Synthesis, characterization of Ag@PANI core-shell nanostructures using solid state polymerization method

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ABSTRACT
One-step reaction has been developed to obtain Ag®Polyanilin (Ag@PANI) core-shell nano-structures. Aniline sulphate was oxidized by silver nitrate using solid-state polymerization method at room temperature. The structure and morphology of the core-shell were characterized by the Fourier transform infrared (FTIR) spectra, Ultraviolet-Visible (UV–Vis) absorption spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The XRD patterns displayed both the broad amorphous polymeric and sharp metallic peaks. The results from TEM and SEM images showed that the nano-composites have core-shell structures. The changes occurring in the structure of PANI are discussed on the basis of infrared and UV-Vis spectroscopy. The spectra revealed the formation of the nano-composites.

Keywords: PANI, solid state polymerization; core-shell; nanocomposites.

1. INTRODUCTION
Preparation of nano-composites from metal–polymer is a vast research point in technological fields. Nano-composites have extensively attracted the researchers’ consideration due to their advanced properties [1–4]. Numerous nano-composites combining PANI with different inorganic nano-materials have been investigated. The addition of metal or metal oxide to PANI improves physical and mechanical properties, due to interfacial interactions between PANI and inorganic nanoparticles, creating materials having new properties [2,5].

The conjugating PANI is one of the promising polymers due to its high processability, intrinsic redox reaction, ease of preparation, good environmental stability and several applications [6,7]. Among the several types of nano-composites, core-shell nano-composites are especially interesting. According to the mentioned introduction, core-shell may be regarded as nano-composite synthesized by mixing several kinds of materials such as dielectric materials, metals and semiconductor materials. One could also add some pigment materials. In core-shell the core and shell could be from the same material or from different materials [8-10]. Nano-composites add new properties to the original materials, like the tremendous increase in the surface area related to their size and also the capability of tuning the size and fields distribution around the structure. Recently, researchers spotted more efforts for investigation especially in the fields of chemical sensors and electronics.

Many synthetic methods were proposed to fabricate Ag@PANI nano-composites such as, sol–gel technique [11], chemical polymerization in the aqueous solution with the presence of polymer monomer and inorganic particles [12], emulsion technology [13], and sono-chemical process [1]. Solid-state reaction has barely been used to synthesize Ag@PANI nano-composites. Preparing the core-shell by solid state reaction affords many advantages like, cost-effective preparation, and the high stability of the end product. Also solid state reaction offers low chemical consumption and it could be regarded as the simplest preparation method [14,15].

Solid state reactants do surface reaction to form the desired product [15]. This surface reaction takes place by milling the different constituents of the reaction. The milling process decreases the inter diffusion rate between the reactants, more than that rate in the normal process. Previously, I. Šeděnková [16] prepared the dendritic structure of silver in Ag@PANI nano-composites, with branches diameter of 100nm using two-step reaction, where the PANI (emeraldine base) is prepared in liquid

Scheme 1. The structure of Ag@PANI core-shell nano-structure.

Figure 1. PANI Em nitrate polymerization by oxidizing aniline sulphate using AgNO3, producing silver, Nitric acid and sulphuric acid as by product.
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state then oxidized by silver nitrate in the solid state reaction. I. Šeděnková [17] fabricated a granular PANI structure accompanied by silver nano-particles via the solid-state oxidations of aniline hydrochloride with various oxidants. The usage of aniline hydrochloride reacted with silver nitrate formed silver chloride, due to less polymerization process and can result in aggregation. In this paper, we synthesized the Ag@PANI core-shell nano-structures by solid state polymerization method from one-step reaction and only from two reactants (aniline sulphate and silver nitrate). The monomer salt was oxidized by silver nitrate introduced to nano-silver metal, where the silver nanoparticles as a core and PANI covered the core as a shell. This way is regarded as an interesting and easy way to form core-shell structure because of that, this synthesizing process did not need to special temperature and could be done at room temperature. Additionally, the experiment setup is very simple with no need for complicated steps or surfactant materials. The structure of the designed particles is shown in scheme (1). The oxidation of aniline sulphate with silver nitrate in the solid state was studied as in figure (1). The synthesized core-shell preparation will be discussed in details along with the investigations and analysis with different techniques.

FTIR spectroscopy is one of the most powerful tools in characterizing the molecular structure especially if it is supported with molecular modeling and imaging [18-23]. Single molecule imaging is also one from the recent trends especially for core-shell and nano-structures [24-29].

2. MATERIALS AND METHODS

2.1. Materials.

Aniline sulphate of analytical-reagent grade was purchased from Alfa Aesar Thermo Fischer- Germany and Silver nitrate from Sisco Research Laboratories PVT LTD- India.

