Flow coating ellipsoidal titania nanoparticles into films with controlled thickness and structure

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Thin films deposited on a substrate have many applications, including anti-reflective coatings, photonics, catalysts, microelectronics, and photovoltaics. Various methods, such as sol-gel coating, spin coating, chemical vapor deposition, thermal evaporation, dip coating, and layer-by-layer deposition are used for making thin films. Deposition of nanoparticles in particular can be used to create porous materials. This bottom-up approach to control the properties of the thin films has emerged as one of the key methods to control the structure on the nanometer- to micrometer-scale. Anisotropic particles are emerging as a versatile building block for creating complex structures.

Here, we present the directed assembly of ellipsoidal titanium dioxide nanoparticles into thin films by flow coating [1] over an area with dimensions of centimeters. Due to its electronic, optical and photocatalytic properties, titanium dioxide is an important component in many nanostructured materials and devices [2]. The suspension is confined between glass slides used as a blade and a substrate. The blade makes an angle α with the substrate and is separated by a gap of d. As the substrate is translated with velocity v, the liquid confined due to capillarity, is pulled out due to frictional drag on the suspension and dries to form a film of titanium dioxide particles. Figure 1a shows a schematic of the flow coating process. Figure 1b shows an SEM image of the ellipsoidal titanium dioxide particles used in this work. The major axis is 2b = 260±62nm and the minor axis 2a=48±8nm with an aspect ratio of 5.35±0.88, determined from TEM images.

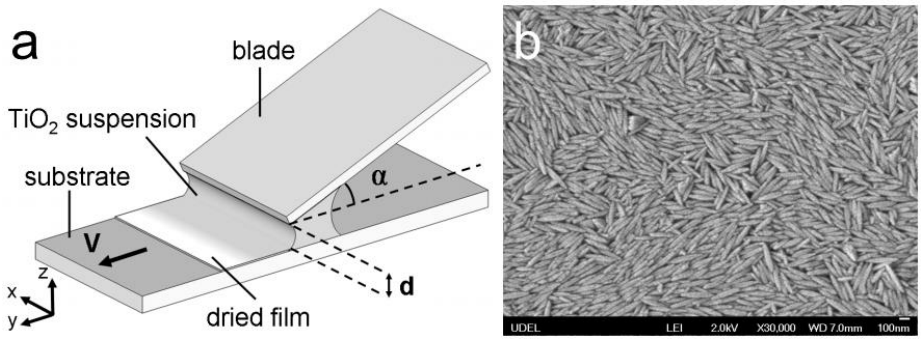

Figure 1: (a) Schematic of the experimental procedure used for assembling titania particles by flow coating. (b) A scanning electron microscopy (SEM) image of the titanium dioxide particles.

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The volume fraction of the particles in the suspension, the blade angle and the substrate velocity affect the thickness and microstructure of the deposited film. The particles undergo an isotropic-nematic transition at a volume fraction Φ^*=0.40. For $\Phi > \Phi^*$ the deposited film consists of particles oriented along the coating direction and below it ($\Phi < \Phi^*$) the particles in the film orient isotropically. Figure 2 shows SEM images of a films deposited at a blade angle α = 25º and a gap d = 200 μm at different coating velocity, v and particle volume fraction, Φ. At a volume fraction Φ = 0.25 and a substrate velocity v = 100 μm/s the particles are randomly orient (figure 2a). Upon increasing the coating velocity to v = 1500 μm/s the particles form domains of similar orientation with dimensions on the order of several micrometers (figure 2b). In contrast, the films deposited from a suspension with particle volume fraction Φ = 0.52, exhibits an orientation along the coating direction, with a substrate velocity dependant orientational order. At a substrate velocity v = 100 μm/s the particles form a wavy microstructure along the direction of translation (figure 2c) and at a substrate velocity v = 1500 μm/s the particles orient with the flow direction (figure 2d). The substrate is snapped to show that the alignment is preserved over the entire cross section of the film.

