Solid–Liquid Adsorption of Calcium Phosphate on TiO₂

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Calcium phosphate (CP) in aqueous solution was exposed to thin-film TiO₂ surfaces at predetermined times ranging from 10 min to 20 h using a liquid reaction apparatus (LRA). Surface analysis was then performed using X-ray photoelectron (XPS) and Auger electron (AES) spectroscopies and time-of-flight secondary ion mass spectrometry (ToF–SIMS) with polyatomic primary ions. XPS revealed that CP nucleated and grew on the TiO₂ surface, with phosphate groups growing on top of an initial 2-dimensional (2D) Ca-rich layer. AES depth profiling of a 4-h solution exposure complemented this finding and gave additional evidence for 3-dimensional (3D) phosphate islands forming on top of the calcium. ToF–SIMS analysis of CP adsorbed on the surface indicated that the predominant phase on the surface was brushite, CaHPO₄·2H₂O. A model for Ca³⁺ cation bridging at the oxide interface is proposed.

Introduction

A molecular-level understanding of the interactions of calcium phosphate (CP) adsorbed on metal oxide surfaces at the solid–water interface is of interest in the study of biomaterials, biomimetics, and soil science. Various phases of CP (such as brushite [CaHPO₄·2H₂O], DCPD, amorphous calcium phosphate [Ca₅(PO₄)₃·xH₂O, ACP], α- and β-tricalcium phosphate [α- and β-Ca₃(PO₄)₂, α- and β-TCP], and octacalcium phosphate [Ca₈H₂(PO₄)₆·2H₂O, OCP]) are involved in the formation of hydroxyapatite [Ca₁₀(PO₄)₆·3H₂O, HAP], the chief component of bone and teeth. The processes involved with HAP incorporation into living tissue and metal oxides at the interface are not well understood and are of current interest due to applications in artificial implants. Phosphate (used in fertilizer) has been shown to have high retention properties for metal oxide particulates in soil. Because of the lack of understanding of adsorption characteristics of phosphates onto metal oxides and bone and teeth, the tendency is to use excess fertilizer in practice; this has resulted in environmental concerns due to excess runoff of phosphates into streams and lakes, which cause eutrophication in aquatic biota.

To gain a better understanding of interactions at the metal oxide surface, experiments have been performed using the constant composition (CC) apparatus5–7 to model nucleation and growth of CP onto high surface area metal oxide colloidal seeds (characterized by Brunauer–Emmett–Teller (BET) methods), particularly for TiO₂, Al₂O₃, and SiO₂. The aqueous CP solution used consisted of 3.5 mM CaCl₂ and 119 μg mL⁻¹ P as KH₂PO₄ and was adjusted to pH = 6.5 using 0.01 M NaCl as background electrolyte. TiO₂ was found to stimulate rapid nucleation and growth, but no growth was observed for SiO₂ or Al₂O₃. Differences in adsorption behavior in the study were attributed to different surface charges that were observed from ζ-potential measurements of the oxides at pH = 6.5. (It should be noted that the relative difference in uptake behavior on the metal oxides is not well understood and is a subject of ongoing investigation.) SiO₂ had a negative potential and resulted in electrostatic repulsion of the CP from the colloidal seed surface whereas TiO₂ had a neutral charge and stimulated growth. The CC methodology is not useful for distinguishing whether the material was largely adsorbed (chemisorbed) or precipitated (physisorbed) onto the colloidal seeds. To better understand CP bonding at the interface, therefore, we turned to surface analytical methods to study the interactions of chemisorbed phosphate with the metal oxide surface. For this purpose, we have developed a liquid reaction apparatus (LRA), fully described elsewhere, in our laboratory. The apparatus consists of a peristaltic pump that delivers liquid though a column. The liquid forms a meniscus to which a substrate can be exposed under a dry N₂ atmosphere. The LRA, suitable for probing predominantly chemisorbed material (since weakly bound species are removed during the outgassing process), is interfaced with an ultrahigh vacuum (UHV) apparatus equipped with X-ray photoelectron (XPS) and Auger electron (AES) spectrometers.

