

Chapter

Applications of Quantum Dots in the Food Industry

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Abstract

Quantum dots (QDs) are spherical particles with a size of <10 nm and, due to their unique properties, have good potential for use in the food industry. Among the various QDs, food industry researchers have highly regarded carbon quantum dots (CQDs) due to their nontoxicity and environmental friendliness. Food analysis is essential for quality assessment as well as safety control. In this regard, QDs-based fluorescence sensors can provide faster, more accurate, more sensitive, and cheaper analysis methods. The use of QDs to detect food additives, pathogens, heavy metals, nutrients, antibiotics, and insecticide residues is investigated in this chapter. QDs in packaging materials, due to their antioxidant, antimicrobial, and inhibitory properties, increase product shelf life, reduce the growth of microorganisms, improve mechanical properties, prevent gases and UV light, and reduce food waste. Their application in improved, active, intelligent, and bio-packaging will also be described. Then, their application in water treatment will be discussed. QDs, due to properties such as high aspect ratio, reactivity, electrostatic, hydrophilic, and hydrophobic interactions, have good potential for use in various water treatment methods, including membranes in filtration, adsorbents, and photocatalysts. Finally, their use to track protein will be investigated.

Keywords: carbon quantum dots, water purification, smart packaging, fluorescence, UV barrier, molecularly imprinted polymer

1. Introduction

Quantum dots (QDs), which are spherical particles with a size of <10 nm, are classified based on the materials used into semiconductor quantum dots and carbon-based quantum dots [1]. Semiconductor quantum dots are three-dimensional nanoparticles composed of inorganic elements like heavy metals and non-heavy materials (such as cadmium, selenide, and zinc sulfide). Semiconductor quantum dots are prepared by a bottom-up approach. They have a spherical shape, crystal structure, and size of fewer than 6 nm, which have quantum mechanical properties due to their small size. Size-dependent photoluminescence, excitation-independent photoluminescence, long life, and good photostability are specific features of QDs. Quantum dots are highly stable against photobleaching and can be considered an alternative to fluorescent index dyes and proteins. Semiconductor quantum dots are

one of the most popular nanoparticles of choice for fluorescent labels, detection, labeling, and tracking [1]. One of the disadvantages of semiconductor quantum dots based on heavy metals is their toxicity, which leads to environmental and health concerns. Graphene quantum dots (GQDs) have been considered in various research fields, including the food industry, due to their lower toxicity and environmental friendliness. The small size of GQDs and their high oxygen content lead to reduced toxicity. The GQDs refer to a 0D graphene plate with a size of less than 10 nm. GQDs have good potential for practical applications due to their specific characteristics, such as excellent luminescence, functional groups, and surface defects. They are widely used as fluorescent probes for several analytes because of their significant properties such as photobleach resistance, low cytotoxicity, good biocompatibility, stable photoluminescence, and high water solubility. Photoluminescence is the most interesting feature of GQD, which can be easily changed by managing its size, surface performance, and chemical doping. In addition, GQDs contain carboxyl, carbonyl, epoxy, and hydroxyl groups that can bind to various biological molecules such as proteins, antibodies, enzymes, and so on [2].

Carbon quantum dots (CQDs) were introduced as environmentally safe alternative nanomaterials that can provide satisfactory optical properties, good biocompatibility, and nontoxicity [3]. CQDs were first discovered in 2004 by Zhu et al. during the purification of single-walled carbon nanotubes. The size of these nanoparticles is less than 10 nm. Like common semiconductor quantum dots, their major advantage over organic dyes is their high optical stability. Also, unlike other QD, CQDs usually have low toxicity and good biocompatibility [4]. In terms of chemical structure, carbon atoms (sp^2 and sp^3) are located as nuclei in amorphous shells consisting of functional groups. Many hydroxyl and carboxyl functional groups are present on the surface of carbon dots, which cause good solubility in water and ease of functionalization by different species. The amount of oxygen in CQDs varies from 5 to 50 wt%, depending on the synthesis method [5].

There is a lot of research on the use of quantum dots in various fields, but few articles report the use of quantum dots in food science. The purpose of this chapter is to review the application of quantum dots in the food industry.

2. QDs in food analysis

The development of modern agriculture and the food processing industry can lead to chemical and biological food contamination. Food analysis is essential for quality assessment as well as safety control. Common methods of analysis include spectroscopy, immunoassay, culture and colony counting, chromatography, nuclear magnetic resonance, and electrochemical methods. The advantages of these methods include reproducibility, sensitivity, and high selectivity. However, these methods require expensive equipment, trained personnel, and long separations [6]. So, finding faster, more accurate, more sensitive, and cheaper methods of analysis has always been the focus of researchers and food manufacturers. In this regard, fluorescence sensors based on QDs can play a key role in ensuring food quality and safety [7]. Various strategies have been developed to improve the performance and selectivity of sensors based on QDs. The following are the most common techniques for food analysis:

- a. **QD/CQD@MIP:** New and effective analytical methods in nanomaterial-based food samples include QDs and CQD. One effective approach to increase the

selectivity of these nanomaterials is their combination with a molecularly imprinted polymer (MIP). Combining the unique optical properties of QD/CQD with a high selection of MIPs is a significant advantage of QD/CQD@MIP. In most cases, the adsorption process in MIP proportionally reduces the intensity of QD/CQD fluorescence, making it valuable for quantitative analysis, so it has promising potential to build sensors with high stability, sensitivity, and selectivity response. Preparation of QD/CQD@MIP conjugates consists of two main steps. In the first step, fluorescent QD/CQD are synthesized as nuclei. Then, the prepared fluorescent nucleus is used directly for QD/CQD@MIP synthesis. In some cases, the surface modification process is performed during or after the synthesis of fluorescent dots. The QD/CQD modification process provides appropriate functional groups or compatibility with synthetic medium for the better embedding of fluorescent nanoparticles in the MIP. Methods used to prepare the nucleus for the synthesis of QD/CQD@MIPs include silylation, treatment with mercaptoperboxylic acids, acrylic acids, oleic acid, polyethylene glycol, polyethylene imine, and L-cysteine. The second step is the MIP printing process, which often uses three polymerization techniques, including the sol-gel method, free radical polymerization, and reverse microemulsion method [3].

