Century Impact of Macromolecules for Advances of Sensing Sciences

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Abstract
Impact of macro molecular theory on the progress of sensing sciences and technology has been presented in the light of materials developments, advances in physical and chemical properties. The chronological advances in the properties of macromolecules have significantly improved the sensing performances towards gases, heavy metals, biomolecules, hydrocarbon, and energetic compounds in terms of unexplored sensing parameters, durability, and working lifetime. In this review article, efforts have been made to correlate the advances in structure and interactivity of macro-molecules with their sensing behavior and working performances. The significant findings on the macromolecules towards advancing the sensing sciences are highlighted with the suitable illustration and schemes to establish it as a potential “microanalytical technique” along with existing challenges.

Graphical Abstract

Keywords Macro molecular theory · Chronological advances · Macromolecules in sensing sciences · Sensing parameters · Applications · And future challenges

1 Introduction

The controversial establishment of macromolecular theory by Hermann Staudinger in 1920 after superseding the established era of aggregation theory for the existence of high molecular
mass natural compounds has opened the newer direction for the applications of several natural compounds along with a base for the synthesis of different synthetic macromolecules also referred as resins and polymer to fulfill the requirements of different industries [1]. In continuation to the structural interpretation and discovery of synthetic polymers, the past hundred years of this theory witnessed the exponential increasing trends in related publications and patents for the foundation of several industrial settlements i.e. automobile, agricultural practices, textile, packaging, and household with the highest annual consumption of 1 MMT tons than other materials [2]. Thus, the huge production and consumption of plastics have granted the status of the current era as the plastic age is the best tribute to the discovery of macromolecules for the advancement of society. Further, the extension and synergized impact of this theory has also boosted up the advances of the other area like aero-space, biomedical device, electronic and life style due to the advantageous features of polymer i.e. light weight, processability, durability, dielectric strength, chemical impotency, and cost-effectiveness. In the above context, the novelty of macromolecules established its suitability as the material backbone of several industries excluding electronic and electrical devices due to their inherited electrical insulation and unresponsive nature. However, the fundamental discovery about the electrical conductivity in polymers i.e. polyacetylene by Alan, Heeger, and Shirakawa in 1977 after doping of halogen has forcefully claimed its applications in electrical and electronic devices viz. solar cell, light-emitting diode, super capacitors, and sensing devices [3, 4].

Furthermore, the natural examples of chemical, physical, and bio sensing after using different biological macromolecules like polysaccharides, proteins, and lipids have inspired scientists to use pristine and hybrid macromolecules to develop the selective interactivity towards interacting analytes to produce induced optical, mechanical, and electrical responsiveness. Thus, the polymer with optimized structure, responsiveness, and interactivity, proposed 100-year backs have laid down the foundation to design and develop the different classes of sensors with unexplored properties for use in analysis, monitoring, coordination, and control. This story of success, failure, and future requirements has been initiated to establish through this article in order to highlight the merit, demand, and need of macromolecule for sensing sciences. The attempt has been also made to incorporate all the significant contributions published on the topic but may be possible for oversight of a few significant discoveries.

2 Macromolecular Theory and Historical Advances

This theory was the cumulative impact of the advance in analytical tool i.e. x-ray diffractometer based mathematical calculation along with observed drawbacks of aggregation theory proposed for structural interpretation of naturally occurring high molecular mass colloidal molecules like silk and cellulose by Grahm in 1861 through self-assembled existence due to non-directed π–π interaction [5]. In this regard, the substantial and convincing XRD data for the polymer i.e. hydrogenated rubber and cellulose confirmed the existence of covalently linked structural identity of larger monomeric units cell in high molecular mass compounds. Thus, the evidence supported the structure of a high molecular mass compound with a larger unit is the basis for the macromolecular theory of Staudinger. The diffraction proposed and covalently linked structure of natural rubber is shown in Fig. 1 along with the photograph of Staudinger.

Further, the x-ray diffraction derived data best fits into the crystallographic unit cell to constitute the giant molecule and later the term “macromolecule” was coined by Staudinger to explain the structure of polymeric materials after correlating the evidence like viscosity and the molecular weight. In an example, in 1923, Brill has correlated the crystallographic study on silk fibroin with varying its molecular weight between 500 and 600 g mol$^{-1}$ [7]. Further, this sustained extension of bifunctional monomers i.e. isoprene into the longer chain-like structure has

![Fig. 1 Photograph of Hermann Staudinger with the proposed structure of natural rubber [6]](image-url)
been also confirmed as macromolecules by the method “uber polymerization”. Further, the theory was successful to explain and predict the structural features of several naturally occurring polymer and laboratory-prepared macromolecules. After that, the macro molecules become a hot and vibrant class of materials with the potential to design and synthesize materials with the extended chain after covalent linking of well-established stable molecules. However, the certificate for the importance of these discoveries has been confirmed through the noble prize of chemistry in 1953 for this breakthrough discovery, which the currently sustained as the giant competing field in materials sciences. Further, the progress of this discovery moved horizontally in verifying the newer naturally occurring molecules as macromolecules as well as to synthesizing newer macromolecules with noble properties to replace several naturally occurring compounds like shellac and ivory. Bakelite was first synthesized as polymer by the scientist at the beginning of the 19th century with the objective of capitalization on the shortages of naturally occurring shellac which was used to insulate electrical cables [8]. Further, with time several other synthetic polymers like nylon, polypropylene, polyvinyl chloride, polyethylene, polymethyl methacrylate were prepared to fulfill the materials demand during the industrial revolution by western countries and leading industries like Dupont.

