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REVIEW ARTICLE

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Nanotechnology-based sensors in geological characterization and mineral exploration: Next-generation approaches

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Abstract

The fast growth of the demand of critical minerals on a global scale has increased the importance of development of efficient analytical technologies with enhanced speed, accuracy, and sustainability of the techniques for geological characterization and mineral exploration. Despite high accuracy of conventional geological, geochemical, and geophysical techniques, their effectiveness is limited by slow analysis, high expenses, and lab-dependent nature of the methods. In this review, current achievements in nanosensors, for geological characterization and mineral exploration are analyzed comprehensively. First, the principle of operation of nanosensors, and the role of specific nanomaterials, including graphene, carbon nanotubes, MXene, quantum dots, and metal/metal oxide nanoparticles, in enhancing the effectiveness of nanosensors are discussed. Later, the use of electrochemical, optical, surface enhanced Raman scattering (SERS) and field-effect transistor (FET)-based sensors in geological characterization and mineral exploration was discussed. In addition, the role of using nanosensors with artificial intelligence, machine learning, Internet of Things (IoT), remote sensing, hyperspectral imaging, and geographic information systems (GIS) was highlighted. Furthermore, current problems associated with practical implementation of sensors like selectivity, matrix interference, long-term stability, standardization, and commercial scale-up were reviewed; future directions for development of hybrid nanocomposites, microfluidic devices, intelligent sensor systems, and decision-making systems aided by artificial intelligence technology were defined. In summary, it was found out that nanotechnology-enabled sensors provide advanced analysis tools which complement conventional analysis techniques and which, combined with advances in interdisciplinary technologies, could provide more efficient and environmentally friendly solutions in mineral exploration.
Keywords: Nanotechnology, nanosensors, geological characterization, mineral exploration, geochemical analysis.

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1. Introduction

At the turn of the 21st century, the fast-growing population of the planet, the process of urbanization, industrialization, and digitalization have resulted in increased need for natural resources, including critical minerals. Lithium, cobalt, nickel, copper, graphite, platinum group elements, and rare earth minerals used in strategic areas such as the production of electric vehicles, renewable energy, batteries, semiconductors, communication systems, and the aerospace industry are among the primary raw materials of our era. According to the International Energy Agency (IEA), the demand for critical minerals is expected to rise rapidly in the future due to the transition to clean energy technologies, which makes the discovery of new mineral resources one of the top priorities around the world. Likewise, the Critical Raw Materials Act published by the European Union, as well as the list of critical minerals released annually by the United States Geological Survey (USGS), clearly demonstrate the significance of the reliable supply of raw materials for economic growth, energy security, and sustainability [1], [2].

Even as demand continues to increase, the reality is that most of the rich deposits of ores that are near the surface have been discovered, pushing mineral exploration into more difficult geological conditions. The reality today is that most of the deposits of ore found are either geologically complex or are found at great depths below thick overburdens. These circumstances not only make the exploration process costly, but it also shows how classical geological methods of exploration lack sensitivity and efficiency in some ways. Specifically, the high cost of drilling processes, the long period taken for laboratory analysis, and the inability to conduct area evaluation quickly have made it necessary to find new ways of exploring through new technology [3], [4].

The field of geological characterization, which constitutes the basis of mineral exploration, is defined as a multidisciplinary scientific endeavor designed to determine the details about the lithology, mineralogy, geochemistry, structure, and alterations of the area under investigation. An appropriate geological characterization procedure is essential to detect mineral occurrences, evaluate resources, develop drilling programs, and ensure sustainable mining activities. For this reason, methods such as field surveys, geological mapping, geophysical studies, geochemistry, petrography, X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), inductively coupled plasma-mass spectrometry (ICP-MS), and hyperspectral imaging are applied [5], [6].

Despite all the above-stated benefits, conventional analytical approaches suffer from several weaknesses. As almost all the analysis is performed in laboratory conditions, sample transportation and preparation before analysis consume a lot of time; thus, not only are these procedures costly, but also make the decision-making process rather slow. Moreover, the number of analyzed samples rises substantially when thousands of samples should be analyzed within large areas of mining sites. The rapid screening capability is particularly valuable during early stages of minerals exploration, while most of the existing techniques cannot perform real-time analysis. The detection of low concentration anomalies often requires special analytical methods, which raises costs of the research. Thus, while being rather accurate, conventional analytical methods can hardly meet requirements to rapidness, mobility, continuous monitoring, and on-site analysis [7].

Advances in materials science and nanotechnology in recent years have offered significant opportunities to overcome these limitations. Nanotechnology and nanomaterials, due to their unique structural and functional properties, have the potential to make innovative applications possible in many fields including energy production, environmental sustainability, health technologies, food safety, electronics, and geosciences [8]–[33]. Nanotechnology is an interdisciplinary field encompassing the synthesis, characterization, and applications of structures with at least one dimension ranging from 1 to 100 nm. Unlike their macroscopic counterparts, nanoscale materials possess unique physicochemical properties such as high specific surface area, superior electrical conductivity, enhanced optical properties, high chemical reactivity, and quantum effects. Thanks to these properties, nanomaterials have enabled groundbreaking developments in many fields, particularly in biomedical diagnostics, environmental monitoring, energy storage, food safety, catalysis, and sensor technologies [34], [35].

Specifically, studies undertaken during the last decade on graphene, carbon nanotubes, metallic nanoparticles, quantum dots, MXene materials, 2D nanomaterials, and hybrid nanocomposites have contributed greatly to improving the capabilities of sensors. High surface areas of the nanomaterials enhance interaction with target analytes, and better electronic transfer properties contribute to improved signal strength, enabling sensing of molecules at even the smallest concentrations. In today's world, sensors based on nanotechnology-based electrochemical, optical, piezoelectric, plasmonic, SERS, field effect transistor (FET), and fluorescent sensors have numerous advantages over conventional sensors, including better detection limits, better selectivity, reduced analysis time, and reduced volume of samples [36], [37].

Sensors based on nanotechnological applications that originally were used mostly for biomedical purposes, environmental monitoring and control, and food security have recently been developing rapidly in the area of geology and mining industry as well. Due to the capability of detecting metal ions, trace elements, alteration minerals, and geochemical markers with high sensitivity in geological settings, it became possible to apply nanosensors for mineral exploration. Specifically, due to the emergence of portable sensing devices, real-time measurements could be conducted in the field without conducting them in the laboratory setting, which makes such approach both economically efficient and fast. At the same time, the combination of sensor technology with unmanned aerial vehicles (UAVs), remote sensing techniques, GIS, IoT, and data analytics based on artificial intelligence is the way in which next-generation digital methods of mineral exploration are being developed [4].

Nevertheless, the use of nanosensors, in the field of geologic characterization and mineral exploration can be considered an area of growing research interest. Indeed, while there are many studies dedicated to the application of nanosensors in such fields as biomedical diagnostics, environment monitoring, food safety, there are not too many papers studying their potential in geosciences and mining industry. Even though a considerable part of existing literature is devoted to the development of certain sensors or measurement of certain metal ions, there are not too many review papers which discuss the comparison of performance of these sensors in various geological conditions, their efficiency in field conditions, and their general implementation in mineral exploration process. In addition, there are still some important research issues concerning the durability, selectivity, long-term stability, and performance of various nanosensors, which were successfully used in laboratory tests, in real-life field conditions and in different geochemical matrices [4], [34], [38].

Assessment from the point of view of geological characterization reveals that sensors utilizing nanotechnology-based not only can be employed for determination of metal ions, but also can be applied in many fields, including detection of hydrothermal alteration minerals, analysis of trace elements in soils and rocks, geochemistry of groundwaters, control of environmental pollutants, and study of ore-forming processes. In particular, graphene- and carbon nanotubes-based electrochemical sensors, plasmonic sensors based on use of gold and silver nanoparticles, quantum dots-based fluorescent sensors, and SERS-based systems allow for detecting metal ions with high accuracy and extremely low concentration. The high sensitivity is an important advantage for the detection of concealed mineralization which forms geochemical anomalies of trace level on the surface. In this way, it is possible to detect anomalies, which cannot be found using traditional geochemical methods, more quickly and inexpensively [34]. Conversely, the development of microelectronics, microfluidics, wireless technologies and low-power electronics has made it possible to combine nanosensors with portable instrumentation. Modern sensor systems are able to function in tandem with smartphones, tablets, and other portable analytical instruments; measurements can be uploaded to cloud databases with the help of wireless communication technologies. Not only does it provide opportunities to acquire real-time data in inaccessible mining locations but it also makes it possible to analyze at once data collected at different locations. Consequently, there is less need to conduct laboratory analyses, field work becomes more efficient, and drilling operations can be guided by more trustworthy geochemical data [4], [34].

