Research and Application of Silane Coupling Agents on Metal Oxide Nanoparticles Surfaces

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Abstract. Metal oxide nanoparticles (MONPs) have garnered significant attention due to their unique nanoscale properties, such as the small size effect, quantum size effect, and photocatalytic activity. These nanoparticles are widely applied in fields such as catalysis, environmental management, energy storage, and antimicrobial materials. However, unmodified MONPs often face challenges related to high surface energy, aggregation, and instability. To address these issues, silane coupling agents (SCAs) have been employed to modify MONPs, enhancing their stability, mechanical properties, and hydrophobicity. This paper examines the modification mechanisms of MONPs using SCAs, focusing on the structure and functionality of common agents such as APTES, GPTMS, and MPS. The advantages of these modified MONPs in various applications are explored, including their role in creating superhydrophobic surfaces, improving photocatalytic performance, and forming antimicrobial and self-cleaning composite materials. Despite the promising benefits, challenges in scaling up production, improving efficiency, and developing environmentally friendly silane agents remain. Future research should focus on addressing these limitations to fully realize the potential of SCA-modified MONPs in industrial and environmental applications.

Keywords: MONPs, silane coupling agents, modified, hydrophobic.

1. Introduction

In recent years, the development of micro-nanomaterials has led to a growing interest in metal oxide nanoparticles (MONPs). MONPs exhibit unique characteristics, such as the small size effect, quantum size effect, and quantum tunneling effect commonly seen in nanoscale materials [1-4]. Additionally, many metal oxides possess antibacterial properties by releasing cations [5-7], while some MONPs demonstrate photocatalytic activity and enhanced absorbance [2,8-10]. As a result, MONPs find applications in various fields, including catalysis, chemical batteries, environmental management, energy storage, and antimicrobial materials [1-2,4,11].

However, unmodified MONPs have high surface energy due to surface effects, and this energy can increase as particle size decreases, as seen in silver oxide nanoparticles (Ag_2O NPs) [12]. Consequently, many MONPs tend to aggregate, exhibit incompatibility with polymers, and show high reactivity and hydrophilicity. Silane coupling agents, first synthesized by Union Carbide and Dow Corning in the 1940s, were initially used as chemical surface treatment agents for glass fiber [13-15]. With further research advancements, various silane coupling agents have been synthesized and utilized as molecular bridges between inorganic and organic materials due to their bifunctional nature [13-16]. The hydrolysis of these agents produces silanol groups that bond with hydroxyl groups on the MONPs surface, forming -Si-O-MONPs structures [17], thereby improving the mechanical stability and electrical properties of the nanoparticles [16]. Moreover, certain silane coupling agents, such as 3-aminopropyltriethoxysilane (APTES, KH550), 3-glycidoxypropyltrimethoxysilane (GPTMS, KH560), and 3-methacryloyloxypropyltrimethoxysilane (MPS, KH570), exhibit hydrophobic properties [16,18]. These hydrophobic agents reduce the surface energy of MONPs [16,19], forming a cross-linked, hydrophobic protective layer [20-21], which stabilizes the hydrophobicity of the MONPs' surface [16-17].

This review will discuss the modification mechanisms of MONPs using silane coupling agents, the properties of the resulting coatings, and the potential applications of the modified materials.

2. Silane Coupling Agents

2.1. Principle of Silane Coupling Agents Modification

Silane coupling agents contain two distinct functional groups [13-16]. One end of the silane coupling agent features an organic functional group, which can vary based on the type of silane agent. For example, APTES contains an amino group, GPTMS has an epoxy group, and MPS possesses a methacryloyloxy group. These organic groups primarily bond with organic polymer substrates [21]. At the opposite end, the alkoxysilane group undergoes hydrolysis to form silanol groups. These silanol groups then dehydrate and bond with the hydroxyl groups present on the surface of the MONPs, resulting in the formation of -Si-O-MONPs structures [17], as shown in Figure 1.