2.2. Preparation of Ag@PANI core-shell nano-structures.

The Ag@PANI core-shell nano-composites were synthesized by solid state polymerization method. A typical synthesis process for Ag@PANI nano-structure is as follows, the aniline sulphate (white powder) and silver nitrate (white powder) were mixed together and intensively milled till the powder turned to green. The mixture was then washed with methanol to remove the unreacted chemicals and then the samples were air dried overnight. Different concentrations of silver nitrate were used to prepare Ag@PANI core-shell nano-structure.

2.3. Samples characterization

Transmission Electron Microscope Model JEM 2010from JEOL- Japan, operated at 200 kV accelerating voltage was used to study the morphology, shape and particle size distribution. A droplet of suspension of the sample was prepared, and dropped into a carbon grid then air dried. Scanning electron microscope from JOEL Japan model JEM 2100 was utilized for SEM imaging. X-ray data were recorded using XRD from Bruker AXS-Germany model D8 advance, at wavelength $\lambda=1.5406\text{Å}$ radiated from CuKα tube at voltage and current of 40KV and 40mA respectively at room temperature. The 20 range was from 200 to 800 with a step size of 0.04O and scanning speed of 1o/min. The vibrational spectra were measured in the wavenumber range (4000-400 cm$^{-1}$) using FTIR spectrometer from Bruker-Optics Germany model V70 by ATR technique equipped with diamond crystal. Optical absorption spectra of Ag@PANI core-shell nano-structures suspended in water were recorded in the absorbance mode using Jasco spectrophotometer model UV-VIS-NIR 570 from Japan, at a resolution of 2 nm. The diffuse reflectance spectra were measured also by the same spectrophotometer by means of the diffuse sphere in the range from 1000 to 200 nm.

3. RESULTS

3.1. FTIR studies.

Mid-infrared absorption spectra of Ag@PANI core-shell nano-structure at different concentration of AgNO$_3$ in the wave number range from 4000- 400 cm$^{-1}$ are illustrated in figure (2a-d). It is clear from figure (2a) that the vibrational band at 1585 cm$^{-1}$ is assigned to quinoid structures and that at 1497 cm$^{-1}$ is related to the benzenoid [30]. The appearance of these vibrational bands confirms the formation of PANI, the mentioned positions are characteristic for PANI regardless whether it is doped or undoped PANI [30-31]. The intensity ratio of these two absorption bands reflects the relative content of quinoid imine to benzene ring structure [33]. A strong sharp peak at 1384 cm$^{-1}$ is observed which is related to the nitrate anion NO$_3^-$, this peak could be a strong evidence on the protonation of PANI, and this protonation is resulting from the presence of HNO$_3$ resulting from the reaction shown in figure 1 [32]. Bands at 1297 cm$^{-1}$ and 1242cm$^{-1}$ are assigned to C-N stretching vibration in the quinoid imine unit and C-N$^+$ stretching vibration in the secondary amines respectively. C-N$^+$ stretching could be seen from the band at 1242cm$^{-1}$ which is ascribed to the vibration in the polaron structure.

The appearance of this band confirms that PANI salt contains the emeraldine salt phase The vibrating band at 1112 cm$^{-1}$ is due to

Figure 2. Infrared spectra of Ag@PANI core-shell nano-composites at different concentrations of AgNO$_3$, (a) 0.05, (b)0.1, (c) 0.15, and (d) 0.2g.
the C-H of B-NH\(^+=Q\) in plane bending vibration in quinoid ring [33], which is formed during the protonation process. The broadening of this band could be attributed to so much electron delocalization in PANI Em salt [34]. The vibration range 800–880 cm\(^{-1}\) is identifying the out-of-plane bending vibration of C-H bond in the 1,4-disubstituted aromatic ring. The bands at 690 cm\(^{-1}\), 621 cm\(^{-1}\), and 505 cm\(^{-1}\) are associated with C-C bending vibrations in quinoid and benzenoid ring [35]. The effect of increasing AgNO\(_3\) concentration in the preparation of Ag@PANI core-shell is taken into account. It is clear that no shift in the position of the bands can be detected with increasing the concentration of AgNO\(_3\). While an increase in the peak height is observed, in particular that of quinoid with respect to that of benzenoid. To follow the enhancement in the intensity of the peak at 1497 cm\(^{-1}\) to 1384 cm\(^{-1}\), it is referred to the intensity ratio of benzenoid structure to nitrate ions peak. The ratio is calculated from the following relation and listed in table (1)

\[
R(\text{intensity ratio}) = \frac{I_{N-B-N}}{I_{1384}}
\]

