In situ Polymerization of Polyaniline/Samarium Oxide - Anatase Titanium Dioxide (PANI/Sm$_2$O$_3$-TiO$_2$) Nanocomposite: Structure, Thermal and Dielectric Constant Supercapacitor Application Study

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Abstract: Pure and varying weigh ratio of Sm$_2$O$_3$-TiO$_2$ modified polyaniline nanocomposite has been successfully synthesized using in situ polymerization of aniline solution with Sm$_2$O$_3$-TiO$_2$ binary oxide. The nanocomposite have been characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), X-photoelectron microscopy (XPS), Field emission-scanning electron microscope (FE-SEM), transmission electron microscopy (TEM) thermogravimetric analysis (TGA) and LCR meter. The XRD results show synthesis anatase TiO$_2$ phase with tetragonal structure and (monoclinic and cubic) mixture structure of Sm$_2$O$_3$. The FE-SEM and TEM measurements appear preparing spherical nanoparticles that covered fiber morphology of polyaniline and successfully in situ polymerization process. The TGA measurements are obtain high thermal stability for polyaniline after incorporation by Sm$_2$O$_3$-TiO$_2$ binary oxide nanoparticles. LCR measurement is obtained that the DC conductivity, dielectric constant and dielectric loss of nanocomposite is larger than pure polyaniline and the electric properties increase with increasing the concentration of nanoparticles.

Key words: pseudocapacitive, photolysis, nanoarchitectonics, LCR, nanofibers

1 Introduction

In the last years, a major attention has been concentrates on the fabricate of conducting polymers doping by nanoparticles because of its unrivaled chemical and physical properties. Polyaniline (PANI) has a large attention to researchers and most widely investigated since it shows excellent stability, ease of prepare, tunable properties, low cost and wide use in electric application such as gas sensor, supercapacitor and batteries. Polyaniline with among metal oxide nanoparticles have been studied widely due to their unique size dependent chemical and physical properties creation via the inserting of oxide nanoparticles in the matrix of polymer. Clearly this enhances the electrical conductivity, thermal stability, mechanical properties and conductivity process ability for the matrix of polymer. Usually, there are two methods utilize for synthesis PANI-metal oxide nanocomposite. The most commonplace and generally tried method is the incorporation the nanoparticles of binary oxide in the matrix of polymer, but the negative part of this method is aggregation of oxides nanoparticles. The second method contains the homogeneously dispersion of oxide nanoparticles during polymerization process to reduce the aggregation. The incorporation of oxides nanoparticles into the matrix of PANI is much difficult. The TGA measurements are obtain high thermal stability for polyaniline after incorporation by Sm$_2$O$_3$-TiO$_2$ binary oxide nanoparticles. LCR measurement is obtained that the DC conductivity, dielectric constant and dielectric loss of nanocomposite is larger than pure polyaniline and the electric properties increase with increasing the concentration of nanoparticles.

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and equal 3.2 eV. So many methods were utilized to reduce the band gap of TiO₂ such as doping it by rare earth metal. So the TiO₂ properties can be enhanced by selective doping of ion of metal, which increased the efficiency of anatase TiO₂. 4f and 5d orbitals of rare earth metal play main roles in promoting the catalyst due to incompletely occupied by electrons for orbitals. Among it, the Sm₂O₃ has been more interesting because the trapping effect of Sm²⁺ and Sm³⁺. Thus different properties of doping samarium ions in anatase phase combination with PANI can show new properties that couldn’t be observed from the individual compound. There are a few more researchers which have investigated or studied the supercapacitive of PANI-Sm₂O₃ hybrid structure. Amongst the different polyaniline oxide nanocomposite, the PANI-Sm₂O₃-TiO₂ is a concerning system having an unrivaled set property according to excellent substantial properties of the other oxides. We herein, report synthesis of PANI-Sm₂O₃-TiO₂ binary nano oxides by using photolysis method and study the structural and electrochemical properties using X-ray diffraction (XRD), Field emission scanning electron microscope (FE-SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and LCR meter.