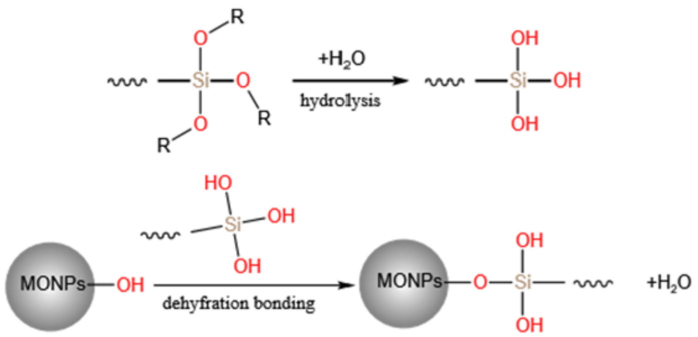

Fig. 1 The reactions that occur in the modification process of MONPs using silane coupling agents (Picture/image credit: Original)

Ultimately, various structures of the silane coupling agents modified MONPs are synthesized [17], Figure 2 shows the various structures of the silane coupling agents' modification of the MONPs.

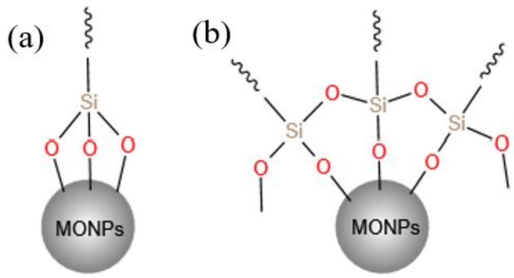

Fig. 2 the various structures of the silane coupling agents' modification of the MONPs (Picture/image credit: Original)

2.2. Structure of Silane Coupling Agents

The APTES is commonly used as surface treatment agent for inorganic materials and glass fibers. In addition, the amino group of the APTES can react with some resins to improve adhesive strength. The GPTMS is commonly used as adhesion promoter for various adhesives and filler. Furthermore, the GPTMS is good resistance to high temperatures and weathering. The MPS is primarily used to improve various physical properties of composite materials, such as mechanical stability, electrical properties and wet properties. Figure 3 shows 3 common hydrophobic silane agents.

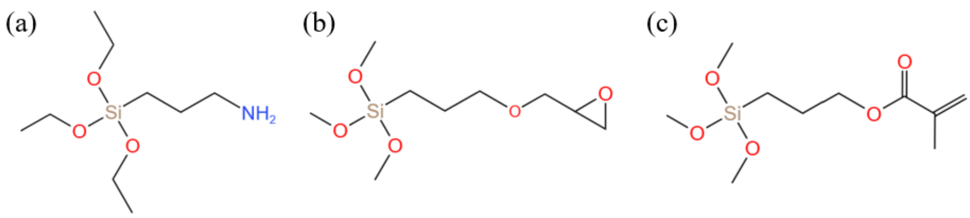

Fig. 3 Three common hydrophobic silane agents: (a)APTES. (b)GPTMS. (c)MPS (Picture/image credit: Original)

3. Application Effects of Different Silane Coupling Agents

3.1. APTES

Wang et al. [22] modified titanium dioxide (TiO_2) with APTES and coated the modified TiO_2 onto the surface of polyurethane foam (PU) using polydimethylsiloxane (PDMS) to create APTES-TiO_2@PDMS@PU. This modification transformed the material from being superhydrophilic (with a water contact angle (WCA) of approximately 0°) to superhydrophobic, exhibiting a WCA of 147.25±1.44°. Moreover, even after 5 minutes of water contact, the WCA of APTES-TiO_2@PDMS@PU remained above 140 °, as shown in Figure 4, indicating the material's excellent hydrophobic properties.

