Uniform amorphous aluminium phosphate thin films with precisely controlled thickness and tunable composition were deposited on nitrogen-doped carbon nanotubes at 150 °C through a new atomic layer deposition approach.

Aluminium phosphate (AlPO₄) has long been known as a catalyst support for numerous catalytic applications.¹² AlPO₄ itself has been used to catalyze the dehydration of methanol to dimethyl ether, which is a clean alternative fuel for diesel engines and a potential aerosol propellant in the cosmetics industry.³ AlPO₄ coating on cathodes has been considered as an effective strategy to improve both the safety and cycle-performance of lithium secondary batteries.⁴ In addition, an AlPO₄ protective layer has been shown to inhibit the oxidation of carbonaceous materials.⁵

AlPO₄ has generally been synthesized previously through a co-precipitation process followed by heat treatment.¹⁻⁵ Unfortunately, this route is incapable of achieving uniform aluminium phosphate thin films and lacks the flexibility to tune their chemical composition (P/Al ratio). Uniformity and tunable composition have been proven to play a critical role in determining the practical applications of AlPO₄.⁶⁻⁸ Recently, atomic layer deposition (ALD) has emerged as a powerful technique for thin film deposition.⁷⁻⁸ Unlike other physical or chemical vapour deposition processes, ALD employs alternative precursor doses and self-limiting surface reactions, which result in material growth of one monolayer (or less) per cycle. Thus, ALD offers exquisite control over the thickness and composition of thin films. However, there have been very few studies on the preparation of aluminium phosphate by ALD.⁹⁻¹¹ Aluminium phosphate was found to form in P-doped aluminium oxide with P doping greater than 10 wt% at 450 and 500 °C using AlCl₃ or aluminium n-propoxide, 2-methyl-2-propanol and P₂O₅ as precursors.¹⁰ However, the high deposition temperature seriously hinders its applications, especially for sensitive substrates. In another study, aluminium phosphate was obtained from AlCl₃ and trimethylphosphite at deposition temperatures between 150 and 400 °C.¹¹ This route simplifies the ALD process by sacrificing the controllability of the chemical composition of the aluminium phosphates. Moreover, the use of metal chlorides is undesirable in the ALD process, because it may lead to the corrosion of the ALD system caused by HCl generated during the reaction and leave Cl impurities in the deposited films.¹¹⁻¹²

Herein, we report a new ALD approach to fabricate amorphous aluminium phosphate ([Al₅P₃O₁₀] thin films. Its features include low-temperature deposition, controllable film thickness, variable film composition, and freedom from metal chlorides. Al₅P₃O₁₀ thin films are deposited by combining subcycles of Al₂O₃ and PO₃ and one ALD cycle consists of 1 Al₂O₃ subcycle and n PO₃ subcycles (5 ≤ n ≤ 20) (Scheme 1). The popular trimethylaluminium (TMA)-H₂O is adopted for the Al₂O₃ subcycle, and trimethylphosphite (TMP)-O is used for the PO₃ subcycle. The composition (P/Al ratio) of Al₅P₃O₁₀ thin films is controlled by varying the PO₃ subcycles while keeping the Al₂O₃ subcycle unchanged.

Nitrogen-doped carbon nanotubes (NCNTs) grown on carbon papers are employed as substrates for the deposition of Al₅P₃O₁₀ thin films, due to their defective surface, which is ready for the  

---

**Scheme 1** Illustration of the ALD process for aluminium phosphate.
growth of metal oxides. The deposition of AlP2O7 is performed at 150 °C by sequentially introducing TMA, H2O, TMP and O3 (9.8 wt% concentration) into the ALD reaction chamber. The ALD sequence is described as 1 × (TMA–H2O)–20 × (TMP–O3). The pulse time is 0.5, 1, 1 and 1 s for TMA, H2O, TMP and O3 respectively, and the purge time after each pulse is 15 s.