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Our previous surface analytical studies using AES and temperature programmed desorption (TPD), with the same solution conditions as described by Song et al., showed that chemisorbed phosphate anions grew approximately 5 times more rapidly on TiO2 than on Al2O3. We attempted further studies of CP adsorption on SiO2 but were unable to observe chemisorbed uptake behavior; CP interactions with the SiO2 surface seemed to be predominantly physisorption. Even after a 48-h solid–liquid exposure to the CP aqueous solution, no uptake by the SiO2 surface was observed; no detectable signal in the XPS of the P 2p core level for phosphate was seen. Our preliminary results thus complement the CC data showing that CP nucleates and grows more readily on TiO2 than either on SiO2 or Al2O3. In this paper, we report our results on CP uptake by TiO2 with attention to Ca adsorption behavior, phase analysis of the CP present, and probing of the CP–TiO2 compositional structure.

**Experimental Section**

**Apparatus.** The LRA consisted of a tubular Teflon column through which prepared solutions can be delivered by peristaltic pump at a flow rate of 5 mL min⁻¹. This provides a continuous fresh surface for solid–liquid adsorption. XPS was performed in an ion-pumped Perkin–Elmer PHI 560 system using a PHI 25–270AR double-pass cylindrical mirror analyzer. A Mg Kα anode was operated at 12 kV and 200 W with a photon energy of hν = 1253.6 eV. The base pressure of the UHV was 7 × 10⁻¹⁰ Torr after bakeout, and the operating system pressure during XP scans was 7 × 10⁻⁸ Torr. The pass energy used for high-resolution XPS was 50 eV (0.1 eV/step and 90 ms/step). AES was performed using pulse counting via an EG&G model 1120 photon counter in the same chamber. For AES depth profile analysis, the substrates were sputtered with a PHI 04-303 ion gun differentially pumped with a 50 L s⁻¹ turbopump. Ar⁺ was used as the primary ion at 3 kV and 15 mPa, and a 25 mA emission current was used with no rastering. The AES electron gun had a primary energy of 3 keV, and a measured beam current of 5 × 10⁻⁹ A (with Ar⁺ sputtering) was used for AES scans. Depth profiling was acquired dynamically, sampling the Auger peak-to-peak heights at 30 s intervals (0.5 eV/step). The system pressure during AES depth profiling experiments remained lower than 5 × 10⁻⁸ Torr. The ToF–SIMS apparatus (separate from the XPS/AES chamber) has been described fully elsewhere. In these experiments, Cs⁺/Cs⁺ projectiles were employed at 20 keV impact energy. Negative secondary ions (SIs) were accelerated to ~7 keV, mass-analyzed by time-of-flight, and detected using a microchannel plate detector. The SIMS measurements were performed using event-by-event bombardment and detection and coincidence counting, which permits ion yield measurements at the level of single ion impacts. The base pressure of the ToF–SIMS analysis chamber was ~3 × 10⁻⁸ Torr or lower. In a previous study using SIMS for CP phase identification (using standardized powders of CP phases), we had determined that the minimum projectile for phase analysis was (Cs⁺)Cs⁺. This projectile produced the highest yield of PO3, with the minimum projectile-induced reduction to PO2, and was thus chosen as the primary ion for these experiments. Phase elucidation on standardized CP powders was necessary because a CP phase change has been reported to readily occur in aqueous media.

**Reagents.** Polycrystalline Ta foil (99.95% purity) obtained from H. Cross Co. (Weehawken, NJ) was cut into 1 cm x 1 cm × 0.1 mm flat substrates to be used for thin-film TiO2 deposition and subsequent solid–liquid adsorption. Reactant-grade H2PO4 and NaCl crystals, 12 M HCl, and 10 M NaOH were obtained from EM Science (Gibbstown, NJ) for CP solution preparation and pH adjustment. In addition, CaCl2 powder (used for the CP solution) and Ti wire (99.99% purity; used for the TiO2 doser) were obtained from Aldrich Chemical Co., Inc. The O2 gas cylinder used for backfilling the UHV for TiO2 thin-film deposition was obtained from Cryogenic Rare Gas (99.99% purity; Metuchen, NJ).

