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Carbon Nanomaterials and Applications in Sensors-A Review

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ABSTRACT: This is a brief review covering the recent developments on the carbon nanostructured materials-based detectors covering recently revealed works is presented. Number of works addressing experimental and theoretical knowledge are reviewed and discussed. The results for carbon nanotubes and hybrid carbon-nanostructured devices that show sensing properties in several fields were thought of for the discussions. The goal of this paper was to focus on sensor mechanisms, and the best results reached up to the current situation are making bases for more applications.
Keywords: Nanomaterials, Carbon Nanotubes, CNTs, Gas sensors, Biosensors.

I. INTRODUCTION

Recent advancements within the field of applied science have created opportunities for the great achievements in biosensing. Emergence of recent materials and their hybrids have raised hopes for development of new biosensors capable of delivering on site results of variety of analytes (at smaller level) at the same time without requiring skillful personnel or refined machinery. A biosensor could be a device consisting of a biological sensing element i.e the bioreceptor which detects the analyte, is connected to a detector or transducer, whichconverts the response into a measurable signal. On the basis of the styles of bioreceptors, biosensors will be classified as immunobiosensors, enzymatic biosensors, genobiosensors and based mostly upon the transduction process, biosensors can additionally be classified as optical, piezoelectric, electrochemical, and thermometric biosensors.

Nowadays, the need to develop new sensors with more specific properties is increasing. There are avariety of sensors for monitoring gases, heavy metals, moisture, biomolecules, pressure, etc. However, most of them are expensive, require pre-treatment, are difficult to use, slow to respond, and do not have the ideal limit of detection, Sensitivity or Selectivity. With a view to improve the above parameters, nanotechnology has provided the most promising update in material properties and has given significant advances in overcoming the limitations conventional materials once faced.

Carbon nanotubes (CNTs), as one of the extensively used 1D nanomaterials, have been applied for the fabrication of numerous high-overall performance sensors and biosensors because of the unique mechanical, electrical, and magnetic properties of CNTs. In addition, the high surface area and high adsorption capacity toward numerous molecules/biomolecule of CNTs make CNTs very good option to manufacture chemical and bio sensors with high sensitivity and selectivity. Besides CNTs, carbon nanofibers (CNFs) have additionally been broadly studied because of their unique chemical and physical properties and comparable structure to fullerenes and CNTs.

This report presents the latest advancements in the field of nanotechnology and it's application with the scope of sensors. This report also deals with the different types of the sensors that can be fabricated as an option. Recent studies will be cited from here.

II. NANOMATERIALS SUITABLE FOR USE

2.1 Carbon Nanotubes (CNTs)

CNTs are sp2 hybridized carbon atom rolled graphene sheets having hollow interior with diameter in nanosize and the length varies from nanometers to microns. Due to their excellent structural, electronic and mechanical properties, CNTs have gained huge interest from the time of their discovery. These showcase variable conductivity and feature small size which lead them to an excellent choice for use within the scope of molecular electronics as molecular wires. Functionalization of CNT may be performed with the aid of using both covalent and non-covalent

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binding with different chemical groups which makes CNTs biocompatible for conjugation with biomolecules and hence making them a appropriate candidate for biosensing. The functional groups which include amine and carboxyl, increase the rate of electron transfer. In practical, the water-soluble polymers based functionalization of CNTs or surface functionalization with ionic or hydrophilic groups of CNTs allows to attain CNT solubilization in aqueous media and is a giant parameter for CNTs to work as a assisting matrix or scaffold for the entrapment of proteins/DNA/ Antibody/enzymes. Functionalization of CNTs additionally improves the direct electron transfer among the biological element active sites and the electrode. Because of the above reason, conductivity of CNTs (especially MWCNTs) is normally stepped forward with the aid of using functionalizing them with redox polymers, hapten molecules, thiol derivatives and N-ethyl-N-(3-dimethylaminopropyl carbodimide-N-hydroxy succinimide (EDS-NHS). An amperometric acrylamide biosensor was fabricated with the aid of using immobilization of Hb onto nanocomposite of cMWCNT and Fe_2O_4 nanoparticles (NPs) electrodeposited onto gold electrode via a polymer chitosan film (Batra et al., 2013). A great improved sensitivity and selectivity was acquired for acrylamide. The sensor offered a short response, wider linear range, decreased limit of detection (0.02 nM), excellent reproducibility, and long stability. Recently, an immunosensor was mentioned for cancer detection making use of poly (diallyldimethylammonium chloride) (PDDA)-functionalized CNTs for assembly of HRP and concanavalin A (ConA) at the gold electrode. Utilizing the biospecific interaction among HRP and ConA, PDDA changed CNTs form a complex of CNTs/PDDA/HRP/ConA which afterward mixed with Ab labeled HRP and form a sandwich. The immunosensor shows a good linear range from 0.05–5 ng/mL to 5–200 ng/mL and a detection restriction of 0.018 ng/mL (Yang et al., 2014). A fresh glucose biosensor was fabricated by the use of free CNTs and enzymatic electrode immobilizing glucose oxidase (GOx), GOx coating and GOx precipitate coating. This sensor contemplated excellent development in sensing, stability and electron transfer (Kim et al. 2015).

