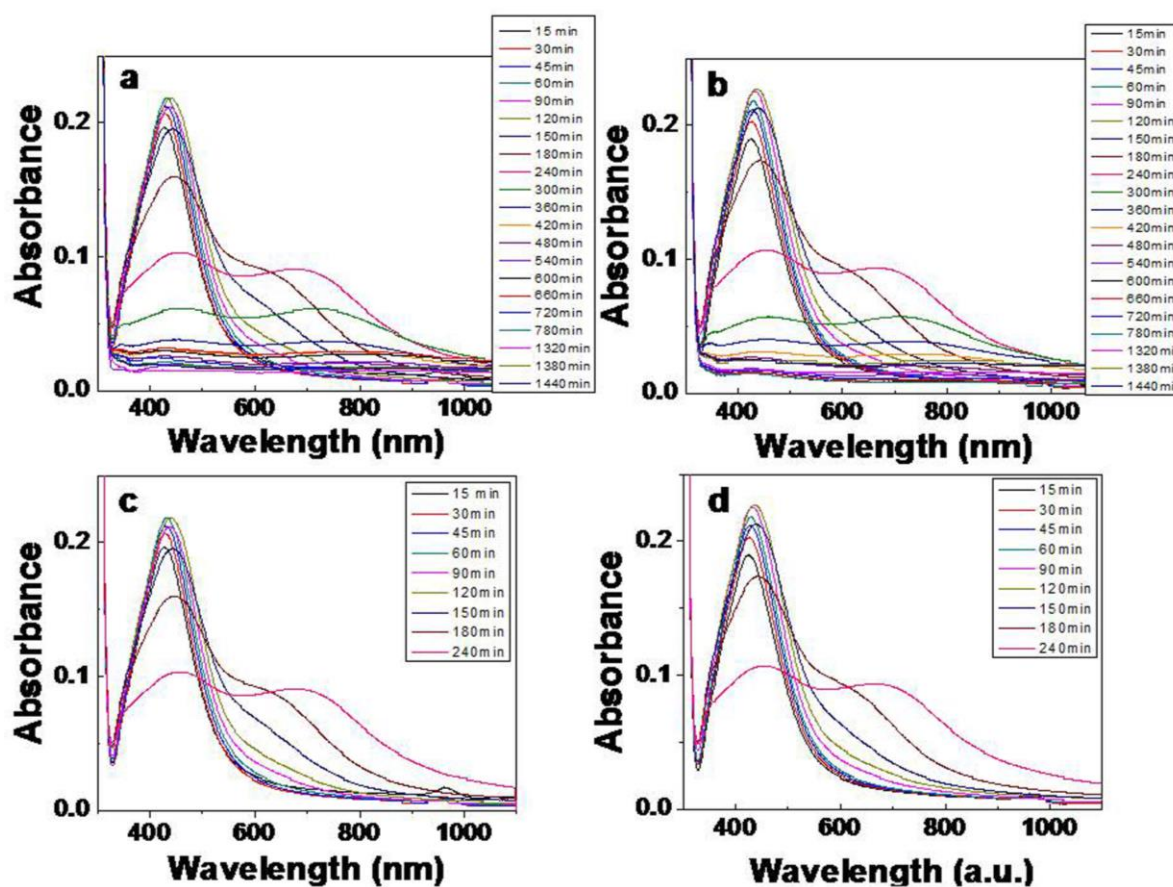


Fig. 1 UV-Vis kinetic study of synthesis of Ag nanoparticles coated with (a) $5\mu\text{L}$ aniline (PANC5) and (b) $10\mu\text{L}$ aniline (PANC10) for 1440 minutes and 240 minutes (c) and (d) respectively

3. Results and discussion

The kinetic study on the UV-Visible spectroscopy on the synthesis of polyaniline/silver nanocomposite was carried out for 1440 minutes in order to understand the completion of the reaction time and to get the *prima facie* indication of formation of anisotropic structure formation. Attempt was also made to find out UV-visible spectral differences on addition of $5\mu\text{L}$ (Fig. 1(a)) and $10\mu\text{L}$ (Fig. 1(b)) of aniline. Based on our previous observation (Ankamwar *et al.* 2012, Sastry *et al.* 2004) and spectral changes observed in Fig. 1 (a) and (b), the reactions were deliberately stopped at 240 minutes as shown in Figs. 1 (c) and (d) in order to get anisotropic structures.