b. MNPs@QDs: Food pollutants are one of the main factors jeopardizing food safety, and with biological accumulation, they are considered as a serious threat to human health. Currently, there are several instrumental analytical techniques for identifying different food contaminants, which, due to having disadvantages such as the need for trained people, complex pretreatment process, and long time, make them unsuitable for quick and on-site detection. MNPs@QDs nanocomposites have good application potential for the analysis of food parameters. Magnetic nanoparticles (MNPs) have a strong magnetic response and are quickly recovered under an external magnetic field, so they have good potential for easy control of adsorption and release of target analytes at low concentrations in complex food samples. MNPs are environmentally friendly because they can be recycled multiple times. In addition to taking advantage of the magnetic properties of MNP, magnetic fluorescent QDs nanocomposites (MNPs@QDs) have QDs-induced fluorescence properties that can rapidly enrich target analytes and separate complex food matrices under a magnetic field. These nanocomposites are also capable of quantitative analysis of analytes, thus greatly simplifying the pretreatment process, which prevents analyte wastage, reduces detection time, and increases detection efficiency [8].

2.1 Detection of food additives

Additives are widely used in food processing to improve flavor and shelf life and enhance nutritional value. Additives have always been abused and are one of the potential causes of food safety problems. It is necessary to develop a rapid and reliable diagnostic method to strengthen the monitoring of food additives [9]. **Table 1** provides an overview of recent studies on using QDs to detect food additives.

2.2 Detection of pathogen

One of the main causes of death in the world is infectious diseases caused by food. Infection caused by food pathogens causes great financial losses to the industry due to delays in product distribution and market recall, in addition to threatening consumer

| QDs | Analytes | LOD | Linear range | Samples | Reference |
|--|------------------|---------------------------------------|--|--|-----------|
| Sulfur. Quantum dots | Tartrazine | 39 nM | 0.1–20 μM | Vitamin water, orange juice | [10] |
| GQDs | Sunset Yellow | 76 nM | 2.5 nm to 25 μM | — | [11] |
| CQDs | Nitrite | 0.15 $\mu\text{mol/L}$ | 0.50– 50 $\mu\text{mol/L}$ | Corn sausage, ham sausage, pickle, and hot dog | [12] |
| CQDs | Nitrite | 0.47 μM | 5–80 μM | — | [13] |
| CQDs | Borax | 8.0 $\mu\text{mol}\cdot\text{L}^{-1}$ | 0.025– 10 $\text{mmol}\cdot\text{L}^{-1}$ | Flour, bread, instant noodle | [14] |
| MoS ₂ quantum dots | Allura red | 1.7 $\times 10^{-6}$ M | ? | ? | [15] |
| Perovskite quantum dots | Rhodamine 6G | 0.01 $\mu\text{g/mL}$ | 0–10 $\mu\text{g/mL}$ | Tap water, food sample | [16] |
| Au@CQDs | Melamine | 3.6 nM | 1 μM to 10 μM | Milk | [17] |
| Fe ₃ O ₄ @SiO ₂ @ CdSe QDs | Bisphenol A | 0.34 nM | 10 ⁻⁹ –10 ⁻⁴ M | Water | [18] |

Table 1.
Application of QDs in the detection of food additives.

health. A common method for detecting pathogens is culturing a specific species and then examining its biochemical and immunological properties, which is very time consuming [19]. For this reason, fluorescence nanosensors based on QDs, which are faster in detecting pathogens, can be effective. The research done in this field is presented in **Table 2**.

2.3 Detection of heavy metals

The presence of heavy metal ions such as lead, mercury, cadmium, and arsenic in food is attributed to water and soil pollution. Heavy metals cause irreversible changes in protein structure and negatively affect cell function. Excessive consumption can cause side effects such as neurological disorders, kidney damage, and bone damage [27].

In one study, fluorescent nanoprobe were used to determine the multiplicity of Hg²⁺, Cu²⁺, and Ag⁺ ions. Nanoprobes (CQDs-QD_x) were designed by mixing CQDs and multicolor CdTe QDs. CQDs were not sensitive to heavy metal ions. At the same time, CdTe QDs showed a size-dependent fluorescence response to different heavy metal ions, thus creating a ratiometric detection scheme by measuring the fluorescence intensity ratios of CQDs-QD_x systems. By evaluating the detection performance, CQDs-QD_x (x = 570, 650, and 702) were successfully used to differentiate and quantify Hg²⁺, Cu²⁺, and Ag⁺ ions. In addition, they also detected heavy metal ions in actual samples with acceptable results [28]. **Table 3** lists other studies for the detection of heavy metals.