Another, breakthrough in the preparation of polymer appears with the discovery of Karl Ziegler and Giulio Natta in the form of hybrid catalyst from the salt of transition and alkali earth metals, which were called “Zigler Natta Catalysts”. This catalyst was prominently used in the polymerization of olefines like polypropylene with stereo structure regularizations and effective methodology as well as yields [9]. In the progress of macromolecules, another turn took place with the discovery of electrical conductivity after doping of halogen i.e. iodine in polyacetylene after using Zeigler Natta catalyst. Thus, polymer integrated with electrical conductivity opened the applications of polymers in electrical and electronic devices like solar cells, light-emitting diodes, supercapacitors, physical and chemical sensors. The important reported conducting polymers are polyaniline, polypyrrole, polythiophene, and PEDOT with different morphology, variable conductivity, and interactivity [10]. Furthermore, the synergism of electrical conductivity with functionality and responsiveness due to encapsulation of metal oxides, grafting biopolymer has significantly improved their applications in the sensing sciences in terms of sensitivity, selectivity, and sensing mechanism [11]. Shukla et al. reported electrically conducting ternary bio nano composite with catalytical nature towards sensing paracetamol after measuring the potential generated after catalytical surface oxidation in the presence of iron oxide [12]. However, the presence of biocompatibility makes conducting polymer suitable for a biochemical reaction for the fabrication of biomedical devices and biosensors. Furthermore, the field of macromolecule is so wide to squeeze the total contents in defined format and length of the manuscript but the brief developments are presented to correlate the fundamental discovery in polymer chemistry, basic macromolecular theory, and physical properties to bring a concise picture about the impact of development in macromolecules in sensing science and technology for common researchers and technocrat.

3 Overview on Macromolecules as Sensing Materials

In general, the development of sensors is a naturally inspired phenomenon after exploiting the different macromolecules with multiple properties for the chronological evolution of different types of sensors for industrial, household, and point of care applications [13]. The initial development of industrial sensors is related to semiconducting devices like silicon-based p-n junction using classical materials, which bear variable properties towards temperature, pressure, chemicals, and biochemicals [14]. However, the innovation in electrical conducting along with functionality and processability in macromolecules encourages the use of polymers in sensing science as membrane, electrode, and absorbent for several physical and chemical responses. The initially, the NAFION, a per fluorinated hydrophobic polymer depicted in Fig. 2, with cluster of ions has been explored as membrane for electrochemical sensors.

The innovation in the principle and polymerization techniques has evolved several features like branching, morphology, and crystallinity in the polymer molecules. The different explored methods of polymerization are i.e. chemical, electrical, mechanical, thermal and photo polymerization are explored for the preparation of different polymers with tunable structure, molecular arrangement, and segmental blocks.

![Fig. 2 Chemical structure of Nafion](image-url)
These methods are used to prepare pristine, hybrid, and doped polymers with controlled dimension, optimized size, and morphology after using different polymerizing as well as crosslinking agents. The basic purpose of cross-linking agents is to improve high thermal and physical stability after inducing the formation of chemical bonds between polymer chains and blocks, however, the excess use of cross-linking agents also reduces the properties. Currently, the cross-linking agents are also used to modify the lattice strength and surface properties for encapsulation of enzymes, electrostatic interaction, solubilization, and surface interacting nature during biochemical applications [15].

For example, Shukla et al. have grafted the polypyrrole chain with chitosan in a micellar structure after using chemical polymerization, under optimized chemical bath, physical condition, and polymerizing agents [16]. The prepared polymeric hybrid nano structure was found suitable for opto-chemical sensing of urea after immobilizing the urease enzyme. Furthermore, the different templates are used to control the size and the morphology of polymers along with uniform dispersion of fillers to improve adsorption capacity, interacting nature, and chemical functionality [10]. In this regard, Rastogi et al. have reported the electrochemical polymerization of polypyrrole in the presence of different surfactants. The nature and functionality of surfactants control the morphology, functionality, conductivity, and polymerization kinetics [17].

However, the contemporary advances in semiconducting properties, selective functionality, and chemical modification have propelled the MM in the fabrication of different sensors and its advances for designing and developments of different sensing devices. In this continuation, the advances in polymeric properties have been also integrated the different polymeric materials electrochemical responsiveness, aligned conductance, multichannel interaction along with inspiration from natural polymer sensor has explored their innovative uses in sensing sciences [18]. For example, the effectiveness of polymers in humidity sensing has been explored to use in breath monitoring due to quacking switching in responsiveness at different humidity levels [19]. Some more polymer-based sensors are given in Table 1 along with advantageous features and applications.

Furthermore, the chemical engineering used in the manipulation of the macromolecules is the chemical modification, grafting, composite formation, shape optimization, dimension alignment, size confinements, and structural optimization in the term of physical, chemical, mechanical, optical, and electrical features to make it fascinating for designing and fabrication of the wide range of physical and chemical sensors. The basic optimized properties explored for sensing science are flexible due to the longer chain of carbon bonds, biocompatibility, functionality in the side chain and active sites along with responsiveness behavior due to tunable electrical conductivity [13, 20]. These modifications in MMVs develop several properties for the fabrication of different types of sensors after using macromolecules and transducers (Fig. 3).

In general, the sensor consists of two parts one is actuators and other detectors, in both parts the properties of macromolecules are substantially updated due to their responsive and communicative properties. Although the sensors are very old measuring devices like temperature for human health, humidity for rain prediction current era hardly any area is untouched with the use of macromolecule-based sensing devices. Initially, the polymer was considered non-responsive for sensing due to its long-chain, non-interacting, chemically stable, and insulating nature. However, in course of time, chemical treatment like plasma treatment made the macromolecule prone to interact with environments to sense chemicals present in the neighborhood due to improved wettability, adhesion as well as biocompatibility [21].

Table 1 Natural sensors and their applications

| Name          | Transducer          | Polymer                  | Features                                                                 | Application                        |
|---------------|---------------------|--------------------------|---------------------------------------------------------------------------|------------------------------------|
| Nerve cells   | Electrical          | Chemically modified protein | Electrical excitations can propagate in the form of action potentials      | Control in body function           |
| Chlorophyll   | Optical             | Metals and porphyrin     | Radiation-induced water splitting at the defined condition                | Formation of glucose and oxygen    |
| Photoreceptor | Molecular recognition | Phototropin               | Natural radiation simultaneously activates more than one photoreceptor in higher plant | Chloroplast reorientation          |
| Ion channels  | Mechanical          | Mechanosensory neurons   | Turgor control in plants, and touch and hearing in animals                | Cell growth                        |
| Neuron        | Thermal             | Temperature sensory neuron | Triggers the nervous response with change in temperature                  | Controls the heat preserving mechanism |
| Chemoreceptors | Celia and olfactory cells | Nervous response        | Stimulate a combination of different neurons                              | Taste and smell                    |
The grafting and developing composite are also used to evolve the properties like ion exchange capacity, conductance, and porosity in hybrid polymers for sensing applications [22]. The grafting of polymer with other one adds different polymer chains through covalent bonding to develop flexibility, porosity as well as functionality due to multiple constituents. The grafting of biomolecules to conducting polymer along with preparation of different types of composites evolves the functionality along with biocompatibility for different classes of sensing like glucose and urea. In an example, Shukla et al. have grafted cellulose with polypyrrole to develop improved flexibility along with porosity for wider range electrochemical humidity sensing due to enhanced adsorption capacity [23]. The incorporation of metals and metal oxides is the other dimension for improvements in sensing ability due to improved interactivity, adsorption capacity, porosity, and electrical properties. The presence of a metallic center also allows the effective catalytic behavior and electron transfer capacity for sensing several gaseous molecules like ammonia. In an example, the presence of ZnO in the matrix of polyaniline allows Lewis acid-base types of interaction for effective ammonia sensing ppm concentration ranges due to protonic doping and undoping nature [24]. The presence of metallic center also advances the catalytic behavior in polymer matrix along with aligned conducting in electrically conducting bio-composites. This catalytic behavior integrated electrically conducting bio-composite was reported suitable for potentiometric sensing of residual paracetamol sensing in hospital waste water and mechanism lying in paracetamol sensing is illustrated in Fig. 4 along with brief finding [12].

