Covalent Grafting of Phenylphosphonate on Calcium Niobate Platelets

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ABSTRACT

Hypothesis

This work explores covalent grafting of phenylphosphonate (PPA) onto exfoliated, protonated calcium niobate (HCN), a Dion-Jacobson layered perovskite. The specific hypothesis is that PPA can be readily grafted onto the face surfaces of exfoliated HCN, which has reactive apical oxygen atoms.

Experiments

Previous research has established the conditions required for full exfoliation of HCN in aqueous solutions of tetrabutylammonium hydroxide (TBAOH), denoted as TBACN. This work first explores the effect of reflux conditions on the dispersion state of TBACN suspensions, and then investigates PPA grafting onto both non-exfoliated HCN and exfoliated TBACN dispersed in deionized (DI) water, TBA solution, and various alcohols. The products are characterized by a variety of techniques including light scattering to assess the TBACN dispersion state, ^{31}P MAS NMR to confirm PPA grafting, and XPS to estimate PPA grafted amounts.

Findings

The results confirm the grafting of PPA on HCN and TBACN, quantify the extent of PPA grafting, and identify various grafting modes (mono-, bi-, and tridentate). All of these aspects are found to be dependent on the layered materials' exfoliation state, suspension processing conditions, and solvent composition. The results are rationalized in terms of a plausible mechanism of the grafting process.

Keywords

phenylphosphonic acid; phenylphosphonate; calcium niobate; exfoliation; grafting; organic-inorganic hybrid

1. Introduction

Inorganic platelets exfoliated in stable suspensions are potential building blocks for making polymer nanocomposites (PNCs) with enhanced properties and performance. In PNCs, the platelet-polymer interface (really an “interphase”) plays two crucial roles. First, the interphase should promote platelet-polymer compatibility and thus platelet dispersion in the polymer, maximizing interfacial area. Second, the interphase should have structure and properties distinct from those of the bulk phases, as well as beneficial to performance in end-use applications. Synergy is achieved when both roles are fulfilled, because the interphase’s beneficial properties are amplified by the high interfacial area/volume ratio achieved when the platelets are well dispersed.

Considerable research has focused on methods of adding organic functional groups to the surface of inorganic platelets to improve polymer-platelet compatibility. The classic example is ion exchange treatment of clay mineral platelets (e.g., montmorillonite) with alkyl ammonium cations to render them more hydrophobic. Although this improves clay platelet compatibility with polymers, it does not (at least by design) contribute significantly to improving composite functionality through beneficial interphase structure or properties.

Covalent organic functionalization of platelet surfaces can be used to tailor the interphase to enhance platelet compatibility with polymers and create “designer” interphase structures. Silane grafting chemistry is well established for layered aluminosilicates (e.g., laponite [1-5] and montmorillonite [6-13]) via condensation reactions with surface silanol or aluminol groups. Surface modification using organophosphonic acids (oPAs) [14, 15], reviewed recently, offers enhanced hydrolytic stability relative to silane grafting [14, 16]. Various oPAs have been used to chemically modify ceramic membranes [17, 18], oxide particles [19-23], oxide thin films [24],

hydroxyapatite [25], and porous zeolites [26]. Grafting of oPAs onto the interlamellar face surfaces of layered inorganics has been reported for kaolinite [27, 28], natural phlogopite [29], hydrotalcite [30], layered silicates [31], and layered double hydroxides [32-35]. Functionalization of polymers with oPAs [36] and polymers carrying oPA functionality [37] have also been studied.

This work explores the covalent surface functionalization of inorganic layered perovskites [38-40] with oPAs. In the past, the surfaces of layered perovskites have been modified via acid treatment [41] or other kinds of ion-exchange [42-47]. Several papers describe various approaches for covalent surface modification of layered perovskites. For example, *n*-alkoxy groups have been grafted to the interlayer surfaces of proton-exchanged niobate [48-51], titanate [52], and tantalite [53] perovskites. Alcohol-functionalized niobates have been used as the starting point for subsequent grafting reactions, such as interlayer polyether grafting [54]. Shimada et al. [55] first functionalized the interlayer surfaces of $\text{HLaNb}_2\text{O}_7 \cdot x\text{H}_2\text{O}$ with *n*-propanol, exchanged it for *n*-decanol, and then proceeded with interlayer grafting using phenylphosphonic acid (PPA) and *n*-alkylphosphonic acids. The work of Shimada et al. is the only report to date of covalent functionalization of a layered perovskite with any oPA.

It is well known that layered perovskites may be exfoliated via cation exchange with bulky alkylammonium cations in aqueous suspensions [38, 39, 56-64]. Much of this work focused on calcium niobate, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (KCN), or its proton-exchanged form, $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ (HCN). Using AFM with quantitative image analysis, Gao et al. [64] proved that complete exfoliation of HCN in aqueous suspensions requires at least a 1:1 molar ratio of tetrabutylammonium cations (TBA^+) to calcium niobate (CN) unit cells. Use of lower TBA^+ concentrations (or less bulky cations) result in incomplete CN exfoliation. Steric

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4 interactions among bulky TBA^+ cations limit the exchange of H^+ for TBA^+ to about 15-20% of
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6 the theoretical cation exchange capacity. Thus the surface of (TBA,H)CN (henceforth denoted
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8 as TBACN) has a significant number of Lewis acid sites (Nb-OH) available for reaction with
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10 oPAs. No one to date has explored the possibility of covalent surface modification of TBA-
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12 exfoliated CN by oPAs.
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16 This work investigates the covalent grafting of PPA onto TBA-exfoliated CN platelets.
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18 In particular, we explore the effect of solvent (water, aqueous TBA solution, alcohols) on grafted
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20 amount and binding mode. Dynamic light scattering (DLS) characterizes the dispersion state of
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22 TBACN platelets in suspension. ^{31}P MAS NMR data prove that PPA has grafted onto TBACN,
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24 and XRD results identify conditions for which grafting occurs on platelet face surfaces, as
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26 opposed to edges and exterior particle surfaces. XPS results provide estimates of the PPA
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28 grafted amount. Finally, FT-IR, NMR, and XPS spectra provide evidence of different binding
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30 modes of PPA on CN platelet surfaces.
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36 Our investigation is timely and relevant for two reasons. First, CN and related layered
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38 perovskite materials are well known as active photocatalysts with significant potential for
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40 hydrogen production via water hydrolysis [65-75]. Recent work has shown that TBA-exfoliated
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42 CN in water can be used to produce hydrogen gas [76-82]. Surface modification of CN may be
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44 useful for maintaining its suspension stability and tailoring its interfacial photocatalytic
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46 properties. However, CN's photocatalytic activity may make it difficult to covalently graft
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48 organic molecules onto its face surfaces, so this question merits investigation. Second, prior
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50 studies of grafting onto layered perovskites (reviewed earlier) all used organic solvents and
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52 examined interlayer reactions without consideration of exfoliation. Compared to the multistep
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54 process of Shimada et al. [55], facile TBA-mediated exfoliation of CN followed by grafting in
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aqueous suspensions may be a more straightforward route to organically-modified CN and related perovskites.

2. Materials and Methods

2.1. Materials

2.1.1. Exfoliated CN Suspension

Calcium niobate ($\text{KCa}_2\text{Nb}_3\text{O}_{10}$, KCN) was synthesized as described previously [64] and proton-exchanged in 6.5 M HNO_3 to produce $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ (HCN). Aqueous stock suspensions of TBACN were prepared following an established protocol [64]. We add 1.0 g of HCN powder and 1.25 g of 40% w/w tetrabutylammonium hydroxide (TBAOH, Sigma-Aldrich) solution to 150 mL deionized (DI) water, followed by stirring at room temperature for a minimum of 7 days. The resulting suspension has a 1:1 molar ratio of TBA^+ to HCN unit cells and contains, based on our previous work [64], more than 95% exfoliated TBACN platelets.

