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Nano-Sensors and Development of Environmentally Friendly Sensors Advanced Opto-Fluidic Nano Biosensor

[1]G. Wyasu, [2*]M.Y. Pudza, [3]Y.M. Ibrahim, [4]S. Moses.

[1]Department of pure and. Applied Chemistry, kaduna state University, kaduna Nigeria.

[2*]Department of Chemical and Environmental Engineering, Faculty of Engineering,

University Putra Malaysia, Serdang, Selangor 43400, Malaysia.

[3]Department of Chemistry, Sokoto State University, Sokoto State - Nigeria.

[4]Department of Science and Laboratory Technology, Federal Polytechnic Kaura Namoda, Zamfara State, Nigeria.

Correspondence E-mail: pudzamusa@gmail.com

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Abstract

Nano-sensors are becoming a generic term in environmental studies and also in related academic disciplines but eco-friendly Nano-sensor is recently evolving into environmental bioremediation and biotechnological application. Nano-sensors technology has been limited to issues surrounding a few special fields. More potentials in environmental applications are yet to be fully unraveled, hence, this review article targets the gap between the previous knowledge and the advancement achieved and the way this could be applied in a yet economical and novel field of an environmental conceptual framework. Environmental damage due to increasing population and industrialization is a serious cause for concern. Remediation, using smarter engineered nanomaterials (NMs) can deliver cost-effective and time-saving in situ clean-up procedures for large-scale contaminated sites. Nanomaterials are self-cleaning, having the potential to eliminate the need for treatment of the contaminated material by reducing the contaminant concentration to zero. With the rapid advancement of nanomaterials, there is the need for a proper evaluation of applications in order to prevent any potential environmental or ecological hazards. The Development of a sustainable novel nano sensor with potential environmental application in the selective detection of heavy metals in aqueous media is futuristic, however, the technique employed should be facile, which will have a commercial and economic benefit to water industries and also other environmental applications.

Keywords: Nanosensors, nanoparticules, biomaterials, fluorescence, Carbon quantum dots. Carbon dots

Introduction

The emergence of carbon dots (CDs) has generated enormous excitement due to their great potential in photocatalysis, optoelectronic devices, bio-imaging, biosensors, and analytical applications [1]. These fluorescent carbonaceous nanoparticles, with a diameter of less than 10 nm, possess fine biocompatibility, high photostability against blinking, excellent up-conversion properties, and low toxicity, which make them promising alternatives to semiconductor quantum dots (QDs) in chemical and biological analyses [2].

Biosensors represent the end product of a rapidly growing field, which combines fundamental biological, chemical, and physical sciences with engineering and computer science to satisfy needs in a broad range of application areas. Therefore, the term 'biosensor' has different connotations depending on what field the user comes from [3]. For this study, we may define a biosensor as "an analytical device, which detects and converts the concentration of the target substance, the analyte (i.e. chemical or biological species or a microorganism), into an electrical signal through a combination of a biological or biologically derived recognition system either integrated within or intimately associated with a suitable physiochemical transducer". The field of biosensors has been active for many decades.

This study reports on biosensors and their classifications along with the synthesis of nanoparticles by green

technologies. Nanotechnology plays an increasingly important role in the development of biosensors. The sensitivity and performance of biosensors is being improved by using nano materials for their construction. The world of nano research requires harnessed understanding of the use of nano materials for the introduction of many new signal transduction technologies in biosensors. Because of their submicron dimensions, nano sensors, nano probes and other nano systems have allowed simple and rapid analysis. Portable instruments capable of analyzing multiple components are becoming possible through the applications of nanoparticles and their characterizations.

Biosensor system

A biosensor in general utilizes a biological recognition element that senses the presence of an analyte (the specie to be detected) and creates a physical or chemical response that is converted by a transducer to a signal [4-6]. The general block diagram [7] of a biosensor system is described in Figure 1.

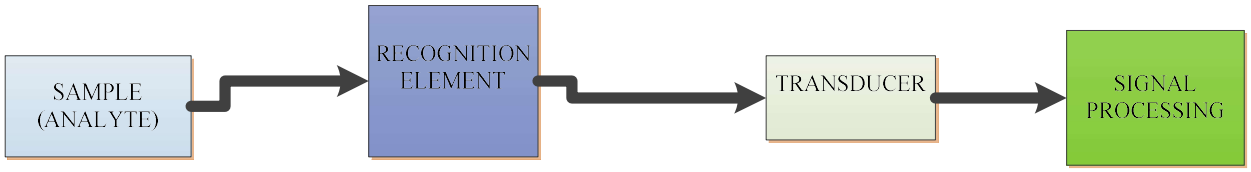

Figure 1: General scheme of Biosensing.

