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Review

Nanoantioxidants: The Fourth Generation of Antioxidants—Recent Research Roadmap and Future Perspectives

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Abstract: Antioxidants work by interacting with free radicals and converting them into harmless chemicals, interfering with the progression of potentially hazardous chain reactions. Antioxidants are useful in treating illnesses induced by free radicals because they help minimize oxidative stress. Antioxidants, whether natural or synthetic, have a limited effect on cellular health and function because of their low absorption, inability to traverse cellular membrane, and disintegration during delivery. The benefits of antioxidants, both natural and synthetic, are comparable. The use of antioxidants that are covalently attached to nanoparticles, or encased in particles with a hollow center, or feature the nanomaterial encapsulation of various origins has been employed to solve these challenges to provide improved stability, slow and slow sustained release, biocompatibility, and targeted administration. This review examines the importance of metal-based antioxidants and methods for enhancing antioxidant activities based on recent studies.

Keywords: nanoantioxidants; DPPH; nanoparticles

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1. Introduction

Age-related disorders have emerged as a major public health concern worldwide in the twenty-first century. The social and economic burden of population aging is becoming increasingly substantial in the modern world. As people live longer, their health span does not necessarily rise at the same rate. Over the last few decades, the burden of age-related illnesses has grown progressively in most developed countries [1,2]. The process of aging is one that occurs throughout time and is a consequence of the degeneration of vital organ structures and functions. It increases the chance of developing a wide array of chronic diseases and contributes to a high death rate [3,4]. The free radical theory is unmatched among several ideas that explain and uncover the ageing process [5]. According to this view, reactive oxygen species (ROS) damage to cells and tissues is exacerbated with age because the body's defense mechanisms repeatedly fail to heal it [6].

Degenerative aging is well understood to be a result of oxidative stress, which is a significant contributor to the overall process. When reactive oxygen species (ROS) are present, the pathophysiology of a number of different biological processes can be affected They have also been linked to heart disease, cancer, neurological illness, and pulmonary

disease, as shown in Figure 1 [7]. ROS formation in cells has also been related to the progression of ageing; nevertheless, this cannot be considered the only factor responsible for the progression of aging. Furthermore, increasing levels of ROS are associated with mitochondrial dysfunction and cellular oxidative damage in age-related disorders [8,9].

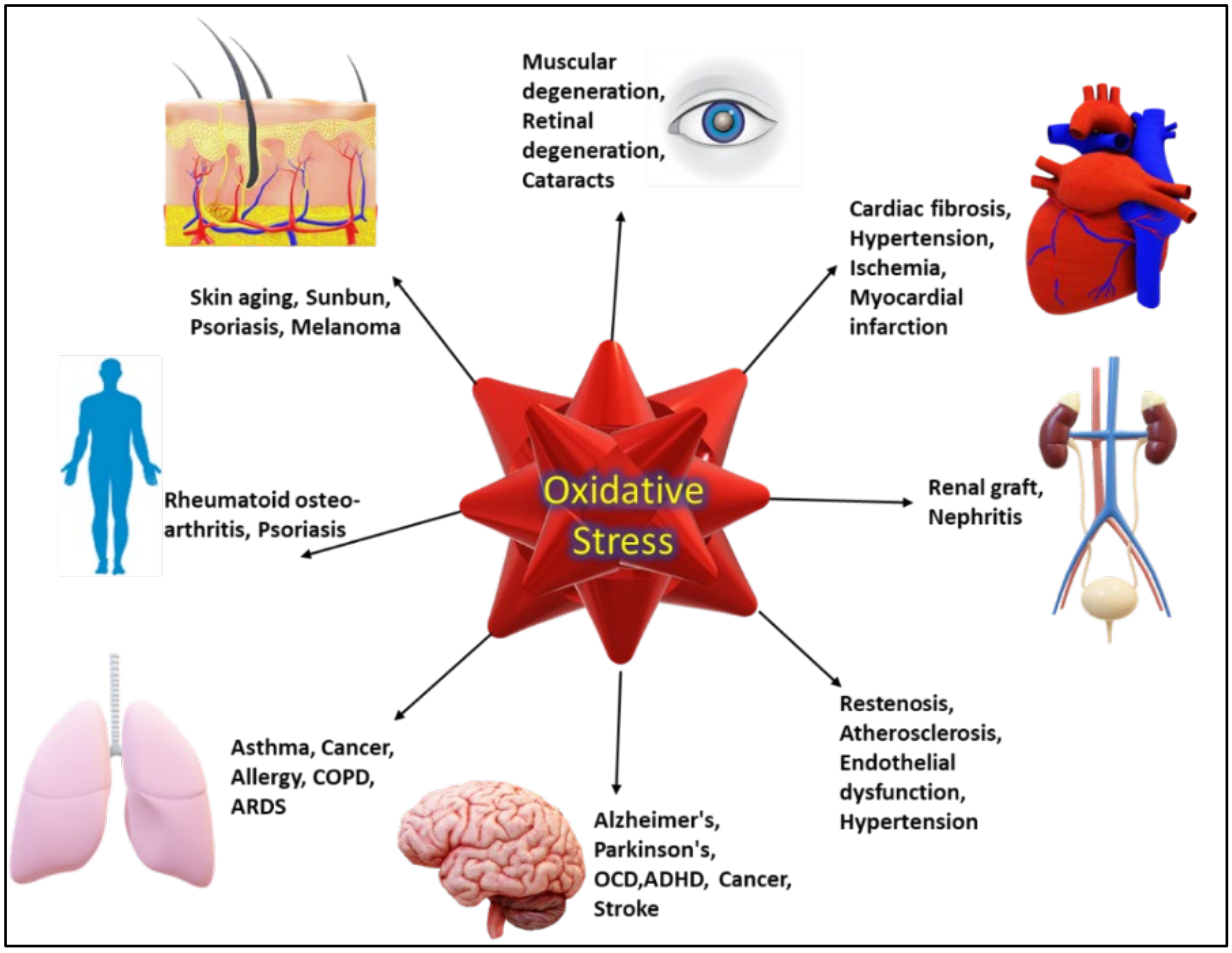

Figure 1. Oxidative stress Adverse Impacts on Human Health.

Organic materials, such as biological components such as proteins and lipids, also include dietary supplements and cosmetics. An oxidative chain is established when atmospheric O_2 reacts with alkyl oxidation products to form peroxyl (ROO) radicals. It is called autoxidation or peroxidation because hydroperoxides (alkyl hydroperoxides and H_2O_2) are the principal first-formed products of the autoxidation process [10]. Due to their unstable nature, hydroperoxides are capable of generating highly reactive hydroxyl (HO•) and alkoxyl (RO•) radicals, two types of radicals that can damage even generally stable molecules, such as DNA bases [11]. The production of reactive carbonyl species (such as 4-hydroxynonenal) due to alkyl hydro-peroxide cleavage exacerbates the oxidative damage [12]. When a cell's ability to produce reactive oxygen species (ROS) exceeds its ability to mount an efficient antioxidant response, it experiences oxidative stress, which leads to cell death and mutation. Oxidative stress causes irreversible damage to proteins, lipids, and DNA, as well as mutation and cell death [13].

Research into bioactive antioxidants that lower oxidative stress and promote immunity is ongoing [14]. Researchers always search for new antioxidant molecules to promote healthy aging and prevent oxidative stress. This review covers the significance of metal-based antioxidants as well as strategies for boosting antioxidant activity based on current research.

2. Antioxidants

Antioxidants are substances or compounds that can prevent the oxidation of a valuable substrate even at low concentrations [10,15]. The discovery of antioxidants sparked a boom in the late 19th and early 20th centuries, thanks to their use in various industrial processes such as corrosion prevention, fuel polymerization, combustion engine fouling, and rubber vulcanization [16]. Antioxidants were formerly used only to protect unsaturated fats from oxidizing, resulting in a rancidity of fats [17]. Any compound's antioxidant properties can be determined by measuring the rate at which fat consumes oxygen when stored oxygen-filled container within a sealed environment. Antioxidant vitamins A, C, and E were discovered and proved to be crucial in the biochemistry of living organisms, revolutionizing the field of nutrition [18,19]. The antioxidant is a stable molecule that donates an electron to harmful free radicals, neutralizing the resulting radical and reducing the amount of damage that it may induce. Generally speaking, these antioxidants either stop or delay cellular damage from occurring [20]. Antioxidants with a low molecular weight can swiftly and effectively interact with ROS, limiting damage to essential molecules from the chain reaction. Our bodies naturally produce antioxidant molecules such as glutathione, uric acid, and ubiquinol during regular metabolic activities [21]. Ascorbic acid (vitamin C), β-carotene, and α-tocopherol (vitamin E) are micronutrients and enzymes found in human bodies that can combat free radicals [22]. Because the body cannot produce these molecules, they must be taken from the food we consume. Endogenous antioxidants are those produced within, while exogenous antioxidants come from outside the body (found in foods such as glutathione and uric acid) [23]. Antioxidants found in nature may help protect against the damage caused by oxidative stress. Numerous fruits, vegetables, and byproducts of fruits contain antioxidants that have been shown to lower the amount of harmful free radicals in the body. These antioxidants include polyphenols (3,6-dihydroxyflavone), carotenoids (lutein), vitamins (ascorbic acid), and metabolic sensitizers (selenium methyl selenocysteine) [24–27]. Bioactive substances from various sources, such as antioxidants obtained from natural resources (such as Rosa rugosa dried flower extracts), have been found to exhibit scavenging and electrophile removal abilities and the ability to prevent the formation of reactive oxygen species [28,29]. On the other hand, natural antioxidants prone towards deterioration and have low bioavailability, poor absorption, and deterioration upon delivery are the main reasons [30]. Antioxidants include synthetic compounds such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA), BHT analogues, GA esters, and other derivatives [24,31,32]. Nanotechnology has opened up new possibilities in a variety of fields. Nanoparticles are ideal for medication and drug delivery because of their small size and versatility. As a result of the integration of nanotechnology with material science and engineering, significant progress has been made in the reduction in free radical production in a variety of fields [31,32]. Antioxidant nanoparticles or nano-antioxidants are the nanoparticles designed for this purpose. Some of these nano-antioxidants have recently shown promise in nanomedicine studies [33,34].

3. Nanoantioxidants

Antioxidants have been proven to be helpful therapeutic and preventative agents for a variety of ailments. Most antioxidants have few drawbacks, such as low permeability, poor water solubility, instability during storage, and digestive tract degradability [35]. Free radical generation has been minimized in several fields by developing nanoparticles, and synthesized nanoparticles are known as nano-antioxidants due to the integration of material sciences and nanotechnology [31,36].

Nanoantioxidants are nanomaterials that capture chain-carrying radicals or reduce the number of initiation processes to lower the overall rate of autoxidation. Vitamin E, 3-carotene, selenium, glutathione, and polyphenols are the most studied dietary antioxidants as a potential pharmacological strategy to reduce ROS levels and combat disorders caused by oxidative stress. However, there have been no conclusive results from clinical trials on the benefits of α-tocopherol, selenium, or (3-carotene supplementation) for lowering

cancer risks [13]. One of the most likely explanations for these surprising outcomes is that most antioxidants fail to reach biologically relevant targets. Nanoantioxidants are a unique possibility in this context since they may be tailored to have more extended stability than small molecules, quickly escape metabolic clearance, and target specific locations [13].

Nanomaterials can either act as passive delivery systems for small-molecule antioxidants or have their built-in antioxidant capabilities. Therefore, a critical step in creating new nano-antioxidants is to conduct in vitro chemical tests to assess their antioxidative activity.