The initial NCNTs have diameters of about 60 nm (Fig. 1a) and exhibit a typical bamboo-like structure (Fig. S1f). Fig. 1b shows a scanning electron microscopy (SEM) image of a 100-cycle AlP2O7 thin film deposited on NCNTs. The selected area diffraction (SAD) pattern in Fig. 1c indicates that the 100-cycle AlP2O7 thin film is amorphous, which is confirmed by the X-ray diffraction pattern (Fig. S2f) and high resolution transmission electron microscopy (HRTEM) image in Fig. 1d. From Fig. 1d, the thickness of the AlP2O7 thin film is measured to be 16.4 nm. Fig. 1e presents the energy dispersive X-ray spectroscopy (EDS) elemental line-scanning result of the 100-cycle AlP2O7 thin film deposited using a sequence of 1 × (TMA–H2O)–20 × (TMP–O3).

The film thickness can be easily obtained by choosing an appropriate number of ALD cycles. The growth rate of Al1.3PO5.0 is slightly higher than that of aluminium phosphate deposited by ALD from AlCl3 and trimethylphosphate (1.4 Å per cycle) at the same deposition temperature.

To demonstrate the flexibility to modify the composition of AlP2O7 through this ALD approach, we varied the number of POx subcycles from 20 to 10 and 5, while the Al2O3 subcycle was kept unchanged. The average P/Al atomic ratio of each sample was obtained from 10 EDS results (Fig. S5f), and is plotted as a function of the number of POx subcycles in Fig. 2b. One can see that the P/Al atomic ratio decreases from ~0.8 to 0.4 to 0.3, when the number of POx subcycles is reduced from 20 to 10 to 5 respectively. It is worth noting that the P/Al ratio in AlP2O7 thin films could be adjusted to be either higher or lower by changing the number of POx subcycles in this ALD recipe. It also should be mentioned that the growth rate of AlP2O7 thin films could be reduced by lowering the P/Al atomic ratio or the number of POx subcycles (Fig. S6f), due to the lower contribution of the POx subcycles to the thin film.

The structure of the amorphous Al1.3PO5.0 thin film was analyzed by X-ray absorption near-edge structure (XANES) spectroscopy. Fig. 3 displays the XANES spectra at the Al L3,2-edge and P L3,2-edge for Al1.3PO5.0, in comparison with those of standard crystalline AlPO4, Al2O3 and P2O5. Fig. 3a indicates that Al1.3PO5.0 has a very similar Al L3,2-edge spectrum to standard AlPO4, except that the first transition of Al1.3PO5.0 exhibits only one broad peak at 78.3 eV, instead of two well resolved peaks at 77.9 and 78.3 eV.

Fig. 1 (a) SEM image of NCNTs; (b) SEM image, (c) TEM image, (d) HRTEM image, (e) STEM-EDS line-scanning and (f) XPS spectrum of NCNTs coated with 100-cycle AlP2O7 thin film deposited using a sequence of 1 × (TMA–H2O)–20 × (TMP–O3).
for standard AlPO₄. This observation is attributable to the amorphous state of Al₁.₃PO₅.₀. The first transition in Al₁.₃PO₅.₀ could be assigned to transitions from the Al spin–orbit split 2p orbitals to the unoccupied densities of states of 3s character (L₁ and L₂ edges), and the second transition corresponds to transitions from the Al 2p orbitals to the upper bands and is sometimes referred to as a multiple scattering resonance of which the energy position relative to the threshold is related to the interatomic distance (r) between Al and its nearest neighbouring O atom with a ∼ 1/r² correlation. A small shift in this resonance to a higher energy indicates that the Al–O inter-atomic distance is shorter in Al₁.₃PO₅.₀ compared to AlPO₄ albeit very slightly. It should be noted that the Al L₁₂,₃-edge spectrum of Al₁.₃PO₅.₀ distinctly differs from that of Al₂O₃, owing to the different local bonding environments of the Al sites, i.e., P–O–Al in Al₁.₃PO₅.₀ and Al–O–Al in Al₂O₃. In Fig. 3b, Al₃PO₅.₀ and standard AlPO₄ exhibit the same four peaks centred at 137.7, 138.7, 140.0 and 147.9 eV in the P L₁₂,₃-edge XANES spectrum, suggesting the same coordination of P (P–O–Al) in both samples and that the local structure of the PO₄ moiety remains intact. The result is in agreement with the P L₁₂,₃-edge XANES spectrum reported for AlPO₄ in the literature. The P L₁₂,₃-edge XANES spectrum of Al₁.₃PO₅.₀ is apparently different from that of P₂O₅ (P–O–P). The XANES results provide strong evidence of P–O–Al bonding being in the amorphous Al₁.₃PO₅.₀ thin film prepared by ALD.

