

SONOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF POLYMERIC NANOCOMPOSITES FOR THE CATALYTIC SENSOR APPLICATION

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Abstract:

Polyaniline decorated Silver nanoparticles (PANI@AgNPs) composites were successfully synthesized by sonochemical oxidative polymerization utilizing an equimolar amount (1:1) of AgNO₃/Aniline dissolved in each 25 ml of water/methanol separately, mixed slowly, and then held in a sonicator for 45 minutes in a dark environment. No other external oxidizing agents were employed for polymerization; only AgNO₃ was used as a metal precursor and as oxidizing agents. Various instrumental techniques HR-TEM, FE-SEM, XRD, TGA, UV-vis., and FT-IR were used to analyze the PANI@AgNPs. The PANI@AgNPs/GCE had good electrochemical responses and electrocatalytic activity over the detection of hydrogen peroxide (H₂O₂), according to a cyclic voltammogram. H₂O₂ is oxidized at the surface of PANI@AgNPs/GCE has clearly reveal by the voltammetry techniques of cyclic, amperometric, and differential pulse voltammetry. The detection limits 0.03 M was found at amperometric analysis for H₂O₂.

Keywords: PANI@AgNPs, Sonochemical oxidative polymerization, Electrochemical sensor, H₂O₂ oxidation

1. Introduction

Conducting polymers and their nanocomposites have acquired great interest for their potential application in a various fields. Nanocomposites can be made in a simple and low-cost manner for a variety of benefits, including environmental stability and flexibility, as well as chemical inertness. As previously stated, the backbone of the polymeric chain along their extended conjugated π -bond is the source of intrinsic electrical conductivity in these polymers. It's vital to remember that due to their extended conjugate-bond structure, conjugated organic molecules can have semiconductor properties. Polymers with this type of inherent structure are known as intrinsically conductive polymers. These polymers can be divided into four groups based on their technological utility: polypyrrole (PPy), polyaniline (PANI), poly (3, 4-ethylenedioxythiophene) (PEDOT), and polythiophene (PTh) [1-5].

The conduction polymers were synthesized utilizing a variety of polymeric processes and several oxidants were used to oxidize its monomers. The oxidation potential of these materials is a critical factor in their selection and predilection for polymerization [6-9]. Different noble metal salts, such as AuCl_4 , PtCl_2 , PtCl_4 , AgNO_3 , and HAuCl_4 , can be employed as oxidation agents in some circumstances to avoid the use of some harmful oxidative agents and to be able to directly deposit noble nanoparticles onto conductive polymer nanostructures. To make "polypyrrole (PPy) nanofiber/Au or Pt nanoparticle" composites, $3\text{H}_2\text{O}$ was used. Because of their lower oxidation potential, oligomers were sometimes employed instead of monomers [10-14]. Carl Julius Fritzsche (a German chemist) was the first to invent the PANI in 1840. PANI has piqued the interest of many scientists since its development, prompting them to examine the polymer from a variety of perspectives. Chemical oxidative and electrochemical polymerization are the most widely utilised synthesis strategies for generating PANI from aniline monomer. Aside from these two ways, the PANI is produced via interfacial, template, seeding techniques, and electro spinning processes. The inclusion of an acid doping agent during the polymerization by acidic medium can make PANI electrically conductive in nature [15-20].

The nature of the structure and varied features of the PANI backbone can be determined by the overall polymeric chain, which is generally formed of successively alternating benzene rings and nitrogen atoms that exist as imine (sp^2 hybridised) or amine (sp^3 hybridised) forms present.

According to their redox proportions, there are four well-known variants of PANI available in prior reports [12]. Pernigraniline has a pink/purple colour when fully oxidised, and Leucoemeraldine has a pale brown colour when entirely reduced, and neither form has a conducting characteristic [13]. Color can be used to distinguish the emeraldine state of PANI, which lacks conducting capacity (blue). Only the protonated emeraldine form (partially oxidized/reduced) has conducting properties, which are derived from protonated charge carriers created following acid treatment (reversible reaction by base treatment) [11]. PANI is a dark green solid with a flexible solid structure that is insoluble, infusible, and intractable. It is soluble in organic solvents and has a processable conductivity of 1 to 10 S/cm [21-26].