2.4 Detection of insecticide and antibiotic residues

Insecticides are widely used in agriculture to control weeds and pests and also to improve food production. Excessive use of insecticides can lead to contamination of

| QDs | Analytes | LOD (CFU/mL) | Linear range (CFU/mL) | Samples | Reference |
|---|-------------------------|--------------------|---------------------------------------|--|-----------|
| Graphene oxide quantum dots | <i>P. aeruginosa</i> | 100 | $1.28 \times 10^3 - 2.00 \times 10^7$ | Drinking water, orange juice, and popsicle | [20] |
| CQDs@MNPs | <i>E. coli</i> | 487 | 500–106 | Milk | [21] |
| Fe ₃ O ₄ @CS@CQDs | <i>S. typhi</i> | 1.38×10^2 | $10^3 - 10^6$ | Lettuce | [22] |
| Fe ₃ O ₄ @SiO ₂ @QDs | <i>E. coli</i> | 2.39×10^2 | $2.5 \times 10^2 - 5 \times 10^5$ | Milk | [23] |
| Fe ₃ O ₄ @ CdZnTe QDs | <i>L. monocytogenes</i> | 1 | $1 - 10^9$ | Tap water, pasteurized milk | [24] |
| MnO ₂ @QDs | <i>S. typhi</i> | 43 | $1.0 \times 10^2 - 1.0 \times 10^7$ | Chicken, meats | [25] |
| CQDs@ gold nanoparticles | <i>S. aureus</i> | 10 | $10^8 - 10^1$ | Milk, orange juice | [26] |

Table 2.
 Application of QDs in the detection of pathogen.

the target environment and, consequently, food contamination. Negative effects of insecticides on humans include neurotoxicity, endocrine disorders, mutagenicity, and carcinogenicity. Therefore, it is necessary to have a sensitive and selective method for analyzing these compounds [36]. A ratiometric fluorescent sensor was synthesized using CQDs in a study to detect acephate, an organophosphate pesticide. The fluorescent quenching mechanism is related to the inner filter effect (IFE). The limit of detection of this method was 0.052 ppb, which is much lower than the standards for acephate from the EU. The ratiometric fluorescent sensor was successfully evaluated for the detection of OPs in tap water and pear samples [37].

Antibiotics are widely used in agriculture, animal husbandry, aquaculture, and pharmaceutical industries. If left unattended, they can harm human health through the food chain and the environmental cycle and can threaten food quality as a potential hazard. Penicillin, for example, causes allergic skin reactions. Streptomycin damages the kidneys and auditory nerve, and tetracycline causes liver damage and yellowing of the teeth. Therefore, it is necessary to develop antibiotic detection methods that have a lower limit of detection than the legal limit [38]. Tetracycline is an antibacterial compound widely used in food-producing animals to treat various bacterial infections due to its low cost and high practicality. Residues of this antibiotic in food products enter the human body through the food chain and cause allergic reactions, digestive disorders, dizziness, muscle pain, and headaches. On the other hand, excessive use of this antibiotic causes the formation of antibiotic-resistant strains. The common methods of determining the residues of tetracyclines include high-performance liquid chromatography and enzyme-linked immunosorbent assays (ELISA). The disadvantages of these methods include a long time and low sensitivity. Therefore, it seems necessary to develop an extremely sensitive method for determining the content of tetracycline. Wang et al. synthesized tungsten oxide quantum dot for tetracycline detection. The fluorescence of the synthesized QDs is quenched after

| QDs | Analytes | LOD | Linear range | Samples | Reference |
|--|--|-----------------|---------------|---------------------------|-----------|
| Nitrogen-doped carbon dots | Hg ²⁺ | 0.24 μM | 0.3–2.0 μM | Beverage | [29] |
| CQDs | Fe ³⁺ | 9.55 μM | 30–600 μM | Aqueous Solution | [30] |
| GQDs | Fe ³⁺ | 0.28 μM | 0–100 μM | Tap and drinking water | [31] |
| Si, N-CQDs | Cr(VI) | 0.995 μM | 0–200 μM | — | [32] |
| Fe ₃ O ₄ @CQDs | Hg ²⁺ | 0.3 nM | 0.003–0.01 μM | Lake/tap water and drinks | [33] |
| CaCO ₃ -Fe ₃ O ₄ -AgInS ₂ /ZnS QDs | Co ²⁺ , Ni ²⁺ , Pb ²⁺ | 10, 100, 100 nM | No data | Water | [34] |
| Fe ₃ O ₄ @SiO ₂ -NH ₂ /CQDs | Cu ²⁺ | 0.16 μM | 0–80 μM | Water | [35] |

Table 3.
Application of QDs in the detection of heavy metals.

the addition of tetracycline due to synergism of IFE, Förster resonance energy transfer (FRET), and photoinduced electron transfer (PET). They successfully tested the sensor to detect tetracycline with a high recovery rate in milk and milk powder [39]. **Table 4** lists some recent research to detect insecticide and antibiotic residues in food.

2.5 Detection of nutritional components

Numerous studies have been performed to use fluorescence sensors to detect nutrients such as ascorbic acid in fruits and vegetables [49], vitamin B₁₂ [50], retinoic acid [51], and others. One of the common mechanisms in the detection of nutrient components is the fluorescence of QDs covered by metal ions and then the fluorescence recovery by the analyte. In other words, electrostatic interactions between metal ions and the surface groups of QDs cause electron transfer and fluorescence coating. By adding an analyte, fluorescence is restored due to analyte chelation and metal ions. This mechanism has been used to detect glutathione and thiamine in food [9].

3. QDs in food packaging

Food packaging is an essential component of the food supply cycle that acts as a shield or barrier against contamination, the external environment, and mechanical damage during transport, and its main purpose is to ensure the quality, health, integrity, and safety of the product. In addition to maintaining product quality, packaging systems also help reduce waste [52]. The use of nanoparticles in food packaging is a new technology that has received much attention due to its many benefits. Nanoparticles as fillers in packaging materials increase product shelf life, reduce the growth of microorganisms, improve mechanical properties, and block gases and UV light. These packages are a good alternative to nonbiodegradable plastic packaging materials due to their high-performance nanostructures and low weight. Food