Furthermore, another contribution of macromolecules in sensing is due to advancements of conducting polymers as well as functionality in biopolymers after chemical treatment, surface optimization, and dimensional control. In an example, the preparation of polymer and clay composites develops porosity and ion exchange capacity along with the interacting ability for sensing applications [25]. The sensing behavior is also dependent and structure-oriented properties of MMs evolved due to structural heterogeneity, which develops short-range structural alignment in the hybrid matrix for effective conduction of sensing response. In an example, the evolution of p-n junction type hybrid structure in the composite of zinc...
Fig. 4 Chemical engineering steps to modify macromolecules

Fig. 5 Evolution of interacting surface for humidity sensing [20]
oxide and polyaniline are evolved due to Lewis acid and base type structure in the composite as illustrated in Fig. 5. This hybrid structure exhibits a reduced band gap and was found suitable for efficient humidity sensing in a reversible manner and wider ranges [26].

The optimization in the microstructural change in polymer surface has been also explored for the development of super selectivity for different analytes. The basic adopted strategies are functionalization and molecular imprinting (MIP) on polymer surface during polymerization of a functional monomer using a selective molecules-based template under optimum conditions [27]. In MIP, the functional monomer is polymerized using different techniques in the presence of target templates and a cross-linking agent. Initially, the precursor was functionalized through covalent and noncovalent interaction between template and monomers. Further, the precursor monomer was polymerized after using a suitable polymerizing agent at an optimum temperature and solvent [28]. Further, the templates were removed, which develops a highly selective interactive structure for water purification and effective sensing of different analytes using molecular lock and molecular key types selective enzyme-like mechanism [29]. Multiple functionalities in polymer have been also developed using composite imprinting material, segment imprinting strategy, and dummy imprinting strategy. In an example, Zhou et al. have demonstrated the molecular imprinting of polymer over SiO₂ coated CdTe quantum dot with fluorescent properties for effective sensing of antibacterial medicine i.e. sulfadimidine in the range of 10–60 µ mol L⁻¹ with good recovery present in the real milk samples. The preparative scheme of molecular imprinting along with constituents is depicted in Fig. 6 along with its fluorescent nature [30].

4 Macromolecules Based Sensors

The chemically-modified and structurally induced synergistic impact in macromolecules is the key to providing a novelty in the design and development of different types of sensors i.e. physical, chemical sensors, and biosensors. The brief classification of the polymer-based sensor is given in Fig. 7 to explain the holistic impact of macromolecules in sensing sciences.

5 Physical Sensors

The basic strategies explored in physical sensing are the monitoring of different induced physical properties like thermoelectricity, piezoelectricity, and pyroelectricity. In this context the porous, flexible and responsive nature of macromolecules and its hybrid forms like hydrogel, micelle, nanostructured polymers, aerogel, and xerogel has huge potential. The processability of polymers to make a film, coating, beads, and sheets, along with surface stability are other additional properties of polymers to be explored in sensing of temperature, pressure, magnetic field, and electromagnetic radiations [31, 32].

The basic principle for temperature sensing is based on the “Peltier–Seebeck effect”, which converts the temperature into electricity. In general, this effectiveness of materials is dependent on the fermi energy and electrical conductivity, which are broadly categorized in dynamic, static, active, or passive according to used macromolecules. The innovation of active nature in composite produces selective oxidizing ability for interacting molecules with change in temperature and has potential in measuring several biochemical reactions as nano calorimeter. Furthermore, the incorporation
of polyelectrolyte nature in macromolecules significantly improves the Seebeck property to overcome the poor conductivity. The composite of a polyelectrolyte, poly(4-styrene sulfonic acid) (PSSH) or poly(sodium 4-styrene sulfonate) (PSSNa), is coated on conducting polymer poly(3,4-ethylene dioxythiophene) synergistically improves the Seebeck coefficient and electrical conductivity 43.5 µVK⁻¹ and 2120 S cm⁻¹ respectively [33]. This structurally synergized hybrid structure of macromolecules also has been explored in effective sensing and monitoring of temperature. The effect of temperature on transistors is a well-established phenomenon and has the potential for temperature sensing. Therefore, polymer-based organic transistors are frequently used for temperature sensing for different ex-situ and in-situ applications with the potential of blue tooth connectivity remote monitoring [34]. Ren et al. has designed unimorph hybrid material from polylactide acid and poly(tetrafluoroethylene) with the potential to convert wind into electricity (0.49 mW) to serve a self-powered low energy blue tooth system. The hybrid also exhibits the change in resistance with temperature for monitoring of change in environmental temperature as a fire detection system [35].

The synergistic approach of mechanical and thermal transitions is explored for efficient sensing of temperature and pressure as a material for soft electronics. In an example, the composite matrix comprised of polydimethylsiloxane filled with universally dispersed nano-sized carbon black and silver platelets is suitable for sensing temperature and pressure based on a wheat stone bridge with excellent compression and release cycle and response time of 52 ms [36]. The optimization in flexibility is also possible through grafting with natural polymer as well as preparing electrostatically stabilized different colloidal structures viz. hydrogel, xerogel, and aerogel. In this regards Zhao et al. have prepared a stretchable and compressible polymer composite aerogel from poly(3,4-ethylene dioxythiophene), poly (styrene sulfonate), and polyimide using integrated freeze-drying and thermal annealing techniques in a controlled constituents ratio. The aerogel exhibits the ordered interconnected porous structure along with excellent compressibility, linear piezoresistive responses at different strains with appreciable reproducibility for 200 cycles with the potential to be used as pressure sensors in harsh environmental conditions [37]. The illustrative explanation of cyclic compressibility along with structural deformation under loading and unloading compression has been illustrated in Fig. 8.

