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A Brief Journey in Nanomaterials: Base and Recent Research Trends

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Abstract

Nano – term is a mimicking dimensional philosophy of natural structure. With same context, nanomaterials in research and processing display a mimic philosophy with particular function(s) in human and other living creatures such as DNA, ribosome, antibody, enzyme, protein, glucose, haemoglobin, and bone (hydroxyapatite or collagen). Also, some microorganisms (bacteria or viruses) are in nano-sized that enabling them for easily entrance to their hosts. According to range definition (1-100(nm)), type, application, toxicity beside environmental impact for short – and long term, nanomaterial and nanotechnology have important achievements starting from discovery to production state. Nanomaterials are high surface materials having enormous selectivity – reactivity resulted from high active sites to area ratio. They prepared by physical, chemical and bio -green reactions that applied to formulate micro- and nano- organic(s) and inorganic(s). These significant materials performe amazing levels in research, discovery, development, and processing in industry, medicine, pharmacy, science, technology, and other life fields. In this mini - review, fast journey with more than seventy references beside their cited books or articles demonstrated that nano sized materials are superior and adjustable in their physical, chemical, and / or biological properties compared to bulk counterparts. Their classification varied according to composition, origin, size (or surface area), and shape that lead to safety – application balance. The dramatically innovation in nano science and technology is a result of surface area to volume ratio that promoted multiple uses and toxicological changing in cell, membrane, or organ. Finally, there is a serious need for more research in these smaller particles to demonstrate what, how, where, and when nanomaterials are safe and eco-friendly through type, concentration, time of exposure, and biological target specifications beside motivate them as more suitable for bio-, agro, food, and medical uses.

1. Introduction

Nano materials are high surface materials compared to their volume giving enormous selectivity – reactivity resulted from high active sites to area ratio. They prepared from physical, chemical and bio-green reactions that applied to formulate micro- and nano- organic(s) and inorganic(s) and performed amazing levels in research, discovery, development, processing in industry, medicine, pharmacy, science, technology, and other life fields (Figures 1 & 2).

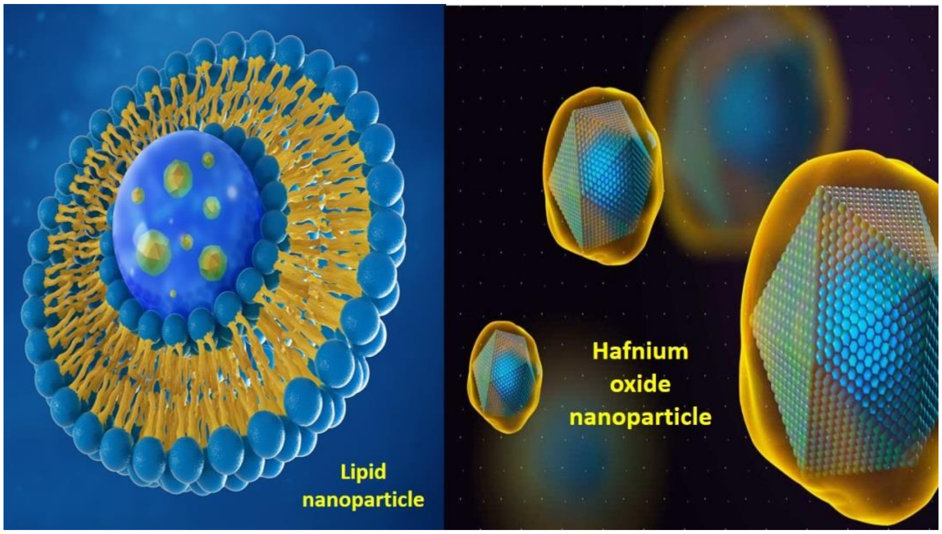

Figure (1). Organic and inorganic nanoparticle.

2. Definition- Classification, and Synthesis Paths – General View

Any main and sub- category of nanomaterials that mentioned above beside other unbound and agglomerated nanowires, nanoplates, quantum dots were classified according to International Organization for Standardization (ISO), EU Commission, US Food and Drug Administration (US-FDA) and/or Environmental Protection Agency (EPA). These definitions were "a manufactured or natural material that possesses unbound, aggregated, or agglomerated particles where external dimensions are between 1nm to 100 nm size range", "material with any external nanoscale dimension or having internal nanoscale surface structure", " material having at least one dimension in the range of approximately ((1 -100) nm) and exhibit dimension –dependent phenomena", and/or " can exhibit unique properties dissimilar than equivalent chemical compound in a large dimension" respect to ISO, EU-Commission, US-FDA, and/or EPA [1-4]. There were many reviews [5-7] that specified these structures depending on chemical base and physical shape as in Table (1).

