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Fluorescent Nanoprobes for Selective Detection of Toxic Pollutants

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Rapid and selective detection systems of intensive and toxic pollutants like heavy metal ions, pesticides, and organic materials have been prepared due to the increasing presence of these pollutants in environmental systems. Conventional methods of analysis though accurate, are usually using complex instruments, costly and time consuming. Over the recent years, fluorescent nanoprobes have become effective sensing platforms because of their distinct optical characteristics such as, high level of fluorescence, tunable emission, good photostability, and surface functionalisation. This mini review identifies the recent developments in the different kinds of fluorescent nanoprobes, including quantum dots, carbon dots, metal nanoclusters, and dye-functionalized nanomaterials, their synthesis, the strategies to functionalize them, and the detection mechanisms of these fluorescent nanoprobes, including the processes of fluorescence quenching, fluorescence enhancement, and energy transfer. Also, their uses in the selective detection of toxic contaminants, especially heavy metals, pesticides, and organic contaminants are discussed. Even though it has made a substantial advance, issues of stability, selectivity in complex matrices, and scalability are still present and the direction of the research in the future is the creation of environmentally friendly, mobile, and extremely selective sensing systems.

Keywords: Fluorescent nanoprobes, toxic pollutants, heavy metal detection, carbon dots, Quantum dots, environmental sensing

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Environmental pollution has become one of the most important global issues because of the rapid industrialization, urban growth and the increased agricultural activity. The constant flow of highly toxic pollutants of heavy metal ions, pesticides, dyes, and pharmaceutical residues into the air, water, and soil systems have caused a dire ecological disequilibrium and health risks [1]. These types of pollutants tend to be non-biodegradable and very persistent and not bioaccumulate and also with long term toxic effects on life. The heavy metals (mercury, lead and cadmium) are particularly dangerous since they are toxic in minute traces, as compared to the organic pollutants (pesticides and dyes) that influence biological systems and contaminate food chains. Therefore, sensitive, quick and efficient methods of detecting these pollutants should be created to monitor and guard the environment [2].

Pollutants have been commonly detected by use of traditional forms of analysis, such as gas chromatography, high-performance liquid chromatography, and atomic absorption spectroscopy, because they are more accurate and reliable [3]. Nevertheless, such techniques frequently involve costly instrumentation, further sample preparation, and trained staff, which do not make them appropriate to be used in on-site and real-time monitoring. Conversely, fluorescence-based sensing methods have also received significant consideration as promising alternatives since they are easy, very sensitive, quick to respond, and low cost. The principle of quantum fluorescence detection involves the emission of energy by a substance when excited and variations in the intensity or wavelength of the fluorescence can be related to the availability of a particular analyte [4].

Over the recent years, the combination of nanotechnology and fluorescence sensing has resulted in the creation of fluorescent nanoprobes that are highly beneficial as compared to traditional fluorescent dyes. These nanoprobes also have some characteristic physicochemical properties including size-dependent optical properties, large surface area-to-volume ratio, and emission properties that can be controlled [5]. This is due to the fact that such properties facilitate

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increased interaction with target analytes as well as better performance in detection. In addition, nanoprobes can be readily functionalized with different chemical groups, biomolecules or ligands to enable specific pollutants in complex environmental matrices to be recognized selectively [6].

The nanomaterials that can be used in creating fluorescent nanoprobes are very diverse and include semiconductor quantum dots, carbon-based nano-materials and metal nanoclusters. The benefits of every category of nanomaterials are different with regard to sensitivity, selectivity, and stability [7]. An example is quantum dots which have high brightness and narrow emission spectrum and carbon dots which has low toxicity and high biocompatibility. Nanoclusters with metallic gastronomy on the other hand, demonstrate a discrete fluorescence property as a result of quantum confinement effects and can be adapted to particular sensing tasks. These properties ensure the great flexibility of fluorescent nanoprobes as a tool of environmental monitoring [8].

Recent improvements in the synthesis methods and surface engineering have improved the performance of fluorescent nanoprobes even more. To enhance selectivity and sensitivity to target pollutants, functionalization has been used to include heteroatoms, polymer coating and biomolecule conjugation [9]. Furthermore, the creation of ratio metric and multi-signal sensing methods has also enhanced the detection precision to a great extent due to the reduction of interference with the environment. Connection to portable devices such as smartphone-based sensors has also allowed real-time and on-site analysis and these systems are therefore very practical in field applications [10].