Moreover, recent achievements in the area of artificial intelligence, machine learning, and big data analysis technologies have opened up new ways of usage of nanosensors. High volume of data evaluation, including geological surveys, satellite images, hyperspectral data, geophysics, drilling logs, and data obtained by means of nanosensors on a single platform makes possible to obtain more precise results in terms of mineral potential evaluation. In particular, due to machine learning algorithms, geochemical correlations can be studied, patterns that demonstrate hidden mineralization can be discovered, and highly accurate mineral potential maps can be built. Moreover, an ability to provide constant data flow by means of IoT-based sensor networks is regarded as one of the main elements of future smart mining technologies [4], [34].

There are some technological and economic aspects that should be addressed to enable the successful use of nanosensors in practice. The stability of sensors, their functioning at different temperatures and humidity levels, the preservation of their selectivity in various geological environments, fouling of their surfaces, their lifespan, the need in calibration, and the costs of production of a large number of them are the most important aspects which influence the field applications of these devices directly. Moreover, the fact that no well-developed international standards for comparing various platforms of sensors by means of standard analytical methods have been created so far complicates evaluation of the results of research. Thus, in the future, the research will probably be devoted not only to creation of new nanomaterials but also to validation of the sensors' performance in the field, standardization and commercialization of them [34].

In this review paper, the latest researches on nanosensor applications in geological characterization and mineral exploration using nanotechnology are reviewed from a broader point of view. The review initially explains the fundamental operation principles of nanosensors and nanomaterials being used in this technology. After that, the fields of application of nanotechnology in geological characterization and mineral exploration are investigated. In addition to that, electrochemical, optical, plasmonic, fluorescent, SERS, and field effect transistor-based sensing technologies are compared and their performance, strengths, and weaknesses in the application to mineral exploration field conditions are examined. Moreover, in light of the integration of these technologies with the help of artificial intelligence, remote sensing, Internet of Things, and big data analytics, the current methods of intelligent mineral exploration systems which might emerge in the future are reviewed [4], [34].

2. Fundamentals of nanotechnology-based sensors

Nanotechnology is the multi-disciplinary science discipline which involves the design, synthesis, characterization, and application of materials having dimensions between 1 and 100 nm in different disciplines of science. The physical, chemical, optical, magnetic and electrical properties of the materials at nanoscale level are quite different from the properties of the same material in macro scale. The main factor behind such variations is the increase in the ratio of surface atoms to total number of atoms in the materials along with quantum confinement effects. Thus, due to increased surface area, increased reactivity, increased rate of electron transfer and enhanced catalytic properties, the sensitivity and selectivity of sensors are greatly improved. Thanks to the above properties, the development of nanosensors has gained increasing importance in various fields of study apart from biomedical diagnostics and environmental analysis [39]. The sensor design involves three main elements, namely, the sensing element, the transducer, and the data processing unit. Whereas the sensing element identifies the particular analyte, the transducer transforms this reaction to an electric, optical, or mechanical signal. Finally, the obtained signal is then treated through appropriate electronic circuits and produces an output that can be understood by the user. Although such classical sensor design is kept intact in the development of nanosensors, much improvement on their efficiency is gained when the sensing surface is modified using nanomaterials. This is because nanomaterials have a larger surface area, which increases the number of binding sites and speeds up charge transfer. Thus, not only is the detection time shortened, but the detection limits are also decreased several times compared to traditional sensors [39], [40].

The mechanism of functioning of sensors based on nanotechnologies is grounded on physical and chemical interaction between the target analyte and the surface of nanomaterials. This kind of interaction may be implemented through adsorption, electron transfer, ion exchange, redox processes, fluorescence quenching, plasmon resonance, and piezoelectric effects. Any changes in physical parameters such as electric current, potential difference, resistance, optical absorption, fluorescence intensity, and Raman effect caused by the target analyte binding with the surface of the sensor are detected. The principle of detection is different for each specific sensor depending on its structure and the target analyte. Especially selective nanomaterials are needed in case the target analyte is metal ions [40], [41].

One of the biggest benefits associated with using nanosensors is the ability of the sensors to recognize the analytes present in very small amounts with very high accuracy. This is mainly because the large specific surface area of the nanomaterials increases the chances of interaction with the target molecules. For instance, a theoretical surface area of the graphene is approximately 2,630 m^2/g and graphene possess very high electron mobility. Likewise, carbon nanotubes promote the transfer of electrons owing to their one-dimensional conductive paths and help amplify the electrochemical signal. In addition, metal nanoparticles increase the sensitivity of the optical sensors due to localized surface plasmon resonance (LSPR) effect. Due to such features, nanosensors are capable of detecting the analytes present at the level less than ppm and in some cases even ppb and ppt level [41]–[43].

In addition to their high surface areas, another factor that is responsible for improved sensors' performance is the ability of nanomaterials to modify their surfaces. Nanomaterials such as graphene oxide, reduced graphene oxide, carbon nanotubes, MXenes, and metal oxide nanoparticles can be easily functionalized with amino, carboxyl, hydroxyl, and thiol groups. Thus, the sensor surface becomes highly selective to particular metal ions, minerals, and chemicals. The above property brings significant benefits in geological practice when there is a need to detect economically valuable ions, such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Au^{3+}, and rare earth elements. Moreover, surface modification ensures sensor stability in case of variations in pH and ionic strength [44], [45].

In assessing the performance of sensors based on nanotechnology, not only their sensitivity but also characteristics like selectivity, accuracy, repeatability, response time, recovery time, stability, limit of detection (LOD), limit of quantification (LOQ), and extended lifetime are analyzed. Especially in cases of geological characterization, sensors should work under varying conditions of mineral phases, high ionic strength, and changing temperature and humidity. The issue of why most sensors that show good results in laboratory tests do not exhibit the same success rates in practical applications has become one of the most important issues in this area today. That is why, in recent years, researchers have not only concentrated on synthesizing new nanomaterials but also have worked on hybrid nanocomposites for improving the environmental stability of sensors [34], [46]–[48]. From the perspective of geological characterization and mineral exploration, the major benefit of nanosensors is the capability for in situ analysis. In contrast to conventional geochemical analysis that takes several days or even weeks due to sample transport and processing in laboratories, the analysis using portable nanosensors takes only several minutes. It helps a lot in detecting geochemical anomalies, optimizing drilling spots, and decreasing expenses on mineral exploration. Moreover, the possibility to use these sensors together with UAVs, robotic systems, and IoT data acquisition systems allows the creation of high-resolution geochemical maps in real time mode. Thus, the nanosensors are seen as one of the core technologies for future smart mining and digital geology applications [34], [49], [50].

2.1. Principles of how sensors work

Sensors using nanotechnology are founded on the idea of transforming the interactions which take place between the target analyte and the active recognition site located on the sensor surface into an analyzable signal. In these types of systems, the transformation of changes in the physical parameters such as the electric current, potential difference, impedance, optical absorbance, fluorescence intensity, Raman signal, or mass changes, caused by the interaction of the analyte with the sensor surface, into digital signals is accomplished through the use of transducers. The main criteria which influence the efficiency of sensors include sensitivity, selectivity, LOD, accuracy, repeatability, response time, and stability. Nowadays, thanks to the use of nanomaterials in these systems, mechanisms of signal amplification have been dramatically enhanced, providing a possibility for quick and reliable detection of analytes in very small amounts [51]–[53].

Electrochemical sensors have been among the most utilized sensing techniques within the nanotechnology-based sensing systems. The variation in the current, potential, or conductivity caused by the oxidation/reduction reaction of the analyte at the electrode surface is monitored in electrochemical sensors. As they are subdivided into amperometric, voltammetric, potentiometric, and impedimetric electrochemical sensors according to their working principle, they provide remarkable advantages in practical applications such as being cost-effective, portable, fast, and highly sensitive. Graphene-, metal-, MOF-, MXene-, and conductive polymer-modified electrodes enhance the electron transfer rate, thus increasing the signal-to-noise ratio and sensor performance. Due to this fact, electrochemical nanosensors have gained a lot of popularity in recent years for the detection of heavy metals and contaminants [54]–[56].

