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Green Synthesis of Ag-Fe_2O_3-Cuo-Pani Nanocomposite and Its Application as An Apple Vinegar Sensor

Madhura S. Walujkar [1] Pooja More[2], Sharda R. Gadale[1,*], Shobha. A. Waghmode[3,]

Abstract

Green synthesis of nanoparticles is inexpensive and environmentally safe, herein we report green approach for the synthesis of Ag, Fe_2O_3, CuO nanoparticles by using Asparagus Racemosus plant to detect carboxylate vapours. Synthesized Ag, Fe_2O_3, CuO nanoparticles were taken in 1:1:1 ratio and PANI (polyaniline) was added in ratio 5:1 to form Ag-Fe_2O_3-CuO–PANI nanocomposite. Synthesized Ag-Fe_2O_3-CuO-PANI were characterized by XRD, FESEM and FTIR whose size was in the range of 16–60 nm. Further, a low cost and portable optical fibre-based sensor was developed using Ag-Fe_2O_3-CuO-PANI nanocomposite, which was coated on unclad optical fibre, in which change in refractive index after exposure to carboxylic acid vapours was measured for 25-200 ppm concentration for Apple vinegar, Vinegar and Lemon juice. Carboxylic acid vapours of Apple vinegar showed the maximum response with optimized Ag-Fe_2O_3-CuO-PANI nanocomposite thickness 11.39 µm on the clad, length of 10 mm with U-shaped sensing probe with 8 mm bent radius.

Keywords: Biomaterial, adsorption, nanocomposite, optical, sensor

INTRODUCTION

The most popular techniques for creating different metal nanoparticles are those that use plant extracts. These processes are less expensive, less time consuming, cost effective than alternative techniques, and are environmentally safe. Synthesizing AgNPs (Silver nanoparticles) using plant extracts has been extensively studied and recognized as a green and efficient way for the synthesis of clean, non-toxic and biocompatible AgNPs [1, 2]. Similarly Green synthesis of Iron oxide nanoparticles and Copper oxide nanoparticles have been studied and utilized in synthesis of ternary system. Conducting polymers have been recognized as a distinct class of polymers holding tremendous potential for sensing applications in present era owing to their high conductivities, simple and green processing route, cost effectiveness and high absorption capacity [3]. Biopolymer is an organic polymer composed of monomeric units of the organic compound, which are covalently bonded to form a biopolymer. Biopolymers are mixed with nanosized particles (i.e., carbon nanotubes, nanocellulose, silver, zinc, copper, magnesium, and gold nanoparticles) to form bionanocomposites Conducting polymer bionanocomposites are composed of gelatin, proteins, cellulose, chitosan, chitin, and polythiophene (PTh), polyaniline (PANI), polypyrrole (PPy) conducting polymers with some metallic components. Amongst the family of conducting polymers polyaniline (PANI) is one of the most promising electrically conducting polymers due to its unique electrical, electrochemical properties, easy polymerization, high environmental stability and low cost of monomer [4].

*__Author for Correspondence__
Sharda R. Gadale

[1]Research scholar, Department of Chemistry, Yashwantrao Mohite College of Arts, Science & Commerce, Pune
[2]Associate Professor, Savitribai Phule Pune University, Pune, India
[1]Associate Professor, Department of Chemistry, Yashwantrao Mohite College of Arts, Science & Commerce, Pune
[3]Professor Department of Chemistry, MES, Abasaheb Garware College, Karve Road, Pune, India

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Optical fiber based chemical sensors have gained growing interest in recent years. These sensors' characteristics, such as their light weight, low attenuation, cost effective, smaller diameter, long-distance signal transmission etc., make them useful for monitoring both industrial and environmental processes.

Sensing of carboxylates is an important concern in sensor development. Carboxylic acids have important role in food industry since they have an impact on the stability and organoleptic qualities of food, such as flavour, aroma, and colour [5]. Citric acid is found in citrus fruits like lemons, oranges, and grapefruits and is widely used as acidulant in jams, candies and fruit juices [6]. Acetic acid is present in vinegar, malic acid is present in apples, lactic acid is present in sour milk, and so on.

Vinegar containing acetic acid is useful for food preservation. Salad dressings, sauces, cheeses, and pickled foods frequently include acetic acid. Addition of vinegar to food materials reduce its pH and restrict the growth of microflora that survive.

Apple cider vinegar is a type of vinegar and it has a pale medium color. Fermented apple juice from smashed apples is used to make apple cider vinegar, which also contains pectin, vitamins B1, B2, and B6, biotin, folic acid, and vitamin C. Numerous advantageous therapeutic components have been discovered in natural vinegar such as carbohydrates, alcohols and organic acids like acetic, formic, lactic, malic, citric, succinic, and tartaric acid. Amino acids and peptides are also important components of it.The blood sugar levels are controlled by apple cider vinegar. Additionally, it regulates blood pressure, which clearly increases after a meal. It aids in weight loss, which is crucial given that diabetes is often caused by obesity. Apple cider vinegar and honey treatment is useful for arthritis and also it is used externally to painful joints. Numerous advantages for the skin, digestion, and immunity are provided by apple cider vinegar organically and without any negative side effects.

Citrus fruits like oranges, lemons, limes and grapefruits make up the majority of the natural sources of citrus acid and has a sour taste. Lemon juice which contain citric acid is universal plant and animal metabolism intermediate. Citric acid is commonly utilised in many foods, beverages, medications, cosmetics, and other products as a flavouring, sequestering, and buffering agent [7]. Humans are aware of the potential for a variety of physiological syndromes, including neurodegeneration, diabetes mellitus, cardiovascular diseases, mental disorders, and oxidative damage to the brain. Citric acid is a popular antioxidant substrate. Citric acid is therefore utilised in the food industry to raise the grade and quality of the product. Thus, it is important to use small, affordable carboxylate vapour sensor to ensure the quality of food everywhere.

