International Journal of Advances in Engineering and Management (IJAEM)
Volume 4, Issue 7 July 2022, pp: 1163-1171 www.ijaem.net ISSN: 2395-5252

Nanotechnology in the Cosmetic Industry: A Review

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Submitted: 10-07-2022 Revised: 18-07-2022 Accepted: 23-07-2022

ABSTRACT: Nanotechnology is an increasingly widespread area of research for its variousapplications and advantages. Hence, it has been the focus of investment and research indifferent areas of science, including for the development of cosmeticsformulations. Nanomaterials allow for deeper skin penetration and an effective release profile ofingredients, which contributes for superior cosmetic effects when compared to conventional cosmetics. There are numerous applications of nanocosmetics, like anti-aging care, make-up, nails, deodorants, oral care, sunscreens, and hair care. However, as it is a nascent area of study, it has now begun toencourage investigations into its toxicology profile, particularly regarding to toxicity andenvironmental pollution.

I. INTRODUCTION:

Nanotechnology is an emerging area that has been extensively explored in the past decades. It is defined as any technology performed at the nanoscale, in the size range of about 1-1000 nm.[1]

The cosmetics industry has boomed in recent years as one of the markets that hold enormous growth potential. The global market for cosmetic products was valued at USD 532.43 billion in 2017 and is expected to garner USD 805.61 billion by 2023, registering a compound annual growth rate (CAGR) of 7.14% from 2018 to 2023.[2] Over the past few years, the cosmetic industry has been flourishing with an expanding rate of around 15%, and it continues to grow.[2]With reference to the nanotechnology-based products, an average of 16.6% growth rate is expected in the global cosmetic market, each year.[2] These projections of significant growth have not yet been validated; however, they highlight the application of nanotech-based products in cosmeceuticals. With increasing consumer demand for beauty products, the use of cosmetics has dramatically intensified. The cosmetic industries continue to explore new ways of product development that provides for more youthful, healthier, and smoother skin.[3]

Incorporation and use of nano-scale ingredients are gaining popularity in the cosmetic industry because of their tiny size and high surface area to volume ratio.[4] These nanostructured materials often have physical and chemical characteristics and biological activities that differ from their bulk equivalents. Some of the essential technological advantages that may be achieved by incorporating nanomaterials in cosmetics are enhanced performance, unique texture, transparency, protection of active substances, and higher consumer acquiescence.[5] For instance, larger particles, i.e., zinc oxide and titanium dioxide, are white and opaque, but these substances become transparent at the nanoscale, enabling their usage in foundations and moisturizers.Therefore, the cosmetics industry has now routinely started the use of nano-ingredients in the formulation of cosmetic products.[4]

The growing interest in sideeffects of nanomaterials led to the development of an important area: nanotoxicology. Since thisfield was recently developed, there are still actions on the different targets that have not beencompletely elucidated. It is alsoimportant to discuss the environmental impact of nanocosmetics.[6] Consequently, it is imperative to ensure the implementation of regulated methods and cosmetic ingredients to ensure their safety, always in accordance with the current legislation.[7]

In this review, we will look at distinct nanosystems involved in the production of nanocosmetic formulations, followed by a brief description of the distinct nanocosmetic formulations. Afterwards, new insights and concerns into toxicological and regulatory aspects of nanocosmetics formulations will be discussed.[1]

Nanosystems:

The nanomaterials used in cosmetics are divided into four large groups: lipid-based nanosystems, polymeric-based nanosystems, metal-based nanosystems and other additional nanosystems.