| QDs | Analytes | LOD | Linear range | Samples | Reference |
|---|--------------------|-----------------------------|---|----------------------------------|-----------|
| Fe ₃ O ₄ @SiO ₂ @CQDs | 4-nitrophenol | 23.45 nM | 0.08–10 μM | Water/fish | [40] |
| CQDs @ MIPs | Lambda-cyhalothrin | 0.5 μg kg ⁻¹ | 1–150 μg kg ⁻¹ | Vegetables and tea | [41] |
| Sulfur-doped graphene quantum dot | Omethoate | 0.001 ppm | — | — | [42] |
| QDs-doped COFs@ MIP | Nereistoxin | 1.60 μg L ⁻¹ | 5–100 μg L ⁻¹ | Tap water | [43] |
| Cerium-nitrogen co-doped carbon quantum dots | Tetracycline | 0.25 μM | 0.4–35 μM | Milk and pork | [44] |
| Nitrogen-doped graphene quantum dots | Tetracycline | 9.735 × 10 ⁻¹³ M | 2.5 × 10 ⁻¹⁰ –5 × 10 ⁻⁶ M | Whole milk, skim milk, and honey | [45] |
| Graphene quantum dots (GQDs) and palladium nanoparticles (Pd NPs) | Tetracyclines | 45 ng.mL ⁻¹ | 100–500 ng.mL ⁻¹ | Raw milk | [46] |
| CQDs | Tetracycline | 0.36 μM | 0.5–30 μM and 30–90 μM | Milk, egg, and chicken | [47] |
| PGr/CdTe QDs/Fe ₃ O ₄ @SiO ₂ /MIPs | Cefoperazone | 0.09 ng/mL | 0.1–25 ng/mL | Milk | [48] |

Table 4. Application of QDs in the detection of insecticide and antibiotic residues in food.

packaging is classified into four groups based on the application of nanoparticles: improved, active, smart, and bio-based packaging [53].

3.1 Improved packaging

The main purpose of this type of packaging is to use nanomaterials applied inside polymeric materials to improve the mechanical properties of the packaging, UV barrier, and the effect on permeability to water vapor and oxygen [54].

3.1.1 Improving the mechanical properties of packaging

Nanoparticles are the potential candidates for the synthesis of polymer nanocomposites due to their small size, high surface-to-volume ratio, high strength, and extremely high surface activity. Polymers reinforced with nanoparticles are very suitable for various applications such as food packaging due to high strength, low weight, and low cost [55]. In one study, CQDs were used to modify the polyvinyl alcohol matrix and cellulose nanofibers. The results showed that the addition of carbon dots to the matrix increases the tensile modulus and tensile strength of the composite due to the formation of hydrogen bonds, van der Waals force, and other chemical bonds

between carbon surfactants, polyvinyl alcohol, and cellulose nanofibers. Electron microscopy images also showed that the carbon-modified film had a denser refractive index than the control film, indicating better composition and bonding in the film with carbon dots [56]. Yu and colleagues synthesized a film based on carbon dots and carboxymethylcellulose (CMC). The tensile strength of the synthesized film was 55% higher than that of CMC film, which indicates that the addition of carbon dots improves the mechanical properties of the film, which is attributed to the strong interaction between the carbon dots and the film [57].

3.1.2 UV barrier

Many nanomaterials can block UV light due to the combination of scattering and absorption effects, so they are used as a light blocker in packaging materials and protect light-sensitive foods. Research has shown that carbon dots are very effective in absorbing UV light. Although the mechanism of blocking UV light at carbon dots is not yet fully understood, some attribute this feature to functional groups on the surface of carbon dots. Transition electrons are transferred from n to π^* or π to π^* , which are mainly supplied by different functional groups, which in turn depend on the precursor used and the synthesis method. In films with carbon dots, intramolecular proton transfer in the excited state by O ... H ... O, O ... H ... N tunnels and abundant conjugate structures provide optical stability and film-blocking properties against UV light [58]. Polyvinyl alcohol is a semicrystalline polymer that is widely used in packaging due to its advantages, such as linear and strong structure, nontoxicity, biocompatibility, and thermal stability. One of its disadvantages is the passage of light, which limits its use in the packaging of light-sensitive products. CQDs were synthesized in one study and combined with the polyvinyl alcohol polymer drying method. The results showed that the ratio of UV light transmission is inversely proportional to the amount of CQDs, so it can be concluded that CQDs improve the inhibitory properties of the polymer against UV light [56].

3.1.3 Impact on gas and water vapor permeability

One of the important features of food packaging materials is permeability to oxygen and water vapor because they affect chemical reactions and microbial growth and thus food safety and quality. The addition of carbon dots to polymer films affects the permeability to oxygen and water vapor, the extent of which depends on the molecular and physicochemical properties of the carbon dots and polymer. Amphiphilic carbon dots are suitable for controlling the wettability and permeability of the polymer layer. Doping carbon dots and radical polymerization can be used to prevent phase separation of carbon dots in polymer networks and thus improve film permeability. The permeability of canola protein films increases after the addition of carbon dots with hydrophilic groups on their surfaces. Also, chitosan films with improved water absorption properties have been made using different types and amounts of carbon dots [58].

On the other hand, CQDs can increase water resistance, which is attributed to the reduction of layer porosity and the abundance of carboxyl groups at the surface of carbon dots, which result in a reduction in free radicals due to the reaction between hydroxyl and carboxyl. The hydroxyl functional group leads to a decrease in water absorption of the film. In one study, CQDs were used to improve the properties of polyvinyl alcohol/nanocellulose layers. By increasing the amount of carbon dots from 0.1 to 4 ml, the water absorption of the film decreased from 119.6 to 42%, which

indicates the improvement of the film barrier property compared with moisture using CQDs [59].

3.2 Active packaging

Food spoilage causes environmental pollution, devastating impact on human health, economic losses, and increased treatment costs; therefore, technology development is needed to reduce food waste and improve food security. One possible way to reduce food waste and spoilage is to develop active ingredients for active packaging to increase product shelf life. Active packaging includes coatings with antimicrobial and antioxidant properties. These agents can be included in conventional nondegradable packaging or used in combination with biodegradable components [54].

