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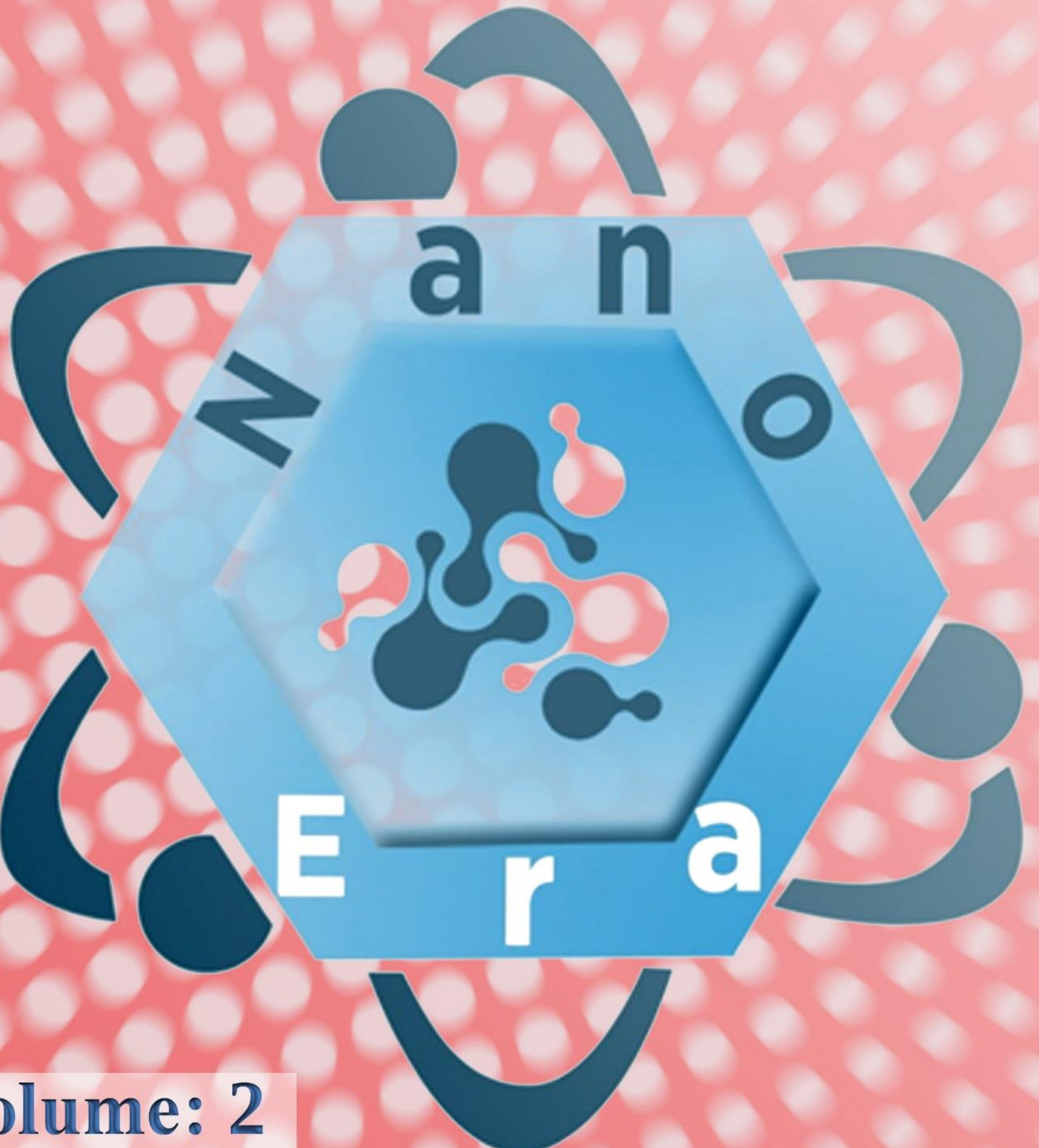

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The NanoEra publishes international scientific research and review articles in English.

Aim

NanoEra journal aims to contribute to the international body of knowledge by publishing articles of the highest quality and importance in all fields of Nanoscience and Nanoengineering.

Scope

NanoEra is an interdisciplinary journal that publishes articles of the highest quality and importance in all fields of nanoscience and nanotechnology. It covers research on the design, characterization, fabrication, and applications of structures, devices, and systems involving the manipulation or control of atomic, molecular, and nanoscale materials, and events.

Research areas covered in the journal

- 2D Materials
- Biomaterials & Nanobiotechnology
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- Nanoelectronic Systems, Components & Devices
- Nanofabrication, Nanoprocessing & Nanomanufacturing
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- Nanomedicine, Toxicology, Drug Delivery Systems & Biopharmaceutical
- Nanotechnology in Construction Industry
- Nanotechnology for Green Energy & Environment Sciences
- Organic and Inorganic Nanocomposites, Polymers
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CONTENTS

NanoEra 2(2), 23-29

NanoEra

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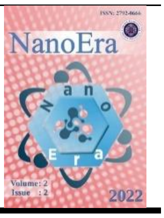

REVIEW ARTICLE

Applications of nanomaterials in highway pavements

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HIGHLIGHTS

\> This study explores the applications of nanomaterials in highway pavements.

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ABSTRACT

Nanotechnology is attracting increasing interest in a broad range of applications. When assessing applications in the field of civil engineering, it is critical to have actual problems that applications can solve for the technology to have a positive impact on the general public's well-being. This article is about pavement engineering advancements that utilize nanomaterials to enhance society by meeting standard requirements and difficulties in the construction sector. These materials research projects are embarked upon to produce more efficient materials. The article has a comprehensive review of the application of nanomaterials, their usefulness, and their applications within the pavement engineering subject. Nanomaterial applications in cold regions, enhancement of physical properties of pavement materials, cost, and application of these materials in soil are all thoroughly covered. Concerns about Nanomaterials Even though nanotechnology and pavement engineering can be used in a lot of different ways and for a lot of different things, it is important to be realistic and accept the limitations and problems that come with the application of these materials, such as health, cost, and other implications. Because of the smaller size of its particles, the use of nanomaterials may present some new difficulties, such as poor packing density, large surface area, and a high cost. A smart design for nanomaterials would take into account these problems and also solve the problems that micrometer-scale materials cause.

1. Introduction

Nanotechnology is the study of matter at the nanoscale. The subject of this article, nanotechnology, deals with matter manipulation on atomic and molecular scales. The unique physical, chemical, mechanical, and optical characteristics of materials on this scale are what nanotechnology seeks to use. Stronger or having distinct magnetic characteristics, nanostructured materials are used in certain cases over other forms or dimensions of the same material. Some others, as far as the conductivity of heat and electricity are concerned, show superior performance. They may also change their chemical composition or even take on a different color when their size or shape changes. When it comes to nanotechnology in pavement materials, there is considerable potential for improvement, powerful enough to significantly alter widely used materials. The need to blend these materials in pavement engineering makes this a worthwhile course. This study investigates the potential application of nanoparticles on highway pavements. Nanosilica, nanoclay, nanocarbon tubes (CTNs), Zycosil, and nanofibers are among them. The use of carbon nano-fibers (CNFS), organic nanoparticles, use of nanomaterials in cold locations, usage of nanomaterials in enhancing the physical features of pavements, the cost of nanomaterials, and application of nanomaterials in soils are among the topics covered in this study.

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2. Nanotechnology

The capacity to understand and manipulate matter on the nanoscale (approximately 1 to 100 nanometers in size) allows for the harnessing of hitherto untapped phenomena and the creation of new opportunities. To create a new universe, it is necessary to use nanoscale science, technology, and engineering, which entails measuring, analyzing, and modifying matter at this length scale [1]. The majority of the current breakthroughs are focused on nanotechnology and the need to incorporate them into civil engineering practice, even if most nano-technical developments originate in disciplines like physics, chemistry, and electrical engineering. When comparing the properties of bulk materials and individual atoms or molecules to those at the nanoscale, there is a clear distinction. Specifically, materials with a nanostructured molecular structure have enhanced strength [2].

Smaller dimensions are just part of the picture when it comes to nanotechnology [3]. It is also possible to use the unique physical, chemical, mechanical, and optical characteristics of naturally occurring materials that exist at the nanoscale. Civilization is working hard to use nanotechnology in paving materials. Material characterization, prediction, and control of material characteristics are possible at the micron level due to nanotechnology. As a result of this technology, most materials, structures, exterior features, and internal components now have a better knowledge of their origins [3,4]. This study aims to improve the performance of materials used in transportation engineering by looking at the latest developments in nanoscience, ideas, and methods and how they are used in pavement engineering.

2.1. Nanotechnology and pavement

Due to the continuing increase in traffic loads and volume with the growing cost of crude oil as a byproduct, the need for better pavement durability, safety, and efficiency has become more important [4–6]. Considering the increasing applications of nanotechnology, asphalt modification is becoming more and more interwoven within the civil engineering industry. Today, asphalt's performance is aided by the addition of nanoparticles. Several experiments and projects have been organized to implement the modification procedure and subsequent improvement results obtained in asphalt, including the road transfer mechanism [7,8].

The use of nanomaterials in pavements is for better, more durable, and longer-lasting asphalt pavements to be used for major infrastructure projects, such as airports, seaports, and roads. This is something that can be achieved by adding different nanoparticles. This topic is always being researched and developed to produce nanoparticles that are simpler to mix and more competitive in cost [9,10]. When conducting research, the use of nanoparticles follows a fast-track route, so the introduction of nanomaterials into asphalt pavements moves at the same pace as its development. High-temperature sensitivity, high ductility, large surface area, and high strain resistance, as well as low electrical resistivity, lead to more widespread use of nanomaterials [10,11]. The morphological characteristics of the nanoscale materials, and in particular, their nanoparticle characteristics, differ greatly from the scale-up [12] "Owing to its unique mechanical, thermal, optical, electrical, and magnetic characteristics, research on polymer grade nanocomposites is gaining increased attention among academics and industry" [13,14]. Included in this combination are a variety of hydrocarbon additives that have a range of hydrocarbon extracts ranging from those of a higher molecular weight to non-metallic additives. Asphalt is often used for its organic bonding properties when it is utilized as a waterproofing substance, a moisture resistance agent, or for corrosion prevention [15]. A summary of the advantageous applications of nano-particles as found in the literature review is presented in Table 1 below.

Table 1. A summary of certain nanomaterials and their applications as presented by the authors.

S/No	Nanoparticles	Application
1	Micro silica (silica fume)	Concrete's compressive and flexural strengths are enhanced.
2	Nano TiO_2	Surface cleaning of concrete pavements
3	Polymer fiber matrix using nano silica	The use of a self-structural health monitoring system in the repair and rehabilitation industries.
4	Carbon nano fibers (CNFs)	The compressive and flexural strengths of concrete may be increased, and self-sensing concrete can be used to monitor the structural state of the pavement. Offers outstanding mechanical characteristics, and high thermal conductivity,
5	Nano-silica (SiO_2)	Improves the viscosity of asphalt, replaces portion of cement to increase concrete strength and early and enhances pavement surface properties.
6	Nano phosphorus	Enhances the visibility on the road
7	Nanotechnology enabled sensors	Temperature, moisture, smoke, noise, strains, vibrations, fractures, and corrosion are all monitored and controlled.
8	Nano Clay	Improves stiffness and tensile strength, tensile modulus, flexural strength, and modulus of thermal stability.
9	Zycosil	In subgrades, it improves CBR value, soil plasticity, and breathability.
10	Nano Fibers	Improves surface-to-volume ratio, high porosity, significant mechanical strength, and flexibility in functionality

2.2. Nanosilica

Silica is abundant throughout the Earth. Colloidal silica, fumed silica, silica gels, and so on are produced by the majority of industrial processes. Recently, there are new applications for nanosized silicas, for example, they are extensively used in the medical and pharmaceutical fields [16]. Nano silica is recommended for use as nanobiopesticides as a result, nanocomposites that include silica are gaining some scientific attention. One of the advantages of these nanomaterials is that they are cheap to produce and have exceptional performance characteristics [17]. To lower the viscosity values of the nano-modified asphalt binder, nano-silica is usually mixed at an appropriate proportion with the conventional asphalt binder. Taherkhani and Afroozi investigated to determine the effects that varying amounts of nano silica had on the engineering qualities of 60/70 asphalt cement [18]. The qualities of modified penetration grade asphalt cement that included varying amounts of nano-silica (i.e. 1, 3, and 5 weight percent) were analyzed. Following the scanning electron microscope evaluation of the modified binder, the penetration grade, softening point, and ductility of the modified binder were determined. The penetration index of the binders was calculated by taking their penetration grade and their softening point into consideration. The findings demonstrated that an increase in nano silica concentration leads to an increase in binder stiffness while simultaneously leading to a reduction in ductility and temperature sensitivity. Taherkhani and Afroozi presented some of the findings graphically [18].