Optical sensors are characterized by alterations in absorbance, reflectivity, refractive index, photoluminescence, and scattering caused by interactions between light and the analyzed target molecule. Due to the distinct optical properties of nanomaterials, such sensors can achieve extremely low detection limits. Gold and silver nanoparticles' localized surface plasmon resonance (LSPR), fluorescent properties of quantum dots, and photonic characteristics of carbon-based nanomaterials greatly improve the effectiveness of optical sensors. Besides that, optical sensors demonstrate immense potential in mineralogical investigations and field studies due to the ability to carry out non-contact measurements, high resolution, and suitability for analyzing multiple analytes. In particular, portable optical sensors provide the possibility to conduct on-site measurements without using laboratory investigations [57]–[59].

SERS sensors are one of the fast-developing nanotechnologies in the last years. The Raman spectroscopy technique is based on inelastic scattering measurements due to molecule-light interactions. Nonetheless, the traditional Raman approach is not very effective for certain purposes because of the low level of signal intensity. The Raman signal in plasmonic nanoparticles-based SERS devices, such as gold or silver nanoparticles, is multiplied by millions because of enhanced electromagnetic field. This makes possible the detection of very small quantities of metal ions, organic substances, and other chemical components on mineral surfaces. It is expected that SERS-based approaches will have an enormous advantage in geological studies with the use of alteration minerals and trace elements connected to mineralization [60]–[62].

The working mechanism of FET nanosensors involves the changes in electrical conductivity caused by charge alterations at the surface of semiconductor channel. The alterations in charge due to the binding of the analyte on the surface of the sensor directly influence the electrical conductivity of the channel. Two-dimensional nanomaterials including graphene, molybdenum disulfide (MoS_2), black phosphorus, and MXene are commonly applied in FET sensors for their high carrier mobility and large active surfaces. FET sensors belong to the category of portable analytical devices of the future owing to their ability to conduct real-time analysis, reagent-free operation, and extremely low detection limits. Moreover, the amount of FET-based platforms increases significantly in the context of environmental sensing and the detection of heavy metal ions [63]–[66].

The piezoelectric sensors function under the assumption that the difference in mass due to the bonding of the targeted molecule to the surface of the sensor affects the frequency of vibration of the piezoelectric crystal. The quartz crystal microbalance (QCM) and surface acoustic wave (SAW) sensors are the most common types of sensors in this category. Due to increased binding sites in piezoelectric sensors because of the modification by nanomaterials, their sensitivity is greatly increased. These types of sensors are highly favored when used for analyzing gases, detecting volatile organic compounds, and in environmental studies. Geologically speaking, they have great potential in monitoring gas emissions in mines and environmental changes caused by mining activities [67]–[70].

One of the major advancements that have been made in the field of sensors recently is the development of the fusion of various types of sensing techniques in one device. Hybrid sensors make use of electrochemical, optical, and plasmonic techniques for the purpose of sensing to ensure higher levels of accuracy as well as minimize false alarms. Moreover, advanced sensor platforms powered by artificial intelligence, machine learning, and big data analytics will be able to provide better output since these sensors will analyze a large amount of measurement data. With respect to geological surveying and mineral exploration, hybrid sensors are likely to form an integral part of future smart mineral exploration technology due to their many advantages [71]–[73].

2.2. Nanomaterials (Graphene, CNTs, MXenes, Quantum Dots, Metal/Metal Oxide NPs, etc.)

When applied to geological characterization and mineral exploration, the choice of the nanomaterial is not only determined by the characteristics of individual nanomaterials like high specific surface area and conductivity, but also the surface chemistry of the material, defects in the structure, morphology, electron transfer characteristics, and type of the interaction between the analyte and the material—these characteristics depend on the method of preparation of the nanomaterial. Thus, derivatives of graphene, carbon nanotubes (CNTs), MXenes, QDs, nanoparticles of metals and metal oxides and their combinations provide additional platforms for the design of new detection methods. Due to the complexity of the matrix of the geological samples, not only the sensitivity of the nanomaterial used in analysis, but also selectivity, resistance to the matrix, reproducibility, and stability of the material in field conditions are important [34], [63].

For graphene and graphene derivatives, important factors that determine the sensor performance include surface defects that form during the synthesis process and the distribution of oxygen-containing functional groups. During the preparation of graphene oxide (GO), the extent of the oxidation process, as well as the oxidizing conditions that are utilized, determine the distribution of the epoxy, hydroxyl, and carboxyl groups. On the other hand, the chemical, thermal, and electrochemical reduction of GO cause the loss of some of the surface functionalities and recovery of the electrical conductivity in the rGO material. Thus, the distinction between GO and rGO is not only based on the electrical conductivity but also on the number and chemical nature of the active sites responsible for the adsorption of the analyte on the surface. The hydrothermal and solvothermal processes can be utilized in the manipulation of the defect concentration, thickness of the layers, and heteroatom doping in graphene derivatives. The combination of these structural parameters' analysis (using the D/G band ratio via Raman spectroscopy, surface elemental composition and functional groups via XPS, chemical bonds via FTIR, interlayer ordering via XRD, and morphology via SEM/TEM) allows us to define the structure-performance relationship [74]–[76].

In the case of the graphene-based geochemical sensors, the process of analyte detection involves the transformation of the binding reaction that occurs on the surface to either the electrochemical or optical signal. Complexation of metal ions with the oxygen-containing groups at the surface, or the retention by means of electrostatic interaction or ion exchange, may change the rate of electron transfer at the electrode interface. Nevertheless, retention of the analytes at the interface is not sufficient for the creation of highly selective device. Competitive adsorption of co-existing ions in the geological samples and interferences from the minerals should be considered. In this context, the control of the density of functional groups of graphene derivatives, addition of the heteroatoms or creation of the composite with the metal/metal oxide nanoparticles may be applied to modify the binding energy and electron transfer pathway of the analyte. In other words, graphene can be treated not only as the conducting support, but also as the interface which includes analyte recognition and signal amplification components. The behavior of sensors made from carbon nanotubes (CNTs) depends greatly on the nanotube diameter, its length, number of walls, surface defects, and functionalization. Since the electronic and surface characteristics of the SWCNT and MWCNT types vary, it is critical to choose the right type of nanotubes for the particular analyte's chemical structure in order to develop a suitable sensor. Polar functional groups on the surface of the nanotubes due to the acid treatment, plasma processes, or non-covalent functionalization will facilitate access of analytes to the nanotubes in an aqueous geochemical medium. However, too much covalent functionalization may interfere with the π-conjugation of the nanotubes and electron transfer [77], [78].

The detection principle behind CNT-based sensors involves adsorption of the analyte on the surface of the nanotube along with the subsequent modification in the charge transfer between the nanotube and the electrode. In the case of CNT/metal nanoparticle composites, the nanotube plays a role in facilitating electron transfer whereas the nanoparticle may serve as an active site for binding or electrocatalytic transformation of the analyte. Likewise, in the case of conductive polymer/MOF/CNT hybrids, there is a clear distinction in the function of individual components. This design allows for the realization of selectivity and signal amplification – two qualities which can be realized only by multiple components, especially in complex geochemical samples. MXenes have unique features in comparison with other two-dimensional materials due to the structure of the interlayer space and the nature of the terminal groups that exist on their surface after the material synthesis. The choice of the etching solvent, temperature, time of treatment, and post-etching conditions has a direct impact on the ratio of –O, –OH, and –F groups on the surface and on defect density. That means that both the isolation and the control of the surface terminations are important parameters in the MXene fabrication process. By jointly investigating changes in interlayer spacing via XRD, structural defects via Raman spectroscopy, surface terminations via XPS, and layered morphology via SEM/TEM, a relationship can be established between the synthesis conditions and the detection performance [79]–[81].