UV-visible spectra clearly indicate the increase in intensity on changing amount of polyaniline from $5\mu\text{L}$ (Fig. 2 (a), curve 1) to $10\mu\text{L}$ (Fig. 2 (a), curve 2). Depending upon the particle size, the silver nanoparticles display a plasmon band that is located between 400 and 520 nm. It can be seen in Fig. 2 (b), Curve 1, the absorption band is observed at 425 nm which confirms the formation of Ag nanoparticles. The absorption spectra of PANI salt (PES) form shows three transitions 306-324 nm, 412- 438 nm, 830-850 nm with a free carrier tail extending into the near-infrared region,

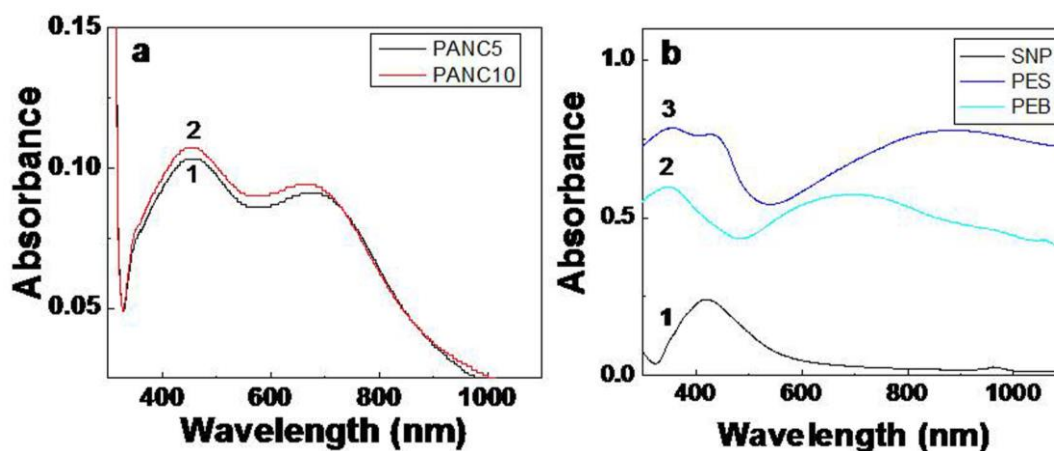


Fig. 2 UV-Vis spectra indicating (a): Ag nanoparticles coated with 5 μ L aniline (curve 1, PANC5) and 10 μ L aniline (curve 2, PANC10) and (b) shows silver nanoparticles (curve 1, SNP), pure polyaniline salt form (curve 2, PES) and polyaniline in base form (curve 3, PEB)

which are attributed to π - π^* transition of benzenoid rings, polaron- π^* transition and π -polaron transition respectively (Fig. 2 (b), curve 2). whereas, pure PANI base (PEB) form shows two characteristic peaks at \sim 350 nm and \sim 650 nm (Fig. 2 (b), curve 3). The earlier band is often associated with a π - π^* in the benzenoid structure. The later absorption band in the visible range is generally associated to the n- π^* transitions. Similar absorption bands with a little red shift appeared in the UV-Vis spectra of PANI/Ag nanocomposites (Fig. 2 (b)). The composite PANC5 exhibits absorption peaks at 436 nm and 670 nm (Fig. 1 (a), curve 1) whereas, PANC10 exhibits absorption peaks at 446 nm and 697 nm (Fig. 1 (a), curve 2). This red shift is caused by the strong interaction between polyaniline and silver. This earlier peaks in the composites are assigned to surface plasmon resonance absorption of the electrons in the conducting silver bands. When a dielectric polymer-metal nanocomposite is excited by light, photons are coupled at the matrix and the additional polaronic bands created due to metal nanoparticles.