3.2.1 Antimicrobial effect

Increasing resistance of microorganisms to antibiotics and other disinfectants has led food industry researchers to look for alternative antimicrobial approaches [51 m]. In one study, sulfur quantum dots (SQDs) were used to prepare food packaging film. The films showed strong antioxidant and antibacterial activity against bacterial food pathogens (*Escherichia. coli* and *Listeria monocytogenes*) and fungi (*Aspergillus niger* and *Penicillium chrysogenum*). When the film was used as a bread wrapping test, the film prevented mold growth for 14 days [60].

CQDs have shown great potential in killing and inhibiting bacteria, fungi, viruses, and drug-resistant species. The mechanisms of this property include the adhesion of CQDs to the bacterial surface, destruction of the bacterial membrane or cell wall, induction of oxidative stress through RNA/DNA degradation, and oxidative induction of proteins and other intracellular biological molecules. The most important killer effect of CQDs on microorganisms is due to the production of reactive oxygen species, which leads to the production of hydroxyl free radicals and single oxygen, which destroys vital biomolecules in the cell, and inactivates intracellular proteins, mitochondrial dysfunction, and lipid peroxidation, and eventually, the cell dies [61]. Ezzati et al. used sulfur-modified CQDs to modify the gelatin/pectin film in food packaging. The resulting film showed strong antimicrobial properties against foodborne pathogens such as *E. coli* and *L. monocytogenes* [62]. In another study, nitrogen-doped CQDs were synthesized and used to modify cellulose nanofibers. The obtained film showed high antibacterial and antifungal activity due to the production of reactive oxygen species. The prepared film was used for packaging tangerine and strawberry fruits. The results showed that the growth of fungi on the fruit surface was effectively inhibited, and their shelf life was increased by 10 and 2 days, respectively, indicating its good potential for use in active packaging [63].

Fan et al. used a combination of CQDs and chitosan to inhibit microorganisms in the packaging of freshly cut cucumbers. CQDs established a strong hydrogen bond with chitosan. The results showed that the diameter of the inhibitory zone against *E. coli* and *Staphylococcus aureus* improved with the increasing concentration of CQDs. In addition, the total number of bacteria, molds, and yeasts decreased during storage [64].

3.2.2 Antioxidant properties

ROs, including single oxygen and free radicals (hydrogen peroxide, hydroxyl, and superoxide), play an important role in food spoilage, chemical degradation,

polymers, and the destruction of biological structures. Therefore, the presence of antioxidant compounds or free radical scavengers in food and food packaging is essential for good health. Recently, a range of carbon nanoparticles such as nitrogen-doped carbon dots, selenium-doped carbon dots, and nitrogen/sulfur-doped carbon dots have been turned into antioxidants to remove ROS. The antioxidant properties of carbon dots are attributed to electron transfer, unpaired electrons due to surface defects, hydrogen donor behavior, doping element, and surface functional groups. The carbon dots synthesized in the NaOH electrolysis medium have more active oxygen-containing groups such as carbonyl and hydroxyl, which can be used as hydrogen donors to scavenge free radicals, resulting in higher antioxidant capacity. In addition, recent studies have shown that carboxyl and amine groups directly or indirectly through the hydrogen atom transfer (HAT) mechanism cause the removal of ROS and thus increase the antioxidant activity of CQDs. In this mechanism, hydrogen or electron is transferred from carboxyl and amine groups to active species such as ROS and deactivates them [65].

3.3 Smart packaging

The purpose of this type of packaging is to monitor the condition of the food or the surrounding environment. In this technology, a visual indicator gives the supplier or customer information about information such as product freshness, packaging leakage, storage temperature throughout the production chain, and corruption. Nanoparticles are used as reactive particles in packaging materials to inform the status of the package. In other words, they are nanosensors that respond to environmental changes (such as temperature, humidity, oxygen level, and microbial contamination). When nanosensors are integrated into food packaging, they can indicate specific chemical compositions and product freshness [66].

3.3.1 Product freshness indicator

This is done using intelligent detection technology and labels that can measure changes in environmental conditions inside the package. Among the many methods, smart labels have received much attention due to their advantages, such as accurate results, high sensitivity, and ease of use. The color change of the smart label attached to the packaging container indicates the freshness of the product. By monitoring the color change of the indicator, it can be seen that the food is unsuitable for consumption. For example, in marking the freshness of meat packaging, the basic principle is that the marker on the label is sensitive to volatile nitrogen compounds and amines in the packaging environment or changes in ambient pH caused by such components. When such sensitive changes are detected, they can be converted to response values, which are usually color changes that can be detected by the naked eye, so that the freshness of the meat is detected in real time [65]. Cauchy and colleagues used soy protein isolate carbon dots in anthocyanin-based smart films to monitor the freshness of packaged pork. When the meat samples were stored at 25°C, the activity of microorganisms increased the amount of volatile nitrogen inside the package, followed by a change in pH. As the shelf life increased, the fresh pork deteriorated, and the color of the detector changed from purple to green [67].

3.3.2 Oxygen indicator

At first, the need for oxygen markers in food packaging may not seem necessary until we realize that the main cause of further food spoilage is oxygen. Much of this spoilage is indirect because oxygen allows a myriad of food spoilage aerobic microorganisms to grow. Oxygen can also cause direct spoilage of many foods through enzyme-catalyzed reactions, including browning fruits and vegetables, ascorbic acid degradation, oxidation of a wide range of flavors, and nonenzymatic reactions such as lipid oxidation. During storage, changes in oxygen levels in the packaging are an important indicator of food freshness and product respiration rate. Given the key role of oxygen in food spoilage, it is not surprising that most foods are packaged in a predominantly oxygen-free environment under a modified atmosphere. The main problem with the modified atmosphere is the lack of a simple, inexpensive oxygen indicator that assures the consumer that the package is safe and that oxygen input is insignificant. At present, this level of quality assurance is not possible in modified atmospheric foods that rely solely on a routine sampling of the packaging line. Typically, one packet out of every 300–400 packets is taken out of line for testing by a technician and checked using an expensive analytical system such as FT-IR or GC, and if sufficient packages are found that are not sealed enough, all 300–400 previous food packages are considered unsafe and are destroyed or repackaged. This unfavorable situation has led to special attention to cheap, reliable, and simple oxygen markers for food packaging [68].