The monitoring of magnetism is an essential tool for most engineering disciplines i.e. automobiles, military, robotics, medical devices, space, geophysics, and industrial measurements, which works on the basis of hall measurement, magneto resistors, and magnetic interference [38]. The flexibility along with heterogeneity in polymer has been widely used for magnetic sensors and several magnetic sensors are commercialized for different electrics and biomedical applications like magneto mammography for muscular motion. The polymer composite with magnetic properties was explored in the sensing application after exploring magneto rheological properties with targeted applications [39, 40]. These polymer-based magnetic composite has been also explored for sensing magnetically active molecules as well as removal magnetic water pollutants like arsenic effectively [41]. Furthermore, the dual active polymer properties for the detection of the photon (light particle and magnetic force) are extensively explored by several scientists using polymer hybrid structures having photovoltaics and magnetic activities in their matrix. Both properties are related to the

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Fig. 7 Different types of polymer-based sensors
arrangement of electrons i.e. paired or unpaired and energy required for their transition for different orbitals, which are optimized by either doping or making composites. The addition of iron oxide has made a polymeric structure magnetically active as well as suitable for magnetic sensing purposes with good parameters. These sensors bear several advanced applications like molecular switches for blading and UV cure in biomedical applications [42], spectroscopy, pulse laser measurement [43], and selective luminescence sensing responses [44]. Some other important polymeric structures used in sensing physical parameters are listed in Table 2 along with their brief descriptions.

6 Chemical Sensor

This class of sensor includes sensing of different gas, metals, organic vapors, explosives, pharmaceuticals, pesticides, and hydrocarbon using selective properties of material i.e. adsorption, catalysis, adsorptive degradation, pi-pi interactions along with electrical and optical responses. Chemical functionalization, structural optimization, doped heterogeneity, and optimized porosity are inherited as well as optimized properties of polymers for their use in chemical sensing. The ordering in bandgap and aligned electrical conductivity also supports quick sensing after using the polymers and their composite [55]. In an example, Shukla et al. has reported the evolution of the carbonyl group in chitin after grafting with polyaniline under optimum conditions. Thus, the obtained polymer-based composite matrix was reported suitable for sensing of cupric ion in trace level after monitoring the induced potential developed after interaction of cupric ion and chitin grafted polyaniline [56]. The explored potentiometric setup was shown in Fig. 9 along with mechanism and sensing parameters.

However, for gas sensing surface adsorptive sites are required for effective sensing of different atmospheric gases. For example, the important property for humidity sensing is hydrophilicity, and the presence of hygroscopic or hydrophilic sites enhances the relative humidity sensing properties. Shukla et al. have increased the humidity sensing range of PANI after grafting with cellulose as well as encapsulating the metal oxides like ZnO and TiO2 for efficient wider range humidity sensing. The presence of transition metal in the matrix of conducting polymer provokes the electron transfer interaction from basic gases like nitrogen of ammonia to lewis acid metal ion bearing vacant d orbital, thus formed composite was used in sensing of ammonia sensing with efficient parameters [24]. The presence of Lewis acidic character in metal and base character in acid generates the formation of hetro-junction like matrix, which is suitable for sensing several gases like hydrogen sulfide, LPG, ammonia, and humidity. Although, the sensing of these gases is the practice in past centuries like humidity for prediction of environmental conditions, in recent times several advanced features are explore for their application.
Table 2  Polymer-based physical sensors

| S. No. | Composition | Analytes | Sensing behavior | References |
|--------|-------------|----------|------------------|------------|
| 1      | Polystyrene sulfonate sodium salt, poly-diallyl-dimethyl-ammonium chloride, multiwalled carbon nanotubes and poly (vinylidene difluoride) | Strain | Improved gauge factor by 9.8 ± 0.3 | [45] |
| 2      | Poly(3,4-ethylenedioxythiophene) and poly(4-styrenesulfonate) | Temperature | Linearity 99.86%, sensitivity 658.5 Ω/°C, and temperature range of 30–40 °C | [46] |
| 3      | Stimulus responsive polymer hydrogels | Pressure | Bio sensitive with quicker response time | [47] |
| 4      | Silver/polypyrrole | Physiological signals | Strain gauge factor (≈ 21 for 18–20 strain) and pressure sensitivity (≈ 0.58 kPa−1 in 300–400 Pa) | [48] |
| 5      | Iron oxide embedded polyester | Magnetic field | High dielectric constant i.e. 78 and tangent loss of 0.45 at 100 Hz | [49] |
| 6      | Poly(l-lactic acid) and poly(tetrafluoroethylene) | Temperature | Nano generation with open-circuit voltage, short-circuit current ≈ 140 V and 16 µA | [35] |
| 7      | Poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) | Temperature | High-temperature sensitivity − 0.77% °C−1 between 25 and 50 °C with excellent stability in 30–80% RH | [50] |
| 8      | Glycerol and polyvinyl alcohol | Temperature | High sensitivity, short response time to temperature, and excellent accuracy under severe weather conditions | [51] |
| 9      | N-(3-trimethoxysilylpropyl) pyrrole monolayer | Pressure | Tuned sensitivity from 0.03 to 17 kPa−1 with varying diameters | [52] |
| 10     | Polymer optical fibres | Pressure | Improved sensitivity and low hysteresis | [53] |
| 11     | Poly(N-isopropylacrylamide)-based hydrogel | Hydrodynamic pressure sensors | Wide detection range with high sensitivity | [54] |

Fig. 9  Chitin-grafted-polyamine based potentiometric copper ion sensor [56]
like monitoring breath rate by humidity and soil index by ammonia. A simple proposed functional self-powered mask for breath monitoring was reported from silica and cellulose nanofiber-based three-dimensional nanostructure high surface area and electron attracting capacity. The composite was used for effective breath monitoring of humans and the illustrative scheme is shown in Fig. 10 [57].

