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Review

Metal Oxide Nanostructures in Food Applications: Quality Control and Packaging

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Abstract: Metal oxide materials have been applied in different fields due to their excellent functional properties. Metal oxides nanostructuration, preparation with the various morphologies, and their coupling with other structures enhance the unique properties of the materials and open new perspectives for their application in the food industry. Chemical gas sensors that are based on semiconducting metal oxide materials can detect the presence of toxins and volatile organic compounds that are produced in food products due to their spoilage and hazardous processes that may take place during the food aging and transportation. Metal oxide nanomaterials can be used in food processing, packaging, and the preservation industry as well. Moreover, the metal oxide-based nanocomposite structures can provide many advantageous features to the final food packaging material, such as antimicrobial activity, enzyme immobilization, oxygen scavenging, mechanical strength, increasing the stability and the shelf life of food, and securing the food against humidity, temperature, and other physiological factors. In this paper, we review the most recent achievements on the synthesis of metal oxide-based nanostructures and their applications in food quality monitoring and active and intelligent packaging.

Keywords: metal oxide; nanostructures; gas sensor; food quality; antimicrobial activity; food packaging

1. Introduction

The monitoring and control of food quality have become important issues. The consumers and the manufacturers are paying more attention to the modern and advanced methods to check the quality of agricultural and food products and to keep them safe for a long time. Besides, the monitoring, control, and maintaining of the quality of food during its transportation from producer to consumer is another important issue. Different analytical methods for food quality control, such as the liquid chromatography–mass spectrometry [1], and surface plasmon resonance [2], have been applied. However, the aforementioned techniques have several limitations. The data acquisition and elaboration processes are slow; the instruments have relatively big dimensions and are not useful to fabricate small-size, portable systems for the real-time analysis. In this regard, the chemical sensors are very promising structures for the manufacturing of small-size and portable monitoring systems to perform real-time food quality analysis. The rotten foods produce toxin gases [3]. In addition, the metabolic activities of microorganisms in dairy foods may contribute to the breakdown of chemical compounds into volatile organic compounds (VOCs) [4]. Therefore, the detection of presence of toxins and VOCs is necessary to avoid the hazards that are related to the food spoilage. Metal oxide based gas sensors are sensitive to a wide range of gases and VOCs. This feature makes them very attractive structures for their integration into the food quality monitoring systems [5–7]. Chemical gas sensors based on metal oxide nanomaterials have been used to evaluate and discriminate the quality and standards of all kinds of food, dairy products, and beverages [8–10]. They can be used to investigate the shelf life, freshness, and maturity of fruits, vegetables, and grains [11–13], and to assess the real-time process monitoring, including the harvesting, processing and storage [14].

The packaging technology is another important subject of research and plays a key role in food protection and storage. The active packaging involves the usage of metal oxide nanostructures in food packaging material that prolongs the shelf life, safety, and quality of the packaged product. The modern model of packaging is the intelligent packaging system with the multifunctional possibilities, such as the sensing, recording, and communication providing information about the possible problems. The spoiled food creates poison and the vapors that can be detected by the chemical gas sensors. The identification of emitted vapors from the food (milk, cheese, meat, fish, fruits, vegetables, eggs, and drinks) will be possible in order to avoid future dangers at the beginning of the spoiling process. Monitoring and control of the humidity and temperature during the food packaging and transport are important as well. Some metal oxides have a good response to the humidity changes [15–17]. This feature of oxide materials can be used for the fabrication of humidity sensors and their integration into food quality monitoring systems in order to overcome the problems that are related to the spoilage of food.

The fabrication of small-size sensing systems based on metal oxide gas sensors and their combination with the modern communications tools is a prospective way to perform qualitative and quantitative multi-component analysis of food products. These kind of systems can be activated and controlled by an operator responsible for organizing the intelligent food packaging, storage, and transport from the producer to consumer [6]. In addition, metal oxides can be used for the development of innovative food packaging materials due to their thermal stability, optical and catalytic properties, non-toxicity, and antimicrobial activities [18]. The research studies that have been published over the last years regarding the application of the metal oxide nanostructures in food quality control and packaging indicate that the interest on oxide materials and the investigation of their functional properties have appreciably increased. Figure 1 reports the number of publications with the topics "Metal oxide* AND food quality control OR food monitoring OR food packaging" since 2000 till 2018 March, retrieved from the "Web of Knowledge" database. This trend demonstrates the growing interest in the aforementioned fields.

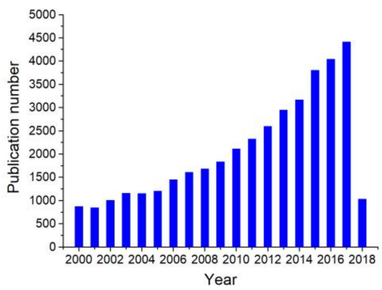

Figure 1. Number of publications with the topics "Metal oxide* AND food quality control OR food monitoring OR food packaging" since 2000, according to Web of Knowledge database.

This paper aims to provide an overview of the most recent achievements on metal oxides-based nanostructures in different food applications, including the quality monitoring, the active and intelligent food packaging, the antimicrobial activities, and the improved nutrition. We have discussed various nanofabrication technologies and strategies, showing their advantages and disadvantages.

We have highlighted the achievements and the challenges in the application of nanostructured metal oxides for the food industry.

2. Metal Oxide Nanostructures Growth and Fabrication Methods

Preparation methods of metal oxide nanostructures have been developed towards the shape, size and crystallinity control of the material. The structures can be prepared by several chemical and physical methods. These synthesis techniques of the nanomaterials are based on the top-down and bottom-up approaches. The top-down approach is advantageous in the semiconductor industry and it has been used for the fabrication of computer chips and other products. This approach is mainly based on the lithographic techniques and has limited capabilities [19]. Instead, the bottom-up approaches are in the development stage and the researchers continue to carry out experiments to improve these techniques. The schematic of top-down and bottom-up approaches is presented in Figure 2.