2.1.2. PPA Grafting Protocol

In a typical grafting reaction, 25 mL of TBACN stock suspension was added to a 100 mL round-bottom flask and stirred, followed by addition of 0.27 g of phenylphosphonic acid (PPA, Sigma-Aldrich, used as received); this quantity represents a 3:1 molar ratio of PPA to CN unit cells. The mixture was then refluxed at a temperature near the solvent's boiling point, with stirring and slow N_2 bubbling, for 3 days. Reflux reactions were usually carried out under lighted conditions in a fume hood. The flask was located approximately 1 m below two standard, 32 W fluorescent bulbs (Phillips 700 series) behind a Plexiglas sheet. In some cases, reflux reactions were carried out in darkness with the lights off and the flask/condenser wrapped

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4 in aluminum foil. The products of grafting reactions prepared following this protocol are
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6 denoted as PPA+TBACN(light) and PPA+TBACN(dark), with the terms in parentheses denoting
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8 variations in suspension and/or reflux conditions.
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11 For TBACN, suspension conditions prior to PPA addition were also varied, including (1)
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13 additional dilution, or (2) drying followed by re-dispersion in a new solvent. For dilution cases,
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15 25 mL of TBACN stock suspension was diluted with 25 mL of either DI water or TBAOH
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17 solution; these suspensions are denoted as TBACN(dil-DI) and TBACN(dil-TBA), respectively.
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21 Experiments were also carried out in which 25 mL of the TBACN stock suspension was
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23 dried and then re-dispersed in 50 mL of a new solvent (DI water; TBAOH solution; 94-96%
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25 anhydrous, denatured ethanol, Alfa-Aesar; 99.5+% ethanol, Sigma-Aldrich; 99.5+% *n*-propanol,
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27 Alfa-Aesar; or *n*-propanol diluted with water to 95% *n*-propanol). The stock suspension was
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29 dried in the flask by heating in an oven at 90-100°C. After adding 50 mL of the new solvent, the
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31 suspension was ultrasonicated for 10 min (Solid-State/Ultrasonic FS-28, Fisher Scientific) and
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33 stirred for at least 1 h at room temperature. These suspensions are denoted, for example, as
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35 TBACN(dried, dil-DI) for the case of re-dispersion into DI water. The product of the grafting
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37 reaction for this suspension is denoted as PPA+TBACN(dried, dil-DI), with corresponding
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39 notation used for other solvents.
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45 For reactions utilizing non-exfoliated HCN without TBA⁺, the corresponding dry weight
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47 of HCN powder (0.30 g) was weighed into the flask, followed by addition of 50 mL of solvent
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49 (DI water, alcohols). The suspension was sonicated for 10 min and then stirred at room
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51 temperature for at least 1 h. Products of grafting reactions are denoted, for example as
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53 PPA+HCN(dil-DI).
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After cooling to room temperature, the suspension was centrifuged at 6000 rpm for 1 h to recover the product. All products were washed twice with DI water (with mixing, sonication, and centrifugation) to remove unreacted PPA. The final products were dried overnight in an oven at 90-100°C.

2.2. Characterization Methods

Powder X-ray Diffraction (XRD) patterns were acquired using an X-ray diffractometer (Rigaku Ultima IV, Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$), typically over the 2θ range of 2-20° with a step size of 0.04° and a scan speed of 0.25°/min.

^{31}P MAS NMR Spectroscopy. Solid-state ^{31}P MAS NMR spectra were collected on either a Varian Inova 500 MHz or a Bruker Avance III-HD 500 MHz spectrometer (202.49 MHz). The Varian spectrometer used a Doty Scientific 4mm XC MAS probe. These spectra were collected at ambient temperature with a sample rotation rate of 10 kHz and TPPM decoupling at a ^1H field strength of 64 kHz. The Bruker system was fitted with a 1.9 mm MAS probe. These spectra were collected at ambient temperature with a sample rotation rate of 20 kHz. ^1H dipolar decoupling was performed with SPINAL64 modulation and 145 kHz field strength. Bloch decays were collected with 50 ms acquisition time over 300 or 400 ppm spectrum width with a relaxation delay of 10 s. Chemical shifts are reported with respect to H_3PO_4 and referenced externally with $\text{NH}_4 \cdot \text{H}_2\text{PO}_4$, which was assigned a value of 0.72 ppm.

Fourier Transform-Infrared (FT-IR) spectra were obtained utilizing a Perkin-Elmer Spectrum 100 FT-IR Spectrometer.

X-ray Photoelectron Spectroscopy (XPS) measurements utilized a Kratos AXIS Ultra DLD XPS system equipped with a monochromatic Al K α source. The energy scale of the

system is calibrated using an Au foil with Au4f scanned for the Al radiation and a Cu foil with Cu2p scanned for the Mg radiation resulting in a difference of 1081.70 ± 0.025 eV between these two peaks. The binding energy is calibrated using an Ag foil with Ag3d_{5/2} set at 368.21 ± 0.025 eV for the monochromatic Al X-ray source. The monochromatic Al K α source was operated at 15 keV and 120 W. The pass energy was typically fixed at 40 eV for the detailed scans. A charge neutralizer was used to compensate for the surface charge.

Thermogravimetric Analysis (TGA) (TA Instruments, model Q5000-0413) quantified the temperature-dependent mass loss of dried CN samples. Samples were placed on a Pt pan and heated in air from room temperature to 700°C with a 10°C/min ramp rate.

Dynamic Light Scattering (DLS) measurements employed a Zetasizer Nano ZS (ZEN3600, Malvern Instruments). Every DLS measurement was accompanied by a calibration test using 0.24 μ m polystyrene latex microspheres (Bangs Laboratories, Inc.) as a sizing standard. Samples for DLS were diluted with specified solvent to a consistent concentration ($\sim 5 \times 10^{-5}$ g/mL, ~ 1 mL sample volume), sonicated for at least 10 minutes, mixed on a vortex mixer, and then characterized at 25°C. DLS theory for platelet-like particles is not well developed [83]. We use the quadratic cumulant method with the Stokes-Einstein equation to determine the effective spherical diameter of CN particles in suspension.

3. Results and Discussion

3.1. Characterization of HCN and TBACN

3.1.1. As-Prepared HCN and TBACN

Proton-exchanged CN (HCN) and TBA-exfoliated CN (TBACN) have physical characteristics similar to those previously reported [64]. Upon heating from room temperature to

150°C, HCN loses about 0.4% of its mass due to loss of residual moisture in the sample (Figure 1a). From 150°C to 700°C, HCN undergoes an additional 2.2% mass loss. Most of this loss (1.9%) occurs between 250°C and 350°C and is due to a dehydroxylation reaction producing calcium hexaniobate ($\text{Ca}_4\text{Nb}_6\text{O}_{19}$), as observed previously [84]. The (001) peak in the XRD pattern for HCN (Figure 1b) is located at $2\theta = 6.05^\circ$, giving a d-spacing of 1.46 nm; the full pattern has been published previously [64].

After exfoliation with TBA^+ (1:1 TBA:CN molar ratio), the resulting TBACN forms a stable suspension of exfoliated platelets [64]. DLS measurements (Table 1) indicate an equivalent spherical diameter of 390 nm for TBACN particles in stock suspension, comparable to the 451 nm size reported previously [64]. Dilution of stock suspension into DI water, stirring for three days, and then further dilution with DI water does not lead to aggregation, since the particle diameter (365 nm) remains about that of the original suspension. After drying the stock suspension, TBACN particles readily re-disperse in aqueous TBA solution ($D = 328$ nm), but not in DI water ($D = 650$ nm).

TGA analysis of dried TBACN indicates a mass loss of 2.5% up to 150°C (assumed to be residual moisture), and a further loss of 11.6% from 150°C to 700°C. The peak rates of mass loss, around 250°C and 325°C, are associated with TBA^+ decomposition. After accounting for an estimated mass loss of 1.6% due to the dehydration reaction, the remaining TBA^+ mass loss leads to a 0.21 molar ratio of TBA^+ to CN unit cells. Repeated measurements give an average TBA:CN ratio of 0.18 ± 0.03 , consistent with previous reports [58]. XRD analysis of dried TBACN powder gives the expected XRD pattern [64] with the broad (001) peak indicating a d-spacing of 2.48 nm, consistent with turbostratic ordering of restacked TBA-coated CN platelets. The small secondary peak at 6° probably represents some non-exfoliated HCN.

Table 1. DLS results for TBACN suspensions (aqueous and alcoholic). The suspension concentrations were 5.0×10^{-5} g/mL for all DLS measurements.

Sample ID	Description	DLS Diluent (a)	Sphere Diam. (b) (nm)	Platelet Length (c) (nm)
As-prepared suspensions				
TBACN	As-prepared stock suspension, TBA+HCN	TBA/DI	390	540
TBACN(dil-DI)	TBACN diluted 1:1 (v/v) in DI, stirred for 3 days	DI	365	488
TBACN(dried, dil-DI)	TBACN dried, then re-dispersed in DI water	DI	650	1159
TBACN(dried, dil-TBA)	TBACN dried, then re-dispersed in TBA solution	TBA/DI	328	416
TBACN(dil-Et95)	TBACN diluted into 95% ethanol for DLS	Et95	352	462
TBACN(dried, dil-Et95)	TBACN dried, re-dispersed into 95% ethanol	Et95	474	723
TBACN(dried, dil-Et99)	TBACN dried, re-dispersed into 99% ethanol	Et99	897	1881
TBACN(dried, dil-nPr95)	TBACN dried, re-dispersed into 95% <i>n</i> -propanol	nPr95	509	805
TBACN(dried, dil-nPr99)	TBACN dried, re-dispersed into 99% <i>n</i> -propanol	nPr99	459	689
Refluxed suspensions				
TBACN(dil-DI, reflux)	TBACN diluted 1:1 in DI, refluxed 3 days in light	DI	398	556
TBACN(reflux)	TBACN refluxed 3 days in darkness	TBA/DI	400	560
PPA-grafted suspension				
PPA+TBACN	TBACN + 3:1 (molar) PPA, refluxed in light	TBA/DI	392	544

(a) Solvent used to dilute sample for DLS; abbreviations: DI = deionized water; TBA/DI = aqueous TBA solution; Et95 = 95% ethanol (balance water); Et99 = 99% ethanol (balance water); nPr95 = 95% *n*-propanol (balance water); nPr99 = 99% *n*-propanol (balance water).

