



Review

A review of current coupling agents for modification of metal oxide nanoparticles

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ABSTRACT

In recent years, metal oxide nanoparticles (NPs) have gained an increasing interest because of their unique size dependent properties; examples include electrical, magnetic, mechanical, optical and chemical properties, which largely differ from those of their bulk materials. The metal oxide NPs are used in a wide range of applications in various fields, such as medicine, energy storage, catalysis, food packaging, optoelectronic devices, semiconductor devices, aerospace, and sensing. One of the main problems of metal oxide NPs associated with different surface structures and surface interactions are represented by a high tendency of metal oxide NPs to adhesion and aggregation. The use of coupling agents is a good alternative to overcome this problem. This paper reviews the application of coupling agents for the modification of metal oxide NPs and summarizes the interaction between metal oxide NPs and coupling agents.

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1. Introduction

Nowadays, nanotechnology is one of the most developing sciences in last decades. Nanotechnology relates to the design,

creation, and utilization of materials whose size varies from 1 to 100 nanometers (nm) [1,2]. This is due to the fact that materials with diameter in nanoscale exhibit different properties than larger materials of the same substance. When particle size is decreased to the nanoscale range, properties often significant change with consequent new product for their application in various areas of life [3,4], for example such as: sensors technology, nanoscale electronics, and optics [5–7].

Nanoparticles (NPs) are defined as primary particles with a nominal diameter smaller than 100 nm [8]. The most common NPs currently implemented have been made of transition metals,

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silicon, carbon, and metal oxides. Among NPs, metal oxide NPs are attracting considerable interest due to their unique physical and chemical properties [9]. These metal oxide NPs can be composed of a variety of materials for example: zinc oxide (ZnO), titanium dioxide (TiO₂), copper oxide (CuO), zirconium dioxide (ZrO₂), Aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), iron oxide (Fe₃O₄), magnesium oxide (MgO), nickel oxide (NiO), manganese dioxide (MnO₂) and etc. Their unique properties of metal oxide NPs strongly depend on NP preparation and dimension [10–12]. The main problem in NPs application is high tendency of metal oxide NPs to adhesion and aggregation. Surface modification of the metal oxide NPs with organic compounds has been employed to overcome the problem and reduce the particle surface energy and decrease their tendency to agglomerate [13,14].

This article reviews the recent utilization of diverse coupling agents for the modification of metal oxide NPs, summarizes the interaction mechanisms between metal oxide NPs and coupling agents.

2. Metal oxide nanoparticles

2.1. Synthesis, properties and applications of metal oxide nanoparticles

Among all the materials to be prepared with diameter in nanoscale, metal oxides are particularly attractive candidates, from a scientific as well as from a technological point of view. The metal oxide NPs research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields [15–17]. The NPs can be produced through either chemical or physical means. Among those techniques, the chemical synthesis of NPs is a rapidly growing field with a great potential in making useful materials [18,19]. For example, sol–gel processing, electrochemical methods, hydrothermal techniques, and chemical vapor deposition. Several synthetic approaches have been developed for synthesizing NPs over the past several decades. All the different methods to synthesize any kind of NPs can be classified in two general groups, which are called “Top-Down” (involves breaking down of large material pieces) and “Bottom-Up” (from molecular scale or nanoscale). The Top-Down method is associated with the use of mechanical force, such as ball milling and grinding. The Bottom-Up is to generate particles of the correct size using crystallization, direct generation or other similar techniques. Both approaches play very important roles in nanotechnology [20,21]. These technical approaches can also be grouped according to the growth media: NPs including vapor, liquid, solid state processing routes, and combined methods. In the gas routes use both inert and reactive atmospheres at a variety of pressures. The gas routes NP synthesis methods include electrospray, flame pyrolysis, vaporization and condensation using lasers and other heat sources, and plasma synthesis. The liquid route involves sol–gel and other wet chemical methods. Solid state route preparations take place via mechanical milling, mechanochemical synthesis, thermal decomposition, solid state reaction, spark discharge [22–25].