One of the common methods for detecting oxygen in food packaging is the use of optical sensors, which use fluorophore nanoparticles in a solid matrix. Zhu et al. used a combination of silane-activated carbon dots as oxygen-insensitive fluorophore and ruthenium dihydrochloride as oxygen-sensitive fluorophore to prepare the fibrous membrane. The fibrous membrane prepared by photoluminescence ratiometric imaging is well able to evaluate the amount of oxygen in the packaging of fruits so that the fluorescence of CQDs is at a wavelength of 400 nm and its intensity does not change with changing oxygen concentration, but the intensity of fluorescence emitted by ruthenium at 600 nm depends on the oxygen concentration. They also used a digital camera instead of an expensive optical spectrometer to monitor oxygen concentration. Then, a fiber membrane was used to wrap the grapes, which initially emitted bright blue fluorescence but changed to purple on the third day of storage due to fluorescent respiration. As the respiration process increased, the fluorescent dye turned bright red on days 6 and 7 of storage. Therefore, it can be said that these fibrous membranes have a good potential for assessing oxygen in the packaging of agricultural products [69].

3.4 Biomaterial-based packaging

Common packaging materials include plastics such as polyvinyl chloride, polystyrene, polyethylene, and polypropylene, which are widely used due to their strength, heat, and moisture resistance. The use of these materials is a threat to the environment due to their nondegradable nature. Therefore, it can be said that biodegradable materials are the best choice for packaging. These coatings and films are monolayers, bilayers, or multilayers of polysaccharides, lipids, and proteins that, due to their sensitive nature, poor mechanical properties, and poor sealing properties, cannot be completely substituted for other materials [70]. Xylan is one

of the hemicelluloses and the second most abundant polysaccharide in plants, which usually has poor mechanical performance due to its relatively low molecular weight. Modifying them with carbon dots improves their filmmaking and mechanical performance. Yang et al. used carbon dots to modify the carboxymethylxylan matrix. The results showed that carbon dots, in addition to creating excellent optical properties, improve the thermal stability and mechanical strength of nanocomposite films, so that by adding 92.1 wt% of carbon dots, due to creating a chemical bond between xylan and carbon dots, the tensile strength and modulus of elasticity increase by 114.3 and 90.7%, respectively. Also, this film can effectively absorb UV light and convert it into blue light. Due to the mentioned advantages, this film has a good capability for food packaging [71].

Schmitz and colleagues synthesized a nanocomposite by combining zein and QDs. The prepared QDs were used as nanofillers to obtain zein-based nanocomposite films that showed good visual appearance, homogeneity, and clarity. The presence of QDs increased hydrophobicity and reduced the water absorption of composite films up to three times compared with pure zein. The presence of QDs in the films led to extensive UV blocking in the absorption spectrum. Antimicrobial assays showed that zinc oxide nanoparticles loaded into zein films were promising antibacterial agents, as growth inhibition of *S. aureus* reached $(96.5 \pm 4.9) \%$ to 44.8 wt% of ZnO nanoparticles [72]. Grzebieniarsz and colleagues synthesized films based on natural resources such as potato starch and chitosan by combining QDs and cadmium sulfide. They performed a storage experiment using poultry meat coated with films produced to assess microbiological quality. The results showed that composites restrict the growth of selected microorganisms in poultry meat [73]. Priyadarshi et al. used sulfur quantum dots (SQDs) as functional fillers for biopolymer films in food packaging. SQDs showed antimicrobial activity with almost negligible toxicity. The addition of SQD to gelatin/agar composite films also increased the UV barrier property without compromising color and clarity. The film showed excellent antioxidant activity, moderate antibacterial effect on *L. monocytogenes*, and inhibitory effect on *E. coli* [74]. Zhang et al. made functional films based on carboxymethylcellulose (CMC) by adding different amounts of CQD. The CQDs were evenly distributed in the polymer matrix to form a very clear UV-blocking film. The addition of CQD increased the tensile strength (up to 27.6%) and elastic modulus (up to 61.5%). The films showed excellent antioxidant and antimicrobial activity. Lemon fruits were coated with film solutions to test the performance of the film. Lemons coated with CMC/CQD film showed an excellent appearance without mold growth even after 21 days of storage [75].

4. Water purification

The development of industry and agriculture leads to the release of various pollutants and their mixing with underground and surface water, which is a threat to human health and the environment. On the other hand, due to the growth of the population in the world, the demand for water will increase in the coming years. Therefore, it seems necessary to purify polluted water for various uses, including drinking, agriculture, and industrial use [76]. Water pollutants include heavy metals, inorganic and organic pollutants, especially dyes, polycyclic aromatic hydrocarbons, pesticides, and pharmaceuticals. Most of the mentioned pollutants exist in very low concentrations, but their risks to humans and living organisms are very

