As an inorganic sunscreen material, nano-titanium dioxide (nano-TiO$_2$) owns broad prospects in sunscreen cosmetics for its small size, non-toxicity, strong covering ability, UV absorption and scattering abilities, etc. Nano-TiO$_2$ has high photocatalytic activity, so it will go through a series of complex chemical reactions under light irradiation and cause damage to its surrounding agents. In addition, it is hard to disperse in various aqueous and non-aqueous mediums due to its high surface energy and hydrophobic property. In order to apply nano-TiO$_2$ to cosmetics effectively and safely, its surface modification is necessary. This paper reviews nano-TiO$_2$'s preparation, modification, and its application in sunscreen cosmetics.

Keywords nano-TiO$_2$, preparation, surface modification, application

Preparation of nano-TiO$_2$

Nano-TiO$_2$ can be prepared by gas, liquid, and solid phase methods. At present, gas and liquid phase methods are mainly employed for preparation of nano-TiO$_2$. Nano-TiO$_2$ prepared by the gas phase method possesses several advantages such as small particle size and good dispersion, but it suffers from large energy consumption and high cost. The liquid phase method is simple, easy to operate and inexpensive, but the morphology of TiO$_2$ is not easy to control.

Gas phase method

Physical vapor deposition method

Firstly, raw materials will be converted into gas or plasma by evaporation, ionization, or sputtering. Then, the gas or plasma will be quenched to form nanoparticles. Nano-TiO$_2$ has characteristics of high purity, uniform distribution, small particle size, and good dispersity. Its particle size and distribution can be controlled by changing gas pressure and heating temperature. It was reported that single-crystal TiO$_2$ nanowires were synthesized by a physical vapor deposition (PVD) method. The thickness of nano-film by PVD is uniform and easy-to-control; moreover, its light transmittance and glossiness are also satisfactory. However, the PVD method requires deposition in a vacuum environment and the devices are more expensive.

Chemical vapor deposition method

Nano-powder is prepared using chemical vapor deposition (CVD) methods using the vapor of volatile compounds as reaction reactants, then reacts and condenses rapidly in the protective gas to get required materials. The fine spherical nano-TiO$_2$ particles prepared by CVD have characters of small size, high chemical activity, well dispersion, good visible light transmittance, strong UV absorb and shielding ability. The CVD process is easy to enlarge and able to use in-
Minireview

Fang et al.

Hydrolysis of titanium alkoxide is a kind of sol-gel method using titanium alkoxide as a raw material. The raw material goes through hydrolysis and polycondensation to obtain sol, then further polycondensation to get gel. The gel is dried and calcined to obtain nano-TiO₂. Music et al. explored the sol-gel process of a ternary system of tetraisopropanolorthotitanate (TTIP)/isopropanol (i-PrOH) concentrated nitric acid. The results presented that adding polyethylene glycol (PEG) into the system could stabilize the sol and avoided the sintering of the particles during the calcination process. So et al. analyzed the effect of the molar ratio of nitric acid/TTIP on the crystalline phase of the gel. The results indicated that the product was amorphous when nitric acid was not added. When mole ratio of nitric acid/TTIP was low, the product was anatase TiO₂. With the increase of the molar ratio, rutile TiO₂ appeared and its content increased gradually. Vorkapic et al. found that different types of alkoxide only affected the size of primary particles. The sol particles were the aggregates of the primary particles, the size of which was mainly controlled by the process of peptization. The most important factor was peptization temperature. Huang et al. prepared TiO₂/ethyleneglycol slurry at room temperature by controlling the water and metal alkoxide molar ratio from 2 to 4 and the hydrolysis rate of titanium glycol. TEM analysis showed that nano-TiO₂ particles with a particle size of 5—10 nm were homogeneously dispersed in ethylene glycol. Chen et al. used butyl titanate as raw materials for preparation of nano-TiO₂, and they used XRD to analyze grain size of colloidal TiO₂ which was calcined at different temperatures. The results showed that TiO₂ particles own anatase structures at calcined temperature of 473 K and its particle size was about 5.5 nm. When calcined temperature was higher than 673 K, the particle size of TiO₂ increased rapidly, and mix-crystal structure of anatase and rutile was formed. TiO₂ particles were completely transformed into rutile TiO₂ at 973 K. Gopalarathinam et al. hydrolyzed titanium alkoxide to form sol under acidic conditions and then heated at different heating rates. At atmospheric pressure and a heating temperature below 100 °C, anatase nano-TiO₂ with particle size of 50—100 nm was synthesized.