(b) Intensity-mean equivalent spherical diameter.

(c) Average platelet length based on Eqn. (3) in ref. [83].

Figure 1. Characterization of as-prepared HCN (solid curves) and TBACN (dashed curves): (a) mass (%) and its derivative as functions of temperature from TGA, and (b) XRD patterns over the low-angle range. Numbers in (a) indicate “total” (non-water) percentage mass decreases from 150°C to 700°C.

3.1.2. Effect of Suspension Processing and Reflux Conditions on TBACN

TBACN suspensions were refluxed in darkness and under fluorescent lights as control experiments for the PPA grafting experiments discussed in section 3.2. For TBACN refluxed in darkness, the dried product exhibits a 9.1% mass loss from 150°C to 700°C (Figure 2a), slightly less than that found for the starting stock suspension. The derivative mass loss pattern is also similar to that of the starting TBACN stock suspension (Figure 1a). Most of the mass loss occurs between 150 and 350°C, presumably due to TBA^+ oxidation and fragmentation. Additional mass loss up to 550°C probably occurs due to oxidation of the residual carbonaceous char (see Figure 1a). XRD results (Figure 2b) show that TBACN refluxed in darkness has a d-spacing of 2.66 nm, close to that of starting TBACN (2.48 nm). These results indicate that refluxing TBACN in darkness does not have much of an effect on the state of the TBACN platelets.

In contrast, the product of refluxing TBACN suspension in the light exhibits a 5.2% mass loss between 150°C and 700°C (Figure 2a), less than half that of the starting stock suspension. The derivative mass loss pattern differs from that of the stock suspension as well; the peak rate of mass loss occurs at 250°C. The d-spacing of TBACN refluxed in light decreases from 2.48 nm to 1.52 nm (Figure 2b). These results indicate that HCN may catalyze the degradation of TBA^+ in the presence of light at elevated temperatures. This should not be surprising, given the well-established photocatalytic properties of HCN and other layered perovskites [65-82].

Figure 2. Characterization of TBACN refluxed in light (solid red curves, “light”) and in darkness (solid black curves, “dark”): (a) mass (%) and its derivative as functions of temperature from TGA, and (b) XRD patterns over the low-angle range. Panel (b) also includes patterns for as-prepared HCN (dotted black curve) and TBACN stock suspension (dashed red curve). Numbers in (a) indicate “total” (non-water) percentage mass decreases from 150°C to 700°C.

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4 TGA and XRD provide useful information on the effect of sample processing conditions
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6 on the state of TBACN. Figure 3 summarizes TGA mass loss results for TBACN suspensions
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8 subjected to various processing conditions and refluxed under lighted conditions. As-prepared
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10 HCN does not contain TBA^+ , so it exhibits only a small mass loss due to dehydroxylation. For
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12 TBACN diluted 1:1 (v/v) with DI water, stirred, but not refluxed (Figure 3, “TBACN(dil-DI,
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14 stir)”), the mass loss values over 150-350°C and 150-700°C are about 15% less than those of the
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16 TBACN stock suspension. This suggests that dilution into DI water may result in desorption of
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18 some weakly bound TBA^+ from the HCN platelets.
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25 The last three samples in Figure 3 are TBACN stock suspensions diluted and refluxed
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27 under lighted conditions. The mass loss values for TBACN diluted 1:1 into DI water and
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29 refluxed [TBACN(dil-DI, reflux)] are 30% lower than those for TBACN stock suspension. This
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31 might be explained by a combination of TBA^+ desorption and photocatalytic-degradation. The
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33 mass loss values are even lower if TBACN is dried before re-dispersion into DI water and
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35 refluxed [TBACN(dried, dil-DI, reflux)]. DLS results (Table 1) indicate that after drying,
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37 TBACN platelets do not fully re-disperse in DI water. While not necessarily favoring TBA^+
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39 desorption, the local environment in TBACN aggregates may be more favorable for photo-
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41 degradation. Finally, TBACN diluted 1:1 into TBA solution and refluxed [TBACN(dil-TBA,
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43 reflux)] has the lowest mass loss values (about 60% less than TBACN stock suspension). This
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45 sample thus had the lowest final TBA content, despite the excess TBA^+ initially present. This
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47 may be explained by active TBA^+ photo-degradation catalyzed by HCN.
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Figure 3. Fractional mass losses measured by TGA for as-prepared HCN and TBACN subjected to various processing conditions: as-prepared stock suspension (TBACN); TBACN diluted 1:1 with DI water and stirred [TBACN(dil-DI, stir)]; TBACN diluted 1:1 with DI water and refluxed [TBACN(dil-DI, reflux)]; TBACN dried, re-dispersed in DI water, and refluxed [TBACN(dried, dil-DI, reflux)]; and TBACN diluted 1:1 with TBA solution and refluxed [TBACN(dil-TBA, reflux)]. The starting suspensions all had the same TBACN wt%, and were refluxed in light. Numbers above each pair of bars denote the total fractional mass loss from 150 to 700°C. Trend lines are drawn to guide the eye.

XRD characterization (Figure 4) generally supports the TGA analysis. TBACN suspension diluted 1:1 in DI water and only stirred [TBACN(dil-DI, stir)] has an XRD pattern (after drying) like that of undiluted TBACN suspension (Figure 1b). The (001) peak gives a d-spacing of 2.57 nm, consistent with restacking of TBA-covered CN platelets. A small peak at 1.52 nm indicates the presence of some non-exfoliated HCN. TBACN suspension diluted 1:1 in DI water and refluxed [TBACN(dil-DI, reflux)] has a similar XRD pattern (primary d-spacing of 2.66 nm), but with a larger secondary peak near 6° (1.48 nm). In this case, desorption and/or degradation of some TBA may have caused restacking of some HCN platelets with less (or no) TBA⁺ in the interlayer spaces. For the TBACN suspension that was first dried, re-dispersed in DI water, and refluxed [TBACN(dried, dil-DI, reflux)], the XRD pattern does not show strong Bragg reflections, indicating disorder in the dried product. Magnification shows that there is a peak near 5.8° (d-spacing 1.55 nm) that could be some non-exfoliated or restacked, bare HCN. The main observation is the near absence of a (001) peak near 3.4° associated with restacked, TBA-coated CN platelets, consistent with desorption and photo-degradation of the TBA⁺. Lastly, the pattern for TBACN suspension diluted 1:1 in TBA solution and refluxed [TBACN(dil-TBA, reflux)] also has no 3.4° (001) peak, but it does have a prominent peak near 6° (1.48 nm). This is consistent with considerable photo-degradation of the TBA⁺, followed by platelet restacking during the drying of the product.

Figure 4. XRD patterns of TBACN subjected to various processing conditions: TBACN diluted 1:1 with DI water and stirred [TBACN(dil-DI, stir)]; TBACN diluted 1:1 with DI water and refluxed [TBACN(dil-DI, reflux)]; TBACN dried, re-dispersed in DI water, and refluxed [TBACN(dried, dil-DI, reflux)]; and TBACN diluted 1:1 with TBA solution and refluxed [TBACN(dil-TBA, reflux)]. The starting suspensions all had the same TBACN wt% and were refluxed in light.

3.2. PPA Grafting in HCN and TBACN Aqueous Suspensions

3.2.1. Evidence for PPA Grafting and Grafted Amounts

We now consider covalent modification of HCN and TBACN using phenylphosphonic acid (PPA). As in previous studies of organophosphonic acid grafting [19-21, 26, 29, 33, 55, 85,

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4 86], ^{31}P MAS NMR (Figure 5) provides direct evidence for PPA grafting onto calcium niobate.
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7 The NMR spectrum for pure PPA (Figure 5a) has a signature peak at 21.4 ppm. The other
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9 spectra in Figure 5 are for the washed, dried products of refluxed HCN or TBACN suspensions
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11 with added PPA. In all cases, the spectra show broad, sometimes multimodal peaks shifted 4-17
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13 ppm upfield relative to the peak for pure PPA. The peak locations for the reflux products
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15 (centered at around 11-13 ppm) are consistent with previous reports for PPA grafting onto titania
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17 [20] and layered lanthanum hexaniobate [55]. None of the product spectra in Figure 5 have
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19 peaks at 21.4 ppm indicative of free, non-grafted PPA. These spectra show that PPA readily
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21 grafts onto HCN and TBACN platelets. The apparent presence of multiple, overlapping peaks
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23 suggests different PPA grafting modes, which will be discussed in section 3.2.4.
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Figure 5. ^{31}P MAS NMR spectra with peak fitting for: (a) pure PPA, (b) PPA+HCN refluxed in DI water and in light, (c) PPA+TBACN refluxed in light, and (d) PPA+TBACN refluxed in darkness. PPA was added to CN in a 3:1 molar ratio.