**Procedure.** The prepared CP solution was made using Milli-pore CO2-free H2O as the solvent. This solution was shown to stimulate nucleation and growth of HAP on the high surface area, BET-characterized metal oxide colloidal seeds used in the CC experiments mentioned above. The solution contained 3.5 mM CaCl2 and 119 µg mL⁻¹ P as KH2PO4 and was adjusted to pH = 6.5 by adding NaOH and HCl dropwise to maintain a point-of-zero surface charge (PZC). This pH resulted in a neutral–pH critical at the surface, as measured in the electronic amplitude and CC experiments. The volume of the CP solution prepared was large (4 L) compared to the amount of NaOH and HCl typically needed for pH adjustment (2–5 mL). The supported background electrolyte was 0.01 M NaCl. The pH of the solution was adjusted prior to all CP solid–liquid exposures to the TiO2 surface. To avoid CO2 contamination of the solution due to air–liquid adsorption from the atmosphere, the CP solution was sparged with dry N2 via fritted glass. Otherwise, CO2 contamination would result in lowering of the solution pH and hence a change of surface charge. Mole fraction measurements (less than 10 atom %) from high-resolution XP scans of the Na 1s and Cl 2p orbitals (which can become high from excess buffering) were diagnostic of fresh solution conditions.

Ta foil was used as a metal support for growing oxide thin films to overcome charging problems during electron spectroscopic analyses while maintaining the same electronic and chemical properties as bulk oxide.14,15 The pressure regions in both the antechamber and the LRA were maintained with the use of differentially turbopumped sliding seals. This setup allowed the transferring of the sample from ambient conditions to UHV without breaking the vacuum. After a solid–liquid exposure, the sample was transferred into the antechamber for outgassing and subsequently into the UHV. The typical time required for outgassing is approximately 2 h, which allows the antechamber pressure to reach the low ~10⁻⁷ Torr region. The Ta substrate (spot-welded to electrical leads from the sample probe) was cleaned by resistive heating by passing current through it with a (1–10 V, 50 A maximum output) power supply. AES survey scans [0–1030 eV kinetic energy (KE) range] verified the surface cleanliness of the Ta foil prior to thin-film deposition. TiO2 was then coated onto the exposed via “hot filament” deposition by passing current through a metal doser under high background pressure (~5 × 10⁻⁷ Torr). AES and XPS confirmed the oxide overlay layer according to its characteristic O KLL and Ti KMM Auger transitions and O 1s and Ti 2p core levels for TiO2. The inelastic mean free path estimation2 of the attenuation of the XPS Ta 4f/2 core level (with cleaned Ta foil) after thin-film oxide deposition showed that the film thickness was approximately 50 Å. This same film preparation was made for all CP solution exposures. After surface characterization of the clean TiO2 thin film, the substrate was translated to the LRA via the antechamber, inverted, and brought into contact with the CP solution meniscus flowing through the LRA under an atmosphere of dry N2. The respective exposures were varied from 10 min to 20 h. After the solid–liquid dose, the surface was rinsed with Millipore H2O for 2 s to remove loosely bound ions that were
weakly bound (physorbed) to the surface. The substrate was then translated back into the antechamber for outgassing and into the UHV for surface analysis.

