Sustainable steric stabilization of colloidal titania nanoparticles

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A B S T R A C T

A route to produce a stable colloidal suspension is essential if mono-dispersed particles are to be successfully synthesized, isolated, and used in subsequent nanocomposite manufacture. Dispersing nanoparticles in fluids was found to be an important approach for avoiding poor dispersion characteristics. However, there is still a great tendency for colloidal nanoparticles to flocculate over time. Steric stabilization can prevent coagulation by introducing a thick adsorbed organic layer which constitutes a significant steric barrier that can prevent the particle surfaces from coming into direct contact. One of the main features of hydrothermal synthesis technique is that it offers novel approaches for sustainable nanoparticle surface modification. This manuscript reports on the sustainable steric stabilization of titanium dioxide nanoparticles. Nanoparticle surface modification was performed via two main approaches including post-synthesis and in situ surface modification. The tuneable hydrothermal conditions (i.e. temperature, pressure, flow rates, and surfactant addition) were optimized to enable controlled steric stabilization in a continuous fashion. Effective post synthesis surface modification with organic ligand (dodecenyl succinic anhydride (DDSA)) was achieved; the optimum surface coating temperature was reported to be 180–240 °C to ensure DDSA ring opening and binding to titania nanoparticles. Organic-modified titania demonstrated complete change in surface properties from hydrophilic to hydrophobic and exhibited phase transfer from the aqueous phase to the organic phase. Exclusive surface modification in the reactor was found to be an effective approach; it demonstrated surfactant loading level 2.2 times that of post synthesis surface modification. Titania was also stabilized in aqueous media using poly acrylic acid (PAA) as polar polymeric dispersant. PAA-titania nanoparticles demonstrated a durable amorphous polymeric layer of 2 nm thickness. This manuscript revealed the state of the art for the real development of stable colloidal mono-dispersed particles with controlled surface properties.

1. Introduction

Titania nanoparticles are used in versatile applications ranging from ultraviolet light absorber [1,2], photocatalysis [3], photosynthesis [4], flame retardancy [5], ceramic industries [6,7], and painting pigments [8]. The sustainable fabrication of titanium dioxide nanoparticles using hydrothermal synthesis has been established [9]. Nano-oxides produced by hydrothermal synthesis are in the form of colloids [10]. Collision during the manufacture process may cause excessive aggregation [11,12]. In colloidal solution, there is an attractive dispersion force (van der Waals attractive force) between particles. This attractive force tends to aggregate the

particles [13]. For particles having a plate like shape separated by a distance h, the attraction potential (V_A) is given by Eq. (1) [14,15].

$$V_A = \frac{A}{12\pi h^2} \tag{1}$$

where A is Hamaker constant (it is the material property, its value in the order 10^{-19}–10^{-20} J), h is the distance from the particle surface (m). The attraction force decays in proportion to $1/h^2$ for plate particles, and it decays in proportion to $1/h^6$ for atoms [16]. Einstein showed that, the average square displacement X^2 of a particle of radius r in a medium of viscosity η could be evaluated using Eq. (2) [17].

$$X^2 = \frac{RTt}{3\pi N_0 \eta r} = 2Dt \tag{2}$$

where D is the diffusion coefficient, R is the universal gas constant, T is the absolute temperature, t is the time, and N_0 is the Avogadro's number. According to Einstein's equation, a particle of 1 nm radius in water at 20 °C can travel 1 μm in 2.3 ms. Consequently, this ran-

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dom Brownian motion can cause rapid colloidal flocculation [18]. A stable nano-colloidal suspension is vital to prevent aggregation and to produce mono-dispersed particles for different applications [19–21]. A route to produce a stable colloidal suspension is an urgent need if mono-dispersed particles are to be successfully synthesized, isolated, and used in subsequent composite manufacture [22–26]. It is possible to stabilize colloidal particles and to prevent coagulation by introducing a thick adsorbed polymer layer which constitutes a steric barrier [27].

1.1. Steric stabilization of colloidal nanoparticles

Certain organic ligands, with polar anchoring groups, have been reported to stabilize colloidal nanoparticles and to prevent coagulation by introducing adsorbed organic layer which constitutes a significant steric barrier that can prevent the particle surfaces from coming into direct contact [28]. The employed interfacial dispersants should be capable of hydrogen bonding with the metal oxide surface [29,30]. Carboxylate ligands are often used to modify metal oxide nanoparticles [31]. Fig. 1 demonstrates the adsorption mechanisms of carboxylate dispersants to nano-oxide surface [31].

Multi functional ligands containing carboxylic groups have been used effectively for coupling with metal oxide colloids [8]. These surfactants can be designed to strongly bind to the nanoparticle surface, in the mean time bind to selective target compounds such as polymer chain. Thus proper nanoparticle dispersion can be achieved [15,31].