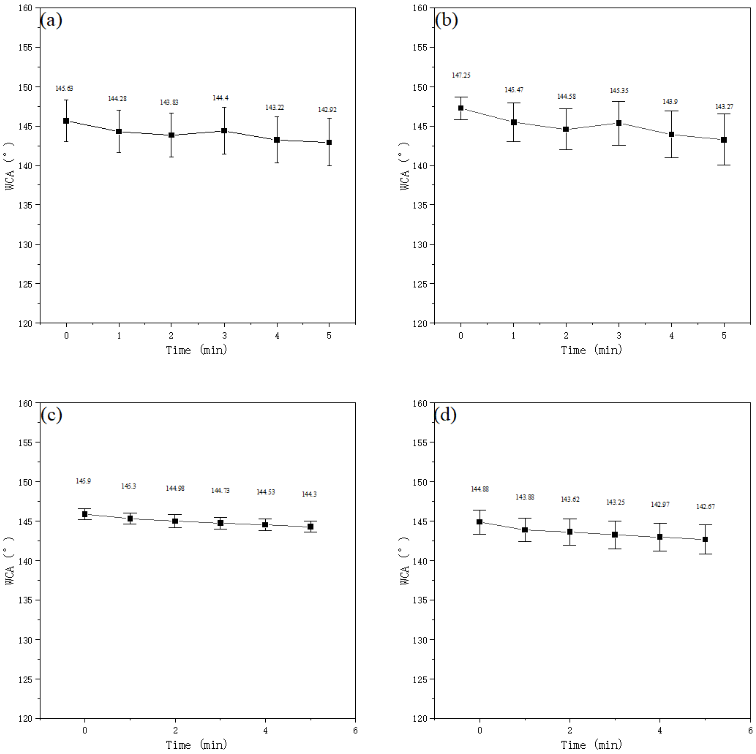

Fig. 4 Variation trend of the WCA of the APTES-TiO_2@PDMS@PU: (a)sample 1. (b)sample 2. (c)sample 3. (d)sample 4. (Picture/image credit: Original)

Teng et al. [23] modified TiO_2 NPs with APTES and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) and coated the modified TiO_2 NPs onto the surface of paper using epoxy resin (EP) as an adhesive to create a superhydrophobic coating. The coating exhibited a water contact angle (WCA) of 153±1.5° and a water sliding angle (WSA) of 3.5±0.5°. Additionally, the superhydrophobic coating demonstrated excellent mechanical stability, maintaining a WCA above 150° after being soaked in strong acid and strong base for 96 hours and stored at room temperature for six months. These results indicate that the superhydrophobic coating possesses durability and robust hydrophobic properties.

Zhang [24] modified zinc oxide microparticles (ZnO MPs) and zinc oxide nanoparticles (ZnO NPs) with APTES to synthesize APTES-ZnO MPs and APTES-ZnO NPs, achieving low surface energy, roughness, and excellent hydrophobicity, with WCAs exceeding 90°. Zhang further reduced the surface energy and utilized a micro-nano dual-structure to create stabilized antimicrobial superhydrophobic coatings. These coatings were applied to various substrates, producing superhydrophobic coating samples with WCAs exceeding 150°, ranging from 154.8° on PET to 162.4° on stainless steel. Moreover, after soaking the stainless-steel sample in pH=2 acid, pH=13 base, and 3.5 wt% NaCl for 24 hours, and subjecting it to UV irradiation for 144 hours, the WCA remained above 150°, and the WSA stayed below 15°, as shown in Figure 5. This indicates that the superhydrophobic coatings possess excellent chemical stability. Zhang [24] also noted that these coatings exhibit strong mechanical stability and self-cleaning properties.

