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The Analysis of Toxicity and Safety of Nano Particles Applied in Sunscreen

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Abstract. Nano particles (NPs) with size from 1 to 100nm had been developed fast from 1950s. They are highly stable, hydrophilic and biocompatible. These NPs possess transparency and UV-absorbing properties, making them effective as protective filters. Different kinds of NPs had been applied in sunscreen. However, due to the size of metal NPs, they can easily pass-through human skin. After that, these NPs could enter the organs and the circulation system in human body. For the biochemical reactions with nano-catalysts, the adsorption and the whole reaction rate could be increased greatly due to the high ratio of surface area to volume of NPs. The evaluation of the safety of NPs is still essential to prevent any potential issues. They could cause damage to the skin or even organs in human body. The toxicity and safety of NPs including Ag, TiO2, ZnO and other ingredients are analysed, and further research are needed to be carried out to modify the recipe of sunscreen.

Keywords: NPs, sunscreen, toxicity, safety.

1. Introduction

The study of NPs had increased quickly when Richard Feynman talked about 'There is plenty room at the bottom' in his lecture from 1950s [1]. NPs are the tiny particles with diameter ranged from 1 to 100nm. This kind of particles could be used as a special material in various areas such as pharmaceuticals, medical science, cosmetics and engineering, due to its unique properties.

One of the properties of NPs is the high ratio of surface area to volume. This increased their reactivities and interaction with other substances. One of the applications of this property of NPs is the sunscreens, which is used widely for protecting skin from the damage of sun light which can cause sunburn, photoaging, melanoma and skin cancers [2]. For the ingredients of sunscreen, many types of nano particles are applied, including organic and inorganic nano particles. The organic nano particles are used in small amount in sunscreen while in pharmaceuticals they are used more widely. The most common nano particles used in sunscreen are the metal nano particles, including Al, Ti, Au, Fe, Ag and Zn with zero carbon percentage. They are highly stable, hydrophilic and biocompatible. These nanoparticles possess transparency and UV-absorbing properties, making them effective as protective filters [3]. However, due to the size of metal NPs, they can easily pass-through human skin. After that, these NPs could enter the organs and the circulation system in human body. For the biochemical reactions with nano-catalysts, the adsorption and the whole reaction rate could be increased greatly due to the high ratio of surface area to volume of NPs. The evaluation of the safety of NPs is still essential to prevent any potential issues. The toxicity of the metal NPs is mostly concerned because of its high penetrating ability to human skin. They could cause damage to the skin or even organs in human body.

When exposure to nano particles, people would meet risk of health problem due to the toxicity if these particles. There are many reported indicated that the ionised metal nano particles are able to penetrate the skin easily. For example, the Ni nano particles could be ionised and dissolved by sweat at the surface of skin. Then they pass through the skin and cause immune issues. It is also shown that the Ni salt-water solution could penetrate the stratum corneum and the penetrating ability of nano particles of Ni is higher than other metal nano particles, which means it could be potentially risky to human health [4]. In sunscreen, TiO_2 and ZnO are the nanoparticles that are used most commonly,

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they usually appear in mixture. But they are also potentially dangerous to human health. Although it is not clear that the strength of toxicity correlated to the size or shape or other factors, this kind of risk should not be ignored [5]. Since SCCS had said the concentration of ZnO used in sunscreen could not exceed 25% to ensure no toxicity to human body. And TiO_2 was evaluated by SCCS in the similar way [6]. So, for the safety of people, further evaluation of nano particles of TiO_2 and ZnO is needed to clarify the uncertain variables that influences the toxicity of these particles.

Metal nano particles, including Ni, TiO_2, ZnO and Ag showed above, can be beneficial to humans but contain potential risks, especially toxicity. This paper aims to discuss the toxicity of these nano particles comprehensively and evaluate the risk of these particles in sunscreen in past papers and articles to help find corresponding strategies to ensure they can be utilised properly and safely for people.