The sampling unit introduces an analyte into the detector. The recognition element binds or reacts with a specific analyte, providing bio-detection specificity [8]. Enzymes, antibodies, receptors, DNA or even cells such as yeast or bacteria have been used as biorecognition elements [9-12]. Stimulation, in general, can be provided by optical, electric, or other kinds of force fields that extract a response as a result of misrecognition. The transduction process transforms the physical or chemical response of misrecognition, in the presence of an external stimulation, into an optical, electrical or any other form of signal that is then detected by the detection unit. The detection unit may include pattern recognition for identification of the analyte. Research communities from various fields like, physics, chemistry, biology, material science have come together to develop more sophisticated, reliable, and mature biosensing devices. Biosensors find a wide range of real-world applications [13,14]. Potential applications are basically clinical and nonclinical [15,16]. More recent interest is the use of biosensors to detect toxins [17], microorganisms [18,19], bacteria, viruses [20] and chemical and biological defense [21] against terrorism. It is also popular in agriculture [22] and environmental [23] applications. Nowadays nanotechnology-based application [24] are also in development.

Classification of biosensors

Biosensors are classified based on two parameters. Based on the transduction mechanism and second based on the biorecognition elements [25]. The classification is shown in the following Figure 2.

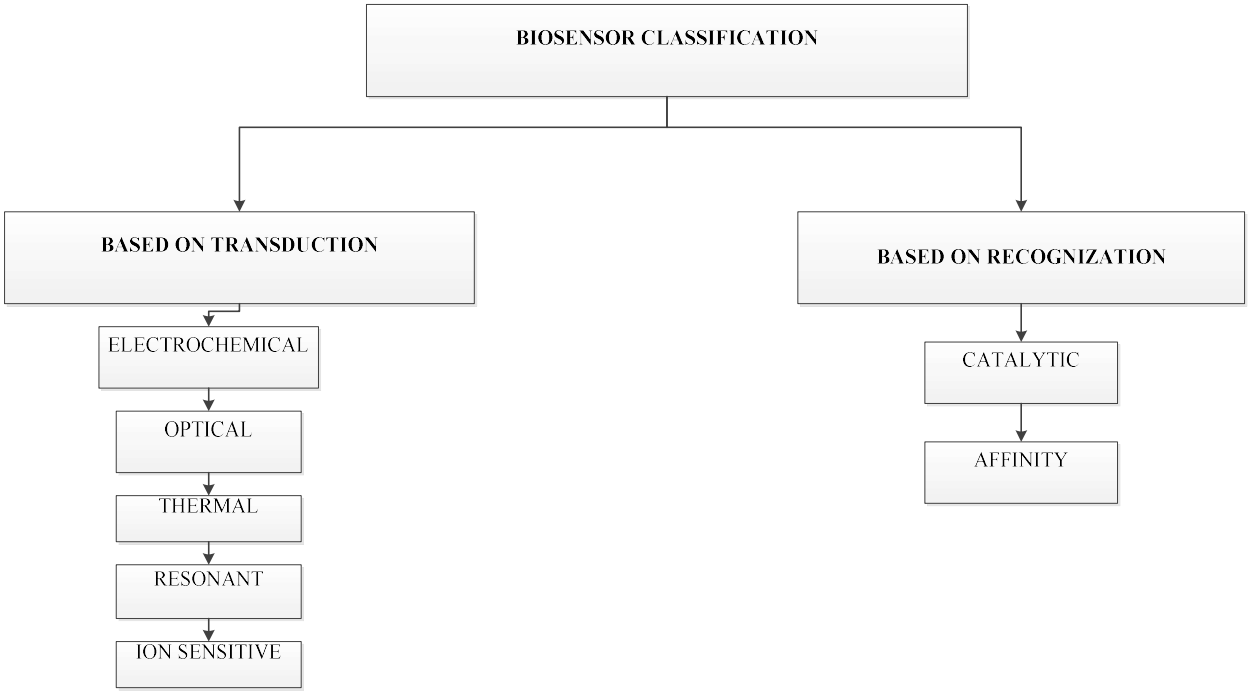

Figure 2: Biosensor Classification

Electrochemical biosensors [26,27] Are mainly used for the detection of glucose concentration, DNA-binding drugs, hybridized DNA, etc. The underlying principle for this class of biosensors is that many chemical reactions produce or consume ions or electrons which in turn cause some change in the electrical properties of the solution which can be sensed and used as measuring parameter. In resonant biosensors, an acoustic wave or piezo-electric transducer is coupled with a bio-element. When the analyte molecule gets