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Synthesis and Characterization of Interfacial Silver Doped Polyaniline/Graphene/SrTiO₃ Composites

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Abstract: Studies on Polymer composites with a unique properties are the recent fields of increasing scientific and technical interest, offering great opportunity to improve their respective properties by means of additives, fillers etc. Graphene has been an effective filler material to enhance the mechanical and electrical properties of the composite. The IPANI-Ag-Graphene-SrTiO₃ composites were synthesized by insitu polymerization using ammonium per sulphate as an oxidising agent with varying compositions of SrTiO₃ (10, 20, 30, 40, and 50 wt%) in IPANI-Ag-Graphene. The structural characterization of the synthesized polymer composites were investigated using FTIR and XRD techniques. XRD spectra reveals some degree of crystallinity in the of IPANI-Ag-Gr-SrTiO₃ composite, due to the presence of sharp peaks. The FTIR spectra of IPANI shows characteristic vibrations in the region 1100-1600 cm⁻¹. A characteristic broad band observed at 3200 cm⁻¹ is due to N-H stretching of aniline. In IPANI-Ag-Gr-SrTiO₃ composite, the bands of SrTiO₃ and graphene are also visible.

Keywords: Composites; Polyaniline; Spectroscopy; FTIR; XRD

I. Introduction

Nowadays, the overall insight into polymer science and technology is so deep that a material scientist can create an almost limitless range of new polymer materials. Emerging research in the field of such polymer composites aims mainly at some suitable modifications, so that the applicability can be improved. Conducting polymers and its blends shows a wide range of novel electrochemical and chemical properties that led to their use in diverse application viz., sensors [1-2]. Conducting polyaniline blends and composites are prepared mostly via the chemical oxidation route, although electrochemical synthesis is also employed in some cases [3-4]. The large number of reports were found in the literature that explains synthesis of poly aniline and its blends [5-7,8-9]. Graphene blended IPANI is more suitable for designing electro chromic devices [10]. Structural conformation, size, distribution and thermal properties of the composites were investigated using FTIR, XRD techniques, and the results are presented here.

II. Experimental

A. Materials and Methods

All chemicals used were of analytical reagent grade. The monomer aniline was doubly distilled prior to use. Ammonium per sulphate, hydrochloric acid, chloroform and nitric acid from S.d.fine chemicals were used as recieved. We procured graphene from Adnano Technologies. Strontium titanate was synthesized in the laboratory. Milli-Q water, an ultra-pure water is used for dissolution purpose.

B. Synthesis of IPANI and IPANI-Ag-SrTiO₃-Graphene

Polyaniline was synthesized by in situ chemical oxidative interfacial polymerization using ammonium peroxydisulfate as an oxidising agent. 2N HCl is added in to beaker, add about 1.5 ml of aniline, then 10ml of chloroform organic solvent was added. Then add 0.2m ammonium peroxydisulfate dropwise, along the sides of the beaker to start oxidation at room temperature for about 4-6 hours. The two solutions were then carefully transferred into a beaker, generating an interface between the two layers. After 5 min, a green layer was formed slowly at the liquid-liquid interface and then gradually diffuses into the aqueous phase. After 24 h, the entire aqueous phase was homogenously filled with dark green indicating the beginning of the polymerization, and the organic layer showed an orange colour due to the formation of aniline oligomers. The aqueous phase was then collected and washed with ethanol and water to remove the unreacted aniline. A dark green colour polymer produced by oxidation were collected on filter and washed several times by distilled water, and dried in vacuum at room temperature for 36hr .

1ml of aniline was dissolved in 1m nitric acid in a beaker, 10ml of chloroform was added. Then add 0.1m ammonium per sulphate solution and 0.1m silver nitrate solution separately dropwise, along the sides of the beaker to start oxidation at room temperature for about 4-6 hours. After 5 min, dark- green layer was formed slowly at the interface and then gradually diffused into the aqueous phase. After 24 h, the entire aqueous phase was

homogenously filled with dark-green, and the organic layer observed shows orange colour due to the formation of aniline oligomers. The aqueous phase was then collected, and washed with ethanol and water to remove the unreacted aniline. A dark greenish colour polyaniline doped with silver particles obtained. SrTiO_3 powder was added to polymer solution with continuous stirring in order to keep the SrTiO_3 suspended in the solution. The reaction mixture was agitated vigorously for 3hrs. During this process, the solution was always kept at 0°C . The precipitated powder recovered was vacuum filtered, followed by washing with milli-Q water and acetone. Composites were dried in an oven at $60\text{--}70^\circ\text{C}$ to achieve a constant weight. Following this procedure, five different IPANI-Ag- SrTiO_3 composites were prepared by varying 10, 20, 30, 40 and 50% by weight of SrTiO_3 in IPANI-Ag.