Where I is the relative absorption intensity. From figure (3), by comparing the initial ratio at the sample 0.05 g to other sample, we found that the ratio decreased from 1.614 to 0.967 with increasing the concentration of silver nitrate. This may refer to the increase in bonding of nitrate ion groups (NO\(_3^−\)) with quinoid structure. This reflects the increase in silver content. The intensity ratio slightly increased to 1.218 at the sample 0.15 g but still less than that of 0.05 g. It may indicate that the benzenoid structure increased in the chain, and the bond between quinoid structure and nitrate ions groups NO\(_3^−\) decreased. The oxidation strength could be investigated from the ratio (R) of the peak intensities of both quinoid and benzenoid. In the case of R equal to zero, PANI is fully reduced and it is in the form of Leucoemrladine, while if it is in between 0.5 and 1, PANI is partially oxidized and it is in the form of Protoemrladine. The fully oxidized state takes place at R>1 which refers to the Pernigraniline form [36].

**Table 1.** The intensity ratio of the absorption bands of benzenoid structure to the nitrate ions for Ag@PANI core-shell nano-composites at different concentrations of AgNO\(_3\).

| Concentration (g) | Intensity ratio\((I_{1497}/I_{1384})\) |
|------------------|----------------------------------|
| 0.05             | 1.614                            |
| 0.1              | 0.83378                          |
| 0.15             | 1.218                            |
| 0.2              | 0.967                            |

The calculated R values of the quinoid structure to benzenoid structure are listed in table (2).

**Table 2.** The intensity ratio of the absorption bands of quinoid to benzenoid structure for Ag@PANI core-shell nano-composites at different concentrations of AgNO\(_3\).

| Concentration (g) | Intensity ratio\((I_{1985}/I_{1497})\) |
|------------------|----------------------------------|
| 0.05             | 0.61022                          |
| 0.1              | 0.7474                           |
| 0.15             | 0.69314                          |
| 0.2              | 0.81326                          |

From figure (4), it is clear that the intensity ratios of \(I_{1985}\) to \(I_{1497}\) are increasing with increasing the concentration of AgNO\(_3\) for the sample at 0.05, 0.1 and 0.2 g from 0.612 to 0.81326. This indicates that the benzenoid unit changed into quinoid structure in PANI. It also indicates the increase in the oxidation state of PANI, and the formation of Ag@PANI core-shell in the emeraldine salt form.

**Figure 3.** The intensity ratio of the benzenoid structure to nitrate ions band vs concentration of AgNO\(_3\).

**Figure 4.** The intensity ratio of the quinoid to benzenoid structure.

**3.2. UV-Visible spectra for Ag@PANI core-shell nano-structure.**

The absorption modes in diffuse reflectance spectra of the Ag@PANI core-shell nano-structures are shown in figure (5:a-d). In figure (5: a), it was found that, four characteristic absorption bands appeared. The first characteristic peak around 250 nm was corresponded to anilinium cation [37]. This is due to the presence of aniline oligomer in nano-composites. Electron transfer from HOMO to LUMO states is noticed from the bands at 328 nm and 388 nm. This electron transfer is related to the \(\pi→\pi^*\) electronic transition of the benzene ring [37].

**Figure 5.** UV-Vis absorbance spectra of Ag@PANI at different concentrations of silver nitrate (a) 0.05, (b) 0.1, (c) 0.15 and (d) 0.2 g.
It is noticed as a specific protonation PANI property in the UV which is the polaron- π* transition. This transition is clear from the presence of the electronic peak at 428 nm [38]. It is also noticed from the presence of the peak at 674 nm. Normally in PANI the electronic transition from n to π* is always related to this peak. It denotes in PANI the conformation of the benzoid ring into quinoid ring. The effect of concentration of AgNO₃ on the spectra is shown in figure (5:a-d). It is observed that the polaron-π* peak at 428 nm is slightly shifted towards higher wavelength (bathchromic shift) to 430nm and 436 nm in the sample at 0.15 and 0.2 g respectively. The electronic band at 674 nm is slightly shifted to 692 nm in the sample at 0.15 g and to 744 nm in the sample at 0.2g. This band at 744 nm is attributed to π -polaron transitions of PANI backbone, which indicates the formation of π-polarons and PANI is in the doped state and in emeraldine salt form [39].

From the discussed spectral shift, one could conclude that there is enlargement in the PANI conjugation. This enlargement is expected to reduce the absorption energy [40]; moreover, due to the successful interaction of metal-nano-particles with the polymer chain [41].