2.2 Pure Carbon NanoFibers(CNFs)

Due to their high specific surface area and good electrocatalytic ability towards the oxidation of specific organic matter, pure CNFs are normally preferred to observe small molecules, viruses, proteins, and nucleic acids in food quality check and clinical analysis. For example, yue et al. said mesoporous CNF-modified pyrolytic graphite electrode for the cooccurring determination of uric acid, ascorbic acid, and dopamine. Koehn et al. made a vertically aligned CNF electrode array by the PECVD method, then integrated the CNF array with the wireless instantaneous neurotransmitter detector system to detect dopamine by quick scan cyclic voltammetry. Rand and coworkers developed a biosensor supported vertically aligned CNFs for the cooccurring detection of serotonin and dopamine within the presence of excess ascorbic acid. Periyakaruppan et al. says similar CNFs primarily based nanoelectrode arrays for label-free detection of cardiac troponin-I in the early diagnosing of heart muscle infarction.

2.3 CNFs modified with metal oxides

Since some acid gases and organic gases will cause changes within the impedance of metal oxide-decorated CNFs, metal oxide-decorated CNFs will be used for the detection of specific acid gas and organic gas. Lee and coworkers made ZnO/SnO_2 nanonodules-decorated CNFs for dimethylphosphonate gas detection by single nozzle co-electrospinning by 2 phase-separated polymer solutions. Later, this group changed WO_3 nanonodule to the surface of CNFs for the detection of NO_2 gas using an equivalent method, and observed that the sensitivity of the WO_3 nanonodule-decorated CNFs enhanced the quantity of the decorated WO_3 on the CNFs surface. Hu and colleagues showed the electrospun preparation of mesoporous MnO_2 and Mn_3O_4NPs-decorated CNFs, and observed that the hybrid CNFs have a diameter of 200–300 nm with high surface area. In another case, Xia and co-workers showed the overall synthesis of ultrafine transition metal oxide (Zn, Mn, and Co) NPs-embedded porous CNFs via a facile electrospinning strategy, following through the oxidisation method. As shown in Figure 4, there are plenty interconnected pores distributed within theZnO/CNFs, MnO/CNFs, and CoO/CNFs, and therefore the Zn, Mn, and Co elements are homogeneously distributed within the porous CNFs, respectively.

2.3.1 Zinc Oxide

Features a wide band gap of 3.37 eV that makes it a good nanomaterial in comparsion to others. ZnO may be a semiconducting material that exhibits high surface area to volume ratio, high biocompatibility, extremely stability, biomimetic, less toxicity and have a decent electron transferring feature. ZnO nanoparticles (NPs) are good supply for immobilization of proteins because of high isoelectric point.Various biosensors with ZnO are reported for biomolecules like cholesterol, glucose, urea, cortisol, H_2O_2, glutamate and so on totally different shapes of ZnO were exploited to fabricate biosensors. For example, spherical and flower shaped ZnO NPs were immobilized on Au electrode to fabricate 2 cholesterolbiosensors (Umar et al., 2009a; Umar et al., 2009b). A layer of nafion was additionally applied to flower shaped ZnO. The sensorwith nafion offered additional sensitivity and reproducibility, low km value, lower detection limit and fast response that were because of the network shaped by nafion which prevents protein leaking. Totally different structure of ZnO like ZnO nanorod and nanocom were also executed to construct glucose biosensor by modifying conductor (Wei et al., 2006; Wang et al.,2006). GOx was immobilized to each ZnO structure and nafion was used to cowl nanocombs. Presence of nafion will increase the enzyme–electrode interaction and therefore increased performance of biosensor. 2 label free, low price immunosensors for detection of cortisol were made by using one dimensional ZnO nanorods (ZnO-NRs) and two dimensional ZnO nanoflakes (ZnO-NFs) (Vabbina et al., 2015). Both the nanostructures givemassive surface area, stability, biocompatibility and enhances the sensing ability of sensor. Theimmunosensors show selective electrochemical cortisol detection At 1 pM 100 times higher than enzyme connected immunosorbent assay (ELISA). 7.74 μA/M and 11.86 μA/M values were the sensitivity measured for ZnO-NFs and ZnO-NRs respectively. Kumar et al. (2015) showed a chemical biosensor for hydrazine that is ultra-highly sensitive and relies on ZnO nanocones. The sensor offered a high sensitive of 50×10^4μA/μM/$cm^2$and low detection limit of 0.01 μM.