The titanium alkoxide hydrolysis method owns several advantages. Firstly, nano-TiO₂ with specific pore structures can be formed by adding an appropriate amount of surfactants or template agents that will make nanoparticles grow in a particular direction. Secondly, the purity of raw materials is high and impurity ions are not introduced in the whole process. Thirdly, reaction conditions are relatively mild. Finally, high purity, small particle size, and narrow size distribution nano-TiO₂ can be obtained by controlling process conditions. However, the method suffers from high cost for raw materials. Furthermore, the gel will go through volume shrinkage in the drying and calcination process, causing agglomeration of nano-TiO₂ particles.

Considering grain size distribution, cost, crystal form and other factors, the liquid phase method is mainly employed to prepare nano-TiO₂ for cosmetics.

Application of nano-TiO₂ in cosmetics

From the point of view of developmental trend of sunscreen cosmetic, there are two types of sunscreens with great potential including inorganic and bionic sunscreens. It is difficult to promote bionic sunscreen for its high cost presently. However, inorganic sunscreen is more affordable possessing superior sun-protect performances and great market potential. Nano-TiO₂ has the best potential among inorganic sunscreens.

Select nano-TiO₂ for cosmetics

Select crystal structures

Commonly used TiO₂ is a square crystal including three crystal forms: anatase, rutile, and brookite. Rutile TiO₂ could be obtained by...
As nanoparticles have a large specific surface area, the surface energy between particles, such as electrostatic attraction force, van der Waals ability, scattering ability, and weak absorption capacity. In the presence of oxygen, the photoactivity of rutile TiO$_2$ is weaker than that of anatase TiO$_2$.[30,31] Generally, the effect of rutile TiO$_2$ shielding UV is more significant than anatase TiO$_2$, so the mainly used nano-TiO$_2$ in cosmetics is rutile TiO$_2$.

Select particle sizes

The UV resist ability of nano-TiO$_2$ is closely related to its particle size. When the particle size is equal to or less than half wavelength of incident light, the amount of light reflection and scattering reach its maximum. Hence, the shielding effect is the best. Since the UV ray’s wavelength is between 190 and 400 nm, the particle size of nano-TiO$_2$ should be no more than 200 nm, preferably, no more than 100 nm. In addition, particles that are too small are easy to agglomerate, which is not conducive to its dispersion. Tiny particles are also easy to plug the pores on human skin and then affect skin breathable and sweat discharge. The particle size is controlled between 30 and 100 nm. When the particle size is between this range, the UV shielding effect is the best and the visible light can also be transmitted, which bring out more natural beauty of the skin.[32-35]

Select preparation methods

Wet and dry methods are performed to prepare nano-TiO$_2$. The rutile TiO$_2$ synthesized by wet methods owns better dispersibility, but it suffers from impure crystal form and high photocatalytic activity. However, rutile TiO$_2$ obtained by dry methods possesses higher purity and less photocatalytic activity, but its dispersion is poor.[36] Nowadays, the liquid-based methods are widely employed for preparation of nano-TiO$_2$ in cosmetics considering crystal form, particle size distribution, cost, and other factors. TiOSO$_4$ or TiCl$_4$ is used as a raw material to prepare a solution with a certain concentration, then alkaline solution is added to obtain TiO$_2$ hydrate by hydrolysis. After depolymerization, washing, drying and calcinations, nano-TiO$_2$ can be produced. TiO$_2$ with different particle size and crystal form can be obtained by changing calcination temperatures.[12]

Sun protection mechanism of nano-TiO$_2$

Nano-TiO$_2$ protects the skin by reflecting and scattering UV radiation.[37,38] The surface effect of nano-TiO$_2$ can cause surface atoms of nanoparticles to deform, changes in electron spin conformation and electron spectroscopy, and new photochemical properties. The quantum size effect of nano powders results in “blue-shift phenomenon” at the absorption of a certain wavelength light and “broadening phenomenon” at the absorption of various wavelengths light, and a significant enhancement of the absorption effect of UV light.[39] The size of nano-TiO$_2$ particle is less than 100 nm, so it can effectively absorb and scatter UV light. When UV light irradiates nano-TiO$_2$ particles, the electrons of the nanoparticles are forced to vibrate (the frequency of the vibration is the same as that of the incident light). The electrons become secondary wave source, and emit electromagnetic waves in all directions, and that is the scattering of ultraviolet light. In addition, TiO$_2$ is an $n$-type semiconductor. Anatase TiO$_2$’s band gap width is 3.2 eV, while rutile TiO$_2$’s band gap width is 3.0 eV. The electrons on the valence band can absorb UV light, be excited to the conduction band, and generate electron-hole pairs at the same time. That is why TiO$_2$ can absorb UV light.[32,40-41]

Problems of nano-TiO$_2$ as sunscreen in cosmetic

Aggregation problems

Smaller the size of nano-TiO$_2$ particles, stronger the interactions between particles, such as electostatic attraction force, van der Waals force and capillary force, which will cause aggregation of particles. As nanoparticles have a large specific surface area, the surface energy is also very large so the system will be in a relatively unstable thermodynamic state. Particles will aggregate to reduce free enthalpy of the system, which is an unavoidable spontaneous process. The instability of nano-TiO$_2$ limits its application in cosmetics greatly.