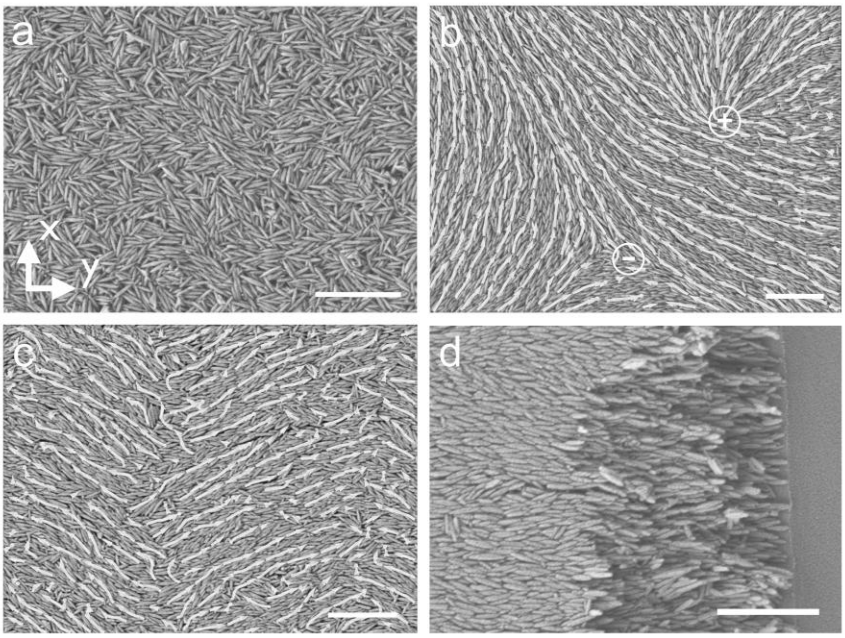

Figure 2: The substrate moves along the y-axis and the scalebar is 1 μm for all the images. The streamlines shown in figure b and c are calculated using Mathematica. (a) SEM image of a film deposited at velocity v=100 μm/s and volume fraction Φ=0.25. (b) SEM image of a film deposited at velocity v=1500 μm/s and volume fraction Φ=0.25. (c) SEM image of a film deposited at velocity v=100 μm/s and volume fraction Φ=0.52. (d) SEM image of a film deposited at velocity v=1500 μm/s and volume fraction Φ=0.52.

Figure 3 shows the effect of volume fraction and substrate velocity on the structure of the deposited film. Below the I-N transition ($\Phi < \Phi^* \approx 0.40$) particles form domains of similar particle orientation (D), with the domain size increasing with increasing substrate velocity. The black filled circles indicate large domains (figure 2b) and the light gray circles indicate isotropic orientation (figure 2c). Above the I-N transition particles align in the coating direction. The filled squares indicate fully aligned particles (F) and an SEM of the microstructure is shown in figure 2d. Upon reducing the substrate velocity the particles forma wavy structure shown in figure 2c

and indicated by open triangles in figure 3. Finally the particle form an isotropic structure (I) shown by filled gray circles.

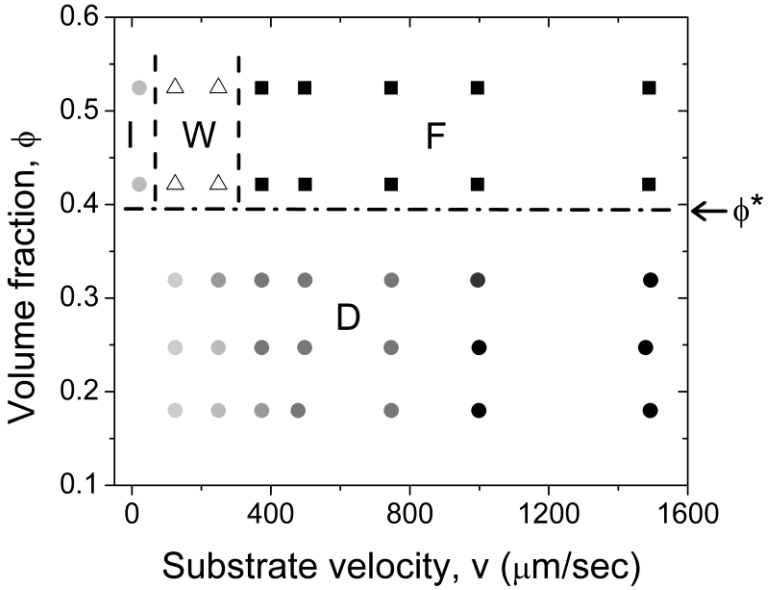

Figure 3: Effect of volume fraction on the structure of the deposited film. At volume fraction below the I-N transition (Φ < Φ*) the particle form domains (D) as shown in figure 2b. The size of the domains depends on the substrate velocity. Above the I-N transition the particle align in the coating direction. The region F indicates the fully aligned region (figure 2d), region W, shown by open triangles, indicates the wavy structure (figure 2c) and the isotropic structure (I) is shown in gray circles. The films were deposited using a blade at an angle α=25 and a gap d=200 μm.