2.3. Nanoclay

The addition of nanoclay to some materials improves their compatibility with organic monomers and polymers. Nano-composites are composed of a mix of polymers with layered silicates with a layer thickness of around one nanometer. Clay minerals exist naturally, and their development is subject to natural fluctuation. A nano-clay (up to 700–800 m^2/g) is created when clay discs are separated from each other. In the process, the nanoclay and bitumen interact more intensively, with better output [18,19].

Even when a single kind of montmorillonite nano-clay is added, the stiffness and viscosity of particular bitumen are usually positively altered. In practice, some physical characteristics of bitumen (stiffness and tensile strength, tensile modulus, flexural strength, and modulus of thermal stability) may be improved when small quantities of clay are used. The elasticity of the nanoclay generally tends to be greater, as is the dissipation of mechanical energy [19]. To strengthen and alter the asphalt binder, bentonite clay and organically modified bentonite are employed. They were made using a mixture of modified asphalt binders, which are created through a melting process through the process of shearing stress. Rutting resistance is significantly improved in bitumen with the addition of Nano clay, an increase in asphalt rheological characteristics, and resistance to cracking significantly improves when bentonite clay is added to asphalt [20–22]. Polymer nanocomposites are one of the most intriguing materials discovered recently, and the physical properties are effectively improved by modifying a polymer with tiny amounts of nano clay, provided the clay is distributed at the nanoscale level [22,23]. Nanoclays are used as a secondary modification to further improve the performance characteristics of modified asphalt [24]. The potential of nanoclays included in sodium montmorillonite and organophilic montmorillonite seems promising to minimize continuing deformation or rutting of asphalt pavements. The combination of clay and polymer leads to a greater dispersion of polymer in asphalt, thus affecting the ultimate rheological characteristics of asphalt [25].

2.4. Nanocarbon Tubes (CTNS)

Taking into account the existing building materials, carbon nanotubes prove to be the most solid material because of the characteristics they have. As a result, carbon nanotubes are 120 times stronger than steel and much lighter than steel [26]. Asphalt combined with carbon nanotubes is very durable and weather-resistant, which makes it recommended for applications on bridges and boat surfaces [26,27]. CTN materials are currently being used for state-of-the-art bridges with enormous hanging cables composed of steel wire that are smaller and more resistant than traditional steel materials [28,29]. Nano carbon tubes (CTNs) in concrete may fill pores; their compressive strength is increased and the pore wall structure is made homogeneous [30]. The world's first test section of road pavement with graphene nanotubes showed a 67% increase in resistance to cracks and ruts [30]. Meanwhile, Graphene is a two-dimensional carbon material made up of sheets of carbon atoms organized in a honeycomb lattice, each sheet being one atom thick.

2.5. Zycosil

Zycosil is a novel nanomaterial that was created for waterproofing with ultraviolet resistance, thermal resistance, and wind erosion resistance. Its nano-size penetration and eco-friendly capabilities make it highly advantageous. It also has certain common characteristics, such as a permanent water-resistant coating over various kinds of soil, stones, and other building materials on roads. Unending critical underground drainage problems in road construction and repair can be achieved by using the Zycosil reactive bonding ability. Research shows that Zycosil in subgrades maintains California Bearing Ratio (CBR) value, soil plasticity, and breathability. However, Zycosil has some restrictions. The solvent used had a negative impact on pre-existing cracks [31]. Ashraf presented Zycosil application to a road [32].

2.6. Carbon Nano-Fibers (CNFs)

Carbon nanofibers (CNFs) are also excellent for interfacial bonding and high tensile modulus and have large surface areas like other nanomaterials. Carbon nanofibers are highly graphical, very compatible, and may be distributed in isotropic or anisotropic modes with most polymer processing methods. You may disperse them into many other matrices, including elastomers, thermoplastics, metals, ceramics, thermosets, and so on, and they will retain their exceptional mechanical properties and great heat conductivity. Carbon nanofibers have a distinctive surface state to make it easier to function and adapt the nanofibers to host polymers or applications with other surface modification methods [32].

2.7. Nanofibers

Nanofibers can be made from different kinds of polymers, both natural and man-made. They have different physical properties and uses, but they are all part of the Nano carbon family [33,34]. The size of the nanofibers varies depending on the polymer used and the manufacturing process [35]. All polymer nanofibers have the same huge surface-to-volume ratio, high porosity, significant mechanical strength, and flexibility in how they can be used.

2.8. Organic nanoparticles

If organic nanoparticles are added to asphalt, the chemical compatibility issue between nanoparticles and asphalt may be resolved. It also prevents the expense of surface functioning of inorganic nanoparticles. The carbon nanostructures, nanotubes, and nanofibers are another fascinating family of organic nanoparticles. Their primary usage has been discovered to be electronics-related applications, such as in electronic and optoelectronic devices or as electrodes and component buffer layers in polymer solar cell components [36]. This behavior of "filling" may be transmitted to construction material fields too.

Using nanostructured carbon materials generally provides better durability [36,37]; graphene, for example, when used as a modifier in asphalt impacts rigidity and improves elastic behavior. The major disadvantage, however, of using graphene as a bitumen modifier—and in general as an ingredient to enhance the mechanical performance of building materials—is the high cost of production. That is why graphene investigations are extremely limited and have been moved on to graphene-derivated nanomaterials such as graphene oxide (GO) and graphene Nanoplatelets or some inexpensive carbon nanotubes and carbon nanofibers [38].

Carbon nanotubes have been discovered to enhance rigidity and lower stress and also improve the mechanical efficiency of hot mix asphalt (HMA) [39]. Multi-wall carbon nanotubes also enhance the rheological characteristics. In this instance, the authors assume that greater defectiveness in multi-wall carbon nanotubes leads to improved rheological characteristics. Organic nanoparticles are undoubted of a chemical nature inherently compatible with that of bituminous materials, and their usage eliminates expenses of additional procedures involving the chemical alteration of the surface of nanoparticles, as in the case of inorganic nanoparticles. However, in certain instances, their costs are still considerable (graphenes, nanotubes). The growing market in the families of carbon and the development of technology specialized in the manufacture of materials of this type will cause a reduction in their prices and likely make carbon nanostructures more attractive to large-scale uses such as asphalt modification [40].

3. Application of nanomaterials in cold regions

According to research, adding nano clay changes to bitumen increases asphalt rigidity and rutting resistance [41]. The indirect tensile strength is also enhanced by the input of nanoclay modifications, which improves the resistance to aging. The elasticity of modified bitumen increases at high temperatures and the energy dissipation decreases due to the nanoscopic dispersion of the clay [41,42]. This improves the durability and life of asphalt pavements, which saves money for maintenance and repairs. However, the nano-material pavement may have certain drawbacks at low temperatures. Research indicates that nano clay-modified bitumen's fatigue resistance is less than untreated bitumen at low temperatures [43]. Despite the drawback of poor fatigue resistance, nano-modified bitumen has several benefits at low and high temperatures. Studies have also revealed that nano $CaCO_3$ modified bitumen has enhanced anti-deformation and anti-aging capabilities in low temperatures [44]. The increased tensile strength of modified asphalt in nano clay is another significant advantage [45]. This is very important because snow and ice can quickly destroy asphalt roads in colder climates. If roads could be designed to cause less damage from deicers, huge amounts of time and money could be saved by reducing the frequency of necessary repairs.

4. Use of nano materials in improving the physical characteristics of pavements

The usage of CNTs in bituminous binders and mixes affects their different characteristics. Its rheological properties, in particular, can be significantly extended [45,46]. It also reduces the underlay thickness and thus the use of stone materials [46]. It may also contribute to improved rutting resistance and reduced oxidative sensitivity. When changed with tiny quantities of nano clay, many physical characteristics (for example, rigidity and tensile strength, the modulus of tensile strength, resistance to bending, and modular thermal stability) of bitumen may be improved if the clay is distributed at the nanoscopic level. The bitumen modified by the nanoscale is typically significantly more elastic than untreated bitumen [47].

The use of nanoclay in asphalt usually improves the viscosity and fatigue of asphalt binders. Research shows that even a tiny portion of nano clay may substantially enhance thermoplastic materials' compressive and shear strength. Adding titanium dioxide (TiO_2) to bitumen leads to a softening point greater than the bitumen base [48]. The performance of bitumen is enhanced while its visco-elastic performance significantly improves at higher temperatures. In comparison with conventional bitumen, this results in a reduction in penetration value as well as an increase in viscosity owing to the better relationship between bitumen particles produced with the integration of nano-particles. Finally, the improved efficiency of bitumen in softening point tests makes it more sensitive to variations in temperature.

Under different conditions and stresses from the outside, a nanomaterial is said to have different mechanical properties. Nanomaterials' mechanical characteristics have been the focus of considerable research for some time now. Although nanoparticles are not nanomaterials, this research aims to improve their mechanical characteristics by incorporating them into a matrix made up of materials that are. Few studies have examined the mechanical characteristics of pure nanomaterials. In Table 2, you can find out more about the mechanical properties of the metal nanostructures that were made.

This information includes the Vickers hardness, fracture toughness, ultimate tensile strength, fracture strength, and impact strength. Nanomaterials, including metal nanoparticles, have a much better fracture strength and toughness than solid Al_2O_3. Nanoparticle incorporation is the likely cause of this phenomenon. The nanocomposite's grain size is less than that of monolithic Al_2O_3 due to the pinning action of metal particles, which also leads to grain refinement and an improvement in the nanocomposite's mechanical characteristics [12]. Interestingly, nanocomposites containing nano-Cu are softer than monolithic Al_2O_3, while nanocomposites containing nano-Ni-Co are harder. This is likely because Cu has a lower hardness than Al_2O_3, and the addition of nano-Cu weakens the hardness of nanocomposites. Comparatively, nano-Ni-Co is harder than Al_2O_3. Adding nano-Ni-Co to nanocomposites makes them harder, up to a point [49]. The final three groups of numbers in Table 3 above demonstrate that the hybrid composites outperform the single-reinforced composites in impact strength, ultimate tensile strength, and Vickers hardness. The mechanical qualities of non-metallic nanoparticles are listed in Table 3.