IPANI-Ag-Graphene- SrTiO_3 composite was prepared by mixing graphene powder with varying 10, 20, 30, 40 and 50% by weight of IPANI-Ag- SrTiO_3 powder. First IPANI-Ag- SrTiO_3 was powdered by using mortar & pestle, manually. Then graphene powder was added to it. The resulting composites were crushed and grinded in to fine grained powder.

III. Results and discussion

A. FTIR analysis

FTIR analysis was done using Perkin Elmer IR Spectrophotometer (L16100217) in the range of $4000\text{--}200\text{cm}^{-1}$ by pelletizing (thickness of the pellet is approximately 1mm) the synthesized polymer composite samples with dry KBr. Figure 1 shows FTIR spectra of (a) IPANI (b) IPANI-Ag (c) Graphene (d) SrTiO_3 (e) IPANI-Ag-Gr- SrTiO_3 -50%. The IR bands appearing at 1572 and 1498cm^{-1} are attributed to $\text{N}=\text{Q}=\text{N}$ and $\text{N}-\text{B}-\text{N}$ ring stretching vibrations in IPANI (where -B- and $=\text{Q}=$ stands for benzenoid and quinoid moieties in the IPANI backbone) [13-15, 22, 23]. The presence of these two bands clearly shows that the IPANI is composed of benzenoid as well as quinoid units [22, 23]. A characteristic broad band at $2950\text{--}3300\text{cm}^{-1}$ is due to N-H stretching of aniline [12, 14]. The band at 834cm^{-1} is due to C-H stretching of aromatic ring [13, 24]. The peak at 1296cm^{-1} might be ascribed to C-N and C=N stretching modes in IPANI [13, 15]. In fig 1b, the bands at 1140cm^{-1} corresponds to IPANI in IPANI-Ag composite [13]. Another characteristic absorption band at 1250cm^{-1} is associated with polaronic structure of IPANI [13, 14, 17]. The additional bands at 494 and 422cm^{-1} are due to Ag [14]. The evidence of formation of polyaniline with 1,4-substituted phenyl rings occurred at 879cm^{-1} . IR peaks at 806 and 1140cm^{-1} were attributed to C-H out-of-plane and C-H in-plane bending vibrations of IPANI [15]. In fig 1c, the absorption band at 1125cm^{-1} infers the doping effects of graphene fragments on the IPANI quinoid rings [25]. The IR spectra of IPANI-Ag-Gr exhibits characteristic graphene band along with the silver doped IPANI. The IR spectrum of SrTiO_3 exhibits a characteristic broad band at 583cm^{-1} which is due to the Ti-O stretching vibration and the band at 1452cm^{-1} may be ascribed to carboxylate group stretching mode [15, 16]. The FTIR spectra of graphene shows a characteristic vibration at 3435cm^{-1} which is due to absorbed moisture [26]. The initial band at 610cm^{-1} and a little hump around 1500cm^{-1} are due to aromatic ring deformation and sp^2 hybridized C=C stretching in aromatic ring of graphene [20]. In FTIR Spectra of IPANI-Ag-Gr- SrTiO_3 -50% composite, the major bands of graphene and SrTiO_3 are visible. Thus, the FTIR result confirms the presence of graphene and SrTiO_3 in IPANI-Ag-Gr- SrTiO_3 composite.

