Facile self-assembly and stabilization of metal oxide nanoparticles

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ABSTRACT

This paper describes a facile method of self-assembling different metal oxide nanoparticles into nanostructured materials via di-carboxylate linkers (oxalic acid) using TiO_2 as an example. In this method, the di-carboxylate linkers react with surface hydroxyls on metal oxide nanoparticles forming covalent, ester-like bonds, which enable the binding of two metal oxide particles, one at either end of the linker and facilitates efficient self-assembly of one group of metal oxide nanoparticles homogeneously distributed onto the surface of another group. The oxalate linkers can then be removed by thermal decomposition. This approach is shown to be effective using differently-sized TiO_2 nanoparticles, namely in-house synthesized 3–5 nm anatase nanocrystals and Degussa P25 titania particles (mean 21 nm particle size). Our data show that the application of a high temperature heat treatment (450 °C for 30 min), conventionally applied to achieve a stable porous structure by thermal decomposition of the linker molecules and by inducing inter-particle necking, damages the surface area of the nanostructured material. However, here we show that sintering at 300 °C for 30 min or by flash near infrared radiation sintering for 12 s efficiently decomposes the oxalate linkers and stabilizes the nanostructure of the material whilst maintaining its high surface area.

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1. Introduction

Nanostructured materials can be defined as substances which contain either the same or different types and/or sizes of nanoparticles assembled into a particular structural arrangement [1]. Hence, optimizing both the mixture of different component nanoparticles and their structural arrangement can produce attractive and often unique combinations of chemical and physical properties. As such, nanostructured materials are becoming an increasingly important group of materials which have been widely studied in areas such as photovoltaics [2], optoelectronics [3], energy storage [4,5], gas sensors [6], photocatalysis [7] and medicine [8].

In this context, whilst the technical definition of a nanoparticle is <100 nm, most are much smaller (1–30 nm) because the desired chemical and physical properties are often linked to size (e.g. for quantum dots [9] or medical applications [8]). However, the controlled processing and assembly of very small nanoparticles into nanostructured materials are very challenging [10–12]. In particular, nanoparticles tend to be synthesized in solution creating colloidal suspensions which must be destabilised to enable recovery. However, the recovered nanoparticles often have a tendency to agglomerate. This limits both their advantageous size-related phenomena (e.g. surface area and quantum-related electronic and optical properties) and the ability to assemble them into a chosen structural arrangement. In addition, nanoparticle agglomeration greatly influences powder flowability, particle re-wetting and suspension rheology [13–16]. To try to minimize these problems, nanoparticles (e.g. quantum dots) are usually surface derivatised to improve handling but this often involves long-chain organic molecules and organic solvents which need to be removed after processing [17].

Processing nanoparticles into nanostructured materials is further complicated because the final material is often stabilized onto a substrate in a controlled design or architecture, e.g. single *vs.* multi-layered [18], or compact *vs.* porous structures [19]. One approach to control the architecture of nanostructured materials is to self-assemble the nanoparticles into the desired configuration which has led to many reports for metallic nanoparticles such as gold or silver [20]. However, the self-assembly of metal oxide particles has been much less studied. In part, this may be due to the challenges of controlling the self-assembly of metal oxide particles. This may also reflect the need to apply post-assembly, high temperature heat treatments to promote interparticle bonding and substrate
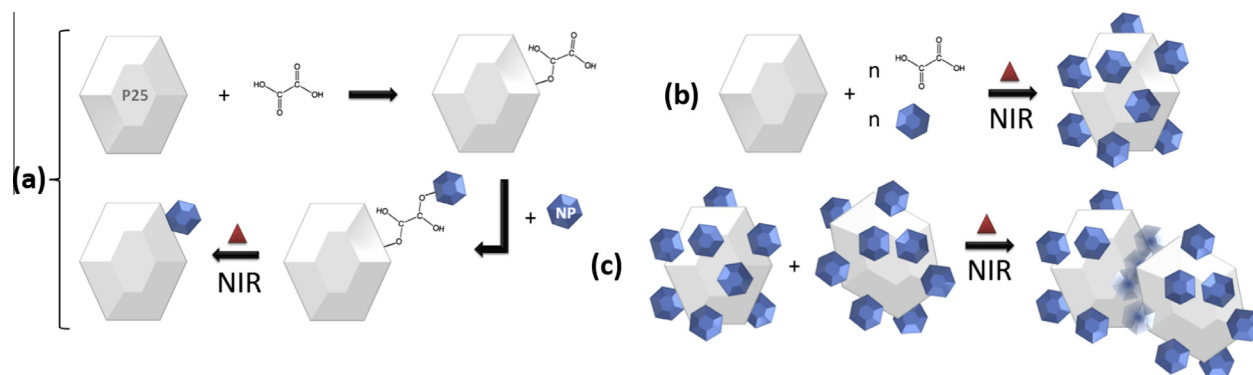
Scheme 1. (a) self-assembly of larger (grey) and smaller (blue) nanoparticles using oxalate linkers and sintering, (b) smaller nanoparticles enhancing surface area and (c) smaller nanoparticles promoting inter-particle necking. (For interpretation of the references to colour in this scheme legend, the reader is referred to the web version of this article.)

adhesion whilst also evaporating/combusting the colloidal matrix used to process the nanoparticles [21]. For example, mesoporous TiO_2 coatings used as photoanodes for photovoltaic devices or photocatalytic water treatment [19–22] are printed onto glass from suspensions containing solvent and rheology modifiers both of which are removed using heat treatment typically at 450 °C [23]. This can be a problem because the very high surface:volume ratio of nanoparticles can accelerate surface energy driven phenomena over bulk transformations. This is why heat often exacerbates agglomeration of nanoparticles both in dry powders and in liquid suspensions. If not controlled, this can lead to Ostwald ripening and particle growth [24]. These issues are particularly problematic for very small nanoparticles (<30 nm) which exhibit both highly reactive surface characteristics and high surface areas.