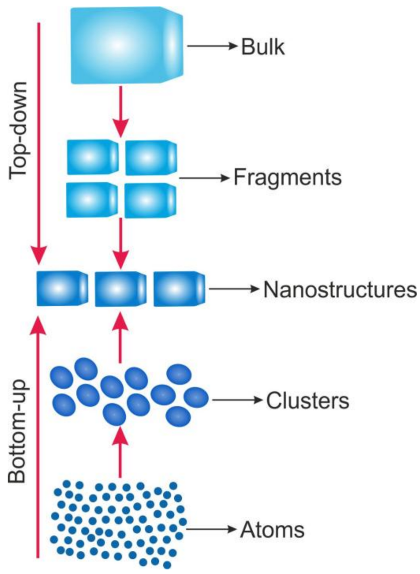

Figure 2. The schematic representation of the top-down and bottom-up approaches for the fabrication of metal oxide nanostructures.

The studies have shown that the bottom-up preparation methods may offer unique capabilities in nanofabrication. Based on this approach, the metal oxide nanostructures can be synthesized in the shape of nanowires, nanorods, nanotubes, nanobelts, etc. [5,20,21]. The assembly of molecular building blocks or chemical synthesis through the vapor phase transport, electrochemical deposition, and solution-based or template-based growth are on the basis of preparation procedures. These procedures may include the vapor-solid or vapor-liquid-solid growth, chemical or physical vapor deposition, metal organic chemical vapor deposition, and the thermal oxidation of metals [21–24]. The vapor phase deposition method is mainly performed at elevated temperatures under the gas flow in a chamber [23,25]. Great efforts have been made for the fabrication of one dimensional (1D) and thin film metal oxide nanostructures using the chemical vapor deposition (CVD) method, which involves the formation of nanomaterials onto the substrate by the chemical reactions of vapor phase precursors [5,26–28]. In this case, the reactions can be enhanced by higher frequency radiation and plasma [26,29,30]. The structure and morphology of the prepared materials depend on the substrate temperature, composition, and the chemistry of the vapor phase. Further improvements of the CVD process allowed for the fabrication of doped 1D metal oxides [26,30,31]. However, the growth rate of the nanostructure can be decreased depending on the doping concentrations [26]. Some dopants can affect the crystal quality of the material and the material growth may become disordered due to the phase separation [30].

Atomic layer deposition (ALD) can also be used for the fabrication of 1D metal oxide materials. ALD is a modification of the CVD, in which gaseous precursors are introduced sequentially to the surface of the substrate and the reactor is purged with an inert gas to remove the unreacted precursor and the reaction byproducts [5,32]. This is a very precise template-based technique to grow well-ordered structures with uniform dimensions. The template material, its preparation and post-growth removal procedure have crucial effects on the fabrication of materials. The most used template for the ALD is the anodic aluminum oxide (AAO) [6]. Well-ordered nanotubular arrays, nanorods, nanopillars, and nanochannels were obtained using the ALD method. The diameter of the structures can be controlled by varying the pattern dimensions. Similarly, it is possible to increase the length of the obtained structures by repeating the deposition cycles [33–35].

Vapor-liquid-solid or vapor-solid growth mechanism can be involved in the physical vapor deposition (PVD) procedure for the fabrication of metal oxide nanomaterials as well. The deposition process is carried out in the furnace that is connected with a vacuum pump. The catalyst on the substrate, temperature, and pressure during the material fabrication affect the morphology of the obtained structures [5,32,36]. This is an effective method to obtain metal oxide nanowires, nanorods, nanoneedles, etc. [37,38]. The thermal oxidation of metallic layers can be used in order to obtain single crystalline metal oxide nanowires and nanorods [24,39,40]. This method may be included in the PVD category. The thermal oxidation procedure is the simplest in the PVD category and it can be carried out under atmospheric pressure. The growth conditions can be controlled by modifying the preparation procedure, the temperature, and time, as well as the metal-catalyst and gas atmosphere. Nevertheless, the fabrication procedure at high temperatures can limit the choice of the substrates, especially the use of polymeric flexible films that have relatively low-temperature stability. In this regard, the electrochemical anodization of metallic films is an effective method for the fabrication of 1D oxide materials on flexible polymeric substrates. The anodization procedure is performed in a two-electrode system electrochemical cell. This procedure consists of the oxidation and etching of the metallic films. The metals can be anodized in normal ambient conditions at room temperature [22]. Well-ordered and highly aligned tubular arrays and porous structures can be obtained by means of the anodization method. The length and diameter of the structures are controlled by a variation of the electrolyte composition, the reaction time, and the anodization voltage [41–43]. The synthesis procedure at relatively low temperatures allows for fabricating the nanomaterials on flexible polymeric substrates [44,45]. More complex architectures (Figure 3) can be obtained by coupling the electrochemical anodization and the thermal decomposition methods [45].

Chemical methods, such as the spin-coating, dip-coating, and sol-gel have been applied for the preparation of metal oxide thin films and nanoparticles [46–48]. The aforementioned methods are very convenient for the fabrication of composite structures due to the availability of precursor materials [47–49]. The morphology, alignment, density, aspect ratio, and crystalline quality of the materials that were prepared by sol-gel are directly related to the seed layer parameters [46]. Recent investigations have shown that the hydrothermal growth using different chemical solutions is another efficient method for the preparation of pure and doped oxide materials with various shapes (nanorods, nanofibers, nanowires, and nanosheets) [50–53]. The morphology of the structures during the preparation process is changed depending on the solution composition, the reaction temperature, and time [6,54].