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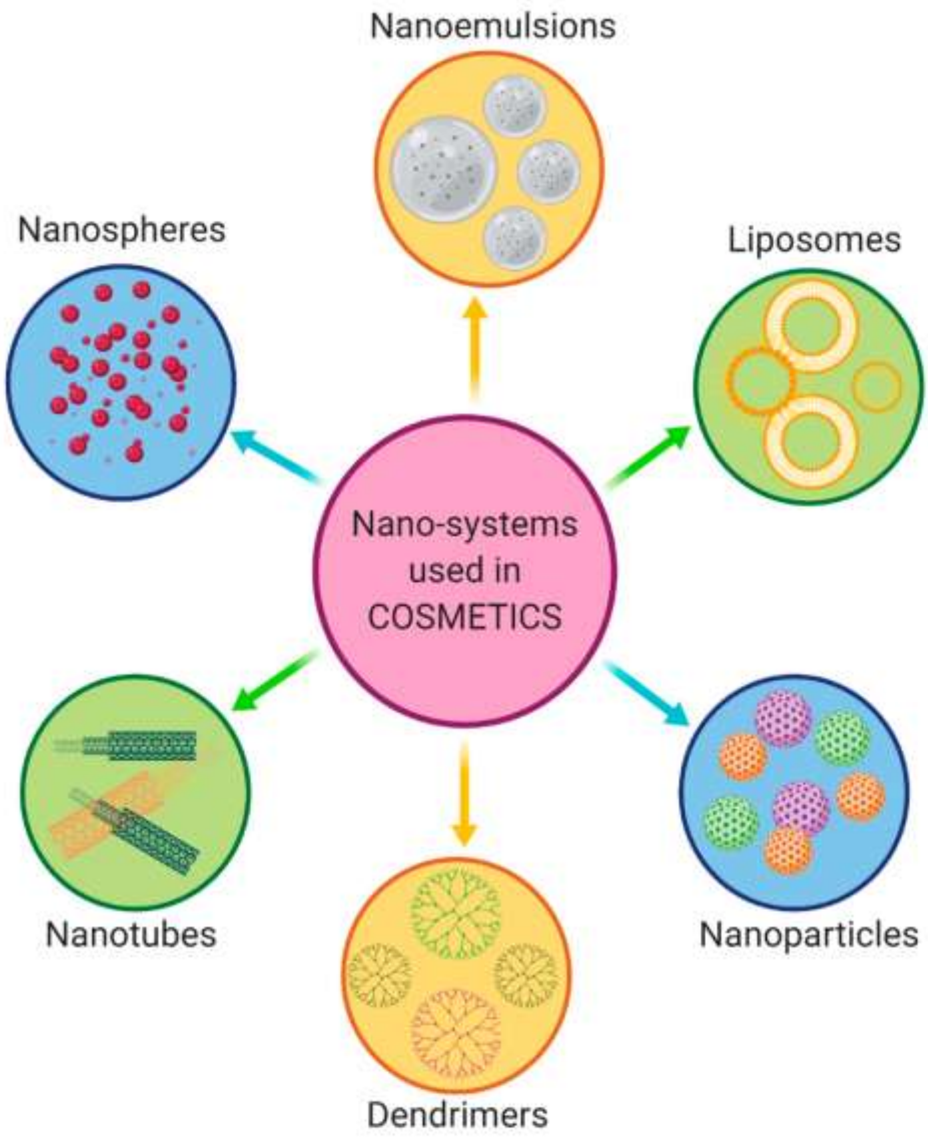

Fig.1. Various nanostructures used in cosmetics.[2]

1. Lipid-based nanosystems: Lipid-based nanosystems have demonstrated to be a proper bet in terms of dermal carriers due to their biocompatibility, stability, penetration improvement, effective active ingredient delivery and possibility to be incorporated in diverse and innovative dosage forms.

1.1. Solid lipid nanoparticles and nanostructured lipid carriers: According to the lipophilic matrix structure, two generations of lipid nanosystems are distinguishable. Solid Lipid Nanoparticles (SLNs) are the first generation of lipid-based NPs, constituted bysolid lipids, with attributes of controlled release and lower probability of skin damagedue the lower quantity of active ingredient immediately released to the skin.[8,9] The efficiency of SLNs strongly depends on varied factors such as the manufacturingmethod and physicochemical properties of the activeingredient, namely its lipophilicity.[10] Duringthe SLNs storage, crystalline structure rearrangements occur for a more ordered and stable form, thematrix imperfections are reduced and so is the space to accommodate the interest active ingredient,leading to its loss or scape. To overcome this issue, a second generation of lipid-based nanoparticles (NPs) wasdeveloped, the Nanostructured Lipid Carriers (NLCs). NLCs are constituted by acombination of solidand liquid lipids, in which the active ingredients are entrapped. The amorphous structure enhances the active ingredientsloading, avoiding its leaking during storage.The intimate contact among SLNs and NLCs with the skin, results in their greater ability to penetrate the stratum corneum. Their occlusive effect disrupts stratum corneum lipidic structures,improving skin hydration and nanosystems penetration properties, as well as the therapeuticefficiency. In addition, SLNs present UV resistance, conferring photoprotection features.[8,11,12]In cosmetic formulations, SLNs and NLCs are mainly incorporated into skin care products such asmoisturizing creams and sunscreens.[11]

