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Significance of particle size and charge capacity in TiO_2 nanoparticle-lipid interactions

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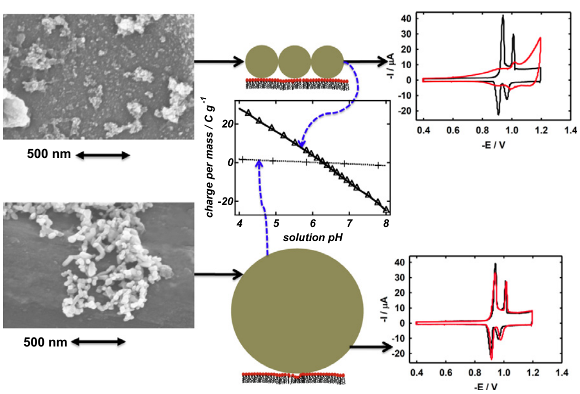
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: The activity of submicron sized titanium oxide (TiO_2) particles towards biomembrane models is coupled to their charge carrying capacity and their primary particle size.
Experiments: Electrochemical methods using a phospholipid layer on mercury (Hg) membrane model have been used to determine the phospholipid monolayer activity of TiO_2 as an indicator of biomembrane activity. The particles were characterised for size, by dynamic light scattering (DLS) and scanning electron microscopy (SEM), and for charge, by acid-base titration.
Findings: TiO_2 nanoparticles aggregate in 0.1 mol dm^{-3} solutions of KCl. The charge capacity of TiO_2 nanoparticles depends on their primary particle size and is unaffected by aggregation. TiO_2 particles of ~40 nm primary particle size interact significantly with phospholipid layers. Aggregation of these particles initially has a small effect on this interaction but long term aggregation influences the interaction whereby the aggregates penetrate the lipid layer rather than adsorbing on the surface. Fulvic acid does not inhibit the ~40 nm particle/phospholipid interaction.

P25 TiO_2 particles of larger particle size interact less strongly with phospholipid layers and the interaction is alleviated following particle aggregation. The semiconductor properties of TiO_2 are evident in voltammograms showing electron transfer to TiO_2 adsorbed on uncoated Hg.

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1. Introduction

Titanium dioxide (TiO_2) nanoparticles are one of the most widely used nanomaterials in current application and have extensive use as sunscreens and paints. Accordingly they have a considerable release into environmental systems. Recent estimations have predicted surface water concentrations of discharged TiO_2 to be 21 ng dm^{-3} [1] although these values have yet to be confirmed experimentally. TiO_2 is refractory with a very low water solubility as well as showing a strong tendency to aggregate [2–6]. In spite of this, its biological activity remains uncertain with conflicting reports as to its hazard to environmental and human health [7–10]. A specific feature of TiO_2 is its semiconductor properties which means that the material can absorb UV which enables its photoactivity [11] and photocatalytic activity [12] and may enhance its incipient toxicity [13]. Another property of TiO_2 is its existence in three mineral phases anatase, rutile and brookite respectively [11]. The metastable anatase and brookite phases convert irreversibly to the equilibrium rutile phase upon heating above temperatures in the range 600–800 °C [14]. Rutile and anatase are the more common forms of TiO_2 with rutile being the most common [11]. In all mineral phases, Ti is octahedrally co-ordinated to oxygen atoms [11].

The aggregation of TiO_2 dispersions in aqueous conditions is mainly due to their lyophobicity promoted by their mineralisation and surface features as well as their overall dimensions [15]. Previous studies in this laboratory have looked at SiO_2 [16,17], ZnO [18] and CdTe [19] nanoparticles correlating their chemical and physical characteristics with their activity towards biological membranes (biomembranes) and/or biomembrane-like layers. Biomembrane activity is defined as the tendency of nanoparticles to structurally modify and/or permeate in, biomembranes and/or biomembrane-like layers. Although SiO_2, ZnO and CdTe nanoparti-