2 Experimental

2.1 Materials

All source chemicals were supplied from Sigma Aldrich company with purity (98%) and used without any future purification.

2.2 synthesis of Sm₂O₃-TiO₂ binary oxide

The synthesis of Sm₂O₃-TiO₂ binary oxide nanoparticles was carried out by photolysis method and use irradiation system with 15 watts (Fig. 1), wherein equivalent moles with mole ratio (1:1) of Sm(NO₃)₃.6H₂O and Ti[OCH(CH₃)₂]₂ were mixed together. Then it transferred to reactor of irradiation system and irradiated under icing condition for 2 h and white precipitate formed, which was collected by decantation method and washed with acetone and deionized water for several times. The precipitate was centrifuged to remove excess of ions, and dried at 80°C. Finally it annealed at 400°C for 3 h in ambient.

2.3 PANI/Sm₂O₃-TiO₂ nanocomposite synthesis

To synthesis nanocomposite, the Sm₂O₃-TiO₂ was added through PANI polymerization. Firstly, 0.2M ammonium persulphate (APS) was added drop wise drop to the mixture of 0.2M aniline and hydrochloric acid. During dropping of APS with continuous stirring in ice bath, the mixture mutation from colorless to dark green color. At this stage, the (20 wt. %) 0.02 g Sm₂O₃-TiO₂ binary oxide was added to the reaction mixture and kept at same conditions 24 h. After that, the formed was filtered and washed several times by ammonium solution to remove acid ions and natural the pH and deionized water. Finally, the produce precipitate was dried at 60°C for 3 h. The prepare process was summarized by the following diagram (Fig. 2).

2.4 Measurements

The structure of synthesized polyaniline and binary oxide modified polyaniline was investigated and recorded and white precipitate formed, which was collected by decantation method and washed with acetone and deionized water for several times. The precipitate was centrifuged to remove excess of ions, and dried at 80°C. Finally it annealed at 400°C for 3 h in ambient.
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3 Results and Discussion

3.1 XRD analysis

The XRD of PANI, Sm$_2$O$_3$, TiO$_2$ and PANI/Sm$_2$O$_3$-TiO$_2$ nanocomposite are exhibited at Fig. 3. According to Fig. 3 (A), three diffraction peaks localized at $2\theta = 25.47, 20.51$ and 14.67 assign to (121), (113) and (322) crystal planes, which may be corresponding to the scattering from chains of polymer at interplanar spacing. The results are in good agreement of JCPDS card no. 72-0634. The diffraction peak at 25.47 obtain that the PANI with good degree of crystallinity. Figure 3(B) illustrates the XRD of TiO$_2$ with a maximum peak at $2\theta = 25.46^\circ$ which corresponding (110) Bragg reflection and it’s in a good agreement of JCPDS (card no. 21-1272), which indicate the high crystallinity of tetragonal structure of TiO$_2$ anatase phase. The XRD of Sm$_2$O$_3$ is shown in Fig. 3 (C). The results are display (monoclinic and cubic) phases of Sm$_2$O$_3$ with maximum peak at $2\theta = 28.30^\circ$ and it’s in a good agreement of JCPDS (card no. 11-0609). The mixed phase has been may assign to the transformation phase during annealed process. In the pattern of PANI/Sm$_2$O$_3$-TiO$_2$ shown in Fig. 3 (D), diffraction peaks of Sm$_2$O$_3$ and anatase TiO$_2$ were observed clearly, the diffraction peaks of PANI obtain more sharp, which indicating the excellent crystallinity of prepared composite and the binary oxides nanoparticles do not obstruct the crystallinity chains of PANI. Compared with pure PANI, the diffraction peak of PANI/Sm$_2$O$_3$-TiO$_2$ that centered at 25.47 shift to high position, which indicate incorporation of Sm$_2$O$_3$-TiO$_2$ that cause induced strain in matrix of polymer. In addition to shift diffraction peak of PANI, the maximum diffraction peak of anatase shifted to low position due to incorporated (Ti$^{4+}$) ions with the high radii (Sm$^{3+}$)ions in the matrix of nanocomposite. The crystallite size was calculated using Scherre equation (Eq. 1):