Though these improvements have been made, some challenges have been faced such as the possible toxicity of some nanomaterials, stability in different environmental conditions, and interference with other co-existing materials. These issues are critical in the large-scale application of fluorescent nanoprobe-based more sensing systems. The purpose of this mini review is to present a brief update on the recent advances on fluorescent nanoprobes on selective detection of toxic pollutants as follows; their types, methods of their production, their detection mechanisms and their use in the monitoring of the environment.

Types of Fluorescent Nanoprobes

Fluorescent nanoprobes are classified according to their composition and optical properties and each has its advantages of selective detection of harmful pollutants. These nanomaterials can be tuned fluorescence-wise, are incredibly sensitive, and can be surface-functionalized to identify a specific analyte [11]. Quantum dots, carbon dots, metal nanoclusters and dye functionalized nanoprobes are the most commonly used types.

Quantum Dots

Quantum dots are size-dependent nanocrystals of semiconductor material, which have optical properties due to quantum confinement effects. They are photostable, narrow-emission spectrum, high-fluorescence quantum yield. The properties allow sensitivity and multiplexing of the pollutants, particularly the heavy metal ions. However, the toxicity of the quantum dots heavy metal has invited concern that has seen the development of safer alternatives [12].

Carbon Dots

Carbon dots are emerging non-toxic, water soluble, and biocompatible low-toxicity fluorescent nano-particles. They can be easily made with several organic products and are very fluorescent. Carbon dots have gained wide applications in the detection of metal ions and organic pollutants through fluorescence quenching or enhancement mechanism and thus are suitable to be utilized within the environment [13].

Metal Nanoclusters

Metallic nanoclusters (typically including a noble metal such as silver or gold) consist of a small number of atoms and behave like molecules with regard to their fluorescence. They are quantum confined; thus, they are highly luminescent and can be functionalized on their surfaces with ligands to enhance selectivity to specific analytes. More so, these nanoclusters can detect biomolecules and metal ions effectively [14].

Dye-Functionalized Nanoprobes

Nanomaterial supports are functionalized with organic fluorescent dyes using Dye-functionalised nanoprobes to improve sensitivity and selectivity. This is because the intensity of fluorescence is enhanced when dyes are used, but the stability and surface properties are provided by the nanomaterial. These nanoprobes find wide use in the detection of individual chemical compounds and organic contaminants with particular interactions [15]. The major categories of fluorescent nanoprobes and their structural diversity are illustrated in Figure 1.

Table 1. Comparison of Fluorescent Nanoprobes, Their Properties, and Applications.

Nanoprobe Type	Key Properties	Advantages	Typical Applications	References
Quantum Dots	Size-dependent emission, high quantum yield	High sensitivity, photostability	Heavy metal ion detection	[16]
Carbon Dots	Low toxicity, water soluble	Eco-friendly, easy synthesis	Metal ions, dyes, pollutants	[17]
Metal Nanoclusters	Strong fluorescence, small size	High selectivity, tunable	Ion and biomolecule detection	[18]
Dye-Functionalized	High fluorescence intensity	Target-specific detection	Organic pollutant sensing	[19]

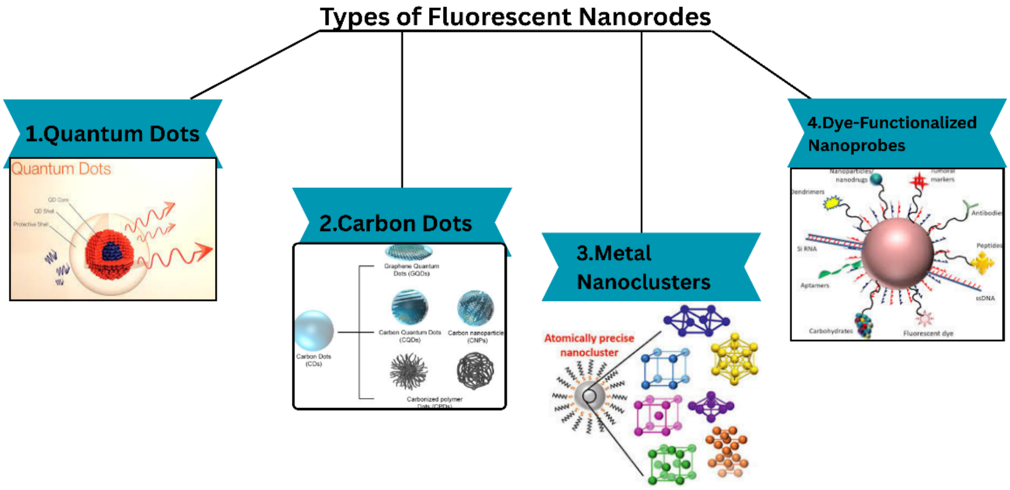

Figure 1. Types of fluorescent nanoprobes used for toxic pollutant detection.