ZnO usually shaped nanocomposite with polymers, AuNPs, graphene MWCNTs and so on and these hybrids are documented for immobilization of enzymes that helps in direct electron transfet. Between the conductor and active site which ends in superior properties for amperometric sensing. An amperometric glucose biosensor with great selectivity, stability, reliableness and repeatability was made-up by the use of the ZnO and MWCNTs on glassy carbon electrode (Palanisamy et al., 2012). The sensor exhibited a linear vary of 0.2–27.2 mm, 20 mM as limit of detection and a sensitivity of 4.18 mA/ mM. A ZnO/graphene and S6 aptamers primarily based biosensor for detection of SK-BR-3 breast cancer cells was made on ITO electrode (Liu et al., 2014). A low detection limit of58 cells mL^{-1} and a dynamic linear range of10^2-10^6cells mL^{-1} was observed. Lately, extremely sensitive uric acid biosensor was developedwith the use of ZnO nanosheets grown on electrode with high sensitivity, stability, duplicability and selectivity (Ahmad et al., 2015). ZnO nanosheets give additional surface to interact and lead to higher electron transfer between active sites of electrode and enzyme. Extent of communication between enzyme and electrode plays a key role in defining the level of sensitivity, i.e., more the interaction, higher the electron transfer and thus increased sensitivity.

III. APPLICATION OF THE NANOMATERIALS IN SENSORS

3.1 Gas sensors

Li and coworkers made CNFs of graphitic nanorolls employing a straightforward electrospinning-assisted solid-phase graphitization method, graphitic CNFs exhibit sensitivity to H_2, CO, CH_4, and ethanol gases at room temperature, and therefore the detection limit for CO gas is as low as 50 ppm. Zhang et al. reported a H_2S detector using ZnO-CNFs composites, the as-prepared H_2S sensor showed a linear response within the limits of 50–102 ppm of H_2S. Claramunt et al. deposited metal alloy NPs-decorated CNFs on Kapton for checking the level of NH_3. The results show that the sensitivity of Au and Pd NPs-decorated CNFs to NH_3 may be improved by dominant proportion of Au and Pd. Moreover, the latency of the detector is up to five minutes at 110–120 ◦C. However, when put next with the spectroscopical sensor like mid-infrared sensor and quartz-enhanced photoacoustic sensor, that have the benefits of fast detection at room temperature with no reagent, the operation temperature of Au, and Pd NPs-decorated CNFs is a lot higher. So as to scale down the detection temperature, Lee et al. changed WO_3 nanonodules onto the CNFs, and the ready WO_3 nanomodule-decorated CNFs not only provides a better sensing surface area, but also WO^{2+} on the surface of the fabric will mix with the O22 of NO_2, realizing the detectionof NO_2 gas at room temperature, and the detection limit for NO_2 reach 1 ppm.

