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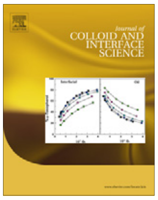

Quantitative analysis of exfoliation and aspect ratio of calcium niobate platelets

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ABSTRACT

This work employs tapping-mode AFM and dynamic light scattering (DLS) to investigate the effects of suspension composition (alkylammonium cation type, concentration) on the degree of exfoliation of a layered perovskite, calcium niobate ($HCa_2Nb_3O_{10}$, denoted as CNP). It is well known that in aqueous suspensions, tetrabutylammonium (TBA) cations intercalate CNP's layered structure, producing exfoliated platelets. This work shows that tetramethylammonium and tetraethylammonium cations do not produce significant levels of CNP exfoliation. However, TBA leads to complete exfoliation of CNP (>95%) in suspensions prepared with TBA:CNP ratios greater than 1:1. TGA and XRD data indicate that TBA uptake is limited by steric packing constraints. After depositing TBA–CNP platelets on mica surfaces for AFM imaging, quantitative image analysis provides the degree of exfoliation and distributions of platelet thickness, lateral size, and aspect ratio. The aspect ratio of TBA–CNP platelets has a lognormal distribution. Sedimentation of TBA–CNP suspensions under unit gravity removes unexfoliated particles from suspension, and centrifugation leads to differential sedimentation. The lateral size and aspect ratio of residual suspended TBA–CNP platelets decrease with increasing centrifugation speed. For all fractions of TBA–CNP platelets, the number-average lateral size from AFM agrees remarkably well with the effective spherical particle diameter measured by DLS.

1. Introduction

The building blocks of polymer nanocomposites include particles of various shapes, such as spheres (dots), cylinders (tubes), and sheets (platelets), each having a characteristic dimension on the nanometer scale. The nanoscale dimension determines the amount of polymer–particle interfacial area in the composite per unit particle mass ($\hat{S}$). For dots, tubes, and platelets with density ρ and diameter d or thickness t, the specific areas are $6/\rho d$, $4/\rho d$, and $2/\rho t$, respectively. Platelets are particularly efficient at creating interfacial area: for a layered silicate such as montmorillonite with $\rho = 2.86\ \text{g/cm}^3$ and $t = 1$ nm, $\hat{S} = 700\ \text{m}^2/\text{g}$. Comparable silicate spheres with $d = 10$ nm only deliver $\hat{S} = 210\ \text{m}^2/\text{g}$.

Achieving and maintaining a high degree of exfoliation is a prerequisite for efficient utilization of platelets as building blocks in polymer nanocomposites. Compared to N individual exfoliated platelets, a plate-like stack of N platelets (e.g., a tactoid) results in an N-fold decrease in $\hat{S}$. Hence, much work has been done to tailor the surface chemistry of layered materials, especially layered silicates, perovskites, and (more recently) graphene, to maximize exfoliation to produce individual platelets. Progress in this area has been limited, in part, by the difficulty in quantifying the degree of exfoliation of platelets dispersed in solvents or polymers.

Studying platelet exfoliation in liquid solvents [1–5] offers two advantages: First, solution composition and processing conditions can be easily varied to explore their impact on exfoliation of layered materials in liquid suspensions. Second, depositing particles/platelets on a surface and removing the solvent enables characterization by atomic force microscopy (AFM) [6–15]. This enables us to quantify the degree of exfoliation and relate it to solution chemistry, platelet surface chemistry, and processing conditions. Quantitative analysis of platelet exfoliation in solution also helps us develop methods to tailor platelet surfaces for maximal exfoliation.