Analyte-surface interactions in the case of MXene sensors arise due to both the chemistry of the surface termination and the electrostatic and coordinative interaction between them. The hydrophilicity of the surfaces as well as open layers to the penetration of the ions provide for the transportation of the analytes to the interface of the sensors in aqueous geochemical samples, while the charge of the surface and functional groups could contribute to the selective uptake of ions. Moreover, the conductive nature of MXene allows converting any adsorption or redox process taking place at the surface into the electrochemical signal. Nevertheless, the reduced structural stability of the MXenes in oxidative conditions is a considerable drawback, which needs to be taken into account. For this reason, the combination of MXenes with graphene, polymers, or metal nanoparticles is under consideration. In the case of QDs, synthesis parameters govern their optical sensing performance. The particle size, crystallinity, surface passivation, heteroatom doping, and nature of the surface ligands affect the quantum efficiency of fluorescence, emission wavelength, and analyte sensitivity. Hence, during the synthesis of CQDs, GQDs, and other carbonaceous quantum dots through hydrothermal, microwave-assisted, or pyrolysis approaches, one needs to control these parameters. While UV–Vis and fluorescence spectroscopy are used to determine optical properties, TEM enables the assessment of particle size and distribution, and XPS/FTIR enables the assessment of surface chemistry [82]–[85].

Some of the basic principles involved in the QD-based geochemical sensing include fluorescence quenching/recovery, electron/energy transfer, surface complexation, and, in some cases, redox-based optical switching. The binding of the analyte onto the QD surface leads to fluorescence quenching or enhancement through changes in the energy or charge states of the surface. Though this principle facilitates the determination of the presence of the analyte in the geological sample at low concentrations with the help of proper surface ligands, there could be problems associated with selectivity arising from the presence of other ions in the sample that exhibit similar optical or binding properties. Hence, it is essential to combine QDs with molecular ligands, polymers, or metal/metal oxide NPs. The following factors affect the working of nanoparticles made up of metals and metal oxides: synthesis procedure, particle size, crystal structure, surface defects, and morphology. Particle size and surface characteristics of nanoparticles synthesized using chemical reduction, sol-gel, hydrothermal, solvothermal, and precipitation techniques can be controlled through manipulation of precursor concentration, pH value, temperature, and reaction time. Whereas noble metal nanoparticles like gold, silver, platinum, and palladium serve as active surfaces for optical and electrocatalytic sensing applications, metal oxides like ferric oxide, zinc oxide, titanium oxide, copper oxide, and tin oxide have various roles in electrochemical, photocatalytic, and adsorptive sensing schemes [86]–[88].

The role of metal nanoparticles in sensing is not limited only to increasing the active surface area. For example, in Au and Ag nanoparticles, surface plasmon resonance may enhance local optical signals in response to the binding of the analyte to the nanoparticle surface. Metal oxide nanoparticles can demonstrate activity associated with oxygen vacancies on the surface, as well as hydroxyl and redox active centers that can affect the interaction of analytes and electron transfer process. The magnetic properties of Fe_3O_4 nanoparticles, on the other hand, can be used for enrichment and magnetic separation during the stage of sample preparation, irrespective of the sensing surface itself. Various hybrid nanostructures are currently being created to incorporate the complementary attributes of various nanomaterials into one sensing platform. For example, in the cases of graphene-metal nanoparticles, CNT-metal oxides, MXene-polymers, GQDs-metal oxides, and other similar combinations, the particular function of each constituent decides the sensing efficiency of the composite. In such structures, whereas the conductive material enables the flow of electrons, the second material can be used for performing functions like analyte detection, catalysis, signal production, or magnetic separation. But it must not be considered that the performance of the hybrids is necessarily enhanced simply by using hybrid structures. The important factors affecting the performance of the hybrid include contact resistance, interphase electron transfer, and agglomeration of nanoparticles [89]–[93].

Thus, the choice of nanomaterials for application in geological studies depends on the combined analysis of chemical characteristics of the analyte and the matrix of the sample. In those cases when adsorption dominates as the mechanism, surface functionality and zeta potential become crucial; in electrochemical detectors, electron transfer rate and nanomaterial-electrode interface become the decisive factors, and in optical detectors, surface passivation, energy transfer, and fluorescence/plasmonics characteristics become crucial. However, matrix constituents such as pH, ionic strength, coexisting metal ions, minerals, and organic material can change the interaction between the analyte and the nanomaterial. Thus, the efficiency of the nanomaterial has to be estimated not only through its LOD in lab settings but also from the perspective of selectivity, recoverability, reproducibility, stability, and applicability to field samples [90], [92], [94].

In such case, the use of nanomaterials in geological sensors as selective detection of the analyte at the surface, transformation of binding/reaction into electrical/optical signal, and amplification of this signal through the nanostructure can be analyzed at these three basic levels. Thus, the choice of materials in future sensors cannot be reduced to just listing all good properties of the nanomaterial, but on what synthesis process influences surface modification, and consequently, analyte recognition and signaling processes. Such approach is especially relevant for the development of portable devices for in-situ and multiplex detection of important minerals and geochemical markers. Various synthesis methods for different nanomaterials, basic parameters of nanomaterials characterization, dominating detection mechanism, strengths and weaknesses of nanomaterials in geological sensors and main fields of application are listed in Table 1.

Table 1. Representative nanomaterials for geological sensing: synthesis approaches, characterization parameters, sensing mechanisms, advantages, limitations, and major applications.

Nanomaterials	Representative synthesis approaches	Key characteriztion parameters	Dominant sensing mechanism(s)	Advantages for geological sensing	Key limitations	Major geological applications
Graphene and graphene derivatives (GO, rGO)	Chemical oxidation/reduction, hydrothermal/solvothermal synthesis, electrochemical exfoliation, heteroatom doping	XRD: interlayer structure; Raman: D/G ratio; FTIR/XPS: surface functional groups; SEM/TEM: morphology; BET: accessible surface	Surface complexation, electrostatic interaction, adsorption, electron-transfer modulation, electrocatalytic amplification	Tunable surface chemistry, efficient charge transport, compatibility with hybrid architectures	Restacking/agglomeration, batch-to-batch variation, possible loss of functional groups during reduction	Trace metal detection, geochemical anomaly assessment, electrochemical sensing, mineral-associated contaminant analysis
Carbon Nanotubes (CNT)	Arc discharge, laser ablation, CVD, post-synthesis oxidation/functionalization	Raman: structural defects; TEM/SEM: diameter and morphology; TGA: purity/functionalization; XPS/FTIR: surface chemistry	Adsorption-induced charge transfer, electrocatalysis, interfacial electron-transfer modulation	Rapid electron transport, high aspect ratio, good mechanical stability, suitable for conductive networks	Aggregation, difficult homogeneous dispersion, excessive functionalization may reduce conductivity	Metal-ion analysis, portable electrochemical sensors, water and rock sample analysis

MXene	Selective etching of MAX phases, followed by delamination and surface modification	XRD: interlayer spacing; XPS: surface terminations; Raman: structural defects; SEM/TEM: layered morphology; zeta potential: surface charge	Surface adsorption, electrostatic/coordination interactions, charge-transfer modulation, electrocatalysis	Tunable surface terminations, rapid charge transport, aqueous compatibility, easy hybridization	Oxidation and structural degradation, sensitivity to synthesis/storage conditions	Heavy-metal sensing, environmental geochemistry, field-deployable electrochemical sensors
Quantum Dots	Hydrothermal/solvothermal synthesis, pyrolysis, microwave-assisted synthesis, colloidal synthesis	UV–Vis/fluorescence: optical response; TEM: particle size; XPS/FTIR: surface chemistry; XRD: crystallinity	Fluorescence quenching/recovery, electron/energy transfer, surface complexation, optical signal modulation	High optical sensitivity, tunable emission, suitability for multiplexed detection	Photobleaching/surface instability in some systems; toxicity concerns for Cd-containing QDs; synthesis reproducibility	Trace-element analysis, fluorescence sensing, optical geochemical analysis
Metal Nanoparticles (Au, Ag, Pt, Pd)	Chemical reduction, seed-mediated growth, photochemical/green synthesis, electrodeposition	UV–Vis: LSPR; TEM/SEM: size and morphology; XRD: crystallinity; XPS: surface chemistry	LSPR modulation, SERS enhancement, electrocatalysis, surface adsorption	Strong optical/electrocatalytic signal amplification, high sensitivity	High cost for noble metals, aggregation, surface contamination/fouling	Raman/SERS sensing, trace-element detection, mineral-surface analysis
Metal Oxide Nanoparticles (ZnO, TiO_2, Fe_3O_4, CuO)	Sol–gel, precipitation, hydrothermal/solvothermal synthesis, combustion methods	XRD: crystal phase; SEM/TEM: morphology; BET: surface area; XPS/FTIR: surface chemistry; VSM for magnetic Fe_3O_4	Adsorption, surface redox reactions, catalytic/electrocatalytic processes, magnetic preconcentration	Chemical stability, catalytic activity, low-cost synthesis for many oxides; magnetic separation for Fe_3O_4	Relatively low conductivity in some oxides, aggregation, surface-dependent selectivity	Electrochemical sensing, groundwater/soil analysis, magnetic preconcentration, environmental geochemistry
Hybrid Nanocomposites	In-situ growth, self-assembly, chemical coupling, electrodeposition, hydrothermal/solvothermal integration	XRD: phase composition; SEM/TEM: interfacial morphology; Raman/FTIR/XPS: interfacial chemistry; EIS: charge-transfer behavior; BET: accessible surface	Synergistic adsorption, interfacial charge transfer, electrocatalysis, SERS/optical amplification, multi-modal sensing	Combines complementary properties, enhanced signal amplification, improved selectivity, potential for multi-analyte detection	Complex synthesis, interface reproducibility, possible phase aggregation, more difficult scale-up	Multiplexed metal-ion detection, smart field sensors, mineral exploration, integrated geochemical monitoring