3.2 Sensors for small molecules

CNFs-based nanomaterials being used to detect gas molecules and strain sensing, can also be used to detect micro molecules. Huang et al. loaded palladium NPs on CNFs to organize a Pd/CNFs modified carbon paste conductor for the detection of dopamine (DA), uric acid (UA), and ascorbic acid (AA). Once being modified with Pd NPs-loaded CNFs (Pd/CNFs), the oxidation overpotentials of DA, UA, and AA were considerably reduced compared to the bare carbon paste electrode. The detection limits of Pd/CNFs changed carbon paste conductors for DA, UA and AA were 0.2 µM, 0.7 µM, and 15 µM, respectively, and therefore the the} linear range was 0.5–160 µM (DA), 2–200 mm (UA), and 0.05–4 mm (AA). Liu et al. rumored another Pd NPs-loaded CNFs modified carbon paste electrode for oxalic acid detection, had the detection limit of the sensor for oxalic acid as low as 0.2 mM, and shows a linear range from 0.2 to 45 nM. Liu et al. also made a Ni/CNFs composite electrode by electrospinning for glucose detection. The Ni/CNFs hybrid shows higher sensitivity towards glucose due to the electrocatalytic activity of the Ni NPs and therefore the stability of the carbon conductor. In the absence of chloride poisoning, the detection limit of the Ni/CNFs composite electrode for glucose is 1 µM, with a linear range of 2 µM–2.5 mm (R = 0.9997). Li and coworker successfully created a magnetic composite through polymerization of dopamine, laccase, and Ni NPs loaded CNFs. The as-prepared magnetic composite exhibited high selectivity towards catechol, and showed a linear range from 1 to 9100 µM, with a detection limit of 0.69 µM for catechol in water samples. Lee et al. created a ZnO/CNFs composite for detecting DMMP, and ZnO NPs on CNFs enhanced the precise surface area of the detector and its affinity for DMMP. The detection limit of ZnO/CNFs composite for DMMP is 0.1 ppb, with a linear limits of 0.1–1000 ppb.

3.3 Biosensors

Ways to regulate and monitor health issues have attracted intensive attention, and even a lot of economic resources are designated to new technologies researches and development. The quicker the changes on the organism operate are detected, the simpler their control can be. Furthermore, identification systems with low detection limit, which implies more sensitivity, will increase the chances of medical intervention on unwellness treatment more efficiently. During this way, devices for biomolecules detection and quantification are of nice importance to boost life quality.

CNT field-effect transistors (CNTFET) have been with success enforced in dna sensors. Tran et al. rumored detection of influenza a virulent disease employing a CNTFET-based polymer sensor, achieving a limit of detection of 1 pM in a linear range from 1 pM to 10 nM. Dudina et al. reported the development of biosensors through an array of 9216 CNTFETs, detecting resistance within the 50 kΩ to 1 GΩ range, achieving a noise performance of 2.14 pARMS at a 1 kHz bandwidth and 0.84 pARMS at a 1 MHz bandwidth.

IV. LIMITATIONS

Carbon nanostructures have some limitations in their application due structural characteristics and properties, like functionalization, defects, and particles aggregation. All of these limitations are regarding sensor system responses and might decrease the standard of the device. This subject can present some limitations for the carbon nanostructures mentioned previously in this paper. CNT based sensor application is restricted due some of its structure characteristics. CNTs can not be applied directly in medical specialty applications due their metallic characteristic, being insoluble in several solvents. This characteristic can be a problem looking on the kind of device for biological concerns, that is being developed. Also, CNT sizes obtained from the synthesis sometimes aren't homogeneous, which may lead one to get results that are not consistent. CNT are often used as CNT-based biosensors operative with a field-effect transistor configuration (CNT-bioFET) to find biomolecules. Although this sort of system presents superior performance, the presence of background noise of electrostatic nature can phase out the reliable information being measured. As recognized by Camilli and Passacantando, the noise has identical scale range of the signal, and its origin is associated to substrate interactions and surface adsorbates. Another concern is that the presence of defects in CNT structure and even the functionalization methodology used for CNT application. They will influence CNT Young's modulus, which may yield many issues for sensor devices based on CNT specially those ones accustomed measure stress and strain properties.

V. CONCLUSION

Carbon nanostructure-based sensors are systems with excellent properties, giving us many prospects of application.Although carbon nanotubes have high reactivity just like the alternative allotropes, their mechanical properties conjointly imply within the development of sensors for physical parameter detection, like stress and strain. Their high surface-to-volume rate also permits the development of gas sensors nearly as good as those made using graphene structure. The devices reported throughout this review represent the utmost development found these days for carbon nanostructure-based sensors, presenting the most analysis areas being explored and therefore the potentialities for the future. Several remained challenges regard on the carbon-based manufacture to terminate contaminants also as to improve the functionalization process. In addition to this, new synthesis methods for CNFs could be developed, also the biological modification of CNFs for subsequent biomedical applications including biosensors, anti-bacterial materials, bone tissue engineering, and others could be further explored. Improving these aspects can increase the sensor selectivity and manage defect densification, which is strictly regarding physical and chemical properties that has got to be overcome.

Conflict of interest
The authors declare no conflicts of interest.

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