Table 2. The nanomechanical characteristics of nano metals [12,49]

Material Sample	Fracture toughness (MPa√M)	Impact Strength (J/cm^2)	Ultimate Tensile Strength (MPa)	Fracture strength (MPa)	Vickers hardness (GPa) Fracture
Al_2O_3/Cu(oxide)	4.9±0.7	---	---	819±53	17.0
Al_2O_3/Ni-Co	4.3±0.5	---	---	1070±72	19.0
AA6061/nano B4C	---	12.36	201.54	---	69.39
AA6061/nano SiC	---	15.5	190.21	---	96.38
Monolithic Al_2O_3	3.6±0.3	---	——	536±35	17.8
AA6061/1.5SiC+1.5B4C	---	19.75	280.18	---	173.97
Al_2O_3/Cu(nitrate)	4.8±0.2	---	---	953±59	17.2

Table 3. Nonmetallic Nanomaterials structures and their mechanical properties [50]

Material Sample	Compressive strength (MPa)	Flexural strength (MPa)	Vickers hardness (GPa)	Tensile strength (MPa)	Young's/ Bending modulus(GPa)	Elongation at break (%)
p-type skutterudites+ 1.5 wt%	255±10	45±5	569±70	---	33±10	---
p-type skutterudites+ 0.5 wt	355±15	65±7	513±52	---	40±6	---
p-type skutterudites	630±20	105±10	576±52	---	44±8	---
p-type skutterudites+ 1.0 wt%	320±15	54±7	563±85	---	39±8	---
Kenaf fiber	---	---	---	500-600	40-53	1.5-3.5
oil palm empty fruit bunch fiber	---	---	---	50-400	1-9	8-18
90% nano- PLLA+ 10% nano-HA	---	142.5	---	53.2	3.5	---
100% nano-PLLA	---	135.6	---	55.6	3.3	---
70% nano- PLLA+ 30% nano-HA	---	130.3	---	42.3	3.9	---
80% nano- PLLA+ 20% nano-HA	---	156.8	---	48.6	3.8	---
60% nano- PLLA+ 40% nano-HA	---	125.9	---	38.6	4.1	---

5. The cost of nanomaterials

The cost of most equipment and materials in nanotechnology is presently quite expensive, partly because it is an emerging technology but also because of the intricacy of the technology. In the case of nanomaterials, however, over time, prices have proven to drop. The assumption is that the cost of materials will drop as production methods improve. Since 1990, for example, CNT production costs have fallen significantly and may reach lower values in the future [48]. Bitumen accounts for approximately 0.5% of the mass in ordinary asphalt pavements and 5–17% of the cost of asphalt concrete. With the worldwide depletion of crude oil supplies, the price of bitumen may rise dramatically in the future. Nanotechnology may thus play a part in easing this issue. Also, both construction and maintenance costs need to be looked at in terms of how nanomaterials could be used in pavement engineering, with a focus on the short-term, long-term, and total cost of ownership. As far as maintenance costs are concerned, actions that can ensure minimum pavement maintenance have a direct impact on the life cycle cost during the maintenance period, which is preventable by the development of automatic crack filters and corrosion treatment. In addition, the life of the pavement may generally be enhanced by improving the pavement's resilience to environmental effects. The materials needed for the development of stronger pavement materials are decreasing (e.g., thinner pavement layers) and therefore influence the cost of construction. Life cycle impacts should be considered in any cost assessment in terms of improved paving durability and decreased maintenance needs [48].

6. Application of nanomaterials in soils

Although not formally described as such, many geotechnical substances may be termed nanomaterials, and their behavior has been researched on a nanoscale for many years. Soil is essentially a particulate substance with a large range of particles from less than 1 mm to 75 mm. A vast variety of particle sizes has made soil one of the most complex materials to study, simulate, and use. Unbound materials may also be called natural soils and gravel and consist of soil materials chosen for their particular features. Usually, water is added to these materials to guarantee optimum content, then the material is compacted. Changes in moisture content usually affect the behavior of these materials. A major difference in the usage of a mineral at the nanoscale is that the volume ratio of the surface area usually rises dramatically. Of course, one of the materials frequently seen in paving engineering is clay. Their reaction to changes in the moisture content of the material causes extremely unique difficulties in the pavement engineering area since most clays have low friction angles and some of them are expansive [12,49–53].

7. Future prospects

In light of the findings of this literature study, there are numerous properties of nanotechnology that may be used in the construction of pavements to improve their overall performance. Depending on the client's needs, flexible, breathable, ductile, permeable, or impermeable concrete qualities may be designed for specific purposes. The application of nanotechnology in engineered materials will facilitate the optimization of regional resource use and the minimization of wasteful transportation. With nanotechnology's continued development, there could be a reduction in the cost of pavement maintenance and an extension of the lifetime of pavement. It may also aid in the development of cement concrete and asphalt blends that can withstand environmental stresses such as freezing and thawing, sulfate, corrosion, acid rain, and others. This new idea could help make materials that can withstand blasts and conduct electricity, as well as materials that can sense changes in humidity, temperature, and even stress.

8. Conclusion

By enhancing building materials' performance and lowering energy consumption, nanomaterials may help reduce the use of natural resources. The use of nanomaterials in construction gives the construction of pavements a cheaper, quicker, safer, and more durable advantage. The inclusion of nanoparticles has been clearly shown to enhance the performance of asphalt binders. Properties like the softening point and viscosity of asphalt may be enhanced (raised) along with bitumen penetration. Furthermore, compared to conventional asphalt, the tensile strength of the modified bitumen is enhanced. The same goes for the rutting resistance, which is far better than conventional asphalt. Nanoparticles (considered additives) have not been very appealing to researchers since they are considerably more expensive than typical additives like polymers. Today, the constant commitment of more and more researchers in the area of nano-technology has resulted in the creation of many new creative and low-cost manufacturing techniques for nanomaterials and made them suitable for use in pavement materials such as asphalt binders. Many advanced research and development applications for asphalt mixtures that are made with nanomaterials are still being made to meet different needs in pavement engineering today.

Conflict of Interest

No conflict of interest was declared.

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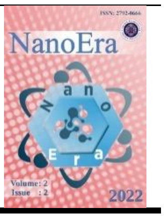

REVIEW ARTICLE

Using nanobiosensors in the determination of food safety and quality

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HIGHLIGHTS

> The unique properties of nanomaterials expand the application possibilities of nanobiosensors in the food industry.
> Nanobiosensors enable the rapid detection of contaminants and nutrient content in foods.
> A growing number of publications and patents demonstrate the outstanding development of nanobiosensors in the food industry.

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ABSTRACT

Today, there is a growing demand for fast, reliable, and cost-effective systems for the detection, monitoring and diagnosis of food ingredients and contaminants. Quantitative/qualitative analysis of foods is carried out using traditional analytical methods, such as chromatographic and spectroscopic techniques. Despite their sensitivity and accuracy, these methods are challenging because of the multi-stage and complex sample preparation procedures, requiring specialized personnel and expensive instrumentation for analysis. In addition, their labor-intensive and time-consuming nature eliminates the possibility of on-site and high-frequency monitoring of the analytes. A wide variety of nanotechnology-based new nanobiosensors are being developed in order to eliminate the difficulties posed by these techniques. In this context, in the present study, nanomaterials used in the development of nanobiosensors for use in foods, their working principles and their use in foods were examined.

1. Introduction

In recent years, with the change in consumer preferences and awareness, interest in quality and safety issues in food has increased. For this reason, all parties operating in the food industry are under pressure to pay maximum attention to the supply of products in terms of quality and safety. These grounds are accurate, real-time, selective, cost-effective, free from interaction with other contaminants, etc. making it necessary to develop new methods [1]. Based on this need, biosensors have been defined by the International Union of Basic and Applied Chemistry as “a device that uses specific biochemical reactions generated by isolated enzymes, immune systems, tissues, organelles or whole cells to detect chemical compounds, usually with electrical, thermal or optical signals” [2]. Biosensors tend to interfere with signal generation due to the influence of the sensing matrix and co-existing molecules. In this context, metallic nanomaterials, polymers, carbon nanomaterials, quantum dots, etc. Today, nanomaterials with different sizes, shapes, and properties, such as nanomaterials, are widely used both in the scientific world and commercially to increase the efficiency of biosensors and reduce interference from the sensing matrix [3].

Basically, biosensors comprise three units, a biological recognition element (BRE), a transducer, and an amplifier and processor [4]. Biosensors have been developed for the sensitive detection of the analyte via BREs on a functionalized supporting matrix (sensor matrix). For this purpose, carbon paste, paper, graphite, and screen-printed electrodes (SPE) are some of the most widely used sensor matrices. BREs (enzymes, aptamer, antibody, nucleic acid, cell and tissue, etc.) are immobilized on the transducer surface so that the biological recognition event occurs with analyte molecules more effectively and selectively. On the other hand, the transducer (optical, electrochemical, thermal,

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and acoustic) transforms the biological recognition event into a measurable signal and enables it to be detected [5,6].

In light of current knowledge, various applications of biosensors, including quality and safety control in foods, have been revealed in many studies. Currently, biosensors are actively applied in foods for different purposes (pathogen, toxin, heavy metal, nutritional component, detection of prohibited substances, etc.). Moreover, these biosensors have been integrated into nanomolecules for the development of nanobiosensors to improve the performance of the detection system [7]. In this context, the development and application of nanobiosensors, which have a wide place both academically and commercially in the determination of food safety and quality, increase the interest in these materials. In the present review, the materials used in the development of nanobiosensors, their working principles and their applications in food are discussed.

2. Materials needed to build a biosensor

2.1. Nanomaterials

2.1.1. Metal and Metal Oxide Nanoparticles

Metal nanoparticles (MNPs) have many advantageous properties that make biosensors useful as a component of nanobiosensors. Many metals and metal-organic nanoparticles (NPs) are used in the development of nanobiosensors. Of these, gold, silver and platinum nanoparticles are the most popular. While these noble metals are chemically inert in bulk, they exhibit unique physicochemical properties at the nanoscale. It is possible to classify MNPs according to the physical/electrochemical changes that occur as a result of the binding of the analyte to be analyzed and the receptor target immobilized on the surface of the MNPs. MNPs contribute to the development of nanobiosensors by playing roles such as immobilization platform, accelerating electron transfer, catalyzing the reactions of chemical luminescence with their substrates, amplifying mass changes and improving refractive index (RI) changes [8].

Currently, among these MNPs, gold NPs (AuNPs) are widely used for biosensor applications due to their biocompatibility, unique opto-electronic properties, and relatively simple fabrication and modification techniques. AuNPs, which typically have a size between 1-100 nm, have a high surface-to-volume ratio. This property of AuNPs allows them to be used to immobilize a wide variety of biomolecules. Its superiority over other MNPs is that it supports quick and direct electron transfer, has excellent conductivity, and is a good stimulator for signal amplification with light scattering properties. All these features have allowed using AuNPs to improve the performance of optical, Electrochemical, and piezoelectric biosensors. On the other hand, they also provide the opportunity to adjust the light absorptions in the entire visible spectrum through their size, surrounding environment, and capping material [9]. Silver nanoparticles (AgNP), another important MNP, have a size of less than 2 nm and have attracted attention due to their photoluminescence in the ultraviolet (UV) region, just like AuNPs. Again, its molecule-like properties have allowed its use in biosensor applications. AuNPs have unique optical, catalytic, and electronic properties, which have enabled their use in the production of various biosensor platforms [10]. Their ultra-small size, strong fluorescence, good stability, low toxicity, good biocompatibility, and being cheaper than precious metal nanomaterials and having the same properties as precious MNPs have made copper nanomaterials (CuNP) preferable for the use of biosensors [11]. Among other materials included in MNPs, NPs based on iron oxide (Fe_2O_3) and manganese oxide (MnO_2) are considered the best-known magnetic nanomaterials due to their higher electron transfer rates. These are also components that are widely used in the construction of nanobiosensors in bioanalytical applications [12]. Cobalt oxide-based nanoparticles (Co_3O_4 NP) are of great interest in nanobiosensor applications due to their physical, chemical, magnetic, optical and electronic properties. It is especially used commercially for gas and chemical sensors [13]. As a bulk material, titanium dioxide (TiO_2) powder is applied in personal care products and paints as well as giving white color to some food products and increasing the brightness of food. In their different forms, TiO_2 NPs show features such as photocatalysis, n-type semiconductor, non-toxic, biocompatible, low cost, high stability and environmentally friendly. These features provide a good use of transforming materials in the development of biosensors for food safety and quality [14].