Polymeric dispersants differ from low molecular weight species because of their long backbone chains. Additionally, they are able to bind to numerous surface sites at the same time, forming a durable adsorption surfactant layer [32–34]. Anchoring groups that can be used to anchor polymeric chains to oxide surface are amine [35], ammonium [36], carboxylic [37,38], sulphonic, and phosphoric acid functional groups [31]. The molecular weight of the polymeric dispersant should be sufficient to provide the optimum chain length to produce a molecular barrier of sufficient thickness. This barrier should overcome van der Waals forces of attraction between particles [39,40]. The molecular weights that are too high can cause dispersion instability, as there will be an increased tendency for the long chains to fold back onto themselves causing flocculation [40,41]. Polymers with molecular weight above 10^6 g mol^{-1} are generally used as flocculants [40], whilst the preferred molecular weight for polymeric dispersants was reported to be less than 20,000 g mol^{-1} [8]. The conformation of the adsorbed polymer is a major controlling factor in determining the steric barrier stability [42]. The adsorbed polymer has three possible segments: (a) segments at the solid–liquid interface, called trains; (b) segments bound at both ends, called loops; (c) segments bound at one end, called tails [43]. Non-interacting groups are responsible for the occurrence of tails and loops [42]. Variation in train, loop, and tail
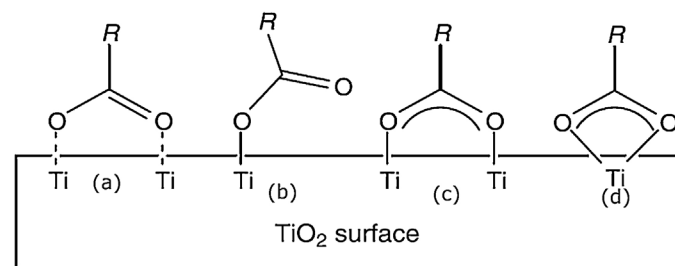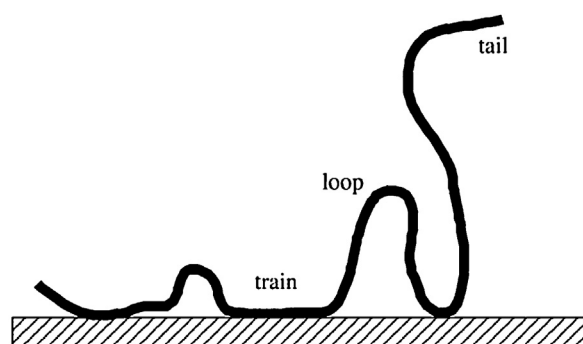
Fig. 2. Schematic of adsorbed polymer molecule at the solid–liquid interface [29].

length controls the adsorbed layer thickness [8]. Fig. 2 is a schematic drawing of polymer conformation at the solid–liquid interface.

There are two main routes for nanoparticle surface modification including:

1) Post-synthesis modification approach: Where the functionalized nanoparticles are synthesized in two steps, which are distinctly separated from each other. The first step is the formation of the nanoparticles (core). The second step is the functionalization, where the functional organic molecules are introduced later in a separated stage.
2) In situ functionalization: In this technique the nanoparticles are formed in the presence of functional organic molecules. The clusters assembly occurs where organic groups are exclusively bonded to the atom surface [15]. The growth of the cluster core is controlled by the organic groups; It has been reported that the attached surfactant could counteract further particle growth [44]. The sequences of reactions that may lead to surface modification are rarely known and not always obvious.

1.2. Integration of nanoparticles into polymers

Inorganic–organic nanocomposites are a special class of inorganic–organic hybrid materials with improved mechanical, optical, electrochemical, thermal, and flame resistance properties [45]. It has been reported that surface modification could offer enhanced compatibility between inorganic particles and the organic hosting medium [9]. Furthermore, the surfactant itself can undergo chemical bonding and integrate the nanoparticles into the polymeric matrix chains [46]. There are two principle routes to integrate the nanoparticles into the polymeric matrix including.

1.2.1. Grafting to approach

This approach includes coupling of the nanoparticles with polymers that have reactive groups to attach the particles to the polymer surface. Many kinds of interaction that may range from the van der Waals force to covalent bonding can be developed between the nanoparticle surface and the polymer [8,31]. This type of interaction depends mainly on the specific surface area of the particles, the molecular weight of the polymer, and the portion of reactive substituent at the polymer chains [42,43]. Polymers with pendent reactive groups such as sulfonates or carboxylates were grafted to the surface of nano-ferrite, silica, or titania [31,35]. This technique has many drawbacks, such as insufficient surface coverage due to steric hindrance or macromolecule's competition between adsorption and chemical bonding [15].

1.2.2. Grafting from approach

Grafting from approach includes polymerization on or from the surface of organic modified particles. It is one of the main routes

Fig. 1. Adsorption mechanisms of carboxylate ligands on titania nanoparticles. Keys: (a) physical adsorption, (b) monodentate coordination, (c) bridging chemisorption, (d) chelating chemisorptions.