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Applications of graphene in quality assurance and safety of food

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ABSTRACT

There is tremendous interest in graphene and its derivatives [graphene oxide (GO) and reduced GO (rGO)] due to their superior mechanical, thermal, electrical, optical, and chemical-adsorption properties. In the past few years, graphene-based materials attracted much attention and were used for a myriad of practical applications in various industries. In this review, we present a comprehensive, state-of-the art assessment of graphene applications in the food industry. We critically examine recent developments on graphene synthesis from foodstuffs, use of graphene for food analyses, and graphene-based analytical methods in detection (e.g., composition, contaminants, toxins, and volatile organic compounds), which help to ascertain quality and/or safety of foods. We also discuss antibacterial properties of graphene-based nanomaterials and their applications in food packaging.

Contents

1. Introduction

The food industry is one of the largest, worth several trillions of dollars worldwide. The heart and soul of this complex, global enterprise is ensuring high quality and safety of the foods that we consume. While the food industry typically lags other industries, such as electronics and automobiles, in adopting new technologies, nanomaterial-based applications have found their way into the food industry. There are several examples where nanotechnology has helped to improve taste, texture, shelf life, nutrient delivery, and the overall quality and safety of foods [1,2]. For example, titanium dioxide (TiO_2) and silver (Ag) nanoparticles (NPs) have been used as antimicrobial agents in storage containers for foods and beverages. According to the US Food and Drug Administration (FDA), direct addition of Ag salts up to 17 μg/kg is allowed as disinfectant in bottled water [3].

However, increased use of engineered nanomaterials in the food industry has also raised concerns regarding their potential toxicity and impact on human health. For example, TiO_2-NPs extracted from chewing gum were investigated for their toxicity [4]. Though they were considered safe, a few studies suggest that TiO_2-NPs could pass through the gastrointestinal tract and slowly distribute and

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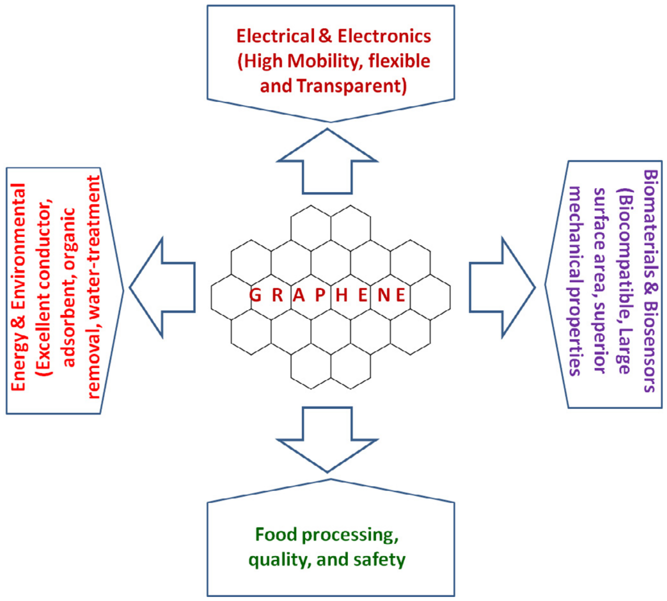

Fig. 1. Graphene applications span various fields of science, engineering, and technology.

accumulate in other organs [5]. Efforts to investigate further our understanding of the cytotoxicity of engineered NPs used in foodstuffs are ongoing [6].

Biosensors incorporating nanomaterials have the potential to improve the speed, the sensitivity and the analytical accuracy needed to detect the presence of molecular contaminants or adulterants in complex food matrices [7]. Gold NPs (AuNPs) are popularly employed in biosensors, since the aggregation of AuNPs leads to visibly perceptible color change, signaling the presence of the analyte being tested. The use of AuNPs [8,9], Au nanorods [10,11], and carbon nanotubes (CNTs) [12] particularly helped to detect the presence of gases, aromas, chemical contaminants and pathogens, or respond to changes in environmental conditions.

Graphene is one atom thick, two-dimensional (2-D) nanosheet of graphite discovered by Novoselov et al [13]. It possesses high electron mobility (250,000 cm^2/V s), exceptional thermal conductivity (5000 W m^{-1} K^{-1}), superior mechanical properties (e.g., Young's modulus of 1 TPa), large specific surface area (>100 m^2 g^{-1}), good electron transfer ability and good biocompatibility [14]. High-quality graphene (i.e., without structural defects) can be synthesized by chemical-vapor deposition (CVD) [15]. Furthermore, graphene oxide (GO) or reduced GO (rGO) can be derived from graphite by chemical oxidation [16] or electrochemical exfoliation [17].