The other class of chemical sensing over polymer matrix are organic vapors and molecules, which are performed through different interactions like π-π interaction due to the nature of polymers and analytes. The interaction generates different induced sensing responses like ions, fluorescence, and induced color impact after surface elective interaction of vapors over sensing substrate [58]. In an example, Temel and Ozyaytekin have prepared polybenzimidazole coated quartz crystal using electrospinning techniques. The modified crystal was explored in sensing of hydrocarbon vapors of toluene and ethylbenzene in the ppm level concentrations i.e. 1–10 ppm with effective sensing parameters like detection limit 0.41 ppm for toluene and 0.45 ppm for ethylbenzene [59].

Table 3  Polymer-based chemical sensor along with sensing parameters

| S. No. | Composition                                   | Analytes          | Sensing behavior                                                                 | References |
|-------|-----------------------------------------------|-------------------|----------------------------------------------------------------------------------|------------|
| 1     | Cerium(III)-melamine coordination polymer     | Explosive         | Unique spectral fluorescence signal at 400, 700, and 785 nm for TNT vapor         | [60]       |
| 2     | Chitosan-grafted polyaniline                  | Malathion         | Range 62.5–2.0 µM, sensitivity 2.26 mV µM⁻¹ cm⁻², detection limit 3.8 µM, response time 8.0 min, and recovery time 30 s | [61]       |
| 3     | Nickel oxide intercalated chitosan-grafted-polyaniline | Lead            | Sensing range of 1.0 × 10⁻⁶ M⁻¹ × 10⁻³ M, sensitivity 0.2379 mV µM⁻¹ cm⁻², limit of detection 3.8 µM and stability for 64 days | [62]       |
| 4     | Iron Oxide Encapsulated in Chitosan-Grafted-Polyaniline | Paracetamol     | Sensing range 5–100 µM, limit of detection (LOD) 5.7 µM, response and recovery time of 50 and 20 s | [12]       |
| 5     | Cupric oxide/polyaniline                      | Humidity          | Sensing range 10–95, response time 40 s, and recovery time 55 s                 | [63]       |
| 7     | Zinc oxide encapsulated polyaniline grafted chitosan | Urea            | Self-activating with a detection limit of 29.84 ppm                             | [64]       |
| 8     | Nickel oxide encapsulated polypyrrole         | H₂O₂              | Sensing ability in both gas and liquid with excellent sensing parameters like the limit of detection 0.073692 ppm in gas and 0.073649 ppm in the liquid | [65]       |
| 9     | Polyethylene and ZnS                         | Hydrazine         | The efficient and high sensitivity of ~89.3 µA cm⁻² with a detection limit of 1.07 µM | [66]       |
| 10    | Chitosan and dipeptide                       | Ochratoxin A      | The linear range of 0.1–100 ng mL⁻¹ and detection limit of 0.03 ng mL⁻¹        | [67]       |
| 11    | ZnO, polyvinyl alcohol and polypropylene     | H₂S               | Enhances the electronic characteristics for chemical sensing                     | [68]       |
Some other significant polymers-based gas sensing materials are listed in Table 3 along with brief details of sensing behavior.

7 Biosensors

Screening and quantification of the different biomolecules using a biological molecule or biologically derived components in combination with a transducer are explored worldwide to enrich analytical and biomedical sciences employing the different polymers with biocompatible nature. In general, the polymer provides suitable surface properties for immobilization of enzyme, interactive as well as adsorptive sites for different biomolecule i.e. metabolites, biological components, and metabolic regularity molecules related to health issues and conditions. The enzyme immobilization is used to achieve improved stability, activity, and reusable of enzymes for various applications of different enzyme surface reactions under harsh conditions like pH and temperature. The enzymes are immobilized through binding, entrapment, and cross-linking after using a suitable mediating agent. The immobilization by binding can be physical, ionic, or covalent, while entrapment of enzyme is by the polymeric network, however, the crosslinking is either by aggregation or crystal formation using a bifunctional group. The use of stabilizing agents like ethylene glycol, polyethylene glycol, trehalose, dextran make the enzyme use even at pH 10 with excellent activity. Thus, the synergistically bounded enzyme and polymer substrate has been explored in different industrial applications like the distillery, water purification, and biosensing of different organic compounds [69]. Generally, in biosensors, the use of biopolymer provides biocompatibility and optimized isoelectric point, while the conducting polymer effectively channelizes the induced electrical impulses from transducers to detectors for effective sensing of biomolecules such as glucose and urea [16, 70, 71]. The structural optimization of macromolecules is another dimension in improving the properties of macromolecules to optimize surface reactivity, conductivity, and porosity. In an effort, Shukla et al. has prepared micellar structure from polypyrrole after grafting with chitosan having self-reporting properties for effective optical sensing of urea in the range 0.01–30 mM and sensing response for a few seconds. The scheme of preparation and basic involved principle during optical sensing of urea after immobilization of urease is shown in Fig. 11 [16].

Synergism in sensing and delivery is another noble aspect in biomedical advances with the capability to deliver medicine at selective sites along with control of side effects. The terminologies are called theragnostic, in this dimension multifunctionality of polymers are successively used.
for sustainable drug release in the cure of serious diseases like cancer as well to provide supplements to the body [72, 73]. The other area for biosensing is monitoring biological active water pollutants like pesticides and pharmaceuticals. The presence of these organic pollutants is not only reported in water bodies but also in different edible products including fruit and vegetable. In this regard, the enzymes are used to hydrolyze these molecules for sensing of different biomolecules selectivity and the resultant hydrolysis products were generate induced current and potentials for efficient sensing. The instability of enzyme and biological components has encouraged scientists to explore the nonenzymatic routes for biosensing using selective catalyst and molecular imprinting techniques. In this context, Singh et al. has prepared NiO encapsulated polyaniline nanocomposite for effective nonenzymatic sensing of glucose present in biological fluid and fruit juices with comparable properties of the standard commercial method [74]. The sensing setup and brief results are shown in Fig. 12 with the brief mechanism.

Furthermore, the induced functionality in polymer composites is also exhibited selective reactivities, lab on a chip, bioreactor towards sensing of different pharmaceuticals, organic molecules, and infectious microorganisms like virus and bacteria [75]. Some important macromolecules-based biosensors are compiled in Table 4 along with their technical details.