XRD patterns for the washed, dried products (Figure 6) provide evidence about the location of PPA grafting. The pattern for PPA refluxed in DI water with non-exfoliated HCN has one peak at 6.05° (d-spacing 1.46 nm), essentially the same as that of the as-prepared HCN (Figure 1b). This shows that PPA does not penetrate HCN's interlayer space, but instead grafts solely on the exterior of the non-exfoliated HCN particles. The patterns for PPA added to TBACN suspension and refluxed (in light or in darkness) have distinct, broad peaks centered

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4 near 4.2° with d-spacings in the 2.1-2.2 nm range, in between the d-spacings of as-prepared HCN
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6 (1.46 nm) and TBACN stock suspension (2.48 nm). These patterns also have smaller peaks at
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8 5.84° (1.51 nm), but no evidence of a peak at 3.56° (2.48 nm) consistent with the starting
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10 TBACN; this shows that PPA grafting at least partially displaces adsorbed TBA⁺.
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14 Taken together, the NMR and XRD data show that PPA has been grafted onto the face
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16 surfaces of the exfoliated TBACN platelets. Upon drying, these “PPA+TBACN” platelets
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18 restack with turbostratic order with an average interlayer gap width expanded by about 0.7 nm
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20 relative to HCN (for PPA+TBACN prepared in the light, 2.17 - 1.46 nm = 0.71 nm). This
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22 expansion is consistent with that reported previously for interlayer grafting of PPA on layered
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24 double hydroxides [33, 35], interpreted in terms of a bilayer of grafted PPA molecules with tilted
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26 orientation. Alternately, the 0.71 nm expansion approximately equals the length of a PPA
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28 molecule [34, 55, 87-90], possibly consistent with an “interdigitated” bilayer of grafted PPA
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30 molecules oriented normal to the surface [29]. Although these pictures of the interlayer structure
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32 are speculative, the NMR and XRD data provide clear evidence that PPA has been grafted onto
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34 the face surfaces of the exfoliated TBACN platelets. We are not aware of any previous reports
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36 of covalent grafting onto any kind of exfoliated niobate platelets.
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43 Previous studies suggest the possibility of side reactions between PPA and TBACN to
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45 form small quantities of layered calcium or niobium phenylphosphonate (CaPPA, NbPPA).
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47 Reports of the synthesis of layered CaPPA [91, 92] provide XRD patterns and ³¹P NMR spectra.
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49 The XRD pattern for CaPPA [92] has three distinct peaks (at about 5.7°, 11.5°, and 17.4°) that
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51 are difficult to distinguish from those of residual unexfoliated HCN. The ³¹P NMR spectrum of
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53 hydrated CaPPA [92] has two peaks: one at 20.0 ppm is not seen in the product spectra in Figure
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55 5, and the other at 12.4 ppm overlaps with those seen in Figure 5. Thus the quantity of CaPPA
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produced in the grafting reactions carried out in this work is likely to be small or nonexistent. The synthesis of NbPPA has not been reported in the literature. We have recently synthesized NbPPA via a melt process, to be reported in a future publication. The peaks in the XRD pattern attributable to NbPPA do not match the peaks in XRD patterns for our products, so we can rule out the presence of NbPPA as a byproduct.

Figure 6. XRD patterns for: TBACN; PPA+HCN refluxed in DI water and in light; PPA+TBACN refluxed in light; and PPA+TBACN refluxed in darkness.

The XRD patterns in Figure 6 imply that PPA grafting removes at least some of the adsorbed TBA^+ from the surfaces of the PPA+TBACN products, as evidenced by the absence of peaks at 3.56° . TBA^+ could be eliminated by photocatalytic-degradation or physical

displacement from the HCN surface by grafted PPA. FT-IR spectra (Figure 7) provide additional insight. The FT-IR spectrum for TBACN shows strong bands at 2961, 2933, and 2874 cm^{-1} associated with CH_3 stretching and symmetric and asymmetric CH_2 stretching vibrations, respectively [93-95]. However, these bands are much weaker in the PPA+TBACN products. The same is true for CH_3 and CH_2 bending vibrations in the 1500-1370 cm^{-1} region (see section 3.2.4) [93, 95]. These observations indicate that the amounts of residual TBA^+ in the PPA+TBACN products are relatively small.

Figure 7. FT-IR spectra in the 3500-2500 cm^{-1} range for: TBACN; PPA+TBACN refluxed in light; and PPA+TBACN refluxed in darkness.

The TGA mass loss and derivative mass loss curves (Figure 8) also provide additional information. The mass loss curves (Figure 8a) appear to be shifted vertically relative to each other, mainly due to differences in water loss below 150°C. Between 150 and 350°C, the PPA+HCN product loses 2.0 wt%, almost equal to that of as-prepared HCN (1.8 wt%, Figure 1a); the peaks in the derivative mass loss (i.e., mass loss rate, Figures 1a and 8b) are similar, as well. This implies that the 150-350°C mass loss for PPA+HCN is due to CN dehydroxylation. The PPA+HCN product loses 4.2 wt% from 350 to 550°C (Figure 8a) and has a distinct peak in the mass loss rate curve at 500°C (Figure 8b). As-prepared HCN loses almost no mass (0.2 wt%, Figure 3) over the same temperature range. From this, we infer that the decomposition of PPA in PPA+HCN occurs only in the 350-550°C temperature range, consistent with previous reports for PPA decomposition after grafting onto other metal oxides [21, 34].

Figure 8. TGA characterization of mass percentage (a) and its derivative (b) as functions of temperature for: PPA+HCN refluxed in DI water and in light; PPA+TBACN refluxed in light; and PPA+TBACN refluxed in darkness. Numbers in (a) indicate percentage mass decreases from 350°C to 550°C.

The derivative mass loss patterns for the PPA+TBACN products in the 150-350°C range (Figure 8b) are similar to that of TBACN suspension refluxed in light (Figure 2a). Presumably, these mass losses are associated with residual TBA^+ . The PPA+TBACN products lose significant additional mass in the 350-550°C range (Figure 8a) with distinct acceleration between 425 and 500°C (Figure 8b), again consistent with PPA decomposition in oxidizing environments [21, 34]. Figure S1 (Supporting Information) quantifies the TGA mass losses over the key temperature ranges. Both of the PPA+TBACN(light, dark) products have significantly larger losses in the 350-550°C range than the corresponding refluxed TBACN stock suspensions (Figure S1). The additional mass losses must be due to the decomposition of grafted PPA.

For refluxed the TBACN suspensions (Figure S1), most of the mass loss occurs over 150-350°C, but TBA^+ decomposition continues through the 350-550°C range. Thus, we cannot assume that the 350-550°C mass losses are entirely due to PPA decomposition for the PPA+TBACN products.

TGA-based estimates of PPA grafted amounts are also complicated by uncertainty in the stoichiometry of PPA oxidation during TGA. For the TGA residue from PPA+TBACN refluxed in light, ^{31}P MAS NMR and FT-IR results (Figures S2 and S3, Supporting Information) indicate the presence of free $(\text{PO}_4)^{3-}$ and $(\text{HPO}_4)^{2-}$, perhaps as $\text{Ca}_3(\text{PO}_4)_2$ and CaHPO_4 . Thus, during TGA in air, PPA loses its phenyl ring but gains oxygen atoms as it is oxidized to phosphates, which may have complex stoichiometry [96, 97]. This makes it difficult to estimate the moles of PPA from the net mass loss without additional data or making strong assumptions. TGA results for PPA+TBACN products prepared using TBACN suspensions processed in various ways may be found in Supporting Information (Figures S4 and S5).

PPA grafted amounts can be estimated from XPS results (Table 2). For as-prepared HCN and TBACN stock suspension, the O:Nb ratios are close to the expected value of 3.33 (10:3). The Nb:Ca ratios for HCN (2.73) and TBACN (1.75) are higher than the expected value of 1.5, perhaps due to shielding of the Ca atoms within the CN structure.