attached to the membrane, the mass of the membrane changes. The resulting change in the mass subsequently changes the resonant frequency of the transducer. This frequency change is then measured. Thermal biosensors, exploits one of the fundamental properties of biological reactions, namely production of heat, which in turn changes the temperature of the medium in which the reaction takes place. Due to the biological reactions, the temperature of the medium changes. This temperature change is measured. It is constructed by combining enzyme with temperature sensors. When the analyte comes in contact with the enzyme, the heat reaction of the enzyme is measured. The measurement is done by thermistor known as 'enzyme thermistor'. Used for the detection of pesticides and pathogenic bacteria. Semiconductor FET having an ion-sensitive surface (ISFET) is used in ion sensitive biosensors. Sensor electrode is covered with a polymer layer. Polymer layer is selectively permeable to the analyte ions. When the ion concentration in solution changes, the ions diffuse through the polymer layer. It causes a change in the FET surface potential. It is known as ENFET (Enzyme Field Effect Transistor) and is primarily used for pH detection.

Optical biosensors

In the most commonly used form of an optical biosensor [28-

30], the transduction process induces a change in the phase, amplitude, polarization, or frequency of the input light in response to the physical or chemical change produced by the bio recognition process. Some of the advantages offered by an optical biosensor are selectivity and specificity, remote sensing, isolation from electromagnetic interference, fast, real-time measurements, multiple channels/multi parameters detection, compact design, minimally invasive for in vivo measurements, choice of optical components for biocompatibility, detailed chemical information on analytes, The main components of an optical biosensor are: light source, optical transmission medium (fiber, waveguide, etc.), immobilized biological recognition element (enzymes, antibodies or microbes), optical detection system. Optical biosensors can be broadly classified based on the different parameters as shown in Figure 3.