high because they are very persistent in normal environments and water treatment systems. Organic compounds are important pollutants that come out of manufacturing plants. These organic pollutants lead to the reduction of dissolved oxygen and endanger human health. Heavy metals such as lead, nickel, cadmium, essential oil, copper, manganese, chromium, and cobalt are very harmful to human health even in low concentrations, and their frequent consumption can damage the liver and brain and cause cancer [77]. The most important water purification methods are filtration, crystallization, sedimentation, gravity separation, flotation, coagulation, ionic oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electrodialysis, electrolysis, absorption, centrifugal and membrane fluid separation, neutralization and remineralization, reduction, and oxidation. None of the mentioned methods are completely effective for providing safe drinking water. Nanotechnology has provided new solutions for water purification. Nanomaterials are suitable for adsorption, catalysis, and sensing applications due to properties such as high aspect ratio, reactivity, adjustable pore volume, electrostatic, hydrophilic, and hydrophobic interactions. Nanomaterials are widely used in various water treatment methods, including membranes in filtration, adsorbents, and photocatalysts for pollutant degradation and detection. Recently, much research has been conducted on the potential application of QDs in water treatment due to their unique properties. Of course, it should be noted that nanomaterials used for drinking water purification must also be environmentally friendly and nontoxic, because unsafe particles in contact with the human body cause severe damage to vital organs and their dimensional properties aggravate biological damage slowly [78]. There is a lot of research on the use of CQDs in water treatment. In general, the use of CQDs in water purification can be investigated from two aspects.

4.1 CQDs as membranes

Nanofiltration membranes have good potential for water purification. One disadvantage of the traditional water filtration methodology is that soluble salts and a few soluble minerals and organic substances cannot be removed. Nanotechnology provides new solutions for water purification. This is done using nanoporous polymers, nanomembranes, etc., which usually have pore sizes between 1 and 50 nm and separate most bacterium and harmful substances. Desalinization also belongs to the current methodology. The general structure of the membrane consists of many layers. In a simple membrane structure, CQDs are uniformly distributed between the dense upper layer and the porous substrate. The addition of CQDs to thin-film nanocomposite (TFN) membranes will increase membrane efficiency, water flux, power density, and water purity. Also, because of the electrostatic repulsions between the deposits and also the membrane surface, a major improvement in antifouling properties happens within the designated layer. Efficient and large surfaces and large intermediate spaces with several functional groups are the most reasons for increasing fluxes. The presence of specific hydrophilic groups in CQDs reduces the nonspecific absorption and therefore will increase the selectivity within the needed absorption of pollutants. These membranes also are utilized in reverse osmosis because of enhanced water permeability, high permeation flux, and antifouling capability. By incorporating CQDs on the membrane surfaces, all processes like desalination performance, porosity, permeability, hydrophilicity, selectivity are increased [79].

4.1.1 Thin-film nanocomposite (TFN) membranes

In recent years, many studies are conducted on modifying selected skins by adding CQDs. The CQDs disperse within the aqueous phase and then participate within the surface polymerization process to create TFN membranes. CQD-modified TFN membranes will perform higher than virgin membranes, even with a small addition of CQD in the water phase. The resulting membranes show surface hydrophilicity and better permeability while maintaining solute selectivity, excellent stability, and improved antifouling features. The performance of TFN membranes can be maximized by properly functionalizing CQDs and optimizing their value [80]. In one study, CQDs were used to make new thin-film nanocomposite (TFN) membranes. First, the amino carbon quantum dots (ACQDs) were synthesized through a simple single-pot hydrothermal method and then used in surface polymerization to fabricate the ACQD-TFN membrane. Using ACQDs in membrane led to a water flux increase of $23.2 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 70°C during the treatment of a 10 wt% NaCl solution, which was 44% higher performance than thin-film composite membrane without modification [81].

4.1.2 CQD/polymer composite membranes

In this method, CQDs are added to polymeric dopes to form homogeneous solutions and to form mixed matrices membranes through various spinning methods. The small size of CQDs leads to better dispersion of particles in doped solutions and the formation of membranes with a uniform structure without loss of mechanical strength. One of the challenges of this method is finding a suitable solvent for CQD and polymer. Another challenge is how to control the distribution of CQD in membranes. Therefore, in addition to ensuring the long-term stability of CQDs within the membrane, practical tools for the formation of chemical bonds between CQDs and the polymer matrix must be identified [80].

Colbum's team used an ionic liquid (1-ethyl-3-methylimidazolium acetate) as the common solvent for both CQDs and cellulose to create uniform membrane properties. CQDs are bound with the cellulose domain through hydrogen bond networks, and a stable composite membrane was formed. The presence of CQDs on the surface can also make the membrane negatively charged and more hydrophilic. Also, Field Emission Scanning Electron Microscopy images of the cross section of the membrane indicate that CQDs act as pore formers and help to form membranes with higher permeability [80].

4.1.3 Membranes with CQDs on top of substrates

In this method, CQDs are coated above the membrane surface with the help of various coating agents such as polydopamine (PDA) and trimethoxy silane (3-aminopropyl) (APTMS). One way to stabilize CQDs is to create a covalent bond between the oxygen-containing groups in CQDs and the amine-containing agents on the membrane surface [28]. In research, CQDs were fabricated from citric acid *via* a simple method. Subsequently, they are immobilized onto the polydopamine (PDA) layer grafted on. The carboxylic groups of CQD react with the $-\text{NH}_2$ group of polydopamine, resulting in increased resistance of the modified membrane to deposition. The modified membranes possess much enhanced antibacterial activity and anti-biofouling propensity. The continuous PRO operations at 15 bar also confirm

that the CQD-modified membranes exhibit a much higher power density (11.0 vs. 8.8 W/m²) and water recovery after backwash (94 vs. 89%) than the unmodified ones [82].

4.2 CQDs for removal of pollutants

One of the appropriate strategies for water treatment is photocatalysis. Both sunlight and UV light are employed to destroy pollutants. It is an oxidation process, which is stable and environmentally friendly for water purification. CQDs show excellent photoluminescence. They are excellent fluorescent materials and efficient photocatalysts in UV light. CQDs also are sensitive to visible light, which results in enhanced charge carriers and photocatalytic performance. CQDs transfer electrons at different positions and can reduce the recombination of light-generated charges. All the mentioned properties have made them an appropriate candidate for water purification and removal of organic and inorganic pollutants from water [79].