Our previous work [15] describes the use of AFM to quantify the degree of exfoliation and size distribution of montmorillonite (MMT) dispersed in water. MMT, a naturally occurring clay mineral, readily exfoliates upon dispersion in deionized water – but not completely. Starting with a 1.0 wt% suspension, 0.13 wt% of the MMT settled out after a few days under unit gravity, leaving a suspension containing 0.87 wt% of primarily exfoliated MMT platelets. After centrifugation of the parent suspension for 1 h at 2000g followed by deposition of the supernatant onto mica, about 87% of the MMT particles seen in AFM images were isolated, single platelets; the other particles were primarily single platelets carrying small fragments resulting from incomplete exfoliation. We also quantified the MMT aspect ratio distribution as a function of suspension centrifugation speed. The MMT platelet aspect ratio was

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maximal for centrifugation at 125*g* (1000 rpm). This suggests that centrifugation at speeds below 125*g* removed primarily unexfoliated MMT particles from suspension, while centrifugation above 125*g* also removed larger exfoliated platelets from suspension.

In this work, we use AFM and dynamic light scattering (DLS) to quantify the degree of exfoliation and size distribution of calcium niobate perovskite (CNP) platelets in aqueous suspensions. Potassium calcium niobate ($KCa_2Nb_3O_{10}$) is a synthetic, layered, Dion–Jacobson perovskite [16,17] with interlayer K^+ cations readily exchanged for protons [18] to produce $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ (HCNP), and the starting point for subsequent exchange with alkali metal cations [19,20] or organic amines [21–33]. HCNP can be exfoliated by some organic amines [23,28] and ammonium cations, with tetrabutyl ammonium hydroxide (TBAOH) receiving the most attention [25–27,29]. Exfoliated CNP platelets have been used to prepare various multicomponent, multilayer, or catalytic structures [29,31,34,35] formed by controlled platelet aggregation or layer-by-layer assembly.

In most studies of CNP exfoliation [23,25,26,29,33,36], TEM and AFM images show platelets with lateral dimensions on the order of 0.1–2.0 μm. Early work [23] using scanning TEM with high-angle annular detection (STEM–HAAD) demonstrated that polyether amines exfoliate at least some of the HCNP into unilamellar sheets. Mallouk et al. [25,26] found that excess TBAOH exfoliates HCNP into unilamellar platelets, which sometimes form closely packed ("tiled") films after deposition on surfaces. The uniform contrast of platelets in the TEM and AFM images implies that the platelets were unilamellar; this was later verified quantitatively by high resolution TEM with electron diffraction analysis [29,36]. AFM images in past studies [25,26,28,33] give qualitative evidence of exfoliation. Shiguihara et al. [37] explored the effect of TBAOH concentration on the exfoliation of layered hexaniobate $H_2K_2Nb_6O_{17}$, but they did not use AFM for quantitative analysis. To the best of our knowledge, no published studies have used AFM to quantify the degree of exfoliation or aspect ratio distribution of any layered perovskite as a function of solution and processing conditions.

In this work, we use AFM and DLS to identify conditions, including alkyl ammonium cation type, cation concentration, and processing conditions (dialysis and centrifugation), resulting in nearly complete CNP exfoliation. We use centrifugation to separate unexfoliated CNP particles and larger platelets from TBAOH-treated HCNP suspensions. AFM and image analysis are used to quantify the mean platelet thickness, lateral size, and aspect ratio distributions of HCNP remaining in suspension as functions of centrifugation speed. Dynamic light scattering measurements provide the effective spherical particle diameter of CNP platelets in suspension. The effective HCNP platelet size from DLS correlates well with that obtained from AFM image analysis.