Deprotonation of carboxylic acids can result in the formation of carboxylate ions. Here, citric acid from lemon juice is tribasic in nature while acetic acid from vinegar is monobasic in nature.In addition to acetic acid, apple vinegar also contains formic, lactic, malic, citric, succinic, and tartaric acids.

In this study, we present the evanescent wave optical fibre sensor for the detection of carboxylic acid vapours from Apple Vinegar, Vinegar and Lemon juice with low ppm detection and good sensitivity.

According to a survey of the literature, numerous researchers for example, Mehmet Turemis et al. [8] reported ZnO-Polyaniline, Qingwen Wu et al. [9] reported Graphene-PANI/PVDF films, or Tauseef Ali et al. [10] reported hybrid PANI/holmium oxide nanocomposites. In literature several reports on ammonia gas sensor or humidity gas sensor using nanocomposites are reported. Here for the first time we are reporting cost effective Ag-Fe2O3-CuO–PANI (Ternary system) nanocomposite as a carboxylate vapour sensor. Herein, we report the successful fabrication of optical fiber sensor based on Ternary system nanocomposite for the detection of carboxylate vapours from lemon juice, Vinegar and Apple Vinegar.

EXPERIMENTAL TECHNIQUES

Materials

All of the chemicals and monomer utilized in this experimentation were of reagent grade quality. The solutions were prepared using double distilled water Silver nitrate ($AgNO_3$), Ferric nitrate ($Fe(NO_3)_3$) Copper Sulphate ($CuSO_4.5H_2O$), Aniline ($C_6H_5NH_2$) ,Ammonium persulphate (APS) and Hydrochloric acid (HCl 36%) were purchased from SRL chemicals, India. Aniline was distilled before use. All other chemicals were used as received.

Preparation of Plant Extract

The method used to prepare Silver nanoparticles we have used similar procedure reported by us earlier, where we have showed the optical sensor based on Ag-PANI for detection of carboxylate vapours [11]. Plant extract preparation was done by using powder of Asparagus Racemosus plant with double distilled water taken in 1:4 ratio in 250 ml conical flask . Solution was boiled for 15 minutes. Aqueous extract obtained was centrifuged at 3000 rpm for time of 10 minutes followed by filtration. This extract was stored at 4°C for further use.

Green Synthesis of Silver Nanoparticles

For the synthesis of plant mediated Ag nanoparticles the plant extract and 1mM silver nitrate solution were taken in 1:20 ratio respectively. The reaction was allowed to take place in 250 ml conical flask at room temperature. The solution was sonicated for 15 minutes and alkaline pH of solution was adjusted with the help of 1N NaOH. Conical flask was kept overnight at room temperature and colour change of the solution from light yellow to dark gray was monitored, which was the indication for $AgNO_3$ conversion into Ag nanoparticles. Formation of AgNPs were confirmed by UV-Visible spectroscopy. The nanoparticles were separated using centrifugation at 4000 rpm and then washed three times with deionized water which were dried in an oven for time duration of an hour at 80°C.

Green Synthesis of Iron Oxide Nanoparticles

For the synthesis of plant mediated Iron oxide nanoparticles the plant extract and 1mM Ferric nitrate solution were taken in 1:20 ratio respectively. The reaction was allowed to take place in 250 ml conical flask at room temperature. The solution was sonicated for 15 minutes and alkaline pH of solution was adjusted with the help of 1N NaOH. Conical flask was kept overnight at room temperature and colour change of the solution from light yellow to dark brown was monitored, which was the indication for $Fe(NO_3)_3$ conversion into Iron oxide nanoparticles. Further, formation of nanoparticles was confirmed by UV-Visible spectroscopy. These nanoparticles were separated using centrifugation at 4000 rpm and then washed three times with deionized water which were dried in an oven for time duration of an hour at 80°C.

Green Synthesis of Copper Oxide Nanoparticles

For the synthesis of plant mediated Copper oxide nanoparticles the plant extract and 1mM Copper sulphate solution were taken in 1:20 ratio respectively. The reaction was allowed to take place in 250 ml conical flask at room temperature. The solution was sonicated for 15 minutes and pH of solution was adjusted to neutral. Conical flask was kept overnight at room temperature and colour change of the solution from light blue to brown black was monitored, which was the indication for Copper Sulphate conversion into CuO nanoparticles which was confirmed by UV-Visible spectroscopy. The nanoparticles were separated by centrifugation at 4000 rpm, washed three times with deionized water and dried in an oven for one hour at 80°C

Synthesis of Ternary System (Ag-Fe_2O_3-CuO –Polyaniline) Nanocomposite

PANI was prepared by oxidative polymerization of aniline monomer in acidic medium using ammonium peroxide sulphate. Synthesized Ag, Fe_2O_3,CuO nanoparticles were taken in 1:1:1 ratio in a conical flask and synthesized PANI was added in ratio 5:1. The mixture was sonicated for half an hour. 0.1 mM $NaBH_4$ was added dropwise as a reducing agent. Again, solution was sonicated for half an hour and kept overnight at room temperature. The solution was centrifuged, filtered ad dried at 80°C for one hour.

Optical Sensing Measurements

In the present setup we have build a less expensive ,simple and portable LED based intrinsic optical fiber sensor for sensing of carboxylate vapour from Lemon juice, Vinegar and Apple Vinegar. LED is used as a monochromatic light source which is relatively efficient, having reduced maintenance with longer life time and compact. In comparison with traditional source of light it offers low input voltage and high intensity. Because of its narrow emission band (λ = 25 nm) it can be used without a monochromator system. The LED source along with optical fiber is integrated with the detection system which is a phototransistor so as to yield a compact and handy device. The sensing chamber with dimension of 324 cm^3 was a fabricated rectangle box ,which has facility for inserting the modified cladded fiber optic sensor for conducting experiment.. The ends of Intrinsic Optical fiber sensor were connected to the Transmitter (LED Light source) and Receiver (Detector) as indicated in the Figure.1.

