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Short Communication Polyaniline-CdS nanocomposite/GOx matrix modified optical fiber based biosensor for glucose detection

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Abstract

In the present study, polyaniline-cadmium sulphide (PANI-CdS) nanocomposite material was synthesized by simple chemical polymerization method using $FeCl_3$ as an oxidant. The prepared matrix was deposited as an active cladding material for the fabrication of cladding modified fiber optic intrinsic biosensor. The cladding modified material was used for the immobilization of biomolecules-enzyme-glucose oxidase (GOx) with the help of cross-linking technique. The nature of deposited nanocomposite material was confirmed using X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FE-SEM) techniques. Moreover, optical microscopy was used to observe the thin layer of deposited nanocomposite matrix on fiber optic sensing element. The prepared sensor can be used further for the detection of glucose solution of various concentrations. From the results, it has been found that PANI-CdS nanocomposite is biocompatible for the fixation of biomolecules on fiber optic sensing element. The results have been presented.

Keywords: Polymer, Nanocomposite, Cladding modification, Glucose oxidase, Optical fiber, Biosensor.

Introduction

Polymer matrices have been increasingly utilized as a main constituent of sensing element of electrochemical and optical biosensors. Polymer offers supportive media to immobilize biomolecules¹⁻⁶. Moreover, polymers have superior qualities like good optical transparency, chemical stability, low oxidation potential, sensitivity and environmental stability^{6,7}. Recently, biosensors utilizing nanomaterials have been attracted considerable attention in the area of sensing technology.

The nano-sized CdS showed potential applications in protein/enzyme electrochemistry due to its remarkable physicochemical properties. CdS nanoparticles were used to incorporate with GOx for realizing the direct electron transfer, and CdS has been found efficiently enhancing the electron transfer reactivity of $GOx^{8,9}$.

In the present study, polyaniline-cadmium sulphide (PANI-CdS) nanocomposite material was synthesized by simple chemical polymerization. The prepared matrix was deposited as an active cladding material for the fabrication of fiber optic intrinsic biosensor. Enzyme-glucose oxidase (GOx) was immobilized over modified cladding through cross-linking via glutaraldehyde solution. Prepared nanocomposite matrix was characterized using X-ray diffraction (XRD) analysis, field emission scanning electron microscopy (FE-SEM) and optical microscopy.

Materials and methods

Cadmium chloride (CdCl₂), sodium sulphide (Na₂S) and Larginine were purchased from Sigma Aldrich, USA to prepare nanoparticles. Aniline and ferric chloride were purchased from Fisher Scientific, India. Glucose oxidase (GOx, Aspergillus Niger, 125 units/mg) was procured from Sisco Research Laboratories (SRL), India. Glutaraldehyde solution (25%), potassium dihydrogen orthophosphate and sodium hydroxide pallets were purchased from SD Fine chemicals, India⁶. All the synthesis processes were carried out in freshly prepared double distilled water⁶. All the chemicals were of analytical grade and used as it is without further purification.

Structural and morphological study of PCdS nanocomposite was done by powder XRD using Rigaku diffractometer Miniplex II with nickel filtered CuK α radiations (λ =1.5406 Å) and FE-SEM, Hitachi S-4800, Japan. Optical images were recorded using optical microscope, AxioCam, Germany.

Preparation of FOIGB: The FOIGB sensing element was fabricated on half-meter long piece of multimode optical fiber of $425/300\mu m$ (core/cladding) diameter⁶. 2 cm portion of the optical fiber was removed mechanically using stripper and surgical blade to expose the fiber optic core. Cleaned uncladded portion of the fiber was coated with a very thin layer of nanocomposite material using in-situ deposition method during polymerization at room temperature⁶. The sensing element was

rinsed with phosphate buffer solution to generate a hydrophilic surface⁶. GOx was immobilized over modified PCdS nanocomposite matrix surface through cross-linking via glutaraldehyde solution using layer-by-layer technique^{6,7,10-12}. Figure-1 depicts the mechanism and arrangement of fiber optic sensing element.