XPS also provides the molar percentage of P atoms in samples with added PPA; each HCN unit cell contains 3 Nb atoms, so 3(P:Nb) gives the PPA:CN molar ratio. The maximum possible PPA:CN ratio is 2, assuming one reactive apical oxygen on each face surface of the CN unit cell and monodentate PPA grafting. The maximum “practical” ratio may be less than 2 due to steric hindrance, since the reported 0.24 nm² parking area for a phosphonate graft [17, 19, 20, 55, 98] is greater than the 0.148 nm² area of one CN unit cell [99]. Based solely on steric considerations, the maximum PPA:CN ratio may be as little as 1.23 (=2×0.148/0.24). PPA grafting via bi- or tridentate binding modes (discussed below in section 3.2.4) might further reduce the PPA:CN ratio.

For PPA+TBACN suspensions refluxed in light or in darkness, the measured PPA:CN ratios are both just over 0.5 (Table 2). This represents a graft density of about 1.70/nm² [=0.5/(2×0.148)], which is less than the 4.8/nm² reported for PPA grafting on TiO₂ [20]. In addition to the factors mentioned above, PPA must displace adsorbed TBA⁺ in order to graft onto the CN surface, which probably hinders grafting. PPA’s acidic protons probably assist by exchanging for TBA⁺, but ion exchange, and thus displacement, do not appear to be complete. For PPA grafted onto unexfoliated HCN particles, XPS yields a higher PPA:CN ratio, 0.785, equivalent to a graft density of 2.65/nm². In this case, PPA does not compete with TBA⁺ for space on the surface. The PPA:CN ratio may be underestimated in this sample because PPA

grafts only on the exterior surface of the HCN particles, while the XPS X-rays may penetrate multiple CN layers.

Table 2. XPS results for elemental compositions and PPA:CN ratios of PPA+CN products.

Sample ID	Composition (mol%)				PPA:CN Molar Ratio Based on P:Nb	PPA Graft Density (1/nm ²)
	P	Ca	Nb	O		
HCN (H ₂ Ca ₂ Nb ₃ O ₁₀ •1.5H ₂ O)	0.00	5.76	15.7	52.2	0	n.a.
TBACN	0.00	8.40	14.7	49.1	0	n.a.
PPA+HCN(light)	3.01	3.71	11.5	42.8	0.785	2.65
PPA+TBACN(light)	2.28	7.94	13.6	47.0	0.504	1.70
PPA+TBACN(dark)	2.47	7.72	13.1	46.4	0.566	1.91
PPA+TBACN(dil-DI)	1.64	7.69	14.1	50.5	0.349	1.18
PPA+TBACN(dried, dil-DI)	1.59	7.60	14.3	48.3	0.333	1.13
PPA+TBACN(dried, dil-TBA)	1.10	7.99	14.0	50.5	0.235	0.79
PPA+HCN(dil-Et95)	0.76	5.12	14.1	45.1	0.162	0.55 (a)
PPA+HCN(dil-nPr99)	1.09	4.87	13.4	43.8	0.245	0.83 (a)
PPA+TBACN(dried, dil-Et95)	0.70	8.71	15.3	50.7	0.138	0.47
PPA+TBACN(dried, dil-Et99)	0.38	8.57	15.7	52.1	0.073	0.25
PPA+TBACN(dried, dil-nPr95)	0.49	8.99	15.5	51.6	0.095	0.32
PPA+TBACN(dried, dil-nPr99)	0.71	8.67	15.0	51.2	0.142	0.48

(a) Values reported for consistency; NMR, FT-IR, and TGA data (Supporting Information) support the conclusion that little or no PPA grafts onto unexfoliated HCN in alcoholic suspensions. See section 3.3.

3.2.2. Influence of Light on PPA Grafting

TGA and XRD results presented in Figures 2-4 demonstrate that adsorbed TBA⁺ cations undergo at least partial degradation when TBACN suspensions are exposed to light, attributed to photocatalytic activity of the layered calcium niobate perovskite. Does exposure to light affect PPA grafting on TBACN? XRD patterns (Figure 6), FT-IR spectra (Figure 7 and, presented later, Figure 11), and TGA data (Figures 8 and S1) do not reveal significant differences between the product of PPA+TBACN refluxed in light versus that refluxed in darkness. XPS results (Table 2) indicate that the PPA:CN molar ratio for PPA+TBACN(dark) is 12% higher than that for PPA+TBACN(light). For PPA+TBACN(dark), the TGA mass loss in the 350-550°C

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4 temperature range (Figure 8a) is about 9% higher than that for PPA+TBACN(light). This may
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6 seem counterintuitive, since photo-degradation of TBA⁺ should open up space on the TBACN
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8 surface for additional PPA grafting.
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11 However, the ³¹P MAS NMR spectra (Figure 5c and d) provide evidence that some
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13 grafted PPA may undergo TBACN-catalyzed photo-degradation, which accounts for the lower
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15 PPA grafted amount in PPA+TBACN refluxed in light. The upfield shift of the peak in Figure
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17 5d suggests that for PPA+TBACN refluxed in darkness, PPA grafts primarily in a bidentate
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19 grafting mode (deconvolution into two peaks may not be justified). The same probably occurs in
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21 PPA+TBACN refluxed in light. However, for PPA+TBACN(light), prolonged light exposure (3
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23 days) under acidic, aqueous reflux conditions may result in some PPA photo-degradation,
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25 accompanied by reversion of a fraction of bidentate grafts to monodentate form. This
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27 rationalizes the two separate deconvoluted peaks (with upfield shifts corresponding to a mixture
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29 of mono- and bidentate grafts) observed in the NMR spectrum (Figure 5c) for
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31 PPA+TBACN(light). PPA grafting modes are discussed more thoroughly in section 3.2.4.
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41 *3.2.3. Effect of Suspension Processing Conditions on PPA Grafting*

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44 This section explores the effect of suspension processing steps, such as dilution or drying
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46 and re-dispersion, on PPA grafting onto TBACN platelets. Figure 9 displays ³¹P MAS NMR
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48 spectra for washed, dried PPA+TBACN products made from TBACN suspensions processed in
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50 different ways. Each spectrum has a dominant monomodal peak centered at just above 11 ppm.
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52 This upfield shift of about 10.4 ppm (relative to PPA's peak at 21.4 ppm, Figure 5a) shows that
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54 PPA has been grafted onto TBACN. The PPA signature peak does not appear in Figure 9,
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56 indicating the absence of non-grafted PPA. These results demonstrate that PPA grafting occurs
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4 in TBACN suspensions diluted into DI water or dried and re-dispersed in DI water or TBA
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6 solution.
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9 XPS and XRD results (Table 2, Figure 10) indicate that the location and amount of PPA
10 grafting are affected by suspension processing conditions. For TBACN stock suspension diluted
11 1:1 into DI water [TBACN(dil-DI)], DLS (Table 1) shows that the TBACN platelets are well
12 dispersed, if not fully exfoliated [64]. Thus, PPA has access to all of the CN platelet surfaces in
13 this case. After PPA grafting, the product [PPA+TBACN(dil-DI)] has a PPA:CN ratio of 0.349
14 (Table 2), indicating less PPA grafting than in the PPA+TBACN(light, dark) products discussed
15 earlier. The PPA concentration in PPA+TBACN(dil-DI) is only half that in the
16 PPA+TBACN(light, dark) cases. This reduces the driving force for PPA grafting, resulting in
17 the lower PPA:CN ratio. The XRD pattern for the PPA+TBACN(dil-DI) product (Figure 10) has
18 a relatively broad peak centered near 5.1° . The peak shape suggests weak turbostratic ordering
19 with considerable polydispersity of interlayer spacing centered at 1.72 nm. The product (after
20 drying) has a d-spacing less than that of PPA+TBACN(light, dark) (2.12-2.17 nm, Figure 6),
21 also consistent with the lower PPA grafted amount.
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41 For TBACN suspension that is first dried and then re-dispersed/diluted in DI water
42 [TBACN(dried, dil-DI)], DLS (Table 1) shows that TBACN platelets do not fully re-disperse,
43 but remain partially aggregated. After PPA grafting, the PPA+TBACN(dried, dil-DI) product
44 has a PPA:CN ratio of 0.333 (Table 2), comparable to that of the PPA+TBACN(dil-DI) product.
45 This indicates that the TBACN aggregates are sufficiently open to allow PPA access to the
46 platelets' surfaces over the three-day reaction period. The ^{31}P MAS NMR spectrum for the
47 PPA+TBACN(dried, dil-DI) product (Figure 9b) confirms PPA grafting, but the XRD pattern
48 (Figure 10) has no peak (other than residual non-exfoliated HCN), and thus no evidence of CN
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platelet ordering in the dried product. If the suspension initially contained disordered aggregates of TBACN before PPA grafting, then the lack of layering order in the dried PPA+TBACN(dried, dil-DI) product seems reasonable.