3. Nanotechnology-based sensors used in geological characterization

Geological characterization is a multi-stage research procedure performed in order to analyze the mineralogical and geochemical characteristics of the rocks, discover the zones of alteration, clarify the mineralization processes and find out possible mineral deposits. The current need for critical minerals makes it necessary to investigate mineralizations occurring at bigger depth levels and in more complicated geological conditions. As a result, the current interest is rising not only in traditional laboratory methods but also in innovative sensor technologies allowing highly precise, portable and real-time analysis. Sensors based on nanotechnology are considered one of the most promising technologies for geological characterization investigation because of such characteristics of sensors as high specific surface area, sophisticated signal amplification and low detection limits [95]–[98].

The determination of metal ions and trace elements in the samples taken from soil, rocks, sediments, and groundwater is one of the most important uses of nanosensors for geological profiling. The analysis of trace elements in particular of economic or environmental importance, such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, As^{3+}, and Hg^{2+} ions at very low concentrations, is especially important in order to identify geochemical anomalies associated with mineralization processes. Though laboratory analysis techniques like ICP-MS, ICP-OES, or AAS allow performing accurate analysis, due to the development of portable electrochemical nanosensors it became possible to conduct an analysis with a similar level of sensitivity on-site [99]–[101].

Electrochemical sensors based on nanotechnology constitute one of the most popular platforms employed in the detection of metal ions in geological samples. Electrodes functionalized with graphene, carbon nanotubes, MXene and metallic nanoparticles are capable of providing much lower detection limits compared to unfunctionalized electrodes as a result of the fast electron transfer rates in such materials. Moreover, the functionalization of nanomaterial surfaces using selective chelating molecules allows for the precise detection of specific metal ions, eliminating the presence of ions from the rest of the sample. It has been shown that electrochemical nanosensors show great promise especially in the detection of the distribution of trace elements in hydrothermal ore deposits [102]–[105].

Nanosensors have been increasingly employed in the field of geological characterization. In such nanosensors, the variations in absorption, fluorescence, or plasmon resonance due to the interaction between the analyte and the nanomaterial are observed. The unique property of localized surface plasmon resonance of gold and silver nanoparticles, along with the intense fluorescence property of carbon quantum dots, facilitates the detection of minute amounts of metal ions. It is particularly helpful in the fast detection of hazardous components like arsenic, mercury, and lead in the groundwater samples. The capability to use optical sensors with portable spectrometers is believed to be one of the major advancements that makes laboratory testing unnecessary in fieldwork [106]–[108].

SERS nanosensors have also become another subject of interest in recent years in terms of characterizing geologic samples. Plasmonic surfaces produced using gold and silver nanoparticles can increase the intensity of the Raman signal by several million-fold, allowing for the detection of trace chemical species attached to the surface of mineral grains. This technique is extremely beneficial, especially in characterizing sulfides, hydrothermal alteration minerals, and secondary minerals developed in the course of ore genesis. The lack of sample preparation and extremely fast analysis time offered by SERS-based systems makes it a good choice for developing future portable mineral analyzers [109]–[111].

Some of the main strengths of nanosensors in geological characterization include their capability of being integrated into microfluidic devices. With microfluidics, it is possible to conduct multiple analyses at once through the use of a small amount of sample. With the help of sensing zones equipped with nanomaterials in the microfluidic devices, different metal ions and geochemical signatures may be analyzed at once with a single chip. It is expected that this will facilitate development of portable "lab-on-a-chip" devices. It is believed that these technologies will help in speeding up decision-making in remote mining locations [99], [112], [113].

In addition to that, the combination of such sensors with remote sensing technologies can also serve as an additional argument for the usage of nanosensors in geological mapping. Nowadays, information received via hyperspectral imagery, satellites, UAVs, and ground sensors is analyzed together. The integration of geochemical information obtained in situ with the help of nanosensors together with remote sensing data makes it possible to model zones of alteration and mineralization much better. It provides opportunities not only for the analysis of surface geochemistry but also for mineral distribution and structural geology [95], [114], [115].

Nevertheless, there are certain technological limitations that need to be solved for wide applications of sensors based on nanotechnology in geological studies. The interactions between different ions in complex geologic samples, high ion strength, pH variation, the influence of temperature changes, as well as the presence of organic matter, may be harmful to the sensors' operation. Moreover, the problems of surface fouling, durability concerns, the necessity of calibration, and the absence of standard measuring procedures for such conditions prevent the broad application of these innovations. This is why modern scientific efforts in this sphere do not involve just creation of highly sensitive sensors but rather the development of robust platforms as well [116]–[119].

In general, the utilization of nanosensors can provide a range of benefits to the geological characterization process, including sensitivity, portability, quick analysis, and real-time data generation. In combination with such technologies as artificial intelligence, big data analysis, microfluidics, and remote sensing, such sensors will not only enhance the quality of geological data available currently but will become one of the primary components of smart mineral exploration systems in the future. In particular, along with the growing interest in the exploration of critical minerals and increasing sustainability of mineral extraction, the application of nanosensors will gradually increase both in research and industry spheres [120]–[122].

Another useful application of nanosensors in geological characterization involves hydrogeochemistry. As groundwater interacts with rocks for a long period of time, it contains geochemical information about the processes of mineralization. In particular, dissolved ions, trace elements, and nanoparticles formed by ore deposits in deep geological settings can be conveyed to groundwater. Thus, high-precision analysis of hydrogeochemical samples becomes an important exploration method used for locating mineral deposits buried under rocks. Modern nanotechnology-based electrochemical and optical sensors become a great alternative to standard lab analyzes that allow carrying out direct in-situ analysis of trace elements, including Cu, Zn, Ni, Co, Mo, U, rare earth elements in groundwater. Analytical methods that focus on detection of nanoparticles at single-particle scale help interpret hydrogeochemical anomalies [123]–[125].

Another fast-growing field of research related to the characterization of nanoparticles formed naturally in geological settings is the subject of increasing interest. A number of geological substances like clay minerals, iron oxides, manganese oxides, and silicate minerals can occur in the size of nanometers and affect element mobility. Natural nanoparticles can affect geochemical signals by absorbing metal ions and determine the creation of anomalies in mineralization. Due to advanced nanosensors which have been developed nowadays, it is possible to study chemical compositions, properties of surfaces, and environmental behavior of natural nanoparticles, and thus understand the process of ore genesis better. Recently, studies which describe the cycle of nanomaterials on Earth have proved that natural nanoparticles are important geochemical indicators which cannot be overlooked in mineral exploration [126]–[128].

Sensors developed through nanotechnology have a range of benefits not only for geochemical analysis, but also for detection of alteration zones related to mineralization. Clay minerals, iron oxides, carbonates, and sulfates are some of the secondary minerals that serve as key markers of mineralization; however, even minor changes in their chemical compositions are easily identified with the help of optical and electrochemical nanosensors. Moreover, a combination of portable sensor devices along with hyperspectral imaging helps identify the spatial location of alteration zones more precisely. Thus, it is possible not only to map out the zone, but also to carry out the geochemical analysis of alteration zones in real time [38], [129].