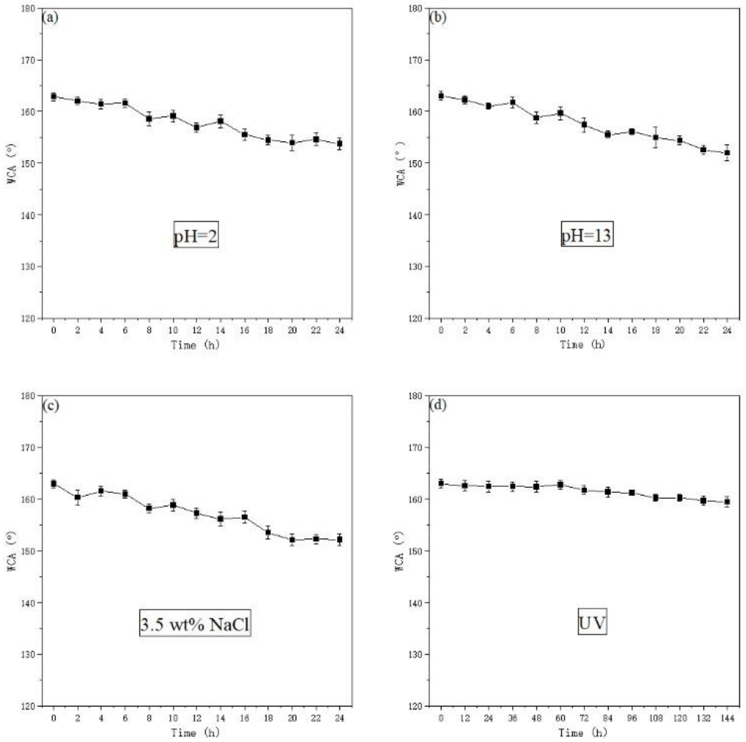

Fig. 5 The stainless-steel sample's chemical stability test: (a)pH=2 acid soak test, (b)pH=13 base soak test, (c)3.5 wt% NaCl soak test, (d)UV irradiate test. (Picture/image credit: Original)

3.2. GPTMS

Safdar et al. [25] modified TiO_2 NPs with varying volumes of GPTMS and octadecyltrimethoxysilane (ODS), producing hydrophobic TiO_2 NPs. The optimal superhydrophobicity, with a WCA of 156.69°, was achieved using 4% ODS and 6% GPTMS, while the WCA without GPTMS was only 136°. Additionally, GPTMS enhanced the durability of the TiO2 NPs by stabilizing their properties under UV irradiation, maintaining antimicrobial activity, and imparting self-cleaning properties. Safdar et al. [25] also noted that this modification technique could be applied to various surface engineering applications.

Rivero et al. [26] modified TiO_2 NPs using GPTMS and methyltriethoxysilane (MTEOS), resulting in GPTMS-MTEOS-TiO_2 NPs with mechanical stability and hydrophobicity, demonstrating WCAs of 98.61° and 98.51° after six soaking cycles, confirming the durability of the coating. To further enhance hydrophobicity, Rivero et al. [26] introduced POTS, increasing the WCA to 107.11°, while adding PFAS boosted the WCA to 120.76°. Electrochemical impedance spectroscopy and potentiodynamic polarization tests showed that the modification improved the corrosion resistance of TiO_2 NPs.

3.3. MPS

Zhang et al. [16] prepared three distinct ZnO nanostructures through electrochemical and hydrothermal growth methods, including an electrochemical ITO sample, an electrochemical powder sample, and a hydrothermal powder sample. They modified these nanostructures using MPS (3-Methacryloyloxypropyltrimethoxysilane) to enhance their hydrophobic properties. The WCA of the electrochemical ITO sample increased from 26.8° to 126.9°, indicating hydrophobicity, while the electrochemical powder sample's WCA rose from 0° to 154.2°, achieving superhydrophobicity. Similarly, the hydrothermal powder sample's WCA increased from 0° to 129.7°, also indicating hydrophobicity.

Li [27] further modified TiO_2 NPs with varying mass fractions of MPS and applied them to PET fiber filter media, resulting in superhydrophobic coatings. The WCA reached a maximum of 156.29° at a 1% MPS mass fraction, as shown in Figure 6, while coatings using unmodified TiO_2 NPs remained superhydrophilic, with a WCA of approximately 0°. Additionally, the superhydrophobic coatings retained WCAs above 150° even after being soaked in pH 1 acid and pH 13 base for 30 hours and enduring 50 abrasion cycles, demonstrating good mechanical stability and a robust superhydrophobic effect.