In this present investigation, PANI@AgNPs/GCE modified electrode used as an electrocatalyst for the detection of H₂O₂. Generally, H₂O₂ is the simplest peroxide (a compound with an oxygen-oxygen single bond). Hydrogen peroxide is a clear liquid, slightly more viscous than water. In dilute solution, it appears colour less. Due to its oxidizing properties, hydrogen peroxide is often used as a bleach or cleaning agent. It is considered a highly reactive oxygen species, due to its strong oxidizing capacity. Hydrogen peroxide has wide range of application in various fields like environmental, pharmaceutical, clinical, industrial research and it is the by- product of a large number of oxidize enzymes of the reaction catalyst. The detection of hydrogen peroxide is an important aspect in biomedical and environmental applications. Electrochemical sensors are of particular interest for their practicality, simplicity, low cost, and suitability for real time detection. H₂O₂ is oxidized at the surface of PANI@AgNPs/GCE has clearly reveal by the voltammetry techniques like cyclic, amperometric, and differential pulse voltammetry.

2. Experimental Methods

Chemicals

S.D. Fine Chemicals P.Ltd. India supplied the aniline, AgNO₃, and other chemicals. Qualigens Pvt. Ltd. in India provided all solvents, and deionized water was used to make all stock solutions.

Synthesis of PANI@AgNPs nanocomposite

Synthesis of PANI@AgNPs using oxidation polymerization (**scheme 1**). 0.068 g of AgNO₃ was dissolved in 20 mL ultra-pure water in a beaker. Subsequently, 0.037 g aniline was dissolved in

20 mL methanol by sonication, which was added slowly in to the aqueous phase resulting in the formation of a completely miscible. After 10 minutes the reaction mixture turn in too deep red colour is due to the formation of AgNPs in static condition, and the reaction was allowed to kept 2 days for the complete formation PANI@AgNPs nanocomposites which is confirmed by the formation of green precipitate in a beaker. PANI@AgNPs isolated by filtration and by extensive washing with corresponding solvents and methanol to remove all un-reacted monomer and other soluble oligomers and dry the composite in room temperature [18].

Instrumentation

PANI@AgNPs were disseminated in N-Methyl-2-pyrrolidone using an ultrasonicator to obtain electronic spectra using a SHIMADZU-1800 (UV-Vis. Spectrophotometer) from Japan and FT-IR spectra using a Perkin Elmer Y-40 from the United States. Philips, JSO debye Flex 2002 Seifert with 10°/min scanning speed was used to evaluate the XRD pattern. HITACHI, SU6600 with voltage 0 kV (FE-SEM), Japan validated the morphology, size, and forms of the nanoparticles, while HR-TEM images were taken with a JEOL-3010 apparatus.

3. Results and Discussion

The UV-vis spectrum of PANI@AgNPs generated using the oxidative polymerization technique is shown in Figure 3. For the UV-vis. spectral analysis, N-Methyl-2-pyrrolidone was utilised as a solvent. Only two peaks are seen in spectral analysis at 302 nm and 570 nm, which are attributed to the benzenoid ring's π - π^* transition and molecular exciton for the quinoid form of the PANI backbone [4, 20].

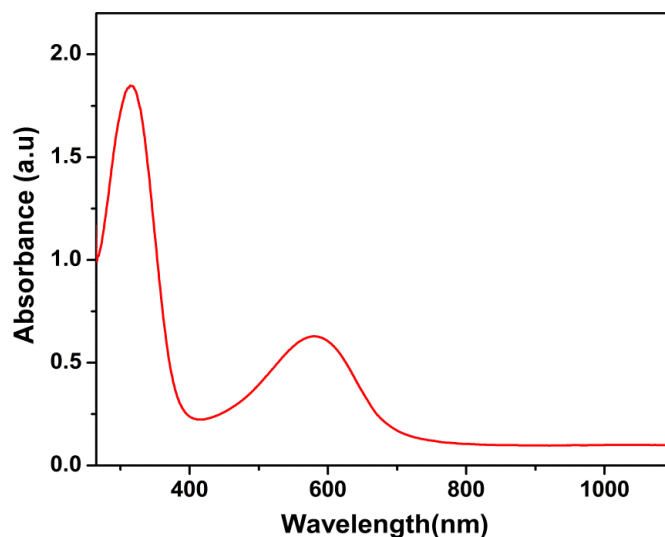


Fig.1: UV-visible spectrum of PANI@AgNPs

The FT-IR spectral response of PANI@AgNPs is shown in Figure 4. The N–H stretching is visible in the spectra of PANI@AgNPs bands at 3380 cm^{-1} , whereas the C–H stretching is visible at 2988 and 2870 cm^{-1} . The C–N stretching is assigned to the band at 1316 cm^{-1} , whereas the responses at 1119 and 882 cm^{-1} correspond to the C–H in-plane and out-of-plane bending of the polymer matrix, respectively. The quinoid and benzenoid rings present in the polymer matrix are responsible for the peaks detected at 1598 and 1500 cm^{-1} . All of these results indicate that PANI@AgNPs were produced sequentially using a single oxidation polymerization technique [4, 20].