1.2. Liposomes: Liposomes are spherical vesicular structures in which the aqueous core is surrounded by a phospholipid bilayer. Their external lipid bilayer enables hydrophobic active ingredients transport while the hydrophilic active ingredients are confined in their core. According to the number of bilayers, liposomes can be classified as unilamellar vesicles (ULVs) or multilamellar vesicles (MLVs).[13,14]This formulation entails a set of strategic advantages to cosmetic products, like a higher solubility of the ACI, higher biocompatibility towards the skin tissues, controlled release behaviour and ACI protection from degradation phenomena, increasing its accumulation at the target site and enabling for therapeutic effects at lower doses.[15] These nanosystems may be developed to deliver fragrances in antiperspirants, body sprays, deodorants, and lipsticks.[11]Low drug loading, low reproducibility and physical and chemical instability have limited their commercialization and application.[16,17]

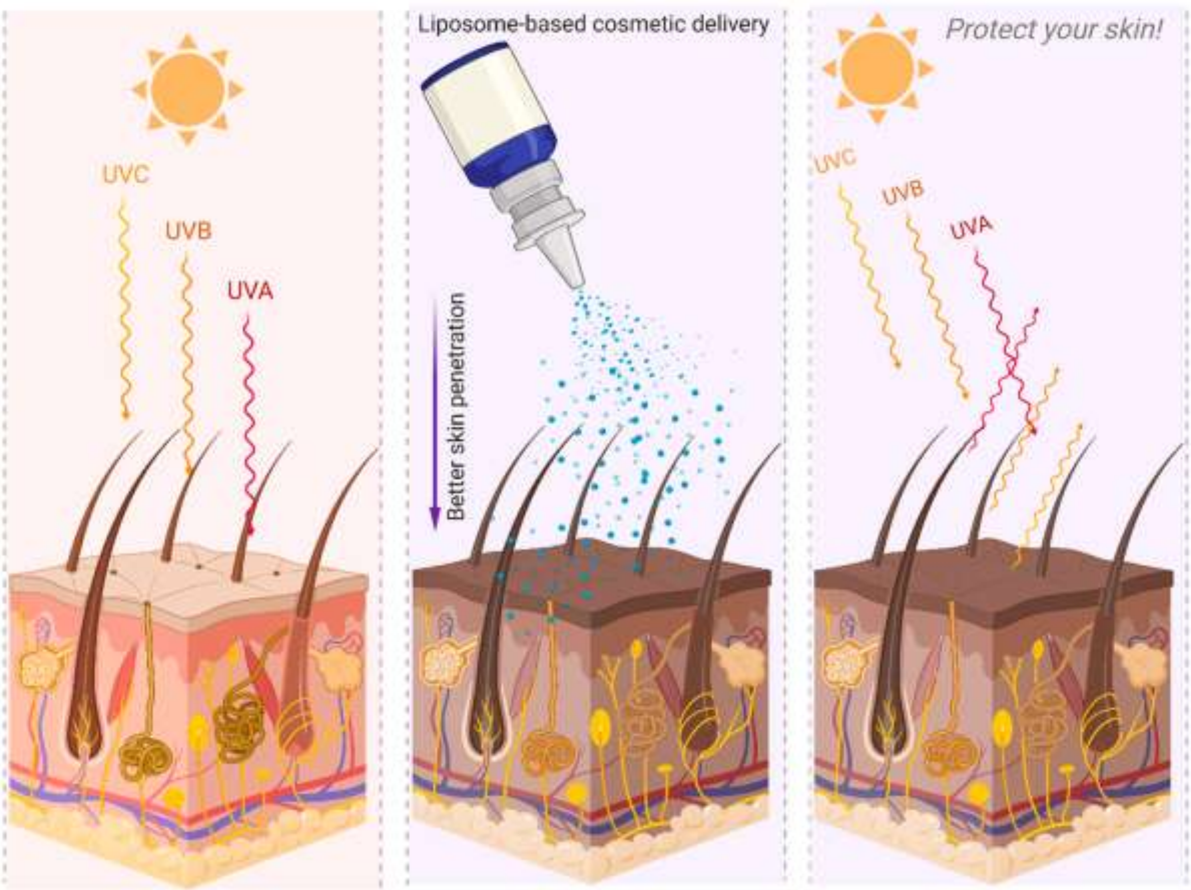

Fig.2. Liposome-based cosmetic delivery via skin. The liposome-incorporated cosmeceutical formulations offer better skin penetration and help to protect the skin from harmful radiations.[2]