Different forms of antioxidants have been discovered as a result of recent research trends. Nano-antioxidants have been made with a variety of materials until now (Figure 2). Nanoparticles of metal and metal oxide, CNTs and other carbonacious nanomaterials, and polymer-loaded antioxidant nanoparticles have all been reported to possess antioxidant capabilities. Different forms of antioxidants have been discovered as a result of recent research trends. Biodegradable nanoparticles have recently received a great deal of attention due to their high encapsulation efficiency, controlled release properties, and a lack of toxicity, among other factors. As a carrier for various forms of nano-antioxidants throughout history, biodegradable polymers have proven to be the most essential materials to be explored [37,38]. Metal-based nanoparticles with high antioxidant activity are being used to develop new antioxidant materials.

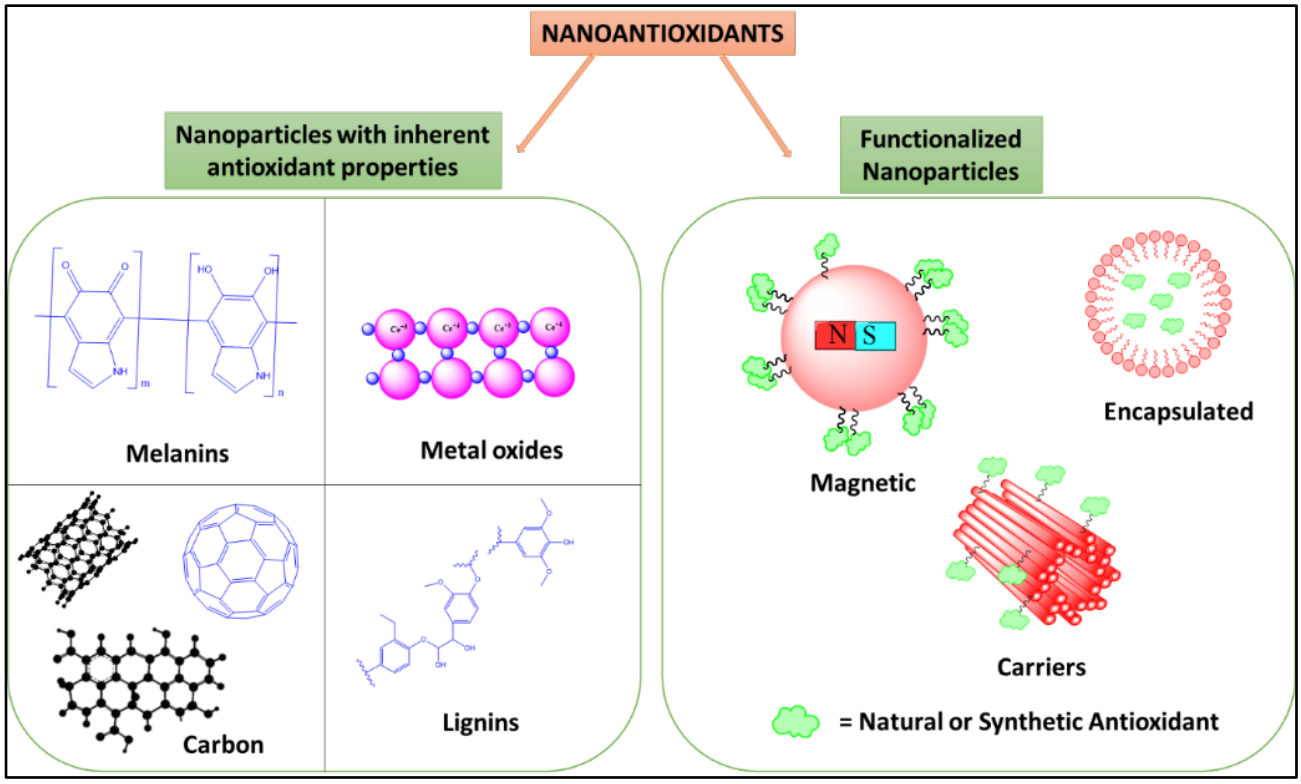

Figure 2. Nanoparticles with Antioxidant Activity: "Nanoantioxidants".

The antioxidant enzymes GSH-Px and thioredoxin reductase use selenium in selenoproteins to regulate hemostasis and the redox system [39]. Furthermore, as documented in several studies, selenium nanoparticles activate selenoproteins and display antioxidant activity in both in vivo and in vitro environments [40]. When administered to rats, nanoselenium has been found to significantly diminish nicotine-induced nephrotoxicity by inhibiting the production of reactive oxygen species and inflammation. This impact has been attributed to the small size of nanoselenium, which has a greater surface-to-volume ratio and, as a result, has better bioavailability than larger particles [41].

A dose-dependent antioxidant activity has been demonstrated for ZnO nanoparticles produced from Polygala tenuifolia root extracts [42]. Antibacterial and anticancer characteristics of silver nanoparticles have made them popular for medical applications. They are used in a variety of applications. The use of plant-based silver nanoparticles, on the other hand, has the advantage of having free radical scavenging action, which is becoming increasingly important in the treatment of oxidative stress-mediated toxicities [43].

Additionally, carbon-based nanoparticles have the potential to perform a radical cleaning up activity. Carbon nanotubes, for example, have antioxidant properties due to their strong affinity for electrons [44]. Specifically, single-walled carbon nanotubes exhibit significant antioxidant effects in the oxygen radical absorbance capacity assay, which has been validated [45].

A variety of nanoparticles coated with antioxidant CNTs and metal or metal-oxide nanoparticles have antioxidative properties [36]. Nano-oxidant synthesis has used various preparation strategies over the last few decades, including solvent/emulsion drying, solvent displacement, nanoprecipitation, templating, and solvent displacement methods [36].

Due to their intrinsic physicochemical features, reactive nitrogen and oxygen species can be cleaned up by using oxide nanoparticles, which mimic the antioxidant molecule [46]. There has been a great deal of interest in the biomedical field for cerium oxide nanoparticles (CONPs) because of their multi-enzymatic ROS scavenging abilities [47]. In addition to coexisting in both oxidation states, these CONPs exhibit a reduction potential of 1.52 V and can flip between both oxidation states [48]. However, Cerium dioxide in the form of a bulk crystal consists of Ce^{4+}, whereas when it is reduced to nano-size, it considerably increases the relative proportion of Ce^{3+}, resulting in improved catalytic activities. After three weeks of intravenous administration, researchers found that nanoceria dramatically reduced lipoperoxidation, demonstrating that CONPs effectively treat oxidative stress in an in vivo test on mice conducted by Hirst et al. (2013) [49]. Caputo et al. (2015) compared the antioxidant capacity of CONPs with NAC (*N*-acetyl-cysteine) and Trolox (soluble analogues of vitamin E) in a study [50].

Additionally, liposomes are used to deliver antioxidants to their intended areas. Since these liposomes are both amphiphilic and biocompatible, they can hold a variety of chemicals, including antioxidant enzymes that are both water-soluble and water insoluble [51]. Chitosan is the most commonly used substance to make nanoparticles, whether as a standalone substance or in combination with another [52]. Chitosan has mucoadhesive characteristics, rendering it superior for delivering drugs to mucosal surfaces, including the intestinal and nasal epithelium [53]. It has been found that curcumin coated with chitosan, which protects it from free radicals, is more effective in scavenging free radicals than curcumin alone [54]. By adjusting the pH and oxidative stress levels of inflamed tissues, Pu et al. (2014) found that curcumin-based nanocarriers can encapsulate curcumin antioxidant molecules and regulate their release, which in turn increases the generation of RNS/ROS by lipopolysaccharide-stimulated macrophages [55].

4. Classification of Antioxidant Action

4.1. Preventive Antioxidants

Preventive antioxidants work by lowering the rate of initiation [56]. This is a heterogeneous class of compounds that comprise scavengers [57], metal chelators [58], agents capable of degrading hydroperoxide [59], and both smaller molecules and enzymes such as superoxide dismutase (SOD) and glutathione peroxidase (GPX) or their analogs [60].

4.2. Chain-Breaking Antioxidants

An antioxidant (AH) and a peroxyl radical can create a hydroperoxide and a radical of the antioxidant (A•), which also trap a second ROO• and results in the production of non-radical end products if a formal H-atom transfer occurs between them [10]. Antioxidants that break chains are destroyed during the reaction. Therefore, they function stoichiometrically when regeneration mechanisms are absent. In this context, it is essential

to keep in mind that chain-breaking antioxidants exclusively react with peroxyl radicals, but the interactions with other radical species produced during autoxidation are of lesser importance. Because R• interacts so quickly with oxygen, an antioxidant's chances of catching it are minimal to none. With regard to the OH- and RO-initiating radicals, these radicals have extremely high reactivity towards all organic molecules, making it impossible for the antioxidant to compete with these reactions because the antioxidant, which, by definition, is only found in trace quantities, is unable to compete with these reactions [56]. Figure 3 shows characteristics of a molecule (AH) that makes it a chain-breaking antioxidant.

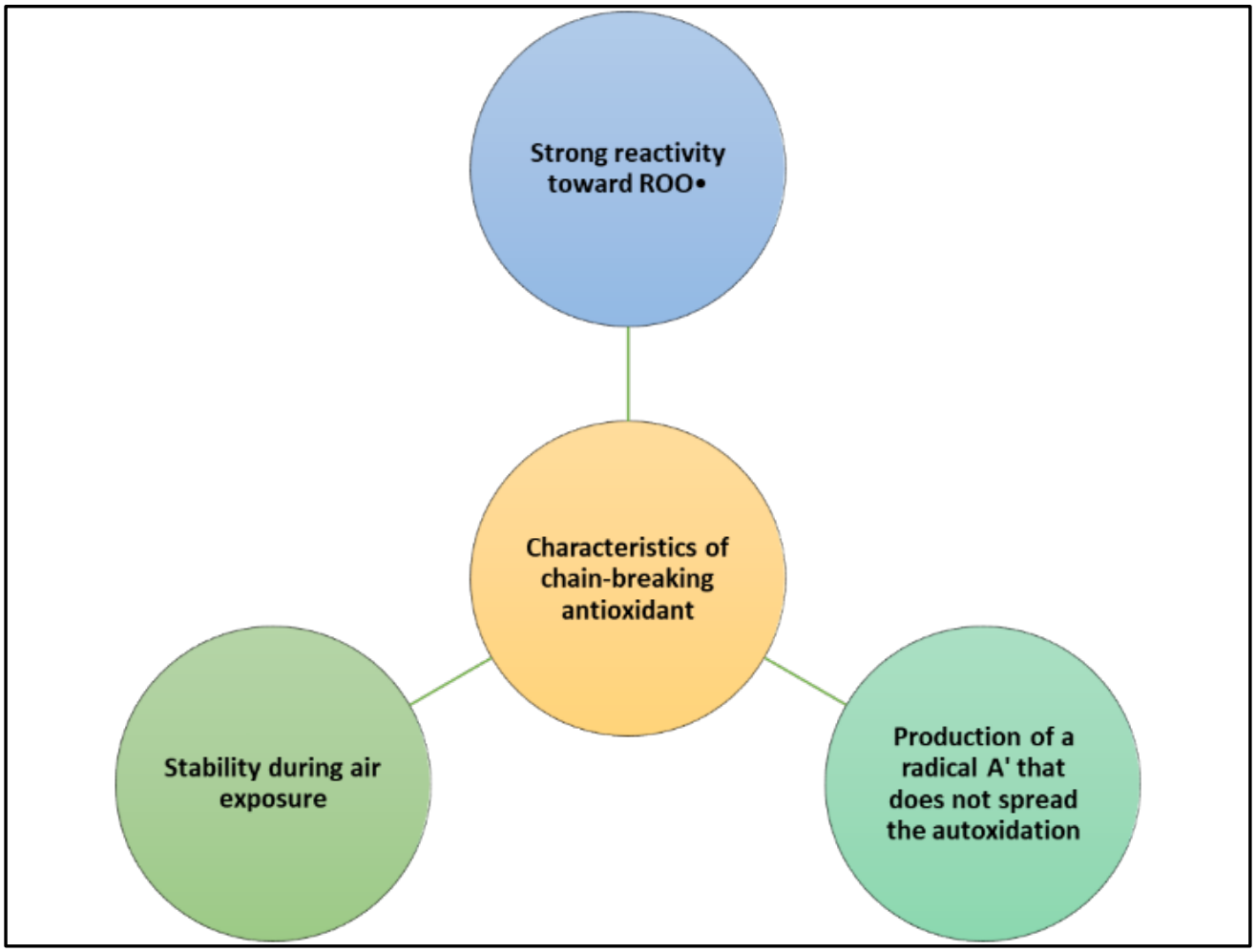

Figure 3. Characteristics of a chain-breaking antioxidant.