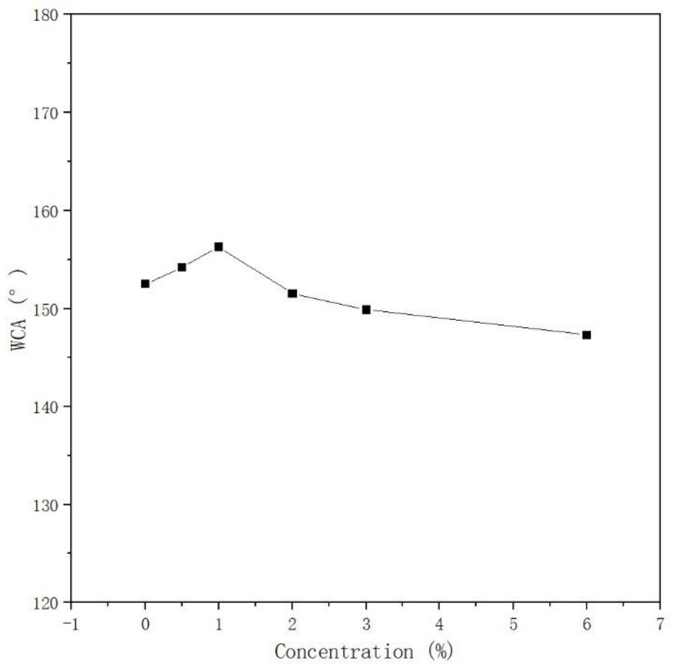

Fig. 6 The WCA of the coating modified by different mass fractions of the MPS. (Picture/image credit: Original)

4. Applications Prospect of Silane Coupling Agents' Modified MONPs

4.1. Recyclable Photocatalysts

The MONPs play a significant role in photocatalysis, with several MONPs, such as Ag_2O, ZnO, TiO_2, Al_2O_3, and CuO nanoparticles, demonstrating catalytic capabilities in this field. The surface modification of MONPs with silane coupling agents can effectively lower their surface energy, reducing the tendency for aggregation and thus improving their dispersion in reaction systems. The silane coupling agents also create a cross-linked hydrophobic protective layer on the MONP surfaces, enhancing their chemical stability and enabling their use in more extreme environments, such as strong acids, bases, and UV irradiation. This improved stability and protection provided by the silane modification can significantly enhance the recyclability of MONP-based photocatalysts [28]. Therefore, the modified MONPs-based photocatalysts can play a long and wide role in air purification, sewage purification, deodorization and anti-odor fields. For example, the modified MONPs-based photocatalysts may be used in the vehicle exhaust treatment after a series of researches, which will play a key role in the environmental protection.

4.2. Antimicrobial, Hydrophobic and Self-cleaning Composite Materials

MONPs have wide-ranging applications in antimicrobial materials, with many MONPs, including Ag_2O, ZnO, TiO_2, and CuO nanoparticles, demonstrating strong antibacterial effects through the release of cations. Silane coupling agents serve as molecular bridges, linking MONPs to organic polymer materials, such as fibers in fabrics, to create antimicrobial composite materials [29]. These composites not only exhibit effective antimicrobial properties but also possess hydrophobic or even superhydrophobic surfaces, providing self-cleaning capabilities. These enhanced properties make the silane-modified MONP composites ideal for various applications requiring antimicrobial and low-maintenance materials. The antimicrobial, hydrophobic, and self-cleaning composites can be used in some pharmaceutical excipients and protective clothing, but research and consideration are needed to control costs and to select to process suitable for mass production.

5. Conclusion

The MONPs possess significant potential in various fields, including catalysis, chemical batteries, environmental management, energy storage, and antimicrobial materials, due to their unique properties. When modified with hydrophobic silane coupling agents, these nanoparticles experience enhanced physical and chemical attributes. For instance, APTES-modified MONPs exhibit excellent mechanical stability, self-cleaning properties, and durability, along with superior superhydrophobic effects, enabling them to maintain chemical stability even in harsh environments like strong acids, bases, and UV irradiation. GPTMS-modified MONPs also demonstrate good mechanical stability and hydrophobicity, and when exposed to UV light, they retain antimicrobial activity and self-cleaning properties. Similarly, MPS-modified MONPs show improved mechanical stability and hydrophobic properties, with some achieving superhydrophobicity.

The reduction of surface energy due to silane coupling agent modification prevents the aggregation of MONPs, making them highly effective in photocatalytic applications. These modified photocatalysts can operate in extreme environments and be reused multiple times. Furthermore, the hydrophobic nature of silane coupling agents facilitates bonding between MONPs and organic polymer materials, creating antimicrobial, hydrophobic, and self-cleaning composites.

However, challenges remain in the modification process. Shorten modification times and the need to control reaction conditions to improve efficiency are key concerns. Additionally, the development of consistent coating processes for mass production and the pursuit of greener, eco-friendly silane coupling agents require further research.

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