2. Polymeric-based nanosystems:

2.1.Polymeric nanoparticles: Polymeric NPs are one of the most studied nanosystems in nanotechnology, evidencing a diameter between 200 to 300 nm. The encapsulation mechanism, the chemical and viscosity properties of ingredients, the size and active ingredient-release behaviour seem to be the main features affecting the extent of the active ingredients' delivery. The interest of polymeric NPs is based on their ability to change the active ingredients physicochemical features, controlling, this way, their efficacy.[18,19]These nanosystems are very promising to drug delivery, due to their high stability, encapsulationefficiency and controlled release ability. Their rigidity and bioadhesiveness allow the formation of afilm on the skin surface, enabling an efficient drug release and retention, locally.[20,21] Incosmetics, polymeric NPs are used in skin care products, such as anti-aging and moisturizing creams.[22]

2.2. Nanofibers: Nanofibers are nanosystems with potential cosmetic applications due to their remarkable features. Their diameter, reaching 500 nm, great surface area, porous structure, appropriate drug molecules release, distinct physical and mechanical properties and high production rate make them a unique choice to deliver ACIs, whether hydrophobic or hydrophilic. For cosmetic purposes, these nanosystems have been attracting great attention, since their porous structure provides an appropriate drug release from the polymeric matrix, reducing drug systemic absorption and required dosage. Their efficiency is dependent upon their porosity, morphology, polymer type and size. Nanofibers yielded with natural and synthetic polymers express the biological advantages of natural polymers of synthetic ones.[23,24]

3. Metal – based nanosystems:

3.1. Silver nanoparticles: Silver NPs (AgNPs) have been widely used in many consumer products, particularly due to its antimicrobial and antifungal spectrum of activity. Since antimicrobial resistance has been shown to be a great matter of discussion, AgNPs appear to be an effective alternative to this health issue. The antibacterial mechanism of action is based on a modification in the cell wall permeability associated to an assumed bactericidal activity. Inside the bacterial cell, the silver ions interact with the respiratory chain, causing an increase of reactive oxygen species (ROSs) production and, consequently, inhibition of bacterial cell growth; also, it can be seen a binding of AgNPs to the phosphorous and sulfur groups of DNA with consequent unwinding and loss of transcriptional and translationmechanisms. It is observed an inversional proportional behavior between the antimicrobial activity and AgNPs size: the effectiveness grows with the decrease of AgNPs size, since smaller NPs evidence higher contact surface. AgNPs can be broadly found in different cosmetic products, as toothpastes, creams, soaps, lotions or deodorants.[25,26]

3.2. Titanium oxide and zinc oxide nanoparticles: Titanium oxide (TiO_2) and zinc oxide (ZnO) NPs have been successfully incorporated in various cosmetic products as UV filters.[1] In fact, TiO_2 is responsible for reflecting UVB radiation, whereas ZnO has the capacity of reflecting UVA radiation. The combined use of these two oxides reveals a profitable protection against sun radiation alongside with optimal characteristics, like the transparency, the spreadability and better texture, without skin irritation, which is normally a consequence of chemical UV filters. The UV protection of these systems is widely exploited since TiO_2 and ZnO NPs deposit on the external surface of the stratum corneum.[27,28]ZnO has also proved to be an attractive option to the cosmetic and pharmaceutical industries, due to its antimicrobial property. Its antimicrobial activity is owed to the production of ROS, followed by the release of Zn^{2+}, which is cytotoxic to the bacteria and induces the destabilization of bacteria cell walls. Thus, the association of ZnO and TiO_2 shows a synergistic activity. However, ZnO NPs effectiveness is largely dependent on the ingredients used in topical formulations, since they can interact and minimize the ZnO antimicrobial activity, as is the case of antioxidants or EDTA.[1,29]