The most effective examples of this family of antioxidants may be phenols (such as resveratrol) and ascorbate (vitamin C), whereas synthetic equivalents include aromatic amines, BHT, BHA, and the nitroxide compound. Figure 4 despicts system for classifying nanoantioxidants based on structural and mode of action.

Besides direct antioxidants, substances that do not themselves have antioxidant activity but can promote and enhance the effectiveness of biological systems' endogenous antioxidant defenses are usually classed as indirect antioxidants.

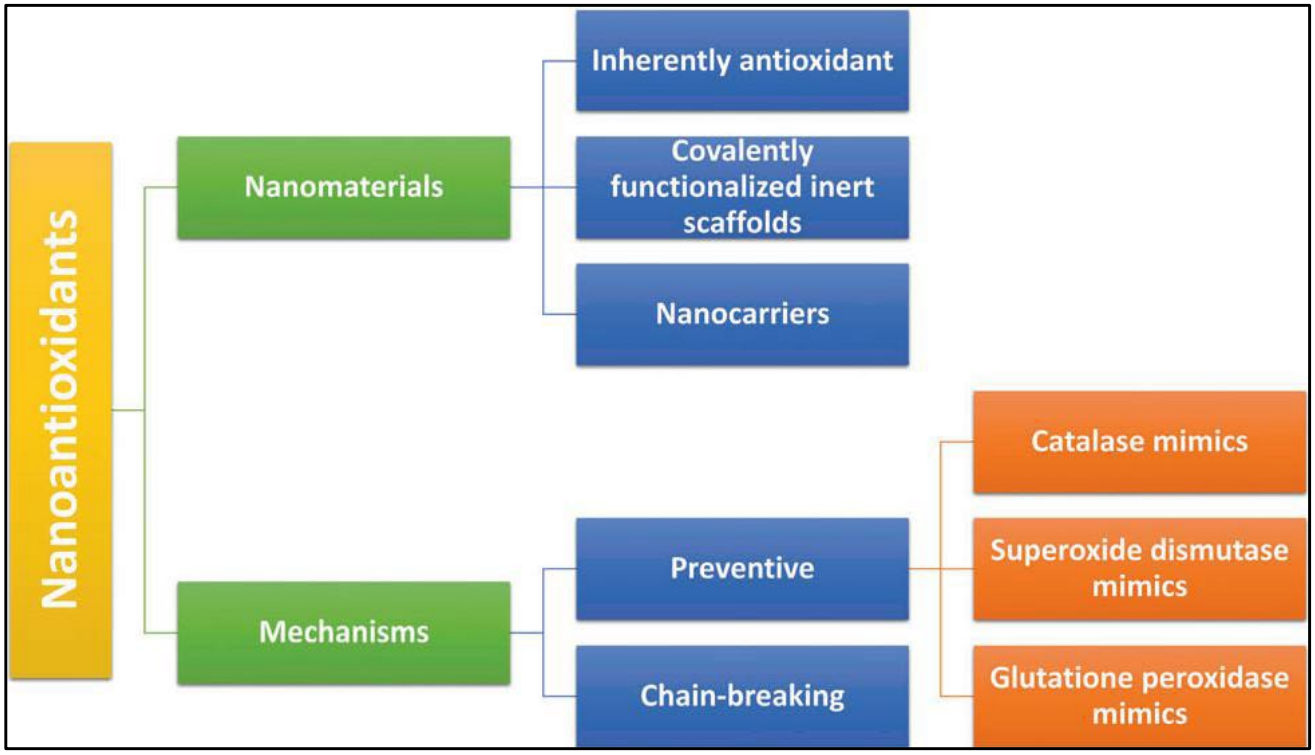

Figure 4. System for Classifying Nanoantioxidants Based on Structural and Mode of Action.

5. Nanomaterials with Inherent Antioxidant Capabilities

There are variety of nanomaterials with inherent antioxidant capabilities that do not need to be functionalized with antioxidants; instead, their properties come from the surface features of the nanomaterials. Nanoparticles of inorganic metal are the most common type of such materials. On the other hand, organic nanoparticles are becoming increasingly essential, with a few examples below.

Metals such as silver, gold, platinum, and palladium, as well as metal oxide, are examples that can be found throughout the literature [46,61–66]. NPs act as catalase substitutes, but only at neutral or basic pH levels; at acidic pH values, on the other hand, a pro-oxidant impact starts to develop. The production of HO• radicals causes the prooxidant activity of the nanoparticle as a result of the occurrence of the Fenton reaction on the nanoparticle's surface [67].

$$H_2O_2 + e^- \rightarrow HO\bullet + HO^- \quad (1)$$

Colorimetric glucose or DNA sensing uses this reaction for nanomaterials with peroxidase activity [68]. These nanoantioxidants have a two-sided activity, restricting their effectiveness and providing an exciting opportunity to build pH-responsive redox modulators of the cell's oxidative stress [69].

There is still some debate about the mechanisms that underlie catalase activities in cerium oxide nanoparticles, although it appears that very stable surface peroxo/hydroperoxo species are at play [70]. The degree of oxidation of a nanomaterial may have an effect on its catalytic activity. Highly persistent surface peroxo/hydroperoxo species are implicated in the case of cerium oxide nanoparticles in catalase activity; however, the processes behind catalase activity are still a mystery [70,71]. The degree of oxidation of a nanomaterial determines whether or not it exhibits CAT-like behavior [70].

The material with a higher Mn^{3+}/Mn^{2+} ratio, generated by oxidation with $NaIO_4$, showed improved CAT activities in comparison to materials with a lower Mn^{3+}/Mn^{2} ratio in Mn_3O_4 NPs with flower-like morphology ("nanoflowers") [63].

When it comes to Co_3O_4 nanomaterials, nanoplates were the most common, followed by nanorods and nanocubes. For three distinct Co_3O_4 nanomaterials, the amount of CAT-like activity reduced inversely due to their redox potential. In order to explain this result, it was found that the rate-determining step in the CAT catalytic cycles is the cleavage of the O-O bond that occurs during the nanomaterial's reduction of H_2O_2 [72]. In low pH environments, switching from Fenton chemistry to catalase activity is controlled by the pH of the environment (high pH). A possible explanation for this unusual behavior is the pH dependency of the interaction between HO• and HOOH (Equation (2)), which is predicted to be aided by the partial deprotonation of H_2O_2 (pKa = 11.6; see Equation (2)) [67].

$$H_2O_2 + HO\bullet \rightarrow O_2\bullet- + H_2O + H^+ \quad (2)$$

Changes in pH in gold nanorods, core–shell gold–platinum nanorods, and gold–palladium nanorods are thought to result from the metal surface absorbing H+ or HO^- [73].

Unlike catalase activity, which has been found in many oxides, glutathione peroxidase (GPX) activity has only been found in vanadium [74] and manganese [63] oxides (see Table 1).

Table 1. Mechanisms of Action and Chemical Assays for Evaluating the Activity of Antioxidant Nanoparticles.

Nanoantioxidant	Assay	Ref.
	Catalase mimic (pH > 7)	
PVDF coated Au NPs	Spectrophotometric H_2O_2 decrease Oxygen evolution	[75]
-	(EPR)	-
Cerium Oxide Nanoparticles	Spectrophotometric H_2O_2 disappearance Oxygen evolution	[62]
Cobalt Oxide nanoparticles	Clark electrod Oxygen evolution from H_2O_2	[61]
Gold Plantium Nanorods; Core shell	H_2O_2 decrease (spectrophotometric), O_2 evolution	[73]
Gold Nanorods; Core shell	(Clark electrode)	-
Gold Palladium Nanorods	-	-
Apoferritin-coated Pt NPs	H_2O_2 consumption, evolution of O_2 bubbles	[76]
Platinium Nanopowder	O_2 detection by EPR line broadening	[77]
Trimanganese tetraoxide nanoflowers	Spectrophotometric H_2O_2 decrease	[63]
Dimercaptosuccinic acid coated Fe_3O_4 NPs	O_2 formation (Clark electrode)	[64]
Eumelanin-silica NPs	Ferrous Xylenol orange assay decrease in H_2O_2 concentration.	[65]
	GPX mimic	
Vanadium Nanowires	Change in coenzyme NADPH absorbance at 340 nm in a glutathione reductase coupled assay (spectrophotometric)	[74]
GO supported Selenium nanoparticles	Spectrophotometric Glutathione reductase coupled assay	[78]
Trimanganese tetraoxide nanoflowers	Spectrophotometric Glutathione reductase coupled assay	[63]
	Chain-breaking	
Polyacrylic acid (PAA)- protected Pt NPs	DPPH (spectrophotometric), linoleic acid peroxidation, and AAPH-derived radical scavenging are inhibited (EPR detection)	[79]
Oleic acid coated cerium oxide NPs	Radical scavenging from AAPH (ORAC assay)	[80]
ZrO_2 NPs	DPPH (spectrophotometric)	[81]
PEG coated melanin NPs	DPPH (spectrophotometric and EPR)	[82]
	SOD mimic	
PEG-coated melanin NPs	5-Diethoxyphosphoryl-5-Methyl-1-Pyrroline N Oxide Reaction with $O_2^{\bullet-}$ and EPR Study of O_2 Evolution (Clark electrode)	[83]
PVDF coated Gold nanoparticles	spin-trap with EPR detection and xanthine/xanthine oxidase	[75]
Glycine-coated $Cu(OH)_2$ NPs	Iodonitrotetrazolium chloride and Xanthine/Xanthine Oxidase (spectrophotometric)	[84]
PEG coated MnO NPs	cytochrome C and xanthine/xanthine oxidase (spectrophotometric)	[85]
PEG-coated carbon nanoclusters	EPR analysis of the O_2 reaction	[86]
Pd nanocrystals	spin-trap with EPR detection and xanthine/xanthine oxidase	[87]
Platinium Nanopwder	Xanthine/Xanthine Oxidase with an EPR-detection spin-trap	[77]

Table 1. *Cont.*

Nanoantioxidant	Assay	Ref.
Trimanganese tetraoxide nanoflowers	Iodonitrotetrazolium chloride and Xanthine/Xanthine Oxidase (spectrophotometric)	[63]
Dimercapto succinic acid coated Co_3O_4 NPs	spin-trap with EPR detection and xanthine/xanthine oxidase	[66]
MWCNTs	cytochrome C and xanthine/xanthine oxidase (spectrophotometric)	[88]
Functionalized fullerene	Reaction with $^1O_2$ (spectrophotometric)	[88]

GPX Mimics: Until now, GPX activity has only been identified in vanadium [74] and manganese [63] oxides, in contrast to the ubiquitous catalase activity present in many metals and metal oxides.

Glutathione (GSH) is sacrificed when V_2O_5 nanowires are used in physiological settings to mediate the H_2O_2 to H_2O reduction because of V_2O_5's unique ability instead of producing polar peroxido species in comparison to HO• radicals (Equation (3)) [85].

$$2\ GSH + H_2O_2 —* GS\text{-}SG + 2\ H_2O \quad (3)$$

Compounds with heavy chalcogen atoms, such as selenium and tellurium, are more likely to exhibit GPX-like activity. GPX-like activity was observed in graphene oxide-supported selenium nanoparticles, likely attributable to their high surface area and high rate of reaction [78].