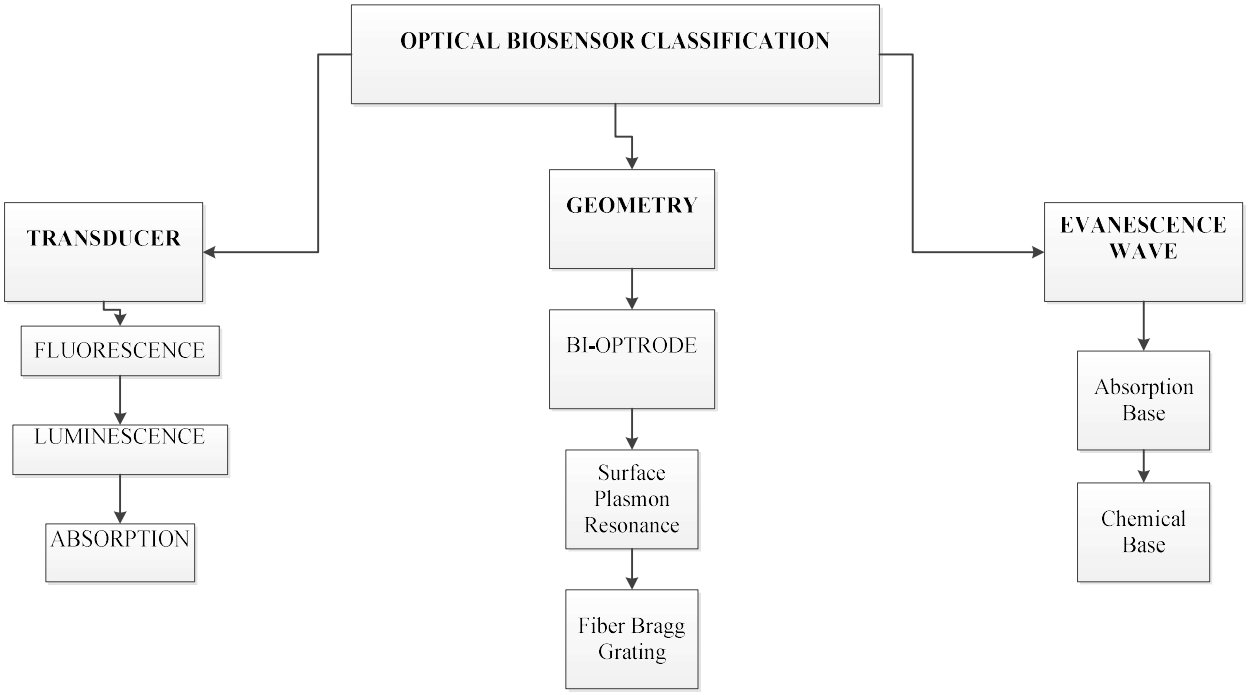

Figure 3: Classification of Optical Biosensors

Optical nano biosensors

Nanotechnology [31] Is playing an increasingly important role in the development of biosensors. The sensitivity and performance of biosensors is being improved by using nano materials for their construction. The use of nano materials has allowed the introduction of many new signal transduction technologies in biosensors. Because of their submicron dimensions, nano sensors, nano probes and other nano systems have allowed simple and rapid analyses. Portable instruments capable of analyzing multiple components are becoming possible. Using micro- and nanotechnologies [32,33], optical biosensors could be integrated in "lab-on-achip" microsystems which could be used in real applications in many different scenarios (home, patient office, work, etc.) for real-time and on-line monitoring.

Synthesis of nanoparticles using green technology

Pattanayak *et. al*. [34], described in their paper titled "Ecofriendly synthesis of Iron Nanoparticles from various Plants and Spices extract": Biosynthesis from different parts (mostly leaf) of the plant is found to be the most effective process of synthesis at a very affordable cost. Appropriate precursors such as Ferric Chloride can be used for the reduction of plant extracts. Scientists report the synthesis of nanoparticles, reducing Ferric ions present in the aqueous solution of Ferric chloride by the help of different plant extracts.

Vincenzo and Moreno [35], in their paper titled "Laser Ablation synthesis in solution and size manipulation of noble metal Nanoparticles" Laser Ablation mechanism; Absorption of incoming photons, which can produce the heating and photo ionization of irradiated area, subsequently, some material can be torn away from the target as vapors, liquid drops, solid fragments or as an expanding plasma plume, The atomic density and temperature profiles are not homogeneous everywhere in the plasma plume, since two boundary regions exist with the surrounding liquid and metal target.

Iravani., *et. al*. [36], described in their paper titled "Green synthesis of metal nanoparticles using plants": This study reveals that in recent years, the development of efficient green chemistry methods for synthesis of metal nanoparticles has become a major focus of researchers. Investigations in order to find out an eco-friendly technique for production of well-characterized nanoparticles have been carried out. One of the most considered methods is production of metal nanoparticles using organisms. Among these organisms plants seem to be the best candidates and they are suitable for large-scale biosynthesis of nanoparticles. Nanoparticles produced by plants are more stable and the rate of synthesis is faster than in the case of microorganisms.

Wenbu *et. al.* [37], Described in their work titled "Economical, Green synthesis of Fluorescent carbon nanoparticles and their use as probes for sensitive and selective Detection of Mercury (II) Ions." The article presented reports on a simple, economical and green preparative strategy toward water soluble, fluorescent carbon nanoparticles (CPs) with a quantum yield of approximately 6.9% by hydrothermal process using a low cost waste of pomelo peel as a carbon source.

Sandhya, *et al.* [38], stated in a journal titiled "Heavy metal ion sensing in water using surface Plasmon resonance of metallic nanostructures". It reviewed on techniques to improve selectivity and sensitivity of surface Plasmon response sensors. Effects of particle size and shape, the material type and the surrounding environment were found to be effectual in the surface Plasmon surface frequency.