Photocatalytic activities

Nano-TiO$_2$ has excellent photocatalytic activities. Under light irradiation, it can catalyze some chemical reactions. Nano-TiO$_2$ directly used in cosmetics will decompose fragrances/nutrients and oxidize grease in cosmetics, causing deterioration of cosmetics. In addition, nano-TiO$_2$ may damage human skin. In clinical trials, TiO$_2$ can cause severe human skin tissue necrosis and non-specific dermatitis, which can lead to deposition of melanin in the skin.[6,44]

Hydrophilic and oleophobic properties

As a kind of inorganic additive, nano-TiO$_2$ is difficult to disperse in an organic medium, which limits its application in cosmetics. It is necessary to modify nano-TiO$_2$ and increase its compatibility with organic medium.[44-47]

Surface modification of nano-TiO$_2$

In view of the problems existing in the application of nano-TiO$_2$ in sunscreen products, researchers hope to improve its safety and dispersity by applying the surface modifications. The surface modified methods of nano-TiO$_2$ include inorganic and organic treatments.[48-54]

Inorganic treatments

Inorganic treatment of nano-TiO$_2$ is depositing inorganic compounds or metals on the TiO$_2$ particles (by certain methods) to form a covering film or build a core-shell structure particle. Then the covered particles will be treated by washing, dehydrating, drying, and calcining, so that the covering film could firmly attach to the particle surface. Many inorganic treating agents are used to improve surface properties of nano-TiO$_2$ particles such as oxides of aluminum, zirconium, silicon, zinc, chrome, tin, etc. By coating the nanoparticles with inorganic materials, less UV irradiation is able to reach TiO$_2$, which leads to less UV light absorption for TiO$_2$ particles. Meanwhile, this treatment can also change the crystal structure of the particles’ surface layerand, consequently, change the particles’ electrochemical behavior. The covering materials can be used as an effective barrier to restrain the photocatalytic activity of the TiO$_2$, increase the dispersion ability of the nano-TiO$_2$ particles, and reduce direct contact between skin and harmful groups on the surface of the particle.[55] In inorganic treatment, if only one kind of coating agent is used, the modification effect is limited. For example, performance of nano-TiO$_2$ coated with aluminum or silicon alone is not as good as co-coated with aluminum and silicon.[56] Wei et al.[57] used sol-gel method to incorporate silver into TiO$_2$ and used silver-loaded TiO$_2$ as raw material to prepare antimicrobial sunscreen cream, then they have studied the effect of silver-loaded TiO$_2$ on sun protection performance, color stability and antibacterial property of the cream. The results showed that silver-loaded in TiO$_2$ can promote the transformation of crystal structure from anatase to rutile and improve the sun protection effect. When silver-loaded TiO$_2$ was used as a skin cream or sunscreen, the high silver content significantly affects the color of the product. In addition, silver-loaded TiO$_2$ can fully meet the cosmetics’ antibacterial requirement.[58,59]

Organic treatments

Nano-TiO$_2$ with hydrophilic surface can be obtained by inorganic treatments and it is suitable for using in polar solvents. However, hydrophilic particles are difficult to disperse in organic systems such as oily cosmetics and they can’t demonstrate special functions of nano-TiO$_2$. In order to improve compatibility and dispersibility of nano-TiO$_2$ in organic systems, organic surface treatment can be carried out. Organic treatment agents included surfactants, coupling
agents, and organic polymers.[69,60]

Surfactants
Surfactants include anionic, cationic, and nonionic surfactants. One end of surfactant molecules is a long-chain alkyl group, and another end is a carboxyl group, ether group, amino group, or other polar groups. Surfactants can be physically or chemically absorbed on the surface of nano-TiO₂ particles using the polar groups.[33,55]