2. Toxicity of Metal NPs in sunscreen

2.1. Ag NPs

Ag are commonly used as anti-bacterial agents in medical treatment. These particles can cause genotoxicity, cytotoxicity or even cell death after penetrating skin [7]. In the process of using sunscreen containing Ag NPs, this kind of particles would enter human body through breath and skin penetration. Some studies indicated that the nano particles of Ag could exist in body by ingestion and halation. Then they can be transferred to other tissues and organs through body circulation system. Lung damage, oxidative stress, DNA damage, apoptosis and chromosome aberration can be caused by the exposure to Ag nano particles in sunscreen. It is possible for the Ag nanoparticles to appear toxicity effects by exerting reactivity [1]. To figure out the effects of Ag nano particles, porcine skin, human skin samples or 3D models were used. Among the samples used in researches, porcine skin is an excellent model because the skin thickness and adsorption rate are very similar to human skin (**Figure 1.**) [8].

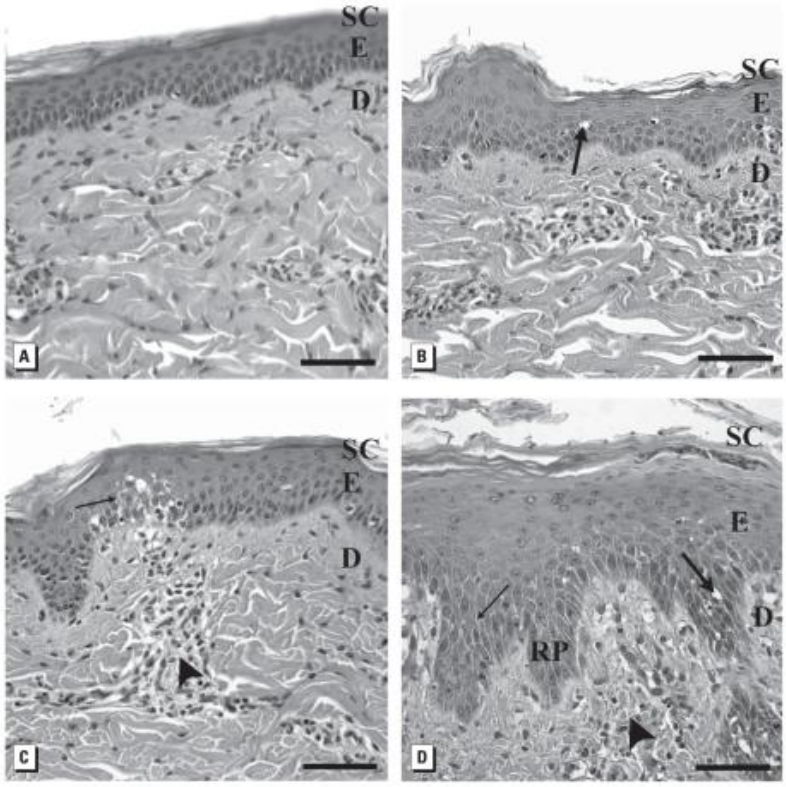

Figure 1. 20-nm washed silver nano-particles on porcine skin (haematoxylin and eosin staining). (*A*) Untreated control. Skin exposed to 0.34 μg/mL (*B*) 3.4 μg/mL (*C*) and 34 μg/mL (*D*) 20-nm washed Ag-nps in lighting images [8]

In 2016, the Vivek A. M group reported that Ag NPs would be less dangerous to human safety with equivalent human skin model experiments [9]. They found that Ag NPs would not be irritative to human skin with preparation of solutions and NPs, epidermal organ test and data analysis. Because the adsorption of Ag NPs by human body is limitative, which means the amount of Ag NPs penetrating human skin is too small to cause damage whether it is toxic or not. Apart from the risky properties and amount of Ag NPs, the size of them should also be considered. In 2023, the Tamanna J group reported that Ag NPs with size ranged from 10nm to 100 nm, can penetrate human skin, which means it is easier for Ag NPs to enter human body.

