

# Characterization of Silver Doped Polyaniline-SiO<sub>2</sub> Nanocomposite

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**Abstract:** Polyaniline/silica and polyaniline-Ag/silica nanocomposite were prepared from naturally available rice husk silica after adopting the treatment process. The synthesized materials were characterized by various spectroscopic techniques and suggested that the formation of polyaniline in salt form exist in benzenoid and quinoid forms. The thermal analysis shows that the stability of Ag doped composite is enhanced greatly compared to raw polyaniline. The UV-Vis spectra of Pan-Ag/RHA, shows two absorption bands obtained (~250-300 and ~ 400-500) is due topolymer in contact with silver nanoparticles. Ft-Raman resuts shows the bands at 1426 and 1519 cm<sup>-1</sup> are due to the C=N stretching vibrations in quinonoid diimine and in polyaniline, a strong band appears at 1598 cm<sup>-1</sup> due to the C-C stretching vibration of the benzenoid-like rings. Morphology of polyaniline has been studied and observed as fibers and polyaniline/Ag-silica composite forms the petals of flowers morphologies for silver doped nanocomposite.

**Keywords:** Nanocomposite, sol-gel processes, polyaniline, rice husk silica, silver nanoparticle.

## 1. Introduction

Polyaniline is one of the most studied conducting polymers for electronic, optical, gas sensors and as corrosion protection due to its tunable conducting property, thermal stability, and unique doping/dedoping and redox properties [1, 2]. However, the poor mechanical properties, insolubility in common solvent and low processability have some drawbacks. In order to overcome these problems, strategies have been developed such as conventional thermoplastic-electro conductive polymer composites with unique properties [2]. In recent years, the preparation of metal nanoparticle polymer composites with synergistic chemical and physical properties has been studied with great attention [3, 4]. It can be synthesized easily through either chemical or electrochemical polymerization methods [5]. However, conventional bulk chemical synthesis produces large amount of irregular particle agglomerates and a small amount of polyaniline nanofiber formation. Chemical polymerization of aniline is conducted using relatively strong oxidants like ammonium peroxydisulfate, ferric permanganate, bichromate or hydrogen peroxide. Synthesis of polyaniline by glucose oxidase was

reported to depend on the initial generation of H<sub>2</sub>O<sub>2</sub> in a broad pH range [6]. Synthesis of conductive composites of polyaniline and inorganic metal ion doping compounds could provide materials with modified properties [7-9]. Among these inorganic materials, silica (SiO<sub>2</sub>) has received great attention due to its unique properties and wide application [10, 11]. The incorporation of metal particles in conducting polymers has attracted considerable attention in the last two decades because of its numerous applications such as biosensors, electro catalysis and energy storage [12]. The incorporation of metal nanoparticles could effectively improve the electrical, optical and dielectric properties of the polyaniline composite and these properties are very much sensitive by tuning the quantum properties [13]. Recently, Choudary et al., reported polyaniline-supported recoverable and recyclable Sc, In, Pd, Os, and Rh catalysts for a variety of organic transformations [14]. The polyaniline/Ag nanocomposite synthesised by in-situ chemical polymerization exhibit remarkable improvement of electrical conductivity and dielectric properties compared with pure polyaniline [15]. Huang et al. synthesised nanocomposites of polyaniline combined with Ag/Pt nanoparticles simultaneously [16]. Efficient enzyme bio-electrochemical electrodes could be built by polyaniline and silver nanoparticle stabilized with polyvinyl alcohol [17]. The present study reports a facile route for the synthesis of polyaniline (pan) and its composites with waste biomass like rice husk silica and (pan/RHA) and silver doping on RHA (pan-Ag/RHA). The crystalline and thermal stability are explained by XRD, TGA, and DSC. The surface and textural properties has been analysed by BET and electron microscopy techniques. The organic property and chemical environment of polyaniline and silver doped silica nanocoposite has also been studied by H-NMR and Si-NMR technique.

## 2. Experimental

### 2.1 Materials Preparation

Polyaniline was synthesised by direct oxidation of aniline with H<sub>2</sub>O<sub>2</sub>. In a typical synthesis, aniline (5.0 g, HmbG Chemicals, 99 %) was dissolved in

conc. HCl (15.0 mL, J.T. Baker, 36.5-38.0 %) and it was diluted with distilled water (100 mL) and stirred magnetically for 10 minutes. To this, H<sub>2</sub>O<sub>2</sub> (20.0 mL, J.T. Baker, 30 %) was added and heated initially at 293 K for 10 minutes with continued stirring. The precipitated material of polyaniline was filtered after 3 h, washed with distilled water and followed by washing with acetone and dried at 373 K overnight. The blackish green material thus obtained is collected and labelled as polyaniline.