CQDs can be used to take away organic and inorganic pollutants Cd²⁺ and Pb²⁺ ions from wastewater by absorption treatment. N-CQDs were with success incorporated into this treatment. Another adsorbent, polyethyleneimine-functionalized CQDs onto the magnetic materials (MnFe₂O₄) to provide a nanocomposite (PECQDs/MnFe₂O₄), is applied for the removal of uranium [79].

5. Protein tracking by QDs

Proteins are the main components of food and play an important role in nutrition, formation, and maintenance of food structure. Today, the function of protein in food matrices is well known, but it is necessary to study the role of protein in different food matrices. For example, in bread dough, gluten causes the dough to be elastic and viscous and forms a matrix to hold gases in the bread. On the other hand, knowing the function and amount of gluten in the dough is not enough. In the past, gluten function was studied by extracting gluten proteins and studying the behavior of the extracted proteins, but the behavior of the extracted gluten due to its interaction with other proteins may not be similar to that found in the food matrix. Knowing the distribution of proteins leads to a better understanding of their function. One of the effective strategies in this field is labeling proteins with QDs, which leads to a better understanding of their function [83].

Gluten and zein, the most common and consumed proteins, are cereals. The main storage protein of wheat grain is gluten. Gluten is a complex mixture of hundreds of protein components, mainly gliadin and glutenin. Based on solubility in alcohol-water solutions, gluten proteins are divided into soluble gliadin and insoluble glutenins. Both parts play an important role in the rheological properties of dough, but their functions are different. Gliadins contribute to the viscosity and expandability of the dough system, while glutenin is responsible for the strength and elasticity of the dough. In terms of amino acid composition, gluten has high amounts of glutamine and proline and low content of amino acids with charged side groups [84]. The most important storage protein in corn is zein. Zein contains four components (alpha, beta, gamma, and delta) with different peptide chains, molecular sizes, and solubilities. Zein is rich in glutamic acid, leucine, proline, and alanine, but it is exceptional among vegetable proteins in terms of the lack of tryptophan. This protein is considered hydrophobic due to significant amounts of nonpolar amino acids. Also, the high

proportion of nonpolar amino acids and the lack of basic and acidic amino acids lead to a decrease in the solubility of zein [85].

Suzer et al. were the first to use QDs to image and label food structures. The distribution of gluten and zein in the cereal matrix strongly affects the structure and texture. Thus, knowledge of their distribution offers new insights into how distribution affects food structure. In this study, they used nucleus/shell CdSe/ZnS QDs to image the gluten network in flatbread and zein in corn extrudates. A confocal laser scanning microscope (CLSM) was used to observe the structure of QD-labeled cereal proteins and visualize their location in the food matrix. The results showed that QDs could be covalently conjugated with gluten and zein [86]. In one study, QDs were conjugated to gliadin antibodies and used as fluorescent probes to detect gliadin proteins in dough and baked bread samples. CLSM was used to investigate QDs-gliadin antibody conjugates and obtain 3D images of the gliadin distribution in the dough and flatbread matrix. CLSM images showed significant changes in the fluorescence intensity distribution generated by the gliadin-QD conjugate with cooking time. Based on the results obtained from the dough and flatbread samples, they stated that the distribution of gliadin in different layers (top, center, and bottom) is nonuniform and the baking time and location of the layers play an important role in the distribution of flatbread gliadin protein. From the successful binding of QDs to gliadin antibodies, it can be concluded that QDs have good potential as a probe to target protein subunits in food matrices [87].

In the mentioned studies, the antibody-antigen method was used to label the proteins. When the antibodies were conjugated with the QDs, to break the disulfide bonds in the antibodies, and then crosslink the QDs to the new free-SH groups, diethritol (DTT) was used in the antibody. The antigen detection region is strong in antibodies with disulfide bonds. Therefore, the use of DTT may lead to antibody damage. A new method has been proposed for the conjugation of QDs to antibodies in which disulfide bonds are not broken performed with acetylglucosamine. The next step is the integration of azides from modified N-acetylgalactosamine monosaccharides into antibody glycans. The third step is the catalyst-free click conjugation of desferrioxamine-modified dibenzocyclooctynes to the azide-bearing sugars. And the last step is the radiolabeling of modified chelator antibodies with zirconium. In this method, there is no risk of reducing the effectiveness of the antibody protein, because the antibody binding site is not manipulated in any way [83].

6. Conclusion

Undoubtedly, quantum dot-based sensors have promising prospects for food analysis. Quantum dots are superior to fluorescent dyes due to their relatively long luminescence lifetimes, photobleaching resistance, and high quantum yield. Because food samples have different biological and chemical components, identifying a specific target without the involvement of other sample components is a challenge. This highlights the importance of using connectors that can detect a specific target, one of the most important of which is the integration of QDs with MIP, which provides sensors with a low detection limit. QDs offer many benefits for food packaging, including improved mechanical properties, better thermal stability, increased water resistance, UV barrier properties, and antimicrobial and antioxidant activity. In this review, we reviewed recent research using quantum dots in water treatment as nanomembranes, nanosensors, and absorbent photocatalysts. Despite recent advances in this area, more


fundamental research on the antifouling mechanism, biofilm growth, and industrial development is needed. Although CQDs are more secure than other QDs, are within the appropriate concentration range, and are not toxic to human and animal cells, research into the toxicity, migration, and degradation of CQDs is still in its infancy, and further studies are carried out to examine toxicity, behavior. Possible migration of CQDs from sensor films or packaging to food systems and their effect on the gastrointestinal tract is required.

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