Table (1). Classification of Nano-sized materials.

Category	Physical structure(s)	Examples
Metals or their oxides	Particle	Metal or its oxide such as Au, Ag, Si, Pt, TiO_2, ZnO
Composite - based	Multiphase including nanofiber, metal- organic framework	Combination of metal- organic base known as ceramic
Carbon – based on physical - chemical methods such as Arc discharge, laser ablation, chemical vapour deposition	Hollow tube, sphere, ellipsoid	Carbon nanotube or nanofiber, fullerene (C_{60})
Organic – based	Non-covalent based structure such as dendrimer or micelle	Chitin, cyclodextrin, protein, polymer, supramolecule, porphyrin

Preparation of nanomaterials is a mimic strategy of natural nanostructures that achieve their function(s) in human and other living creatures such as DNA (2.2-2.6 (nm)), ribosome (25 nm), antibody (2-200 (nm)), enzyme, protein (3-6 (nm)), essential organic material [like glucose (1 nm), haemoglobin (6.5 nm)], and bone (hydroxyapatite or collagen). Also, some microorganisms (bacteria or viruses) are in nano-sized enabling easily entrance their host [8, 9]. All natural and synthesized nano-scale materials were categorized according global scientific agencies targeting the same goals of range definition (1-100(nm)), type, application, toxicity, and environmental impact for short – and long term [10, 11], (Figure 2.).

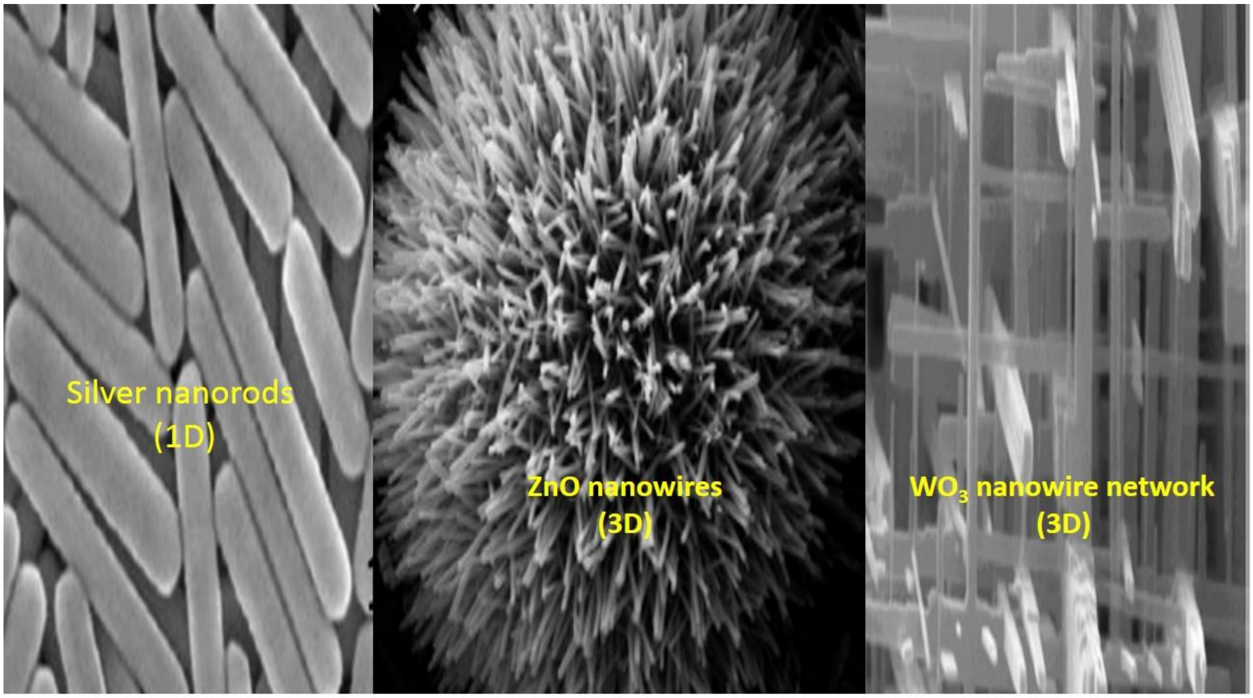

Figure (2). Various shaped inorganic nanoparticles [9].