To prepare the hierarchically assembled poly- and single-crystalline 1D metal oxide nanostructures, the ALD, PVD, CVD, and thermal oxidation methods have been well developed comparing to the chemical approaches. Meanwhile, the template-assisted approach, such as the ALD, makes the integration of the material difficult with the existing planar structures. The growth rate and the crystallinity of the nanostructures that are prepared through the vapor phase transport can be reduced depending on the dopant material type and concentration. The anodization is a cost-effective and precise method to obtain well-ordered and doped nanotubes or nanoporous structures at room temperature without the use of any vacuum technique. Nevertheless, the anodized materials are mainly amorphous and they can be crystallized by post-growth thermal treatment. The doping and functionalization of metal oxides with the different materials can be successfully performed by means of the hydrothermal growth. In this case, the structure synthesis is performed at high temperatures, which limits the choice of substrates.

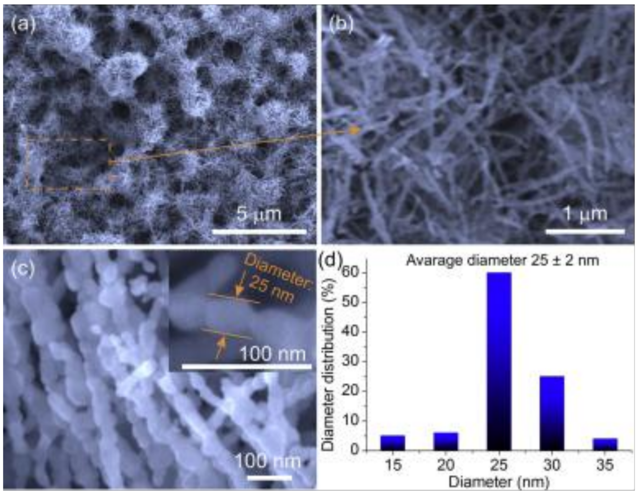

Figure 3. (**a**–**c**) SEM micrographs with different resolutions and (**d**) corresponding histograms of thermally annealed ZnO nanoparticles diameter distribution. Reprinted from [45] with permission. Copyright (2015) Elsevier B.V.

3. Food Quality Control

This section reports the recent developments in metal oxide chemical sensor devices for their applications in food analysis, in particular, the food quality control, process monitoring, authenticity, and freshness determination. The sensing mechanism of metal oxides is related to the adsorption and desorption processes of different gaseous compounds on the structure surface, followed by the changes in the material electrical conductance (or resistance). The sensing mechanism is described in more detail in our previous works [5,6]. Recent studies have shown that the metal oxide nanomaterials-based gas sensors can be used for the assessment of food products. Chemical sensors and more complex systems have been used to detect the gases that are present in the rotten or spoiled food.

Trimethylamine (TMA) is a gaseous compound that is formed naturally due to the biodegradation of fish and animal products. TMA detection may give useful information to determine the fish and the seafood freshness. TiO_2, WO_3, and ZnO with different shapes showed a good response towards TMA [55–58]. The functionalization of WO_3 nanorods, ZnO (Figure 4) and MoO_3 by Au improved the material's response due to the catalytic effect of Au [56,58,59]. Introduction of Cr^{3+} in 1D ZnO nanostructures or their coupling with Cr_2O_3 and In_2O_3 can enhance the response and selectivity of the materials towards TMA [57,60,61]. In addition, the heterostructure based on p-type Cr_2O_3 and SnO_2 nanowires showed a good and selective response towards low concentrations of TMA [62]. Lou et al. fabricated the α-Fe_2O_3/TiO_2 hierarchical heterostructure with a good sensing performance when compared with the pure Fe_2O_3 and TiO_2 1D nanostructures [63]. Dimethylamine (DMA) and ammonia (NH_3) are the other substances that are responsible for fishy odors, and directly related to the fish quality [64]. During the last years, only a couple of works have been published on metal oxide-based DMA sensors. Investigations have shown that 1D ZnO materials have very good sensing properties for the fabrication of DMA gas sensors [65,66]. However, there is no detailed information in the literature on the studies of other metal oxide materials for their application in DMA detection. Hence, the perspectives of the application of other oxide materials in the fabrication of DMA sensors are still not clear. Besides the fish quality control, NH_3 was used as an analyte to determine the shelf life and spoilage of other meat products [67]. The sensing performance of oxide materials towards NH_3 was improved by combining them with polymers. SnO_2 nanosheets and ZnO nanorods were polymerized by the polypyrrole [68,69]. The response of the polypyrrole-SnO_2 composite towards a low concentration of NH_3 was improved because of the p-n junction that was formed at the interface of two materials [68]. Excellent conjunction and interaction between the polypyrrole chains and the ZnO nanorods improved the charge transfer in the composite enhancing the structure response [69]. Moreover, both of the composite materials showed a selective response towards NH_3 at room temperature (RT), which is an important achievement to fabricate low power consumption sensing devices. The coupling of TiO_2 and ZnO with the polyaniline also improved the response and selectivity of the materials at RT [70,71]. The functionalization of ZnO nanorods by Au enhanced the sensing performance of the structure at RT, and in the meantime, decreased the response and recovery time of ZnO [72]. Li et al. improved the response of SnO_2 nanotubes towards NH_3 at RT by fabricating a SnO_2/SnS_2 composite material [73]. This improvement was attributed to the heterojunction that was formed at the boundaries of SnO_2 and SnS_2 crystallites and the higher work function of SnS_2 as compared with SnO_2.

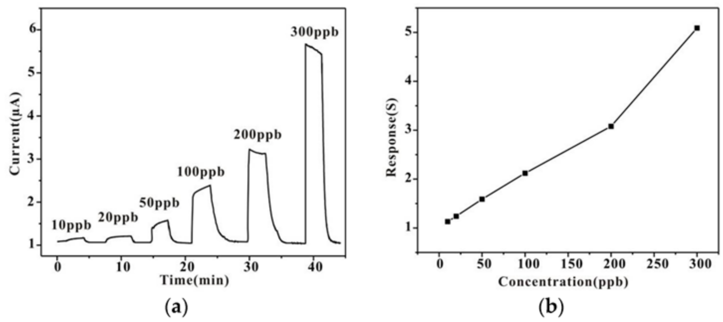

Figure 4. (**a**) Responses of the Au-modified hierarchical porous single-crystalline ZnO nanosheets to different concentrations of trimethylamine (TMA) and (**b**) the corresponding calibration curve. Reprinted from [58] with permission.