SOD Mimics: Due to the fact that although the superoxide radical is a member of the peroxyl radical family, its unique chemistry distinguishes it from other radicals such as the alkylperoxyl radical, and antioxidants that trap the radical must be taken into consideration independently.

As the conjugated acid (HOO•) has a pKa of 4.5, O_2• is the more common form of superoxide. Superoxide, in its protonated (neutral, HOO•) form, exhibits dualistic behaviour, as it can either abstract or donate a H atom to form HOOH and O_2, respectively [89] when the superoxide is protonated (in the neutral state). On the other hand, deprotonated O_2• has the majority of the properties of a reducing agent.

A diverse variety of nanomaterials, including noble metals (gold, platinum, and palladium) as well as metal oxides (cerium, cobalt, and manganese oxides), carbon clusters (carbon nanotubes, and fullerenes), and melanin, have been shown to have SOD-like activity.

SOD- and GPX-like activity were concurrently achieved by a "multi-nanozyme" based on MnO_2 nano-nanoparticles deposited on V_2O_5 nanowires by polydopamine [90].

Instead of chain-breaking antioxidant activities, a given nanomaterial must be capable of quenching alkylperoxyl radicals by converting them to hydroperoxides [79–82]. Alkylperoxyl radicals (ROO•, where R is an alkyl, such as lipids) can be quenched by either an H-atom donating antioxidant AH or an electron-donating antioxidant (D) and a protic solvent SolvH, as shown in Figure 5.

In the same manner, nanoparticles with cleavable O-H groups, such as lignin and melanin, behave. The antioxidant activity of lignin nanoparticles has been observed in apolar polymers such as natural rubber and methanol, for example [91].

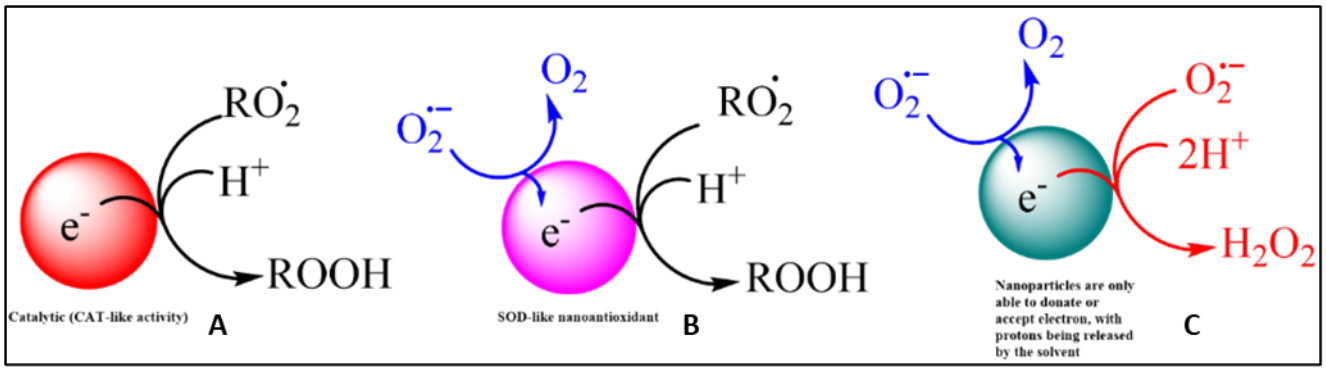

Figure 5. Comparisons and contrasts between sacrificial (**A**), catalytic, and (**B**) SOD-like nanoantioxidants (**C**). Nanoparticles as the electron donor or accepter.

6. Antioxidant Functionalized Nanoparticles

Bioactive substances such as terpenoids, alkaloids, polyphenols, and phenolic acids have been found in bacteria, algae, fungi, lichens, and plants. These bioactive chemicals could lead to improved results. The antioxidative properties of these compounds have been demonstrated to decrease and stabilize metallicions.

Table 2 presents the various types of antioxidant nanoparticles with functionalized antioxidants from different biological sources.

Table 2. Nanoparticles with Antioxidant Functionalization.

Types of Nanoparticles	Biological Extract	Morphology	Size	Antioxidant Activity	Ref.
Iron	*Amaranthus dubiusleaf* extract	Spherical	43–220 nm	DPPH	[92]
Iron	*Amaranthus spinosus* leaf extract	Spherical	-	DPPH	[93]
Iron	*Asphodelus aestivus Brot.* Extract	Spherical	20–25 nm	DPPH, ABTS	[94]
Iron oxide	tea-pruning waste	Spherical	20–35 nm	DPPH	[95]
Iron oxide	*Phoenix dactylifera* L.	Spherical	2–30 nm	DPPH	[96]
Iron oxide	curcumin	Spherical	-	DPPH	[97]
Iron oxide	*Coriandrum sativum* L. *(cilantro)*	Spherical	-	DPPH	[98]
Iron oxide	*Blumea eriantha DC*	spherical and irregular shapes	10–60	DPPH, ABTS, Hydrogen peroxide scavenging activity and Reducing power assay activity	[99]
Nickel Oxide	*Stevia rebaudiana* Bertoni leaf extract	Spherical	20–50 nm	DPPH	[100]
Gold	*Lactobacillus kimchicus* DCY51T biomass	Spherical	13 nm	DPPH	[101]
Silver	*Streptomyces griseorubens AU2* cell free supernatant	Spherical	5–20 nm	DPPH	[102]
Gold	*Enterococcus* species cell free extract	Sphere	8–50 nm	DPPH	[103]
Gold	*Snail slime*	Spherical, hexagonal, trapezoidal, and rod shape	14 ± 6 nm	DPPH, ABTS	[104]
Gold	*Achillea biebersteinii*	Spherical	2–30 nm	DPPH	[105]
Gold	*Centaurea behen*	Spherical	50 nm	DPPH	[106]

Table 2. *Cont.*

Types of Nanoparticles	Biological Extract	Morphology	Size	Antioxidant Activity	Ref.
Types of Nanoparticles	Biological Extract	Morphology	Size	Antioxidant Activity	Ref.
Gold	*Cannabis sativa* L.	Spherical	-	DPPH	[107]
Gold	*Curcumae Kwangsiensis folium*	Spherical	8–25 nm	DPPH	[108]
Gold	*Kaempferia parviflora rhizome*	Spherical	20–60 nm	DPPH	[109]
Gold	*Atriplex halimus and Chenopodium amperosidies*	Spherical	2–10 nm	DPPH	[110]
Gold	*Brassica rapa var. pekinensis*	Spherical	25 nm	DPPH, ABTS	[111]
Gold	*Sambucus wightiana*	trigonal, cubic, hexagonal, and polygonal	15.96 nm	DPPH	[112]
Gold	*Curcuma pseudomontana*	Spherical	20 nm	DPPH, RP, H_2O_2, NO and Cupric ion reducing antioxidant capacity (CUPRAC) assay	[113]
Gold	Quercetin	Spherical	100 nm	ABTS, DPPH and NO assay	[114]
Gold and Silver	*Escherichia coli* cell *protein*	Triangular, circular, hexagonal (AuNPs), Sphere (AgNPs)	10–100 nm (AuNPs), 10–50 nm (AgNPs)	EC75	[115]
Gold and Silver	*Crassocephalum rubens*	spherical	15–25 nm for AgNPs, 10–20 nm for AuNPs	lipid peroxidation and DPPH	[116]
Silver	*Streptomyces griseorubens AU2* cell free supernatant biomass	Sphere	5–50 nm	DPPH	[117]
Silver	*Cuscuta japonica*	oval-spherical	30–50 nm	DPPH	[118]
Silver	*Striga angustifolia*	nanoflakes	106.40 nm	DPPH	[119]
Silver	*Olea europaea*	Spherical	10.47 ± 9.19 nm	DPPH	[120]
Silver	*Galphimia glauca*	Spherical	19–37 nm	DPPH	[121]
Silver	*Cannabis sativa*	Spherical	10–50 nm	DPPH	[122]
Silver	polyphenol-rich kiwi peel	Spherical	200–300 nm	ABTS	[123]
Silver	*Tilia cordata*	Spherical	50 nm	FRAP	[124]
Silver	*Cissampelous pairera*	Spherical	60 nm to 118 nm	DPPH	[125]
Silver	*Rhus javanica*, *Rumex hastatus*, *and Callistemon viminalis*	-	1–100 nm	DPPH, ABTS	[126]
Silver	*Annona muricata*	Spherical	35 nm	DPPH, ABTS	[127]
Selenium	*Streptomycesminutiscleroticus RT M10A62* biomass	Spherical	10–250 nm	DPPH	[128]
Selenium	*Pantoea agglomerans* UC-32	Spherical	100 nm	High antioxidant activity in human umbilical	[129]
Selenium	*Spirulina platensis*	Spherical	32–86 nm	DPPH, ABTS	[130]
Selenium	*Morinda citrifolia*	Spherical	12–160 nm	DPPH	[131]
-	*Polygonatum sibiricum* polysaccharide	Spherical	105 nm	DPPH, ABTS	[132]
Gold and Silver	*Gordonia amicalis* HS-11 cell free supernatant	Grain	5–25 nm	CFS synthesized AgNPs and AuNPs	[133]
Silver	*Streptomyces violaceus MM72 exopolysaccharides*	-	30 nm	DPPH	[134]
Silver doped zinc oxide	*Morinda citrifolia*	Spherical	-	DPPH	[135]

Table 2. *Cont.*

Types of Nanoparticles	Biological Extract	Morphology	Size	Antioxidant Activity	Ref.
Zinc Oxide	*Pichia kudriavzevii* cell free extract	Hexagonal	10–61 nm	DPPH	[136]
Silver	*Pestalotiopsis microspora* filtrate	Sphere	2–10 nm	-	[137]
Gold	*Cladosporium cladosporioides* filtrate	Cubic	100 nm	DPPH	[138]
Silver	*Cladosporium*	Sphere	100 nm	−DPPH	[139]
Copper	Cissus arnotiana	Sphere	60–90 nm	DPPH	-
Copper oxide	*Sargassum longifolium*	Sphere	40 and 60 nm	DPPH	[140]
Copper	*Blumea balsamifera*	Sphere	30–55 nm	DPPH	[141]
Copper	*Borreria hispida*	Sphere	121 ± 37 nm	DPPH	[142]
Copper	*Fragaria ananassa*	Sphere	10–30 nm	DPPH	[143]
Copper	*Persea americana*	Sphere	42–90 nm	DPPH	[144]
Copper	*Falcaria vulgaris*	Sphere	20–25 nm	DPPH	[145]
Copper Oxide	*Cissus arnotiana* leaf extract	Spherical	80–90 nm	DPPH	[146]

7. Inert Scaffold with Antioxidant Functionalities

About fifteen years ago, researchers Liu and coworkers coupled Trolox, a synthetic a-tocopherol analogue, or salvianic acid [147] to gold nanoparticles encapsulated with thiol to demonstrate the efficacy of antioxidants grafted onto a nanomaterial [148].

The radical trapping ability of Au@Trolox was shown to be superior to that of Trolox itself, indicating that this technique will not decrease the antioxidant characteristics of the compound. The food-grade antioxidants caffeic acid [149] and gallic acid [150] were covalently attached to SiO_2 NPs of different sizes by using aminopropyl-triethoxysilane (APTES) as the linker. Due to the fact that silica is regarded biochemically inert, it is used as a flowing aid in the production of nutraceutical and pharmaceutical products. Gallic acid coupled to SiO_2 demonstrated excellent radical trapping capabilities and was capable of being reused without losing its activity. For the first time, however, the authors demonstrated that, following the reaction with free radicals, these nanoparticles exhibited considerable agglomeration, which they attributed to the presence of cross coupling between free radicals on the surface [151].