Finally, for TBACN stock suspension dried and then re-dispersed/diluted into TBA solution [TBACN(dried, dil-TBA)], DLS (Table 1) again shows that the TBACN platelets are well dispersed, as expected, with all face surfaces accessible to PPA. After adding PPA (3:1 molar ratio to CN unit cells), its concentration is again one-half of that in the PPA+TBACN(light, dark) samples. However, because TBACN(dried, dil-TBA) was dried and then re-dispersed into fresh TBA solution, the $\text{TBA}^+:\text{CN}$ ratio was 2:1, double that of the starting TBACN stock suspension. The lower driving force for PPA grafting and the greater competition from TBA^+ for the CN surface result in a lower PPA grafted amount: PPA:CN is 0.235 (Table 2) for PPA+TBACN(dried, dil-TBA). The XRD pattern for this product (Figure 10) again has a relatively broad peak centered near 5.1° , consistent with turbostratic ordering and a polydispersity of d-spacing centered at 1.73 nm. Despite the lower PPA grafted amount, grafting still appears to occur on the face surfaces of exfoliated TBACN platelets. Upon drying, the platelets in PPA+TBACN(dried, dil-TBA) restack with turbostratic order and a mean d-spacing less than that of TBACN (2.48 nm) or PPA+TBACN(light, dark) (2.12-2.17 nm), but more than that of the starting HCN (1.48 nm).

Figure 9. ^{31}P MAS NMR spectra with peak fitting for PPA+TBACN products prepared using TBACN suspensions processed in various ways: PPA added to (a) TBACN diluted 1:1 with DI water [PPA+TBACN(dil-DI)]; (b) TBACN dried and re-dispersed in DI water [PPA+TBACN(dried, dil-DI)]; and (c) TBACN dried and re-dispersed in TBA solution [PPA+TBACN(dried, dil-TBA)]. The resulting suspensions all had the same TBACN wt% and 3:1 PPA:CN ratio, and all were refluxed in light.

Figure 10. XRD patterns for TBACN and PPA+TBACN products prepared using TBACN suspensions processed in various ways: PPA added to TBACN diluted 1:1 with DI water [PPA+TBACN(dil-DI)]; PPA added to TBACN dried and re-dispersed in DI water [PPA+TBACN(dried, dil-DI)]; and PPA added to TBACN dried and re-dispersed in TBA solution [PPA+TBACN(dried, dil-TBA)]. The curve for PPA+TBACN(dil-DI) is shifted upwards for clarity.

The ^{31}P MAS NMR results provide another piece of evidence suggesting that the driving force for PPA grafting is lower in the diluted suspensions. For PPA grafting in TBACN suspension dried and re-dispersed in TBA solution [PPA+TBACN(dried, dil-TBA)], the NMR spectrum (Figure 9c) has an additional peak at -11.5 ppm, consistent with the production of polyphosphate or polyphosphonate species [19, 20, 98, 100]. To reiterate, in this reaction mixture, the TBA:CN ratio is 100% higher (2:1) than in TBACN stock suspension, but the PPA

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4 concentration is 50% lower. The adsorbed TBA^+ presents a more formidable steric barrier that
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6 may inhibit PPA grafting, especially when the PPA concentration is low. Some of the PPA may
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8 oligomerize in solution to form poly(phenylphosphonate) esters that may be adsorbed or grafted
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10 on the CN platelets. Alternately, the forcing conditions may result in the production of a small
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12 amount of precipitated calcium phenylphosphonate [20, 86, 91, 92, 101].
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16 TGA results for PPA+TBACN products prepared using diluted or dried/re-dispersed
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18 TBACN suspensions are consistent with the NMR, XPS, and XRD results; full details may be
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20 found in the Supporting Information section. In general, the total mass losses for these
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22 PPA+TBACN products over the 150-700°C range are less than those for the corresponding
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24 TBACN suspensions processed the same way, but containing no PPA. This tells us two things.
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26 First, these PPA+TBACN products contain less TBA^+ than the dried TBACN in the starting
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28 stock suspension. Second, the PPA grafting process facilitated the removal of TBA^+ from the
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30 CN platelets: more TBA^+ remained on the CN platelets when the stock suspensions were simply
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32 diluted and refluxed (Figure 3) in the absence of PPA. However, the presence of both PPA and
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34 residual TBA^+ (or its degradation byproducts) make it difficult to extract more quantitative
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36 information on their relative amounts in these products.
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3.2.4. PPA Grafting Modes

Phenylphosphonic acid has three functional groups (two P-OH and one P=O) available for covalent bonding with CN, with a total of five possible grafting modes (two monodentate, two bidentate, and one tridentate) [86, 102-108]. ^{31}P MAS NMR, FT-IR, and XPS spectra can aid in identifying the dominant grafting modes for different experimental conditions.

PPA and HCN. The FT-IR spectrum for pure PPA (Figure 11) agrees with those previously published [109, 110]; band assignments may be found within these references. The FT-IR spectrum for as-prepared HCN has a shoulder at 779 cm^{-1} identified [111] as the bridging Nb-O-Nb stretching vibration; split peaks at 904 and 942 cm^{-1} associated with the terminal Nb-O stretching vibration [111]; and the H-O-H bending vibration at 1635 cm^{-1} . The only significant overlap of PPA and CN bands lies in the $900\text{-}950\text{ cm}^{-1}$ range, where two of PPA's P-O stretching vibrations [110] overlap with the aforementioned CN terminal Nb-O stretching vibration [111]. Figure 11 also shows the spectra for three PPA+CN products; Table 3 lists the tentative band assignments based on the relevant literature.

PPA+HCN. The PPA+HCN product has the same bands as HCN, except that the HCN peak at 904 cm^{-1} appears as a shoulder in PPA+HCN. This may be due to an overlapping peak at 940 cm^{-1} usually ascribed to a P-O stretch [109, 110]. PPA+HCN has distinctive peaks at 1153 cm^{-1} (probably P-C stretch), 1439 cm^{-1} (aromatic C-C), 1597 cm^{-1} (weak, aromatic C-C), and 3059 cm^{-1} (aromatic C-H stretch, not shown), all indicative of PPA grafting. This spectrum also shows a strong, broad band in the $1200\text{-}1250\text{ cm}^{-1}$ range due to the P=O stretch (refs. in Table 3). The survival of this group tells us that PPA grafting in PPA+HCN primarily involves PPA's P-OH groups. The PPA+HCN spectrum also shows a broad band in the $975\text{-}1100\text{ cm}^{-1}$ range normally associated with a variety of P-O stretching vibrations (refs. in Table 3). The lack of

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4 distinct peaks in this range probably indicates a distribution of Nb-O-P grafts, as one might
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6 expect for PPA grafting on edges and faces of unexfoliated HCN particles.
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9 The ^{31}P MAS NMR spectrum for PPA+HCN (Figure 5b) can be deconvoluted into three
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11 overlapping peaks centered at 17.7, 11.5, and 4.6 ppm. Increasing upfield shifts (to lower ppm
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13 values) are consistent with stronger binding or grafting modes [102]. Thus these three peaks
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15 could represent mono-, bi-, and tridentate PPA grafting; as observed for PPA grafting onto
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17 amorphous zirconia and titania [20, 21, 85, 86, 101, 105]. The occurrence of bidentate grafting
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19 with P=O surviving might be expected at the edges of CN platelets where “broken” niobate
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21 octahedra expose Nb-(OH)₂ sites available for PPA grafting via condensation with P-OH groups.
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23 The availability of Nb-(OH)₂ sites also facilitates the formation of tridentate-grafted PPA, which
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25 does not seem to occur much for PPA grafting onto TBACN face surfaces.
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31 *PPA+TBACN.* For the products of PPA grafting onto exfoliated TBACN, the FT-IR
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33 spectra have the same vibrational bands for grafting in light or darkness (Figure 11), and for
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35 various suspension processing conditions (Figure S6, Supporting Information). All of the
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37 PPA+TBACN spectra inherit the 779 and 942 cm⁻¹ bands from HCN. The HCN 904 cm⁻¹ band,
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39 however, is either weak or absent, perhaps due to reaction of PPA with terminal Nb-O groups.
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41 The 904 cm⁻¹ band may also be hidden by the superposition of the HCN 942 cm⁻¹ band and the
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43 P-OH bands at 930 and 945 cm⁻¹, inherited from PPA. This would suggest that residual P-OH
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45 groups survive after mono- or bidentate PPA grafting.
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Figure 11. FT-IR spectra for (bottom to top): PPA; HCN; PPA+HCN refluxed in DI water and in light; PPA+TBACN refluxed in darkness; and PPA+TBACN refluxed in light. Spectra are shifted vertically; and the PPA spectrum rescaled, for visual clarity. Table 3 lists band (peak) assignments.

Table 3. Band assignments for numbered peaks in the FT-IR spectra shown in Figures 11 and 14 (and Figures S6 and S13, Supporting Information).