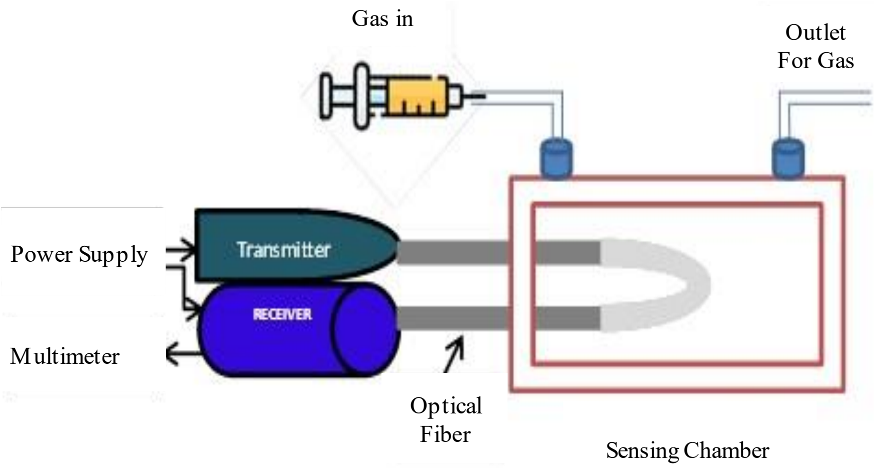

Figure 1. Optical Sensing Measurement Setup

The transmitter from Siemens (660 nm, SFH 756V) with RED light is introduced in the fiber and the light passing through the optical fiber sensor is received by the photo detector of Siemens (200–1100 nm, SFH350 , responsivity of 0.3 A/W,) as shown. The transmitter and receiver used are low-cost components. The power supplied to the transmitter and the receiver is +5 V. We have made efforts to build a room temperature optical fiber gas sensors using Ag-Fe_2O_3-CuO-PANI nanocomposite as sensing medium.

RESULTS AND DISCUSSION

Material Characterization

As shown in Figure 2 the XRD spectra of Ag-Fe_2O_3-CuO-PANI determines the crystal structure of crystalline phase of Ag-Fe_2O_3-CuO –PANI which is indicated by Rigaku Miniflex instrument equipped with CuKα radiation (λ =1.5406 Å, 30 Kv,15 mA) with Ni- filter. By using a step size of 0.05° and scan rate of 10°/min, data were gathered in the 2θ range of 10-80°. The development of single crystalline Ag nanoparticles in Ag-Fe_2O_3-CuO –PANI was confirmed by characteristic peaks in the XRD spectra at 46.508°(200), 68.56°(220) and 76.938°(311) and is referred as JCPDS file No. 03-0921. Broad peaks at two angles of 14.98° (weak), 21.46° (low intensity), and 25.44°, which correspond to (011), (020), and (200) plane reflections, were visible in the XRD diffractogram of PANI. [1,2] . These PANI peaks may have developed as a result of the aniline monomer unit's frequent repeating. The observed diffraction peaks of CuO (32.89°,35.99°,36.88°) are close to the diffraction patterns reported in the X-ray database of JCPDS CuO (45-0937). XRD pattern of iron oxide has sharp peak of maximum intensity at 32.508° corresponding to plane (121) and it is in accordance with standard JCPDS values (JCPDS No. 85-0987).

The Scherrer formula ($D = K\lambda/\beta \cos\theta$, where D= size of particle in nm, K is constant (0.94), λ = wavelength and β = full width at half maximum at the θ angle) was used to calculate the average crystalline size of the AgNPs, Fe_2O_3 NPs and CuO nanoparticles and it was 38.6 nm, 41.2 nm and 61.5 nm respectively.

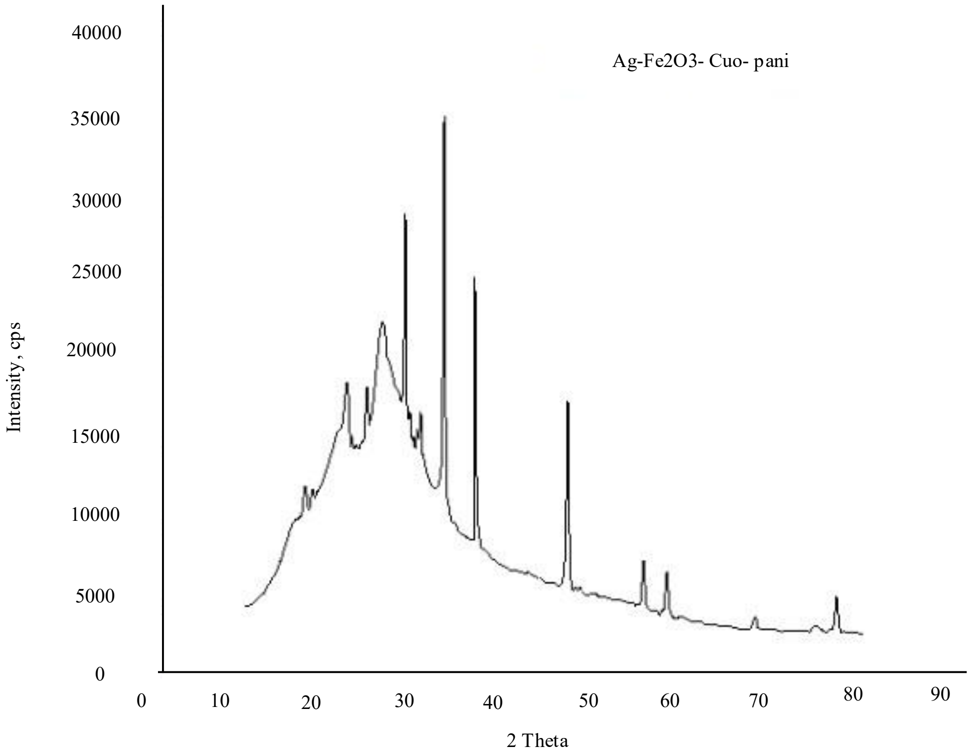

Figure 2. XRD of Ag-Fe_2O_3-CuO -PANI nanocomposite

FESEM of Ag-Fe_2O_3-CuO-PANI nanocomposites as indicated in Figure 3. with its polydispersed nature which confirms the Ag-Fe_2O_3-CuO-PANI ternary system. Base structure is broad sheet of Fe_2O_3 nanoparticles on which medium size 60.63 nm CuO nanoparticles are dispersed and on it small little spherical shape. Ag nanoparticles bearing size of 47 nm are embedded.