Nanosensors which have been designed in the last few years have evolved into multiplex sensors that help in analyzing various analytes at one go rather than analyzing only one component. The reason behind this is the use of microelectromechanical systems (MEMS), microfluidics and nano-sensor arrays which allow the simultaneous analysis of multiple metal ions or geochemical signatures at one go through the single compact instrument. This method allows saving of analysis time, especially during geochemical surveying on a larger scale, while helping analyze the relationship between different elements at one go. With the help of this method, complex geochemical reactions occurring in geological environment can be better interpreted [129]–[132]. Moreover, the combination of advanced-generation nanosensors working under field conditions with cloud data management systems plays an important role in the advancement of the digital geology concept. Data gathered by the sensors may be transferred wirelessly to central data banks and analyzed at the same time along with the information provided by the GIS, remote sensing, and geophysical data. Thus, it becomes possible to monitor dynamically changes in the geochemical composition in wide spatial ranges (not only at one measurement point) and to create real-time mineral potential maps. The use of big data and artificial intelligence algorithms within such systems makes it possible to reduce the degree of human influence on decision-making processes [95], [129], [133].

Another research direction in relation to the future of nanosensors is sustainability. Over the past few years, numerous studies have been carried out to explore the use of biodegradable nanomaterials, environmentally friendly synthesis techniques, and energy-efficient sensor platforms. In particular, the efforts directed towards the development of green nanotechnology technologies designed for reducing negative environmental effects associated with mining activities seek not only to create more efficient sensors but also to make them environmentally-friendly throughout the whole life cycle. Such approach became one of the major trends in the development of new generation sensor systems that comply with sustainable mining policy [130], [134]–[137].

4. Sensors used in mineral exploration

Mineral exploration can be defined as a research procedure where geological, geochemical, geophysical and remote sensing information is combined to locate mineral deposits of economic significance. Many discoveries of high-grade mineral deposits near surface level in recent times have resulted in exploration activities being conducted in deep and complex geological environments lying under cover rocks. High resolution geological information and next generation sensor technologies have been essential in such situations to conduct quick, accurate and inexpensive on site investigations. The ability to detect at low concentrations, selectivity, fast response time, and portability due to the use of nanotechnology based sensors makes them very useful in such cases, especially in reconnaissance exploration, targeting, and field investigations [138], [139].

One of the most vital objectives of sensors technology in mining exploration is the early identification of direct or indirect geochemical indicators of mineralization. The analysis of metal ions, trace elements, and alterations in the samples from rocks, soils, sediments, stream sediments, vegetation, and ground water can be done with the help of sensors. Detection of elements like copper (Cu), gold (Au), silver (Ag), lithium (Li), nickel (Ni), cobalt (Co), molybdenum (Mo), uranium (U), REE, arsenic (As) and antimony (Sb) at low levels becomes highly significant for the indication of mineralization. Although ICP-MS and ICP-OES analysis is highly accurate, it causes loss of time because of the sample preparation process in laboratories. In contrast, portable nanosensor technology makes real-time analysis possible in field conditions [140]–[142].

Mineral exploration sensors can indirectly detect not only metal ions but also minerals formed during the mineralization process. Iron oxide minerals, clay minerals, carbonates, sulfates, and products of silicification that arise in the alteration zones are the most significant markers of mineral deposits. Sensors designed on the basis of nanomaterials and having optical and electrochemical nature are capable to detect specific chemical signatures from those minerals with high sensitivity, thus providing prompt verification in the field conditions. Therefore, it is possible to combine geological mapping, geochemical sampling and geophysical studies in one evaluation procedure which will provide more accurate conclusions about drillhole location [115], [143]–[145].

Nowadays, sensors are not used separately in the course of mineral exploration but together with remote sensing, hyperspectral analysis, UAV technology, GIS and GPS, and computer-assisted decision making. In the course of field investigations, geochemical data collected using nanosensors are analyzed along with mineral alteration maps collected via satellite images and geophysical anomalies in order to create three-dimensional models of mineral potential. This approach makes it possible to expand the application of a certain method to several methods, which enhances the efficiency of the process. The scheme of the integration of nanosensors and other digital technologies in the course of mineral exploration is presented below see Figure 1 [4], [95], [146].

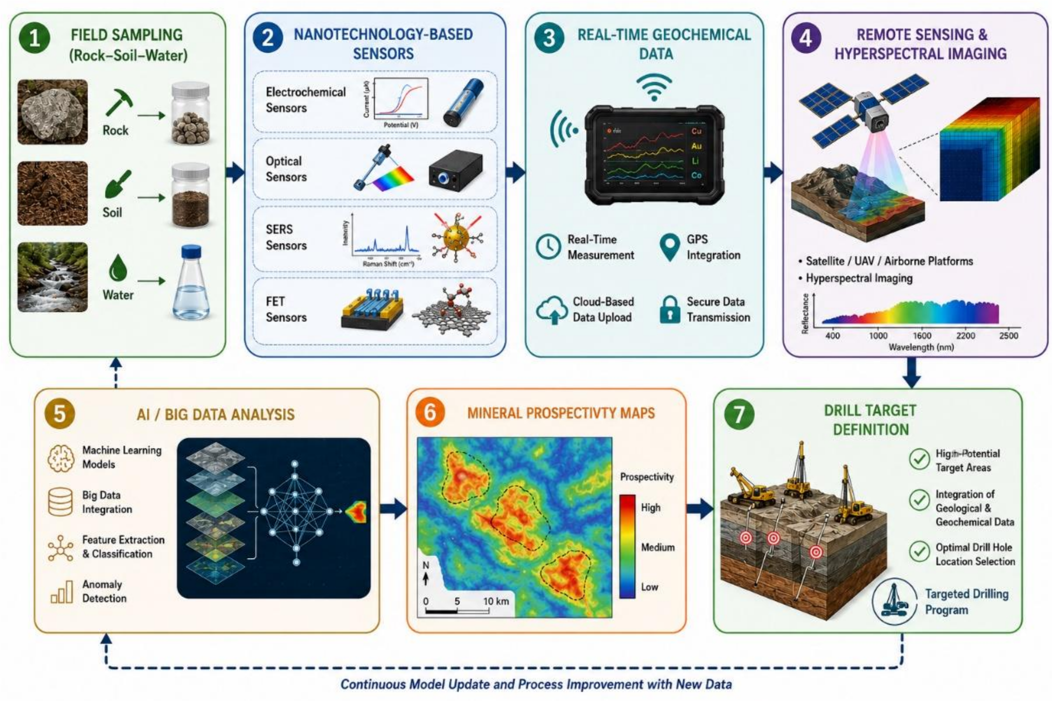

Fig.1. Integrated workflow of nanosensors with digital technologies for mineral exploration.

Continuous monitoring is among the major benefits that come with using the novel generation of sensors for mineral exploration. In particular, by continuously monitoring the chemistry of groundwater, drainage waters, and gases emitted from mines, any geochemical changes related to the formation of minerals may be registered. The use of IoT sensor networks allows sending the data obtained from different sources instantly to centralized databases where its analysis is carried out. Such systems help not only in discovering new mineral deposits but also in monitoring the impact of operations on the environment and sustainable mining practices [147]–[149]. But there are some technical issues that require further solving before nanosensors become common in mineral exploration. The existence of several kinds of ions in the natural geological environment, high ionic strength, variations in temperature, organic matter and mineral matrix composition may affect the work of sensors. Moreover, fouling of the surface, necessity of long calibration period, resistance to harsh conditions and absence of standardization for different geological environments are some of the main research subjects. Therefore, the current research does not concentrate just on the development of sensors with higher sensitivity but also on creation of smart sensors with prolonged life span, recyclability and self-calibration capacity [116], [150]–[152].

When viewed holistically, however, nanosensors emerge not as technologies that completely replace the conventional methods used in mineral exploration but as revolutionary tools that supplement them and hasten the process of work. Combined with artificial intelligence, machine learning, remote sensing, and digital geology, nanosensors are regarded as some of the technologies that can help find critical minerals faster, cheaper, and more accurately. In light of the advent of nanosensors that will be able to perform multi-analytical analysis, coupled with microfluidic systems and autonomous field platforms in the future, the use of decision-making process through data analytics is set to grow significantly in mineral exploration operations [4], [153], [154].