3. Inorganic Nanoparticles – General Remarks

Many nanoparticles had encountered considerable attentions resulted from their remarkable properties and probable applications such as calcium oxide, zinc oxide, aluminium oxide, iron, rhodium, gold, silver, aluminium beside bimetallic nanoparticles (Figures 1-3) [12 – 17]. Several published articles related to the preparation, properties, and applications of several nanoparticles were tabulated in Table (2).

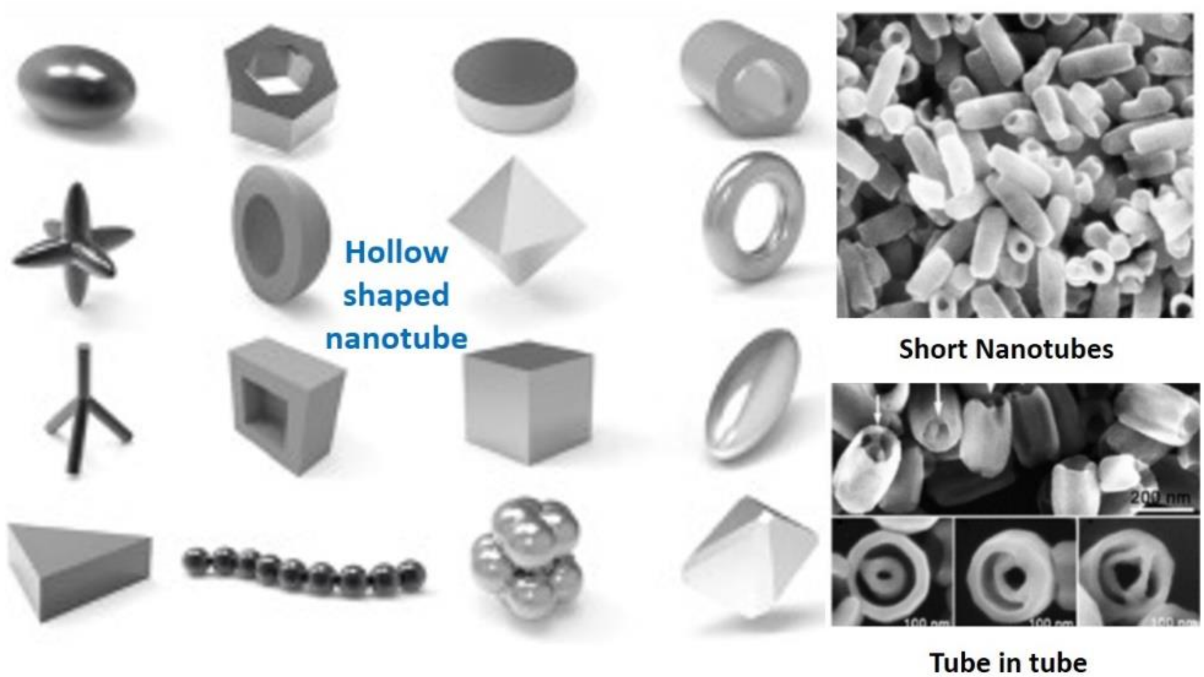

Figure (3). Magnetic Iron oxide nanoshapes.

Table (2). Nanomaterials in general observations.

Nanoparticle	Preparation method	Properties	Application(s)	Remarkable notes	Ref.
Calcium oxide	Calcium nitrate in Basic medium	Active catalyst	Adsorption of heavy metals such as Chromium- 6+. Trans-esterification, photosynthesis toxic dye degradation	Highly basic, non-corrosive, reusable, recyclable, non-explosive, non-volatile	16, 18-20
Zinc oxide	Acetate salt with organic base	Catalyst, supporter	Anticancer, antibacterial, diabetic treatment, drug delivery, sunscreen, bio-imaging	Less toxic, biocompatibility, strong UV- absorber, luminescent	21- 23
Iron	Polymer as a capping agent in H_2O, using natural polyphenols	Active catalyst	Organic contamination, hydrogenations	Remarkable catalytic activity	24- 27
Rhodium	Green hydrogen reduction		Hydrogenation, cancer treatment	Successfully absorbed on various supports such as TiO_2	28- 30
Platinum	Green Hydrogen reduction	Nano-catalyst	Fuel cell, optics, coating, textile, plastics, sensor, coating, organic reaction, petroleum cracking, oxidation reduction,	High catalytic activity	31 -34
Gold	Green synthesis of gold salt, photocatalytic method, photochemical method	Active catalyst, antimicrobial	Conductor, fuel cell, drug delivery, catalysis, textile, medical and personal care products	High X-ray absorption coefficient, strong binding affinity to various organic, optical – electronic properties	35 -38