Rice husk (from a rice mill in Penang, Malaysia) was washed and rinsed several times with distilled water in order to remove all the adhered dirt. The washed rice husk (RH) was dried at room temperature and about 30.0 g of the clean RH was stirred in 750 mL of 1.0 M HNO<sub>3</sub> at room temperature for 24 h to remove all metallic impurities. The acid treated RH was washed with distilled water until the pH of the rinse became constant (around 4.6- 5.0), dried in an oven at 373 K for 24 h and kept in a muffle furnace at 873 K for 6 h for complete combustion. The white rice husk ash (RHA) thus obtained was used as source of silica for further material preparation. Polyaniline-silica composite was synthesised by same procedure with addition of 1.0 g of RHA directly into the aniline/conc. HCl mixture. The product was collected after 3h, washed with distilled water followed by washing with acetone and dried at 373 K overnight. The product was labelled as polyaniline-RHA (PanRHA).

For the synthesis of silver doped polyaniline-silica composite, aniline (5.0 g) was dissolved in water (100 mL) and conc. HNO<sub>3</sub> (5.0 mL) and stirred magnetically. The RHA (1.0 g) and 0.1575 g of AgNO<sub>3</sub>, (10 wt.%) were added into this solution and repeated the same procedure with addition of the oxidant, H<sub>2</sub>O<sub>2</sub>. Product obtained after 3 h was filtered, washed with distilled water and dried at 373 K overnight. The dark black composite obtained was labelled as Pan-Ag/RHA. Synthesis strategies of polyaniline and polymerization reaction route are given in scheme 1 & 2.

## 2.2 Characterization

The prepared materials were characterized by elemental analysis (Perkin Elmer Series II, 2400), powder X-ray diffraction (Siemens Diffractometer D5000, Kristalloflex operated at 40 kV and 10 mA with nickel filtered CuK $\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ ), N<sub>2</sub>-sorption porosimetry (NOVA 2200e surface area and pore size analyzer, P/P<sub>0</sub> between 0.05 and 0.21) and thermo gravimetric analyses in N<sub>2</sub> atmosphere (TG/DTG 851 $^{\circ}$  Mettler Toledo). The absorption as well as reflectance spectra were collected on Perkin Elmer Lambda 35 spectrometer in acetonitrile and also with diffuse reflectance technique using KBr pellets as the reference in the

range 200–550 nm. FT-IR analysis was carried out on a Perkin-Elmer System 2000 using KBr pellet method. The <sup>1</sup>H NMR spectrum of synthesized polyaniline was recorded in acetonitrile on Perkin spectrometer at 300 KHz. The solid state <sup>29</sup>Si and <sup>15</sup>N MAS NMR spectra were recorded at 59 MHz on a Bruker DSX 300 spectrometer using TMS and glycine as internal standards respectively. The morphology and elemental loading were observed by SEM (Leica Cambridge S360), (Edax Falcon System) and TEM (Philips CM12).

## 3. Results and discussion

### 3.1 Elemental analyses and surface area measurement

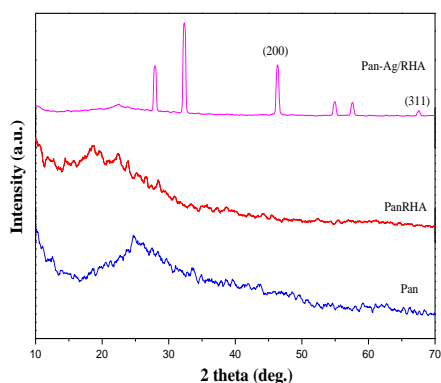
The amount of C and N obtained from polyaniline *via* elemental analysis is compared with the element content obtained by EDX analysis. The amount of N was found to be more in polyaniline and it decreased further upon incorporation with silica. In Pani-RHA and Pan-Ag/RHA, the reduction in carbon content suggests successful incorporation of silica into the polymer. The elemental compositions and amount of silicon, silver and chlorine obtained from EDX analysis are shown in Table 1. The presence of chlorine in polyaniline was confirmed from the EDX analysis. Upon silica incorporation the Cl content was decreased. The incorporation of silica and silver in Pan-Ag/RHA was also confirmed by the EDX analysis. The BET surface area of the Pan-Ag/RHA was found to be 87.2 m<sup>2</sup>/g.

Table 1. The elemental analysis results of Pan and PanRHA-Ag.