Subramanian *et al.* [39], in an article titled "Cultivation of Chlorella on brewery wastewater and nano-particle biosynthesis by its biomass" stated the method of bio-nanoparticle synthesis using chlorella (is a genus of single-cell green algae belonging to the phylum Chlorophyta), The algal biomass grown in single water sample were harvested from culture medium by centrifugation at 4000mg for 5 min followed by washing with ultrapure water for 3 times to remove any impurities present. Iron nanoparticles were synthesized by mixing 0.5 g (dry weight) Chlorella sp. MM3 with 5 mL of 0.1 M FeCl3 (Sigma–Aldrich) solution followed by incubation at 37 C for 48 h.

Gupta *et. al.* [40], Described in their work titled "Paper strip based and live cell ultrasensitive lead sensor using carbon dots synthesized from biological media" It reported a formulation of sensor through microwave heating of biocompatible biological media such as potato-dextrose agar (PDA) for detection of lead (pb^{2+}) in solution.

Applications of nanoparticles

Ajay and Mona., [41], described in their paper titled "Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications" : Super paramagnetic iron oxide nanoparticles (SPION) with appropriate surface chemistry have been widely used experimentally for numerous in vivo

applications such as magnetic resonance imaging contrast enhancement, tissue repair, immunoassay, detoxification of biological fluids, hyperthermia, drug delivery and in cell separation, etc. All these biomedical and bioengineering applications require that these nanoparticles have high magnetization values and size smaller than 100 nm with overall narrow particle size distribution, so that the particles have uniform physical and chemical properties. To this end, most work in this field has been done in improving the biocompatibility of the materials, but only a few scientific investigations and developments have been carried out in improving the quality of magnetic particles, their size distribution, their shape and surface in addition to characterizing them to get a protocol for the quality control of these particles.

Chengkun *et al.* [42] stated in their paper titled "Presence of photoluminescent carbon dots in Nescafe original instant coffee: Application to bioimaging" it reported the finding of the presence of photo luminescent (PL) c-dots in commercial Nescafe instant coffee which indicates that c-dots are amorphous and the cytotoxicity study revealed that the c-dots did not cause any toxicity to cells at concentration as high as 20mg/ml. the c-dots have been directly applied in cells and fish imaging.

xiaoming *et al.* [43] detailed in their work titled "Novel and Green synthesis of high-fluorescent carbon dots originated from honey for sensing and imaging". An innovative and green approach of production and application exhibiting various advantages including fluorescent quantum yield, excellent photo stability and employed for assay of Fe2+ of collected blood samples, cell imaging and coding.

Ruizhong and Wei., [44] Outlined "Nitrogen-doped carbon quantum dots: Facile synthesis and application as a turn-off fluorescent probe for detection of Hg^{2+} ions." Where highly photoluminescent nitrogen doped carbon dots was synthesized and detection application of mercury with detection limit of 0.23um which is as result of the fluorescent quenching mechanism attributed to the surface/molecule states in quantum dots and the mercury induced conversion of special functional group(-CONH-) from spirolactam structure to an opened-ring amide.

Rui-jun Fan *et al.* [45] in a paper titled "Photoluminescent carbon dots directly derived from polyethylene glycol and their application for cellular imaging." Mentioned how polyethylene glycol (PEG) was used to synthesize carbon dots with cytoxicity conducted alongside cellular imaging. The PEG is a biocompatible non-conjugated polymer, used as both carbon source and passivating agent. The pH value of the carbon dots was at ph.3 because of the formation of carboxyl groups.

Roberto and Francesco [46], in their paper titled "Mitochondrial Biosensors." Deposited the facts of mitochondria as a potent biosensor by direct targeting and selective targeting of mitochondrial matrix, in most cases mitochondrial sensors where deployed in animal cells (human, mouse, rat, Drosophila) and only few studies exist in the plant field.

Zhaoxia *et al.* [47] stated in a paper work titled "Carbon dots with turnable emission, Controlled size and their application for sensing hypochlorous acid." As a member of carbohydrates that is widely distributed in living organism, sucrose was chosen as carbon source with assistance of microwave irradiation, the thermal pyrolysis produced strongly fluorescent carbon dots without post-passivation. By increasing the concentration of phosphoric acid under UV lamp various fluorescent (blue, green and yellow) emissions of carbon dots of variable sizes where obtained. It was found that the green carbon dots have excellent sensitivity for the detection of HCLO.