5. Types of sensors

The nanosensor technologies make use of the physical and chemical interactions between the sensor and the targeted analyte to generate an electrical or optical output using different detection methods. Sensors used for geological characterization and mining can be broadly classified into electrochemical, optical, and FET-based systems. In such sensors, nanomaterials including graphene, carbon nanotubes (CNTs), quantum dots, MXene, and metal and metal oxide nanoparticles act as the sensing interfaces; due to the high surface area and enhanced electron transfer capacity of these materials, the performance of sensors is greatly increased. The SERS, FET, and nanohybrid sensors in particular have shown promising results in the detection of metal ions and geological minerals in geological samples in recent years. Therefore, the majority of sensors nowadays are shifting towards being multifunctional sensors that incorporate several nanomaterials and detection methods [155]–[157].

5.1. Electrochemical sensors

Electrochemical sensors are among the most popular nanosensors applied for geological characterization and mineral prospecting. Electrochemical sensors measure the changes in current, potential, or impedance that represent the oxidation/reduction reactions created by the target analyte at the electrode surface. Graphene-, carbon nanotubes-, MXene-, and metal nanoparticle-modified electrodes facilitate the electron transfer process, allowing detecting metal ions at extremely low concentrations. Electrochemical nanosensors have high sensitivity and detection capabilities especially concerning the elements needed for the mineralization such as Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, As^{3+}, Ni^{2+}, and Co^{2+}. Moreover, the inexpensive character, portability possibility, and the capability of performing real-time analysis give a significant edge to the use of electrochemical nanosensors in field studies. Thanks to the recent advances in microfluidics-based electrochemical sensors, it became possible to analyze several metal ions at once [158]–[161].

5.2. Optical sensors (SERS, FET, Quantum Dots)

The basic principle behind optical sensors is to detect the changes in absorption of light, fluorescence, plasmon resonance, or Raman signal produced due to the presence of the analyte of interest. In optical sensors, fluorescent sensors, SERS-based sensors, and field effect transistor (FET)-based optoelectronic sensors have been studied. Some of the frequently used nanomaterials in optical sensors include quantum dots, gold/silver nanoparticles, graphene hybrids, etc. The Raman signal can be amplified millions of times using the plasmon effect produced by gold or silver nanoparticles. Thus, SERS-based sensors help in the detection of trace levels of mineral markers or metal ions. In FET-based sensors, nanomaterials with high conductivity such as graphene or carbon nanotubes are used to convert surface charge changes caused by the target analyte into an electric signal. These sensors possess not only ultra-low detection limits but are highly promising candidates for developing portable mineral analysis systems due to their fast response and high selectivity. The current integration of optical sensors with hyperspectral imaging, microfluidics, and artificial intelligence-based data analysis technologies is advancing the progress of next-generation intelligent sensors for conducting multiparametric analysis in mineral exploration [162]–[166].

To compare the applications of nanoparticle- and nanomaterial-based nanosensors developed in recent years in geological and geochemical analyses, representative studies reported in the literature are summarized in Table 2. Table 2 provides a comparative overview of different nanosensor platforms in terms of the detection technique used, the type of nanomaterial, and the target analyte or geological parameter. This comparison enables an assessment of the potential of different nanomaterial architectures in geological characterization, geochemical analysis, and mineral exploration applications.

Table 2. Representative recent nanoparticle-enhanced nanosensors for geological characterization, geochemical analysis, and mineral exploration.

Source / Year	Detection Technique	Nanoparticle / Nanomaterial	Target Analyte / Geological Parameter
[167]	Electrochemical	RGO–MWCNT–AuNP	Cd^{2+} and Pb^{2+} in soil
[168]	SERS	Ag nanoparticles	Au^{3+}, Ag^{+}, Cu^{2+} and Zn^{2+}; gold mineralization
[169]	SERS	Ag nanoparticles	Hg^{2+} in cinnabar
[170]	SERS	Au nanostars	Hg^{2+}
[171]	Electrochemical	BiNP@LIG	Cd^{2+} and Pb^{2+} in soil
[172]	Electrochemical	Silica isoporous membrane	Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} in soil
[173]	Electrochemical	rGO/polydopamine/alanine	Cd^{2+}, Pb^{2+}, Fe^{2+} and Cu^{2+}
[174]	SERS	Au nanostar@Ag satellite	Hg^{2+}
[175]	Electrochemical	Bi/GO	Cd^{2+} and Pb^{2+}

6. Integration of artificial intelligence, iot, and remote sensing

The capability of sensors developed using the principles of nanotechnology in terms of conducting precise measurements is not the only factor that determines the efficiency of such devices in mineral exploration and geological surveying tasks. At present, the capabilities of the real-time processing, integration, and automatic interpretation of the huge amount of data provided by sensors considerably change conventional approaches to mineral exploration. Thanks to the integration of artificial intelligence (AI), IoT, remote sensing, GIS, and cloud computing systems, it became possible to process the geological data much faster and create mineral potential maps with a high degree of accuracy [176]–[178]

AI algorithms are increasingly being employed for analyzing the multivariate geochemical data provided by nanosensors. Specifically, ML and DL-based models have been quite successful in achieving noise reduction in signals received from sensors, detecting anomalous geochemical values, classifying several metal ions, and predicting mineralization zones. AI algorithms such as Random Forest, SVMs, ANNs, and CNNs are capable of uncovering intricate geochemical relations that are hard to discern using conventional statistical methods. Consequently, large data sets provided by nanosensors can be analyzed more effectively, and better-informed decisions can be taken in relation to drilling targets [122], [179], [180].

Through IoT technology, nanosensors can be set up at different places to collect data on an ongoing basis and send that data to a central database through wireless communication channels. With the help of IoT sensor networks, it becomes possible to monitor soil, rock, groundwater, and other environmental parameters in real time; instant detection of geochemical changes taking place in a particular area is also made possible through these technologies. Such systems make it possible to cut down on manual sampling work especially in mining areas and increase the frequency of data collection while cutting down measurement errors due to human interference [181]–[183].

Also, remote sensing techniques are quite useful in supplementing field information collected by means of nanosensors. Images produced through hyperspectral imaging, multispectral imagery captured by satellites, LIDAR systems, and UAVs are often employed to determine surface mineralogy, areas of hydrothermal alteration, structural geology, and lithological variations. In the process of field investigation, the analysis of geochemical anomalies detected by nanosensors along with remote sensing data makes possible better modeling of the mineral system. As a result of such an approach, 3D models of mineral potential may be developed based on multivariate data rather than surface data alone [184]–[186].

The combination of artificial intelligence, IoT, and remote sensing technologies as part of the digital mining techniques that have been invented in the last few years is combined with digital twins, big data analysis, and GIS. With the help of the digital twins, the actual state of affairs can be monitored online and different exploration scenarios can be simulated beforehand. The ongoing data flows from the sensors allow for the updating of the mineralization models dynamically and thus contribute to the optimization of exploration processes. The benefits of such systems are provided not only during the process of the search for new deposits but also during the production planning and environmental monitoring in existing mines [187]–[189].

In summary, the development of nano-sensors, along with other technological advancements, such as artificial intelligence, IoT, and remote sensing technology, is helping in making decisions based on data for mineral exploration processes. In the coming years, with the help of wide use of smart sensor networks consuming less power, autonomous ground vehicles, UAVs, and AI-enabled decision-making system, it is likely that real-time geological characterization will be a routine process. It will not only lower down the cost of exploration process but will also make an important contribution to discovering critical minerals [190]–[193].

7. Current challenges and future prospects

Despite the obvious benefits of sensors developed using nanotechnology such as high sensitivity, low detection limit, and real-time analysis in the processes of geological characterization and mineral exploration, there are certain scientific and technological problems that need to be solved before applying this technology in the field on a massive scale. The problem is that most of the sensors which give the required results in laboratory conditions fail to work properly in real geological samples. Indeed, samples of rock, soil, sediment, and groundwater include many ions, organic substances, and suspended particles, and all these elements have an effect of interference on the surface of the sensor. Therefore, the selectivity may decrease, false positives and negatives may arise, and the reliability of the sensors may be reduced. That is why modern studies pay attention not only to the reduction of the detection limit but also to the development of the new generation of selective nanomaterials [194]–[196].