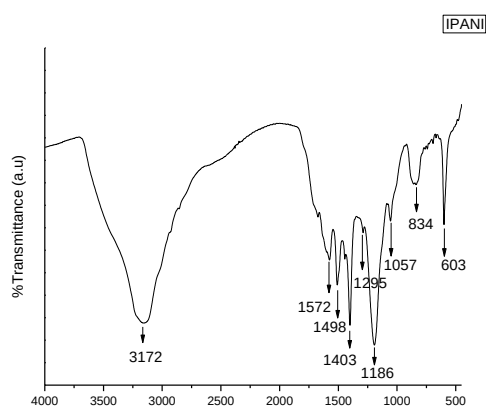


Figure 1a

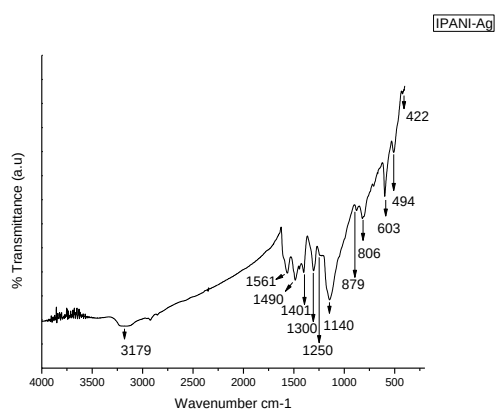
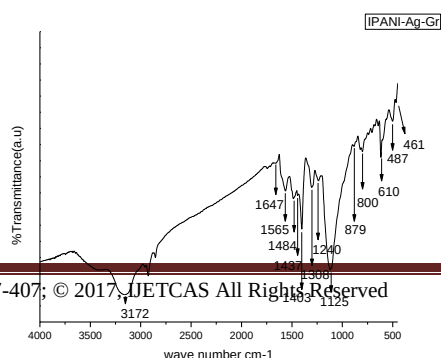


Figure 1b



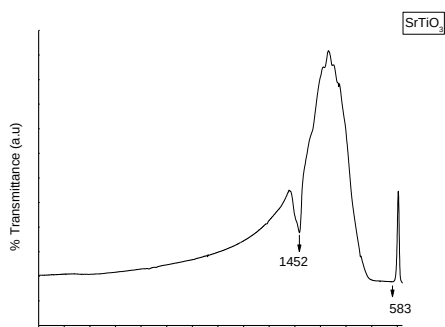


Figure 1c

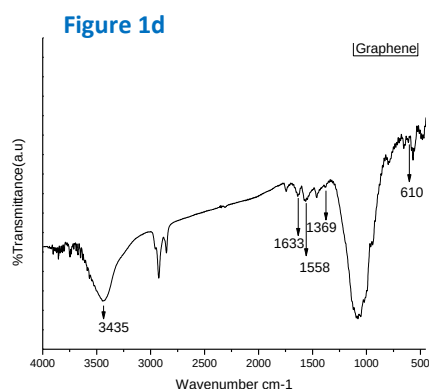


Figure 1d

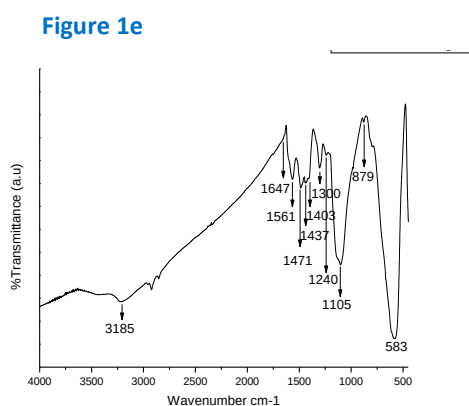


Figure 1e

Figure 1f

B. X-ray diffraction Study

XRD spectra of synthesized polymer composites was done using PANalytical X'pert³ powder instrument with Cu-K α radiation source ($\lambda=0.15406$ nm) operated at 40kV and 30mA. XRD pattern of IPANI exhibited two broad diffraction peaks at about $2\theta = 23.5^\circ$ and 26.1° are on par with those observed by others[18]. These peaks can be attributed to the periodicity in parallel and perpendicular directions of the polyaniline chain, respectively [18]. The XRD pattern of silver particles in IPANI matrix shows characteristic bragg's reflections at $2\theta=16.1^\circ$, 19.2° , 23.6° , 26.3° , 44.7° , 46° and 63.6° corresponding to (220), (100), (111), (101) and (200) diffraction planes respectively, for the face-centered cubic structure of silver particles embedded in IPANI[14]. The average crystallite size of silver particle in IPANI determined through the (111) diffraction plane was estimated to be 13.5nm. In IPANI-Ag-Gr-SrTiO₃-50 composite diffraction pattern, the peaks centered at $2\theta= 23.6^\circ$, 26.3° , 30.5° and 46.4° are assigned to (100), (111), (101) and (200) diffraction planes of silver particle exist in the polymer composite. All the peaks can be indexed to the face centered cubic pattern of silver particles. The average crystallite size of silver particle in the composite through the (111) diffraction plane, calculated by Scherer formula was ~ 9 nm. This suggests that the successful incorporation of silver particle in the polymer composite. The diffraction peaks at $2\theta=32.4^\circ$, 40.0° , 46.5° , 57.7° and 67.7° to the (110), (111), (200), (211) and (220) diffraction planes, respectively, ascribed to the cubic structure of SrTiO₃. The XRD pattern for SrTiO₃ compared well with the JCPDS Pattern