The substrates were scanned with XPS as a check prior to both AES depth profiling and SIMS analysis. XPS core level peak centers of sputter-cleaned Cu 2p3/2 (932.7 eV) and Au 4f7/2 (84.0 eV) from foils were used to calibrate the spectrometer’s binding energy (BE) range. The signal from adventitious carbon (C 1s) at 284.7 ± 0.2 eV was used to correct for charging and as a BE standard. XPS high-resolution scans of the surfaces were carried out for the Ta 4f7/2, Ti 2p3/2, Ti 2p1/2, Ca 2p3/2, Ca 2p1/2, P 2p, Cl 2p, Na 1s, C 1s, and O 1s core levels. Intensities from these orbitals were normalized by their respective sensitivity factors. The following KE ranges were used for the AES depth profile (with respective Auger transitions in parentheses): 255–300 (Ca LMM), 485–540 (O KLL), 105–135 (P KLL), 150–180 (Ta NOO), and 360–405 (Ti LMM) eV. These AES narrow scans were differentiated, and the peak-to-peak heights were taken. An atom % profile was determined from the respective atomic sensitivity factors of the Auger transitions and was plotted as a function of sputtering time. A 1002-A-thick SiO2 wafer (RBD Enterprises, Inc.) was used as a standard for determining the sputtering rate for depth estimation in the AES profile. The analyte substrate (after CP solution exposure) was removed from the XPS/AES surface analysis chamber and spot-welded onto the stainless steel SIMS target cube (2 cm × 2 cm × 2 cm); sample and cube were then transported (in a dry N2 atmosphere) and mounted onto the ToF-SIMS apparatus for analysis.

Results and Discussion

XPS. The average BE peak centers of these orbitals remained relatively constant at different CP solution exposure times. The measured average of the core level BE peak centers (12 measurements) at different solid–liquid solution exposures was as follows: P 2p at 133.8 ± 0.3 eV, Ca 2p3/2 at 351.2 ± 0.3 eV, Ca 2p1/2 at 347.5 ± 0.3 eV, O 1s at 532.2 ± 0.3 and 530.6 ± 0.2 eV (deconvoluted), Ti 2p3/2 at 464.2 ± 0.2 eV, and Ti 2p1/2 at 458.6 ± 0.2 eV. These core levels were consistent with those measured for standardized DCPD powder (within the ±0.2 eV precision of the BE measurement).

The overall O 1s XPS core level had a broad envelope, greater than 3 eV full-width-half-maximum (fwhm), and was thus deconvoluted with two peaks. Figure 1 shows the deconvolution of the O 1s levels after (A) 10-min and (B) 12-h exposures of the TiO2 substrate to the CP solution. The BE of (1) is 530.6 eV, corresponding to the TiO2 metal oxide state. This state was fitted with a fixed fwhm of 2.2 eV was likely an average of hydroxyl O from H2O (reported to be at 532.5 eV) and phosphate O (reported to be at 531.6–531.8 eV). Peak (3) was a BE-center of 532.1 eV and a fwhm of 3.4 eV, denoting an increased population of phosphate and hydroxyl O. Peaks (2) and (3) were not further deconvoluted because we felt that in doing so we would overinterpret the data; if the 2.2 eV fwhm (from TiO2) were used, third and fourth oxidation states would appear in (3). There was an obvious increase in hydroxyl O/phosphate O in the 12-h exposure. In comparing peaks (2) and (3), there was an increase in intensity of these states as well as an increase in the fwhm, from 2.4 eV in (2) to 3.4 eV in (3). In addition, a proportionately larger phosphate O to hydroxyl O ratio at higher exposure may be responsible for the ~0.4 eV BE shift in the O 1s level.

The CP uptake on TiO2 performed by XPS is shown in Figure 2. To quantify the amount of CP on the surface, XPS peak areas of the O 1s, C 1s, Ca 2p3/2 and P 2p core level intensities (normalized to the Ti 2p signal) as a function of solution exposure time. The dashed line represents a 1 MLeq of CP on the surface. The CP uptake on TiO2 was exposed to CP solution at (A) 10 min and (B) 12 h. Peak 1 denotes TiO2 oxygen. Peaks 2 and 3 denote hydroxyl O.

Figure 1. XPS of O 1s core level spectra after the TiO2 surface was exposed to CP solution at (A) 10 min and (B) 12 h. Peak 1 denotes TiO2 oxygen. Peaks 2 and 3 denote hydroxyl O.