Zou et al.[64] prepared stearic acid surface modified nanoparticles in a mixed solvent by a sol-gel method, which were characterized by FT-IR, XPS, XRD, and TEM. They confirmed organic coating on the surface of the nanoparticles and carbonyl groups in the stearic acid molecule bounded to inorganic core in bidentate coordination. Li et al.[62] synthesized oleic acid-modified nanoparticles by surface modification method. The surface modified nanoparticles were characterized by IR, TEM and XPS, and the effect of oleic acid concentration on the surface coverage and the dispersibility of modified nanoparticles in oil was further investigated. The results demonstrated that after the surface modification by oleic acid, the nano-TiO₂ with well dispersion performance in the oil phase was successfully prepared. Jiang et al.[63] used stearic acid and adipic acid as a modification agent; they modified the surface of nanoparticles by a sol-gel supercritical drying method, and well solved the dispersion problem of nanoparticles in organic medium. It was found that the growth and aggregation of nanoparticles were controlled because the presence of the surface modification layer. Zhao et al.[64] successfully synthesized the surfactant coated TiO₂ particles by hydrolyzing titanate in the water center of W/O type micro emulsion, which was comprised of water/Span-80 (or DBS) or n-amyl alcohol/cyclohexane. Li et al.[65,66] modified nanoparticles using organic silanes, titanate coupling agents, sodium dodecyl benzene sulfonate, and sodium laurate. In terms of the lipophilic degree of nanoparticles, they found that the best surface treatment agent was sodium laurate. They discussed the mechanism of nano surface modification and the optimization of modification process conditions. The change of the bonding state and particle size of nanoparticles before and after modification was also studied. Nussbaumer et al.[67] selected dodecyl benzene sulfonic acid as an organic modifying agent for surface modification of rutile nano-TiO₂. The resulting product was almost transparent in toluene, but it could absorb ultraviolet light over a wide range of wavelengths.[25]

Coupling agents
Coupling agents are substances with amphiphilic structures, and their functional groups can react with active groups on the surface of nano powders to form strong chemical bonds. Other functional groups can interact with molecules of organic polymers to cause chemical reactions or physical entanglements. As a result, nano-TiO₂ particles and organic media produce a special function molecular bridges that improve comprehensive performances of nanocomposites.[23,68,69] The coupling agents are involved in silicates, titanates, aluminates, etc..

Li et al.[70] pre-treated nano-TiO₂ particles with butyl titanate firstly, and then modified them using methyl methacrylate (MMA) as a coupling agent. The results indicated that the reaction between butyl titanate and TiO₂ surface hydroxyl groups resulted in the formation of crosslinking reactions on the surface of the particles. The further reaction of crosslinking reactions with methyl methacrylate caused the formation of polymethylmethacrylate (PMMA) and the PMMA uniformly coating on the surface of TiO₂ nanoparticles. The nanoparticles modified by polymerization own good dispersibility in toluene. Deuss et al.[71] utilized two kinds of organosiloxanes for dry surface treatment of nanosized TiO₂ (P25), and Kerner et al.[72] treated nano TiO₂ with amino-containing silanes. Their results showed that the treated nanopowders could be well dispersed in hydrophilic and lipophilic medium.[73,74]

In addition, other literatures presented that nano-TiO₂ composite particles with uniform dispersion, high stability and good UV protection could be obtained by coupling agent treatment.[15,56]

Polymer coating method
The van der Waals force between particles can be reduced by coating polymers on the surface of TiO₂. Moreover, a new repulsion force, which is steric resistance, is produced. It is helpful to enhance the compatibility between nano-TiO₂ composites and organic matrices and improve the nano-TiO₂ dispersibility in organic medium. Polymer coating methods include a pretreatment method and a direct coating method.[77]

Due to the presence of free radicals and positive/negative ions on the surface of TiO₂, the direct coating method can directly lead to monomer polymerization. As to the pretreatment method, it is difficult for organic monomers and polymers to be adsorbed on the surface of particles due to the strong polarity on the surface of TiO₂, resulting in low treatment efficiencies. Pre-treatment with silane coupling agents, surfactants, polymers, and so on, is usually performed firstly to reduce surface activity, then followed by polymer coating modification on the surface of TiO₂.[77,78]

Zhang et al.[79] prepared TiO₂ coated with polymethylmethacrylate (PMMA) using in-situ emulsion polymerization. They found that nano-TiO₂ did not inhibit the polymerization of methyl methacrylate. The results suggested that the coating of PMMA on the surface of nano-TiO₂ was mainly covered physically, while chemical coating was little. Tan et al.[80] used sodium dodecyl sulfate for pre-modification of TiO₂ particles, and then the pre-modified particles were employed as nuclei. Methyl methacrylate and styrene were used as monomers to coat TiO₂ by the polymerization method to obtain TiO₂-polymer compounds encapsulated particles with good surface coating properties.[77] Xu et al.[81] used toluene 2,4-diisocyanate (TDI) as wall materials by the interface polymerization method under different conditions to prepare a series of TiO₂ polypurea microcapsules. It was found that the density and hydrophilicity of polypurea microcapsules decreased greatly, and its affinity with ethanol was greatly improved.

Conclusions
Nano-TiO₂ has received the favor of sunscreen cosmetics producers for its unique properties of scattering and reflection of UV. Though preparation and modification of nano-TiO₂ is successful, its theoretical and application is not satisfactory. Therefore, the industrial application of nano-TiO₂ in sunscreen cosmetics is still limited.[56] How to ensure the strong absorption UV property of nano-TiO₂, weaken or eliminate its photocatalytic activity, and improve its dispersibility in cosmetics, is an urgent problem that needs to be solved in the future.

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