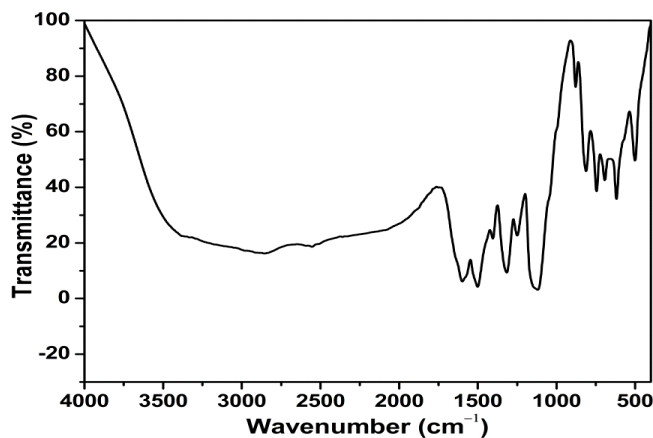


Fig.2: FT-IR spectrum of PANI@AgNPs

PANI@AgNPs (Fig. 5) were subjected to a thermogravimetric analysis (TGA) at RT-800 °C in N₂ atm with a heating rate of 20 °C/min. It was discovered that the produced nanocomposites decomposes in three stages. first the degradation of (~100 °C), is due to the removal of water molecules/moisture from the polymer and second in the temp range 271-310 °C is the removal of acid dopant and third has rapid weight loss (483-583 °C) is attributed the decomposition of PANI. The mass percentage of composition of metal that remains after the degradation of the polymer for PANI@AgNPs is approximately 65.0 ± 0.5 %. It confirms the PANI@AgNPs have a greater thermal stability by the presence of Ag NPs, which control heat motion in the composite [27, 28].

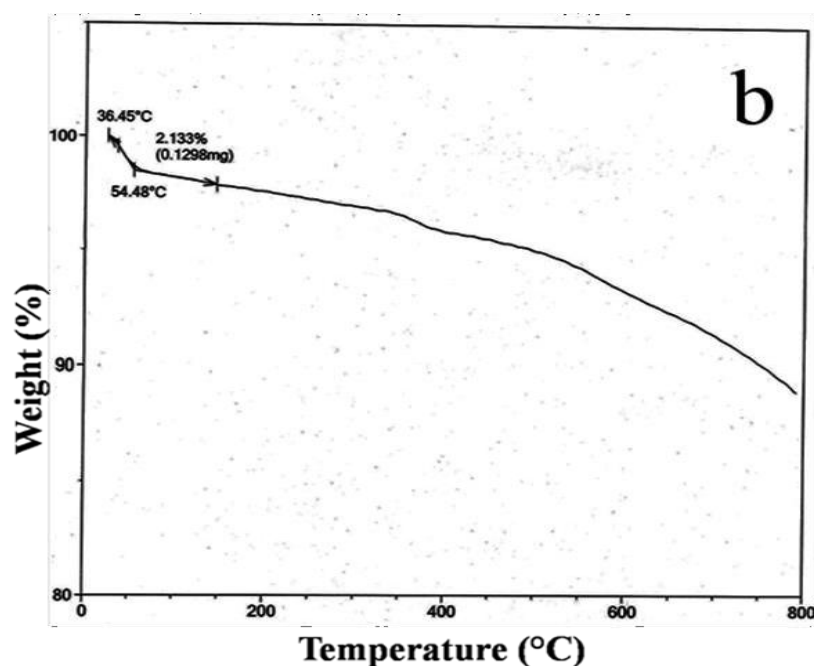


Fig.3: TGA spectrum of PANI@AgNPs

Figure 6 shows the XRD pattern of PANI@AgNPs. The spectrum reveals a broad background peak with a typical superimposed peak at $2\theta = 20^\circ$, indicating that the polymer is amorphous and somewhat crystalline. The other four peaks at $2\theta = 38.0, 44.5, 64.5,$ and 77.7 are attributed to the (111), (200), (220), and (311) Bragg reflections of the Ag plane, respectively. The XRD patterns demonstrate the existence of Silver nanoparticles trapped within the polymer matrix [20, 28].