2.1.2. Semiconductor Quantum Dots

Semiconductor Quantum Dots (QD) are one of the most preferred nanoparticles for researchers as fluorescent labels in recent years. They play an important role in the development of different platforms for the detection of many analytes using their semiconductor-like electrical properties and narrow and size-tunable emissions. QDs with different compositions and emissions, such as CdS, Pbs, and ZnS, are widely used today to detect antibiotic residues by labeling them with complementary strands of aptamer specific to antibiotic residues [15].

2.2. Bioreceptors (Biological recognition element)

Biological materials such as antibodies, aptamers, cells, enzymes, receptors, or neurons are used as recognition/sensing elements in biosensors. BREs are known for their high specificity and selectivity towards the target molecule compared to their counterparts. These properties allow for ease of functionalization and amplification against any antigen in animal and microbial models. On the other hand, the unstable structure of BREs, which is one of the most important problems encountered in biosensor applications, is a problem that needs to be solved. Therefore, they must be immobilized [16].

Enzymes are common biocatalysts that are effective in increasing the rate of biological reactions. The working principle of enzyme-based biosensors can be explained by the following possible mechanisms: (a) The analyte is metabolized by the enzyme and thus the enzyme concentration is estimated by measuring the catalytic conversion of the analyte by the enzyme, (b) the enzymatic product formation as a result of an enzymatic reaction inhibited or activated by the analyte, and (c) changes in enzyme characteristics are monitored. Antibodies, also known as immunoglobulins, are preferred biorecognition elements in the development of biosensors for the detection of food contaminants, as they have good selectivity against their antigens [17].

Recognition of DNA sequences is necessary to control and detect molecular structures. Using single DNA/RNA strands or synthetic oligonucleotides called aptamers as BRE is a rather new and interesting approach. DNA-based biosensors use DNA probes for BRE, which are then converted into a signal using the transducer. Aptamers are small chain synthetic oligonucleotides that can bind specifically to toxins, peptides, ions, whole cells or proteins. Aptamer-based detection methods have attracted important attention in biosensor applications due to their high selectivity and affinity for bio-recognition elements [18].

2.3. Transducer

According to their working principles, transducers are generally classified as electrochemical, optical, thermal, electronic and gravimetric. Electrochemical transduction, which is among the available sensing modes, provides high sensitivity and specificity and portable analyzers, allowing the necessary instrumentation to be miniaturized [19]. Especially with advances in nanotechnology, these transducers allow simultaneous parallel monitoring of multiple chemicals or biological parameters or monitoring of a single parameter in several samples.

Fluorescence is another physical process used to develop sensors. Surface plasmon resonance (SPR), which is one of the optical techniques for pathogen detection, has widespread use. Techniques based on optical-based sensors monitor optical signal changes that occur between a functionalized nanomaterial and a toxin or bacteria. Used in this sense, SPR is the basis of many standard tools for measuring the adsorption of material onto planar metal surfaces or the surface of metal NPs. An SPR sensor can be used to measure the amount of analyte captured as it records the shift of the resonant wavelength as a function of time. In this context, fluorescent approaches are used in numerous biosensing applications [20].

Another type of transducer, piezoelectric sensors, consists of a piezoelectric material (usually a crystal) whose surface undergoes mechanical deformation and displacement of electric charge when pressure is applied, or vice versa when pressure is reduced. The quartz crystal microbalance (QCM) developed for this purpose is the most popular piezoelectric detector today. It works based on sending an electrical signal through a gold-plated quartz crystal with a biological recognition element on its surface. When bonding occurs, the mass change produces vibrations in the crystal, and the oscillation frequency in the crystal changes [21]. Thermal biosensors take advantage of the fundamental properties of biological reactions (exothermic or endothermic), namely the measurement of heat energy absorbed or released during the reaction. With this feature, the amount of thermal energy released as a result of the reaction with signal detection components is converted into quantitative data, revealing the detection and amount of the analyte [22].

Colorimetric nanobiosensors are of great interest because of their simple and versatile functions. The frequency of absorbed light can vary depending on the shape, size, composition and aggregation state of the nanoparticles. In this regard, MNPs offer an extremely high molar extinction coefficient. Colorimetric nanobiosensors are widely used today for foodborne pathogen detection and work based on the principle of changing plasma coupling between NPs [23,24].

3. Working mechanism of nanobiosensors

Nanobiosensors are used today as a way to detect different analytes, such as antibodies, nucleic acids, pathogens and metabolites, toxic substances, prohibited substances, and the detection of components in the normal composition of food. In simple terms, the working principle of a nanobiosensor starts with the binding of the relevant bioanalytes to the bioreceptors, and then continues by modulating the physicochemical signal associated with this binding. Next, a transducer captures the physiochemical signal and converts it to a signal (Electrical, optical, etc.). The variation in the exposed signal is monitored. Analysis of variation in one or more of the different parameters resulting from signal-induced changes quantifies the presence or absence of the analyte (Figure 1). In addition, the nanostructures in nanobiosensors act as an interlayer between biological agents and physicochemical detector components or biological agents, and the transducer is combined with nanomaterials to form a biosensor [25].

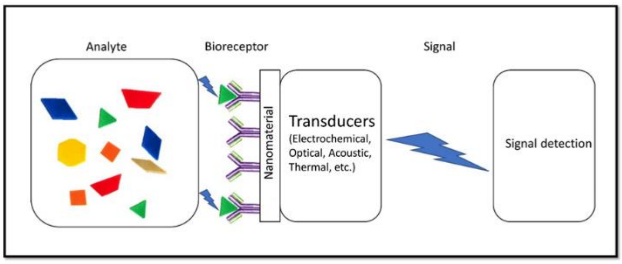

Figure 1. The construction diagram for a nanosensor

4. Their use in food

Today, in terms of food safety, the potential presence of various food additives, drugs, pesticides and fertilizers, pathogenic microorganisms including viruses and bacteria, dioxins, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), heavy metals and biotoxins in foods poses important risks. Moreover, it is clear that various components such as sugars, amino acids, alcohols, organic acids, cholesterol, polyphenols, fatty acids, and biogenic amines must be monitored nutritionally in order to monitor food quality. This situation reveals the need for multidimensional consideration of food safety and quality assurance, and therefore the importance of protecting public health with interventions at every step of the food supply chain [26]. In this context, fast and cost-effective methods should be preferred for the measurements of analytes in the field or on the production line. Moreover, it is possible to perform such analyzes quickly and cost-effectively with nanobiosensors and nanobioanalytical tests instead of time-consuming, costly, and complex applications [27]. The current use of nanobiosensors in foods is discussed in the following subheadings according to their intended use.

4.1. Determination of food components

The food industry needs fast, reliable, and robust sensors at different stages of food processing as well as the final product. Nanotechnology-based biosensor approaches have found their place in various applications for the detection of food components. In this context, Szydłowska-Czerniak et al. [28] developed an AgNP-based nanobiosensor. The performance of AgNP-based nanobiosensor was compared with traditional FRAP, DPPH and FC methods, which show linear correlations in the antioxidant content of 15 types of rapeseed oil. The results revealed significant positive correlations between AgNP-modified FRAP, DPPH, and FC methods for all extracts of rapeseed samples studied. In terms of sensitivity and accuracy, it is remarkable that the analysis of the antioxidant capacity of rapeseed samples with this method gives inexpensive and fast results.

It is known that high intake of caffeine, which is in the structure of some foods, poses a risk to human health. A nanobiosensor capable of detecting caffeine with magnetic molecular imprinted polymeric microspheres (MMIP) prepared using Fe_3O_4 as the supporting core, mesoporous SiO_2 as the intermediate shell, α-methyl acrylic acid as the functional monomer and caffeine as the template has been developed [29]. In this method, MMIPs removed caffeine from beverages, then AgNPs were rapidly screened by colorimetric method. Caffeine, measured semi-quantitatively as ≥ 5 mg L^{-1}, was accurately measured in the 0.1-5 mg L^{-1} range by UV-vis spectroscopy at 393 nm, consistent with HPLC analytical results. The researchers suggested that this method could be used to quickly and precisely analyze caffeine in beverages. In another study, a core-shell molecular imprinted fluorescent nanosensor was developed for the proportional fluorescence and visual detection of folic acid (FA) in foods. For this purpose, the nanosensor was prepared by fixing the printing shell on silica nanoparticles and embedding CdTe quantum dots in the printed shell to provide FA-dependent fluorescent signals. The resulting data revealed a favorable linearity relationship between a limit of detection (LOD) of 48 nM and fluorescence intensity ratio (I449/I619) and FA concentration above 0.23-113 µM under optimum conditions. Qualitative evaluation with visual perception was carried out by evaluating abundant fluorescent color changes from red to pink, and purple to blue. This developed sensor has been evaluated by researchers as having excellent sensing performances such as fast response, high and selective recognition. On the other hand, it has been suggested that satisfactory instantaneous recoveries between 94.8% and 104.2%, which are consistent with the measurement results, were obtained with HPLC-UV [30].

4.2. Food packaging and shelf life

The purpose of food packaging is to increase food shelf life by protecting food against spoilage and bacterial growth in a food or by preventing food nutrient loss. For this purpose, nanotechnology-based approaches used in food packaging offer higher hopes in food packaging by promising longer shelf life, safer packaging, better traceability of food products, and healthier food. Intelligent and active packaging systems produced with nanotechnology will be able to repair tears and leaks (self-healing feature) and respond to environmental conditions (e.g. temperature and humidity changes) [31]. Due to their simplicity, low cost, affordability, and efficiency, Time and Temperature Indicators (TTIs) are widely used today to monitor and demonstrate the quality of foodstuffs [32]. Zhang, et al. [33] developed a nanobiosensor that can show the quality of cakes with AgNP-based TTI. According to the color change resulting from the reaction, they stated that the dark purple color may represent the deterioration and inedibility of the cakes. In another study, a protein-based halochromic nanosensor was designed to evaluate the quality of rainbow trout fillets. In the study, zein nanofibers containing alizarin as an indicator dye were electrospun. The color of the sensor changed to magenta on the 10th and 12th day of cold storage, indicating deterioration. It has been stated that this developed halochromic nanosensor can monitor fish freshness in real-time through color changes [34]. In a similar study [35], cerium nanoparticles (CeNPs) were also used as a multifunctional enzyme mimetic material based on xanthine oxidase to monitor fish freshness, measuring the release of hypoxanthine (HX), a product of nucleotide degradation, in meat and fish, and as a redox-enhancing and chromogenic indicator. The researchers noted the potential for use of this technology as an inexpensive approach to monitoring HX levels, as opposed to traditional multi-step enzyme-based solution assays. In another study [36] an electrospun nanofiber mat based on polyvinyl alcohol and a natural pigment derived from red cabbage (*Brassica oleracea L.*) extract (RCE) was prepared to act as a pH biosensor. The pH sensitivity was calibrated using a color spectrum colorimeter at different pH values of the nanofibers tested using a range of different pH solutions. It has been revealed that this designed mat can be used as a pH sensor and accurately displays pH values in the 2-12 range.

Optical biosensors are widely used in the rapid evaluation of foods due to their simplicity and visualization. In this context, smartphones with high-resolution cameras and advanced computational capabilities draw attention to the development of nanobiosensors as an instrument to reflect the sensitivity of optical sensing. For this purpose, AuNPs show different *E. coli* O157:H7 concentrations and a new biosensor that uses the imaging feature of the smartphone to monitor the color change of AuNPs has been developed [37]. Magnetic nanoparticles (MNPs) modified with capture antibodies and polystyrene microspheres (PSs) modified with detection antibodies (PSs) and catalases were used simultaneously to react with target bacteria in the first mixing channel of the microfluidic chip, a system was developed to quantify bacteria. The color was measured using the smartphone imaging feature. It has been suggested that this biosensor exhibits good specificity and sensitivity for the detection of *E. coli* O157:H7 in chicken samples with a lower detection limit of 50 CFU/mL.