Synthesis and Functionalization of Nanoprobes

Synthesis Methods

The production of fluorescent nanoprobes is a crucial process that defines their size, morphology, and optical response. Some of the common methods to prepare carbon based nanoprobes, and in particular carbon dots, include hydrothermal and solvothermal processes, among other methods, under controlled temperature pressure environment [20]. The techniques allow homogenous particle production, high crystallinity and increased fluorescence. The reduction of metal ions to generate metal nanostructures is also used to synthesize metal nanoclusters, in which the metal ions (e.g., gold or silver) are reduced in the presence of stabilizing ligands to produce extremely luminescent nanostructures [21]. Moreover, microwave-assisted synthesis is a fast and energy-efficient method of production, having a better control in particle size. In the recent past, eco-friendly green synthesis methods that involve plant extracts or biomolecules have attracted interest because of their low toxicity and environmental friendliness, and, therefore, can be applied in the environment [22].

Surface Functionalization Strategies

The surface functionalization is necessary in the impartation of selectivity and stability to the fluorescent nanoprobes. Not only does the introduction of functional groups, like hydroxyl, carboxyl and amine group, onto the surface of the nanoprobe, but also promotes the effective interaction of the nanoprobe with target pollutants, either via an electrostatic interaction, a coordination reaction, or a hydrogen bond [23]. The changes of fluorescence resulting of such interactions are measured and form the basis of detection. Also, the dispersion stability is enhanced by surface alteration with polymers or certain ligands, which inhibits aggregation when complex environmental media are used. The optical properties of nanoprobes can also be tuned through functionalization, which makes them both more sensitive and selective to a single analyte [24].

Role of Doping and Biomolecule Conjugation

The application of doping and biomolecule conjugation is important in enhancing the performance of fluorescent nanoprobes. The non-metallic element doping, e.g. insertion of nitrogen, sulphur or phosphorus elements, changes the electronic structure of nanomaterials, resulting in the increased fluorescence intensity and better sensing performance [25]. Conversely, conjugation with other biomolecules including aptamers, enzymes and antibodies allow high specificity as they allow selective recognition of target pollutants on a molecular basis. The method is especially instrumental in the determination of complex contaminants like pesticides and organic toxins in environmental samples. Doping and functionalization of biomolecules leads to very sensitive and selective nanoprobe systems that can be used in the implementation of high-quality sensing [26]. The overall synthesis, functionalization, and detection process of fluorescent nanoprobes is illustrated in Figure 2.

Detection Mechanisms

The principle of detection of toxic pollutants by fluorescent nanoprobes relies on the principle of an alteration of fluorescence intensity, wavelength, or emission ratio upon reaction with the target analytes. These alterations are as a result of various photophysical processes, which take place when the nanoprobe is in contact with particular pollutants [27]. High sensitivity and selectivity in environmental sensing applications depend on the choice of a suitable detection mechanism.

Fluorescence Quenching

One of the most widely studied phenomena in nanoprobe-based sensing is known as fluorescence quenching, which involves a decrease in fluorescence of the probe in the presence of a target analyte. This may be done by dynamic (collisional) quenching or by statical quenching by the formation of complexes between the nanoprobe and the analyte [28]. Non-radiative decay of the excited nanoprobe is common in cases where the excited nanoprobe transfers electrons or energy to the analyte, which causes the electron transfer to occur, thereby reducing the fluorescence emission. Heavy metal ions, Hg^{2+} and Fe^{3+} ions, are commonly detected in this mechanism because of their strong binding with surface functional groups of nanoprobes [29].

Fluorescence Enhancement

The fluorescence enhancement mechanism, is an assay process in which the fluorescence intensity is increased as a result of interaction with the analyte of interest. This is where the analyte either competes non-radiative processes or causes structural alterations in the nanoprobe to prefer radiative recombination [30]. In other cases, the binding of analytes inhibits molecular motion or passivates surface defects, resulting in intensive emission. This process is beneficial as it suppresses the background interference and increases the sensitivity of the detection [31].

