Regular Article

Time-resolved viscoelastic properties of self-assembling iron oxide nanocube superlattices probed by quartz crystal microbalance with dissipation monitoring
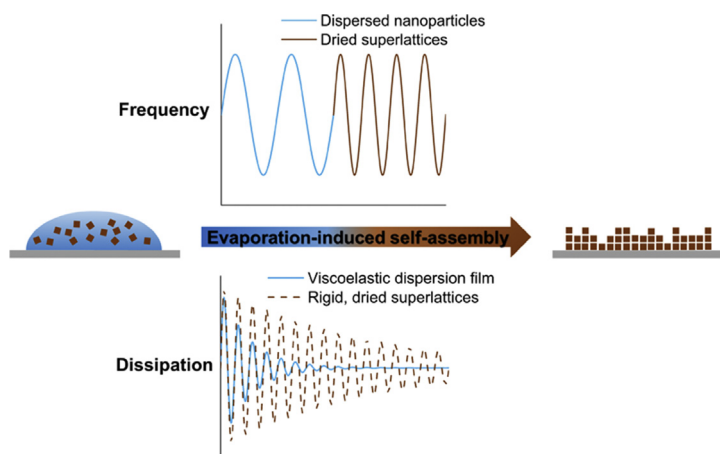
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Self-assembly of nanoparticles into superlattices can be used to create hierarchically structured materials with tailored functions. We have used the surface sensitive quartz crystal microbalance with dissipation monitoring (QCM-D) technique in combination with video microscopy (VM) to obtain time-resolved information on the mass increase and rheological properties of evaporation-induced self-assembly of nanocubes. We have recorded the frequency and dissipation shifts during growth and densification of superlattices formed by self-assembly of oleic acid capped, truncated iron oxide nanocubes and analyzed the time-resolved QCM-D data using a Kelvin-Voigt viscoelastic model. We show that the nanoparticles first assemble into solvent-containing arrays dominated by a viscous response followed by a solvent-releasing step that results in the formation of rigid and well-ordered superlattices. Our findings demonstrate that QCM-D can be successfully used to follow self-assembly and assist in the design of optimized routes to produce well-ordered superlattices.

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1. Introduction

Assembly of nanosized particles into large arrays with long-range translational and orientational order is a promising route to produce materials for optoelectronic, magnetic and structural applications [1]. Nanoparticle arrays and superlattices can be produced by a range of techniques, including e.g. drop casting [2], self-assembly at fluid-fluid interfaces [3], and dip coating [4]. Drop casting is an evaporation-induced self-assembly technique [5] where the solvent evaporation rate, Marangoni flow and the coffee-ring effect have a strong influence on the sizes and shapes of the formed superlattices [6–8].

In-situ X-ray crystallographic methods have been extensively used to probe the self-assembly process [9–11]. A recent small-angle x-ray scattering (SAXS) and grazing incidence SAXS (GISAXS) study of drop cast iron oxide nanoparticle dispersions has shown that at low evaporation rates of the solvent, self-assembly mainly takes place at the solid-liquid interface and is driven by capillary forces at the drying front of the droplet [12]. Although previous studies provided important insight to the development of the crystalline order of the self-assembling nanoparticles, studies on the evolution of the rheological properties of the self-assembling arrays are sparse.

Quartz crystal microbalance with dissipation monitoring (QCM-D) is a technique that provides time-dependent information on the depositing mass and its viscoelastic properties. Thus, it can be seen as a high-frequency interfacial rheometer [13]. The QCM-D has been successfully used for obtaining information on the rheological properties of soft organic films, consisting of DNA [14,15], proteins [16,17], or polymers [18,19]. QCM-D has also been proven to be a powerful technique in studies on aggregation and deposition of nanoparticles [20,21], including laterally heterogeneous colloidal films [22,23].

In this study, we have investigated the time-dependent viscoelastic properties and deposited mass of assembling arrays by QCM-D. Dispersions of superparamagnetic, truncated iron oxide nanocubes [24] in toluene were drop cast under controlled conditions in a closed custom-built compartment that allowed simultaneous monitoring of the QCM-D response and the growth of the self-assembled arrays by video microscopy (VM). The time-dependent viscoelastic properties obtained by a Kelvin-Voigt based model displayed for the arrays a distinct transition from a viscous-dominated response to a response, characteristic for rigid films later in the self-assembly process. The viscous-elastic transition was related to the expulsion of solvent and transition from solvent-swollen to dense arrays.