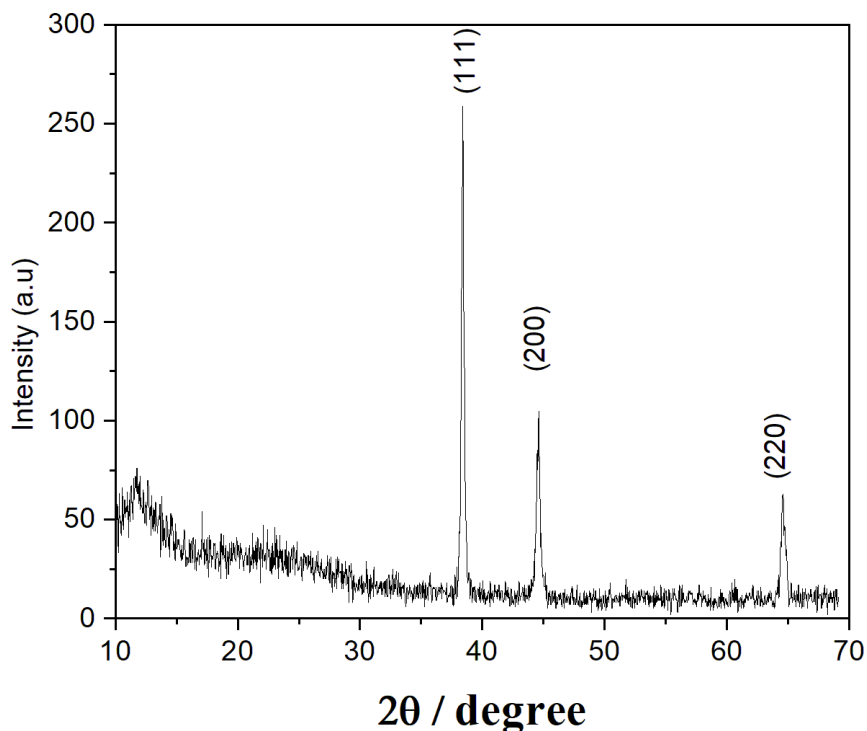


Fig.4: XRD spectrum of PANI@AgNPs

The FE-SEM images of the PANI@AgNPs nanocomposites are shown in Figure 7(a-c). The nanocomposite's shape resembled that of a polymer matrix, with chunks arranged in a fibrous pattern. EDX spectrum (d) and percentile table (inset) showed the existence of immobilised Silver nanoparticles in the polymer matrix, and HR-TEM pictures are displayed in Fig. 8. (a-c). PANI@AgNPs nanocomposites have a spherical morphology of the Ag nanoparticles located inside the polymer matrix, as seen in the photos, with sizes ranging from 10 to 30 nm, with the majority of them falling within the 20 nm range [4, 27,33,34]. The data presented above will be sufficient to demonstrate the creation of Au NPs during the oxidative polymerization process.