The FTIR spectra of pure polyaniline (PES and PEB), polyaniline/Ag nanocomposites (PANC5 and PANC10) and Ag nanoparticles (SNP) are shown in Fig. 3. Curve 1 shows the FTIR spectra of the silver nanoparticles; the bands at 3445, 1660, 1380, 1275 and 836 cm^{-1} have been obtained which may be attributed due to O-H stretching vibrations, C=O stretching vibrations, C-H bending vibrations, C-O-C stretching vibrations and C-H deformation vibrations out of planes respectively. These bands may be attributed due to presence of citrate ions in the sample. All of the spectra except for the spectra of silver nanoparticles, exhibits peaks corresponding to the stretching of quinoid (N=Q=N, at around 1570 cm^{-1}) and benzenoid (N-B-N, at around 1490 cm^{-1}) rings. These results are in good agreement with previous spectroscopic characterizations of polyaniline (Pillalamarri *et al.* 2005, Hasik *et al.* 2001). An FTIR spectrum suggesting the molecular structures of products obtained with APS and silver nitrate as oxidants are shown in the Fig. 3. The spectra corresponding to oxidation products obtained with the later oxidant (curve 2 and curve 3), however, differ in shape and include an additional peak at 1384 cm^{-1} corresponding to nitrate counter-ions, indicating that the PANI in the samples was in emeraldine salt form. The absence of the band at 1189 cm^{-1} in the composites (curve 2 and 3), is due to protonated chain vibrations. This band is characteristic of protonated chain vibrations Q=NH⁺-B or B-NH⁺-B (Q = quinoid, B =

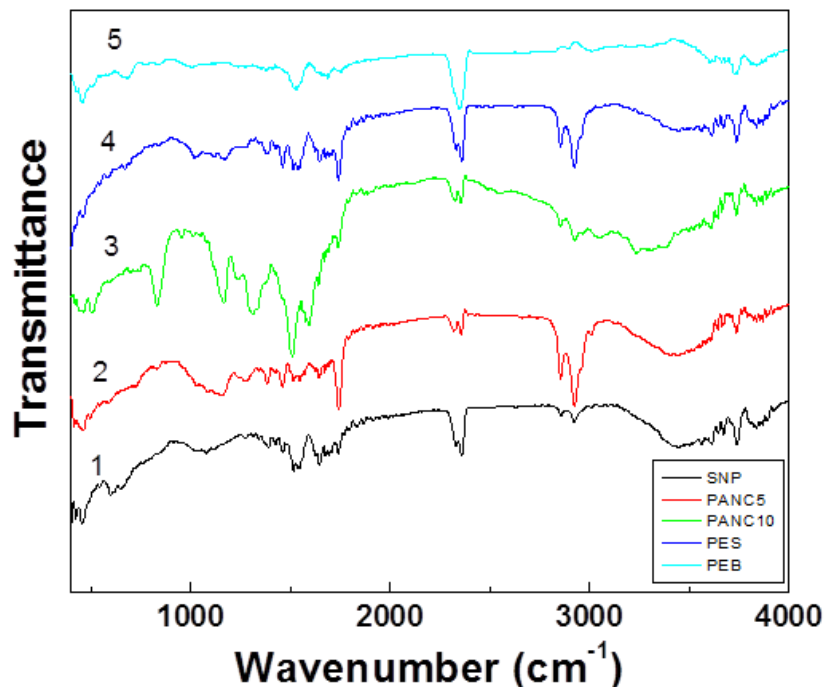


Fig. 3 FTIR spectra of silver nanoparticles (curve 1), PANC5 (curve 2), PANC10 (curve 3), polyaniline in salt form (curve 4) and polyaniline in base form (curve 5)

benzenoid units of polymer) which can be due to hydrogen bond to the -NH- or =N- groups in PANI. When the Ag is incorporated into the polymer matrix this bonding is weakened (as Ag^+ is reduced to Ag^0 and the -NH- groups of the polymer chain are oxidized to -N=). In all the spectra of the composite samples, characterized peaks of PANI at around 1120, 1240, 1300, 1460, and 1575 cm^{-1} were found, which can be assigned to the C-H in plane bending, C=N stretching, C-N stretching, C=C stretching of benzenoid ring, and C=C stretching of quinoid ring, respectively (Wang *et al.* 2001, Lee *et al.* 2003, Khanna *et al.* 2005). The weak peaks at 1440 and 1640 cm^{-1} were assigned to the phenazine structure of PANI. The broad band in the region between 3100 and 3700 cm^{-1} corresponds to stretching of N-H bond. A peak observed at around 3410 cm^{-1} (PANC5) and 3420 cm^{-1} (PANC10) was due to the N-H stretching vibrations. The appearance of a broad band instead of a sharp peak can be attributed due to the presence of a high concentration of N-H groups in the nanocomposite. The peaks around 2850 and 3000 cm^{-1} (curve 2 and curve 3) corresponds to C-H stretching vibrations, whereas the peak at ~ 1384 cm^{-1} can be assigned to aromatic C-N stretching vibrations. The 3500 cm^{-1} was assigned to the hydrogen bond interaction in the PANI. Fig. 3 shows the IR spectra of PANI salt and PANI base (curve 4 and curve 5 respectively). The peaks for the polyaniline base and salt appear at the same region and with similar intensities but can be recognized by marginal differences. IR spectrum of the polyaniline base shows six principal peaks at 1591, 1507, 1311, 1236, 1165 and 829 cm^{-1} . The peaks at 1591 and 1507 cm^{-1} are assigned to C-C ring stretching vibrations. The peaks at 1311 and 1236 cm^{-1} corresponds to N-H bending and the symmetric component of the C-C (or C-N) stretching modes.