Yingshuai *et al.* [48] in a publication titled "One-step green synthesized fluorescent carbon nanodots from bamboo leaves for copper (II) ion detection." Posits the exploration of bamboo leaves as a carbon source with high carbohydrate constituent. Carbon quantum dots was synthesize hydrothermally and a resultant high quantum yield quantum dots with sensitive CU^{2+} detection with limit of detection as low as 115nM and a dynamic range from 0.333 to 66.6uM, the zeta potential of the pristine carbon quantum dots is

measured as -4.78 mV which changes to +13.8mV after treatment with positive charged polyethyeneimine (a water soluble cationic polymer).

Soon-Bee et al., [49] in their work "In-line deoxygenation for organic carbon detections in seawater using a marine microbial fuel cell-biosensor." Described a two-chambered microbial fuel cell physically separated by cation exchange membrane filled with conductive graphite granules with internal anolyte and catholyte volumes of 100ml. the result of the discussion demonstrated that activated organic carbon detection in seawater is possible by seamless combination of electrochemical cell with microbial fuel cell, but the long term operation could lead to the buildup of an aerobic biofilm on the graphite.

Kuo-Chih *et al.* [50] Experimented In their work titled "Percutaneous fiber-optic biosensors for immediate evaluation of chemotherapy efficacy in vivo (part 1): Strategy of assay design for monitoring non-homogeneously distributed biomarkers." And identified the optimal exogenous fluorophores for the cell distribution indicators, phospholipids modified marina blue can provide timely quantifiable values indicating only the cell densities (spatial distribution index), independent of the treatment of the apoptotic initiator and without interfering with the optical characteristics of FM 1-43 (fluorophores).

Huilin *et al.* [51] in a research paper titled "Carbon dots as fluorescent probe for "off-on" Detecting sodium dodecyl-benzenesulfonoate in aqueous solution (SDBS)." Posit that in order to obtain homogeneous solution, the pristine carbon dots were synthesized from sodium citrate through a simple, convenient and one-step hydrothermal method and characterized by fluorescent spectroscopy, UV-vis absorption spectroscopy, transmission electron microscopy and FT-IR spectra. Fluorescent recovery was achieved with the application of SDBS, of which detection of SDBS in real water samples is proportional to the concentration in the range of 0.10 to 7.50 ug/mL.

Characterization of nanoparticles

James *et. al.* [52] described in their paper titled "Characterization and Properties of Metallic Iron Nanoparticles: Spectroscopy, Electrochemistry, and Kinetics": Superparamagnetic iron oxide nanoparticles (SPION) with appropriate surface chemistry have been widely used experimentally for numerous in vivo. All these biomedical and bioengineering applications require that these nanoparticles have high magnetization values and sizes smaller than 100 nm with an overall narrow particle size distribution, so that the particles have uniform physical and chemical properties.

Yu-fu *et al.* [53]. Described in their paper titled "40 GHz RF biosensor based on microwave coplanar waveguide transmission line for cancer cells (HepG2) dielectric characterization. This paper presented a 40-GHz RF biosensor that involves using microwave coplanar waveguide transmission line for the dielectric characterization of cancer cells (Hepatoma G2, HepG2). Most application is in postoperative cancer diagnosis.

Chaudhary *et al.* [54] Explicitly stated the characterization techniques in nanomaterials which include the following processes; AFM; Raman Spectroscopy; Scanning electron microscopy; Scanning probe microscopy; TEM; X-RD.but do not include the Fourier transform infrared spectroscopy (FTIR) spectra which will detect functional groups responsible for characteristic biomaterial composition.

The unique properties of nanoparticles (NPs) are mainly because of their large surface area (the surface-to-volume ratio is much larger in NPs) which relates to the fine-grained dispersion of the organic-nanoparticle in the dispersing medium. The diameter of atoms and molecules cluster are usually in range of several of tens of nanometers, and generally, the size of the nanoparticle under investigation lies in the 1-50 nm range. Therefore, in nanoparticle systems, the percentage of atoms or molecules at a boundary is significantly higher than in the bulk material. This high percentage of atoms/molecules near to the boundary leads to the unique properties of nanoparticles; hence, as volume is connected to

the mass, the energy (mass) of nanoparticles is strongly governed by surface effects.

Chemical characterization is to determine the surface and interior atoms and compounds as well as their three-dimensional distributions. Many chemical analysis methods have been developed for surface analysis or thin films, Hence focusing on Optical spectroscopy, Electron spectroscopy.