4. Biology, Chemistry and Nanoscale – Between Green Target and Practice

By green synthesis of nanomaterials, several points can be achieved towards less damage to human health and environment and more reasonable uses of natural resources and / or wastes such as sustainability, minimizing of energy consuming across decreasing global overheating issue, minimum toxicity of introduced to the produced materials, and applying more maintainable synthesizing chemical, physical, or biological routes [39, 40].

Many published research and review articles demonstrated modern trends in this important subject (Green Nano-sized material) in synthesis, fabrication, characterization, application of all kinds (organic, inorganic [metal, non-metal, oxide, salt], coordination, hybrid, composites, polymers, and other sub-titled materials). Green methods were microwave, sonication, hydrothermal, magnetic, mechanical, solventless beside bio- techniques. In bio-techniques, plant part extraction, using bacteria, fungi, yeast and even viruses were accomplished so more profitability and availability of green non- contaminating methods can be efficiently obtained [3-7].

To get nanoscale material, two paths of synthesis named as Top - down and Down – Top. In top- down, bulk size materials converted to the corresponding nano size by mechanical milling, etching, sputtering, laser ablation, and electro-explosion [11, 46, 47, 48, 49]. These physical – mechanical methods are effective techniques in producing various phases having excellent properties compared to original material (s) as shown in Table (3).

Table (3). Top – down synthesis method.

Method	General description	Example(s)
Ball Milling	Simple, Cost – effective Used in Energy storage or conversion	Oxide, carbide, alloy, coating, composite, blend
Electro-spinning	Liquid(s) with viscous appearance in electric field	Ultra- thin, Nanofiber, polymer, organic, inorganic, hybrid, hollow materials
Sputtering	Deposition process of energetic gaseous ion on the target surface by radio-frequency diode, magnetron, or DC diode	Thin film
Masked or maskless lithography	Using focused light or electron source Masked technique includes scanning probe, ion beam, and electron beam Maskless technique carries out by combination of ion implantation and wet chemical etching	Suspended, 3D, or hybrid structures
Arc discharge	Driven chamber by arc discharge filled with gas containing two graphite rods as a surface of deposition Ar gas: C-C bonding; N_2: C-C, C-N bonding, H_2: C-C bonding and etching	Carbon – based (fullerene, nanotube, graphene, amorphous sphere, nanohorn, polyhedral or pyrolytic graphite)
Laser ablation	Laser beam hits the target	Metal, carbon, oxide, ceramic or composite

In Bottom – Up approaches, sol – gel, Chemical Vapour Deposition (CVD), solvothermal, hydrothermal, soft template, hard template, and reverse micelle are known methods for generation of nano scale materials. As in Top – down methods, down –up methods produce different phases and show superior characters compared to original material(s) [50 - 54] as shown in Table (4).

Materials in the term and shape of nano classification are well– synthesized, characterized, developed, and applied in drug delivery, imaging, theranostic (diagnosis – therapy) including polymeric type having considerable highly controlled chemical composition, completely easier metabolic - elimination pathways, bio degradable – compatible, immunogenic, mimicking natural type, and unique physicochemical properties [55].

Nano – RNA, DNA, protein, sugar, lipid, albumin, and other polymerics that had long – term stability, extremely controlled quality and characterization, and uncomplicated storage – management facilities may be collected after precipitation or freeze –drying steps from suspension medium to get over their instability character. Minimizing salt, aggregation centres, and toxic impurities during processing are essential step(s) done by ultra-filtration, dialysis, or centrifugation to ensure novel results in the clinical research [56, 57, 58, 59, 60].

Property - Target relationship determines what method should be applied for nano-polymeric synthesis. Base material or monomer categorized synthesis into one-step or two- step methods as shown in Tables (3-5).[38-60].

Emulsion step combined by solvent evaporation or diffusion besides salting out, precipitation, dialysis, supercritical fluid, and interfacial or radical or Ultraviolet polymerization are most utilized techniques in nanomaterial subject. Non- biodegradability is a susceptible challenge related to health – environment acceptance of the base material, final product, and by-product especially in drug or bioactive encapsulation, protection, delivering, research and development (Table 5) [55, 60, 61].