2. Experimental methods

2.1. Materials

2.1.1. CNP synthesis

Calcium niobate perovskite ($KCa_2Nb_3O_{10}$, denoted here as KCNP) was prepared by reacting stoichiometric mixtures of $CaCO_3$, Nb_2O_5, and K_2CO_3 with 10% molar excess of K_2CO_3 added to compensate for volatilization losses. The reaction mixture was heated at 3 °C/min to 1250 °C and maintained at that temperature for 72 h. The reacted powders were washed repeatedly with deionized water to remove excess potassium ions and then air-dried. To exchange H^+ for K^+, KCNP powder was dispersed in 6.5 M nitric acid, stirred for 3 days, and then washed repeatedly with deionized water until free of K^+ ions. After drying, PXRD analysis revealed phase-pure, proton-exchanged HCNP ($HCa_2Nb_3O_{10}$). Exposure to ambient humidity swells $HCa_2Nb_3O_{10}$ with water [18], producing $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ (denoted as HCNP). The PXRD patterns for dry and hydrated HCNP (Supporting information) agree well with those reported previously [18]; all peaks can be indexed on the basis of tetragonal symmetry, indicating the formation of phase-pure layered materials.

2.1.2. Suspension preparation

Several alkyl ammonium bases were used to promote HCNP swelling and exfoliation, including tetramethylammonium hydroxide (TMAOH, 20 wt% in water, Alfa Aesar), tetraethylammonium hydroxide (TEAOH, 35 wt% in water, Alfa Aesar), and tetrabutylammonium hydroxide (TBAOH, 40 wt% in water, Aldrich), all used as received. In a typical exfoliation procedure, 0.3 g of HCNP powder was added to 150 mL of 3.66 mM aqueous solution of alkyl ammonium base to achieve a 0.20 wt% HCNP solution containing a nominal 1:1 molar ratio of cations to CNP unit cells. Alkyl ammonium concentration was varied to change the cation:CNP molar ratio. The solutions were ultrasonicated (Fisher model FS-28) for 1 h and stirred at room temperature for at least 7 days.

In some cases, suspensions were centrifuged (Eppendorf model 5403, Brinkmann) to remove a fraction of the suspended particles. The dimensionless centrifugal acceleration *A* (centrifugal acceleration divided by *g*) is

$$A(g) = \left(\frac{2\pi n}{60}\right)^2 \frac{r}{g} \tag{1}$$

where *n* is the rotation speed in rpm, and *r* is an equivalent radius (0.122 m here) that depends on the particular geometry of the centrifuge's rotor and tubes. After centrifugation for 1 h at different centrifugal speeds, the supernatant suspension was retained for analysis.

For TBAOH-treated HCNP (TBA–CNP), the amount of TBA–CNP remaining in suspension after centrifugation was measured by dry weight analysis. For these experiments, we started with 1.0 wt% TBA–CNP suspension containing 1:1 TBA:CNP. After centrifugation, we measured the residual weight of TBA–CNP in the supernatant after drying.

To prepare CNP samples for AFM imaging, suspensions were first dialyzed for 8 h to remove excess alkyl ammonium ions. The dialysis tubing (MEMBRA-CEL Tubing, MD10-14, Viskase Companies, Inc.) has a pore size of about 25 Å and a nominal molecular weight cutoff of 14,000 daltons. Prior to use, the dialysis tubing was soaked in deionized (DI) water for at least 24 h and followed by at least three rounds of copious rinsing. About 5 mL of CNP suspension was sealed inside the tubing, immersed in a DI water bath (about 2.0 L), and stirred. The DI bath water was replaced three or four times during dialysis.

2.2. Methods

2.2.1. Powder X-ray diffraction

Powder X-ray diffraction patterns were obtained using two X-ray diffractometers (Miniflex II and D-MAX-2100, Rigaku, Japan) with monochromatized Cu Kα (λ = 1.5418 Å) radiation. In general, CNP powders were ground and sieved using a 270 mesh sieve and then mounted in the sample holder.

2.2.2. Organic cation uptake

We measured the uptake of organic cations by HCNP using two methods. The first method followed an established protocol for measuring the cation exchange capacity of clay minerals [38,39] based on the bis(ethylenediamine) copper complex, $[Cu(en)_2]^{2+}$. After dispersing HCNP powder in standard $[Cu(en)_2]^{2+}$ solutions, the residual solution concentration of $[Cu(en)_2]^{2+}$ is quantified by