Hydrogen sulfide (H_2S) is produced from eggs and egg products due to their heating. Moreover, low concentrations of H_2S contribute to the flavor of heated proteinaceous foods, such as beef, chicken, fish, and milk products, and its production increases at higher temperatures. The detection of H_2S can give useful information to identify the overcooked and rotten food [74]. Various oxide materials and their compositions have been studied for the fabrication of H_2S sensors [75–84]. Porous metal oxide nanostructures, such as TiO_2, NiO, and CuO are very attractive materials for H_2S detection [75–77,85]. They have shown a good response towards low concentrations of H_2S. In addition, the porous NiO and CuO with p-type conductivity could detect H_2S in ppb level at relatively low operating temperatures [76,77]. TiO_2 nanoparticles have been used for the functionalization of Fe_2O_3 nanorods [83]. The obtained structure showed a better sensing performance when compared to the pristine Fe_2O_3 nanorods. The enhancement was related to the modulation conduction channel width and potential barrier height of the material. The functionalization and doping of ZnO have been proven as the promising strategies to improve the material response towards H_2S [86,87]. Guo et al. fabricated a composite material based on ZnO and SnO_2 [80]. The obtained ZnO/SnO_2 heterogeneous nanospheres showed selective and high response in the presence of low concentrations of H_2S. Ag-loaded yolk-shell SnO_2 nanostructures showed a high and reversible response towards H_2S [81]. Yang et al. reported the synthesis of Ag_2O/SnO_2 porous structures with the stable and selective response towards H_2S in ppb level [82]. The H_2S sensing performance of a p-n junction based on Co_3O_4-SnO_2 nanocomposite was improved with an increase in the structure annealing temperature [79]. CuO/V_2O_5 hybrid nanowires showed a better response towards H_2S when compared with the pristine V_2O_5 nanowires [78].

Fruits and vegetables are perishable products with a very short shelf life. The detection of VOCs is an accessible way for the monitoring of changes in the fresh produce. The majority of the latest studies have been carried out to develop metal oxide sensors for the detection of ethanol and acetone. SnO_2, ZnO, TiO_2, Cr_2O_3, WO_3, Co_3O_4, NiO, and In_2O_3 based nanostructures with different morphologies have been studied for the ethanol [4,88–92] and acetone detection. Reported results have shown that the functionalization and introduction of specific dopant materials can improve the response, selectivity, and recovery time of oxide materials. Furthermore, the composite structures based on metal oxides have shown a promising sensing performance for their application in ethanol and acetone sensing devices. Table 1 summarizes the recent achievements in sensing properties of the metal oxide-based structures for the food quality analysis.

Table 1. A selected list of references on metal oxide materials for the fabrication of gas sensors and their application in food quality analysis.

Material and Morphology	Target Gas and Concentration	Operating Temperature (°C)	Reference
TiO_2 nanotubes	TMA, 40–400 ppm	-	[55]
Au-WO_3 nanorods	TMA, 100 ppm	280	[56]
Au-MoO_3 nanobelts	TMA, 5–100 ppm	280	[59]
Cr^{3+}-ZnO nanorod	TMA, 0.01–100 ppm	255	[57]
ZnO-Cr_2O_3	TMA, 5 ppm	400	[60]
ZnO-In_2O_3 nanofibers	TMA, 0.05–5 ppm	375	[61]
Cr_2O_3-SnO_2 nanowire	TMA, 0.25–5 ppm	450	[62]
Au-ZnO porous nanosheets	TMA, 10–300 ppm	260	[58]
α-Fe_2O_3/TiO_2 nanofibers/nanorods	TMA, 10–200 ppm	250–320	[63]
ZnO pencil-like	DMA, 5–300 ppm	340	[65]
ZnO nanorod/nanosheet	DMA, 1–1000 ppm	370	[66]
polypyrrole-SnO_2 nanosheets	NH_3, 1–10.7 ppm	RT	[68]
polypyrrole-ZnO nanorods	NH_3, 50 ppm	RT	[69]
Polyaniline-TiO_2 thin films	NH_3, 23–141 ppm	RT	[70]
Polyaniline-ZnO nanoparticles	NH_3, 20–100 ppm	RT	[71]
Au-ZnO nanorods	NH_3, 5–100 ppm	RT	[72]
SnO_2/SnS_2 nanotubes/nanoparticles	NH_3, 20–500 ppm	RT	[73]
TiO_2 nanotubes	H_2S, 1–50 ppm	300	[85]
TiO_2 nanotubes	H_2S, 6–38 ppm	70	[75]
NiO porous	H_2S, 1 ppb–100 ppm	RT-92	[76]
CuO porous nanosheets	H_2S, 10 ppb–60 ppm	RT	[77]
TiO_2-Fe_2O_3 nanoparticle-nanorods	H_2S, 1–200 ppm	300	[83]
Au-ZnO nanorods	H_2S, 3 ppm	25	[86]
Cu-ZnO thin film	H_2S, 5–50 ppm	250	[87]
ZnO/SnO_2, nanospheres	H_2S, 0.5–100 ppm	300	[80]
Ag-SnO_2, yolk-shell	H_2S, 0.25–5 ppm	350	[81]
Ag_2O/SnO_2 porous	H_2S, 300 ppb	100	[82]
Co_3O_4-SnO_2 nanobox	H_2S, 50 ppm	180	[79]
CuO/V_2O_5 nanowires	H_2S, 7–23 ppm	220	[78]
PbO-SnO_2 nanowires	Ethanol, 5–200 ppm	300	[88]
Reduced graphene oxide-ZnO, nanoparticles, chain-like agglomerates	Ethanol, 100–250 ppm	250	[4]
TiO_2 nanotubes	Ethanol, 10–50 ppm	200–500	[89]
Cr_2O_3-WO_3, nanoparticle, nanorods	Ethanol, 5–200 ppm	300	[90]
Co_3O_4 porous nanosheets	Ethanol, 1–100 ppm	220	[91]
Cd-NiO thin film	Ethanol, 1000 ppm	100	[92]
PtO_2-SnO_2 nanofiber	Acetone, 0.6–5 ppm	400	[93]
Fe-C-WO_3 walnut-like particles	Acetone, 0.2–10 ppm	300	[94]
W-NiO, flower-like spheres	Acetone, 10–1000 ppm	250	[95]
In_2O_3-reduced graphene oxide, nanocubes	Acetone, 5–25 ppm	175	[96]