Material	Elemental analysis (%)			EDX (%)			
	C (%)	H (%)	N (%)	EDX	Cl	Si	Ag
Pan	98.10	-	6.41	7.25	9.05	-	-
PanRHA	19.41	1.58	2.51	1.48	2.95	36.84	-
Pan-Ag/RHA	14.19	1.11	1.64	-	-	30.72	1.78

### 3.2 Powder X-ray diffraction

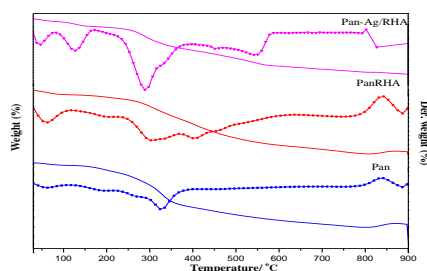
The wide-angle powder X-ray diffraction pattern of the Pan and Pan-Ag/RHA composites are shown in Fig. 1. In polyaniline, a weak reflection observed at 2theta-value at 25 $^{\circ}$  is characteristic peak of the weak polymer chain. In Pan-Ag/RHA, the sharp peaks centered at 2-theta = 28, 33, 45 and 77 $^{\circ}$  are assigned to (111), (211), (200) and (311) planes of silver particle exist in the polymer composite. All the peaks can be indexed to the face centered cubic pattern of silver nanoparticles with space group *Fm3m* [4]. Crystallite size of silver calculated by Scherer formula was 12.4 nm. This suggests that the successful incorporation of silver nanoparticle in the polymer composite.



**Fig. 1: The powder X-ray diffraction pattern of the materials**

### 3.3 Thermo gravimetric analysis

The thermal analysis of polyaniline and its composites obtained in  $N_2$ - atmosphere is presented in Fig. 2. The pattern exhibits various mass losses in the region of 100-600 °C. As seen in the pattern, the weight loss below 150 °C can be ascribed to the removal of loosely bound water molecules and HCl on the surface of the polymer. In polyaniline, the degradation polymer backbone of occurs at 300-400 °C [18].



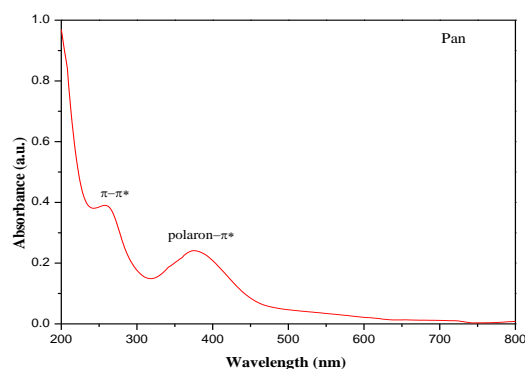
**Fig. 2: The TG-DTG analysis of Pan, and Pan-**

In PanRHA and Pan-Ag/RHA, the thermograms show higher onset temperatures of degradation due to the presence of more thermally stable silica and silver. This suggests an enhancement in the thermal stability for the prepared polyaniline nanocomposites than that of pure polyaniline.

### 3.4 UV-Vis absorption and DR UV-Vis spectra

The UV-Vis spectrum of polyaniline recorded in acetonitrile is presented in Fig. 3. Two absorption maxima were observed at 260 and 370 nm. The band in the region 240-300 nm is associated with a transitions of the benzenoid rings of polyaniline [19]. The band at 330-450 nm is assigned to the polaron/bipolaron resonance absorption of the electrons [20]. This suggests the formation of the conductive emeraldine salt form of polyaniline by this method in the presence of oxidant. The high

intensity of this peak may suggest more conductivity of the polymer composite.



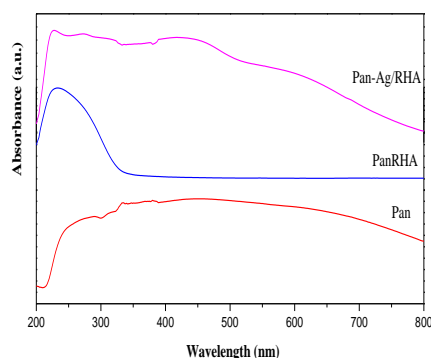
**Fig. 3: The UV-Vis spectrum of polyaniline in acetonitrile**

The diffuse reflectance spectra of the prepared materials were obtained with KBr as reference as shown in Fig. 4. The diffuse reflectance UV-Vis spectra of synthesized polyaniline and its composites obtained with KBr pellet shows absorption in the range 250-400 nm with tail extending to higher absorption. Long range absorption of polyaniline suggests more conductivity associated with it. In Pan-Ag/RHA, two absorption bands obtained (~250-300 and ~400-500) and have been distinguished corresponding to polymer in contact with silver nanoparticles.