No.	σ (cm ⁻¹)	Source	Mode (a)	References
1	691 (sh)	PPA	C-H oop	[34, 55, 109, 112, 113]
2	748	PPA	C-H oop	[34, 55, 112, 113]
3	779 (sh)	HCN	Nb-O bridge	[111]
4	904	HCN	Nb-O term.	[111]
5	942	HCN	Nb-O term.	[111]
6	962	PPA+HCN	Nb-O-P	this work
7	975-1100	PPA	P-O	[17, 19, 20, 28, 55, 109, 110, 112-114]
8	1145, 1153	PPA	P-C	[19, 20, 110, 115]
9	1220	PPA	P=O	[17, 19, 20, 28, 55, 109, 110, 114, 116]
10	1379	TBA ⁺	aliph. C-H	[93]
11	1439	PPA	arom. C-C	[109, 110, 112, 113]
12	1462	TBA ⁺	aliph. C-H	[93]
13	1484	TBA ⁺	aliph. C-H	[93]
14	1597	PPA	arom. C-C	[110]
15	1636	H ₂ O	H-O-H bend	[93, 111]

(a) Abbreviations: oop = out-of-plane bending; sh = shoulder; term. = terminal; aliph. = aliphatic; arom. = aromatic.

The PPA+TBACN spectra exhibit various vibrational bands (C-H, C-C, P-C) expected due to the presence of grafted PPA. We see almost no absorbance due to the P=O band (1200-1250 cm⁻¹) in the PPA+TBACN spectra, indicating the primary role of P=O in the grafting of PPA onto TBACN [17, 19, 20, 55, 116]. In the 975-1100 cm⁻¹ range, PPA has a series of distinctive P-O bands (refs. in Table 3). In PPA+TBACN, this wavenumber range has several distinct, overlapping peaks (996, 1018, 1036, 1052 cm⁻¹) also attributed to various P-O vibrations, including those of PO₃²⁻ and HPO₃¹⁻ [109]. The presence of P-OH and Nb-O-P vibrational bands is also likely, but we cannot make definitive assignments for these bands. Lastly, the spectra in Figure 11 for PPA+TBACN products have a distinct peak at 962 cm⁻¹ (peak 6) that does not appear in the spectra for PPA, HCN, or PPA+HCN. Shimada et al. [55] ascribed a band at ~950 cm⁻¹ to P-OH, but it seems more likely due to Nb-O-C in their starting material, lanthanum niobate with interlayer-grafted decanol. In PPA+TBACN, the absence of the terminal

Nb-O band at 904 cm^{-1} and appearance of the 962 cm^{-1} peak suggests that the latter may be a stretching vibration of Nb-O-P.

^{31}P MAS NMR spectra for PPA+TBACN products (Figures 5 and 9) show that experimental conditions influence PPA grafting modes. For PPA grafting on TBACN in the light (Figure 5c), the NMR spectrum may be deconvoluted into two peaks, one smaller and one larger centered at 16.4 and 10.7 ppm, respectively. These peaks likely correspond to mono- and bidentate grafting modes involving P=O (primarily) and some P-OH groups. Although the FT-IR band(s) for residual P-OH groups cannot be conclusively identified, locations at 945 cm^{-1} and in the $975\text{--}1100\text{ cm}^{-1}$ range seem plausible. The blend of mono- and bidentate grafting can be rationalized in two ways. As mentioned earlier, PPA initially grafted in bidentate mode may, upon prolonged exposure to light during reflux, undergo TBACN-catalyzed photo-degradation, resulting in reversion of some bidentate grafts to monodentate form. Alternately, over time, photo-degradation of adsorbed TBA^+ could free some space on the TBACN surface, permitting additional PPA grafting in the monodentate mode via P=O reaction with niobate Lewis acid sites.

For PPA grafted onto TBACN in the darkness (Figure 5d), the peak in the NMR spectrum may be deconvoluted into two closely overlapping peaks (13.1 and 10.8 ppm). The overall upfield shift suggests primarily bidentate grafting, and the two peaks could correspond to different bidentate modes (bridged and chelated, *vide infra*). The bidentate-chelating mode may be somewhat more prevalent in this case due to the steric hindrance of adsorbed TBA^+ .

The PPA graft density may also be a relevant factor. For the PPA+TBACN(light, dark) products, the PPA:CN molar ratios are greater than 0.5 (Table 2), which is half of the maximum ratio assuming 100% bidentate grafting (PPA:CN = 1.0). PPA+TBACN products prepared in

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4 diluted TBACN suspensions have lower PPA graft densities (PPA:CN ratios between 0.24 and
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6 0.35, Table 2) due to the lower PPA concentration and driving force for grafting. The ^{31}P MAS
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8 NMR spectra for these products (Figure 9) have one main peak centered in the 11.1-11.6 ppm
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10 range, associated (as argued above) with the bidentate grafting mode. These spectra also appear
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12 to have small secondary peaks centered in the 3-5 ppm range, possibly consistent with the
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14 tridentate grafting mode. The lower graft density may make it easier for bidentate-grafted PPA
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16 molecules to find an open neighboring site for a third covalent bond. However, the large
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18 majority of the PPA molecules appear to be grafted in the bidentate mode.
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24 The complexity of the FT-IR band structures in the 975-1100 cm^{-1} range and the overlap
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26 of PPA and HCN bands (Figure 11) make it difficult to conclusively assign any band to P-OH in
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28 the FT-IR spectra of the PPA+TBACN products. On the other hand, XPS O1s spectra
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30 (Supporting Information, Figures S7-S9) provide strong qualitative evidence for the presence of
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32 surviving P-OH groups in the PPA+TBACN products. Specifically, deconvolution of the XPS
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34 O1s spectrum for PPA (Figure S7) gives two peaks at 531.1 and 532.5 eV with a 1:2 area ratio,
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36 consistent with P=O and P-OH, respectively [106, 117-120]. The O1s spectrum for HCN
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38 (Figure S7), similar to that found previously [121], can be deconvoluted into two peaks at 530.0
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40 and 531.4 eV, which we ascribe to bridging Nb-O-Nb and terminal Nb-OH. The P-OH peak
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42 from PPA (532.5 eV) does not appear in the HCN spectrum, but it does appear in the O1s spectra
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44 of all the PPA+TBACN products (Figures S8 and S9). This shows that at least some P-OH
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46 groups survive the grafting process. Variations in PPA grafted amounts and sampling depth
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48 preclude a more quantitative analysis based on peak areas. Nonetheless, the XPS O1s results
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50 support our argument that PPA grafts onto the face surfaces of TBA-exfoliated CN platelets
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52 primarily in the bidentate mode.
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Figure 12 illustrates a proposed mechanism, consistent with the results presented, for grafting of PPA (and possibly other organophosphonic acids) onto the face surfaces of crystalline, protonated calcium niobate (HCN) layers. Grafting begins with the coordination of the PPA's phosphoryl oxygen with a surface Nb atom, a Lewis acid site, accompanied by cleavage of a Nb-O-Nb bridging bond in the HCN lattice. Similar reactions have been previously proposed for cleavage of Si-O [14], Al-O [19], Ti-O [20], and other kinds of metal-oxygen bonds in metal oxides [110]. Initial monodentate grafting is then followed by secondary heterocondensation between P-OH and apical Nb-OH groups, producing bidentate grafts with either bridging or chelating modes. Geometric considerations favor both bidentate modes. Based on PPA bond distances and angles derived from molecular simulations [90], the distance between O atoms in O=P-O-H is about 2.62 Å. Considering the surface atoms in a layer of HCN (Figure S10, Supporting Information), the Nb atoms reside in a square array with an Nb-O-Nb distance of 3.855 Å [98] and a diagonal distance of 5.452 Å. Thus the HCN surface can readily accommodate PPA grafting in the bidentate-bridging mode with Nb-O-P-O-Nb spanning either the side or diagonal of the square Nb atom array, depending on the Nb-O-P bond angles. The bidentate-chelating mode may form when the graft density is high because it does not require an adjacent apical Nb-OH site.

Geometric considerations do not appear to favor additional heterocondensation reactions of bidentate-grafted PPA to produce tridentate grafts. The geometry of the octahedral niobate lattice would require considerable deformation of (approximately) tetrahedral PPA to form the third leg of a tridentate graft. Evidence of surviving P-OH groups from XPS O1s spectra (and possibly FT-IR spectra) appear to rule out extensive tridentate grafting.

In summary, the proposed mechanism in Figure 12 accounts for the primary role of P=O in grafting, as indicated by the absence of P=O groups in the FT-IR spectra of all PPA+TBACN products. The mechanism also illustrates how secondary heterocondensation may produce two kinds of bidentate grafts, depending on the availability of adjacent sites. The coordination of Nb remains at six in this mechanism, avoiding a concern about seven-fold coordination raised in the one previous study of PPA interlayer grafting on a niobate [55].

