

Synthesis of Titania Hollow Spheres Using Non-aqueous Emulsions

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Hollow titania spheres ranging in diameter from 100 nm to a few micrometres were synthesized by a novel method using surfactant-stabilized non-aqueous emulsion droplets. Well-defined micron-sized hollow spheres with amorphous titania walls typically 50 nm-thick were prepared by addition of water to formamide dispersions of hexadecane droplets containing titanium ethoxide. In contrast, addition of titanium ethoxide to formamide/water droplets dispersed in hexadecane produced hollow spheres of amorphous titania only 100nm in diameter. Doping of the hollow spheres with manganese salts and porphyrins is also demonstrated. In both cases, hydrolysis/condensation reactions at the formamide/oil interface gave rise to intact shells that could have uses as low-density pigments, dyes, self-repairing coatings, photoactive storage/release agents, as well as compartmentalized structures in nanotechnology.

Key words: Titania, Hollow Spheres, Non-aqueous Emulsions

1. INTRODUCTION

Titania ceramics produced by sol-gel routes¹ are commonly used as paint pigments abrasives, electronics coatings, membranes and filters.² Titanium dioxide absorbs UV light and is of key interest use in the development of solar power cells.^{3,4} For example, coupling of the photo-induced band gap excitations to a circuit and tri-iodide complex has been used to produce a device that can be powered by sunlight. By sensitising titania with ruthenium-based dyes, photo-catalysts have been developed for the degradation of organic molecules, such as pollutants,⁵ within the visible range of the electromagnetic spectrum. Recently, sol-gel doping techniques have been used to produce more sensitive and efficient solar cells.

Previous work on the formation of hollow ceramic spheres has been predominantly concerned with silica. In particular, unilamellar and multilamellar silica colloids have been synthesized using surfactant vesicles,^{6,7} or by spray drying of reaction solutions containing cationic surfactant templates.⁸ Hollow shells with thin walls of amorphous silica⁹⁻¹¹ or ordered mesostructured silica¹²⁻¹⁵ have been prepared by sol-gel reactions at the surface of oil droplets containing

tetraethoxysilane (TEOS) dispersed in aqueous reaction solutions. Other studies have used supersaturated metal salt solutions or nanoparticle-containing sols, in association with polystyrene latex spheres^{16,17} or microemulsion water droplets,¹⁸ or combinations of these¹⁹ to prepare silica, zeolite or calcium carbonate hollow microspheres, respectively.

In this paper we describe a method for the synthesis of TiO₂ hollow microspheres using non-aqueous normal or inverse emulsions. Previous work has shown that TiO₂ foams can be prepared by sol-gel reactions using a surfactant-stabilized formamide in a 25% titanium (IV) iso-propoxide 74% isooctane and 1% silicone oil concentrated emulsion.²⁰ Formamide is highly polar and can be used to prepare stable emulsions, and here we demonstrate that this non-aqueous reaction system can be used to control the hydrolysis and condensation of titania precursors for the formation of continuous thin shells of amorphous titania. Moreover, we show that the diameter of the hollow titania spheres can be modified from 100 nm to several micrometres depending on the phase behaviour of the reaction system

Titania hollow microspheres were prepared from normal or inverse formamide/hexadecane emulsions by two distinct methods based on a formulations developed by Landfester *et al* in the field of polymer particle preparation.²¹

Addition of small amounts of water to a normal emulsion consisting of surfactant-stabilised hexadecane droplets of titanium (IV) ethoxide dispersed in formamide immediately gave a white flocculant that separated and floated to the liquid surface. SEM and EDX analysis revealed the product to consist of titania hollow spheres as may be seen from figure I. A wide size range can be observed ranging between 500 to 3000 micrometers.

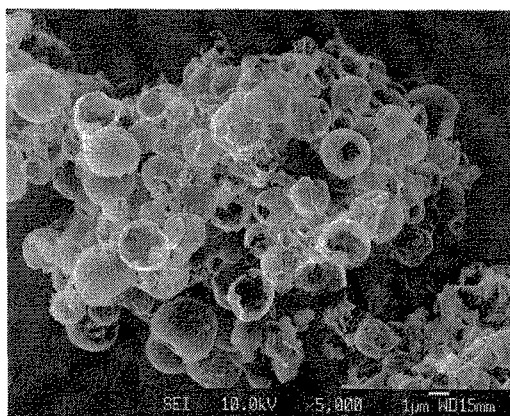


Figure I. SEM image of titania microspheres.

The spheres were collapsed due to evaporation of trapped hexadecane and partially fragmented in the SEM to reveal the hollow interior and external wall indicating that the hydrolysis and condensation reactions occurred specifically at the droplet interface. Although a range of reaction precursors and oils were tested, a water to alkoxide molar ratio of 4:1 in the presence of hexadecane consistently gave well-defined titania microspheres provided that the starting pH was around 10.5 (final pH \approx 9.0). Only unstructured particles were

produced below pH 6 due to destabilisation of the emulsion droplets.

