Direct Growth of Layered Intercalation Compounds via Single Step One-pot *in situ* Synthesis

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A single step one-pot *in situ* synthesis method was developed to directly grow layered intercalation compounds. This methdology is expected to be applicable to a wide range of layered materials.

Inorganic-organic hybrids with an intercalated structure have been the research focus for decades due to their potential of preserving combined properties of organic and inorganic components within a single molecular composite.[1, 2] Applications of such intercalated hybrids include batteries,[4, 5] solar cells,[6] catalysts,[7] and drug release materials,[8] which widely exist in our daily life.

Currently, the preparation of layered intercalation compounds has been mainly limited to a two-step process: pre-synthesis of a layered compound (or obtaining a natural layered compound) followed by the intercalation reaction (Fig. 1A).[9-12] However, the second step of intercalation could be very challenging. Some guest species are impossible to be intercalated because of size mismatch[13] and/or lack of interaction with the host layered material. Thus, it is highly desirable that a new synthesis method can be developed to avoid the above challenges and directly grow intercalation compounds *via* a one-step reaction without the need of the pre-formation of layered compounds (Fig. 1B).
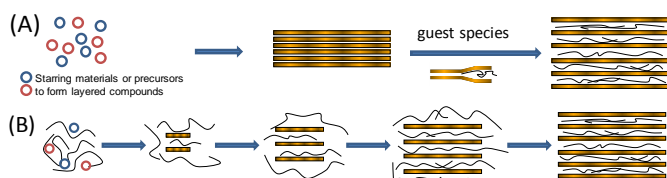

Figure 1. Schematic of intercalation approaches: (A) traditional intercalation; (B) single step one-pot *in situ* synthesis (the intermediate steps are intentionally added to illustrate the growing progress of the layered intercalation compounds, but the reaction itself consists of one step).

Crystal growth of layered structures is typically anisotropic, with faster growth along the layer planes, driven by the formation of strong covalent or coordinate bonds. Interlayer growth is dominated by the formation of weaker bonds, such as Van der Waals forces,[14] weak electrostatic interactions,[15] or hydrogen bonds[16] in various layered systems. We hypothesize that the direct growth of intercalation compounds requires the formation of a network of interactions between the intercalant and the inorganic sheet structure. α-Zirconium phosphates ($Zr(HPO_4)_2 \cdot H_2O$, α-ZrP)[17] (Fig. S1a) appears to be an ideal model layered compound for this fundamental exploration. α-ZrP crystallizes with acidic hydroxyl groups projecting from the sheet surface.[18] This surface is ideally suited to form hydrogen bonded networks with a hydrogen bond acceptor such as polyethylene glycol (PEG, Fig. 2). In addition, α-ZrP sheet surface can form electrostatic interactions with positively charged guest species since the acidic hydroxyl groups on α-ZrP sheet surface can ionize to form negatively charged layers, as well as forming Van der Waals forces with guest species, which universally exist.

Herein, using α-ZrP as an example, we report the direct growth of layered intercalation compounds by applying a layer growth coordinator, PEG (Fig. 2). Thanks to the hydrogen bonding with α-ZrP sheets, PEG molecules can "guide" the growth of the layers in the Z-direction, during which the PEG coordinators are embedded within the growing layers to form an intercalation compound (like assembly of building blocks, Fig. 2). Such a novel methodology opens new routes for achieving intercalated morphology, and may lead to new materials.
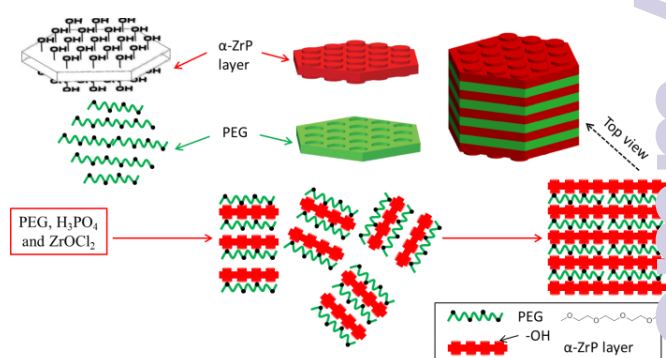

Fig. 2. Direct growth of layered intercalation compounds (not drawn to scale).

Preliminary studies have shown that it is not possible to intercalate PEG into pre-synthesized α-ZrP using conventional methods (See Fig. S2). However, when PEG is added to the hydrothermal reaction mixture used to synthesize α-ZrP, the interlayer distance of the formed compounds increases from the native 7.6 to 10.4 Å, indicating the formation of an intercalated