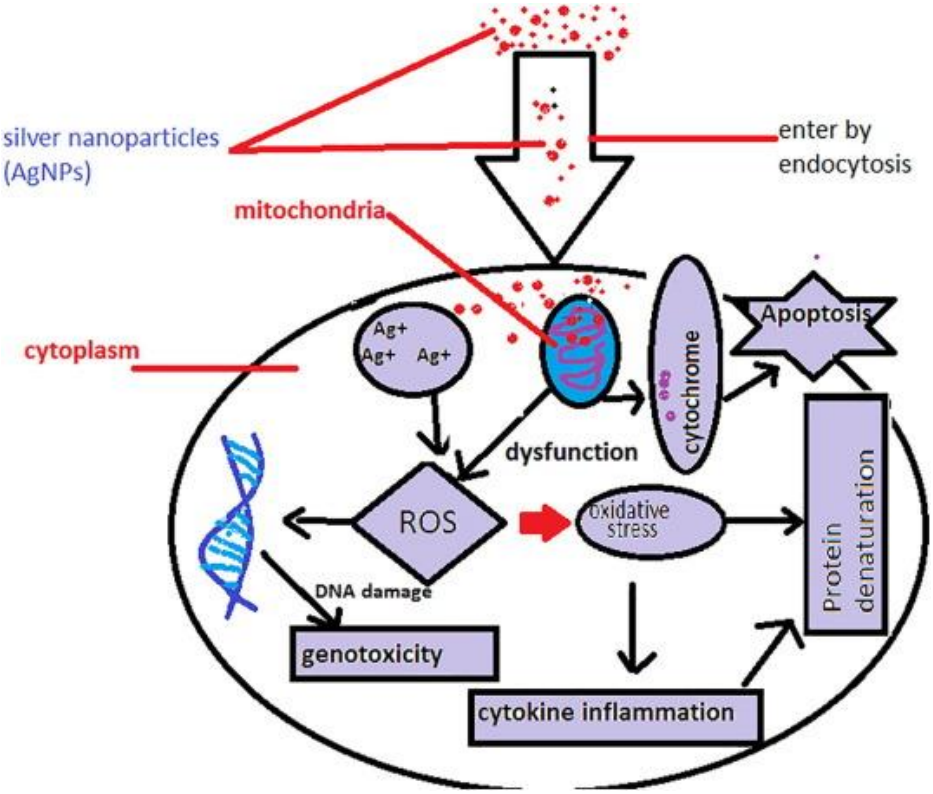

Figure 2. Possible Ag nano-particles in cell: consumption & cytotoxicity. [7]

Compared with small-sized Ag NPs, the larger ones could be less toxic because it has less surface area to mass ratio. Thus, the cytotoxicity of Ag nano particles with size greater than 10 nm could appear when they interact with macrophages (**Figure 2.**) [7]. The discussion of the toxicity or safety of Ag NPs is always controversial, but solutions and strategies to resolve this problem should also be considered. And more research is needed to help understanding the toxicity of Ag NPs.

2.2. TiO2 NPs

Compared to Ag NPs, TiO_2 NPs are used more commonly in sunscreen, since it can protect skin from the damage of UV lights in sunscreen. TiO_2 NPs were classified by IARC, which is International Agency for Research on Cancer, as group 2B carcinogen, since it was shown that the TiO_2 NPs could lead to respiratory tract cancer in rats in experiment [5]. For the control and safety assessment of TiO_2 NPs, the European Union legislated that the concentration of titanium dioxide and zinc oxide NPs should not exceed 25% [5]. TiO_2 NPs could be harmful to human body if they are used in sunscreens because TiO_2 NPs can penetrate skin or be inhaled in. In 2010, the Nakissa S group indicated that the TiO_2 NPs could not penetrate human skin because it was found that the intact epidermis was fine [6]. For further study, in 2011 the Smijs TG group reported that long time period of exposure to TiO_2 NPs could also increase their toxicity by 25%. The strength of toxicity of TiO_2 NPs were shown to be correlated with their size, shape and surface chemistry. The TiO_2 NPs toxicity was also associated with their photocatalytic activity because they would produce superoxide anion radicals and hydroxyl radials when they were present in light (**Figure 3.**). These radicals could be directly measured by ESR

(Electron Spin Resonance) or indirectly tested through light-induced cell damage. The results of these tests showed that rutile-type TiO_2 NPs had highest photocatalytic activity, which meant that this type of TiO_2 NPs could produce hydroxyl radials in higher cytotoxicity [10].