4.3. Food Processing

Some metabolites that are known to be harmful to human health may be released as a result of some undesirable reactions during the processing of foods. In this context, it can contribute to rapid detection, intervention and process regulation in the processing process. Acrylamide is an amide-type organic compound, which is classified as a probable human carcinogen (Group 2A) by the International Agency for Research on Cancer and formed as a result of the Maillard reaction. A nanobiosensor developed for the detection of raw potato glucose content at 150 °C ($r = 0.8985$, $P<0.01$) and 176 °C ($r = 0.9949$, $P<0.01$) revealed a high correlation between the level of acrylamide in fried potato chips [38]. This developed biosensor can be used to quickly predict the formation of acrylamide during industrial potato processing. An electrochemical biosensor based on DNA-carbon dots of N-nitrosodimethylamine (NDMA) and N-nitrosodiethanolamine (NDEA), another mutagenic and carcinogenic food component, has been developed [39]. In this study, after the chitosan carbon dot was deposited on the glassy carbon electrode (GCE), DNA was electrostatically immobilized on the surface of the carbon dots and a sensing electrode (DNA/chiCD/GCE modified electrode) was produced. It was emphasized that it could be a fast and alternative method for the detection of nitrosamines in foods with detection limits of 9.9×10^{-9} M and 9.6×10^{-9} M. In another study [40], a graphene-based nanosensor was developed for in situ monitoring of polycyclic aromatic hydrocarbons (PAHs) in aqueous solutions. The sensor was fabricated using photolithography and etching Au/Ti film on a silicon layer followed by the transfer of a single sheet of graphene prepared separately by chemical vapor deposition (CVD). It has been suggested that this developed sensor can be applied to many contaminated water bodies or engineering systems due to its low detection cost, portability, and ease of use.

4.4. Microbial contamination

Today, a wide variety of biosensors have been developed to detect foodborne pathogens and their toxins [28]. For this purpose, a nanobiosensor based on Förster resonance energy transfer (FRET) between semiconductor nanocrystals (quantum dots, QDs) and dark quencher-labeled peptide probes has been reported for botulin-BoNT serotype E (BoNT/E) detection. Peptide probes contain a specific cleavage site for active BoNT/E. The detection limits were reported as 0.02 and 2 ng/mL for BoNT/E light chain and holotoxin, respectively, and the sensor was reported to give results in a total of 3 hours. It has been suggested that this nanobiosensor, which has been developed with its advantages such as high sensitivity, simple operation, short detection time and can be used in parallel with probes developed for other BoNT serotypes, will be useful for rapid BoNT/E detection and serotype discrimination in food analysis [41].

A nanobiosensor has been developed for fast, easy and high-sensitivity detection of *Staphylococcus aureus (S. aureus)*, another important food pathogen [42]. In this study, a paper-based portable device was produced to detect bacterial cells and a value between 102 – 108 CFU/mL was determined as the linear dynamic range of the colorimetric Au/Pt NC-based optical sensor. Moreover, it has been suggested that this microfluidic paper can detect entire bacterial cells very quickly in five minutes, with high sensitivity in real samples. In a similar study, a biosensor based on superparamagnetic ultra-small iron oxide nanoparticles (USIO NPs) combined with membrane filtration and low-field nuclear magnetic resonance (LF-NMR) was developed for rapid detection of *Salmonella* [43]. In this study, firstly, specific binding of free biotin capture antibodies and detection antibodies to different *Salmonella* targets in milk samples was achieved. The streptavidin-coated USIO NP probes were then coupled with the biotinylated monoclonal antibody to capture *Salmonella*. Finally, polyethersulfone membrane filtration was performed in the final reaction system to remove unbound probes, and the transverse magnetization time of the filtrate was measured by NMR to indirectly reflect the content of the target substance retained in the filter membrane. The researchers reported that this method showed high specificity against *Salmonella* and the limit of detection (LOD) in pure culture and real samples was 2.3×10^3 CFU mL^{-1} in 150 minutes. With a similar approach, direct detection of *Escherichia coli (E. coli)* in food samples is also possible by measuring and detecting light scattered by cells. This type of sensor operates on the basis of binding with a known protein and can be characterized as a bacterium on a silicon chip that can bind to any other *E. coli* bacteria present in the food sample [44].

4.5. Detection of toxic chemicals

The presence of toxic materials such as pesticides, foodborne toxins, and heavy metals in foods is considered a risk to human health. It is also among the possible risks that the materials used in the packaging of foodstuffs leak into the food and cause unwanted exposure [45]. AuNP (30 nm)-based dipstick competitive immunoassay (anti-DDT antibodies (IgY)) assay to detect organochlorine pesticides such as DDT at the nanogram level (ppb) was developed by Lisa, et al. [46]. In this study, the lowest detection limit of DDT was determined as 27 ng mL-1 with optimized conditions. According to the results obtained, the researchers reported that AuNPs nanobiosensor is an appropriate and rapid application for the detection of organochlorine pesticides in food and environmental samples, since AuNPs have agglomeration properties associated with color production.

Cantilever nanobiosensors have emerged as an alternative to traditional analysis methods to monitor heavy metals, highlighted by the detection of substances at the micro and nanoscale through the use of sensor layers. In a study [47] a new cantilever nanobiosensor functionalized with urease enzyme by self-assembled monolayers was developed for the detection of heavy metals (lead, nickel, cadmium, zinc, cobalt, and aluminum) in water. This developed nanobiosensor presented high sensitivity, good stability, and a detection limit over a wide ppb range during 30 days of storage. Researchers reported that the cantilever nanobiosensor with urease enzyme can detect heavy metals in water sensitively and accurately. In another study [48], Au–Ag nanostructures were developed to detect pesticides in tea samples based on a SERS (surface-enhanced Raman spectroscopy) substrate. Pesticides in tea (dichlorophenoxyacetic acid and acetamiprid) could be detected using the potential difference exhibited by different nutrients in complex matrices. It has been suggested that the developed nanosensor has linearity from 1.0×10^{-4} to 1.0×10^3 μg g^{-1}, 2 s detection time, 99.85% recovery and, 4.85% reproducibility.

4.6. Detection of food allergens

Food allergies can cause life-threatening type I hypersensitivity immune responses. While treatment and emergency care interventions can limit the damage of an allergic episode, there is currently no cure for food hypersensitivities. Due to the complexity of food preparation methods in the modern diet, many patients may be accidentally exposed to a known allergen [49]. In this context, rapid and on-site detection of food allergens is of vital importance. To this end, Weng and Neethirajan [50] developed an integrated microfluidic system with quantum dot (QDs) nanoparticles and aptamer-functionalized graphene oxide (GO) for the detection of Ara h 1 allergen. Researchers reported that this nanobiosensor they developed has a detection limit of 56 ng/mL. In a similar study, Speroni et al. [51] developed an enzyme-linked immunosorbent assay (ELISA) based on antibody-coated magnetic microparticles for the detection of Ara h 3/4 allergen in foods. The limit of detection was found to be 0.2 mg, with a linear response range of 2.5 to 15 mg peanuts/kg. In another study, Zhang and Zhou [52] developed an aptamer-based nanosensor immobilized on graphene oxide (GO) and fluorescent surfaces for the detection of tropomyosin. It has been suggested that this nanobiosensor operates in the concentration range of 0.5 to 50 $\mu g/mL^{-1}$ with a detection limit of 4.2 nM.

5. Conclusion

Nanobiosensors are newly emerged quality and safety detection tools with various applications in foods. It is not possible to limit the current developments in our review with this research. There are currently developed and more sensitive nanobiosensors. While current research focuses on the range of applications and advances made in recent years, several challenges remain. Besides the sensible choice of fabrication method, a number of variables can affect the performance of such detection approaches. It is assumed that it is too early to conclude that nanobiosensors developed based on nanotechnology can provide solutions as a single point of solution. Nevertheless, the use of nanobiosensors in food is promising solutions for the future and is considered to have potential for current food quality and safety assessment applications.

Conflict of Interest

No conflict of interest was declared.

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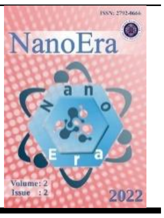

REVIEW ARTICLE

Protein nanoparticle interaction

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HIGHLIGHTS

> Effects of protein properties such as interactions between proteins and target molecules or structures interactions, isoelectric points (pI) and pH on protein corona formation.

> Effects of nanoparticle such as size, shape, surface, charges properties on protein corona formation.

> Protein corona size, quantitative and structural analysis techniques.

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ABSTRACT

With the rapid development of nanotechnology in recent years, nanoparticles (NPs) have started to be used in the pharmaceutical industry for imaging, treatment and diagnosis. For the use of NPs in drug delivery, it is necessary to clearly determine how nanoparticle-based drugs will behave in the biological environment. After these drugs enter the biological environment, they interact rapidly with the proteins in the biological environment and forming a complex called protein corona (PC). The formation of the PC form affects many important events such as the adsorption and distribution of drugs, whether the drug reaches the target area, and the removal of the drug from the body. In order to design a more safety nanoparticle-based drug, the interaction of NPs with protein should be well understood, the physicochemical properties of the resulting PC form and its behavioral characteristics in the biological environment should be clearly clarified. In this review, the factors affecting the protein nanoparticle interaction and the analysis methods of the resulting PC form are briefly mentioned.

1. Introduction

The field of nanotechnology has advanced rapidly in the last decade. Nanoparticles (NPs) are used in various fields such as electronic components, some foods, industry, cosmetics, pharmaceuticals and medicine [1,2]. Recently, the use of NPs in the pharmaceutical field has been expanded for cellular therapy, tissue repair, drug delivery, as sensors metabolites and other biomolecules, implantable biosensors, nanosurger, tissue engineering, nanoparticle-enabled diagnostics [1,3].

The purpose of using nanoparticles in drug delivery is to improve the interaction between drug and target, that is, to create a better therapeutic possibility. Drugs with water solubility problems are either dispersed with nanospheres or enclosed in a nanocapsule by being surrounded by a single polymeric membrane. The efficacy of therapy administered in this way can be altered by varying the residence time and excretion of the drug or by changing site-specific targeting [1].

The application of NPs for diagnostic, therapeutic and imaging purposes depends on different parameters such as the physicochemical properties of these nanoparticles, drug loading efficiency, drug release, and most importantly, low or no toxicity [2].

Interaction between NPs and biomolecules causes the formation of a biological corona form. The biological corona form formed on the surface of NPs belonging to the same pile with different surface properties causes different biological results, as well as contains different proteins [4,5].

NPs with advanced bio-interface capabilities are easily taken into the cell by interacting with the cell membrane. In this way, intracellular receptors can be easily targeted. NPs can generally be taken into the cell in two ways.

First, when nanoparticles interact with the cell membrane, they can be taken up into the cell by endocytosis. By fusion of this endosome with the lysosome, degradation or denaturation of the protein cargo by acidic media or proteases can occur before it enters the cytoplasm. Second,

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when NPs come into contact with biological media, they are rapidly coated with proteins [3].

Looking at the inner and outer layers of the PC formation, the inner layer is characterized by strong bonds in slow change with the environment (hard corona) with a lifetime of several hours, while the weakly bonded proteins (soft corona) in the outer layer have a faster rate of change [4,6]. PC formation is a thermodynamic process.

In protein-nanoparticle interaction, defining the proteins adsorbed on the nanoparticle surface, the lifetimes and conformations of these formed forms, as well as preparing and stabilizing the NPs and giving the nanoparticle a feature, may result in the design of more reliable NPs.