### 3.3. Morphology.

SEM images of Ag@PANI core-shell are shown in figure (6: a-c). From the images it is clear that Ag (light particles) is completely encircled by dark layer of PANI; also there are aggregations in some regions from silver-capped by a polyaniline cage from core-shell Ag@PANI.

TEM images are presented in figure (7: a-d). It is clear that the TEM images of PANI-coated Ag nano-particles indicate a uniformly spherical shape with diameters of 3-20 nm and the well-dispersed nano-composites have core-shell structure. The polymer shell looked like a shadow encircling the silver particles which appear as a core of darker color.

### 3.4. X-Ray Diffraction.

From the XRD spectra, one could calculate several useful structural parameters like lattice constant, d-spacing, and the amount of crystallinity of the compounds, in addition to other important information about the particles itself like the particle size.

The XRD spectra are presented in figure (8). The diffraction patterns show amorphous as well as crystalline components with diffraction peaks at 20 around 20.09°, 25.05°, 38.04°, 44.13°, 64.30°, and 77.31°.

The peak around 20.09° is related to the parallel periodicity parallel to the polymer chain while the other one at 25.05° could be related to the orthogonal periodicity of the polymer chain [42,43]. According to (JCPDS no-01-1164) and the literature silver have (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes. Also silver is arranged in the 3D space as a cubic face centered crystal structure with its planes emerging in the XRD at 20 around 38.04°, 44.13°, 64.30°, and 77.31° [44]. The additional peaks in the spectra are referred to the silver NPs which are embedded in PANI structure which is also proved by the TEM images. One could predict that there are Silver NPs from the presence of XRD peak at 20 around 37.9°. The intensity ratios between the phases (2 0 0) and (1 1 1) shown in figure (8), for the investigated concentrations are 0.69, 0.92,0.96, and 0.93. The calculated ratios are slightly higher than the conventional value which is 0.45 according to the literature [45]. The increase in the (2 0 0) to (1 1 1) ratio may be because the Silver NPs are enriched in the (1 0 0) plan, or in other words, their (1 0 0) planes tend to be the preferentially oriented parallel to the surface of the supporting substrate. It is noticed that the mentioned ratio's increase with the increase of AgNO₃ concentration is attributed to the growth of the (1 0 0) planes more with the silver ion concentration through allowing more silver atoms to accumulate onto them.
Figure 8. X-Ray diffraction pattern of PANI prepared at different concentrations of APS (a) 0.05, (b) 0.1, (c) 0.15, (d) 0.2 g.

Figure 9. Williamson-Hall plot of nano-crystalline silver sample assuming uniform deformation mode the used $\beta_{hl}$ value is the corrected values.

Using Scherrer method for powder by means of Bragg's relation one could calculate the d-spacing of different samples.

$$n\lambda = 2d\sin\theta$$

where $\lambda$ is the X-Ray wavelength, $n$ is an integer number and is equal to 1,2,.....,and $\theta$ is the angle of deviation of the diffracted beam, and is measured in the plane of the incident and diffracted beams. While for n value is more than one, the signal intensity becomes very weak compared with the first order so the relation is always approximated to $n=1$.

The lattice constant (a) can be determined from any line in an indexed cubic pattern by making use of the cubic formula for the inter-planer spacing.

$$a = d\sqrt{h^2+k^2+l^2}$$

where h, k and l are Miller indices.

For silver, the crystal structure is FCC. Theoretically, the unit cell edge value ‘$a$’ could be calculated by [46]

$$a = \frac{4r}{\sqrt{2}}$$

While $r_{Ag}=144$ pm, the silver edge value will be 4.07 Å. Experimentally the edge value has been calculated from the peak intensity of the plane (1 1 1) and it is found to be 4.09 Å which is approximately the same as the theoretical value. The lattice constant ‘a’ details are listed in table (3) which are in good agreement with the literature [46].

Miller indices (h k l) of the crystal are important to be determined for each peak to index. It is calculated by two different methods and tabulated in table (4). Another important parameter which is the particle size (D) is determined from the XRD pattern in terms of a factor called the shape factor (K) and the peak full width at half max. $\beta$ by the following Scherrer equation

$$D = \frac{K\lambda}{\beta\cos\theta}$$

The average particle size of Ag@PANI core-shell nanocomposites was calculated for the most intense peak i.e., (1 1 1) Bragg reflection [47-50]. Also both d-spacing and particle size have been calculated and listed in table (3).

In table (3), it is clear that with increasing the concentration of AgNO$_3$, the particle size decreased and d-spacing increased for the samples of 0.1 and 0.2 g. The sample of 0.15 g has less d-spacing and high value of intensities ratio of $I_{(2 0 0)}/I_{(1 1 1)}$ and $I_{(2 2 0)}/I_{(1 1 1)}$, this indicates that the sample have more relative abundance of (1 1 0) facets on the surfaces than other samples.