4. Additional nanosystems:

4.1. Dendrimers: Dendrimers are a new class of nano-sized, unimolecular, and highly branched nanostructures with globular, regular branching and structural symmetry. The total number of series of branches determines the generation of the dendrimer.[30] The first-generation dendrimer has one series of branches, while there are two series in the case of second-generation dendrimers. Dendrimers are very small, with an approximate diameter of 2–20 nm.[31] A wide variety of dendrimers exists, and biological properties such as polyvalence, monodispersity, solubility, low cytotoxicity, chemical stability, self-assembling, and electrostatic interactions render dendrimers a promising carrier for drug delivery with high selectivity and precision. These nanostructures are being employed in various cosmeceutical products such as sunscreen, shampoos, anti-acne cream, and hair-styling gels.[32] The dendrimers have shown potential in the effective delivery of dermal preparations through the skin barrier.[33] Intrinsic viscosity is one of the important dendrimer characteristics that make them useful for cosmetic formulations.[34] Many cosmetic companies, such as Dow Chemical Company, L'Oréal, Revlon, and Unilever, have many patents on dendrimer-based cosmetic formulations for applications in skin, nail, and hair care products.[2]

4.2. Nanospheres: Nanospheres are spherical particles of polymeric matrix. They range from approximately 10 to 200 nm diameter in size. These amorphous or crystalline nanoscale carriers can be categorized into biodegradable and non-biodegradable nanospheres. The notable examples of biodegradable nanospheres include albumin-based nanospheres, pristine or modified starch-based nanospheres, and gelatin-based nanospheres, whereas polylactic acid (PLA) is included in the non-biodegradable category of nanospheres. The incorporation of nanospheres in cosmeceutical related products, such as skincare or body-care items, induce the delivery of active constituents into the deep layer of the skin. This, in turn, provide some favourable therapeutic effects to the affected area of the skin more efficiently and precisely. The nanospheres have potential uses in cosmetic products such as anti-acne, anti-wrinkle, and moisturizing creams.[1,29]

Nanotechnology-based cosmetic formulations:
In this section, the applications of nanosystems in cosmetics are described, keeping in mind their function in the different presented formulations.

1. Beauty care: So et al. described the use of SLNs in whitening skin cosmetics. 6-methyl-3-phenethyl-3,4-dihydro- 1H-quinazoline-2-thione (JSH18) is a tyrosinase inhibitor with recognized depigmentation properties. In this case, this molecule was incorporated in SLNs to evaluate the inhibition of melanin synthesis and its application in topical formulations. After 7 days of UV radiation exposure and application of the formulation described for 4 days, the skin was evaluated by using reflectance spectrophotometry, showing a total recover of sun induced pigments.[35] Jiménez et al. also studied the effects of AuNPs with Panax ginseng extract incorporated in whitening cosmetic products. This plant is known for its antioxidant and anti-aging properties, and it was incorporated in synthetized AuNPs. Then, the whitening properties were investigated, and the tyrosinase activity and melanin synthesis of skin melanoma cells have shown meaningfully reduced levels,[36] proposing the cosmetic applications of AuNPs.[1]
2. Sunscreens: Sunscreens belong to a vast field of cosmetics in which the development of nanotechnology has seen a tremendous growth. Many studies have been published to evaluate nanosystems applicability in this type of product. Shetty et al.[37]described the incorporation of morin polymeric NPs into sunscreen. Morin is a natural flavonoid with antioxidant and UV-protection activity. They developed PLGA polymeric NPs, incorporating morin inside the NPs. These NPs showed great in vitro results related to morin antioxidant activity, skin deposition and permeation when compared to morin in plain form. The creams comprising morin-loaded PLGA NPs were produced, and their evaluation indicated marked UV protection values, coupled with great deposition of morin, without cytotoxicity effects to the cells. These outstanding results confirm the value of these optimized PLGA NPs in sunscreen formulations.