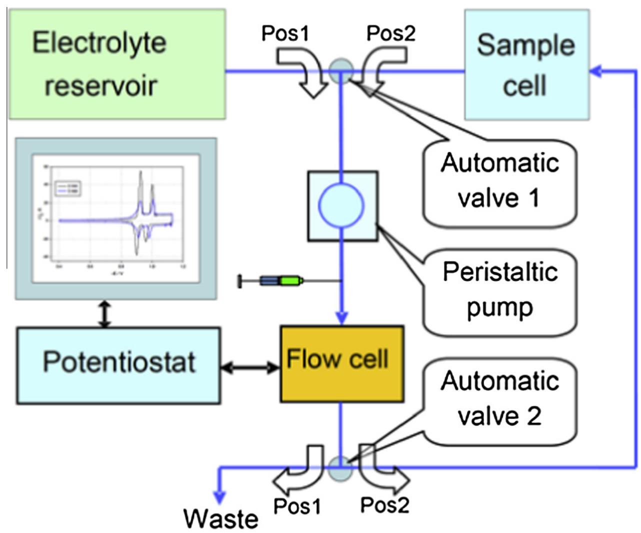

Fig. 1. Schematic view of flow system (modified from Ref. [18]).

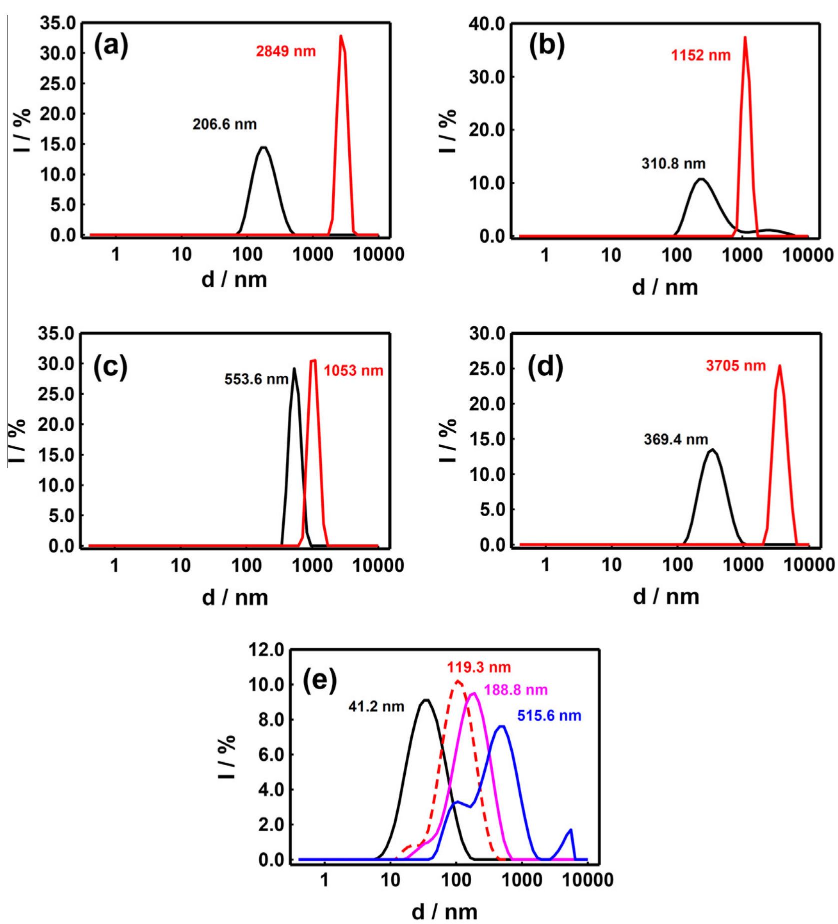

Fig. 2. DLS particle size distribution of 0.1% dispersions of: (a) P25, (b) rutile powder, (c) mixed anatase/rutile (4:1) powder, (d) rutile "stock dispersion" and, (e) anatase "stock dispersion" in, MilliQ water (black line) and 0.1 mol dm^{-3} KCl incubation at 0 (red line), 1 (red dash line), 15 (purple line) and 30 (blue line) min expressed as intensity (I%) versus particle diameter (d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)