No.35-734. The sharp peaks of SrTiO₃ associated with other peaks of low intensity indicate its crystalline nature. However, the doped composites exhibited diffused peaks which substantiates its amorphous behaviour. The sharp peaks of SrTiO₃ are visible and superimposes over the diffraction peaks of composite pattern. This indicates that PANI undergoes interfacial interactions with SrTiO₃ crystallites and thus, confirms the formation of composite [19]. The diffraction peak of graphene located at $2\theta=26.6^\circ$ correspond to (003) diffraction plane, with a d-spacing 0.335 nm is on par with JCPDS Pattern No. 26-1079, attributed to rhombohedral phase. The relative intensity of graphene in the composite is weakened compared with that of graphene due to encapsulation by IPANI [21]. The average crystallite size of the particle is calculated by using Debye-Scherer equation [19]

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

Where D is average crystallite size of particle, $\lambda=0.15406$ nm is X-ray wavelength of Cu-K α radiation source, K=0.89 is the scherrer constant, θ is half diffraction angle and β is full width at half maxima (FWHM) of the diffraction peak in radians. The average crystallite size of SrTiO₃ particle and IPANI-Ag-Gr-SrTiO₃-50 composite through the diffraction plane (110), calculated by using Debye-Scherer equation are 68.5 nm ($\theta=0.2835$ radians; $\beta=0.0020$ radians) and 59.3 nm ($\theta=0.2835$ radians; $\beta=0.0023$ radians) respectively.

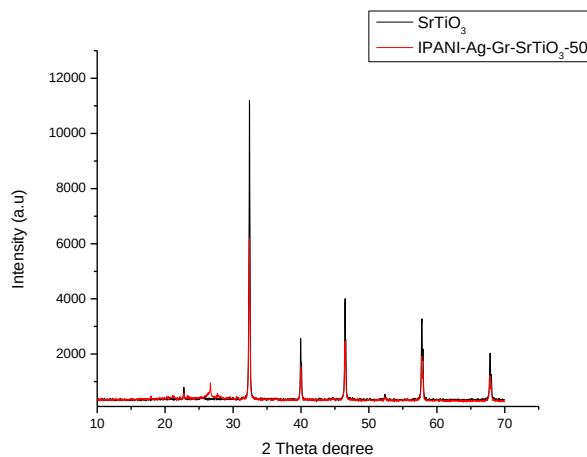


Figure 2a

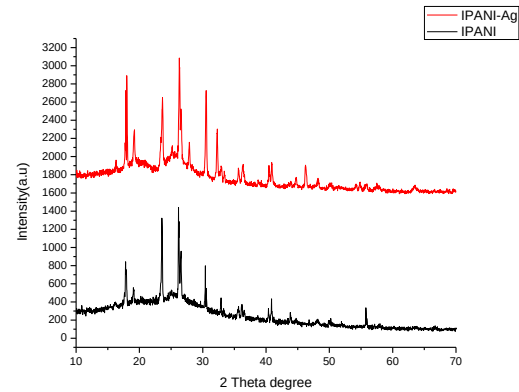


Figure 2b

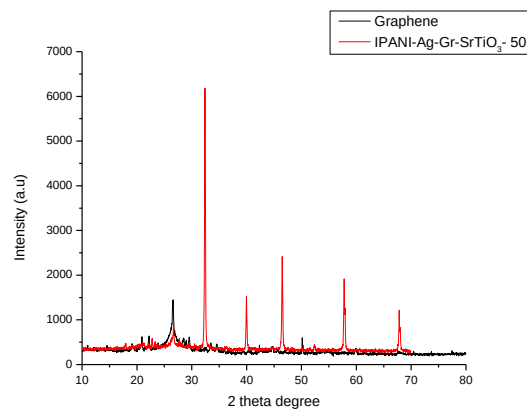


Figure 2c

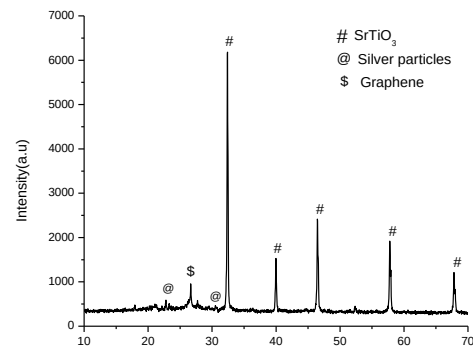


Figure 2d

IV. Conclusion

We have synthesized polyaniline by using interfacial polymerization technique in presence of chloroform and also their composites with varied percentage amount of strontium titanate /graphene nano particles. Spectroscopic data reveals the formation of interfacial polyaniline and their composites. XRD spectral data indicates highly ordered structure composites were obtained and it is confirmed based on the sharp peaks observed in the spectra. It was found that, the additive has considerable effect on particle size of the composite. The characteristic stretching frequencies of benzenoid and quinoid moieties observed in the FTIR spectra confirm the formation of the composite and distribution of particles uniformly.