The presence of VOCs in food is a complex aroma bouquet, which includes different compounds due to the aging and bacterial putrefaction of food. In this regard, the fabrication of a more complex and multicomponent system is a proper way for the precise monitoring of food quality and discrimination. The concept of this artificial system is called Electronic nose (EN). An EN consists of different metal oxide gas sensors, where each sensor has particular application requirements with a specific response and selectivity to recognize simple or complex gaseous compounds.

Konduru et al. used SnO_2 and WO_3 based sensors array to differentiate ethanol, acetone, acetonitrile, and ethyl acetate for the onion quality evaluation. The fabricated EN sensing system was able to detect the presence of the two key volatile compounds that were emitted by diseased onions, and in the meantime, to differentiate them at two concentration levels [97]. An EN based on SnO_2 chemical sensors was applied for the identification of the geographical origin of licorice roots [98]. E-nose results were compared to the results that were obtained by the other techniques. The investigations showed that this is an effective and non-destructive method for the authentication of licorice roots. Pacioni et al. used SnO_2 sensors array that was functionalized with different metals to obtain a good and selective response towards acetaldehyde, ethanol, acetone, dimethylsulfide, and ethylacetate for the discrimination of truffle-flavored oils [99]. The SnO_2 is the most studied metal oxide material for the fabrication of gas sensors. The material has a good response towards different gases. Therefore, the SnO_2 based chemical sensors have been mostly used for the fabrication of EN systems. The ENs based on SnO_2 gas sensors have been applied for the classification of black tea and the diagnosis of Enterobacteriaceae in vegetable soups, to study the global aromatic profile of coffee, as well as for the meat and fish freshness control. The applications of EN systems based on SnO_2 and the other metal oxides are summarized in Table 2. Unfortunately, the composition of oxide materials in some studies on EN systems was not presented. This fact makes it difficult to perform a more detailed comparison of the results that were reported in the literature.

The recent studies of oxide materials are mainly focused on the nanostructures and the thin films, with an increasing attention to improve the sensing performance of the material at relatively low operating temperatures for the prototype sensing devices [100–102]. Furthermore, the water molecules can be formed on the surface of metal oxides due to the adsorption of some reducing gases [103]. Therefore, to obtain the gas sensors with stable and reversible response, the sensor device should operate above room temperature to avoid the effects that are related with the water molecules. The aforementioned issues should be considered when comparing the operating temperature and the power consumption of the sensing devices. The different sensing behaviors that were reported for the doped and functionalized oxide materials towards different gaseous compounds are encouraging, and together with the use of ENs, will reduce the problem of the selectivity. The accurate control of the structures shape, composition and dimensions will contribute towards the synthesis of new and interesting nanomaterials, which will open unexplored possibilities for future sensing technologies for food quality control applications.

Table 2. A list of Electronic nose (EN) systems based on metal oxides for the food quality monitoring.

Sensing Material	Target Gases	Application	Reference
SnO_2, WO_3	Ethanol, acetone, acetonitrile, ethyl acetate	Onion quality evaluation	[97]
SnO_2	Ethanol, ethyl acetate, isobutyl alcohol, etc.	To identify geographical origin of Licorice roots	[98]
SnO_2, SnO_2-SiO_2, Ag-SnO_2, Au-SnO_2, Pd-SnO_2, WO_3	Acetaldehyde,ethanol, acetone, etc.	To distinguish truffle-flavored oils	[99]

Table 2. *Cont.*

Sensing Material	Target Gases	Application	Reference
SnO_2	Aromatic compounds	Classification of Indonesian black tea	[104]
SnO_2	Alcohols, aldehydes, ketones, etc.	To study the global aromatic profile of coffee	[105]
SnO_2, MoO_3	Acids, alcohols	Diagnosis of Enterobacteriaceae in vegetable soups	[106]
SnO_2	Aromatic compounds	To study the quality of tea	[107]
Metal oxide sensors, Hanwei Electronics Co., Ltd.	Alcohols, NH_3	Prediction of banana quality	[108]
Metal oxide sensors, Hanwei Electronics Co., Ltd. and Figaro Inc.	Sulfur compounds, H_2S, NH_3	Classification of garlic cultivars	[109]
Metal oxide sensors, PEN2, Airsense Analytics, Germany	Alcohol, NH_3, aromatic compounds	Strawberry juice quality control	[110]
Metal oxide sensors, Figaro USA Inc.	VOCs	Fish species discrimination	[111]
Metal oxide sensors, Alpha M.O.S., France	Organic acids, caffeine	Aromatic profile of Espresso coffee	[112]
Metal oxide sensors, Ogam Technology, Futurlec, e2v and Figaro Engineering	VOCs, NH_3, alcohol, etc.	Meat and fish freshness control	[113]
Metal oxide sensors, Alpha M.O.S., France	Ethanol, NH_3, VOCs	To trace peanuts quality	[114]
Metal oxide sensors, Win Muster Airsense Analytics Inc., Germany	Alcohol, methane, aromatic compounds	Analysis of edible oil oxidation	[115]
Metal oxide sensors, Hangzhou Ke Na Sensors Inc., and Figaro Inc.	TMA, DMA, Ethanol	Freshness control of hairtail fish and pork	[116]
Metal oxide sensors, Figaro Inc., Japan	Ethanol, NH_3, VOCs	Classification of honey	[117]

4. Food Packaging and Antimicrobial Actions

In this section, the most active metal oxide nanostructures that have been exploited for use in the food packaging systems are reviewed, along with their structure, effects, and applications.