Table (4). Bottom –Up synthesis method.

Method	General description	Example(s)
Solvothermal Or Hydrothermal	Heterogeneous reaction in presence of solvent (non- aqueous, Solvothermal) or aqueous (hydrothermal) medium at high temperature in sealed vessel	Nanogeometric materials in of one dimension (rod or wire), two dimensions (sphere or sheet) structure
Chemical Vapour Deposition (CVD)	Catalysed chemical reaction of vapour precursors having high volatility, purity, stability, shelf – life with safely use on the substrate surface heated to high temperatures	Thin film, nanotube of Carbon -based
Sol – gel	Wet chemical reaction involve conversion of liquid to sol state Steps: hydrolysis of metal oxide in H2O, forming gel phase, polycondensation resulting metal- hydroxo or metal- oxo in polymer structure, forming colloidal particle during aging, removing used solvent, then calcination Controllers: precursor, time, (water: precursor) molar ratio, pH, hydrolysis rate, and temperature	High quality of homogenised metal oxide, composite, complex
Reverse micelle	Oil in water emulsion where Core: hydrophobic tail of micelle traps oil droplet (normal micelle). Reverse micelle is nano-reactor formed in water in oil emulsion where Core: water having hydrophilic head. Water concentration controls nanoparticle size (water: surfactant ratio)	Precisely controlled size (uniformed nanoparticle) Magnetic lipase – immobilized material

Table (5). General variations in Microbial and physical - chemical technologies.

Technology	General description
Solvent evaporation during emulsification	*Variation of applied step according to hydrophobic – hydrophilic ratio of used material, vacuum or heat to perform evaporation, capacity can be by size*
Solvent diffusion during emulsification	*High in size capacity, reproducibility, solvent quantity, effected by water presence in water – soluble material*
Precipitation	Low energy, single step, effected by stirring rate, reproducible, capacity can be by size.
Salting out	*High speed for homogenization of lipophilic materials, RNA, DNA, protein, expending more time, absence of heating, giving low size capacity*
Microbiological	*High eco- friendly and biocompatible with using safe material with more cost compared to physical - chemical technologies*

In organic chemistry, heterocycles are important N-, O-, S-, P- containing compounds having wide applied range. Many published papers demonstrated their preparation by nanoparticles catalysed organic synthesis giving remarkable results compared to conventional catalyst. With recyclable, reusable, and benign nano- catalysts, these promising heterocyclic materials were in an extensively increasing in simplicity, selectivity, productivity, linear - multi component synthesis, and presenting more accelerating green approach. Based metal nano-catalyst (Mg, Fe, Co, Mn, Ni, Cu, Ti, Si, Au, Ag, Zn, Sm, Zr, Ce, Ru, and their oxides) used in synthesis pyridine, polysubstituted N- bearing heterocycles, Schiff bases, enaminones, triazoles, tetrazoles, oxazepines, dihydroprimidinone cores, and others. Roles of these heterocycles were varying as ligand, stabilizer, antimicrobial, antitumor, calcium channel blocker, explosive, and other important applications [62].

Hetero- Polycyclic Aromatics are two – dimensional π- conjugation compounds provide unusual features having ring fusion structure with heteroatom replacement and displaying electronic 3 D – aromatic behaviour of solid – state molecules. These enlarge fused ring patterns and their B, Se, and Te frameworks such as pyrrole –based, porphyrinoids, and azaacene were synthesized by remarkable on – surface routes and changeable properties between carbocyclic bases and targets (Table 6.). Novel 1D, 2D polymers, fluorophores, dyes, charge transfers, semiconductors, hetero-junction photo-voltaic, phosphorescent emitter and other functional platforms had broad range of research area by utilizing shape and rigidity characters of the starting materials [63 – 67].

Table (6). Synthesis of nano- heterocyclic material by nanocatalyst**.**

Heterocycle	**Nano-catalyst**	**Brief description**	**Ref.**
Pyrrole	$Fe_3O_4@SiO_2@$ propyl-ANDSA Magnetic Nanoparticle (MNP)	Various conditions (temperature, solvent) by re-generable and reusable nanocatalyst	68
	Fe_3O_4 @ DTPA	Various conditions (catalyst amount solvent)	69
	Cu@imine / Fe_3O_4 Magnetic Nanoparticle (MNP)	Reusable catalyst for preparation of polysubstituted pyrrole under low reaction time, free solvent, excellent yield	70
Pyrazole	ZnO	Efficient benign procedure gave moderate yield at low time, room temperature, and water as a medium.	71
	TiO_2	One – step condensation route, under room temperature and solvent – free through Knoevenagel condensation, Michael addition, and cyclization	72
	$CuFe_2O_4$	Eco-friendly four – component reaction, Knoevenagel condensation, Michael addition, and cyclization by Lewis acidic ferric ion	73
Imidazole	Recoverable magnetic $Fe_3O_4@PVA-SO_3H$ separated by a magnet	*in situ* condensation reaction	74
Triazole	Graphene oxide Cu(I) complex	*Green and simple work – up procedure for 1,2,3 – triazole preparation by three component cycloaddition reaction under microwave irradiation*	75