8 Integrated sensors

Integration of sensing component, transducer with action is another innovation for developments in smart sensing sciences with synergized properties like multifunctionality, reproducible, self-calibration, communication, multiple sensing for a wider range of applications due presence of multifunctional properties in polymers and their hybrid structure [89]. This class of technology integration of sensing with action enriches problem-controlled analysis for improvement in biomedical, food processing techniques, and agricultural practices. In this regards, the self-reporting materials along with multifunctionality in different polymeric structure and assembly such as hydrogel and micelle are promising tools for this type of advanced sensing applications with action like on-site drug delivery with the lesser side effect, prediction of communicative disease using several polymers, release microbial suppressant and release soil micronutrient on requirement [90, 91]. In an example, the biocompatible chitosan-based beads were prepared after gamma radiation-induced copolymerization with the porous, high swelling index of 426% and pH-responsive nature. The hydrogel beads were explored for effective localized delivery of Doxorubicin an anticancer agent under a controlled manner by 81.33% for localized

![Fig. 12 Nonenzymatic PANI-based glucose sensing in fruit juices [74]](image-url)
cancer therapy [92]. This concept of curing specified organs for the particular problem is referred to as the point of care concept for several advanced applications in biomedical science like drug delivery, organ transplants, and tissue engineering. This concept of integrated sensing and delivery of drugs for therapy is referred to as an advanced tool in biomedical science called theragnostic, while the same concept of point of care is also used in the field of packaging and agricultural practices. In the field of packaging, these types of packaging are referred to as smart packaging to deliver antimicrobial agents on the requirement to extend the self-life or indicate the quality of packed items. In this regard, Shukla et al. have extracted the carboxylated cellulose in greener routes. Further, the packaging film was developed from blending of extracted cellulose and polyvinyl alcohol, thus obtained film was found suitable for the release of carbon dioxide in the presence of hydronium ions to preserve the meat product from microbial degradations. The brief extraction, and application of developed film was depicted in Fig. 13 [93].

The vaporization of gases from the soil is the indicator for the presence of precursor molecules in soil like the formation of ammonia after decomposition of nitrogenous fertilizer like urea. This type of point of care application is not only suited for quantifying the presence of ammonia but assists an agriculture scientist for fertilizer retaining capacity of soil as well as to supply at time need. In this regard, Shukla et al. have reported resistive type ammonia sensors from ZnO and PPY nanocomposite for portable sensing of ammonia for estimation of volatile ammonia from the soil with good sensing parameters and stability for 90 days without the aspect of supply the micronutrient [94].

The brief representation of the sensing properties of representative polymer-based biosensor is summarized in Table 4.

| S. no. | Composition                  | Analytes                  | Sensing behavior                                      | References |
|-------|-----------------------------|---------------------------|-------------------------------------------------------|------------|
| 1     | ZnO and Polyvinyl alcohol   | Glucose                   | Tuneable potential with efficient parameters i.e. detection limit of 0.2 mM | [76]       |
| 2     | Indenoquinoxalinone based conjugated polymer | Laccase                   | The linear range of 0.005–0.175 mM, the limit of detection of 9.86 µM, and sensitivity of 153.6 µA/VmMcm² | [77]       |
| 3     | 1, 3, 6, 8-Tetraphenylpyrene and α, α’-dibromo-p-xylene | Trace ampicillin         | Limit of detection of 1.33 fg mL⁻¹ (3.30 f. M) with pi-pi inter-cation | [78]       |
| 4     | Bi-functional PEDOT         | NADH and lactate          | The linear range of 20–960 µM, the detection limit of 2.04, and sensitivity of 0.224 µA µM⁻¹ cm⁻² at the PEDOT-COOH50% interface | [79]       |
| 5     | Alginate based hydrogel     | E-coli                    | Rapid and cost-effective with better parameters like the limit of detection 10² colonies forming unit per mL | [80]       |
| 6     | Chemically treated polyvinylchloride | Ethanol                  | Sensing range 0.01–42 mM, the limit of detection (LOD) of 0.0001 µM and stability for of 180 days at 4 °C | [81]       |
| 7     | PVC Membrane                | Antileukemia Drug Cytarabine | Linear range of 1.0 × 10⁻⁶–1.0 × 10⁻³ M at pH 2.8–4 with a detection limit of 5.5 × 10⁻⁷ M | [82]       |
| 8     | Polystyrene                 | SARS-CoV-2 antibody       | Sensitivity lower than 25 PFU/mL                      | [83]       |
| 9     | Glycol-modified polyethylene terephthalate | Dopamine                | Excellent substrate for fabricating the electrode with good sensitive parameters                   | [84]       |
| 10    | Cu/chitosan/Phosphorus      | Hydrogen peroxide         | Sensing range of 10 µM–10.3 mM and limit of detection 0.390 µM.                                      | [85]       |
| 11    | Au, Chitosan and Phthalocyanine | Catechol                 | Surface-induced sensitivity with detection limit 8.55 × 10⁻⁴ µM                                      | [86]       |
| 12    | Silver, Chitosan and reduced graphene oxide | Glucose                  | Linear response for glucose sensing in the range from 0.25 to 25 mM with a detection limit close to 53 µM | [87]       |
| 13    | Alginate and methacrylate   | Bacteria                  | Fluorescence based whole-cell sensor for bacteria                                                   | [88]       |
sensing of humidity in exhaled and inhaled gases for monitoring of breath rate at the precise level. A simple functional mask on this principle was developed by Wang et al. for monitoring the breath rate after monitoring the humidity level. The developed mask and parameters are exhibited in Fig. 14. The change in humidity level of exhaled gas also indicates the dehydration process going during breathing out due to the presence of different organic vapor like alcohol [95].

The monitoring of active sensing properties from remote or mobile is another important area in sensing science after employing polymer substance, in this context, the conducting polymer has played and significant contribution in terms of providing data in remote places using simple electronic gadgets and software like Arduino. The other areas of integrated monitoring are environmental fluctuations, electrical faults, oceanic disturbance, and biomedical information for telemedicine to cure patients and ratification for integration of diagnosis and treatment [90, 96, 97]. Some important integrated multifunctional sensors prepared by polymeric structure are listed in Table 5 along with significant features.

The integrated sensor with action is a newer area for sensing and recovery of different heavy metals present in water, soil, and different edible items like fruits, seafood, and vegetable. In this context, Shukla et al. have reported a chemically functionalized ternary composite of PANI for effective extraction and recovery of lead and mercury present water in the soil by the effective percentage of 84% and 78% [110]. The proposed experimental setup and scheme for extraction of Hg $^{2+}$ ion over chitosan grafted polyaniline is shown in Fig. 15 along with brief data of sensing and extraction.