Figure 2. XPS uptake curves of CP on the TiO2 surface of the Ca 2p3/2 and P 2p core level intensities (normalized to the Ti 2p signal) as a function of solution exposure time. The dashed line represents a 1 MLeq of CP on the surface.

outgassing and introduction into the UHV, an XPS spectrum was taken, and the P/Ti value obtained (0.07) was used for estimating the coverage of CP on the surface. Different areas of the substrate were AES depth-profiled to ensure a consistent phosphate–TiO₂ surface composition; the atom % mole fractions as a function of depth were the same for each area probed. Previous studies using this methodology, with TPD-integrated peak areas along with AES, determined that this 1 MLeq corresponded to \(~5\) µmol cm⁻² CP on the surface. The quantity of CP was reached after a 10-min solution exposure, which agreed with previous solid–liquid CP solution adsorption results as measured by AES. The AES rollover that corresponded to the first MLeq occurred at 10 min. This rollover was not observed in XPS due to the greater surface sensitivity of AES; comparatively larger amounts of Ca and P seen in XPS is due to its ability to probe deeper layers invisible to AES. The surface was exposed to the soft Mg Kα X-rays for an extended period (2 h) and further scanned by XPS to ensure that there was no X-ray induced damage to the surface. No change in the P 2p level line shape was observed; we were thus confident that there was very minimal, if any, photodegradation of phosphate during XPS analysis. The first MLeq on the oxide surface denoted the onset of 2-dimensional (2D) structure formation and growth of further layers to 3-dimensional (3D) islanding. In our plot (Figure 2), Ca depletion is observed after initial growth on the TiO₂ surface along with P growth. The Ca/Ti signal reached a maximum and began to decrease after \(~5\) h of solution exposure. The drop in the Ca/Ti signal denotes attenuation of the Ca 2p photoelectrons underneath overlayering phosphate groups and the onset of islanding by phosphate. The P/Ti signal appears to reach a saturation point at a 5–6 MLeq coverage; the exact solution exposure time when this occurs is not certain due to the relatively large error bars in the P/Ti intensity, which seem to increase with solution exposure time. The error bars are standard deviations of averaged data points. The increase in the error bars is likely due to interference of the spectator ions, Na⁺(aq) and Cl⁻(aq), from the background electrolyte. The relatively lower error bar in the Ca/Ti measurements, especially at the 20-h exposure, suggests greater stability of the Ca-rich first layer relative to the phosphate overgrowth. To determine whether the increased amount of material on the surface resulted in increased attenuation of the Ti 2p photoelectrons from the thin-film oxide substrate, hence affecting its sensitivity for normalizing the amounts of Ca and P, additional uptake experiments with TOF–SIMS were undertaken to complement the XPS findings (see TOF–SIMS results below).

**AES Depth Profiling.** Calibrated to the depth, a sputtering rate (S₁) was determined for the SiO₂ calibration wafer. The sputtering rate of the TiO₂ substrate (S₂) was estimated from the relation S₂ = (S₁d₁j₁A₁γ₁)(d₂j₂A₂γ₂)/d₂j₂A₂γ₂. The terms d₁ and A₁ are the density and molecular weight of TiO₂, respectively; d₂ and A₂ are those of the SiO₂. The current densities, j₁ and j₂ (in µA cm⁻²), were measured during Ar⁺ sputtering on the SiO₂ and TiO₂ surfaces, respectively. The sputter yield values used (γ₁, γ₂) for TiO₂ and SiO₂ were used 0.11 and 0.21, respectively. Figure 3 shows an atom % elemental compositional depth profile of a 4-h CP solution-exposed TiO₂ surface. The differentiated peak-to-peak heights of the Ta NOO Auger transition, from the substrate thin-film TiO₂ deposition, were not plotted for clarity of presentation. The crossover point on the AES profile plot between the Ti LMM and Ta NOO transitions occurred at (1) \(~275\) s; between the O LMM and Ta NOO, crossover occurred at (2) \(~380\) s. The P atom % was initially larger than that of Ca at the beginning of the depth profile; it decreased as top layers of material were etched away. Beginning at \(~200\) s of sputtering, the Ca atom % increased above that of P. At this point, the topmost layer of phosphate was sputtered away, leaving behind the initial Ca-rich layer. From this profile, it appears that the thickness of the phosphate islands was \(~20\) Å at the 4-h CP solution exposure. The initial Ca-rich layer was about 25–30 Å-thick between the Auger Ca–P and Ta–Ti crossover points. The AES depth profile further supports this scheme of phosphate layering (3D cartoon) on top of Ca at the onset of sputtering. Removal of phosphate left behind the Ca-rich layer (2D cartoon).