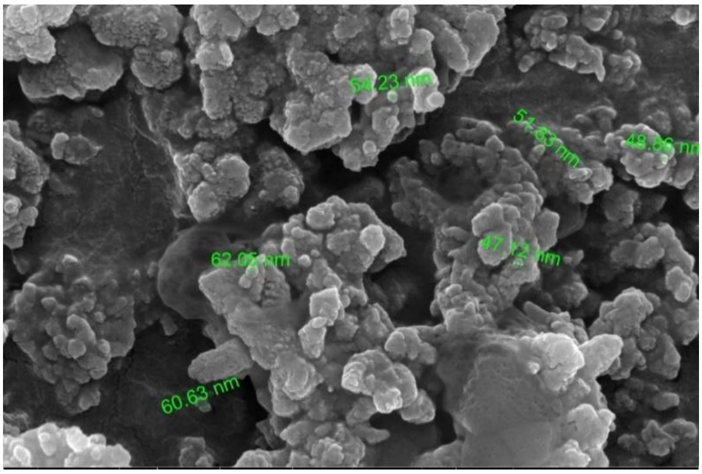

Figure 3. FESEM of Ag-Fe_2O_3-CuO - PANI

FTIR analysis as shown in Figure.4 was used to characterize the chemical structure of synthesized Ag-Fe_2O_3-CuO - PANI. In FTIR shows the bands at 860,1018, 1287and 1419 cm^{-1} which corresponds to polyaniline. Band at 3361.94 cm^{-1} is assigned to N-H stretching vibrations. Band at 2908.48 and 3047.08 cm^{-1} is assigned to aromatic C-H stretching vibration. The iron oxide characteristic peak, known as Fe-O stretching vibration, is visible at a wavelength of 559 cm^{-1}. For PANI , the band corresponds to C=N quinoid ring stretching vibration at 1549 cm^{-1}.