### 3.5 FT-IR spectral characterization

The FT-IR spectra of polyaniline and other materials are presented in Fig. 4. The molecular structure of synthesized polyaniline and nanocomposite were confirmed by the Fourier transform Infrared (FT-IR) analysis. In all the pattern, the band observed at  $1564\text{ cm}^{-1}$  can be assigned to the stretching vibrations of  $C=N$  and  $C=C$  of the quinoid ring of polyaniline. The bands at  $1495$  and  $1448\text{ cm}^{-1}$  are typical for  $C=C$  stretching vibration of benzenoid ring of the polymer. In polyaniline, the bands observed at  $1283$  and  $823\text{ cm}^{-1}$  are due to the  $C=N$  stretching of secondary aromatic amine. However, pan-Ag/RHA, the band at  $1283\text{ cm}^{-1}$  is not seen or it might be hidden by the large and strong band at  $1097\text{ cm}^{-1}$ . This suggest that the possibility of  $Ag \rightarrow C = N$  interaction in PanRHA-Ag. In PanRHA and PanAg/RHA, the additional peaks appear at  $1097\text{ cm}^{-1}$  corresponds to the vibrations of silica backbone ( $Si-O-Si$ ) in the polymer. In all the materials synthesized, the O-H and N-H vibrations

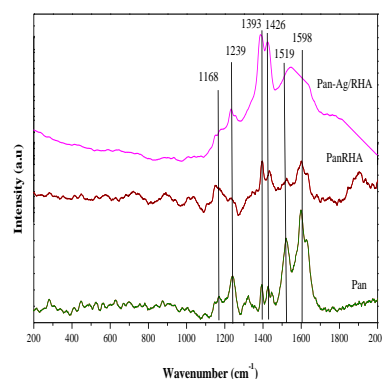
appear at 3450 and 3231  $\text{cm}^{-1}$ , respectively[21].



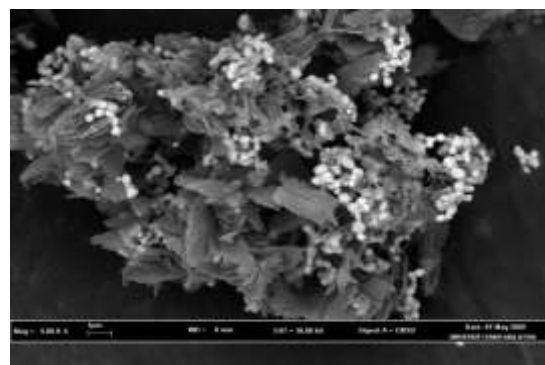
**Fig. 4: The DR UV-vis spectra of Pan, PanRHA and Pan-Ag/RHA.**

### 3.6 FT-Raman spectral characterization

The FT-Raman spectra of polyaniline and its composites are shown in Fig. 5. The band at 1168  $\text{cm}^{-1}$  is due to the C-H bending vibrations of benzenoid-like aromatic rings in polyaniline. The decreased intensity of this band in Pan-Ag/RHA suggests progressive oxidation of polymer to form quinoid-like rings. The band at ca. 1239  $\text{cm}^{-1}$  can be assigned to the C-N stretching of the secondary aromatic amine (diimine), which is indicative of the emeraldine salt form of polyaniline. The bands at ca. 1393  $\text{cm}^{-1}$  is due to the stretching vibrations of C-N<sup>+</sup> fragments coupled to an aromatic ring and having an intermediate single-to-double bond order. The bands at 1426 and 1519  $\text{cm}^{-1}$  are due to the C=N stretching vibrations in quinonoid diimine [22]. In polyaniline, a strong band appears at 1598  $\text{cm}^{-1}$  due to the C-C stretching vibration of the benzenoid-like rings indicating that it is less oxidized. The intensity of this band is very much lowered in Pan-Ag/RHA, suggesting a more oxidized form obtained by the present methodology.



**Fig. 5: The FT-Raman spectra of Pan, PanRHA and Pan-Ag/RHA.**



**Fig. 6: The Scanning electron micrographs of PanRHA, and Pan-Ag/RHA**

## 4. Conclusions

A simple and facile methodology has been developed to prepare polyaniline in emeraldine salt form by oxidative polymerization of aniline using  $\text{H}_2\text{O}_2$  as an oxidant in acidic media. Thermal analysis suggests that the thermal stability was improved after incorporation of silica and silver particle into polymer matrix. Morphology analysis shows the fibrous nature of polyaniline and polyaniline-silica as flower shaped. In addition, silver nanoparticle in pan/RHA appeared as white globules on the surface of these flower petals.

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