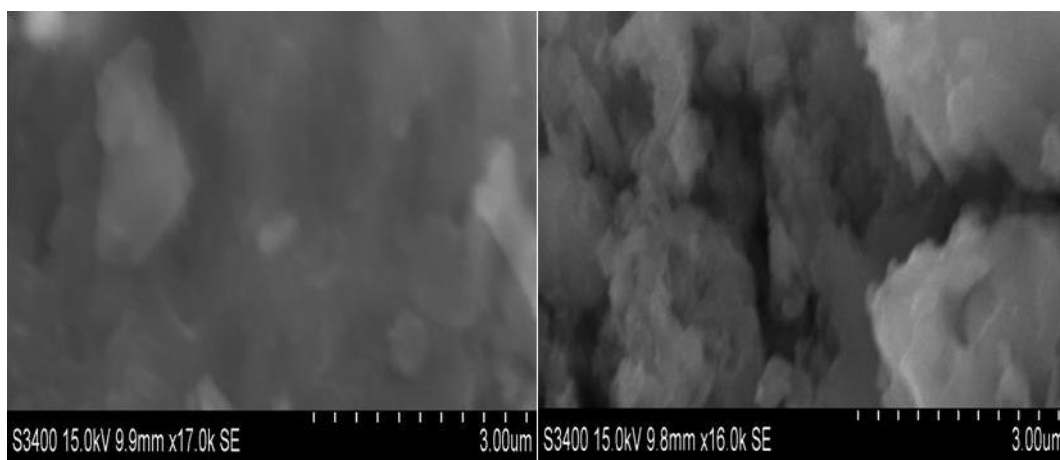


Fig. 5: FE-SEM images of oxidation polymerized PANI@AgNPs

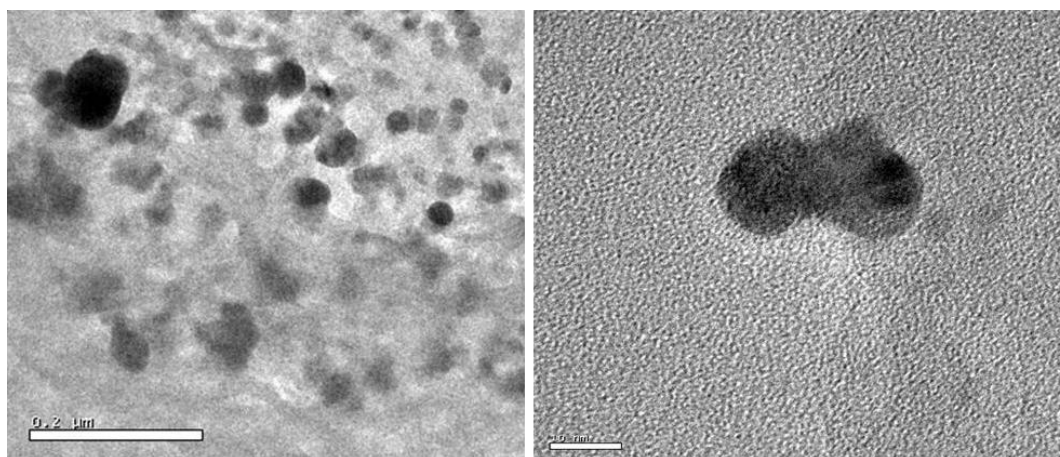


Fig. 6: HR-TEM images of PANI@AgNPs.

Electrochemical oxidation of H₂O₂

Figure 7 shows the electrocatalytic oxidation of H₂O₂ using PANI@AgNPs composites modified GCE in presence of 0.1 M PBS (pH 7) at scan rate 50 mV/s and it reveal the good electrochemical responses during successive addition of 1.0–5.0 μM H₂O₂. As seen, the anodic peak current increases linearly with each addition of 1.0 μM concentration, so it could be concluded that the PANI protected silver composites modified GCE showed good electrocatalytic activity towards H₂O₂ [29].

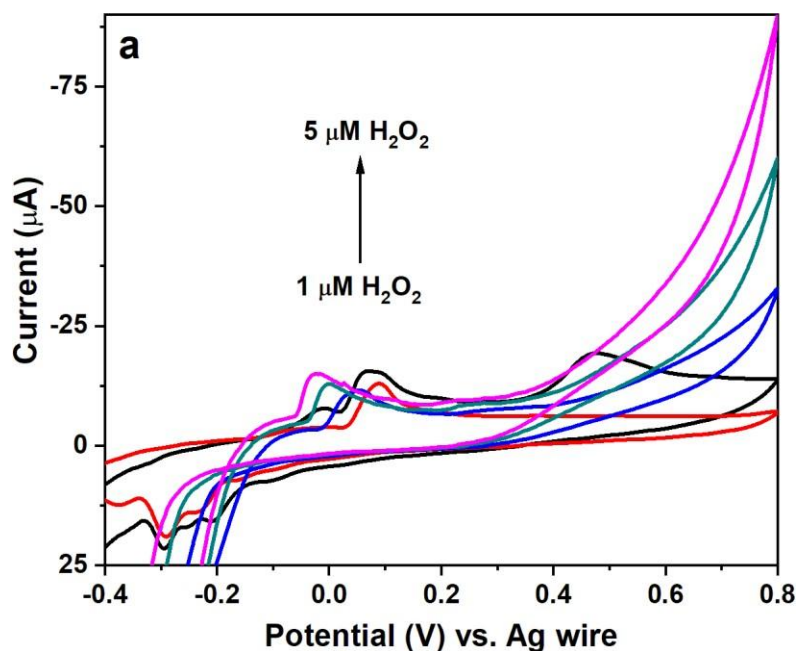


Fig. 6. CV for the oxidation of H_2O_2 at scan rate 50 mV/s with successive addition of H_2O_2 (1–5 μM) in 0.1 M PBS ($\text{pH} = 7.0$)