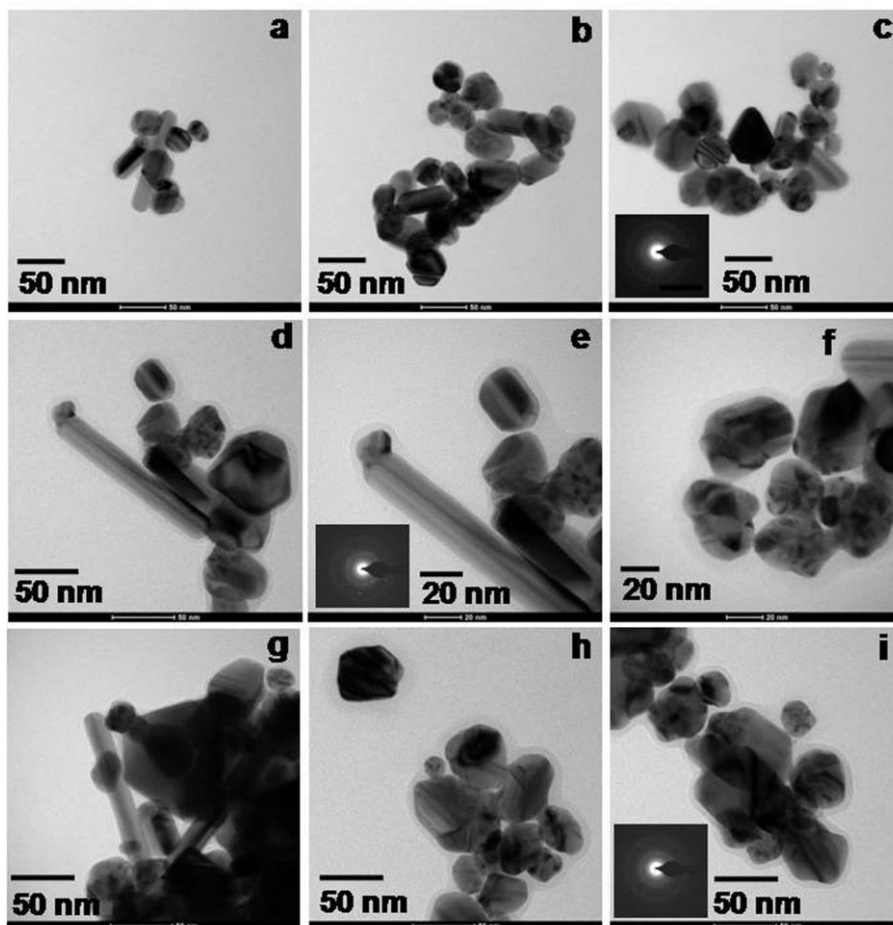


Fig. 4 Representative TEM micrographs of Ag nanoparticles (a-c), Ag nanoparticles coated with 5 μ L aniline at lower (d), higher (e-f) magnification and Ag nanoparticles coated with 10 μ L aniline (g-i)