Similarly, the phenolic antioxidants, Trolox or curcumin, were covalently linked to graphite-coated cobalt magnetic nanoparticles using a similar technique [152]. Alternatively, on the outside of halloysite nanotubes [153,154]. The tubular hollow structure of inorganic alumino-silicate clay halloysite (HNTs) (up to 800 nm in length and 80 nm in external diameter) is made up of siloxane groups (moderate acidity) on the outer surface and aluminol (basicity) on the inner surface, allowing for a variable selectivity of molecules grafted onto either surface. Halloysite nanotubes were employed to covalently attach curcumin to the surface using a disulfide bridge, allowing for thiol-dependent release while preserving curcumin's free radical trapping capabilities [153]. To create a bi-functional nanoantioxidant, a synthetic tocopherol (Trolox) was grafted onto the HNT's external surface using APTES as a linker (HNT-Trolox). This was combined with quercetin, a naturally occurring polyphenolic antioxidant, to create a hybrid nanoantioxidant [154] (Figure 6). With regards to the model's substrate peroxidation, this material demonstrated good antioxidant capabilities due to Trolox acting as the primary radical quencher and quercetin serving as a co-antioxidant.

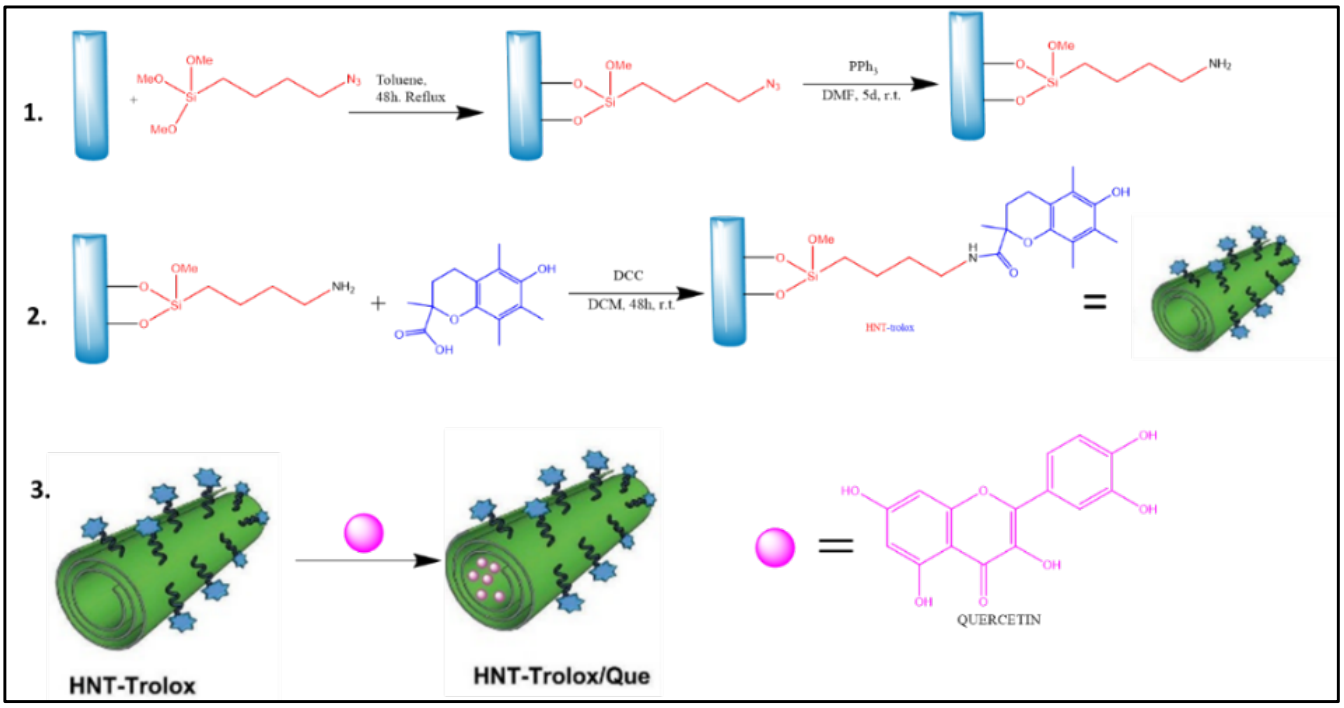

Figure 6. Trolox grafting procedure on halloysite nanotubes; the incorporation of the antioxidant quercetin in the nanotubes' interior.

Cerium nanoparticles can act as antioxidant enzyme mimics in addition to the scavenging ability of ROS and RNS. Nanoscale physical and chemical properties such as oxygen absorption/release capability and the relative thermodynamic efficacy of redox cycling between cerium nanoparticle surface Ce^{3+} and Ce^{4+} are responsible for this phenomenon [46,155]. Combining CNPs with curcumin in a single formulation may result in increased physiological activities due to curcumin's anticancer properties. Curcumin-loaded nanoceria (CNP-Cur) and dextran-laden nanoceria (Dex-CNP-Cur) were studied in MYCN-amplified and non-amplified cells for their anticancer effects [155]. Antioxidant nanoparticle efficacy testing methods and mechanisms are summarized in Table 3.

Table 3. Antioxidant nanoparticle efficacy testing methods and mechanisms.

Nanomaterial	Antioxidant	Method to Determine Activity	Ref.
Halloysite nanotubes	Curcumin	Pressure sensor method (inhibited autoxidation oxygen consumption), spectrophotometric method (DPPH assay)	[153]
Halloysite nanotubes	Trolox	Pressure sensor method (inhibited autoxidation oxygen consumption), spectrophotometric method (DPPH assay)	[154]
Graphite coated cobalt nanoparticles	Trolox	Pressure sensor method (inhibited autoxidation oxygen consumption)	[152]
Silica	Rutin or Caffeic acid	ORAC	[149]
Gold Nanoparticles	Trolox	DPPH• (EPR detection)	[148]
Gold Nanoparticles	Salvianic acid	DPPH• (EPR detection)	[147]
Silica coated Silver nanoparticles	Gallic acid	DPPH• (spectrophotometric and EPR)	[150]
Silica nanoparticles	Gallic acid	DPPH• (spectrophotometric and EPR)	[151]
Single walled CNTs	BHT	ORAC	[45]
Fullerene	BHT	Inhibited autoxidation, O_2 consumption (pressure sensor)	[156]
Fullerene	Flavonoids	Inhibited autoxidation, O_2 consumption (pressure sensor)	[156]

Table 3. *Cont.*

Nanomaterial	Antioxidant	Method to Determine Activity	Ref.
double hydroxide NPs	SOD	Xanthine and xanthine oxidase, nitroblue tetrazolium (spectrophotometric)	[157]
Cerium nanoparticles	SOD	Xanthine and xanthine oxidase, hydrosoluble tetrazolium salt (spectrophotometric)	[158]
Cerium nanoparticles	CAT	Amplex red assay	[158]
MSN	Surface functionalization; morin(2′,3,4′,5,7-pentahydroxyflavone)	An effective scavenger of HO• and quencher for $^1O_2$	[159]
MSN	Poly Tannic acid; crossing linking	Trolox equivalency antioxidant capacity (TEAC)	[160]
MSN	Caffeic acid and Rutin; covalent grafting	Functions of antiradicals, cell toxicity alleviation, and oxidative stress prevention	[149]
MSN	3,5-di-tert-butyl-4-hydroxybenzoic acid; grafting	Oxidation induction time (OIT) determined by DSC	[161]
MSN	Curcumin; loaded	Quantification of cellular ROS	[162]
Polyethylene glycol coated AuNPs	Salvianic acid; Surface functionalization	Thiobarbituric acid reactive substance (TBARS)	[147]
AuNPs	Trolox; Self-assembly	DPPH(spectrophotometric) DPPH• radical scavenging assay (spectrophotometric)	[148]
AuNPs	3,6-dihydroxyflavone, lutein and selenium methyl selenocysteine; embedded	Radical scavenging tests using hydroxyl, hydrogen peroxide, nitric oxide, and DPPH (2,2-diphenyl-l-picrylhydrazyl)	[23]
AgNPs	Coated with Lignin	Human pathogens *S. aureus*, *E. coli*, and *A. niger* are combated, antioxidant assay DPPH (spectrophotometric) and antifungal and antibacterial agent.	[163]
Fe_3O_4NPs	Functionalized with Gallic acid	Superior antibacterial and antifungal activity; antioxidant properties and are magnetically separable	[164]
Fe_2O_3NPs	Coated with Carboxymethyl inulin	Non-toxic to cancer cell lines that have been immortalised.	[165]
Fe_2O_3NPs	Coated with carbon	Potential antioxidant; compatible with peripheral blood mononuclear cells	[166]
Fe_2O_3NPs	Coated with Poly GA	Reduces oxidative stress significantly; biocompatible and bioactive	[167]
Magnetic-silk core-shell nanoparticle	Loaded with Curcumin	Cellular uptake and cytotoxicity in breast cancer cell lines from human breast cancer patients	[168]
Ceria nanoparticles	dextran-coated and loaded with curcumin	inherently anti-cancer	[155]
Ceria nanoparticles	PEG-Phospholipid coated	A less toxic, biocompatible, oxidative stress-reducing, and effective treatment for patients with intracerebral hemorrhage.	[169]
PLGA-PEG	Coated with Curcumin	Neonatal hypoxic-ischemic encephalopathy can be protected by this therapy	[170]
Se-Ag Bimetallic	Gallic acid and Quercetin	Antimicrobial and antioxidant activities	[171]

7.1. Gold Nanoparticles (AuNPs)

Recently, interest in gold nanoparticles (AuNPs) has grown because of their size, shape, and optical properties, which are biocompatible [172]. Gold nanoparticles of various sizes and shapes have found medicinal applications in cancer detection and medicine administration (e.g., Paclitaxel) [172]. Table 2 reveals that antioxidant AuNPs are typically obtained from plant parts such as leaves and fruits and that they are particularly effective

in combating free radicals. Markus et al. (2016) employed an internal membrane-bound technique to identify Kimchi-isolated probiotic strain *Lactobacillus kimchicus* DCY51T and then used this bacteria to produce antioxidant functionalized AuNPs [101]. When exposed to malignant cell types, such as human colorectal adenocarcinoma (HT29) and murine macrophages, AuNPs developed an amino acid capping layer, and the proteins attached to their surface rendered them harmless (RAW264.7). It has been discovered that biologically synthesized gold nanoparticles are superior scavengers of free radicals, notably DPPH, when compared to gold salts. In this study, techniques such as FT-IR and UV-visible spectra HRTEM were used to confirm the identification and usage of an Enterococcus species that lives in food for the synthesis of gold nanoparticles [103]. Extracellular proteins from *Escherichia coli* were employed to create anisotropic gold nanoparticles by Veeraapandian et al. (2012) [115]. When it comes to the size and structure of AuNPs, the amount of protein present has a significant impact. Extracellular proteins operate as a capping agent for nanoparticles, increasing their shelf life and improving their stability. When it comes to the size and structure of AuNPs, the amount of protein present has a significant impact. Extracellular proteins operate as a capping agent for nanoparticles, increasing their shelf life and improving their stability. Manjunath et al. (2017) produced gold nanoparticles using a fungal endophyte, *Cladosporium cladosporioides*, isolated from the seaweed *Sargassum wightii* [138]. The NADPH-dependent reductase enzyme was shown to be responsible for the utilization of phenolic compounds in the reduction of gold metal salts into gold nanoparticles. Using extracts from the mushroom *Inonotus obliquus*, Lee et al. (2015) produced AuNPs without the use of harmful chemicals [173]. Researchers made AuNPs from extracts of *Gracilaria corticate*, which is a marine red alga used as a reducing agent [174]. Sharma et al. (2014) reduced and stabilized AuNPs using the dried biomass of *Lemanea fluviatilis* [175]. Gold nanoparticles were synthesized by Debnath et al. (2016) from dried lichen biomass collected in the Eastern Himalayas at high elevations, without the need of any external stabilization or reducing chemicals [159]. To compare the antioxidant properties of the two gold nanoparticles, those produced from *Acroscyphus sp.* lichen possessed prismatic and multiplied twinned quasi-spherical shapes, while those made from *Sticta* sp. algae only had multiplied twinned quasi-spherical shapes.