References

- [1] Abhijit V. Shevade, Margie L. Homer, Charles J. Taylor, Hanying Zhou, April D. Jewell, enneth S. Manatt, Adam K. Kisor, Shiao-Pin S. Yen, and Margaret A. Ryan *lectrochem. Soc.* 153(11): 2006, H209-H216.

- [2] A Mirmohseni, A Oladegaragoze. J Appl Polym Sci, 85,2002, 2772.
- [3] Soares DAW, A de Queiroz. Macromol Symp;170,2001:221.
- [4] M Karakisla, M Sacak, U. J Akbulut Appl Polym Sci;59(9): 1996,1347.
- [5] Narsimha Parvatikar, Shilpa Jain, Syed Khasim, M. Revansiddappa, S.V. Bhoraskar, M.V.N. Ambika Prasad Sensors and Actuators B 114(2), 2005, 599-603.
- [6] N. N. Mallikarjuna, S. K. Manohar, P. V. Kulkarni, A. Venkataraman, T. M. Aminabhavi Journal of Applied Polymer Science, Vol. 97, 2005 1868–1874.
- [7] Kaushik Mallick, Michael J Witcomb, Michael S Scurrall, Andre M Strydom, Gold Bulletin 41,2008 , 3
- [8] Suprakas Sinha Ray, Mukul Biswas Synthetic Metals 108,2000, 231–236.
- [9] Akira Kitani, Kousuke Sathoguchi, Kenji Iwai and sutoro Ito. Synthetic metals, 102, 1999, 1171-72.
- [10] Tapan K. Das, Smita Prusty Polymer-Plastics Technology and Engineering, 2013, 52: 319–331.
- [11] Stankovich, S.; Dikin, D.A.; Dommett, G.H.B.; Kohlhaas, K.M.; Zimney, E.J.; Stach, E.A.; et al. Graphene-based composite materials. Nature 2006, 442, 282–286.
- [12] Asha, Sneha Lata Goyal, D Kumar, Shyam Kumar, N Kishore Indian Journal of pure and applied physics, 52, 2014, 341-347.
- [13] Safenaz M. reda, Sheikh M, Al-Ghannam ,Advances in materials Physics and Chemistry, 2012,2,75-81
- [14] Y B Wankede et. al., Adv. Mat. Lett. 2013, 4(1), 89-93
- [15] Syed Shahabuddin, Norazilawati Muhamad Sarih, Muhammad Afzal Kamboh, Hamid Rashidi Nodeh and Sharifah Mohamad, Polymers, 2016,8, 305
- [16] Parinitha M, A Venkateshulu International journal of latest research in science and technology, 2013, 2(1),495-498
- [17] Mahesh D. Bedre, Raghunandan Deshpande , Basavaraj Salimath , Venkataraman bbaraju American Journal of Materials Science, 2012, 2(3): 39-43
- [18] M. A. Gabal, M.A. Hussein, A.A. Hermas , Int. J. Electrochem. Sci., 11, 2016, 4526-4538
- [19] Sneha Lata Goyal, Smriti Sharma, Deepika Jain, D Kumar and N Kishore, Pelagia research library, Adv. Appl. Sci. Res., 2015 , 6(1), 89-98
- [20] Mitesh parmar, Chandran Balamurugan, Dong-Weon Lee, sensors(Basel) 13(12), 2013, 16611-16624
- [21] Prasanna B P, Avadhani D N, Muralidhara H B, Revanasiddappa M IJLTETMAS, 3(5), 2014, 55-60
- [22] Milind kulkarni et.al., chemistry and chemical technology, 5(1),2011
- [23] M.Khalid and F. Mohammed ,eXPRESS Polymer Letters,1(11), 2007, 711- 716
- [24] Bajpai et.al., eXPRESS polymer Letters, 2(1),2008,26-39
- [25] Zhongqiu Tong, Yongning Yang, Jiayu Wang, Jiupeng Zhao, Bao-Lian Su and Yao Li J. Mater. Chem. A, 2014, 2, 4642
- [26] Tagreed M.Al-saadi, Mustafa A.K.Jihad IJARSET , ISSN 2350 – 0328, 2(10), 2015, 902-909.