**TOF–SIMS.** Our previous studies using polyatomic projectile TOF–SIMS analysis on various standardized CP powders showed that the technique was ideal for unambiguously distinguishing between different CP phases involved in the nucleation and growth of HAP. Phase determination was not possible using XPS core-level shifts or X-ray powder diffraction (XRD). There was much overlap in the core level measurements between various phases, which made identification using BE shifts ambiguous. In addition, because much of the O 1s intensity at low CP coverages (e.g., 1 MLeq at 10 min) was from TiO₂ and not phosphate O, phase analysis by comparison of high BE satellites with the core level, as demonstrated by Lu et al., was not suitable for our adsorbate–substrate system. Furthermore, low coverages of CP (e.g., \(~5\) µmol cm⁻² after a 10 min solution exposure) would be insufficient to provide XRD structural information, as shown previously. Secondary electrons emitted from the CP–TiO₂ surface were used to count the number of incident primary ions

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in the SIMS analysis. Thus, only negative SI spectra were acquired. High-yield SI peaks PO$_3^-$ and PO$_2^-$, characteristic of PO$_3^{2-}$ groups on the surface, were observed. Polyatomic primary ions have been shown to be more efficient for generating substrate-specific SIs from inorganic targets than monoatomic projectiles at comparable energy. Differences in the relative PO$_3$-to-PO$_2$- SI peak area ratios allowed for CP phase differentiation and identification of the standardized powders. Each CP phase was shown to have a distinctive [PO$_3$]$_{-}$/[PO$_2$]$_{-}$ ratio except for HAP and α-TCP, in which there was overlap. Figure 4 shows a plot of the SI yields of PO$_3^-$ and PO$_2^-$ as a function of CP solution exposure time. XPS scans of the sample after exposure to ambient conditions for extended periods (over 12 h) showed that the CP–TiO$_2$ surface remained sufficiently stable for transport from the LRA in the XPS/AES chamber to the ToF–SIMS instrument. Each SIMS spectrum of CP–TiO$_2$ exposures were acquired using a primary ion dose of (CsI)$_2$Cs$^+$ at a primary ion energy of 3 keV and 10$^7$ ions cm$^{-2}$. The relative SI yield as a function of CP solution exposure time was obtained from the integrated peak areas of PO$_3^-$ (m/e = 79) and PO$_2^-$ (m/e = 63). These peak intensities were normalized by dividing by the number of incident (CsI)$_2$Cs$^+$ primary projectiles. The general uptake behavior of the PO$_3^-$ and PO$_2^-$ SIs were in agreement with those of the P/Ti XPS uptake (Figure 2). Since SIs are not attenuated by top overlayers, as in the case of Ti 2p core level photoelectrons, the SIMS plot provided further corroboration of the CP growth trend observed in the XPS uptake (Figure 2). SI yields originating from beneath thick phosphate layers (∼100 Å depth) were easily detected. The [PO$_3$]$_{-}$/[PO$_2$]$_{-}$ ratio remained relatively constant at ~2 with increased solution exposure times, indicative of a predominant DCPD phase on the surface. The measured [PO$_3$]$_{-}$/[PO$_2$]$_{-}$ SI ratio from standardized powder was 2.6 ± 0.1. Of the other possible CP phases that could form in aqueous solution, ACP had the second highest SI ratio (1.38 ± 0.50). No phase transformation was observed during the CP uptake.