Spectroscopy is a method of "Seeing the Unseen." Using electromagnetic radiation to obtain information about atoms and molecules that are too small to be seen. Optical spectroscopy has been widely used for the characterization of nano- materials, and the techniques can be generally categorized into two groups: Absorption and emission spectroscopy and vibrational spectroscopy. Absorption and emission spectroscopy: As electrons move between the energy levels of an atom they can emit or absorb light energy. If the electron moves from a lower energy level to a higher energy level, the atom must absorb the energy. If the electron falls from a higher energy level to a lower energy level it will release energy by emitting light. By absorbing specific wavelengths of light, an electron moves from a lower energy level to a higher energy level. Since every kind of atom has a different electronic configuration, the wavelengths of light absorbed or emitted by an atom are unique to that element. By measuring the unique wavelengths and intensities of light, what an atom absorbs is called the Atomic Absorption Spectrum. It can be directly observed; the lines in the "visible" spectrum with our eyes, but many other lines outside the "visible" region exist and can be detected by specially designed spectrometers as Optical Spectroscopy.

Vibrational / Infrared Spectroscopy: Molecules and crystals can be thought of as systems of atoms or ions connected by springs (chemical bonds). These systems can be set into vibration, and vibrate with frequencies determined by the atomic weight and by bond strengths. They are at very high frequencies ranging from 1012 to 1014Hz, which is in the infrared (IR) regions of the electromagnetic spectrum. The oscillations combine with an impinging beam of infrared electromagnetic radiation to exchange energy with it when the frequencies are in resonance. In the infrared experiment, the intensity of a beam of infrared radiation is measured before and after it interacts with the sample. The identities, atomic arrangements, and concentrations of the chemical bonds that are present in the sample can be determined by;

I. Electron spectroscopy

This depends on energy levels of the emission of photons (X-ray) or electrons. When an incident electron or photon strikes an unexcited atom, an electron from an inner shell is ejected and leaves a hole or electron vacancy in the inner shell. An electron from an outer shell fills the hole by lowering its energy, and the excess energy is released through either emission of an X- ray ejection of a third electron that is known as an Auger electron. By measuring the energies of the X-rays and Auger electrons emitted by a material, its chemical compositions can be determined.

II. Ionic spectrometry

This is a popular thin film characterization technique which depends on the use of very high-energy beams (MeV) of low-mass ions. Such ions can penetrate hundreds of nanometers deep into samples and lose their energies through electronic excitation and ionization of target atoms. With the known mass and energy of incident ions and the angular position of the ion detector, their concentrations and depth distribution can all be simultaneously determined by measuring the number and energy of backscattered incident ions.

Generally, Transmission electron microscopy (TEM) measurements can be performed on a transmission electron microscope for the characterization of the shape and size of the nanoparticle by depositing them on 400-mesh C-coated Cu grids. Absorption spectra can be recorded at room temperature on a UV-vis spectrophotometer. The steady-state fluorescence and time-resolved fluorescence decay can be recorded by using a spectrofluorometer in pair with a laser as an excitation source. Time-resolved fluorescence decays can be recorded using the time-correlated single photon counting (TCSPC) method. X-ray diffraction (XRD) can be measured

using an analytical XRD instrument in conjunction with Cu K-alpha radiation. X-ray photoelectron spectroscopy (XPS) spectra can be explored to characterize the chemical composition using x-ray photoelectron spectrometer (Thermo Scientific). The Fourier Transform Infrared spectroscopy (FTIR) spectra can be determined by VECTOR 22 with KBr pellet technique. Atomic Force Microscopy (AFM) is the versatile tool to investigate; Topography of surface, properties of single molecules, and the force within molecules.

Conclusion

Environmental damage due to increasing population and industrialization is a serious cause for concern. The advent of Nano remediation, using smarter engineered nanomaterials (NMs) can deliver cost-effective and time-saving in situ clean-up procedures for large-scale contaminated sites. Moreover, it can eliminate the need for treatment of the contaminated material by reducing the contaminant concentration to zero. With the rapid advancement of this technique, proper evaluation needs to be done to prevent any potential environmental or ecological hazards.

The Development of a sustainable novel nano sensor with potential environmental application in the selective detection of heavy metals in aqueous media is futuristic, however, the technique employed should be facile, which will have a commercial and economic benefit to water industries and also other environmental applications.

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