Figure 8 shows the amperometric determination of H_2O_2 oxidation using Ag@PANI modified in GCE in 0.1M PBS ($\text{pH} 7$) electrolyte with applied potential 0.6 V in every 25 s addition the current was measured and its corresponding calibration plots are noted as (b). In addition that the level of the Cottrell current increases with increasing concentration of H_2O_2 . The response is linearly proportional to the concentration of H_2O_2 in the range of 1.0 – 9.0 μM . The linear regression equation was $(y(\mu\text{A}) = -0.73x - 3.50 \mu\text{M})$ with the correlation coefficient being 0.9802 and the detection limit was computed to be 1.23 μM at a signal-to-noise ratio of 3, and its calibration plot are shown in Fig. (b) and it confirm are higher electrocatalytic activity reveal by the linear oxidation over H_2O_2 oxidation [30-32].

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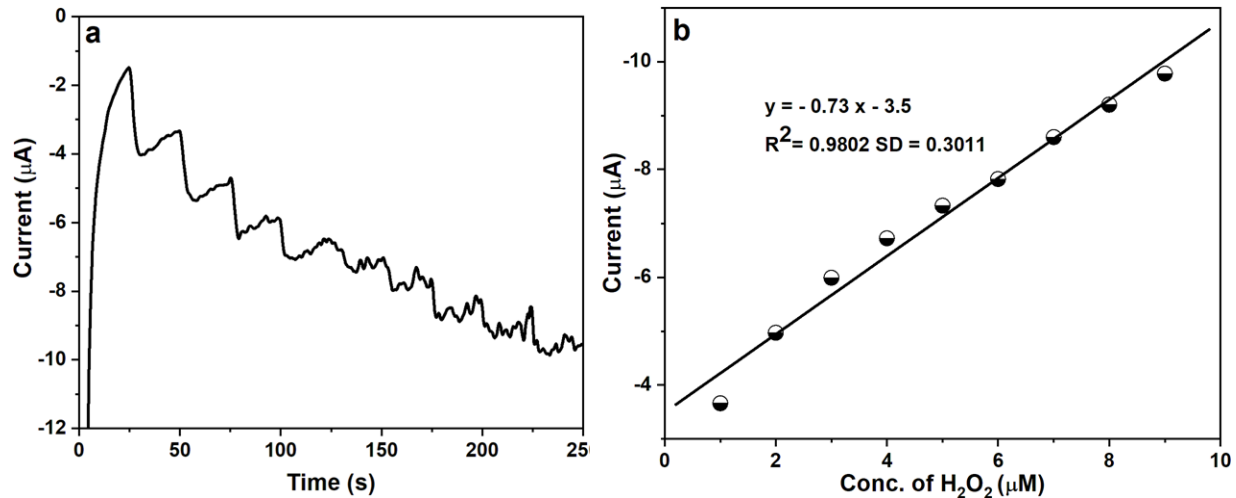


Fig. 8. (a) Amperometric determination for the oxidation of H₂O₂ in 0.1 M PBS (pH = 7.0 and potential of + 0.6 V) with successive addition of 10.0–90.0 μM and (b) its corresponding calibration plot.

4. Conclusion

In summary, we have synthesized PANI@AgNPs successfully using sonochemical oxidative polymerization method. Here, No other external oxidizing agents were employed for synthesis; only AgNO₃ was used as a metal precursor and as oxidizing agents. Various instrumental techniques HR-TEM, FE-SEM, XRD, TGA, UV-vis., and FT-IR were used to analyze to confirm its structure, size and shapes of the nanocomposites and electrocatalytic activity over the detection of hydrogen peroxide (H₂O₂) using cyclic voltammetry and chronoamperometry, which reveals the modified electrode has good sensor activity over the H₂O₂ determination. In this present investigation, the detection limit was computed to be 1.23 μM at a signal-to-noise ratio when we added the successive addition of H₂O₂ (1.0 – 9.0 μM).

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