DPPH-radical-induced free radical scavenging was investigated in both light and dark settings using a gold nanoparticle (AuNP) attached to cellulose fiber (UKP), which is an unbleached kraft paper [176]. The surface functionalization of AuNPs coated with polyethylene glycol PEG and the antioxidant salvianic acid A (Au@PEG3SA) (Figure 7) was successfully performed and their antioxidant activities were evaluated. Compared to pure salvianic acid, the radical scavenging activity was nine times higher with Au@PEG3SA added to the mix. Studying the radical scavenging activity in vitro and in vivo using stopped-flow analysis, laser scanning confocal microscopic inspection, and the thiobarbituric acid reactive substance assay allowed researchers to better understand how radical scavenging activity works. It has been found that AuNPs with antioxidant functions are more effective at scavenging ROS in living cells and could be employed in such applications [147].

Trolox, a vitamin E analogue, was used to produce functionalized AuNPs (Au@Trolox) via Au-S bonding aided by Trolox's thiol (SH) ligand in combination with AuNPs (Figure 8) [148]. Additionally, the inclusion of AuNPs embedded in 3,6-dihydroxyflavone along with other nutrients such as lutein and selenium methly selenocysteine increased maximum inhibition by 87.13% for the reduction of DPPH, 85.11% for the reduction of OH, and 84.02% for the reduction of NO, with an overall increase in antioxidant activity of 29.53%, 26.61%, 25.45%, and 26.07%, respectively [24].

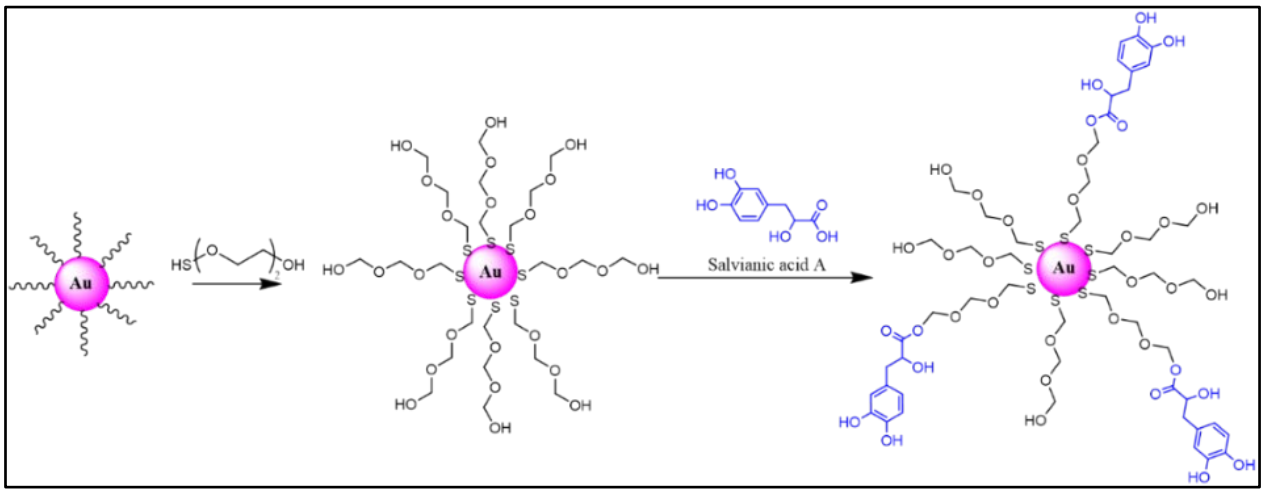

Figure 7. AuNPs (Au@- PEG3SA) Functionalized with Salvianic Acid A.

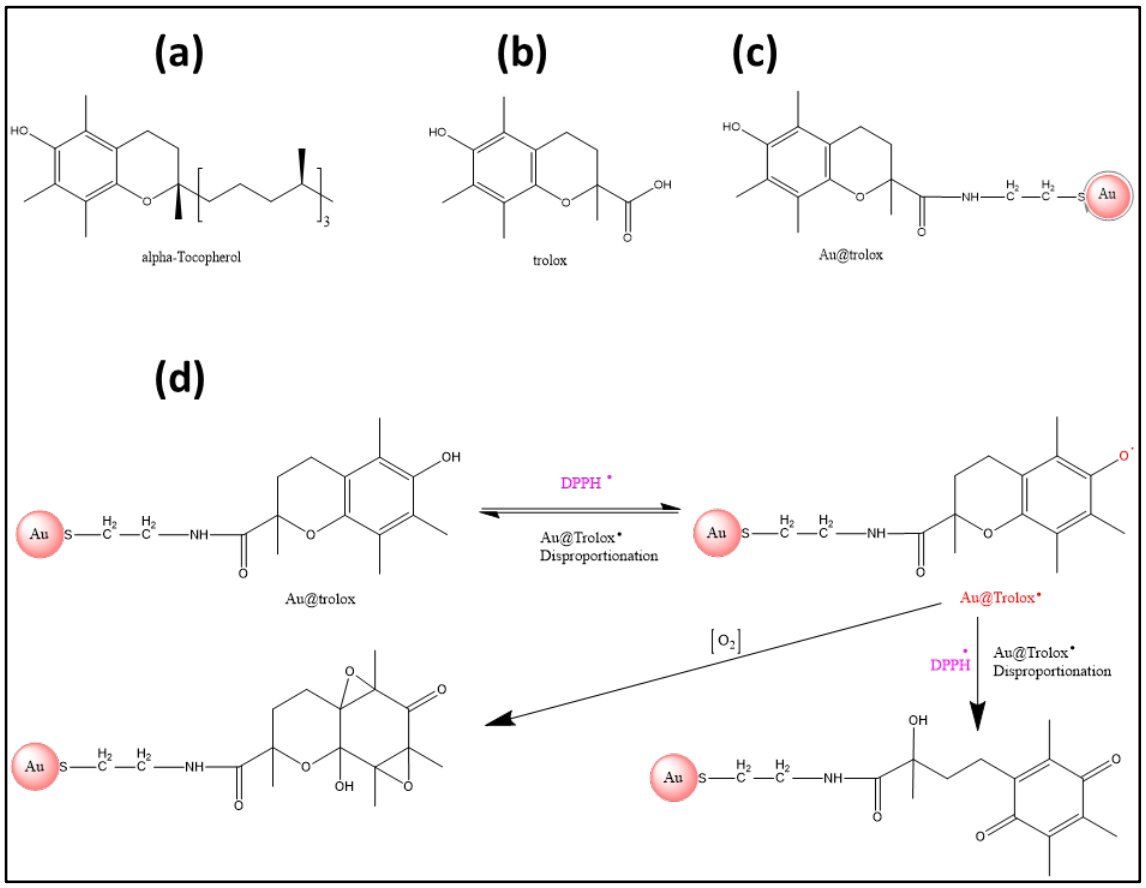

Figure 8. The molecular architecture of (**a**) alpha-tocopherol, (**b**) trolox, (**c**) trolox-functionalized AuNPs, and (**d**) reactions of Au@Trolox with DPPH• radicals.

7.2. SiO_2 Nanoparticles

Due to their mechanical stability, optical and chemical transparency, biocompatibility, and scalability, silica (SiO_2) nanoparticles have numerous applications in chemistry, medicine, pharmaceuticals, and biomedical research [149,161,177]. Nanosized SiO_2 particles can be immobilized with antioxidants to produce high-value hybrid nanocomposites. Natural antioxidants, such as GA-developed nanoantioxidants, were covalently grafted onto the surface of commercially available well-characterized SiO_2NPs (8–30 nm in diam-

eter). The ability of these nano-antioxidants to neutralise DPPH radicals was tested in a single assay (Figure 9). The SiO_2-GA nanoparticles execute quick H-atom transfer (HAT) and secondary/slow radical–radical coupling processes, which are two different types of scavenging reactions. The rapid HAT reactions of all SiO_2NPs can be compared to those of pure GA at stoichiometry ratios of 2 (nfast) [151]. Morin (2′,3, 4′,5,7-pentahydroxyflavone, a flavonoid)-functionalized mesoporous SiO_2NPs (MSN) were also tested for their antioxidant properties as HO• scavengers and O_2 quenchers. On the other hand, the nanoantioxidant composite showed a one order-of-magnitude lower inactivation of O_2 in homogenous fluids and lipid membranes than morin. It was found that the nanoantioxidant composite had a synergistic effect on antioxidant property against HO• that was proportional to morin adsorbed in homogeneous solvents and lipid membranes, compared to morin's one-order-of-magnitude lower inactivation of O_2. Mesoporous poly(tannic acid) (TA) crosslinked SiO_2NPs composites were examined in the same manner for their antioxidant properties, with TA concentrations ranging from 50 mg to 1000 mg and reaction times ranging from 2 to 24 h. Particle sizes varied from 237 to 445 nm as TA concentration and reaction time increased, leading to a decrease in thermal stability of the composite. The highest TA content (1000 mg) and the largest surface area (872 m^2/g) were obtained after 12 and 2 h of reaction, respectively; this material also proved to be the most active antioxidant, with a total phenol content of 140.3 g mL^{-1} GA equivalent and 68 6 mm Trolox (a vitamin E analogue) equivalent [160].

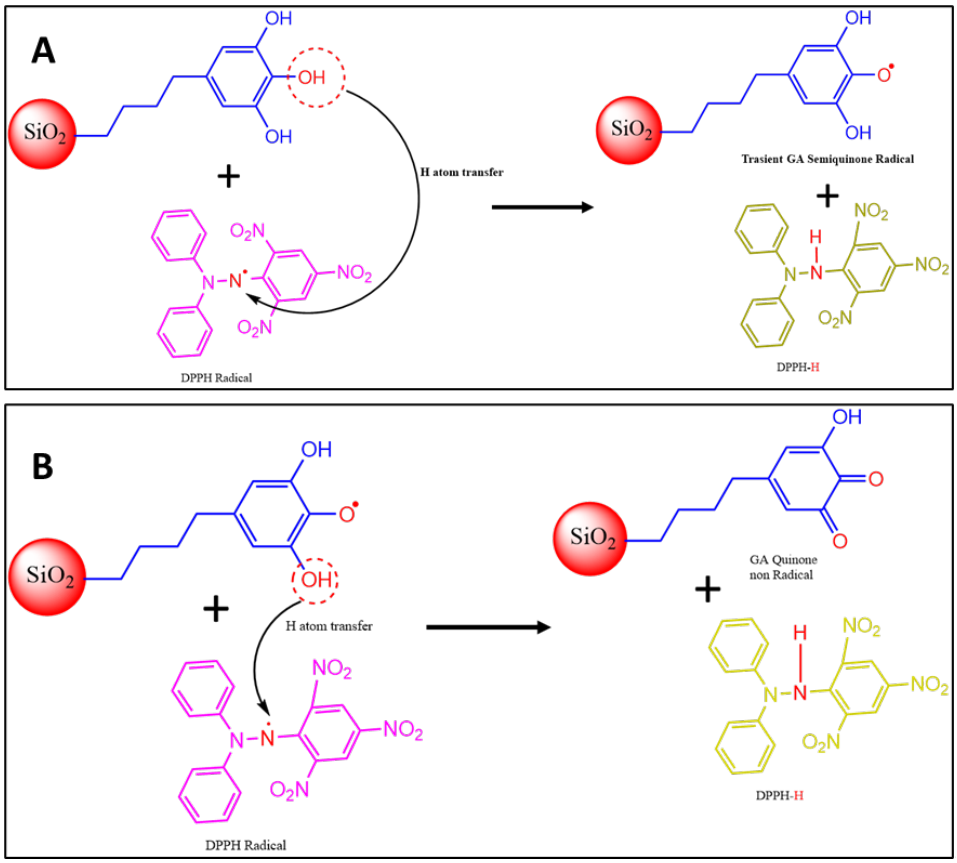

Figure 9. (**A**) Through the H atom transfer (HAT) process from the GA (gallic acid) molecule, one DPPH radical is scavenged by two SiO_2-GA nanoparticles, resulting in the formation of a transitory GA radical. (**B**) HAT from the GA semiquinone results in the formation of a nonradical GA quinone, which SiO_2-GA nanoparticles scavenge.