The phase diagram in figure 3 shows that the alignment of titania particles depends both on the substrate velocity and particle volume fraction. Increasing substrate velocity increases the shear on the colloidal suspension which causes the flow-alignment of the particles. Shear flow in addition to aligning the particles also causes other types of motions like, tumbling, kayaking, wagging and log-rolling. Increasing shear rate finally favor flow-alignment. Therefore, decreasing substrate velocity reduces the propensity of particles to orient in the flow direction. Furthermore, in the nematic regime the rotation of the particles is hindered, leading to a much greater orientation. There can also be a collective orientational motion which leads to the formation of the wavy pattern.

Finally, a third method of controlling the morphology of the deposited film is by varying the blade angle. Since the blade is inclined at an angle to the substrate the extensional component also contributes to the flow. The extensional flow effect is studied by increasing the blade angle and we observe that the orientational order of the deposited film increases with increasing blade angle. Thus, the shear and extensional stresses exerted on the colloidal particles due to the substrate velocity and the blade angle affect the microstructure of the deposited film.

Furthermore, the substrate velocity allows us to control the film thickness, from a monolayer of particle to a film micrometer thick. The thickness of the films deposited at a fixed blade angle α = 25º and a gap d = 200 μm are shown in figure 4. The thickness h of the films deposited range from 46±6 nm (Φ=0.18, v=124 μm/s) to 830±16 nm (Φ=0.52, v=1500 μm/s). Increasing the substrate velocity above v > 250 μm/s leads to deposition of thicker films, which indicates that

the deposition occurs in the Landau-Levich regime [3]. Below this velocity the deposition occurs due to particles advecting towards the air-water contact line, which is referred to the convection-deposition regime.

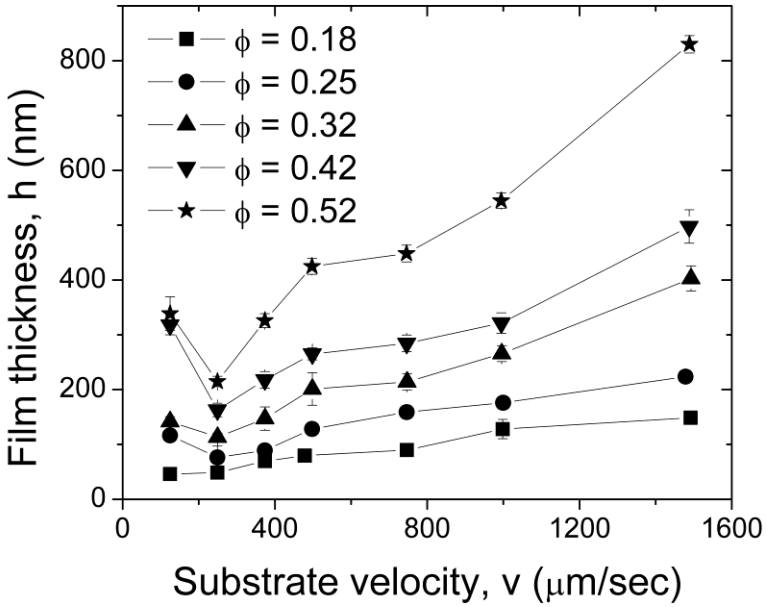

Figure 4: Film thickness as a function of substrate velocity at different particle volume fractions, Φ. The films were deposited using a blade at an angle α=25 and a gap d=200 μm.

To conclude, we report the deposition of thin films of anisotropic particles with controlled thickness and morphology. Both the film structure and the thickness are controlled by varying the particle volume fraction and the substrate velocity. The shear and extensional stresses during the deposition determine the particle orientation in the deposited film. Overall, this work demonstrates a unique approach for tailored thin films of a nanostructured material.

References:

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