Although the integration of sensing and action is an integral part of the different natural and biological phenomena in practical technology forum it needs to be more intensively conceptualized and commercialized for the advancement of different sensing and control phenomena like medical, defense, agriculture, and atmosphere. The integration of sensing information is another equally important area for using international resources and expertise for the safety and sustainability of human settlements. The representative important area that needs to be integrated is depicted in Table 6 for advancing the materials and technology with the objective of sustainability.
### Table 5  Polymer-based integrated sensors

| S. No. | Polymers                                                                 | Analytes                              | Transducers  | Features                                                                 | References |
|--------|--------------------------------------------------------------------------|---------------------------------------|--------------|--------------------------------------------------------------------------|------------|
| 1      | PEDOT: PSS and reduced Graphene                                           | Pressure and anti-electric shock      | Electrical   | Hydrophobic, conducting, durable, and protection from em waves          | [98]       |
| 2      | PEDOT: PSS                                                               | Ammonia and anti-open sensors         | Electrical   | Wireless energy harvesting, data processing, and transmission by standard interfaces | [99]       |
| 3      | Poly(vinylidene undecatri- fluoro-ethylene)                              | Stress and human mechanical stress    | Piezoelectric| Self-powered e-skins and multifunctional wearable micro-/nano-electronic devices | [100]      |
| 4      | Oligoamine and PEG                                                        | Temperature and electricity           | Electrical   | Wireless controlled triggered delivery of dexamethasone                  | [101]      |
| 5      | Cellulose, poly(ethylene glycol), and methyl ether methacrylate          | pH and biological condition           | Optical      | Anisotropic polymer-based chemical responsive drug delivery system for cancer therapy | [102]      |
| 6      | Polymer-Based Superstructure                                             | Bovine serum albumin                  | Mechanical   | Biosensor with antibacterial nature                                   | [103]      |
| 7      | PAA-RGO-PANI based hydrogel                                              | Growth sensor, and ammonia r          | Mechano-electrical | Self-powered plant-wearable sensor for integrated plant growth   | [104]      |
| 8      | Polyacrylamide, dialdehyde β-cyclodextrin, and gelatine                   | Stress and pressure                   | Mechanical   | Wearable sensor to monitor human motions i.e. joint movements and other subtle motions like pulse and speaking | [105]      |
| 9      | Polydimethylsiloxane                                                     | Pressure                               | Mechanical   | Different pressures controlled structural deformation for examining blood vessel health | [106]      |
| 10     | Gelatine/Carrageenan                                                     | pH                                    | Optical      | Antimicrobial to monitor the freshness of packed milk                  | [107]      |
| 11     | Electroactive polymer                                                    | Pressure and attenuated force         | Electrical   | Human like précised griping control in robot and tactile sensing       | [108]      |
| 12     | Carbon coil, poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonate) | Temperature and strain                | Electrical   | Self-powered type strain and temperature dual functional sensor as flexible devices and e-skin applications | [109]      |

**Fig. 15** Integrated sensing and recovery mercury from soil [110]
The integration of electronic, polymer processing, responsiveness, and analytical chemistry develops advanced miniaturized analytical devices for effective screening and sense of different chemical, biochemical, metabolites, DNA, and reaction products [111]. This technique also called microelectromechanical systems as well as micro total analysis systems, explores several polymer-based composites along with microfluidics technology for a single specific test for chemistry, biology, cellomics, proteomic, and manufacturing technology [112]. The processability, chemical stability, variable electrical conductivity, and multiple functionalities are the basic features of macromolecules for use in the development of polymer-based lab on a chip [113]. Advances in processing and integration techniques also explored the applications of LOC for biochemical testing as non-invasive technology. A simple LOC was reported by Ahn et al. for testing of unbound cortisol in human saliva after exploiting fluorescence technology. The sensing of cortisol was based on the measuring of fluorescence intensity using a series of the microchannel in the dynamic range of 7.0 pg mL⁻¹–16.0 ng mL⁻¹ [114]. The multiple stages occurring in the process are also measured through using electrically sensing polymers i.e. conducting polymers. In an example, Varrene et al. has demonstrated the concept of stereolithography in the development of 3D printed separation devices integrated with electrode for electrochemical detection [115]. The steps of preparation and working are shown in Fig. 16.

Further, the observed analytical parameter i.e. good repeatability, linear response, and limit of detection of electrode confirmed as a proof-of-concept for electrically driven separation and analytical techniques. The composition and working properties of significant LOC are listed in Table 7 along with applications.

### 9 Lab on Chip

The integration of electronic, polymer processing, responsiveness, and analytical chemistry develops advanced miniaturized analytical devices for effective screening and sense of different chemical, biochemical, metabolites, DNA, and reaction products [111]. This technique also called microelectromechanical systems as well as micro total analysis systems, explores several polymer-based composites along with microfluidics technology for a single specific test for chemistry, biology, cellomics, proteomic, and manufacturing technology [112]. The processability, chemical stability, variable electrical conductivity, and multiple functionalities are the basic features of macromolecules for use in the development of polymer-based lab on a chip [113]. Advances in processing and integration techniques also explored the applications of LOC for biochemical testing as non-invasive technology. A simple LOC was reported by Ahn et al. for testing of unbound cortisol in human saliva after exploiting fluorescence technology. The sensing of cortisol was based on the measuring of fluorescence intensity using a series of the microchannel in the dynamic range of 7.0 pg mL⁻¹–16.0 ng mL⁻¹ [114]. The multiple stages occurring in the process are also measured through using electrically sensing polymers i.e. conducting polymers. In an example, Varrene et al. has demonstrated the concept of stereolithography in the development of 3D printed separation devices integrated with electrode for electrochemical detection [115]. The steps of preparation and working are shown in Fig. 16.

Further, the observed analytical parameter i.e. good repeatability, linear response, and limit of detection of electrode confirmed as a proof-of-concept for electrically driven separation and analytical techniques. The composition and working properties of significant LOC are listed in Table 7 along with applications.