However, MSN coated with caffeic acid (MSN-CAF) or rutin (quercetin 3-O-[-l-rhamnosyl-(1-6)-d-glucopyranoside]) was examined for its antioxidative stress properties. To prevent ROS formation and biological damage, these catechol antioxidants have ortho-

and meta-hydroxyl groups in their catechol structure that can scavenge or donate hydrogen atoms to free radicals. Caco-2 and HaCaT cell lines were employed to evaluate ROS generation, the activation of the Keap1-Nrf2 pathway, and cell death induced by free and functionalized MSNs in two cellular models (Figure 2). The antiradical test (oxygen radical absorbance capacity (ORAC)) was also used to investigate the antiradical characteristics of free or grafted antioxidant compounds. MSN-RUT had a Trolox equivalent level at 30.3 g/mL, which is much higher than that of naked nanoparticles or amino-propyl functionalized silica nanoparticles ($MSNNH_2$), and its antiradical function was determined to be 3.7 times more than that of MSN. However, MSN coated with caffeic acid (MSN-CAF) or rutin (quercetin 3-O-[-l-rhamnosyl-(1-6)-d-glucopyranoside]) was examined for its antioxidative stress properties. To prevent ROS generation and biological harm, these phenolic antioxidants can scavenge or donate hydrogen atom to free radicals because of the ortho- and meta-hydroxyl groups in the catechol structure they possess. Caco-2 and HaCaT cell lines were employed to evaluate ROS generation, the activation of the Keap1-Nrf2 pathway, and cell death induced by free and functionalized MSNs in two cellular models (Figure 10). The antiradical test (oxygen radical absorbance capacity (ORAC)) was also used to investigate the antiradical characteristics of free or grafted antioxidant compounds. At 30.3 g/mL, Antiradical activity of MSN-RUT was found to be 3.7 times greater than that of MSN-CAF, according to the ORAC test, which found that the Trolox equivalent level of MSN-CAF and MSN-RUT was significantly higher than that for naked nanoparticles or amino-propyl functionalized silica nanoparticles ($MSNNH_2$) [149].

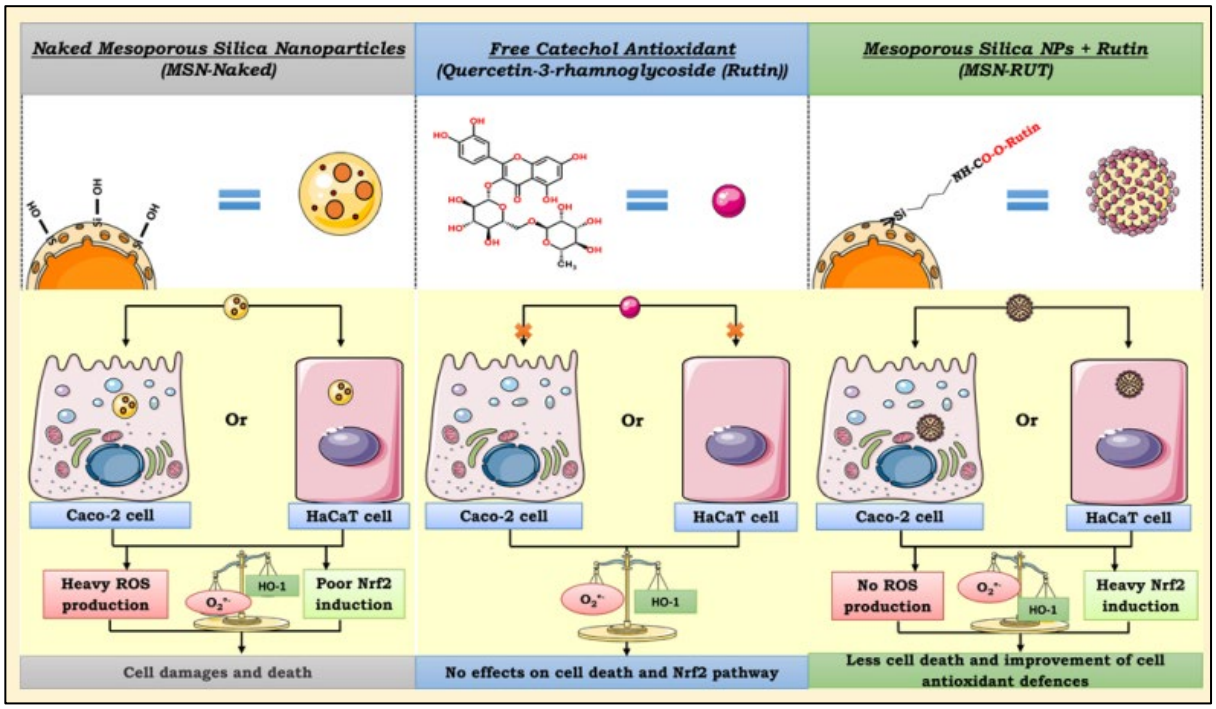

Figure 10. ROS generation, Nrf2 activation, and cell death are all affected by free catechol antioxidant (Rutin), naked MSNs, and MSNs-RUT.

7.3. Silver Nanoparticles (AgNPs)

Silver nanoparticles (AgNPs) have a significantly greater surface area when compared to chemically identical particles, which is due to their outstanding biochemical and catalytic activity [172]. Colloidal silver nanoparticles are agglomerated to create oligomeric clusters, which are then stabilized in order to make AgNPs [172]. It is necessary to use biological catalysts (enzymes) in order to reduce the Ag+ ions, and various plant extracts can be used to create AgNPs with various antioxidant properties. It is necessary to use biological catalysts (enzymes) in order to reduce Ag^+ ions, and various plant extracts can be used

to create AgNPs with various antioxidant properties, as shown in Table 3. Patra et al. (2016) synthesized AgNPs at room temperature under light-exposed conditions using the aqueous watermelon rind component. Silver nanoparticles with potential antioxidant capabilities have been discovered in actinobacteria, and whole-cell biomass and cell free extract of *Streptomyces naganishii* MA7 and *Streptomyces griseorubens* AU2 have been used to create silver nanoparticles with potential antioxidant characteristics [102,117]. Antioxidant-functionalized AgNPs have been synthesized using fungal species such as *Aspergillus versicolor* ENT7, *Cladosporium cladosporioides*, and *Pestalotiopsis microspore* [139,141,148]. Researchers have also discovered that *Ganoderma lucidium* is an important plant source of antioxidant-functionalized AgNPs [178–180]. Venkatesan et al. (2016) synthesized silver nanoparticles using *Ecklonia cava* extracts [181]. *Ecklonia cava* is a marine alga that has been identified as a source of phenolic compounds capable of acting as capping and reducing agents. AgNPs were synthesized using extracts of *Parmeliopsis ambigua*, *Punctelia subrudecta*, *Evernia mesomorpha*, and *Xanthoparmelia plitti* [182]. AgNPs produced from *Clerodendrum phlomidis* leaf extracts have a ferric-reducing potential of 1.63 AU, which is higher than the leaves extract alone [183]. The AgNPs produced from *Clerodendrum phlomidis* leaves had a higher scavenging activity (55.86 g/mL) than the extract (which had a higher IC50 value of 1920 g/mL). The DPPH radical scavenging activity of AgNPs was likewise discovered to be dose-dependent, with the highest inhibition (85.74 percent) being higher than that of the extract alone. AgNPs had a lower IC50 value (9.12 g/mL) than the extract (388.4 g/mL) and standard ferulic acid (182.8 g/mL), showing that they had good antioxidant properties. Das and colleagues discovered that AgNPs produced from *Morus alba* leaves extract improved DPPH scavenging activity to 47.81 percent, compared to 56 percent for conventional ascorbic acid at the same dose, in a study published in 2019. AgNPs mediated by plant extracts, on the other hand, demonstrated 95.08 percent ABTS+ scavenging activity, which is equivalent to the 95.51 percent at 100 g/mL reported for the BTH standard, showing that they have a high scavenging capacity. AgNPs scavenged 64.04 percent of nitric oxide at 100 g/mL, compared to 45.72 percent and 88.62 percent for plant extracts and gallic acid standards, respectively. On the other hand, when applied at a 100g/mL concentration, AgNPs demonstrated a statistically significant superoxide scavenging activity of 81.92 percent, which was equivalent to 85.35 percent when applied to the tocopherol standard [184].

Due to their extensive properties, AgNPs offers a plethora of medical science applications. Synthesizing AgNPs, numerous methods, including new green approaches, can provide environmentally friendly capping agents that are not harmful and toxic [185]. Different green synthesis techniques were used, including lignin-capped silver nanoparticles (LCSN) (grafted on lignin with a spherical shape and a size range of 10–15 nm) [163]. In the presence of sunlight, *Sida cordifolia* leaf extracts stimulated the biogenic production of AgNPs [186], the aqueous extract of *Clerodendrum phlomidis* L. leaves [183], *Seabuckthorn* (SBT) leaf extracts employed by AgNPs (SBT@AgNPs) [187], and poly(vinyl alcohol)-embedded AgNPs (PVA-AgNPs) [188], which have been found to have antioxidant activities.

7.4. Copper Oxide Nanoparticles

For nanoparticle synthesis, copper has recently caught interest because of its availability and desirable properties such as catalysis, electrical, and optical properties [189–191]. In modern technology, as an essential inorganic substance, copper oxide is widely employed, especially for ceramics, catalysis, and superconducting applications. This material can also operate as an electrode to degrade nitrous oxide with ammonia and oxidize carbon monoxide, hydrocarbon, and phenol to produce supercritical water [192]. Cu_2ONPs with antioxidant properties synthesized by plant-derived synthesis are summarized in Table 2. Using leaf extracts from *Cissus arnotiana*, Rajeshkumar and colleagues found that copper nanoparticles have similar radical scavenging properties as ascorbic acid [193].

7.5. Iron Nanoparticles (INPs)

The unique physiochemical properties of iron, such as its low toxicity, good magnetic properties, microwave absorption capabilities, and high catalytic activity, make it a crucial component in nanoparticle synthesis [194–196]. The three types of iron nanoparticles are as follows: iron oxide nanoparticles (IONPs), iron hydroxide nanoparticles (FeOOH), and zero-valent iron nanoparticles (INPs) [197–200]. These new technologies include hyperthermia, bio-separation and bioprocess intensification, ferrofluids for medication delivery and environmental remediation, food preservation and gene therapy, pigments, and thermal-ablation using lithium-ion batteries [201]. The antioxidant capacity of INPs mediated by plants is listed in Table 2. Amaranthine and phenolic chemicals found in the *Amaranthus spinosus* leaf extract mediate iron nanoparticles, which have high antioxidant activities [95] as a capping agent [93].