However, in order to understand these formations, biological environments and systems are required as well as chemical approaches because they are too complex to be modeled in non-biological systems.

2. Effects of nanoparticle properties on protein corona formation

Nanoparticles (NPs) are defined as particles ranging in size from 1-100 nm. The full characterization of NPs includes various measurements such as size and size distribution, the chemistry of the material, surface area, state of distribution, surface chemistry and others.

Most importantly, the chemical composition of the material, surface functionalization, shape and curvature, charges, roughness and hydrophobicity or hydrophilicity, functional groups and targeting moieties will greatly affect the nanoparticle surface properties [1,4]. Therefore, all these features will affect the bionanointerface of NPs and the formation of PC.

The high surface/volume ratio of NPs has an active surface chemistry compared to other bulk biomaterials, and therefore they tend to reduce their surface energy by interacting with the biomolecules in the environment where they are dispersed. Because of the difference in these surface properties, NPs must form a new bio-nano interface between biomolecules and NPs so that they can interact with different proteins [4].

Nanoparticle size plays a role not only in the chemistry of the surface of the NP, but also in the formation of the PC composition and the conformation of this structure.

Also, as the size of the NPs changes, the degree of protein adsorption of the NP also changes. One study shows that the size of NPs with a diameter of 70-200 nm is greater than the size of the proteins they adsorb. Smaller sized nanoparticles (30 nm and above) can suppress the adsorption of certain proteins (possibly larger than NP) [7].

The shape of the NP affects the uptake of NP into the cell and the total amount of protein adsorbed. In one study, in vivo protein formation was followed after gold nanoparticles (nanorods, nanostras) injected into mice reached the bloodstream. As a result of the study, it was determined that the total amount of protein adsorbed on the particle surface was affected by the particle size [8].

In another study, if the shape of the prepared gold NPs is spherical, the interaction with the cell layers increases, while changing the shape to the rod geometry reduces this interaction [4,9].

Charges on the NP surface can interact with proteins electrostatically, and their presence can positively affect binding. Moreover, the adsorption of plasma proteins on the surface of NPs increases in direct proportion to the surface charge density of the NPs [10,11].

Most proteins are negatively charged (pH = 7.2) in the physiological environment, NPs with positive surface charge tend to bind proteins more strongly than negatively charged and neutral NPs due to the electrostatic force [10,12]. However, many NPs are stabilized in a physiological buffer with the help of negatively charged groups (carboxylated, sulfate, phosphate, etc.). In general, despite their negative surface charge, these NPs are immediately covered by plasma proteins when in contact with biological fluids [4]. This shows that many different factors play a role in the formation of PC.

The interaction between the NP protein depends on the hydrophilicity and hydrophobicity of the NPs surface. If the surface of the NPs is hydrophilic, it may interact with the protein via hydrogen bonding, while if it is hydrophobic, it can interact with the protein via a wan der Waals bond.

3. Effects of protein properties on PC formation

Most of the factors affecting protein adsorption are directly related to the three-dimensional conformation that protects the protein itself [10,13]. Due to differences in the structure of proteins, the binding behavior of proteins to NPs is different. Typically, specific interactions between proteins and target molecules or structures are non-covalent interactions such as hydrogen bonds, electrostatic interactions, and hydrophobic interactions. Morever, due to the charge present on the surface of proteins, it can detect electrostatic interaction with NPs depending on the isoelectric points (pI) and pH of the proteins [10,14].

4. PC analysis techniques

Along with the analysis of the modification of the physico-chemical properties of NPs, a qualitative and quantitative study of the formation of PC is required.

Because PC formation exhibits a complex and time-dependent dynamic behavior, there is no single technique that fully characterizes protein-NP interactions. The size distribution, density, composition, and molecular weight of the molecules in this structure cannot be easily and quickly analyzed with a single experimental measurement [5].

Prior to the analysis of PC formation, it also needs to be determined whether purification from unbound excess proteins that could alter the equilibrium is necessary or if in situ measurements can be made without the necessary purification. Analyzes can be divided into two direct and indirect methods, depending on whether purification is necessary or not [15].

When we look at the analysis techniques that can be used on PC formation, we can see these techniques size analysis, quantitative analysis, and structural analysis [5].

Common techniques that can be used for size analysis of NPs on PC formation include ultracentrifugation (UC), differential centrifugal sedimentation (DCS), asymmetric flow field fractionation (AF4), and light scattering-based methods. The combination of data from these techniques allows the determination of the apparent densities of the PC complex for different amounts of NP/protein. Moreover, with the use of small-angle X-ray scattering (SAXS) technique and transmission electron microscopy (TEM) techniques, the comparison of NPs before and after corona formation can be examined, thus evaluating the thickness and size of the protein layer [5,16,17].

The combination of various techniques such as mass spectrometry (MS), liquid chromatography-mass spectrometry (LC-MS), inductively coupled plasma-mass spectrometry (ICP-MS) are effective techniques for the quantitative analysis of PC [5,15,18,19]. While the number of protein layers that make up the hard PC can be investigated using the ICP-MS technique, Protein-protein binding sites can also be identified using MS [5].

For PC, structural changes can be studied using techniques such as Fourier Transform Infrared Analysis (FTIR), X-ray crystallography (XRD), nuclear magnetic resonance (NMR), Raman spectroscopy, circular dichroism (CD), electron paramagnetic resonance (EPR), time-of-flight-secondary ion mass spectrometry (ToF-SIMS). Interactions between proteins and NPs can be characterized by isothermal microcalorimetry (ITC) and fluorescence (FL) techniques, which provide thermodynamic parameters such as binding constant (K) and Gibbs free energy (AG). UV, UV-vis spectroscopy and zeta potential analysis are other methods that can be used [5,20–23].

5. Molecular modeling for PC

Thanks to its atomic-scale resolution, molecular modeling can shed light on the formation of the PC form, highlighting key amino acids involved in protein adsorption, binding and conformational changes on the NP surface. At the same time, simulations at the molecular scale make it possible to evaluate the impact of environmental influences, NP material and surface functionalization on cellular uptake [24]. Due to the few and difficult studies to obtain this information experimentally, preliminary information for these interactions can be obtained by molecular modeling. In a study, researchers investigated protein adsorption on the NP surface and its effect on cellular transmission of NP through dissipative particle dynamics simulations [25].

6. Future perspectives for the PC research

There are many biological barriers in the human body. These barriers must be overcome in order for the nanoparticles to reach their targets. Because of their unique size and affinity for surface functionalization to combine desired properties, NPs are particularly well suited to overcome these barriers.

The key role of NPs protein interactions in the use of nanotechnology in drug discovery has become even more important with the recent investigation of NP-protein interaction.

Understanding protein-nanoparticle interactions is crucial for developing effective NP-based drugs. Considering the studies carried out, it is clear that more comprehensive studies are needed. The physicochemical properties of a nanoparticle affect the behavior of these drugs from adsorption to excretion.

Much less has been done on the complete model of the protein-NP complex, which is highly demanded for a better understanding of the binding mechanism and a more rational design of protein-NP interaction. Moreover, the formation mechanism of PC in NPs should be examined in detail, the formation process, stability, conformations and distribution of PC in the body should be investigated in detail, and more clear information about the behavior of this formed form after ingestion is needed. Most of the studies on PC formation are carried out in vitro. In the biological environment, this process is quite complex and dynamic. There are not many studies on the clinical trials of NPs. If these existing studies are taken furthermore safety-based drugs can be produced.

Conflict of Interest

No conflict of interest was declared.

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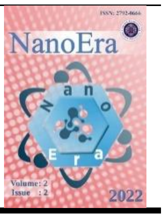

RESEARCH ARTICLE

Photoelectrochemical degradation of methyl orange on CdS–decorated Cr_2O_3/electroreduced graphene oxide nanocomposites

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HIGHLIGHTS

> Chromium(III) oxide /electroreduced graphene oxide (Cr_2O_3/ERGO) nanocomposites were fabricated via electrochemical deposition.

> Prepared Cr_2O_3/ERGO was decorated by CdS nanoparticles using the SILAR technique.

> A ternary CdS/Cr_2O_3/ERGO hybrid nanostructure was used for high-performance photoelectrochemical degradation of methyl orange.

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ABSTRACT

Chromium(III) oxide (Cr_2O_3) and electroreduced graphene oxide (ERGO) nanostructures were synthesized for the first time using a one-pot electrochemical technique on a tin oxide-coated glass (ITO) electrode surface. The surface of the synthesized Cr_2O_3/ERGO nanostructures was decorated with CdS nanoparticles by a simple successive ionic layer adsorption and reaction (SILAR) technique. The characterization of synthesized nanocomposites has been carried out using XRD, FESEM, and EDS techniques. The photodegradation of methyl orange (MO) was investigated in an aqueous suspension containing CdS/Cr_2O_3/ERGO catalyst under artificial sunlight irradiation. The results indicated that the modification of Cr_2O_3/ERGO with CdS nanoparticles exhibits a high performance for the removal of azo dyes.

1. Introduction

Azo dyes, which are highly water-soluble and stable over long periods, are widely used in textile, printing, pharmaceutical, and research laboratories and have been shown to be toxic, carcinogenic, and mutagenic [1–5]. It can enter the human body through the skin and cause lung tissue death, rapid heartbeat, and vomiting. These mostly contain aromatic rings, which are resistant to biodegradation. In addition, due to the presence of the azo group in the dye structure, they can turn into toxic amines [6–8]. Especially for the continuity and development of the textile industry, there is a strong need for the removal of waste dyes by using a non-toxic, highly efficient, and environmentally friendly treatment method [9]. Methyl orange (MO) is the most widely known azo dye [10]. Therefore, MO was chosen as a model dye for photoelectrochemical degradation in this study.

Different metallic oxide-based semiconductor photocatalysts (such as TiO_2, ZnO, CeO_2, SnO_2, MnO_2, ZrO_2, Cr_2O_3 and WO_3, etc.) showed improved performance in dye degradation [11–14]. Among them, Cr_2O_3 is an important transition metal oxide [15]. The Cr_2O_3 remains stable over a wide range of temperature and pressure changes [16]. However, limited by its wide band gap (Eg = 3.45 eV), Cr_2O_3 can only absorb UV light, which leads to exhibit weak photocatalytic activity under visible light irradiation. Therefore, it is necessary to develop a photocatalyst material having improved visible light activity to more effectively use visible light [17]. Recently, many researchers have immobilized catalysts on supporting materials such as

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activated carbon, glass, and graphene. Similarly, decorating the composite with semiconductor metal sulfides such as CdS, PbS or ZnS can be greatly beneficial to extend the light absorption into the visible light region [18–20]. For this reason, CdS nanoparticles decorated Cr_2O_3/electrochemically reduced graphene oxide (CdS/Cr_2O_3/ERGO) electrodes have been considered to be used in photocatalytic applications to collect maximum solar energy.

2. Material and method

Firstly, Cr_2O_3/ERGO was prepared by electrochemical method. Typically, a mixture of 0.1 M KNO_3 aqueous solution containing 2 mg/mL graphene oxide and 10 mM $Cr(NO_3)_3$ was used for Cr_2O_3/ERGO synthesis. Before and during the electrochemical deposition, O_2 gas was passed through the electrolyte solution. CV measurements were recorded at a scanning rate of 100 mV/s in a potential window of 0 V to -1.5 V at room temperature. The Cr_2O_3/ERGO electrochemically deposited on the ITO surface for 5, 10, and 15 minutes under -1.3 V constant potential, were heat treated at 500 °C for 1 hour. Then, the surface of the prepared Cr_2O_3/ERGO nanocomposites was decorated with CdS nanoparticles using the SILAR technique. For the CdS solution medium, 0.1 M $Cd(CH_3COO)_2.2H_2O$ and 0.1 M Na_2S solutions were chosen.