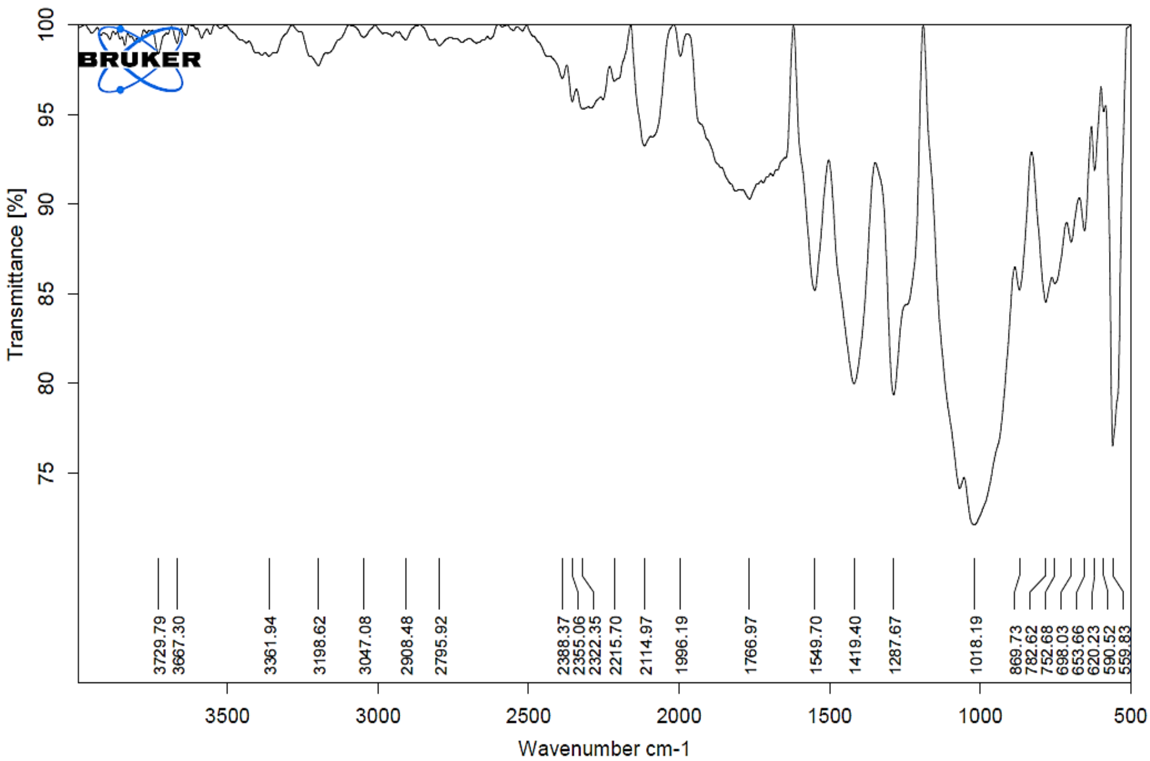

Figure 4. FTIR Spectra of Ag-Fe_2O_3-CuO – PANI

Sensor Fabrication and Working of Ag-Fe_2O_3-CuO-PANI Sensor

Plastic optical fibre is used for the sensor fabrication. The plastic optical fiber's core is constructed of polymethylmethacrylate (PMMA), and it has a thickness of about 980µm. The cladding is made of fluoride-containing carbon polymer, which is 20µm thick and its overall diameter is 2.2 mm. Refractive indices for the core and cladding are 1.492 and 1.417, respectively. The length of plastic optical fibre used was 25 cm. The plastic optical fiber central portion was used for coating, for which initially the insulating layer and a thin layer of cladding of about 10mm length were removed. The unclad part was cleaned with acetone solution and deionised water three times and then manually drop coated with Ag-Fe_2O_3-CuO-PANI nanocomposite. The Ag-Fe_2O_3-CuO-PANI paste was formed by mixing appropriate amount of nanocrystalline Ag-Fe_2O_3-CuO-PANI with ethanol to form lump free paste. The unclad fiber coated was then dried under IR Lamp. Wet polishing the fibre end with 600-grain sandpaper for a predetermined amount of time was used to couple the plastic optical fibre in order to acquire the greatest optical power output. For the purpose of sensing various concentrations of carboxylate vapour, a U-shaped sensing probe with an 8 mm bent radius was created using plastic optical fibre (POF). The sensor is based on evanescent wave adsorption, as seen above, and interacts with the coated sensing film of Ag-Fe_2O_3-CuO-PANI nanocomposite by the extension of guided modes into the cladding region. The peak intensity of the light passing in the fibre shifts outward as a result of the fibre bending, making more optical power available in the sensing region to interact with the gas or vapour in the coated layer.

The experiments were conducted in dark room under normal atmospheric pressure and approximate 73% relative humidity. Before starting the measurements the gas chamber was vacuumed. In the static system the required gas/vapour concentration was achieved by injecting a known volume of test gas with the help of syringe. After every testing cycle i.e. completion of cycle, air was passed into the gas chamber by direct exposure [12].

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By introducing a known volume of test gas through a syringe inside the static system, the necessary gas concentration was attained. Air has to directly enter the gas chamber in order for the testing cycle to be completed. 0.26 mL of carboxylate was injected into a 1.5 l bottle in order to achieve the desired carboxylate vapour concentration (ppm) and allowed to sit for 10 min. As a result, 4.5 mM of carboxylate vapour gas were produced, giving the bottle's interior a partial pressure of 74.80 dynes cm^{-2}.Taking 0.05 mL of carboxylate vapour out of the bottle and injecting it into the gas chamber results in a concentration of 25 ppm.

Ag-Fe_2O_3-CuO-PANI nanocomposite layer transmission qualities alter with gas/vapour adsorption, which results in a variation in refractive index. Since the evanescent tail only has a limited amount of power, efficient interaction between the light and the gas or vapour results, which might cause a detectable change in output, the length of the cladding needs to be greater for the coating.

The thickness and cladding length were optimised for better assessment of the output transmitted, intensity of light with consideration to relative gas/vapour, and other factors. In clad-modified intrinsic optical fibre, sensor light is incident at one end of the fibre, serving as the optical fiber's input, and is received at the other end, serving as the fiber's output. The sensing of light intensity results in the creation of a gas sensor since the light coming from the changed cladding surface may alter as per the concentration of gas present. To measure the output voltage from the receiver a digital multimeter is used.

Gas sensing mechanism of the proposed sensor is that, when at the interface of core/cladding, light undergoes total internal reflection and all the intensity is not reflected back at the interface as a portion of it penetrates inside the cladding nanocomposite. It gives rise to evanescent field whose intensity decays exponentially away from the interface. For the cladding material the depth of penetration (dp) of evanescent field is linked to the refractive index of a core n_{core} and cladding $n_{cladding}$, angle of incidence θ and a wavelength of the light λ. With the interaction of gas/vapours with the evanescent field there is change in intensity of the light propagating in the fiber which leads to variation in the sensor output intensity. The light intensity of output varies depending on the refractive index of the modified cladding n_{mclad} in comparison to the core n_{core} due to changes in the modified cladding's refractive index. Total internal reflections occur at the core-cladding interface and the light intensity propagating through the fibre rises when n_{mclad} becomes less than n_{core}. When $n_{core} < n_{mclad}$, light enters the modified cladding (leaky mode) at the interface after undergoing partial reflection.

The refractive indices of the core and modified cladding affect the light intensity that is reflected at the interface, which in turn reduces the intensity of the light travelling through the fibre and lowers sensor output. The removal of O_2 chemisorption is typically directly related to the sensing properties. The chemisorbed oxygen molecules on the surface of pores and Ag-Fe_2O_3-CuO-PANI nanocomposite layer are adsorbed with the sensor exposure to air, which aids in creation of surface state. These O_2 molecules detent electrons which help in contribution to the formation of chemisorbed oxygen ions [13]. Sensing takes place by desorption and adsorption of gas/vapour molecules on the sensor surface cause a change in refractive index, [14,15]. In the present case there is change in refractive index of the nanocomposite material of the clad in presence of carboxylate vapours.

As shown in Figure 5. Ag-Fe_2O_3-CuO-PANI nanocomposite is exposed to air, they can catalytically assist in the dissociation of O_2 molecules. The Ag-Fe_2O_3-CuO-PANI nanoparticles provide a surface on which the O_2 molecules can interact and break apart. This results in the formation of O^- ions, which are negatively charged oxygen species.

Once the O^- ions are formed, they can "spillover" or transfer onto the surface of Ag-Fe_2O_3-CuO - PANI.

As shown in Fig. 5, the sensing reaction of Ag-Fe_2O_3-CuO -PANI toward carboxylate vapours is as ,the electron depletion layer formed and chemisorption of oxygen ions (O_2^- , O^- , O_2^-) which occurs on the surface of the Ag-Fe_2O_3-CuO -PANI .In the presence of air the oxygen molecules get adsorb on Ag-Fe_2O_3-CuO -PANI surface and captures free electrons from the conduction band.

When exposed to carboxylate vapours, chemisorbed oxygen reacts with carboxylate vapours which returns electrons to conduction band, leading to reduction in the width of the depletion layer. Change in the refractive index is because of the trapping of electrons at adsorbed molecules.

When Ag-Fe_2O_3-CuO-PANI sensor was exposed to Vinegar, Apple vinegar and Lemon juice ,the adsorbed oxygen ions on the nanocomposite surface was reduced by its reaction with acetic acid from Vinegar and Apple vinegar and citric acid from lemon juice and the trapped electrons went back to the conduction band of Ag-Fe_2O_3-CuO-PANI leading to change in refractive index.