### 10 Commercialization and Prospects

The scientific progress in macromolecules has also significantly improved industrial adaptability in terms of patents and sensors and several industries are developed polymer-based sensors for different applications for control, coordination, and multi analytes sensing. Some of the leading

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**Table 6 Integrated proposed polymer-based sensor**

| S. No. | Integration    | Sensing Action                        | Applications          |
|--------|---------------|---------------------------------------|-----------------------|
| 1      | pH            | Release of medicine                   | Drug delivery         |
| 2      | Ammonia       | Release of fertilizer                 | Agriculture           |
| 3      | Acidity       | Release Carbon dioxide                | Food processing       |
| 4      | Explosive     | Defense operation                     | Peace and defense     |
| 5      | The mechanical vibration of the earth| Resettlement                        | Safety management     |
| 6      | Atmospheric gases | Environmental monitoring              | Public security       |

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**Fig. 16 Development and working of 3D printed electrochemical sensors [115]**
Table 7  Polymer-based LOCs, properties, and applications

| S. No. | Composition                  | Transducer and analytes                              | Applications                                                                 | References |
|--------|-----------------------------|------------------------------------------------------|------------------------------------------------------------------------------|------------|
| 1      | Polydimethylsiloxane        | Cantilever and pressure                               | Flow rate with an accuracy of 1.39%, response time 6.3 s and sensitivity of 0.126 µm/(µl/min) | [116]      |
| 2      | Origami paper               | Colorimetric and microcystin                          | On-site using smartphone                                                    | [117]      |
| 3      | Poly aniline and paper      | Electrochromic and glucose                           | 30 s response time of 30 s and 126 µM detection limit of detection           | [118]      |
| 4      | Polyaniline nanofiber       | Ammonia                                              | Excellent reversibility, 25 s response, and 14 s recovery time.              | [119]      |
| 5      | Chitosan and nickel phthalocyanine | Electrical and methanol                       | The highest sensitivity of 60.2 µS.cm and limit of detection i.e. 700 ppm   | [120]      |
| 6      | Chitosan and graphene quantum dots | Surface plasmon resonance and dopamine              | Excellent signal-to-noise ratio in sensing range of 0 fM–1 pM              | [121]      |
| 7      | Cellulose                   | Electrochemical and microbes                         | Proof-of-concept with electrochemical detection of 10^7 colony-forming units mL^-1 | [122]      |
| 8      | Cellulose paper             | Opto-chemical for SARS-CoV-2 N protein               | Point-of-care application for SARS-CoV-2 surveillance                       | [123]      |
| 9      | Poly(ε-caprolactone)        | Organ on a chip                                      | Enhanced function of human liver                                            | [124]      |

Table 8  Some commercialized sensors and patents

| S. No. | Materials                                                                 | Sensors                           | Agency and specifications                                                                 |
|--------|---------------------------------------------------------------------------|-----------------------------------|-------------------------------------------------------------------------------------------|
| 1      | Abbott Diagnostics Scarborough, Inc. 10 Southgate Road Scarborough, Maine 04074 US | Binax NOWTM COVID-19 Ag Card      | Authorized for use at the Point of Care (POC), i.e., in the patient care settings          |
| 2      | Masimo Corporation is headquartered in Irvine, CA                         | Masimo Sleep.™                    | Nightly Analysis with Sleep Halo Index to help you see if disruptions are occurring           |
| 3      | Polyyprrole, PEDOT: PSS                                                   | Flexible pressure                 | US 10,568,579 B2 Korea Institute Of Science and Technology year 2020.                                 |
| 4      | Polytetrafluoroethylene and oxygen-sensitive dyes                         | Glucose and lactate in ng         | WO2020037269A2 The Regents of the University of California                                 |
| 5      | Poly(lactic-co-glycolic acid), polycaprolactone, and polyglycolic acid    | Implantable and bioresorbable sensors for monitoring of traumatic brain injury, neurological disorders | US20170020402A1 University of Illinois and Washington University                        |
| 6      | Polymethyl methacrylate and polydimethylsiloxane                         | Sensing, capture, collection, and storage of biofluids released by tissue | US10653342B2 University of Illinois                                                   |
| 7      | Protein and antibodies                                                    | Selective nucleic acids encoding for the antibodies or antigen-binding fragments | CN111690085B Shanghai ZJ Biotech Co Ltd, Sanyou Biomedical Shanghai Co Ltd.              |
| 8      | Nanocellulose and hemicellulose                                           | An inexpensive, self-energizing Body sensor is simultaneously used successfully to detection of heavy metal | CN108931565A Shandong Agricultural University                                           |
| 9      | The copolymer of polyethylene, terephthalate, polysters, silicones, and fluoropolymers | Sensing muscle signals with the task | US20190247650A1 Bao Tran and Ha Tran, Saratoga                                           |
| 10     | Aptamers DNA and Oligonucleotides                                         | Electrochemical sensing of bisphenol A | CN109521073A Institute of Quality Standards and Testing Technology for Agri-Products Chinese |
| 11     | Polymer type detector a graphene-based sensor                              | Metal detector with data storage   | KR20190133615A Knowles Electronics, Llc                                                    |
industrial products and products are listed in Table 8 along with specific details.

However, the integral aspects of sensing with a cure are still needed to be systematically investigated for object-oriented applications of different sensors. Although, this concept is started by the medical field for the delivery of drug and tissue engineering its impact on other areas like agriculture for the release of nutrients at the time of need. Similarly, the use of integrated sensors for the defense to diffuse arsenal after sensing its remote presence is another important area. Thus, the flexibility of chemical modification in macromolecule to design multi-functionality for wide range sensing and control the atmospheric as well as to enrich other significant branches of science and engineering like robotics [125, 126]. Some other proposed focus area for integrated sensors is controlled delivery in agriculture and biomedical, précised controlled and action in robotics, demining in controlled of terrorism and security for futuristic efforts in sensing sciences.

11 Conclusion and Future Prospects

The advances in macromolecules have been presented in chronological order and their impact on materials sciences. Further, the impact of advances in materials sciences has been discussed in the progress of sensing sciences for their use in physical, chemical, and biosensing with the potential scheme, illustrations, and examples of significant molecules. The existing challenges are also highlighted with their importance along with challenges in solving the issues in terms of selectivity, portability, and reliability in cross-references. Another important dimension of future effort is integrating the sensors with actions for effective technology-oriented initiatives. Although some efforts are initiated in this regard as theragnostic and robotic, which dedicated the delivery of specific drugs at diseased sites at requisites needs and control of temperature and humidity of controlled chamber like medical incubators, however, the commercialization of these concepts is still needed to be expedited.

Declarations

Conflict of interest The author has no conflict of interest to declare.

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