The bands at 1165 cm^{-1} can be attributed to the in-plane C-H bending mode and 829 cm^{-1} due to out-of-plane bending mode. The peaks corresponding to polyaniline salt appear at 1570, 1497, 1302, 1250, 1148 and 822 cm^{-1} respectively. In addition to the above peaks, the spectrum of the polyaniline salt exhibits new peaks around 3216, 1680 and 700 cm^{-1} . The peak at 3216 cm^{-1} could be attributed as due to NH_2 stretching mode and the 1680 cm^{-1} band to the NH_2 bending vibration while the 700 cm^{-1} is assigned as due to NH_2 wagging. The band characteristic of conducting protonated form is observed at 1248 cm^{-1} . It has been interpreted as appearing from bi-polaron structure, related to C-N stretching vibration. The peak at 1570 cm^{-1} confirms the presence of a protonated imine function. The C-Cl stretching peak arises in the region 590 – 700 cm^{-1} .

Fig. 4 (a-c) shows representative TEM micrographs of silver nanoparticles stabilized by citrate ions with an average particle size of ~ 32 nm. The TEM images show that the sample contains spherical, truncated triangular and rod shaped particles. A TEM image clearly indicates the formation of defective particles. Fig. 4(d) represents the TEM micrograph of Ag nanoparticles embedded in the PANI matrix at lower and (e-f) higher magnifications with 5 μ L aniline

concentrations and (g-i) at lower magnification with 10 μL aniline concentrations. It can also be seen that the Ag nanoparticles are dispersed in the PANI matrix. It can be seen through the TEM image that as the aniline concentration is increasing the thickness of the polymeric shell is increased. If we compare the thickness of the polymeric shell, the thickness in case of composite PANC5 was found out to be ~ 5.7 nm which increased to ~ 11.2 nm when the aniline concentration was increased to 10 μL (PANC10) which can be seen clearly in Fig. 3 (c) and (e). We obtained a composite having ~ 37 nm Ag nanoparticles with a polymeric shell of about 5.7 nm in the case of composite with lower aniline concentration whereas, in case of composite with higher aniline concentration ~ 33 nm Ag nanoparticles were coated with a polymeric shell of ~ 11.2 nm thick. The synthesized composite (PANC5) have an average particle size of about 43 nm whereas, the composite (PANC10) has an average particle size of about 53 nm. It can be seen through selected area electron diffraction (SAED) image shown in the inset in Fig. 4(c) that the silver nanoparticles are polycrystalline in nature whereas, the SAED pattern shown in the Fig. 4 (e) and (i) confirms the polycrystalline nature of the composite. These anisotropic defective polyaniline/silver nanocomposites could be promising candidates in sensing, catalysis etc.

4. Conclusions

In this paper a simple technique has been reported to obtain PANI/Ag nanocomposites. The PANI/Ag nanocomposites were successfully synthesized at two different aniline concentrations. The Ag nanoparticles formation and its existence within the composite matrices were confirmed by UV-Vis spectroscopy, FTIR and TEM analysis. TEM analysis shows dispersion of the spherically shaped Ag nanoparticles along with certain rod shaped particles dispersed within PANI matrix. As aniline concentration increases an increase in the thickness of the polymeric shell can be clearly observed in the TEM images.

References

- Ankamwar, B., Mandal, G., Sur, U.K. and Ganguly, T. (2012), "An effective biogenic protocol for room temperature one step synthesis of defective nanocrystalline silver nanobuns using leaf extract", *Dig. J. Nanomater. Biostruct.*, **7**(2), 599-605.
- Correa, C.M., Faez, R., Bizeto, M.A. and Camilo, F.F. (2012), "One-pot synthesis of a polyaniline-silver nanocomposite prepared in ionic liquid", *RSC Adv.*, **2**, 3088-3093.
- Choudhury, A. (2009), "Polyaniline/Silver nanocomposites: Dielectric properties and ethanol vapour sensitivity", *Sens. Actuat. B.*, **138**, 318-325.
- Gould, I.R., Lenhard, J.R., Muentner, A.A., Godleski, S.A. and Farid, S. (2000), "Two electron sensitization: a new concept for silver halide photography", *J. Am. Chem. Soc.*, **122**, 11934-11943.
- Greenwood, N.N. and Earnshaw, A. (1997), *Chemistry of the Elements*, 2nd Edition, Oxford.
- Gangopadhyay, R., De, A. and Ghosh, G. (2001), "Polyaniline-poly(vinyl alcohol) conducting composite: material with easy processability and new novel application potential", *Synth. Met.*, **123**, 21-31.
- Hasik, M., Drelinkiewicz, A., Wenda, E., Paluszkiwicz, C. and Quillard, S. (2001), "FTIR spectroscopic investigation of polyaniline derivatives-palladium systems", *J. Mol. Struct.*, **596**, 89-99.
- Karami, H., Mousavi, M.F. and Shamsipur, M. (2003), "A new design for dry polyaniline rechargeable batteries", *J. Power Source.*, **117**, 255-259.
- Khanna, P.K., Singh, N., Charan, C. and Viswanath, A. (2005), "Synthesis of Ag/Polyaniline nanocomposite via an in situ photo redox mechanism", *Mater. Chem. Phys.*, **92**(1), 214-219.