TiO_2 nanoparticles are good photocatalysts and antimicrobial agents that are used in food packaging [118–121]. They act upon the food spoilage bacteria through lipid peroxidation that is caused by the production of reactive oxygen species (ROS) molecules under visible and UV, DNA damage via hydroxyl radicals, resulting in cell death [122,123]. TiO_2 based bio-nanocomposites have been used as the efficient packaging materials for various oxygen-sensitive food products [124]. An interesting work on TiO_2 based bio-nanocomposite film as a packaging material for soft white cheese was presented by Youssef et al. [125]. The material consisting of chitosan, poly (vinyl alcohol), and TiO_2 nanoparticles (CS/PVA/TiO_2) exhibited good mechanical properties and antimicrobial activities against Gram-positive, Gram-negative bacteria, fungi, and coliform. In another study, they used ZnO nanoparticles, chitosan (CH), and carboxymethyl cellulose (CMC), namely CH/CMC/ZnO nanocomposite, as a packaging material for the same cheese [126]. It showed similar properties as the TiO_2-based material. The CS/PVA/TiO_2 bio-nanocomposites displayed hydrophobic property and when used as a packaging material for the soft white cheese, the moisture content of the cheese significantly increased with increasing storage period. In case of CH/CMC/ZnO packaged cheese, the textural parameters of the cheese reduced with the storage time and few changes were also reported as compared to the control and blank. The films had a significant impact on pathogenic microbial strains presented with the inhibition zone ranging from 5 to 15 mm. A poly(vinyl-chloride) PVC/TiO_2 nanocomposite bears an efficient food packaging property, mechanical strength, and antimicrobial properties [127]. He et al. prepared a TiO_2-protein/polysaccharide (marine red alga) nanocomposite film, wherein the TiO_2 nanoparticles enhanced the tensile strength of the film, showed an antimicrobial action against the food pathogen bacteria *E. coli* and *S. aureus*, and maintained the quality and shelf life of cherry tomatoes when being used as a coating material [128]. By increasing the TiO_2 content in starch/TiO_2 bio-nanocomposite, the hydrophobicity of the nanocomposite increased, and its thermal, mechanical, and UV light-shielding properties were enhanced [129].

The nano-TiO_2-low density polyethylene (LDPE) packaging showed promising results in maintaining the quality and shelf life of Pacific white shrimp [130]. The TiO_2-LDPE nanocomposite material inhibited the growth of spoilage bacteria and lowered the polyphenol oxidase (PPO) activity. It was able to retard the decrease of whiteness and water holding capacity, and reduced the total viable counts (TVC). Bodaghi et al. demonstrated the ability of TiO_2-LDPE nanocomposite film to inhibit the microorganisms *Pseudomonas* spp. and *Rhodotorula mucilaginosa* that are responsible for fruit and vegetable spoilage [131]. The same group developed an LDPE/clay-TiO_2 nanocomposite film showing strong mechanical and barrier properties, and convincing antimicrobial activities against the aforementioned classes of microorganisms [132]. Such film is useful in horticulture product packaging. Similarly, mesoporous TiO_2/SiO_2 nanocomposite with different concentrations of nanoparticles was used to degrade ethylene under UV light as a measure to ensure the shelf life of mature green tomatoes. This could be a successful photooxidative packaging film model for the fresh fruits and vegetables, and their postharvest management [133]. Chitosan/TiO_2 nanocomposite film also demonstrated ethylene photodegradation that helped in the prolongation of tomato storage [134]. TiO_2 nanoparticles were exploited to construct a biodegradable nanocomposite film that was aimed at preserving the microbial and sensory qualities of lamb meat during storage [135]. The whey protein isolate (WPI)/cellulose nanofiber (CNF)/TiO_2 nanoparticles/rosemary essential oil (REO) nanocomposite film was successful in reducing the bacterial load containing food pathogens, such as *L. monocytogenes*, *S. enteritidis*, *E. coli* O_{157}:H_7, *S. aureus*, and *P. fluorescens*, thus increased the shelf life of the meat. Another biodegradable nanocomposite film that was fabricated by incorporating jackfruit filum polysaccharide (JFPS)-TiO_2 nanoparticles displayed reduced moisture content, transparency, and total soluble matter [136]. The JFPS/TiO_2 nanocomposite showed an excellent antimicrobial action that was essential for active food packaging.

In view of the food preservation and safety, various methods and composite materials have been employed for the long-term food storage. AgCl-TiO_2 nanocomposite material was used to study the anti-quorum sensing mechanism [137]. Quorum sensing system has been linked to the biofilm formation in food spoilage bacteria. In this study, the anti-quorum sensing activity of the bioactive AgCl-TiO_2 material in the model bacteria *Chromobacterium violaceum* was confirmed by the absence of signaling molecule oxo-octanoyl homoserine lactone during bacterial growth, endorsing the potential use of AgCl-TiO_2 nanomaterial in the food packaging industry. Peter et al. developed Ag/TiO_2-SiO_2-coated food packaging film for the preservation of fresh green lettuce during storage [138]. The obtained results showed its ability to reduce the level of lettuce spoilage, known as botrytis blight that is caused by *Botrytis cinerea*. The antimicrobial action of TiO_2 nanomaterial is explained by its capacity to produce charge carriers when exposed to UV light, which initiates redox reaction on the microbial cell surface that eventually inhibits the microbial cell. Ag/TiO_2 nanocomposite-based packaging extended the shelf life and microbial safety of the white bread by inhibiting the growth of yeast, molds and Gram-positive bacteria *B. cereus* and *B. subtilis* [139]. In another study, the microbiological and chemical characteristics of the white bread during storage in paper packages using Ag/TiO_2-SiO_2, Ag/N-TiO_2, or Au/TiO_2 in comparison with the non-modified paper packages were investigated [140]. The tensile and breaking resistance of the paper packages decreased with an increase in the composite content. The Ag/TiO_2-SiO_2 based-paper showed the best properties; all three of them exhibited superior water retention and the nanocomposites containing Ag nanoparticles extended the shelf life of the bread together with a strong antimicrobial action.