Environmental safety issues:
The particle size, surface charge and chemical reactivity of NPs are in the origin of toxic pathways activation, with reactive oxygen species production, and consequently with damage to DNA and cell organelles. The incorporation of nanotechnology in sunscreens has been a major step towards skin protection, but it entails unsafe mechanisms for aquatic environments.[38] TiO_2 and ZnO NPs, the most commonly NPs used in sunscreens, are reportedly the source of hydrogen peroxide (H_2O_2) under photoexcitation. H_2O_2 is a stress inductor in phytoplankton. Botta et al. studied the evolution of TiO_2 NPs of four sunscreens in water.[39] The concentration of TiO_2 NPs was analysed. It was possible to observe that a significant part of the TiO_2 NPs was released from the respective sunscreens, forming aggregates which containing about one third of the original NPs concentration. These aggregates raise environmental questions, due to the sediment formed, which may potentially threaten the subaquatic species. To evaluate the effect of sunscreen NPs in aquatic species, TiO_2 and ZnO NPs, at concentrations of 700 mg/L and 70 mg/L, respectively, were put in river water, combined and separately [134]. Only the combined addition of NPs (TiO_2 plus ZnO NPs) or ZnO NPs alone provoked changes in the microbial river species – the NPs aggregated and formed bigger particles, and the genus distribution was altered. Toxicologic

mechanisms of ZnO NPs have also been reviewed.[40] These NPs may be a significant threat to the environment, since low concentrations, such 1 mg/L, can alter the ecosystem. The lack of knowledge in this matter seems to be the major risk to assess the hazard effects of these NPs on the biosphere, namely regarding the long-time exposure to NPs and bioaccumulation.

Asharani et al. carried out a toxicological study to evaluate the effects of Au, Ag and platinum (Pt)-basedNPs in zebrafish embryos.[41]AgNPs lead to circulatory defects with changes in cardiac morphology and, ultimately, death. Both Ag and PtNPs caused hatching delays. The accumulation ofAuNPs did not show any harmful results. The accumulation of these NPs and the alarming effects, because of their exposure, claims further investigations on these matters.[1]

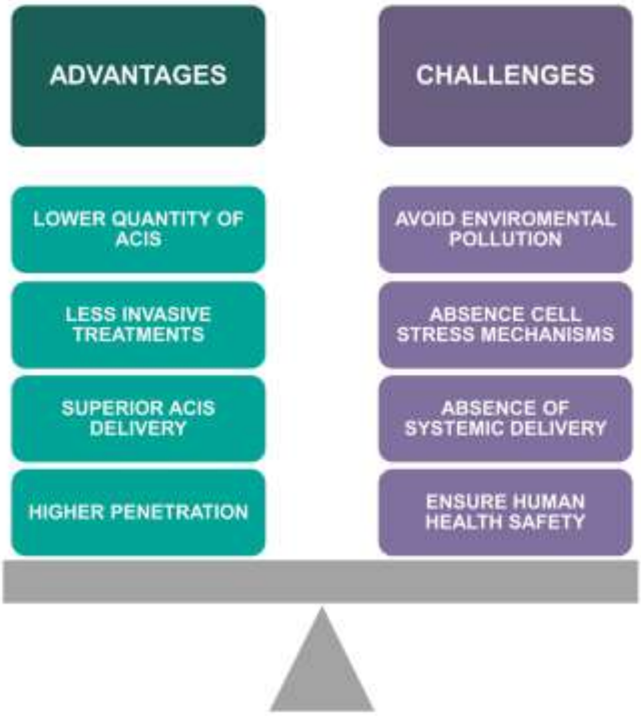

Fig.3. Advantages and challenges of nanocosmetics. ACIS – Active Cosmetic Ingredients.[1]

II. CONCLUSION:

Based on extensive literature study, the use of nanotechnology in cosmetics is becoming a crucial tool for scientific research as well as for the development of new cosmetic and personal care products in industrial sectors. In cosmetics formulations, many nanoscale materials are already being incorporated or recommended for future use as nanosystems or novel nanocarriers to encapsulate active ingredients for their efficient delivery through the skin barriers. These nanosystems have achieved potential in targeted and controlled drug delivery and offered remarkable features such as biocompatibility, better stability, site-specificity, prolonged action, and high drug-loading capability. However, along with their immense technological potential and opportunities, a discussion has been initiated about the safety and toxicity risks related to nanomaterials or nanotechnologies. Various studies are being carried out to identify the possible health hazard and toxicity effects of the nanomaterials.[42,43]Therefore, further research should be directed to provide reliable scientific reports to the consumers regarding the benefits, toxicity, and related safety/regulatory perspectives of nanotechnology-based cosmetics products for the actual realization of the scientific inventions.[2]

Acknowledgements:
I would like to thank my teacher, Mr./Ms.__________ for assisting me with their valuable insights for me to complete this paper.

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