Electrochemical tests were conducted in a standard three-electrode system by a BAS 100i. Ag/AgCl electrode was used as the reference electrode, the Pt wire was employed as counter electrode, and the tin oxide-coated glass (ITO) was used as a working electrode. Structural characterization of the synthesized nanostructures was performed by X-ray diffraction spectroscopy (XRD) and Energy dispersive X-ray spectroscopy (EDS). Field-emission scanning electron microscopy (FESEM) was used for morphological characterization. The photoelectrochemical catalysis ability of CdS/Cr_2O_3/ERGO nanocomposites was investigated for the degradation of MO dye under artificial sunlight. 0.1 M NaCl solution containing 2 mg/L MO was used in photoelectrochemical experiments. Samples were collected from the MO solution at certain times under continuous stirring and absorbance values were measured in the range of 300-800 nm using the Shimadzu UV3101PC visible spectrophotometer. The photoelectrocatalytic performances of the electrodes were calculated using the % decay rates of MO (Equation 1). In Eq.1, A_0 and A_t are the absorbance of MO at 0 min and t min, time respectively.

$$\text{Degradation\%} = [(Ao - At)/Ao]x100 \qquad (1)$$

3. Result and discussion

XRD spectrum was recorded for the structural characterization of CdS/Cr_2O_3/ERGO nanostructures (Figure 1. a). As shown in Figure 1. a, the diffraction peaks could be indexed to Cr_2O_3 with at 39.9°, 44°, 58° and 64° degrees. Also, the observed characteristic diffraction peaks at 24.9° and 43.7° are attributed to the (100) and (110) reflections of CdS. Moreover, 2θ= 24.6° (002) peak was obtained for ERGO. No other impurity peak is detected.

The morphological changes that occurred on the ITO surface with the modification were investigated by the FESEM technique. The surface of the ITO electrode, which has a defined surface, is completely covered with nanostructures (Figure 1. b-c). Before the decoration of CdS nanostructures, the surface of Cr_2O_3/ERGO electrode was investigated by FESEM image. Compared to Figure 1b and Figure 1c, it was seen that the Cr_2O_3/ERGO surface consisted of smaller particles. Nanoparticles with graphene structures are observed more clearly in the FESEM image of CdS/Cr_2O_3/ERGO (Figure 1. c, inner picture) recorded for high magnification. Elemental analysis of the prepared nanocomposites was investigated using the EDS spectrum (Figure 1. d). In the EDS spectrum, Cd and S peaks from CdS, Cr and O peaks from Cr_2O_3, and C peaks from ERGO were obtained. The results of characterizations showed that CdS/Cr_2O_3/ERGO nanocomposites were successfully synthesized.

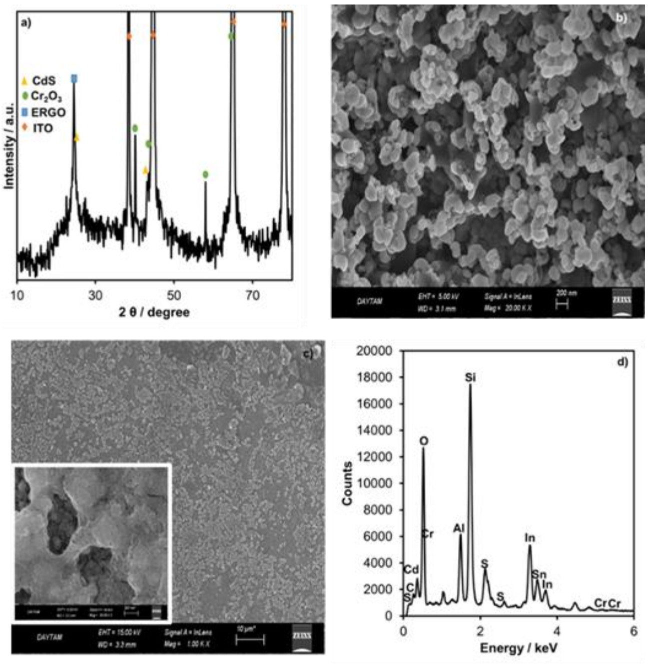

Figure 1. XRD spectra of CdS/Cr_2O_3/ERGO (a). FESEM image of Cr_2O_3/ERGO (b). FESEM images (c), and EDS spectra (d) of CdS/Cr_2O_3/ERGO nanocomposites.

For photoelectrochemical degradation of MO, the photoelectrochemical activities of the prepared CdS/Cr_2O_3/ERGO nanocomposites were investigated depending on the decrease in the UV spectrum peak intensity of MO. Firstly, the effect of Cr_2O_3/ERGO deposition time was investigated. The Cr_2O_3/ERGO nanocomposites deposited at various deposition times (1, 5, and 10 minutes) were examined for removal amount of MO at 1 hour. It was determined that the removal rate (73%) was high in the sample prepared for 5 minutes (Figure 2. a). Secondly; the effect of immersion time (Figure 2. b) and the number of cycles (Figure 2. c) of CdS, which are essential parameters for the SILAR technique, were tested. It was immersed in each ion solution for 10, 20, and 30 s at one cycle. The best immersion time was determined as 20 s in MO removal at 1 hour with a removal rate of ~86%. For the effect of the number of cycles, 1, 3, 5, and 10 cycle samples were prepared at 20 s immersion time. The best photoelectrocatalytic result with a removal rate of 92% in 1 hour of MO removal was obtained in the sample prepared in 5 cycles. According to the above results, CdS/Cr_2O_3/ERGO nanocomposites, prepared for photoelectrocatalytic removal of MO, exhibited high-performance thanks to the synergistic effect between CdS, Cr_2O_3, and ERGO.

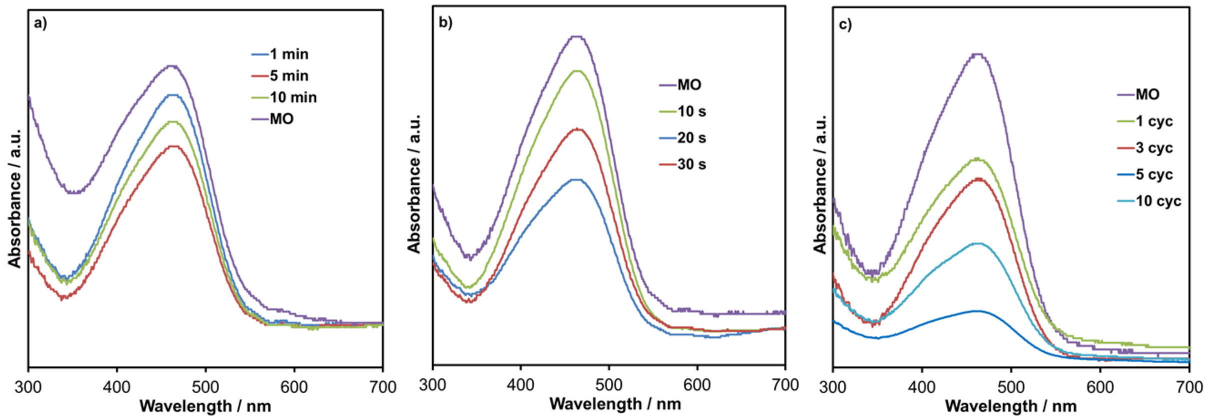

Figure 2. The absorption spectrums of MO on various electrodes: Cr_2O_3/ERGO (a), CdS/Cr_2O_3/ERGO (for the immersion time (b), and the number of cycles (c)).

4. Conclusion

Cr_2O_3/ERGO electrodes were successfully synthesized using an electrochemical technique. The nanocomposite surface was modified with CdS nanoparticles using the SILAR technique. Compared to the Cr_2O_3/ERGO catalyst, the hybrid CdS/Cr_2O_3/ERGO catalyst presented an obvious enhancement in the photocatalytic performance for the MO degradation, resulting from their several merits in both morphology and electronic structure. Furthermore, the deposition time of the Cr_2O_3/ERGO composite, the immersion time of CdS, and the number of cycles were found to be important factors affecting the photoelectrocatalytic degradation of MO in CdS/Cr_2O_3/ERGO electrodes. Experimental results show that CdS/Cr_2O_3/ERGO catalysts with nanoporous structures can serve well to remove organic pollutants from wastewater.

Acknowledgment

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Conflict of Interest

The author(s) declares no known competing financial interests or personal relationships.

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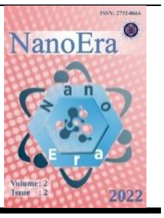

RESEARCH ARTICLE

Nanoparticles supported on Bi_2O_3 for direct formic acid fuel cells

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HIGHLIGHTS

- > Pt nanoparticles obtained over Bi_2O_3 by microwave heating.
- > Formic acid oxidation reaction with this catalyst was investigated.
- > The Pt/Bi_2O_3 showed good catalytic activity and stability.
- > Pt/Bi_2O_3 catalyst is a potential anode electrode material for the electro-oxidation of formic acid.

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Catalyst

ABSTRACT

Direct formic acid fuel cells (DFAFCs) are one of the potential power sources for the rapidly growing requirement of portable devices. Carbon has traditionally been the most common material of choice for DFAFCs electrocatalyst supports. In this study, Bi_2O_3 was used for support material because of some advantages, such as high corrosion resistance and durability. Bi_2O_3 supported Pt catalyst was prepared by using microwave irradiation technique. The catalyst was characterized by using SEM/EDS, XRD and FTIR analyzes. Electrocatalytic activity of Pt/Bi_2O_3 catalyst for formic acid oxidation was tested with cyclic voltammetry (CV) and chronoamperometry measurements.

1. Introduction

In recent years, formic acid has been used as an important fuel either without reformation (in direct formic acid fuel cells). Platinum (Pt) is the most common catalyst in both anode and cathode fuel cell reactions. When formic acid is used as fuel, the oxidation of formic acid on Pt catalysts often occurs via a dual pathway mechanism, which hinders the catalytic activity owing to CO poisoning. This can cause significant problems for the fuel cells. Palladium is found as a solution to reduce the production of CO.

Carbon black has traditionally been the most common material of choice for fuel cell electrocatalyst supports [1]. The other support materials such as carbon nanotubes [2], graphene [3], metal oxides [4] and hybrid structures like carbon-carbon and carbon-metal oxide have critical importance for catalytic activity [5]. In recent years, it is found that certain metal oxides, such as CeO_2 [6], SnO_2 [7] and Fe_3O_4 [8] can enhance the catalytic activity for formic acid oxidation through synergetic interaction with metals such as Pt or Pd. In this study, Bi_2O_3 was used as a support material because of being corrosion resistant and durable. Geng et al. reported that Pt/Bi_2O_3 catalyst is tolerant to CO poisoning and has higher electrocatalytic activity for CO oxidation [9]. In another study, $Pt/Ru/Bi_2O_3$ showed high selectivity toward dehydrogenation and the rate of hydrogen generation is determined [10]. In this study, in order to eliminate CO poisoning problem, it was tried to increase the catalytic activity of Pt nanoparticles over Bi_2O_3 support material.

2. Experimental

2.1. Synthesis of Pt nanoparticles on Bi_2O_3 support

Bi_2O_3 supported Pt catalyst was prepared by using microwave irradiation technique. First, the required amounts of Bi_2O_3 and an aqueous solution of H_2PtCl_6 were added in ethylene glycol and then stirred for 30 min. Then the resulting mixture was operated at 800 W power for 1 min and exposed to microwave energy. The catalyst was washed separately with 300 ml of acetone and 250 ml of distilled

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water and centrifuged to remove impurities. Finally, it was dried at 100°C for 12 h.