Acetic acid and polyphenolic compounds are the main constituents of Apple vinegar due to which it shows higher response as compare to Vinegar and Lemon juice.

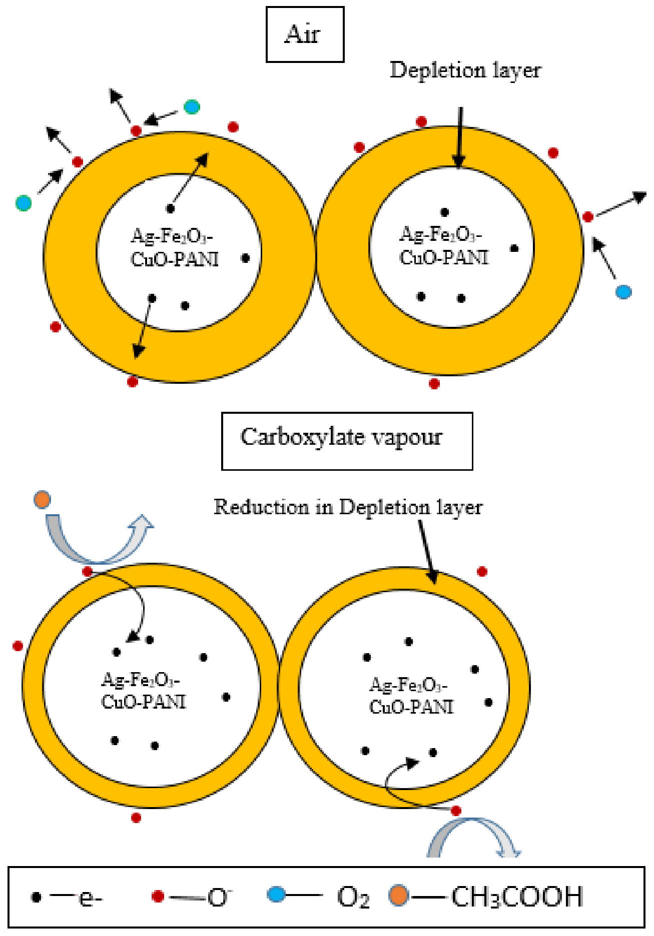

Figure 5. Gas sensing mechanism for Ag-Fe_2O_3-CuO-PANI nanocomposite in air and carboxylate vapour

$$O_2 \text{ (gas)} \leftrightarrow O_2 \text{ (ad)} \quad (5)$$

$$O_2 \text{ (ad)} + e^- \leftrightarrow O_2^- \quad (6)$$

$$O_2^- + e^- \leftrightarrow 2O^- \quad (7)$$

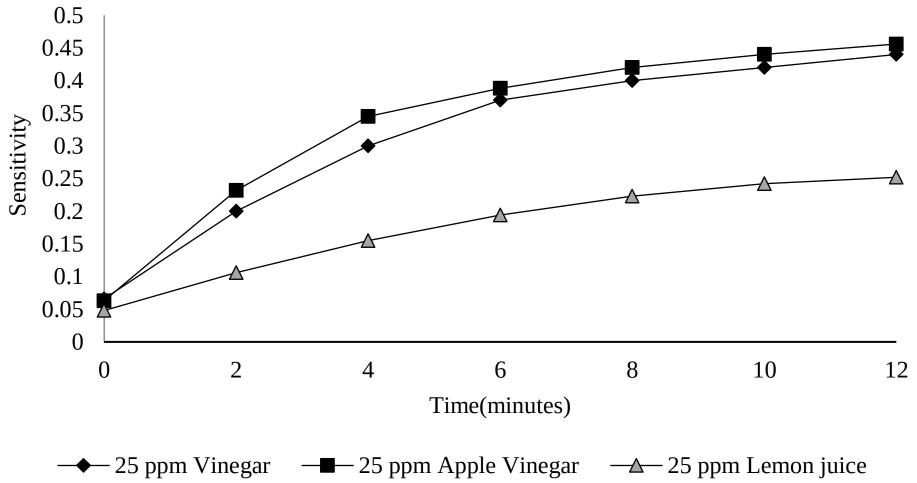

Figure 6. Evaluation of sensor response towards vinegar, apple vinegar and lemon juice using Ag-Fe_2O_3-CuO – PANI at 25 ppm concentration

Figure 6 illustrated the sensing response of Ag-Fe_2O_3-CuO – PANI nanocomposite coated optical fiber sensor towards Vinegar, Apple vinegar and Lemon juice for 25 ppm concentration. It is shown that the Ag-Fe_2O_3-CuO – PANI nanocomposite exhibited a higher response towards Apple vinegar as compare to Vinegar and Lemon juice which indicates that the sensor is highly responsive to Apple vinegar. Carboxylate ion formation in case of acetic acid is more easier as compare to citric acid as it can lose one proton easily to form acetate ion. This acetate ion reacts faster with Ag-Fe_2O_3-CuO – PANI surface giving better response to acetic acid from vinegar than citric acid from Lemon juice. Acetic acid and polyphenolic compounds are the main constituents of Apple vinegar due to which it shows higher response as compare to Vinegar and Lemon juice.