Poly lactic acid (PLA) nanocomposite films prepared from TiO_2 and Ag nanoparticles were applied to study their antimicrobial properties and shelf life of Yunnan cottage cheese [141]. The obtained results showed the essential antimicrobial properties of the PLA/TiO_2 and PLA/TiO_2+Ag packaging films and the packed cheese exhibited better retention in pH value, lactic acid bacteria (LAB) count, and sensory quality. TiO_2-potato starch blend films were studied where TiO_2 nanoparticles reduced the water solubility, water vapor permeability, and moisture uptake of the film [142]. The overall functional properties of the film were improved, illustrating its potential for food packaging. Likewise, a soluble soybean polysaccharide (SSPS)/TiO_2 bio-nanocomposite showed excellent heat seal strength and biocidal activities fulfilling the requisites for a food coating and packaging material [143]. Other TiO_2-based nanocomposite films that were applicable in active and intelligent food packaging are: fish bilayer gelatin/agar film containing TiO_2 [144], wheat gluten/cellulose nanocrystals/TiO_2 nanocomposite [145], and TiO_2/LDPE film assuring the food safety and quality [146]. A chitosan-TiO_2 nanocomposite that was prepared for packaging red grapes was successful in preventing the microbial infection and elongating the shelf life of the grapes [147]. It should be noted that the nanocomposites showed better mechanical properties and enhanced hydrophilicity or high-water permeability. It was efficient against both Gram-positive and Gram-negative bacteria by provoking the leakage of cellular substances through the damaged membrane. Similarly, TiO_2 and Ag-doped TiO_2 nanoparticles were reported to show photocatalytic antibacterial performance under visible-light irradiation [148]. The viability of the test microorganisms: Gram-positive *S. aureus* and Gram-negative *P. aeruginosa*, *E. coli* bacteria was reduced to zero at 3% and 7% doping concentrations of Ag-TiO_2 nanoparticles. TiO_2 offers a good supporting material for the doping of Ag nanoparticles due to its small size and high surface area. A novel bio-nanocomposite material that was developed from wheat gluten, nanocellulose, and TiO_2 nanoparticles coated in kraft paper sheets for food packaging applications showed good antibacterial properties against Gram-positive and Gram-negative bacteria expressed in terms of reduction% of surviving number (CFU) of the tested organisms [145]. A simple example of active food packaging procedure exploiting the polymer nanocomposites is shown in Figure 5.

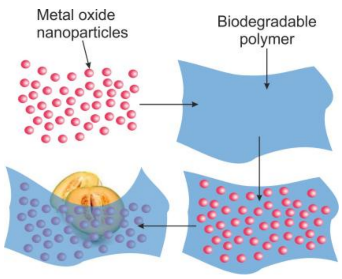

Figure 5. Schematic representation of the active food packaging using metal oxide nanostructure and biodegradable polymeric films.

ZnO nanoparticles are effective antimicrobial agents when they are present in reduced particle size and dimension. They demonstrate an excellent antimicrobial activity against the food pathogens, like *Salmonella*, *Klebsiella*, and *Shigella* via the generation of ROS and the loss of membrane integrity. ZnO nanoparticles also exhibit antibacterial action against spores that are high temperature and pressure resistant [149]. Among the ZnO/LDPE, TiO_2/LDPE, and ZnO-TiO_2/LDPE nanocomposite films that were studied against *E. coli* in fresh calf minced meat, ZnO/LDPE films were identified as the best materials to prevent bacterial growth and to improve the shelf life of the meat [150]. An active emulsified film that was based on carboxymethyl cellulose-chitosan-oleic acid (CMC-CH-OL) with

ZnO nanoparticles that were produced by the casting method was found to be active against the fungi *Aspergillus niger*, and its extensibility increased [151]. The nanocomposite film was effectively applied to increase the shelf life of sliced white bread [152]. All active coatings reduced the number of yeasts and molds in the bread. An active polymer bilayer polyethylene/polycaprolactone (PE/PCL) film that was modified with ZnO or ZnO/casein complex extended the shelf life of food [153]. The addition of ZnO nanoparticles enhanced the barrier, mechanical, thermal properties, and antimicrobial actions of the nanocomposite film. This helps in protecting the food products during their transport. Therefore, such a nanocomposite material is preferred for food packaging when low water loss from packaging is favorable. The use of polyethylene films with chitosan-ZnO nanocomposite for active food packaging prevented the microbial contamination after 24 h incubation and extended the shelf life of food [154]. ZnO nanoparticles that were introduced into the chitosan matrix showed a 42% increase in solubility (water affinity) and an 80% reduction in swelling of the resultant nanocomposite materials. The mechanical, thermal, and antimicrobial effect of TiO_2 and ZnO added PET-poly(ethylene terephthalate) and PBS-poly(butylene succinate) blend thin film was shown by Threepopnatkul et al. [155]. The PET/PBS thin film with TiO_2 seemed to be effective against *E. coli* and *S. aureus* than that with ZnO, showcasing the use of the material for food packaging applications.

