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SHORT COMMUNICATION

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Preparation of monodispersed plate-like particles of tungstic acid

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Abstract To understand the properties of colloidal dispersions it is often vital to prepare model materials with particles that have a small polydispersity in order to make experimental tests of theories or models. However few preparations have been developed that yield anisotropic particles with a narrow size distribution and precise shape. In this paper the preparation of a dispersion of charge stabilized, tungstic acid particles is described. The particles are rectangular and have a length of 7.0 μm, a width of 2.8 μm and a thickness of 0.2 μm. The polydispersity is 8% in length and 10% in width, making it one of the most monodisperse dispersions of anisotropic particles. Each particle is monocrystalline and the crystal orientation is fixed with respect to the particle morphology. Some interesting behavior is observed: these particles aggregate perpendicular and parallel to each other to give flat, ordered flocs when the stability is reduced.

Key words Disc-shaped particles – colloidal dispersion – flocs – tungsten oxide

Introduction

Colloidal dispersions display many properties that are analogous to those observed on atomic and molecular scales. Hence they provide a useful model for such systems as well as being of interest in their own right. These properties, such as crystalline phase transitions, shear thinning and fractal floc structures, are often dependent on the size and shape of the constituent particles. If the sample under study contains particles with a range of sizes and shapes then the details of these phenomena can be blurred and some of the properties may even be lost. For example sterically stabilized spheres have been shown to crystallise only if the polydispersity in the system is less than about 10% where this is taken as the standard deviation in a diameter of the particle quoted as a percentage. In this paper a preparation of tungstic acid is described that yields plate-like particles with a polydispersity of less than 10%.

Preparations have been developed for dispersions of spherical particles with a polydispersity of better than 5% using techniques such as emulsion [1, 2] and dispersion polymerization [3, 4] to produce latex particles. In contrast very few preparations are known that produce anisotropic particles with a polydispersity of less than 20%. One of the most monodisperse systems of anisotropic particles described in the literature is that of tobacco mosaic virus (TMV). The polydispersity of a dispersion of TMV is dependent on the polydispersity of the viruses themselves which can be as low as 2% [5], but also upon the state of aggregation of the sample as the viruses tend to aggregate end-to-end, thus drastically increasing the polydispersity of the system. A major problem with using TMV is making sufficient quantities, as the virus has to be grown within cells of the tobacco plant and then cleaned from cell

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debris. Most experiments performed with TMV have used less than 0.1 g of the virus. The small quantities available make experiments on physical properties of concentrated dispersions difficult.

Another system with monodisperse rods is obtained by preparation of β-FeOOH by room temperature hydrolysis of $FeCl_3$. This can produce rods with a polydispersity of as low as 7% in length. Again quantity is a problem: 1 dm^3 produces between 0.01 and 1 g of particles. Time is a further constraint as the preparation is described as taking between 4 months [6] and 15 yr [7].

Other examples of anisotropic particles with a low polydispersity that can be prepared in the laboratory are heamatite ellipsoids (polydispersity of 18% in length) [8], akaganite rods (polydispersity of 25% in length) [9], boehmite rods (polydispersity of 25% in length) [10], and nickel hydroxide plates (polydispersity of 13% in diameter) [11]. There are several reviews of the preparations of inorganic colloidal particles with uniform morphology [12–14]. A different approach to the preparation of anisotropic particles has been to use monodisperse latices prepared by emulsion polymerisation and deform them uniformly by stretching in a polymer matrix [15]. This provides ellipsoidal particles that can be dispersed subsequently in aqueous media.

Preparation of tungstic acid particles

Zocher and Jacobsohn published a preparation for tungstic acid particles [16] in 1928: this involved acid hydrolysis of sodium tungstate and careful control of the conditions. In 1966 Furusawa and Hachisu [17] referred to the earlier work [16], but altered the preparation slightly by diluting the sample rather more during the washing process and then placing the washed gel in twice the volume of water to ripen. The ripening temperature was also carefully controlled to within ± 0.02 °C and they reported making rectangular particles after one year of ripening with a polydispersity of 18% in area. The detailed chemistry of the synthesis of these materials is slightly obscure as several isopolytungstate ions are reported and can be found in coupled equilibria [18]. The relative stability of the different ionic clusters appears to depend delicately on the pH.