In the past few years, there were numerous exciting applications of graphene in various fields of science, engineering, and technology [18,19]. For example, as illustrated in Fig. 1, graphene is used in transparent conductors, flexible electronics, field-effect transistors, fuel cells, batteries, solar cells, biomaterials, biosensors, and water purifiers [19,20].

Also, graphene-based applications are on the rise, with innovative developments that help ensure food quality and safety [21,22]. To improve agricultural productivity, pesticides, herbicides, insecticides and fungicides are commonly used, and are potentially toxic if allowed to remain in the food chain in high enough concentrations [23], so quality and safety of foods must be evaluated before delivery to the consumer market. In processed foods, preservatives, colorants and other additives are used to enhance consumer appeal and/or shelf life. Some of these agents are deleterious, so their presence needs to be evaluated. Thus, new analytical methods and technologies are needed to generate rapid, reliable, and precise information. Graphene is as a new sorbent in extraction (e.g., cocaine, adenosine, sulfonamide antibiotics, carbamate pesticides, pyrethroid pesticides, phenols, methyl parathion, squalene, and chlorophenols) from environmental, biological and food samples [24]. Graphene-based sorbents are superior to other sorbents, including C18, silica, graphitic carbon, single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) in terms of sorption capacity, ease of elution, cost of material, and recovery of extracted analytes.

2. Graphene synthesis from foodstuffs

CVD is used to synthesize thin films of various nanomaterials using thermochemical vapor-phase reactions in a vacuum furnace to achieve deposition of the desired material on a substrate at high temperature (~1000°C) [25]. Graphene can also be synthesized on a metal-film substrate via CVD by flowing hydrogen and methane gases (carbon source) with a metal catalyst; the methane decomposes, leaving carbon atoms deposited on the substrate to form graphene layers.

Ruan et al. used food materials (e.g., cookies, and chocolate) as the carbon source to synthesize monolayer graphene [26]. They obtained a high-quality graphene film on a Cu foil at 1050°C under H$_2$/Ar flow (Fig. 2A). These films did not exhibit significant disorder (D) bands in their Raman spectra (Fig. 2B,C), signifying the presence of few defects. Also, the large 2 D/G ratio suggested that the graphene synthesized was a monolayer film.

Calcinations of glucose with dicyandiamide produced free-standing monolayers to oligolayered graphene, and layered graphic carbon nitride (g-C$_3$N$_4$) acted as a sacrificial template, which underwent complete thermolysis at 750°C. In the subsequent step, graphene-like sheets were liberated at high temperatures (Fig. 2D). However, graphene obtained from this method contains nitrogen atoms in the graphene lattice, mainly in the form of "pyridinic" nitrogen and a minor amount of "graphitic" nitrogen [27].

Qu et al. synthesized graphene from alfalfa plants by treating alfalfa shoots with nitric acid at 70°C for 300 min and obtained a black graphene precipitate. It is interesting to note that CNTs were produced in the initial stages from plant-cell walls, and were later converted to graphene by unrolling the nanotubes with treatment by nitric acid [28].

Gupta et al. produced a graphene-coated composite to remove organics in contaminated water by heating a mixture of river sand and sugar in a furnace at 750°C under an N$_2$ atmosphere [29].

Kalita et al. used solid camphor as the precursor material in a microwave surface-wave plasma CVD process [30], in which graphene layers were deposited on a Cu foil at a relatively low temperature (<600°C). Moreover, synthesized graphene film could be easily transferred to a transparent plastic substrate by wet etching, and had a sheet resistance of 8.23 kΩ/square.

3. Graphene in detecting food quality

3.1. Detection of chemical contaminants

Surface-enhanced Raman spectroscopy (SERS) is an analytical technique used to study and to identify biomolecules or chemicals by their enhanced (of the order of 10^4–10^{14}) bands in the Raman spectra [31]. The intensity of Raman peaks of the molecules could be enhanced on the substrate (metal NPs) due to electromagnetic or chemical mechanisms [32]. Graphene is a good substrate to investigate the chemical enhancement of SERS [33]. Liu et al [34]. prepared a graphene nanomesh with controlled size and density of holes, by first depositing a Cu film on graphene and then removing the Cu film by annealing to leave plenty of hole rims around the CuNPs. They used this graphene nanomesh to detect rhodamine B (RhB) by SERS. The intensity of the Raman bands on