The refractive index changes when the Carboxylate vapours interacts with the fiber's evanescent field and the output light intensity is influenced by the changed cladding's refractive index relative to the core's refractive index [16]. Greater light will flow through the cladding region when the changed cladding's refractive index is higher than the core's, which causes a second total internal reflection to occur at the cladding-air contact in a leaky mode. [17] The leaky mode condition, in which the material's refractive index is marginally larger than the core, is the primary cause of changes in the output spectrum intensity of fibre optic gas sensors. [18]

As shown in Figure 7. the sensing response of Ag-Fe_2O_3-CuO -PANI nanocomposite –coated optical fiber sensor with different concentrations of tricarboxylic acid vapours from fresh Lemon juice, carboxylic acid vapours from Vinegar and Apple vinegar. When exposed to an environment of carboxylic acid vapours of Lemon juice, Vinegar and Apple vinegar, causes rapid surface adsorption of molecules which results in variation of optical properties. The rise in vapour molecules on the coating surface causes an increase in the actual refractive index due to surrounding medium indicating larger leakage of light from the interface of cladding-air. Adsorption of gas molecules on the coating surface depends on the percentage of Ag-Fe_2O_3-CuO -PANI nanoparticles and its affinity towards it [19]. Due to the air's lower refractive index than the modified cladding and the production of an evanescent wave at the modified cladding-air interface, total internal reflection occurs when a light beam reaches the modified cladding-air contact [20]. The core-modified cladding interface allows the light that has leaked from the optical fibre core to return to the core. As a result, the total light output includes both the light rays that go through the fibre and the light that leaks back into the system. The output light intensity decreases as a result of increased gas adsorption on the cladding surface, which causes light to escape through the cladding-air interface [17].

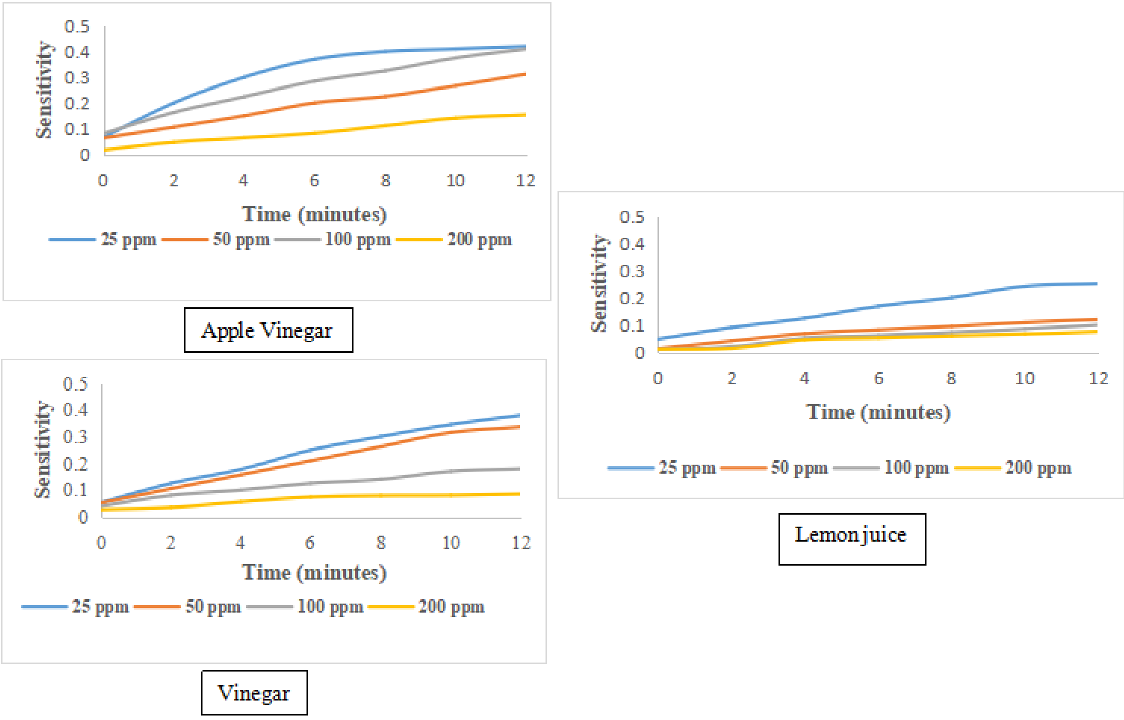

Figure 7. Sensing performance of Ag-Fe_2O_3-CuO -PANI nanocomposite sensor for carboxylic acid concentrations in apple vinegar, vinegar and lemon juice

There is difference in absorption of the evanescent field by air molecules for Tricarboxylic acid of citric acid molecules and carboxylic acid of Vinegar molecules, consequently these molecules affect the signal guided through the core differently. Hence this difference is revealed in the spectral response of the Ag-Fe_2O_3-CuO -PANI nanocomposite coated optical fiber sensor to air and different concentrations [21]. Subsequently the evanescent wave absorption by the molecules of carboxylic acids is larger than that of air molecules, the strength of the spectral response decreases as the concentration of carboxylate ions from vinegar increases [22]. The evanescent field absorption by the carboxylic acid molecules increases as more and more molecules adsorb on the surface of the sensor, which further reduces the spectral response [21].

The sensing performance of Ag-Fe_2O_3-CuO -PANI nanocomposite material coated intrinsic optical fiber sensor for carboxylic acid concentrations in Apple vinegar exhibited a higher response for lower concentration of 25 ppm and as the carboxylic acid concentration increases, the sensitivity decreases.
When the Ag-Fe_2O_3-CuO-PANI nanocomposite is exposed to air, oxygen molecules from the air become chemisorbed oxygen species (O_2^-, O_2^-, and O^-) on its surface by entrapping electrons from the conduction band. The measurements are performed at room temperature, and surface reactions are assumed to be dominated by the species O_2 [23]. The amount of gas/vapour molecules interacting with the gas sensing material nanocomposite (metal oxide) and the attraction of gas/vapour molecules to the gas /vapour sensing medium determine the sensor response [24].

Using the optimized clad length of 10mm more experimentation for effect of material thickness on the unclad optical fiber for different clad thickness of 11.39 µm, 23.16 µm and 34.74 µm using Ag-Fe_2O_3-CuO -PANI nanocomposite is done.

As per Figure. 8 which indicates the performance of Ag-Fe_2O_3-CuO -PANI nanocomposite coated optical fiber sensor for coating variation for carboxylic vapours of Apple vinegar Thickness of 11.39 µm shows a maximum sensitivity and beyond it starts decreasing as observed for 23.16 and 34.74 µm thickness for 10 mm length.