2. Materials and methods

2.1. Iron oxide nanocube synthesis and dispersion preparation

We have synthesized iron oxide nanocubes following a previously described procedure [25]. In brief, nanocubes with edge lengths l_{edge} = 8.9 ± 0.4 nm (C089) and l_{edge} = 12.1 ± 1.0 nm (C121) (edge lengths obtained from small angle X-ray scattering data; Fig. S1) were prepared by first dissolving 10 mmol of an iron oleate precursor in a mixture of 50 mL 1-octadecene (90%, Sigma-Aldrich) and 2.56 g eicosane (99%, Sigma-Aldrich) for C121, and a 9:1 mixture of 1-octadecene and 1-hexadecene (99%, TCI) for C089. We then added 5 mmol of sodium oleate (97%, TCI) and oleic acid (99%, TCI) to the solution. The solution was degassed for 30 min at 140 °C, and afterwards heated with a rate of 3 °C/min to the boiling point of the solution at 325 °C (C121) and 316 °C (C089),

respectively, at which the solution was refluxed for 30 min. The mother liquor was quickly cooled down to room temperature and centrifuged several times in a toluene/ethanol mixture (toluene 99.5%, VWR Chemicals; ethanol 99.5%, Solveco) in order to remove excess organics. Slowly drying the dispersion under vacuum yielded a paste with an iron oxide content of about 54% for C121 and 45% for C089. The paste was redispersed in toluene by adding a small amount of oleic acid (0.05 mg per mg paste) and sonicating the dispersion for several hours. Dispersions with a concentration of c = 0.3 mg$_{iron\ oxide}$/mL were exclusively used in the QCM-D measurements. Previous studies on iron oxide nanocubes synthesized following the same procedure and similar sizes have shown that the nanocubes display a superparamagnetic behavior at room temperature [26,27].

2.2. Quartz crystal microbalance with dissipation monitoring

We have employed a custom-built cell [6] attached to a base module of the QCM-D E1 system (Q-Sense AB) to record simultaneously the frequency change Δf and the dissipation shifts ΔD, i.e. the damping, of the standing wave applied to the quartz crystal up to the 13th overtone. The cell was equipped with a window for droplet monitoring with an optical microscope and with two ports for manipulating the solvent evaporation with a nitrogen gas flow rate of $\dot{m}_{N2}$ = 60 μg min^{-1} using a digital mass flow controller (FMA-2601A, Omega Engineering Inc.) [25].

All used silica-coated sensors (QSX-303, f_f = 5 MHz, Q-Sense AB) were functionalized to limit the droplet (V = 20 μL) spreading of dilute (c = 0.3 mg/mL) dispersions of the oleate-capped iron oxide nanocubes in toluene. The sensor functionalization was carried out according to a previously reported protocol [28]. Briefly, we dusted-off the pristine sensor by sonication in Milli-Q water followed by drying with nitrogen gas. The dry sensor surface was irradiated with UV in a closed chamber (UV/Ozone ProCleaner, Bioforce Nanosciences) for 30 min and hereafter silane-coated (1 H,1H,2H,2H-perfluorooctyltriethoxysilane, 98%, Sigma-Aldrich) at 130 °C for 4.5 h in a sealed pyrex bottle. Afterwards, we placed a Teflon ring with 6 mm inner diameter and 14 mm outer diameter on the silanized sensor and removed the fluorosilane on the exposed area by a UV/ozone treatment for 50 min. The silanized, omniphobic outer region limits the droplet spreading to the highly wettable, annular central region of the sensor.

The measurements were exclusively performed on sensors with a frequency drift below 2 Hz/h and the recorded data were analyzed with the viscoelastic modeling function in the proprietary software package QTools (Q-Sense AB).

2.3. Video microscopy

Video microscopy was performed in reflection mode using a Nikon Eclipse FN1 light microscope. The microscope was equipped with a 50x long working distance (WD = 17 mm, NA = 0.45) and images were obtained by a 2 megapixel CCD camera (Kappa Zelos-02150C GV, Kappa Optronics GmbH) with a time-resolution of 1 s.

2.4. Transmission electron microscopy (TEM)

TEM micrographs were obtained using a JEOL JEM-3010 (Point resolution: 0.17 nm; spherical aberration C_s = 0.6 mm) equipped with a LaB$_6$ filament operated at an accelerating voltage of 300 kV. Selected area electron diffraction (SAED) patterns were recorded at a camera length of 30 cm.