2.2. Characterization

2.2.1. Physical and electrochemical characterization

Crystal structures of the catalyst and support material were analyzed by using XRD (Rigaku Miniflex) with a CuKα (λ = 1,5406 Å) radiation source at a scan rate of 0.6° min^{-1} in the range of 20–90° (2θ). Scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS) was used to identify the surface morphology and elemental analyzes of the catalyst. The functional groups of the obtained Pt/Bi_2O_3 catalyst were characterized by FTIR. Cyclic voltammetry (CV) experiments were conducted at room temperature using the Pt counter electrode, Ag/AgCl reference electrode and glassy carbon working electrode (area = 0.071 cm^2) in 50 mL 0.5M formic acid and 50 mL 0.5 M H_2SO_4 solutions with 100 mL total volume used as an electrolyte solution for determining formic acid oxidation (FAO) activity. CVs were recorded with a scan rate of 20mV/s. The chronoamperometry was recorded at 0.3V for Pt/Bi_2O_3 and Pd black catalysts using the same experimental conditions.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of 10 wt % Pt/Bi_2O_3 and that of the reference Bi_2O_3. The diffraction peaks of Bi_2O_3 were shifted to a lower-angle side with Pt loading. The successive shift of the XRD pattern was partly ascribed to the occupation of interstitial sites in Bi_2O_3 by Pt NPs. All diffraction peaks of bare Bi_2O_3 are assigned to bismite crystallized in monoclinic form corresponding to JCPDS files (No. 41-1449.), namely, α-Bi_2O_3 [11].

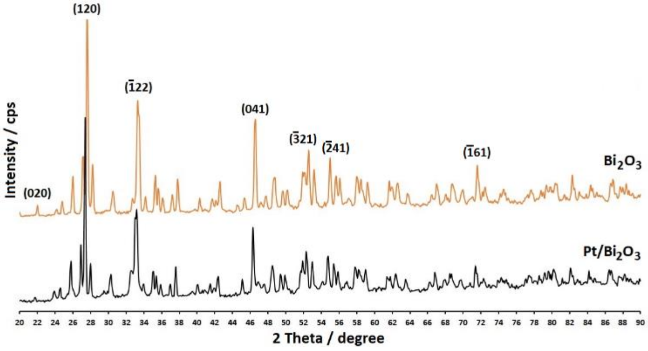


Figure 1. X-ray diffraction patterns of Pt/Bi_2O_3 and Bi_2O_3

Scanning electron microscope (SEM) images of the Pt/Bi_2O_3 and the support Bi_2O_3 are given in Figure 2. SEM image in Figure 2a at high magnification shows the densely packed and well-dispersed α-Bi_2O_3 microrods and Figure 2b shows the Pt clusters on Bi_2O_3. The size of Pt nanoparticles has increased with increasing microwave irradiation time due to the time-dependent nature of coarsening of particles [12]. The Pt domains show a polydispersity in distributions of size may be due to the increasing reaction time from 3–5 min [13]. On the other hand, a short microwave irradiation time will not be sufficient for the doping of Pt nanoparticles on the surface [14]. For these reasons, 1 min. microwave irradiation time is appropriate for catalyst synthesis. The EDS spectrum (Figure 3) of the Pt/Bi_2O_3 catalyst contains Pt, Bi and oxygen.

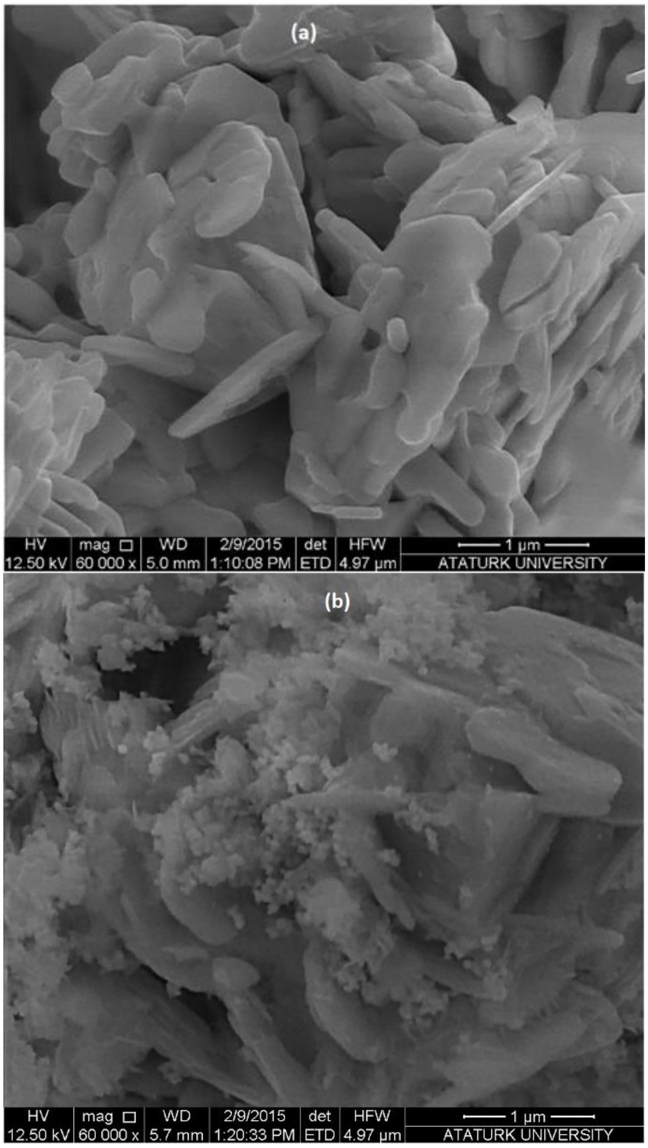
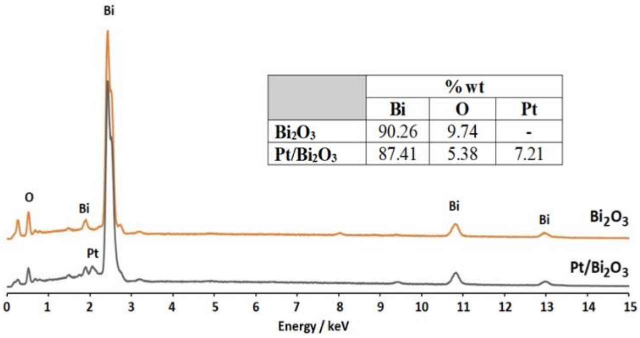


Figure 2. SEM images of the (a) support and (b) Pt/Bi_2O_3 catalyst



	% wt		
	Bi	**O**	**Pt**
Bi_2O_3	90.26	9.74	-
Pt/Bi_2O_3	87.41	5.38	7.21

Figure 3. EDS results of Bi_2O_3 and the Pt/Bi_2O_3

The interaction between pure Bi_2O_3 and Pt doped Bi_2O_3 was studied by FTIR spectroscopy. FTIR spectra were measured in the 4000–400 cm^{-1} range. Fig. 4 shows the FTIR spectra of pure and Pt doped Bi_2O_3. The peak in the region 500-590 cm^{-1} appeared in the FTIR spectrum ascribed to the stretching vibration of Bi-O bond for pure Bi_2O_3 [15]. The C-H-stretching modes can be found between 2700 and 3100 cm^{-1} [16]. The intense peaks at 2980 and 2890 cm^{-1} correspond to the asymmetric and symmetric vibrations of CH_2 groups, respectively, of the Pt/Bi_2O_3 [17]. These C-H stretching modes are probably due to the possible organic molecules available on the surface of the nanoparticles [18].

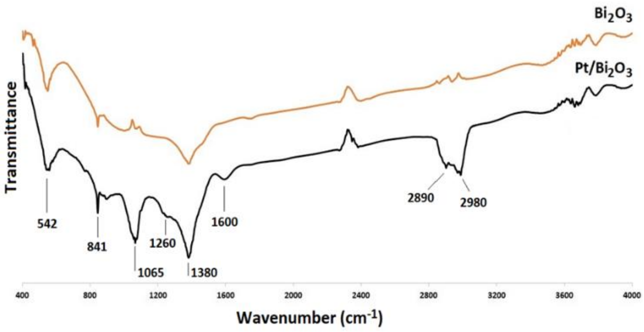


Figure 4. FTIR results of Bi_2O_3 and the Pt/Bi_2O_3

Cyclic voltammetry curves for FAO of Pd black catalyst and Bi_2O_3 supported Pt nanoparticles are shown in Figure 5. It was reported that the electrooxidation of formic acid on catalyst adopts a dual path mechanism, a dehydrogenation path to the direct formation of CO_2 and a dehydration path, and the adsorption of CO intermediate from the dehydration path significantly poisons the activity of Pd catalysts [19]. For the FAO reactions, two peaks were observed in the forward scan. The first peak around 0.30 V results from the direct oxidation of formic acid while the second peak at 0.66 V refers to the indirect path [20]. The reaction mechanisms represented by the following equations [21];

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \quad (1)$$

$$HCOOH \rightarrow CO_{ads} + 2H_2O \rightarrow 2H^+ + 2e^- \quad (2)$$

Pt is blocked by adsorbates in the anodic sweep until the onset of CO oxidation. Thus, Pd is more active than Pt under such conditions, but intrinsic activity of Pt is larger and can be partially seen in cathodic sweep after oxidation of CO, or when adsorption of CO is blocked or reduced [22]. Apparently, the Pt/Bi_2O_3 delivers significantly higher electrocatalytic peak current than that of the commercial Pd black.

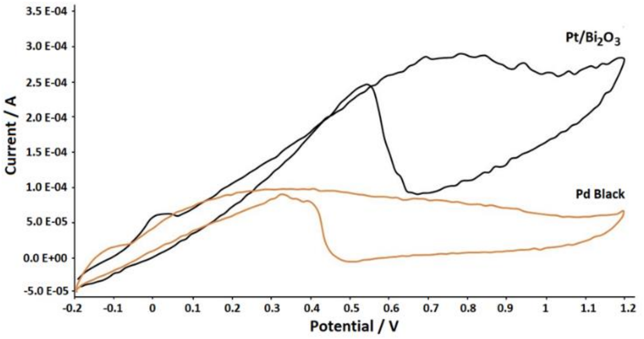


Figure 5. CV results of Pt/Bi_2O_3 and Pd black catalyst

Chronoamperometry for catalytic activity curves were obtained at a fixed potential of 0.3 V for 250 second (Figure 6). Catalyst delivers a similar curve to the results reported in most literature, which drops rapidly at the primary stage and then decays slowly to a limiting value. Obviously, the Pt/Bi_2O_3 exhibits much higher stability than commercial Pd black, which might be contributed from the synergistic effect of Pt nanoparticles and Bi_2O_3 support material.

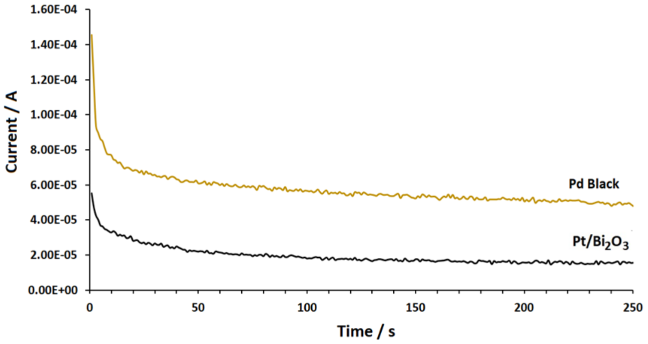


Figure 6. Chronoamperometry results of Pt/Bi_2O_3 and Pd black catalyst

4. Conclusion

Bi_2O_3 supported Pt nanoparticles were synthesized and characterized for possible utilization in FAO. Towards formic acid oxidation, the as-prepared Pt/Bi_2O_3 electrocatalyst exhibits a higher catalytic current and much better stability than the commercial Pd black, thus holding a great promise as a superior anode catalyst in DFAFCs.

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Conflict of Interest

No conflict of interest was declared.

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