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where 0.9 is the shape factor, $\lambda$ is the wavelength of the X-ray source, and $\beta$ is the full width at half maximum of the peak concerned. The results summarized in Table 1 and it demonstrate that the intensity of diffraction peak (322) for PANI increased, crystallite size increase, FWHM decreased and shifted to high position after doping via oxides nanoparticles, which indicate that the crystalline of PANI increasing by doping oxides nanoparticles and in addition to the formation of ordered structure of C6H6 in nanocomposite is enhancing after addition oxide and binary oxide nanoparticle and this helping the planes scattering between C6H6 rings.

![Fig. 3 XRD of PANI, Sm$_2$O$_3$, TiO$_2$, PANI/Sm$_2$O$_3$-TiO$_2$.](image)

| Catalyst             | High intensity peak position | FWHM   | Crystallite size (nm) |
|----------------------|------------------------------|--------|-----------------------|
| TiO$_2$              | 25.46                        | 0.67036| 12.92                 |
| Sm$_2$O$_3$          | 26.60                        | 0.672  | 15.92                 |
| PANI                 | 24.57                        | 0.64933| 12.6                  |
| PANI-20% (Sm$_2$O$_3$-TiO$_2$) | 26.372                  | 0.18377| 44.56                 |

Table 1 Parameters of particles.
3.2 FTIR characterization

The FT-IR spectrum of Sm₂O₃, PANI and PANI/Sm₂O₃-TiO₂ are shown in Fig. 4. Figure 4(A) display the FTIR spectrum of pure Sm₂O₃ and exhibit a peak localized at 3256 cm⁻¹ assign to O-H stretching mode back to adsorbed of water molecules on the surface of nanoparticles. Three peaks centered at 434, 533 and 695 cm⁻¹ corresponding bending modes of Sm-O bond. The FTIR spectrum of pure PANI is appeared in Fig. 4(B). A broad band localize at 3134 cm⁻¹ back to starching mode of N-H, two peaks centered at 2915 and 2859 cm⁻¹ related to the transformation of NH₃⁺ to N-H in the aromatic amine respectively. Two weak peaks at 1561 cm⁻¹ and 1486 cm⁻¹ back to stretching mode of C = N and C = C for benzenoid ring(B) and quinoid ring(Q) respectively, while the two weak peaks center at 1727 cm⁻¹ and 1641 cm⁻¹ corresponding to stretching modes of C-N imine. The stretching vibration of C-N is appears as a weak band localize at 1379 cm⁻¹ in the neighborhood of the(Q) and a broad peak center at 1135 cm⁻¹ corresponding to a stretching mode of N-(Q) -N-(Q) bonding. At 1298 cm⁻¹, observed peak back to C-N bending vibration mode. The bending mode of aromatic C-H in plane is shown at 1040 cm⁻¹ while, the out plane deformation C-H appear as weak peak at 591 cm⁻¹. New three peaks as shown in Fig. 4(C) localize at 433, 554 and 796 cm⁻¹ corresponding to vibration mode of Sm-O-Sm, Sm-O-Ti and stretching mode of Sm-O-H respectively. The results appear blue shifting in vibration mode of PANI after polymerization with Sm₂O₃-TiO₂ binary oxide because of the difference in lattice vacancies and lattice structure.