Another notable problem is related to the stability of nanosensors under field conditions. It is known that such parameters as temperature changes, humidity, pH variations, mechanical vibrations, as well as surface fouling may adversely influence the precision of the measurements made. Since sensor networks are supposed to operate for months continuously collecting data, it makes calibration a difficult task. This is the reason why the creation of intelligent sensor systems that are capable of cleaning themselves, auto-calibration, as well as low power consumption has become one of the main goals of modern researches. Moreover, the creation of hybrid nanocomposites, which are less susceptible to biological and chemical decomposition, is thought to be one of the main solutions [194], [197], [198].

Another problem related to the use of nanosensors that needs to be overcome before they become used in industry is the issue of standardization. As the effectiveness of sensors produced by various research groups is tested using different experimental conditions, it is difficult to compare their performances. The absence of unified standards concerning the methods of preparing samples, calibration of devices, determination of the limit of detection, and other performance criteria hinders the development of commercial systems based on these sensors. The need to establish the performance criteria of sensors for geological purposes by international standardization bodies is considered to be crucial in the future use of such technologies in mining [199], [200].

Moreover, large-scale production and economic viability of nanomaterials are also one of the aspects that need proper evaluation. Despite the high efficiency of materials like graphene, MXene, quantum dots, and certain metal nanoparticles, the cost of synthesis, the difficulty of production process, and instability may restrict their practical implementation. Moreover, at this moment, there is not enough data about the behavior of some nanomaterials in the environment and possible ecotoxicological effects of those materials. Thus, the development of environmentally friendly and recyclable nanomaterials synthesized via the green synthesis is of crucial significance both economically and sustainably mining perspective. As it is clear from Figure 2, the solution of existing problems seems to lie in the integrated development of next generation nanomaterials, big data analysis and smart sensors network supported by artificial intelligence [130], [201], [202].

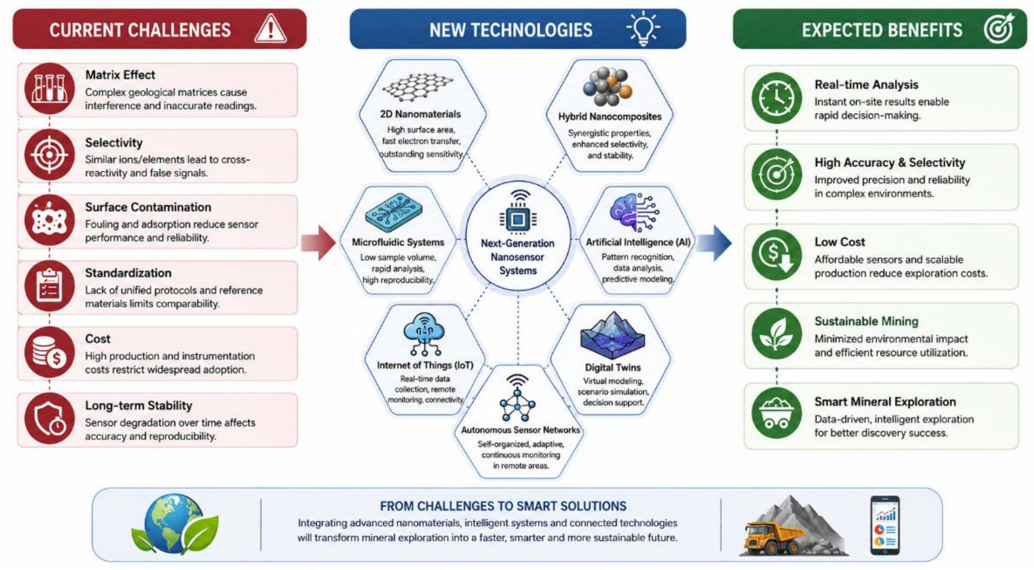

Fig. 2. Current challenges and future directions for nanosensors in geological characterization and mineral exploration.

For the future, the mineral exploration process will not utilize any one technology but will instead make use of a multidisciplinary digital platform. Geological characterization in real-time will be achievable through the combination of artificial intelligence, internet of things, hyperspectral imaging, unmanned aerial vehicles, digital twin technologies, and cloud computing technology alongside nanosensors. Additionally, microfluidic technologies that are able to determine multiple analytes, flexible electronics, wearable sensors, and field robots will form some of the most vital elements in future mineral exploration processes. This combination of technologies not only reduces the cost of exploration but also enables the discovery of critical minerals in a shorter period of time as well as minimizing any negative environmental impact while managing resources sustainably. Therefore, the future of nanosensors will require interdisciplinary cooperation of material science, analytical chemistry, artificial intelligence, and earth sciences [122], [203], [204].

8. Conclusion

The fields of geological characterization and mineral exploration are some of the scientific areas that always keep changing and need new technologies according to the increasing needs for critical minerals, the energy transition, and sustainable mining. While traditional methods of geological, geochemical, and geophysical analyses are highly accurate, their limitation is that these methods are slow, costly, and laboratory-based. However, nanosensors are coming into the picture as the next generation analytical tools because of their capacity to analyze geological samples instantly and accurately by virtue of having nanomaterials with large specific surfaces, effective signal transduction capability, and low detection limits.

The principles of operation of sensors based on nanotechnology, the materials used for their development, and electrochemical, optical, SERS, and FET-based sensors are considered in detail in this review. In addition, the application of these sensors in the processes of geological mapping and mineral exploration has been reviewed; their role in determining metal ions, identifying zones of alteration, detecting geochemical anomalies, and on-site analyses has been assessed. It can be stated that the analyzed literature clearly indicates that sensors based on nanotechnology are not just devices that help in laboratory analyses; they have become an important tool that allows making quick decisions on site, helps with sample selection, and improves drilling target determination.

Technological advancements in nanomaterials science are crucial to improving the effectiveness of sensors. Nanomaterials such as graphene, carbon nanotubes, MXenes, quantum dots, and nanoparticles made of metals and metal oxides substantially improve the sensitivity, specificity, and durability of sensors due to their high electrical conductivity, high surface area and functionalized structure. In addition, hybrid nanocomposites, microfluidics and multiplex analyte detection platforms provide the basis for future intelligent sensors.

In recent years, the use of nanosensors along with artificial intelligence, machine learning, the Internet of Things, remote sensing, hyperspectral imaging and geographic information systems has provided the opportunity for developing an innovative data-based approach for mineral exploration. The analysis of the data coming from sensors through big data analytics helps minimize geological uncertainties and develop more accurate maps of mineral potential and reduce costs associated with exploration. Thus, this technological revolution is the base for changing traditional approaches to mineral exploration into digital, intelligent, and autonomous approaches.

Nevertheless, many obstacles still remain before such nanosensors are used in industry. Selectivity in complex geological environments, stability, sensor standardization, mass production, and cost reduction are some of the most important issues that should be resolved for successful implementation of the technology. Additionally, comparison of the performance of sensors designed by various research teams according to certain evaluation criteria and conducting long-term validation tests under real-life conditions will enhance the application of this technology in industry. Moreover, designing environmentally-friendly synthesis approaches and assessing the impact of nanomaterials on the environment during all stages of their life cycle are important aspects that should be discussed within the framework of sustainable mining practices.

As a result, nowadays, sensors based on nanotechnology cannot be considered as technologies that fully substitute the conventional approaches used in the domains of geological characterization and mineral exploration. Nevertheless, due to the increasing connections between nanomaterials engineering, analytical chemistry, artificial intelligence, data science, and earth sciences, it can be expected that in the future, such sensors will be an integral part of the mineral exploration process, which is automated, autonomous, and highly accurate. With the growing need for the critical minerals, one can assume that sensors based on nanotechnology will play an important role in creating more sustainable and economic mining applications. In this context, future investigations should focus not only on the development of new nanomaterials but also on the integration of these sensors with the decision-making systems supported by artificial intelligence into digital mining platforms.

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Author Contributions

In this article Cumhur Eren IŞIK contributed to design of the study and the final review of the manuscript. Co-author İrem TURK contributed to the literature review, as well as the writing and editing of the manuscript.

Conflict of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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