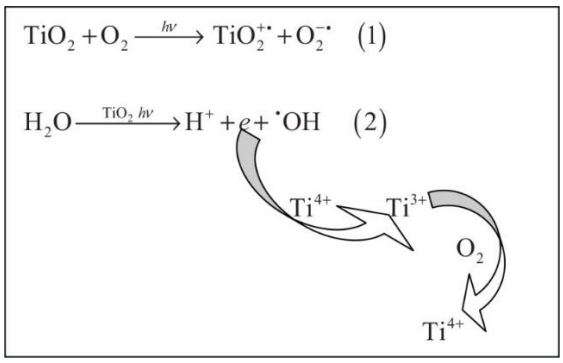

Figure 3. Hydroxyl and superoxide anion radials production mechanism [10]

In 2016 the Vivek A. M group found that the TiO_2 NPs with diameters of 20nm stayed in stratum corneum, which meant that the capability of these kind of nano particles to penetrate skin beyond the stratum corneum was too weak to cause vitro dermal irritancy [9].

2.3. ZnO

The ZnO NPs is another kind of ingredient commonly used in sunscreen NPs. In 2012 the P. Surekha group carried out tests about the skin toxicity of ZnO NPs on rats with different doses of ZnO NPs (**Figure 4.**). [11]

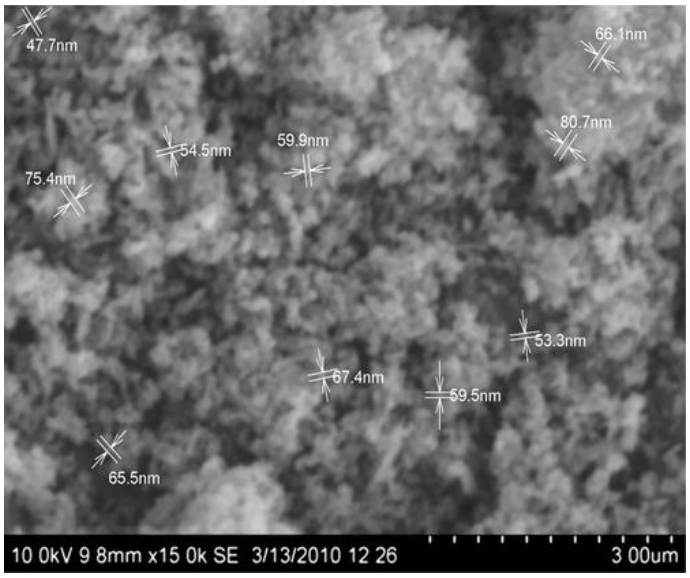

Figure 4. Nano ZnO [11]

For the results, analysis with clinical biochemistry, hematology and pathology were applied. They discovered that the toxicity of ZnO NPs correlates with the time length. For 28 day's tests, the ZnO NPs could penetrate the skin and cause oxidative stress. Then the ROS produced would make collagen oxidate and degrade. The decrease of collagen could lead to wrinkles [11]. However, there was still opposite viewpoint in the discussion of safety of ZnO NPs. In 2017, the Choi J group reported that there were no corrosive and sensitive properties on these nano particles. In this article, human skin models were used as subject and tested with ZnO NPs. The 3-(4, 5-dimethylthiazol-2-yl)-2.5-diphenyltetrazolium bromide method was the method to measure the viability of the cell. The cell viability could help to identify the corrosion and irritation of the skin according to the pre-determined threshold. But the results showed that ZnO NPs did not have corrosion and sensitivity [12]. This research indicated that, there were differences between in vitro tests and real vivo tests. In the same

year, the Ge W group that the exposure to ZnO NPs would cause DNA damage and induction of HFSCs death. ZnO NPs which were unchanged, in bulk and ionized were tested on rats. They also found that the exposure to ZnO NPs would disturb the genes related to apoptosis of HGSCs, cell communication and differentiation [13]. Similar to TiO_2 NPs, the toxicity and safety problems of ZnO NPs are also complicated and confusing.