For this particular study clad thickness of 11.39 µm was considered as the appropriate thickness as the transmitting beam shows maximum confinement of light due to refractive index modulation. It is clear that with increasing coating thickness above 11.39 µm, the amount of content of Ag-Fe_2O_3-CuO -PANI nanocomposite is accordingly increasing. The result is the reduction of the film refractive index with increasing thickness with decrease in the output [25]. For higher thickness there is reduction in the response which may be due to the decrease of the confined light passing through the fiber.

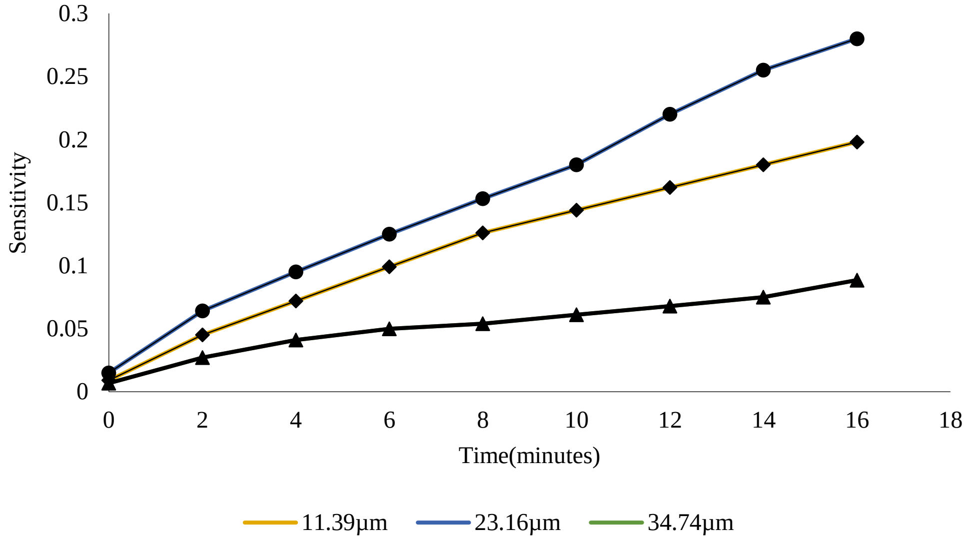

Figure 8. Sensing performance of Ag-Fe_2O_3-CuO -PANI nanocomposite for coating variation of nanocomposite using apple vinegar.

The repeatability of the intrinsic optical sensor using Ag-Fe_2O_3-CuO -PANI nanocomposite was found to be very encouraging as all the cycles are closely overlapping as indicated in Fig. 9, for the thickness of 11.39 µm at 25 ppm as about 3 % uncertainties from cycle to cycle. It is detected that and there is no shift in the wavelength or drop in the intensities.

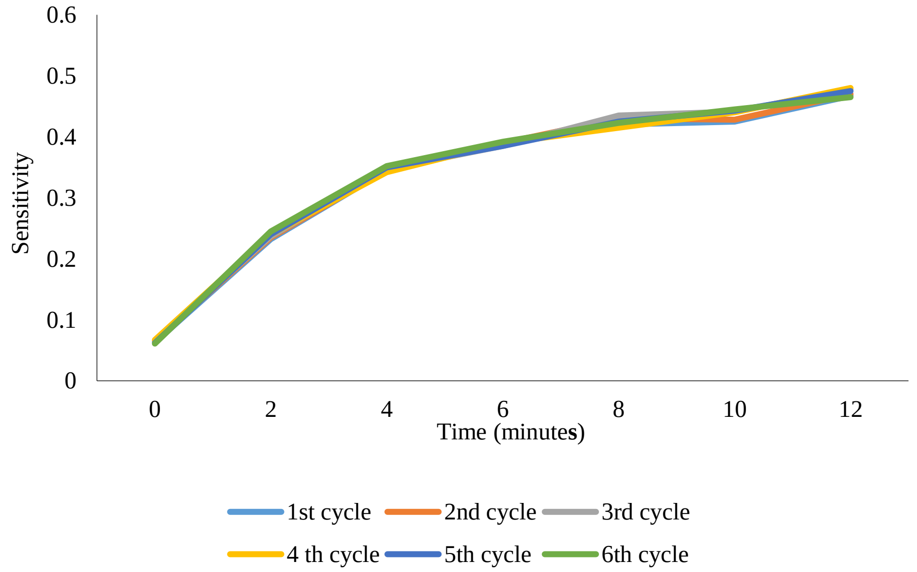

Figure 9. Sensing performance of Ag-Fe_2O_3-cuo -PANI nanocomposite showing repeatability for carboxylic acid concentrations in apple vinegar at 25 ppm concentration

CONCLUSION

In this work we have reported simple, eco-friendly, green synthesis method to create Silver, Iron oxide and Copper oxide nanoparticles and a chemical oxidative procedure to produce trimetallic Ag-Fe_2O_3-CuO -PANI nanocomposite using polyaniline. XRD, FESEM and FTIR were used to validate the final nanocomposite and synthesized nanoparticles were evidently in their crystalline phase based on the XRD signals. FESEM shows polydispersed nature of nanocomposite which clearly represent porous structure of synthesized nanocomposite, which indicated that Ag-Fe_2O_3-CuO -PANI nanocomposite is successful sensitive clad for carboxylate sensing applications. The successfully developed fiber optic sensor with sensitive Ag-Fe_2O_3-CuO -PANI nanocomposite clad for carboxylate vapours from Apple vinegar was low cost, simple and reliable with optimised clad thickness of 11.39 µm in the range 25-200 ppm. At 25 ppm concentrations the developed sensor exhibited maximum sensitivity, good repeatability, better selectivity and stability. This qualifies the developed Ag-Fe_2O_3-CuO -PANI nanocomposite based clad modified fibre optic sensor for monitoring and detection of carbolylate vapours in food industry, environment, and laboratory.

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