TEM studies indicated that the hollow microspheres consisted of walls with a smooth exterior and a slightly roughened interior. The walls of the spheres were an average of 61.3nm with a standard deviation of 10.0nm. Electron diffraction studies indicated that the titania was amorphous. However, the microspheres could be converted to crystalline anatase with no loss of the hollow shell architecture by heating samples slowly to 500°C for at least 2 hours.

Figure 2 indicates the electron diffraction pattern produced by a calcined titania microsphere. The rings correlate to the anatase phase of titania. The spots are due to the presence of residual sodium salts on the surface of the sample.

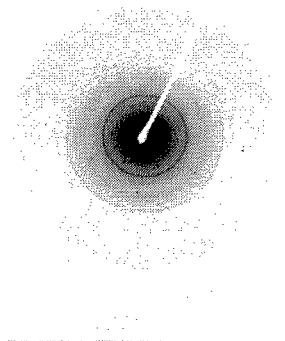


Fig II. TEM produced diffraction pattern taken with a 100cm camera length and an accelerating voltage of 120 KeV. The rings correspond to those observed for an anatase structure. Selected reflections: 101 (3.517 Å) 004 (2.371 Å) 200 (1.895 Å) 105 (1.682 Å) 204 (1.484 Å)

IR data of a calcined sample confirms titania has been produced. The characteristic low frequency band at 1383 cm^{-1} may be assigned to Ti -O-Ti stretching²². There is also a peak at 1626 cm^{-1} indicating the presence of OH groups. Water has already been removed from the product as a result of heating. Thus the OH groups are

present within the titanium dioxide framework. This is expected and is one of the reasons for titanias bioactivity²³. Biomolecules and ions are easily adsorbed to the materials surface. Further work may include the functionalisation of these groups to alter the surface behaviour of the spheres.

Hollow titania microspheres were also synthesized from normal emulsions prepared using ethylene glycol instead of formamide as the continuous phase. Such methods could be useful for example in the fabrics industry as a micro-engineered fabric precursor and pigment. Other experiments currently in progress indicate that it is possible to dope the sphere wall with metal salts without compromising the hollow shell morphology. This shifts the titania band gap interactions in to the visible wavelength.

Nickel, magnesium, cobalt and silver phthalocyanines were successfully embedded in the titania wall. This was characterised by solid state UV-vis analysis of the formed spheres in solution. The porferyns were added to the oil phase of the emulsion solution before reaction.

Titania hollow shells were prepared in inverse emulsions by adding titanium (IV) ethoxide to a dispersion of sorbitan mono-oleate-stabilized formamide/water droplets in hexadecane at a water to alkoxide molar ratio of 4:1. The emulsion immediately turned off-white but remained transparent with no evidence of flocculation, indicating that the products were colloidal and more dispersed than those obtained from the normal emulsions. A white precipitate slowly settled to the bottom of the reaction vessel within 1 hr of mixing. TEM analysis showed intact hollow nanospheres that were morphologically homogenous as can be seen from figure 3.

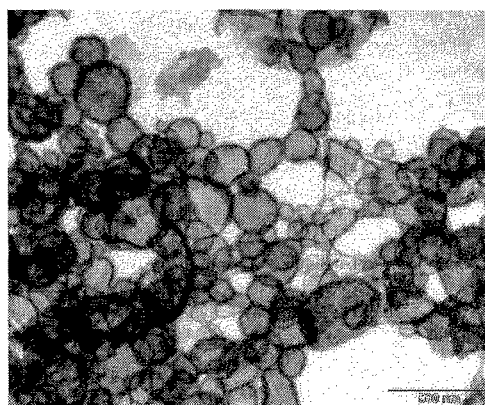


Fig III. TEM micrograph of titania nanospheres.

Image analysis revealed a gaussian size distribution with an average diameter of 141nm and a standard deviation of 49.75nm. This is in contrast to the previous method that has a wide but well-defined size range. Thus, the mean particle diameter was reduced by around ten-times by undertaking the sol-gel reaction within the inverse emulsion droplets. This method also shows a more desirable property towards forming monodisperse shell sizes, exhibiting a control that has been previously unseen in methods of this type. The hollow nanoshells consisted of amorphous walls 19.25nm thick with a standard deviation of 6.69nm. The common observation is a smooth interior and a roughened exterior, which was often fused with other spheres on drying onto the TEM grid.

Significantly, the TiO₂ nanospheres could be redispersed as intact hollow spheres by sonication in aqueous solutions by removing excess hexadecane by ethanol washing followed by centrifugation in water. Thus it should be possible to coat the nanoshells with a variety of oil- or water-soluble molecules for applications in photocatalysis, biomaterials engineering and biomedical applications.

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