In the present work tungstic acid particles were prepared following the procedure of Zocher and Jacobsohn: 10.5 g $Na_2WO_4 \cdot 2H_2O$ (99% purity (ACS reagent) from Aldrich) was dissolved in 150 cm^3 of H_2O (water with resistivity $> 5\ M\Omega\,cm$ was used throughout). This was cooled to 5 °C and 75 cm^3 of 1 M HCl, also cooled to 5 °C, was added quickly and the flask inverted once to ensure mixing. This mix was left undisturbed at 5 °C overnight and gave a white/yellow gel. This gel was then made up to 450 cm^3 with water and shaken vigorously for a few minutes. The dispersion was then centrifuged three times in two buckets at $1100 \times g$ for ten minutes and at a speed of $1800 \times g$ for ten minutes for a fourth time and at $1800 \times g$ for fifteen minutes for the fifth and sixth times. After each spin the supernatant was poured off, water was added to make the sample up to 225 cm^3 in each bucket, and the sample was redispersed by shaking and by passing it through a syringe needle. After the final spin, the sediment was split three ways: one portion was dispersed in 1 dm^3 of water, and stirred continuously (#2), the remaining portion was split in two and half was dispersed in 1 dm^3 of water (#3), and half was dispersed in 1 dm^3 of water and stirred continuously (#4). Hence sample #1 was prepared according to Zocher and Jacobsohn [16], while samples #3 and #4 are diluted as described by Furusawa and Hachisu [17]. These were left at room temperature (about 20 °C) to ripen under identical conditions.

Particles were examined by optical microscopy with a Zeiss Axioplan microscope and transmitted light illumination to study the dispersions in their aqueous environment. Some samples were observed in a scanning electron microscope (Electroscan 2010) to obtain detailed size distributions.

After 24 h the water turned turbid, and in the unstirred samples particles began to sediment. In the stirred samples Schlieren patterns were seen, characteristic of sheared dispersions of anisotropic particles. The particles from all the samples were large enough to be viewed under an optical microscope. Initially all the samples contained flat pointed particles with the same shape as those shown in Fig. 1 and were similar to those observed by Furusawa and Hachisu [17].

Sample #1 is shown in Fig. 1 after two weeks ripening. The particles showed no significant change in shape and were easily dispersed by inverting the container. The particles in sample #2 remained dispersed by the stirring, and ripened to rectangles as shown in the electron micrograph in Fig. 2. This rectangular shape was observed previously only after six months [17].

The polydispersity of sample #2 was measured from three electron microscope images and was found to be 8.4% in length and 10.0% in width. Histograms of the length, width and aspect ratio (length divided by width) are shown in Fig. 3. In contrast the polydispersity of sample #1 (i.e. preparation to the original method of [16]) was found to be 23% in length. This shows that stirring not only increases the rate of ripening but also improves the monodispersity of the resulting particles. This effect is presumably due to concentration gradients forming in the unstirred sample that are not present when stirred.

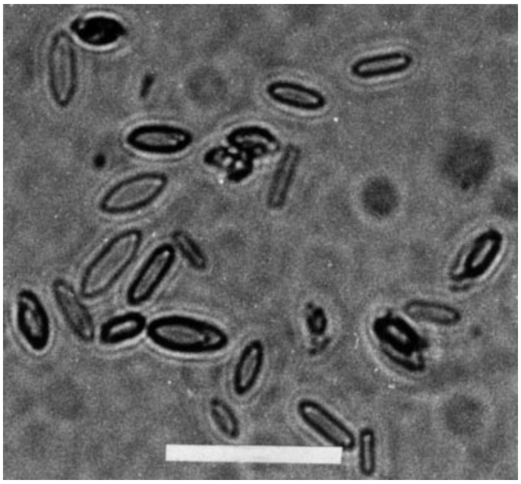


Fig. 1 Optical micrograph of sample #1 after two weeks. The particles are flat and shaped like pointed ellipsoids as they have not ripened significantly. The micrograph provides an image of the particles as a dispersion and indicates that they form a stable colloid. The scale bar is approximately 20 μm