The SIMS results are consistent with XPS core level shift findings, which were also indicative of DCPD on the TiO$_2$ surface. DCPD, along with other phases such as ACP and OCP, was reported to be an important precursor in the formation of HAP. According to Ostwald’s rule of stages, the least thermodynamically stable CP phase nucluates and grows first on the surface, followed by nucleation and growth of more thermodynamically stable phases. This empirical observation has been explained on the basis of structure changes in solution. The ease of nucleation and growth of CP phases follows the trend: DCPD > OCP > α-TCP > HAP. Our findings, indicating that DCPD was the predominant CP phase present, agreed with this trend.

**Compositional Structure.** We postulate that phosphate bonds to the TiO$_2$ via Ca$^{2+}$ cations that bridge O from TiO$_2$ with phosphate O (Figure 5). It should be noted that in this generalized scheme, no statement is being made about bond angles or distances between the atoms depicted. At the Ca$^{2+}$ and PO$_4^{3-}$ concentrations at pH = 6.5 (which is near the PZC for TiO$_2$), CaPO$_4^-$ and CaOH$_2^-$ are the predominant ions in aqueous solution. Ca$^{2+}$ and Mg$^{2+}$ cations, ubiquitous in soil systems, are strongly Lewis acids. They tend to be oxyphilic and can participate in cation bridging. In this scheme, Ca$^{2+}$ cations accept electron pairs from (1) O from the TiO$_2$ metal oxide thin-film surface and (2) phosphate O to form an inner-sphere complex with the TiO$_2$ surface. Phosphate is strongly bonded to the TiO$_2$ substrate via bonding through the Ca. At pH = 6.5, hydronium ions (H$_3$O$^+$) in solution serve as counterions for neutralizing the negatively charged phosphate anions. At this initial layer, hydrogen bonding (3) can occur between H$_2$O and phosphate O. There may be an interaction (4) in which H is abstracted from H$_3$O$^+$ to form hydroxyls with terminal phosphate O atoms. Note that the first M$_{L_{\text{eq}}}$ depicted (5) resembles the molecular formula for DCPD, CaHPO$_4$2H$_2$O, which SIMS showed to be the predominant phase on the surface. A combination of hydrogen bonding from H$_2$O as well as H abstraction

![Figure 4](image-url)  
**Figure 4.** ToF cluster SIMS uptake of PO$_2^-$ and PO$_3^-$ SIs using (CsI)$_2$Cs$^+$ projectiles of CP adsorbed on TiO$_2$ as a function of solution exposure time. The numerical values at each exposure time denote the PO$_3^-$/PO$_2^-$ intensity ratio.

![Figure 5](image-url)  
**Figure 5.** Proposed compositional structure scheme of CP adsorbed on TiO$_2$: (1) O from the TiO$_2$ surface; (2) phosphate O; (3) hydrogen bonding between H$_2$O and phosphate O; (4) electrostatic interaction involving H$_3$O$^+$; (5) a molecular formula similar to that of DCPD; (6) outer phosphate groups.
from $\text{H}_2\text{O}^+$ is likely involved in the growth of additional phosphate overlayers (6), which can continue further until a saturation level is reached. Note that a high BE shoulder develops in the O 1s core level, indicative of an increasing phosphate O/hydroxyl O population between the 10 min and 12 h CP solution exposure (Figure 1). In addition to evidence pointing to the DCPD phase on the surface, the XPS uptake plot and AES depth profile both are indicative of P overlayers covering a Ca-rich initial layer at high CP solution exposures. XPS, AES, and SIMS data are consistent with the above-described scheme.

**Conclusions**

In summary, XPS and AES depth profiling data showed evidence for 3D phosphate islanding on top of a 2D Ca-rich initial layer on the TiO$_2$ surface. The XPS of the O 1s core level suggested that $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ provided a source of protons as the counterions for growing phosphate groups. This scheme also accounts for the DCPD-like CP phase, as detected by ToF-SIMS. There was no indication (in the SIMS data) for CP phase transformation (from DCPD to HAP) up to the observed saturation point. Phosphate reached a level of saturation after ~20 h of solid-liquid solution exposure as shown by XPS and SIMS uptake plots (Figures 2 and 4), suggesting that physiosorption (crystal formation) is necessary for further CP phase transformation into HAP.

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