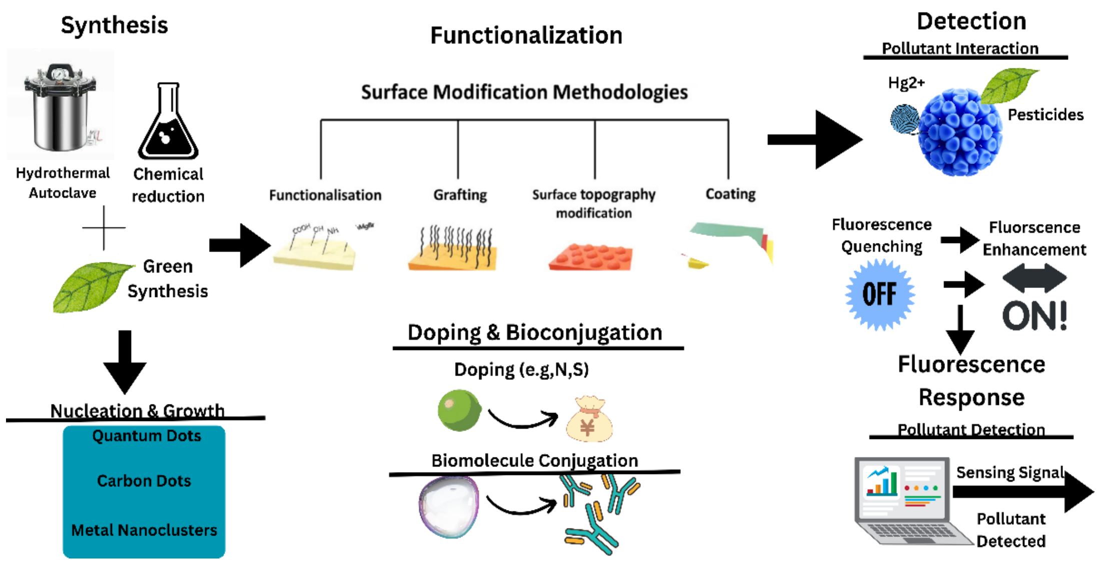

Figure 2. Fluorescent nanoprobe synthesis, functionalization, and detection mechanism.

FRET-Based Detection

Forster Resonance Energy Transfer (FRET) is a distance-dependent process where an acceptor and donor molecule can transfer energy between each other. Under such a non-radiative process, the excitation energy of the donor is moved to the acceptor when the two are close enough, and the fluorescence intensity or emission wavelength is changed in the acceptor [32]. This transfer of energy process can be facilitated or inhibited by the presence of a target pollutant, which allows the detection of pollutants with a high degree of sensitivity. The FRET-based systems find extensive applications as biomolecule, pesticides and ions detectors, owing to their high sensitivity and accuracy [33].

Ratiometric Fluorescence Sensing

Ratiometric fluorescence sensing is a sophisticated detection method, which makes use of two emissions at various wavelengths. The ratio of these two signals is measured instead of just measuring their change of intensity which gives more accurate and reliable results [34]. This approach reduces the impact of environmental factors, including pH, temperature and instrumentation. Ratiometric nanoprobes can be especially used in real-time and in situ tracking of pollutants due to better reproducibility and lower interference than single-emission systems [35].

Applications in Detection of Toxic Pollutants

Fluorescent nanoprobes have been widely used in detection of toxic pollutants because they are very sensitive, respond quickly, and can work in complex environmental conditions. These nanoprobes help detect a broad spectrum of pollutants such as heavy metal ions, pesticides, and organic pollutants which of great concern to the environment and human health. This is one of the main characteristics that give them their high performance: tunable optical properties enable selective interaction with the particular analyte and surface functionalization [36].

The detection of mercury (Hg^{2+}), lead (Pb^{2+}), copper (Cu^{2+}) and iron (Fe^{3+}) are among the most significant uses of fluorescent nanoprobes. These are very toxic metals even in low amounts and are prone to build up in the biology system [37]. Carbon dots and quantum dot-based fluorescent nanoprobes are commonly applied to this effect because of their high fluorescence and functionalization capabilities. This type of interaction between metal ions and the functional groups on the nanoprobe surface results in fluorescence quenching/enhancement, which results in a high sensitivity of detection at trace levels. They have successfully been used in the monitoring of drinking water and industrial effluents [38]. Alongside heavy metals, fluorescent nanoprobes are also beginning to find applications in the detection of pesticides, particularly organophosphorus compounds which are extensively used in agriculture, but are of great health hazard [39]. Examples of these nanoprobes can be functionalized with an individual recognition component like enzyme or aptamers that distinguishes between pesticide molecules. When the alkane is interacted with, a fluctuation in intensity of fluorescence or wavelength can be sensed, which can be detected quickly and selectively. The method also comes in handy in food safety analysis and environmental monitoring of agricultural excess [40].