Figure 12. Schematic illustration of a proposed mechanism for organophosphonic acid grafting onto the surface of HCN. Filled and open circles denote Nb and O atoms respectively in the crystal structure of HCN layers; only surface Nb atoms are shown, and most O atoms in the HCN lattice are omitted for clarity.

3.3. PPA Grafting in HCN and TBACN Alcoholic Suspensions

This section explores PPA grafting onto HCN and TBACN in alcohol-based suspensions, specifically ethanol and *n*-propanol at 95% and 99% (balance water).

PPA+HCN. The Supporting Information section provides NMR, TGA, XRD and FT-IR results for PPA+HCN (Figures S11-S13). In short, NMR, FT-IR, and TGA data indicate little or no grafting of PPA onto unexfoliated HCN in 95% ethanol or 99% *n*-propanol. The XRD patterns are inconclusive about the possibility of PPA penetration and grafting in the HCN interlayer space. XPS results (Table 2) indicate the presence of P in these samples. However, ³¹P MAS NMR data (Figure S11) suggest that this may be non-grafted polyphosphates, essentially a byproduct of prolonged reflux of PPA in alcoholic suspension. Based on the NMR, TGA, and FT-IR results, we conclude that little or no PPA grafts onto unexfoliated HCN in alcoholic suspensions.

PPA+TBACN. DLS (Table 1) shows that direct dilution of TBACN suspension to 5.0×10^{-5} g/mL in 95% ethanol [TBACN(dil-Et95)] results in a stable alcoholic suspension of exfoliated TBACN platelets. However, drying TBACN and re-dispersing in alcohols results in particle sizes larger than that of exfoliated platelets. This shows that dried TBACN does not re-exfoliate in alcohols, but instead incompletely disperses as disordered aggregates, resembling TBACN dried and re-dispersed in DI water [TBACN(dried, dil-DI)].

Figure 13 shows ³¹P MAS NMR spectra for the washed, dried products of PPA added to TBACN that was dried and re-dispersed in alcohols. For grafting in ethanol (95% and 99%, Figure 13a and b, respectively), the spectra of the PPA+TBACN products have monomodal peaks centered between 14-16 ppm, an upfield shift of ~6-7 ppm relative to PPA. This

demonstrates that PPA grafts onto TBACN dispersed in ethanol. The spectra do not manifest peaks at 21 ppm indicative of non-grafted PPA, signifying that all of the detected PPA has been grafted. XPS results (Table 2) imply that the PPA grafted amounts on TBACN in ethanol are about 65% less than in aqueous TBACN suspensions. The XRD patterns (Figure S14, Supporting Information) for these samples have small peaks at angles corresponding to a d-spacing of about 1.5 nm, probably due to residual, non-exfoliated HCN. Otherwise, the absence of any distinctive peaks is consistent with dried aggregates lacking any turbostratic ordering.

The magnitude of the upfield shifts of the peaks in the ^{31}P MAS NMR spectra suggest that PPA grafting on TBACN in ethanol produces primarily monodentate grafted PPA [20, 86, 101, 116]. The FT-IR spectra for these products (Figure 14) do not show any indication of bands at 1220 cm^{-1} , indicating that P=O groups do not survive the grafting process. The spectra show distinct shoulders near 962 cm^{-1} , consistent, in our view, with the formation of Nb-O-P linkages. However, the survival of P-OH groups cannot be definitively established either by FT-IR or XPS O1s spectra. Still, PPA grafting onto TBACN in ethanol appears to follow at least the first step of the mechanism proposed in Figure 12.

For PPA grafting onto TBACN in *n*-propanol, the ^{31}P MAS NMR spectra (Figure 13c and d) also indicate PPA grafting, although the grafted amounts (from XPS, Table 2) are smaller than in aqueous TBACN suspensions. For grafting in 95% *n*-propanol (Figure 13c), the dominant peak at ~11 ppm suggests that PPA grafts onto TBACN primarily in the bidentate mode. A small peak near 4 ppm may indicate some tridentate grafting, or perhaps just noise in the data. For grafting in 99% *n*-propanol (Figure 13d), the NMR spectrum can be deconvoluted into two peaks at 16.5 and 11 ppm. This suggests the presence of both monodentate and bidentate grafting modes. The FT-IR spectra (Figure 14) for the products refluxed in *n*-propanol

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4 are similar to those for ethanol: no band for P=O survives the grafting process. Thus, PPA
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6 grafts onto TBACN (in *n*-propanol) via the P=O group, consistent with the first reaction in
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9 Figure 12.

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11 All of the ^{31}P MAS NMR spectra in Figure 13 could have overlapping peaks that could
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13 not be deconvoluted due to the low grafted amounts and weak NMR signals. Thus, all of the
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15 PPA+TBACN products refluxed in alcohols could have a mixture of PPA grafting modes that
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17 may not be apparent in Figure 13. The peaks at about -11 ppm in Figure 13b and c are again
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19 consistent with PPA undergoing a reaction other than with TBACN. This reaction may produce
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21 polyphosphate or polyphosphonate species [19, 20, 98, 100], or precipitated calcium
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23 phenylphosphonate [20, 86, 91, 92, 101].
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Figure 13. ^{31}P MAS NMR spectra with peak fitting for PPA+TBACN products prepared using TBACN suspensions dried and re-dispersed in alcohol solvents: (a) PPA+TBACN dried and re-dispersed in 95% ethanol [PPA+TBACN(dried, dil-Et95)]; (b) PPA+TBACN dried and re-dispersed in 99% ethanol [PPA+TBACN(dried, dil-Et99)]; (c) PPA+TBACN dried and re-dispersed in 95% *n*-propanol [PPA+TBACN(dried, dil-nPr95)]; and (d) PPA+TBACN dried and re-dispersed in 99% *n*-propanol [PPA+TBACN(dried, dil-nPr99)]. The resulting suspensions all had the same TBACN wt% and 3:1 PPA:CN ratio, and all were refluxed in light.

Figure 14. FT-IR spectra for (bottom to top): PPA; HCN; PPA+TBACN dried and re-dispersed in 99% *n*-propanol [PPA+TBACN(dried, dil-nPr99)]; PPA+TBACN dried and re-dispersed in 95% *n*-propanol [PPA+TBACN(dried, dil-nPr95)]; PPA+TBACN dried and re-dispersed in 95% ethanol [PPA+TBACN(dried, dil-Et95)]; and PPA+TBACN dried and re-dispersed in 99% ethanol [PPA+TBACN(dried, dil-Et99)]. Peak assignments are described in Table 3. Spectra are shifted vertically; and the PPA spectrum rescaled, for visual clarity.

4. Conclusions

This work shows that phenylphosphonate (PPA) can be covalently grafted onto protonated calcium niobate (HCN). PPA grafts onto the face surfaces of TBA-exfoliated HCN (TBACN) dispersed in deionized water, TBA solution, ethanol, and *n*-propanol. However, PPA does not penetrate and graft in HCN's interlayer spaces, but grafts only onto the exterior surfaces of unexfoliated HCN. This work contrasts with other recent reports of interlayer PPA grafting onto niobate sheets that were "pre-expanded" by interlayer grafted decanol [55, 122]. We believe that this is the first report of organic molecule grafting, and certainly organophosphonic acid grafting, onto the face surfaces of exfoliated, niobate-based platelets. Kimura et al. [122] recently reported interlayer PPA grafting on layered hexaniobates, followed by exfoliation in organic solvents. The present work represents the first report of organic molecule grafting onto layered niobate perovskites in aqueous suspensions.

Various characterization results confirm not only the grafting of PPA on exfoliated TBACN, but also quantify the PPA grafted amount and identify the grafting mode (mono-, bi-, and tridentate). The PPA grafting location and grafted amount depends on the exfoliation/aggregation state of TBACN, suspension processing conditions, and solvent composition. Due to the photocatalytic properties of the layered calcium niobate perovskite, the state of light/darkness probably plays some role in the grafting process. In the starting TBACN suspensions, adsorbed TBA^+ cations undergo photo-degradation under reflux conditions in light, but not in darkness. PPA seems to graft onto TBACN primarily in the bidentate mode, but prolonged exposure in light may result in some PPA degradation and/or reversion of some bidentate grafts to the monodentate form. A mechanism proposed for PPA grafting onto HCN and TBACN seems to account for all experimental observations.

The demonstration of PPA grafting onto exfoliated, TBA-exchanged HCN in aqueous and organic solvents may be the first step towards the synthesis of more sophisticated organofunctional niobate platelets. For example, grafting phosphonate-based initiators or chain transfer agents, followed by surface-initiated polymerization, could lead to polymer-grafted platelets (PGPs). Ultimately, PGPs could be used as building blocks for fabrication of polymer nanocomposites with tailored end-use performance for automotive, aerospace, and energy applications.

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