5. Nanomedicine and Nanomaterials – Brief View

Unique features of materials present unparalleled properties for superlative application compared to the corresponding bulk counterpart materials. Here, nanomaterials with all based dimension classifications (0D, 1D, 2D, or 3D) may achieve excellent work with easily recognition between them and micro – dimension (bulk) materials. Therapy and diagnosis related to nanomaterials took huge part in scientific research, development, and application in medicine scope [54] as shown in Table (7). Surface area, magnetism, thermal- electrical conductivity, mechanical, and antimicrobial properties were with high performance range in tissue engineering, sensor, semiconductor, graphene, active catalyst, dealer with pathogen – related diseases, green synthesis in industrial scope, controlling of parasite – host relationship, agro-food, filler, additive, modifier, film, membrane [5, 7, 11, 76, 77].

Table (7). Nanomaterials in Nano-medicine applications.

Nanomaterial	Nano-medicine application(s)
Quantum dot (0D)	Tumour imaging, diagnosis, and treatment, fluorescence observation, early detection of cancer
Rod (1D)	Laser lung cancer treatment, carrier, photo- or chemo- combined by thermal cancer therapy, Near InfraRed (NIR) laser, MRI features
Wire (1D)	Biomarker improve cancer diagnosis and prognosis, Near InfraRed (NIR) hyperthermia to destroy cancer cell
2D of transition metal carbide, nitride, and carbonidride (MXene)	Light- heat conversion
Sheet (2D)	Both Magnetic Resonance Imaging (MRI)or photo-, and photothermal-acoustic wave transducer therapy and diagnosis, Near InfraRed (NIR) laser with photothermal conversion
Cube (3D)	High photoluminescence for cancer cell imaging

6. Nanomaterial: Are They Safe to Human?

In chemistry and biology, every subject has advantages and disadvantages that limit its uses and impact on living creatures and environment. Nanomaterials exposure had been identified with neurological, lung, and heart diseases beside skin problems. These materials may enter human body through ingestion, inhalation, or dermal exposure causing particular hazard on the target depending on time, concentration, aggregation, size, shape, surface area, mechanism, and target location [5, 6, 9, 38, 61, 76]. Table (8) summarizes toxicity mechanism according to applications of various nanomaterials.

Table (8). Nanomaterials in view of toxicity mechanism and applications.

Nano – application field	**Toxicity mechanism**
Bio-polymer, paint, coating, textile, fuel cell	Changing in gene or protein expression, oxidative stress, mitochondrial action
Drug carrier, diagnostic agent	Peroxidation, autophagy, cell viability, reactive oxygen production, mitochondrial action, cell viability, changing in gene expression, liver, nerve, skin, bone, or heart toxicological damage
Semiconductor, heat transfer, medical personal protection , pigment, dye	Cyto- hepato-, spleen, lung, heart, and nephron- toxicology, stress
Body care products (Sunscreen, UV detector, or filler)	Oxidative stress, cell viability, reactive oxygen production, inflammation, mitochondrial action
Some Antimicrobial, corrosion inhibitor, polisher, solar cell	Peroxidation of lipid, apoptosis, membrane damage, inflammation

7. Conclusions

In a comprehensive view, nano sized materials are superior and adjustable in their physical, chemical, and / or biological properties compared to bulk counterparts. Their classification varied according to composition, origin, size or surface area, and shape that lead to safety – application balance. Nanomaterials in their bases are mimic materials to nature to become more suitable for bio-, agro, food, and medical uses. The dramatically innovation in nano science and technology is a result of surface area to volume ratio that promoted multiple uses and toxicological changing in cell, membrane, or organ. Finally, there is a serious need for more research in these smaller particles to demonstrate what, how, where, and when nanomaterials is safe and eco-friendly through type, concentration, time of exposure, and biological target specifications.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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