A comprehensive list of metal oxide nanomaterials and nanocomposites in active food packaging and analysis is given in Table 3. Since the advent of innovative metal oxide nanostructured materials in food packaging, this field continues to grow and evolve. Whereas, these metal oxide nanocomposites serve as a boon in active and intelligent packaging research. There have been concerns about the safety, sustainability, and potential health risks and hazards of the materials that were used. The nanomaterials, when utilized as food additives, could transfer to the food matrix from the nanocomposite. Given the alterations in the nanomaterial surface and properties due to the chemical and physical transformations, the determination of such nanomaterials in a complex food matrix still poses a challenge. Hence, the important concerns that are related to the application of nanocomposites in food packaging are about the size, quantity, and physiochemical properties of the nanomaterials than the polymers, enzymes, or antimicrobial agents that are used to synthesize the nanocomposites. This provides a room for the improvement in key properties and functionalities of the nanomaterials for the food packaging applications.

Table 3. Applications of metal oxide-based nanomaterials in food packaging sector.

Material	Application/ Mode of Action	Reference
CS/PVA/TiO_2	Food packaging	[125]
CH/CMC/ZnO	Food packaging	[126]
PVC/TiO_2	Food packaging	[127]
TiO_2-protein/polysaccharide (marine red alga)	Quality and shelf life of cherry tomatoes	[128]
Starch/TiO_2	UV-protective food packaging material	[129]
TiO_2-LDPE	Quality and shelf-life of Pacific white shrimp	[130]
TiO_2-LDPE	Antimicrobial actions in fruit and vegetable	[131]
LDPE/clay-TiO_2	Antimicrobial action, horticulture packaging	[132]
TiO_2/SiO_2	Degrade ethylene, quality and shelf life of mature green tomatoes	[133]
Chitosan/TiO_2	Ethylene photodegradation, prolongation of tomato storage	[134]
WPI/CNF/TiO_2/REO	Microbial and sensory qualities of lamb meat, antimicrobial action	[135]
JFPS-TiO_2	Antimicrobial action, active food packaging	[136]

Table 3. *Cont.*

Material	Application/ Mode of Action	Reference
AgCl-TiO_2	Anti-quorum sensing, food packaging	[137]
Ag/TiO_2-SiO_2	Preservation of fresh green lettuce, reduction of lettuce spoilage, antimicrobial action	[138]
Ag/TiO_2	Shelf life and microbial safety of white bread, inhibition of yeast, mold and Gram-positive bacteria	[139]
Ag/TiO_2-SiO_2, Ag/N-TiO_2 or Au/TiO_2	Shelf life of white bread, antimicrobial action	[140]
PLA/TiO_2 and PLA/TiO_2+Ag	Shelf-life of Yunnan cottage cheese	[141]
Starch/TiO_2	Reduced water solubility, water vapor permeability and moisture uptake of the film, food packaging function	[142]
Soybean polysaccharide/TiO_2	Heat seal strength, antimicrobial action, food coating and packaging	[143]
Fish gelatin/agar bilayer/TiO_2	Food packaging, food safety	[144]
Wheat gluten/CNC/TiO_2	Food packaging, food safety	[145]
TiO_2/LDPE	Food packaging, food safety	[146]
ZnO/LDPE, TiO_2/LDPE, and ZnO-TiO_2/LDPE	Antimicrobial property against *E. coli* in fresh calf minced meat, shelf life of calf meat	[150]
Carboxymethyl cellulose-chitosan-oleic acid/ZnO	Antimicrobial action against the fungi *Aspergillus niger*, increased extensibility	[151]
CMC-CH-OL-ZnO	Shelf life of sliced white bread, active against yeast and molds	[152]
polyethylene/polycaprolactone-ZnO	Shelf life of food, antimicrobial actions, food packaging and transport	[153]
Chitosan-TiO_2	Food packaging, effective packaging of red grapes, shelf life of grapes	[147]
TiO_2 and Ag-TiO_2	Photocatalytic antibacterial performance, food packaging	[148]
Chitosan-ZnO/polyethylene	Food packaging,antimicrobial properties, shelf life of food	[154]
Wheat gluten/nanocellulose/ TiO_2 coated in craft paper	Food packaging, antimicrobial action	[145]
TiO_2, ZnO-poly(ethyleneterephthalate) and poly(butylene succinate)	Food packaging	[155]

5. Conclusions

In summary, we provide a comprehensive review of recent research activities on the synthesis and application of metal oxide materials in food quality control and active and intelligent packaging. During the last years, the major part of research on the fabrication of metal oxide nanomaterials has been devoted to the improvement of the synthesis procedures for the modification of the shape and size of the structure and the incorporation of dopant or mixture materials onto the obtained structures. Investigations suggest that the move to the nanoscale can significantly increase the response of the material. The doping and fabrication of composite structures is favorable to improve the selectivity of the material. Numerous studies have showed that the gas sensors that are based on metal oxides nanomaterials are very attractive structures. This is due to their promising gas sensing properties caused by their low dimensionality and high surface-to-volume ratio. However, the advantages and disadvantages in the fabrication methods of metal oxide nanostructures should be considered, estimating the preparation speed, cost, and reproducibility.

The EN systems can be used for the selective detection of VOCs and other gaseous compounds, which is very important for the precious determination of quality changes in the food products. ZnO, TiO_2, NiO, Cr_2O_3, WO_3, CuO, Fe_2O_3, Co_3O_4, V_2O_5, and In_2O_3 nanostructures have shown attractive sensing performances for the fabrication of chemical sensors and their applications in food quality control systems. Moreover, SnO_2 has been widely and successfully used in EN systems for the food quality analysis.

The recent studies on metal oxide nanocomposites-based food packaging emphasize the essential role of metal oxide nanomaterials in the fabrication of nanocomposite films coupling the polymer matrices, such as PE, PVC, PLA, chitosan, cellulose, and starch. The obtained bio-nanocomposite structures exhibit antimicrobial actions and effective mechanical, thermal, and barrier properties. Their application in active and intelligent food packaging ensures the food quality and safety and an increased shelf-life of food products.

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