- Karim, M.R., Yeum, J.H., Lee, M.Y., Lee, M.S. and Lim, K.T. (2009), "UV-curing synthesis of sulfonated polyaniline-silver nanocomposites by an in-situ reduction method", *Polym. Adv. Technol.*, **20**, 639-644.
- Khan, J.A., Qasim, M., Singh, B.R., Singh, S., Shoeb, M., Khan, W., Das, D. and Naqvi, A.H. (2013), "Synthesis and characterization of structural, optical, thermal and dielectric properties of polyaniline/CoFe₂O₄ nanocomposites with special reference to photocatalytic activity", *Spectrochim. Acta. A Mol. Biomol. Spectros.*, **109**, 313-321.
- Lin, J.C. and Wang, C.Y. (1996), "Effects of surface treatment of silver powder on rheology of its thick-film paste", *Mater. Chem. Phys.*, **45**, 136-144.
- Lee, M., Kim, B.W., Nam, J.D., Lee, Y., Son, Y. and Seo, S.J. (2003), "In-situ formation of gold nanoparticle/conducting polymer nanocomposites", *Mol. Cryst. Liq. Cryst.*, **407**, 397-402.
- Leroux, Y., Eang, E., Fave, C., Trippe, G. and Lacroix, J.C. (2007), "Conducting polymer/gold nanoparticle hybrid materials: A step toward electro active plasmonic devices", *Electrochem. Commun.*, **9**, 1258-1262.
- Pillalamarri, S.K., Blum, D.F., Tokuhito, T.A. and Bertino, M.F. (2005), "One-pot synthesis of Polyaniline-metal nanocomposites", *Chem. Mater.*, **17**, 5941-5944.
- Sun, Y. and Xia, Y. (2002), "Large-scale synthesis of uniform silver nanowires through a soft, self-seeding, polyol process", *Adv. Mater.*, **14**, 833-837.
- Shiv Shankar, S., Rai, A., Ankamwar, B., Singh, A., Ahmad, A. and Sastry, M. (2004), "Biological synthesis of triangular gold nanoprisms", *Nature Mater.*, **3**, 482-488.
- Stejskal, J. (2013), "Conducting polymer-silver composites", *Chem. Pap.*, **67**(8), 814-848.
- Tamboli, M.S., Kulkarni, M.V., Patil, R.H., Gade, W.N., Navale, S.C. and Kale, B.B. (2012), "Nanowires of silver-Polyaniline nanocomposite synthesized via in situ polymerization and its novel functionality as an antibacterial agent", *Colloids Surf. B.: Biointerf.*, **92**, 35-41.
- Wessling, B. (1994), "Passivation of metals by coating with polyaniline: corrosion potential shift and morphological changes", *Adv. Mater.*, **6**(3), 226-228.
- Wang, Y. and Toshima, N. (1997), "Preparation of Pd-Pt bimetallic colloids with controllable core/shell structures", *J. Phys. Chem. B.*, **101**, 5301-5306.
- Wang, W. and Asher, S. (2001), "A photochemical incorporation of silver quantum dots in monodisperse silica colloids for photonic crystal applications", *J. Am. Chem. Soc.*, **123**, 12528-12535.
- Wang, Y. and Jing, X. (2004), "Intrinsically conducting polymers for electromagnetic interference shielding", *Polym. Adv. Technol.*, **16**, 344-351.
- Wang, H.L., Li, W.G., Jia, Q. X. and Akhadov, E. (2007), "Tailoring conducting polymer chemistry for the chemical deposition of metal particles and clusters", *Chem. Mater.*, **19**, 520-525.