Fluorescent nanoprobes are also useful in the detection of organic contaminants, such as dyes, antibiotics, and phenolic substances. The substances are usually present in industrial wastewater and may lead to serious impacts on the environment when unchecked. The mode of detection is usually either π-mm interactions, hydrogen bonding or electron transfer of the nanoprobe and the pollutant, which leads to the modulation of fluorescence [41]. To illustrate this point, it is possible to detect dye pollutants by using the fluorescence quenching technique and some organic molecules can be used to cause an increase in fluorescence based on their interaction with the nanoprobe surface.

Recently, the use of fluorescent nanoprobes has been expanded to new pollutants like pharmaceutical residues, and microplastics. These chemicals are becoming known as a threat to the environment particularly because of their persistence and possible biological impacts. Their detection can be done quickly and sensitively using fluorescent nanoprobes in both complex matrices like wastewater and biological samples. Further, the use of nanoprobes with portable and smartphone-based sensing devices has also allowed real time and on-site analysis to be used, increasing their practical value [42].

In general, the flexibility, sensitivity and versatility of fluorescent nanoprobes render them effective instruments in the detection of a broad variety of toxic contaminations, which play a significant role in environmental surveillance and pollution control measures.

Table 2. Nanoprobe-based detection of environmental pollutants: categories, mechanisms, and applications.

Pollutant Category	**Specific Analyte**	**Type of Nanoprobe Used**	**Detection Mechanism**	**Application Area**
Heavy Metals	Hg^{2+}, Pb^{2+}, Cd^{2+}, Fe^{3+}	Quantum dots, Carbon dots	Fluorescence quenching	Water quality monitoring
Pesticides	Organophosphates, Carbamates	Carbon dots, Dye-functionalized probes	Fluorescence enhancement / FRET	Food safety, agriculture
Organic Dyes	Rhodamine B, Methylene blue	Carbon dots, Metal nanoclusters	Quenching / Electron transfer	Industrial wastewater
Phenolic Compounds	Phenol, Bisphenol A	Functionalized nanoprobes	Fluorescence change	Environmental analysis
Antibiotics	Tetracycline, Ciprofloxacin	Quantum dots, Nanoclusters	Ratiometric sensing	Pharmaceutical monitoring
Emerging Pollutants	Microplastics, Pharmaceuticals	Advanced hybrid nanoprobes	Multi-mode sensing	Environmental surveillance

Challenges and Future Perspectives

Although the development of fluorescent nanoprobes in detecting pollutants has seen great improvement, there are still various obstacles that restrict their extensive use in practical settings. Stability of nanoprobes in different environmental conditions including change in pH, temperature and ionic strength is also among the major concerns. The effects of these factors can be seen on the intensity of fluorescence and provide misleading detection results [43]. Besides that, selectivity and sensitivity can be impaired by interference with coexisting substances in complicated environmental samples, including natural organic matter or competing ions. The toxicity of some nanomaterials, especially quantum dots based on heavy metals, is another critical problem which makes one question whether they are safe to the environment and can be used over the long-term period [44].

Scalability and reproducibility are also important issues. Most of the synthesis procedures created in the laboratory scale are hard to architect to large-scale manufacturing and retain the consistency and functionality. Besides, commercialization may be constrained by production cost and the requirement of special materials. Detecting protocols and validation in an actual sample should also be standardized to provide reliability and functional use [45]. The future studies should aim at overcoming these limitations by coming up with non-toxic, eco-friendly, and highly stable nanoprobes. Natural precursors and sustainable methods of green synthesis are likely to take an important role in this direction. Further developments in surface engineering and strategies of functionalization will enhance selectivity, resulting in the ability to detect in highly complex matrices. [46]. Real-time and on-site monitoring will be enabled by the incorporation of fluorescent nanoprobes with portable devices, including smartphone-based sensors and microfluidic platforms. Also, the use of artificial intelligence and data-driven methodology can strengthen the analysis of the signals and increase the level of detection. Such advances should increase the number of practical uses involving fluorescent nanoprobes in environmental control and the protection of the health of the population.

CONCLUSION

The application of fluorescent nanoprobes is thought to be highly beneficial in specific detection of toxic pollutants due to their optical property, high sensitivity and rapid response. Their ability to be tailored in structure and surface functionality has allowed them to detect a wide range of contaminants, including heavy metal ions, pesticides and organic contaminants. Developments in their synthesis and functionalization, and in the methods of detecting them, have significantly improved their performance and utility.

Even with the stability, selectivity in intricate environment, and large-scale production challenges, the current research efforts are striving to overcome these limitations by the creation of environmentally viable materials as well as more advanced sensing systems. With even more individuals still inventing and integrating fluorescent nanoprobes into portable technologies, chances are high that they will find a considerable role in the environmental monitoring systems of the future, where they can play a vital role in ensuring an improved control of pollution and sustainable development.

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