To overcome these challenges, this paper describes a facile, aqueous-based approach to self-assemble metal oxide particles which can be applied to differently sized particles and/or different phases using di-carboxylate linkers (Scheme 1a). Here, oxalic acid has been used which can bond through each of its carboxylate moieties [25–27] to two different metal oxide surfaces and in turn link different metal oxide particles together to demonstrate the application of this method to two types of TiO_2 nanoparticles, namely *ca.* 30 nm P25 TiO_2 and 3–5 nm in-house synthesized anatase nanoparticles. Here, P25 is used as a scaffold to host the smaller nanoparticles and produce a nano-structured TiO_2 material with meso- to macroporous characteristics and significantly enhanced surface area. The paper also describes the ultra-fast sintering of the nanostructured TiO_2 materials using near infrared (NIR) radiation which thermally decomposes the oxalate linkers and enables the particles to physically bind whilst preserving the high surface area of the component particles. Our data show that this result is particularly difficult to achieve with conventional high temperature oven sintering techniques, a difficulty also encountered by others [28]. It is thought that the smaller in-house produced nanoparticles can act both as a surface area enhancer (Scheme 1b) and as a particle necking promoter (Scheme 1c) due to their intrinsic high surface area (*ca.* 200 m²/g) contribution and reduced thermodynamic stability.

2. Materials and methods

Mixed TiO_2 colloidal suspensions of mixed TiO_2 particles were prepared using varying ratios of Degussa Aeroxide®P25 TiO_2 (80 wt% in DI H_2O) and TiO_2 NPs nanoparticles (20 wt% in DI H_2O) and concentrations of oxalic acid ranging from 0 to 30 mM. The 3–5 nm TiO_2 NPs nanoparticles were produced by low temperature (80 °C, 30 min) hydrolysis of a 0.125 M $TiCl_4·THF$ precursor using a method adapted from previous work [30]. To prepare a

typical mixed colloid, first an aqueous suspension of P25 (8 wt% in water) was prepared and sonicated for 30 min. A volume of 1 mL of the P25 suspension was mixed with 0, 0.010, 0.030, 0.100, 0.300, 1.000 and 3.000 mL of a 0.1 mol/L oxalic acid solution in separate glass vials and deionised water was added to make each sample up to 8 mL. All vials were shaken for 1 min to promote mixing and to ensure homogeneous adsorption of oxalic acid molecules onto the surface of P25 particles and a 2 mL volume of the 3–5 nm TiO_2 nanoparticle colloid was finally added to each vial. The final TiO_2 concentration of each sample was 1 wt%. These samples were then labelled as 0 mM to 30 mM to reflect their final oxalic acid concentration. After mixing, all samples were dried at 80 °C (30min) before sintering either in a convection oven for 30min at 300 or 450 °C or with a 25 kW NIR radiation lamp at 80 % of the maximum power settings for 12 s (thoroughly described in previous work [33]). To monitor the adsorption of oxalates to P25 in the cases of 3 mM and 30 mM oxalic acid treatments, 8 g of P25 were dispersed in 100 mL of 3 mM and 30 mM aqueous solutions and magnetically stirred. Samples of 5 mL were syringed at 0, 1, 3, 10 and 30min and the P25 particles were filtered using 0.020 μm pore size filters. UV–Vis spectroscopy measurements of the filtered liquid samples were collected using quartz cuvettes (with deionised water as a reference sample) with a Perkin Elmer Lambda 750S over the spectral range 200–800 nm.

The morphological, structural and physicochemical properties of dried and/or sintered samples were analysed to understand the influence of oxalic acid concentration and sintering technique on the nanostructured TiO_2 materials. Thus, electron microscopy imaging was carried out on dried and/or sintered samples prepared on fluorine-doped tin oxide-coated glass substrates (TEC7, NSG-Pilkington) using a Hitachi S-4800 field emission gun scanning electron microscope (FEG-SEM) with a 12 kV/10 μA electron beam at 5 mm working distance. Transmission electron microscopy (TEM) imaging of mixed TiO_2 samples was carried out on a Philips (FEI) CM12 instrument (80 kV). Here, TiO_2 samples were first dispersed in ethanol and then dried at T_{amb} onto carbon film coated copper grids (200 mesh, Agar Scientific) prior to imaging. Surface area and pore size distributions were measured using N_2 adsorption at −196 °C followed by BET and BJH-adsorption analysis on a Tristar II 3020 instrument (Micromeritics, USA). Infrared spectra were collected from dried and sintered samples using attenuated total reflectance (ATR) on a Frontier Fourier Transform-Infrared (FT-IR) spectrometer (Perkin Elmer Inc.). Thermal gravimetric analyses (TGA) were carried out on a Pyris 1 TGA system (Perkin Elmer Inc.) and the differential scanning calorimetry (DSC) measurements on a DSC 4000 instrument (Perkin Elmer Inc.) both under N_2 flow with closed aluminium pans as sample holders.