2.4. Others

Apart from the NPs used in sunscreen above, other NPs are also considered about the toxicity and safety in sunscreen. In 2020, the organic SiO_2 NPs with biocompatibility and biodegradability were proposed by the Park Y-H group to be used in sunscreen. And its toxicity was tested for on porcine skin. The results showed that the nano particles of SiO_2 NPs would not penetrate skin or cause any damage to the skin (**Figure 5.**) [14].

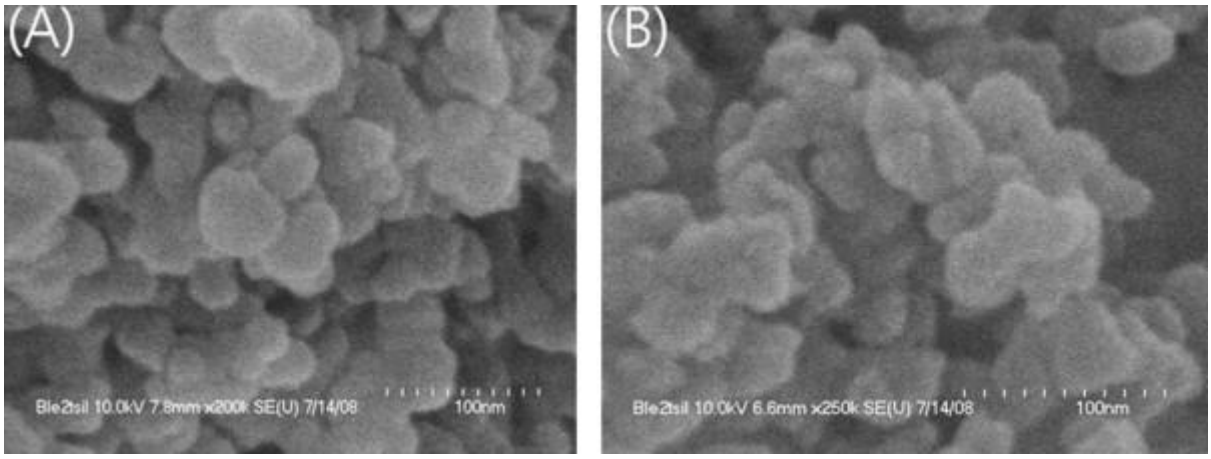

Figure 5. SEM images in (A) 10-20nm-sized nano-silica particles and (B) 7 nm-sized particles [14]

The Au NPs were also used in sunscreen for many years. The preparation, scanning (using SEM and TEM) and analysis of Au NPs were carried out. The stability of these nano particles was shown in the result. Just the nano particles of Au with diameter smaller than 36nm could penetrate human skin but they did not show any harmful effects. But further research was considered to be carried out, because the Au NPs were separated from the sunscreen in this test. So, the further research should include the whole sunscreen to test the toxicity and safety for Au nano particles [15]. In sunscreen, the Ni NPs are not commonly used but it has been applied in sunscreen. The safety test of Ni NPs was carried out for 16 to 24 hours, and no irritation was observed [4].

3. Conclusion

In summary, due to the size of metal NPs, they can easily pass-through human skin. After that, these NPs could enter the organs and the circulation system in human body. For the biochemical reactions with nano-catalysts, the adsorption and the whole reaction rate could be increased greatly due to the high ratio of surface area to volume of NPs. The evaluation of the safety of NPs is still essential to prevent any potential issues. They could cause damage to the skin or even organs in human body. The reported toxicity of Ag, TiO2, ZnO and other NPs used in sunscreen is controversial and complicated. Further research is needed to to investigate potential and definite properties of these NPs to help modify the recipe of sunscreen.

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