The antioxidant properties of Fe_2O_3 nanoparticles have already been studied, and the theory behind it is based on the neutralization of free radicals by the transfer of an electron [202]. However, numerous techniques, such as carbon coating, carboxymethyl-inulin, and poly (GA), modifying the surface with gallic acid, and the incorporation of curcumin in magnetic-silk core-shell nanoparticles, were successful in tailoring Fe_2O_3 nanoparticles. The composites showed improved dispersibility and stability. They were examined for their efficient antioxidant characteristics, antibacterial activities, targeted drug administration to specific organs, and their cytotoxicity and biocompatibility/hemocompatibility [164–168,203]. Magnetically separable ligand-functionalized magnetite with natural antioxidant gallic acid (GA) displayed antimicrobial and antioxidant activities (Figure 11).

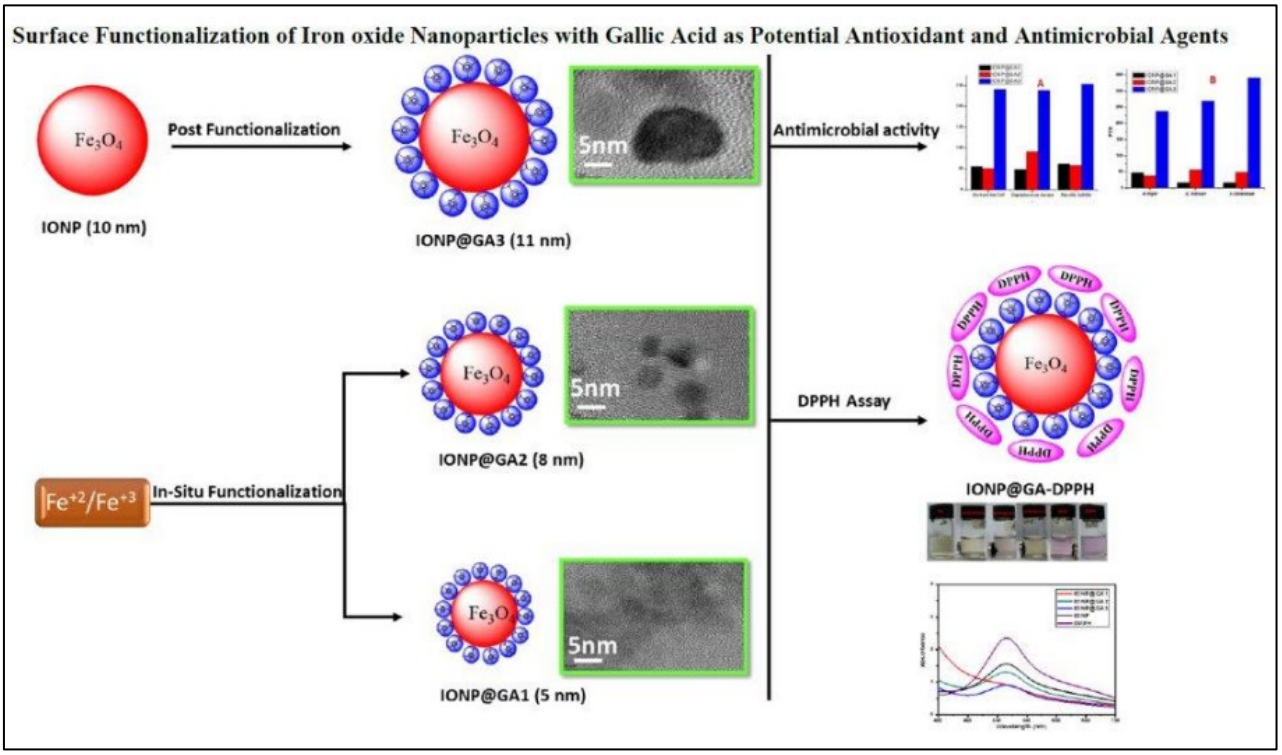

Figure 11. Surface Functionalization of IONP with Gallic Acid.

Post-functionalization techniques successfully synthesized IONP functionalized with multipotent antioxidants (MPAO). PASS analysis and ADMET studies using the structure-based virtual screening technique were used to investigate and anticipate the likely bioactivities and safety profile of the MPAO molecule prior to the synthesis procedure. Magnetite was shown to retain its characteristics after being functionalized with MPAO. The free radical scavenging and antibacterial activities of MPAO functionalized IONP were promising [204,205].

7.6. Selenium Nanoparticles

As part of their research in 2013, Li and his colleagues developed 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox)-coated surface-functionalized selenium nanoparticles (Se@Trolox) with antioxidant activities [206]. Furthermore, Se@Trolox was discovered to inhibit the activation of the AKT and MAPK signaling pathways, the buildup of reactive oxygen species (ROS) generated by cisplatin, and the phosphorylation of the p53 gene in HK-2 cells after DNA damage [206]. Spirulina and biogenic SeNPs have recently been the subject of research into their medicinal potential. A dose-dependent ABTS/DPPH radical removal was achieved by SeNPs, which are capable of scavenging them. The biological activities of Spirulina and SeNPs were found to be linked to their total phenolic content [130]. The antioxidant capability of plant-derived nickel oxide nanoparticles is demonstrated in Table 2.

7.7. Bimetallic Nanoantioxidants

The ability to scavenge ROS or RNS was studied in various combinations of bimetallic nanocomposites in addition to antioxidant-functionalized materials. The antioxidant activity of the stabilized, mono-dispersed Ag-Se bimetallic nanoparticles (Ag-Se) was examined in vitro using the azino-bis-ethyl benzthiazoline-sulfonic acid (ABTS), 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) and DPPH assays [171]. Gallic-acid-functionalized GA-SiO_2@Ag particles demonstrated significantly increased proton-coupled electron transport at near-IR wavelengths (700–1100 nm) when observed at 700–1100 nm (PCET) [150].

It was found that silica-coated AuNPs (Si@AuNP) and PAPM (polyaspartic acid-based polymer micelles) were both glucose sensitive and efficient in targeting the cell. The nanocomposites were made in two steps: First, the primary amine-terminated nanoparticle (either Si@AuNP or PAPM) was functionalized with phenylboronic acid, and then vitamin C was chelated to the nanoparticle via chelation (Figure 12). The resulting Si@AuNP and PAPM have hydrodynamic sizes of 40–50 nm and 40–80 nm, respectively, and contain vitamin C concentrations of 4–8 weight percent and 10–13 weight percent. At micromolar concentrations, vitamin C protects the cell, whereas at millimolar concentrations, it induces oxidative stress and ultimately cell death through the production of H_2O_2.

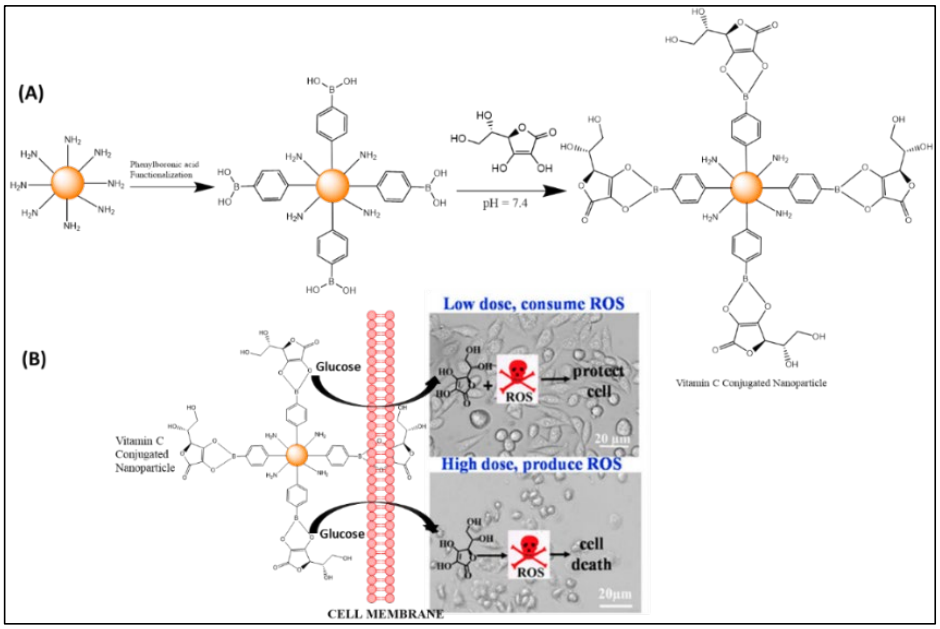

Figure 12. (**A**) Vitamin C-coated nanoparticles (Si@AuNP or PAPM) and (**B**) cellular oxidative Stress at concentrations of micro- and millimolar vitamin C.

Zingiber officinale (ginger) rhizome extract was used as a capping and reducing agent in the synthesis of copper and nickel hybrid nanoparticles. Nanoparticles at a concentration of 200 g/mL were tested against 2,2-diphenyl-1-picrylhydrazyl free radicals, and NPs showed a 42.1 $\pm$ 0.71% percent suppression of the free radicals [207].

8. Conclusions

Numerous treatments have been developed to counteract the negative impact that oxidative stress has on the human body. However, due to many factors, including their inability to cross the blood-brain barrier, conventional antioxidant therapy has been less effective. Therefore, using natural and synthetic antioxidants for the treatment of oxidative stress-induced diseases is no longer recommended. Recent nanoantioxidant research has demonstrated that inorganic nanoparticles can reduce oxidative stress more effectively than organic nanoparticles, with improved sensitivity, cellular antioxidant activity, and the lowest amount of cytotoxicity, as well as the targeted delivery of the nanoantioxidant to specific cells. For example, the covalent attachment or encapsulation of antioxidants with nanospheres derived from various sources has been investigated and is being considered for multiple applications. There are many different types of nanoparticles available, including inorganic, metal, and natural polymer-based nanoparticles; liposomes; and protein polysaccharide-based nanoparticles, to name a few. For nanoantioxidant composites to perform at their peak levels of catalytic and biological activity, it is vital to have a deeper understanding of their origin, physical and chemical properties, and their mechanism of action. Before any potential biomedical applications of nonbiodegradable and insoluble nanoparticles may be considered, extensive toxicity testing must be performed.

Nanoantioxidants synthesized in the lab must also be evaluated in vivo to ensure their safety, especially for long-term treatments, by identifying and analyzing their beneficial and harmful properties. The development of novel and effective delivery strategies for therapeutic nanoantioxidants is vital, as is the development of novel antioxidant activity tests that are accurate and dependable. Research into new compounds as well as the development of very well nanostructures and nanotechnology will play a key role in determining the future of nanoantioxidant-mediated therapy methods.

9. Recommendation for Future Research

The use of natural and synthetic antioxidants for the treatment of oxidative stress-induced disorders is now obsolete. Recently, nanoantioxidants have demonstrated the capacity to minimize oxidative stress with improved sensitivity, cellular antioxidant activity, lower cytotoxic effects, and tailored delivery in inorganic nanoparticles developed over the previous few decades. Antioxidants can be covalently attached or encapsulated with nanospheres of many types, such as inorganic nanoparticles, metal nanoparticles, and many more combinations, for various uses. However, a thorough understanding of the nanoantioxidant composites' origin, physicochemical properties, and the mechanism of action is required to acquire the best catalytic and biological activity. In addition, comprehensive toxicity testing for nonbiodegradable and insoluble nanoparticles is required before any further biomedical application can be carried out. In addition, it is necessary to identify and assess the benefits and negative effects of the synthesised nanoantioxidants before they can be properly utilized in vivo, particularly for long-term treatment.

10. Limitation of This Study

There is a need for new nanoantioxidants and new methods for measuring their antioxidant activity that are more precise and dependable. Because of this, nanoantioxidant treatments in the future will be shaped by advances in molecular knowledge and the development of new nanostructures.

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