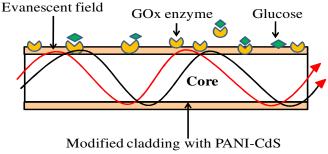


Figure-1: Cladding modification and immobilization of enzymes on sensing element.

Synthesis and deposition of PCdS nanocomposite: The CdS nanoparticles were prepared using a low cost soft chemical route with stock solutions of 1M CdCl₂, 1M Na₂S and 1M Larginine as reported in our previous article¹³. 0.2 M aniline and 0.05 M FeCl₃ solutions were prepared in separate beakers using double distilled water. Already reported powder of synthesized CdS nanoparticles in 10 wt% was used to prepare PCdS nanocomposite. In the solution of aniline, CdS was added under constant stirring. Acidified solution (HCl) was added drop wise in it with constant stirring to dissolve CdS. The polymerization of aniline and CdS was initiated with the drop wise addition of oxidizing agent (FeCl₃) solution under constant stirring at room temperature. While during this process of polymerization, 2 cm uncladded sensing element was submerged in it for the deposition of thin layer of PCdS nanocomposite on it. After polymerization the sensor was removed from polymerization flask and a thin layer of polymer was deposited on the sensing element. Figure-2(a) and (b) exhibit the decladded and deposited PCdS nanocomposite matrix on optical fiber sensing element respectively. The thickness of the deposited film is found to be ~1.7 µm. For further characterizations, PCdS nanocomposite was centrifuged, filtered, washed with distilled water and dried optically.

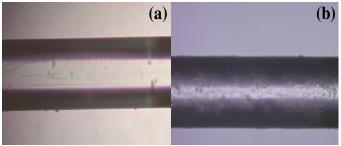
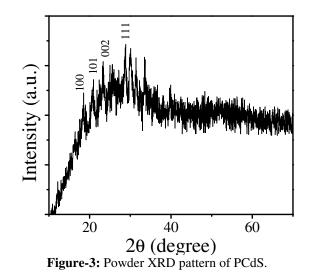


Figure-2: Optical microscopic images of (a) uncladded and (b) PCdS deposited optical fiber.

Results and discussion

XRD analysis: Figure-3 shows the diffuse XRD pattern of PCdS deposited on sensing portion of FOIGB. The diffuse spectra with few weak characteristic diffraction peaks corresponding to the CdS nanoparticles in the 2θ range 15-38° confirms the deposited polymers have amorphous nature with embedded nanocrystalline CdS^{9,14,15}.



FE-SEM study: Figure-4 shows the FE-SEM micrograph of PCdS nanocomposite film used to deposit on FOIGB sensing element. It exhibits a structure with many pores and gaps¹³. It also reveals that the nanocomposite has a mixture of agglomerated and non-agglomerated fluffy particles and scattered granules irrespective of the nature of PANI. From this surface morphology, it can be considered that the nanostructured CdS nanoparticles are embedded within the structure of PANI chains and exhibit different structural morphologies^{6,14}.

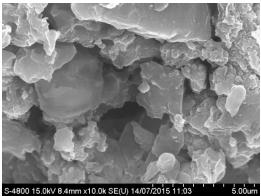


Figure-4: SEM micrograph of PCdS.

Conclusion

As-synthesized PCdS nanocomposite material has successfully been deposited as an active cladding material for the fabrication

of cladding modified fiber optic intrinsic biosensor. It was prepared using a simple in-situ chemical polymerization method. The modified material was further used for the immobilization of enzyme-GOx through cross-linking via glutaraldehyde solution. From XRD, FE-SEM and optical microscopy study, it was confirmed that as-synthesized PCdS nanocomposite can effectively be used as a promising material for the immobilization of biomolecules to prepare biosensors and for other sensing applications. PCdS nanocomposite can accommodate biomolecules for longer duration, which can certainly be useful to enhance the sensitivity and performance of the prepared biosensor.

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