The oxidation resistance of carbonaceous materials (carbon fibres, graphite etc.) needs to be improved in order to reach the full potential of carbon/carbon composites for high-temperature applications. Coating protective layers on carbon materials has been considered as an effective strategy for this purpose. The retarding effect of Al₁.₃PO₅.₀ on carbon oxidation has been demonstrated on powder-based NCNTs. Fig. 4 presents differential scanning calorimetry (DSC) and thermogravimetric (TG) curves of NCNTs and NCNTs coated with a 50-cycle Al₁.₃PO₅.₀ thin film by ALD (around 10 nm in thickness). The DSC results in Fig. 4a show that the exothermic peak for carbon oxidation shifts from about 480 °C for NCNTs to 550 °C for Al₁.₃PO₅.₀/NCNTs, proving the improved thermal stability of NCNTs by an Al₁.₃PO₅.₀ coating. It should be noted that the oxidation temperature of NCNTs in this work (∼ 480 °C) is much lower that of carbon nanotubes reported previously (∼ 650 °C) because of the N doping. An exothermic shoulder observed at ∼ 460 °C in Al₁.₃PO₅.₀/NCNTs is attributed to the transition from amorphous to crystalline AlPO₄. The TG results in Fig. 4b also suggest the delayed oxidation of NCNTs is caused by the Al₁.₃PO₅.₀ coating. For Al₁.₃PO₅.₀/NCNTs, gradual and slow weight loss is found before 440 °C, and could be ascribed to the removal of adsorbed and/or coordinated water. Al₁.₃PO₅.₀ accounts for 20 wt% of the total weight of Al₁.₃PO₅.₀/NCNTs. From the above results, it can be found that Al₁.₃PO₅.₀ thin film made by ALD is an effective protective layer for delaying the oxidation of NCNTs, and its function is comparable to other protective layers, such as zirconia, alumina and/or titania and SiCₐ,O₉. Taking the advantages of uniform, conformal and thickness-controlled film deposition, it is expected that ALD will play an important role in improving the oxidation resistance of carbonaceous materials in the near future.

In conclusion, we report a new low-temperature ALD process to synthesize aluminium phosphate thin films on NCNTs in a well-controlled manner. The film thickness of aluminium phosphates is tunable at the nanoscale level by simply varying the number of ALD cycles, and the film composition (P/Al ratio) is tailored by changing the subcycle ratio between Al₂O₃ and PO₄ during the ALD process. Moreover, the aluminium phosphate film exhibits an inhibitory effect on the oxidation of NCNTs. The strategy reported in this work is applicable to the development of other metal phosphates (FePO₄, TiPO₄) and phosphate-containing compounds (NASICON-type all-solid-state electrolytes, LiM₂(PO₄)₃ (M = Ti, Zr, Ge and Hf)), which will be key components in the next-generation of microbatteries.

**Acknowledgements**

The authors acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Research Chair (CRC) Program, the Foundation for Innovation (CFI), the Ontario Research Fund (ORF), the Canadian Light Source (CLS) at the University of Saskatchewan, and the University of Western Ontario.

**Notes and references**


**Fig. 3** XANES Al L₁₂,₃-edge (a) and P L₁₂,₃-edge (b) spectra of Al₁.₃PO₅.₀ in this work, and standard AlPO₄, Al₂O₃ and P₂O₅.

**Fig. 4** DSC (a) and TG (b) curves of NCNTs and 50-cycle Al₁.₃PO₅.₀ coated NCNTs conducted at a temperature increase rate of 10 °C min⁻¹ in a flowing air atmosphere.