3.3 XPS instruments

The XPS spectrum of PANI/Sm₂O₃-TiO₂ nanocomposite corresponding to C₃s, O₁s, N₁s, Ti₂p and Sm₃d levels of energy are displayed in Fig. 5. As shown in Fig. 5(A), the spectrum of C₁s energy level exhibits three peaks localize at 284.6, 285.5 and 287.1 eV related to the bonding of C-C for sp² carbon, C = N bonding and C-N⁻ bonding. The binding energy noted at 531.2 related to O₁s, Fig. 5(B), which suggesting that the oxygen atoms with O⁺ in state in composite. The XPS spectrum of N₁s energy level is displayed at Fig. 5(C). The spectrum shows four binding energy, two from them centered at 399.5 and 400.33, corresponding to quinoid [ = N· ] and benzenoid [ -N· H ] imine while the remain two peaks illustrate at 400.52 and 402.39 eV back to cationic nitrogen ( = NH⁺ ) and protonated unit of amine (·NH⁺ ) respectively. As appeared in Fig. 5(D), the deconvoluted XPS spectrum of Ti₂p demonstrates two binding energy localize at 458.7 and 464.3 eV corresponding to Ti₂p₃/₂ and Ti₂p₁/₂ while, the last two binding energy that found at 1083.1 and 1110 eV back to Sm₃d₅/₂ and Sm₃d₃/₂ as shown in Fig. 5(E).

3.4 FE-SEM and TEM results

FE-SEM images in (Fig. 6) appear the morphology of Sm₂O₃, PANI and PANI/Sm₂O₃-TiO₂ (20%) nanocomposite respectively, while the TEM result of modify PANI by 20% wt. of Sm₂O₃-TiO₂ binary oxide were demonstrated at Fig. 7. The pure Sm₂O₃ and TiO₂ particles Figs. 6(A) and 6(B) is formed by large nanoplasteres with size less than 100 nm. The morphology shows composed of nanometers agglomeration grans with size between 15 nm to 50 nm. Figure 6(C) illustrates that polyaniline (PANI) consist from irregular distribution of fiber morphology with nanoscale. The morphology of modification PANI by (20% wt.) Sm₂O₃-TiO₂ is shown in Fig. 6(D). the results appear that the nanofibers of PANI don’t appear with little clearly, may be the fibers was crashed or covered by spherical particles of Sm₂O₃-TiO₂ but the modify process obtains clearly by using TEM analysis as shown in Figs. 7(A) and 7(B).

3.5 Thermogravimetric analysis (TGA)

The thermal stability of pure and polyaniline modified Sm₂O₃-TiO₂ binary oxide is displayed in Fig. 8. The results show that are three sequential steps for losing of weight are illustrated for polyaniline and polyaniline modified Sm₂O₃-TiO₂ binary oxide. The first decomposition is obtained between the room temperature and 180°C and its associated to loss of adsorbed water. The middle loss of weight between 200 to 320°C is related with the elimination of oligomers and unreacted monomers while, the final loss of weight is appeared at 430°C and corresponding to decomposition the backbone of polymer. It is evident from results(Fig. 8) that the rate of thermal decomposition for pure polyaniline are much faster than the polyaniline/Sm₂O₃-TiO₂ nanocomposite and this indicate that the
binary oxide nanoparticles are adding better thermal resistance to polyaniline and this fundamentally assign to the improvement interfacial reaction between polyaniline and nanoparticles. The results obtain that the rate of decomposition of 25 wt.% is less as compared to decomposition of 20 wt.% nanocomposite. At higher doping concentration of binary oxide nanoparticles, the inter-distance between the nanoparticles and the polymer matrix is low and thus undergo agglomerate or self-assembly, which lead to formed small agglomerate in the matrix of nanocomposite and as result not a good improvement in thermal stability of 25 wt.% nanocomposite. The reduce of char is remaining for pure polyaniline after 500 °C is only 50.02% while 54.33, 56.15 and 58.32% left for 10, 20 and 25 wt.% nanocomposite. 