In figure (9) the Williamson-Hall plot is presented. The particle size and strain are calculated after plot fitting and determining the interception point on the Y-axis and slope respectively [51].

Table 3. Estimated values of d-spacing, lattice constant, particle size and the intensity ratio of Ag@PANI core-shell nanocomposites at different concentrations of AgNO$_3$.

| Conc. (g) | 20 (°) | d (Å) | D (nm) | a (Å) | Intensity ratio ($I_{(2 0 0)}/I_{(1 1 1)}$) | Intensity ratio ($I_{(2 2 0)}/I_{(1 1 1)}$) |
|----------|--------|-------|--------|-------|---------------------------------|---------------------------------|
| 0.05     | 38.04  | 2.3625| 26.3   | 4.092 | 0.69                            | 0.65                            |
| 0.1      | 38.0   | 2.3647| 24.9   | 4.096 | 0.92                            | 0.83                            |
| 0.15     | 38.14  | 2.3563| 23.4   | 4.081 | 0.96                            | 0.98                            |
| 0.2      | 38.02  | 2.3637| 11.8   | 4.094 | 0.93                            | 0.97                            |
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Table 4. Estimated values of simple peak indexing and peak indexing from d-spacing for Ag@PANI core-shell nano-composites.

| Peak position 2θ(°) | 10^4×sin2θ (°) | 10^4×sin2θ/59.58 (°) | Reflection | Remarks |
|---------------------|----------------|------------------------|------------|---------|
| 38.04247            | 106.3053       | 3                      | (1 1 1)    | 1' + 1' + 1' = 3 |
| 44.20144            | 116.6117       | 4                      | (2 0 0)    | 2' + 0' + 0' = 4 |
| 65.2841             | 283.2489       | 8                      | (2 2 0)    | 2' + 2' + 0' = 8 |
| 77.32235            | 390.5322       | 11                     | (3 1 1)    | 3' + 1' + 1' = 11 | calculated in terms of line broadening (β_{h k l}), Bragg angle (θ_{h k l}) and the lattice constant (a) by [54] 

\[ \delta = \frac{15\beta_{h k l} \cos \theta_{h k l}}{2aD} \]

From table (5), it is observed that the dislocation density of silver nano-particles in core-shell system increased from 24.1×10^{14} to 135×10^{14} m^{-2} with decreasing particle size from 8 to 20 nm. It is well known that the line wideness is proportional directly with the crystalline size. In other words, one could say as sharp XRD pattern as larger crystallite substance.

The presented XRD spectra are shown peak broadening of the nano-particles. The calculated size by Scherrer’s equation for our sample is 24 nm.

Also crystallinity index (I_{cryst}) could be evaluated by comparing the crystallite size as found by SEM particle size determination (D_P) to that calculated from the XRD (D_{XRD}) as in the following equation [55].

\[ I_{cryst} = \frac{D_P(\text{SEM, TEM})}{D_{cryst}(\text{XRD})} \]

The calculated index of crystallinity is listed in table (6) and it is found to be close to 1.

Table 5. Particles size,dislocation density and lattice strain in Williamson-Hall model.

| Sample (g) | Particle size (nm) | Lattice strain (nm) | Dislocation density (x 10^4 m^{-3}) |
|------------|--------------------|---------------------|------------------------------------|
| 0.05       | 20                 | -0.0013             | 24.1                               |
| 0.1        | 19                 | -0.00082            | 26.8                               |
| 0.15       | 18                 | -0.00089            | 30.3                               |
| 0.2        | 8                  | -0.0048             | 135                                |

One from the definitions of the dislocation is that it is just an irregularity or a defect in the crystal structure influencing many of the substance characteristics. The dislocation (δ) could be calculated in terms of line broadening (β_{h k l}), Bragg angle (θ_{h k l}) and the lattice constant (a) by [54]

\[ \delta = \frac{15\beta_{h k l} \cos \theta_{h k l}}{2aD} \]

4. CONCLUSIONS
Ag@PANI core/ shell nanostructures were successfully prepared in solid state. Aniline sulphate was oxidized to polyaniline (shell) and silver ions are reduced to metallic silver(core). The polymerization proceeds well even in the solid state. The result of FTIR and UV-visible spectroscopy support the interaction between PANI and silver nitrate and PANI formed in emeraldine salt form. SEM and TEM reveal that Ag@PANI have core/shell nanostructure. The crystallinity of Ag@PANI core/shell nanostructure improved by increasing concentration of silver nitrate.

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