Among different methods which those broadly in use are: (1) sol–gel processing. This method involves conversion of a precursor solution into an inorganic solid by chemical means. In general, the precursor (metal alkoxide or inorganic salt) hydrolysis, condensation, curing, and then heat treatment, become solid oxide or other compounds [26–28]. (2) Co-precipitation methods. Co-precipitation occurs when a solution (vapor) is supersaturated with the substance forming the precipitate or when a melt is super-cooled. This involves dissolving a salt precursor (chloride, nitrate, etc.) in water (or other solvent) to precipitate the oxhydroxide form with the help of a base [29–31]. (3) Microemulsion technique.

The two basic types of microemulsion are direct (oil dispersed in water) and inverse (water dispersed in oil). The aqueous phase may contain salts or other ingredients and the oil may actually be a complex mixture of different hydrocarbons and olefins [32,33]. (4) Solvothermal/hydrothermal methods. In sealed vessel (autoclave or etc.) solvent can be brought to temperatures well above boiling points by the increasing in autogenous pressures resulting from heating performing a chemical reaction under conditions is referred to as solvothermal processing, in the case of water as solvent, hydrothermal processing [34,35].

Many metal oxide NPs offer unique properties as catalysis, sensing, energy storage and conversion, optics, and electronics [36–39]. Also, the metal oxide NPs have been used as nanofiller in both polymeric nanocomposite [40,41], to improve the electric, mechanical and optical properties, and metallic nanocomposites [42,43].

2.2. Surface modification of metal oxide nanoparticles

The small size of NPs is responsible for the different properties. As the size of a material is decreased below 100 nm, proportion of surface atoms increases, which increases the reactivity and makes them highly reactive sites. When the percentage of atoms on the surface of NP increases, they become more reactive yet less stable. Therefore, NPs have a strong tendency to undergo agglomeration. Surface modification of the metal oxide NPs with physically (by physisorption) or chemically (through covalent bonding) routes have been employed to overcome this problem. Physical modification is usually accomplished with surfactants or macromolecules adsorbed on the surface of metal oxide NPs. The polar groups of surfactants can adsorb on NPs surface due to electrostatic interactions. Surfactants can decrease the particle–particle interactions thus diminishing the agglomerates formation due to the decrease of physical forces [44,45]. A drawback of physical modification is that they are thermally and solvolytically unstable due to the relatively weak van der Waals forces or hydrogen bonding that anchors them

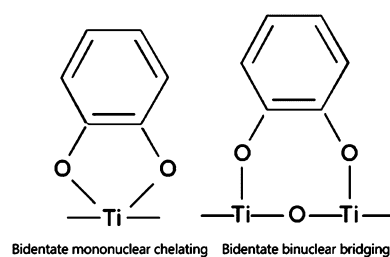


Fig. 1. Proposed molecular structures of catechol with TiO₂ NPs.

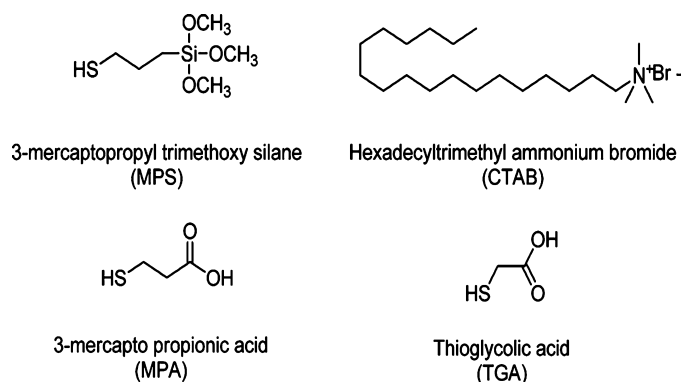


Fig. 2. Chemical structures of the coupling agents.

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