3.6 Electrochemical characterization
3.6.1 Dielectric constant
The dielectric constant of pure and various weight ratio of Sm$_2$O$_3$-TiO$_2$ nanoparticles modified polyaniline is shown in Fig. 9. For synthesized samples, the dielectrics are decreased with increasing the frequency up to 105 Hz and after that, nearly remain constant. With increasing frequency, the polar segment of dielectric is obtained low time to orient it by application field of electric on themselves and this cause decrease the dielectric values. The results show significantly improved the dielectric values with increasing the concentration of Sm$_2$O$_3$-TiO$_2$ binary oxide nanoparticles and the maximum constant is noted for 20 wt.% of composite. The interaction between the Sm$_2$O$_3$-TiO$_2$ nanoparticles and polar part of polyaniline is
accountable for high value of dielectric constant in composite, as well as, the interfacial polarization improved within the composite is higher at this weight ratio of nanoparticles. When the ratio wt% of Sm$_2$O$_3$-TiO$_2$ arrive to 25 wt%, the constant of dielectric found to be decrease due to the lower interaction between the nanoparticles inside the chain of polyaniline which formed an inhomogeneity of the nanocomposite. In the other side, the formation of voids in the structure of nanocomposite reduce the movement of charges and hence decreasing the value of dielectric constant at high concentration of filler particles.

3.6.2 Dielectric loss

The electrical loss when the voltage is applied to the synthesized compound can be mentioned by factor of dissipation $(\tan \delta)$. Figure 10 is demonstrated the effect of doping varying weight ratio of Sm$_2$O$_3$-TiO$_2$ binary oxide in the $(\tan \delta)$ of polyaniline nanocomposite. The results obtained that the value of $(\tan \delta)$ decreases steeply and arrive constant at $10^6$ Hz. Generally, the dielectric loss is depend on the polarization of space charge improved in the nanocomposite via application of electric field. The carriers of free charge tip to align the reversals of field in which move towards the surface of synthesized material for decreasing the defect and pores that presence in the materials. The homogenous arrangement of Sm$_2$O$_3$-TiO$_2$ binary oxide nanoparticles are effect on the surface and the structure of dielectric and hence charge transfer movements are more at low frequency and less at high frequency. As shown in Fig. 10, the dielectric loss of all synthesized nanocomposite is more than polyaniline and the maximum value observed at 20 wt.% of nanocomposite as well as, the relaxation process is higher for 20 wt.% of nanocomposite
due to the strong polarization of space charge which emerge from interfacial reaction between the chain of polymer and binary oxide nanoparticles\textsuperscript{36}.  

2.6.3 DC conductivity

The current voltage (I-V) behavior of pure and varying weight ratio of Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} binary oxide modified polyaniline nanocomposite at room temperature is shown in Fig. 11. The results appeared that conductivity of nanocomposite is more than pure aniline and increased with increasing the concentration of binary oxide. The plots are illustrated a linear variation for current of electric against the voltage which refers to Ohmic behavior of the synthesized polymeric matrix. Generally, the conductivity of nanocomposite materials depends on the quality of electrical, charge carrier movement, polymer chain mobility and the interfacial reaction between binary oxide nanoparticles and the chain of polymer\textsuperscript{37}. Among the synthesized nanocomposite, 20 wt.\% compound appears the high conductivity and this back to the good homogeneous dispersion of binary oxide within the matrix of polymer and the compactness of chain polymer and this cause to internal ordering plane that is responsible for the movement of charge in the polymeric system\textsuperscript{37}.

4 Conclusion

A low temperature photosynthesis is employed to synthesis of Sm\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} binary oxide that multifunctional of PANI during oxidative polymerization to formed PANI/Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanocomposite and it characterized by different techniques such as XRD, FTIR, FE-SEM

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Fig. 8 TGA of PANI and different wt. % of Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} modified PANI.

Fig. 9 Dielectric constant of pure and different wt. % of Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} modified PANI.

Fig. 10 Dielectric loss tangent of pure and different wt. % of Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} modified PANI.

Fig. 11 DC conductivity of pure and different wt. % of Sm\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} modified PANI.
before supercapacitive measurements. The LCR measurements exhibit the pseudocapacitive nature of PANI/Sm$_2$O$_3$-TiO$_2$.

Data Availability
All data generated or analyzed during this study are included in this published article.

Conflict of Interest
We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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