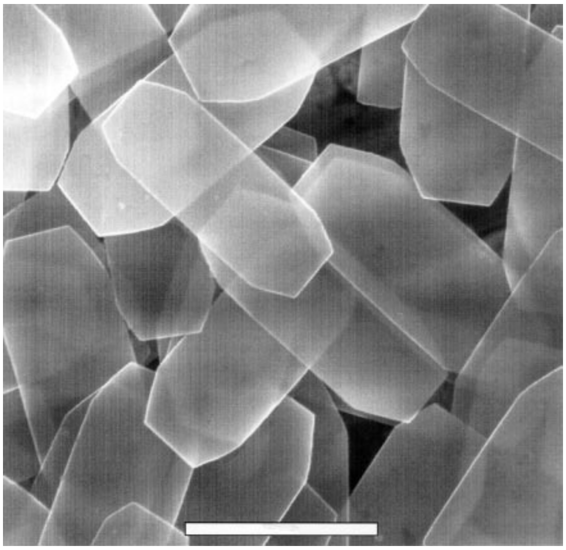
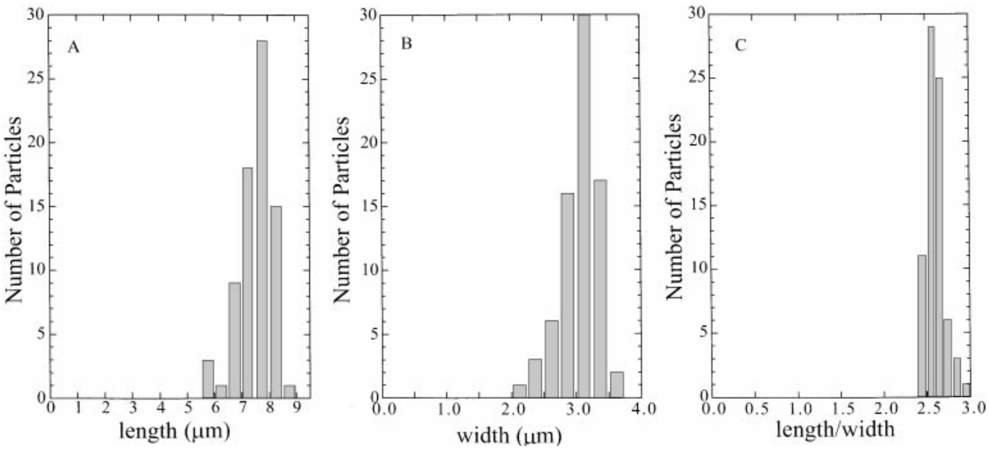


Fig. 2 Scanning electron micrograph of sample #2. These particles have ripened, to give them a rectangular shape. The particles are also very monodispersed compared to sample #1. The scale bar is approximately 5 μm

Fig. 3 Histograms showing the range of *A* lengths, *B* widths and *C* aspect ratio (length/width) of particles from sample #2



Samples #3 and #4 also showed these trends, the particles in sample #3 remained pointed, while those in sample #4 filled out to rectangles. However after two weeks the particles in samples #3 and #4, flocculated into two-dimensional structures. Figure 4 is an image of a floc from sample #4 viewed while still in water with the optical microscope. The particles appear also only to flocculate parallel or perpendicular to each other. This orientational order continued for a distance greater than the size of any floc observed. It is interesting that the more dilute samples flocculated while the concentrated samples remained stable. The sensitivity of the equilibria of the tungstate ions with different solubilities to pH might be responsible for this effect.

Each particle is a single crystal and clear diffraction patterns can be observed in the transmission electron microscope. The orientation of the crystal axes is always fixed with respect to the shape of the particles and this indicates that the different growth rates of specific crystal faces governs the control of shape. The faces may also have different potentials and in this way control the interactions which give rise to the unusual, ordered floc structure.

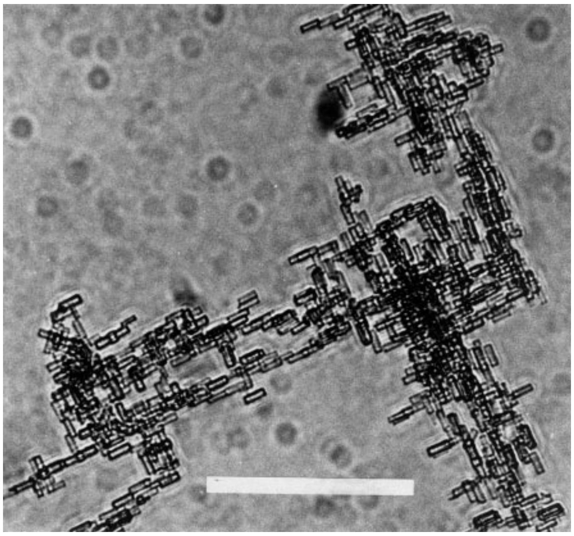


Fig. 4 Optical micrograph of sample #4 with the particles still in the ripening liquid. The particles have orientated and assembled to form two-dimensional flocs where the particles lie parallel or perpendicular to each other. The scale bar is approximately 50 μm

Conclusions

The original preparation of tungstic acid particles [16, 17] was improved by stirring, reducing the polydispersity from 23% to 9% and reducing the aging time required to form rectangular particles. Highly monodisperse particles have recently been shown to display phase behavior that is not observed in polydisperse materials [19, 20]. A monodispersed dispersion of particles such as the tungstic acid described above is ideal for the study of mesophases of concentrated particle dispersions and the study of flocculation of anisotropic particles.

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