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phase. Different mass ratios of PEG with a molecular weight (MW) of ca. 600 g/mol (PEG-600) were added to reaction mixtures to evaluate the ratio effect on intercalation efficiency (Fig. 3a). At low mass ratios (less than 0.50:1 PEG-600:α-ZrP), a mixture of un-intercalated α-ZrP and intercalated PEG/α-ZrP hybrid was observed. At higher mass ratios (≥0.5:1 PEG-600:α-ZrP), only a very small amount of un-intercalated α-ZrP was found. Further increasing the mass ratio did not alter the distribution of the products much, indicating that the mixture has reached an equilibrium distribution. It is possible that the two phases are present within a single crystal, with alternating intercalated/un-intercalated layers. Energy dispersive X-ray spectroscopy (EDX) analysis (Fig. S3) detected C, O, Zr and P from the PEG-600/α-ZrP=1.00/1 intercalation compound (the Cu signal is from the copper sample substrate). The average P/Zr atomic ratio for the intercalation compound is ca. 1.90, which is close to the theoretical value of 2. The TGA results (Fig. S4) suggest that the PEG-600/α-ZrP intercalation compounds contain ca. 6%, 8%, 9%, and 10% PEG for 0.25/1, 0.50/1, 1.00/1, and 2.00/1 ratio intercalation compounds, respectively.
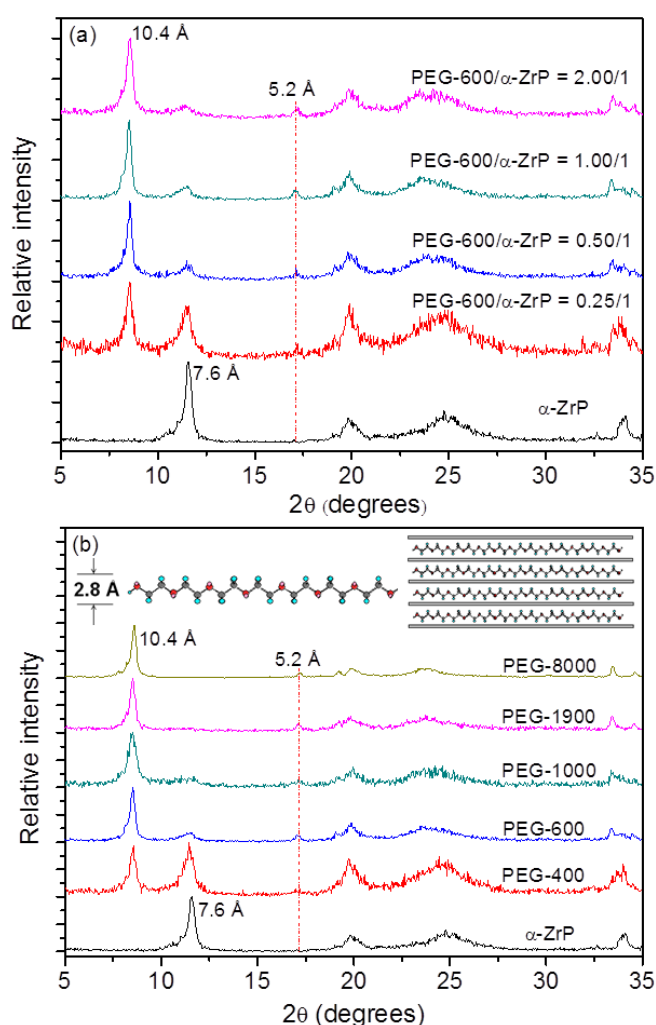

Fig. 3. XRD patterns of the α-ZrP based intercalation compounds via one step direct growth. (a) Intercalation compounds synthesized with various PEG-600/α-ZrP mass ratios (100 °C for 24 hours); (b)

intercalation compounds synthesized with PEGs with different MWs (100 °C for 24 hours, PEG/α-ZrP=1.00:1 in mass ratio).

The degree of intercalation efficiency was found to scale with the chain length of the polymer coordinators (Fig. 3b). When α-ZrP is synthesized in the presence of PEG with a MW exceeding 1000 g/mol, only the intercalated product was observed. This result can be attributed to the cooperative action of ether subunits that allow PEG to be tethered to the growing α-ZrP framework (Fig. 2). In order for PEG chains to be included within the growing crystal they must be sufficiently anchored onto the surface to prevent them from being displaced as the subsequent layer is nucleated. A long chain would statistically favor the anchoring of PEG chains, thus facilitating the formation of an intercalation compound.

It should be noted that the synthesized PEG/α-ZrP intercalation compounds exhibit the same interlayer distance, regardless of the PEG chain length or the PEG/α-ZrP mass ratio. This suggests that the intercalated PEG chains are parallel to the layers. Moreover, the thickness of linear PEG of ca. 2.8 Å (based on ChemDraw Ultra 12.0) is in an excellent agreement with the interlayer distance difference between the PEG/α-ZrP intercalation compounds (10.4 Å) and α-ZrP (7.6 Å), which further suggests that the PEG chains within the layered intercalation compounds are parallel to the layer surface.

While the parallel conformation of PEG chains are expected based on the aforementioned formation hypothesis of the intercalated hybrids (Fig. 2), it should be noted that it is highly in contrast to the dominant trend in which intercalants tilt away from the layer surface to a certain angle, resulting in an interlayer distance proportional to chain length.[19] While many conventional intercalants feature an interacting head group and an organic tail group, PEG forms hydrogen bonds to α-ZrP through its backbone oxygen atoms, favoring an extended conformation.

Figure 4 shows the SEM images of pristine α-ZrP and the intercalated PEG/α-ZrP compounds. Overall, all the intercalation compounds are similar in morphology. They are slightly smaller than the α-ZrP grown in the absence of PEG, which indicates that the presence of PEG only has marginal impact on the crystal growth in the lateral direction. This is consistent with our hypothesis that PEG predominately affects interlayer growth.

Various other coordinators, including other polymers (e.g., polyethyleneimine (PEI), polyvinyl alcohol (PVA)), small molecules (e.g., acrylamide), and ions (e.g., 1-butyl-3-methylimidazolium (BMIM+)) were also evaluated for the direct growth of α-ZrP based intercalation compounds because they can either form hydrogen bonds (e.g., PEI, PVA, acrylamide) or electrostatic force (e.g., BMIM+) with α-ZrP layers. The characterization results proved that they can similarly form intercalation compounds with α-ZrP via the single step synthesis (see Fig. S5), suggesting that the proposed methodology is general.
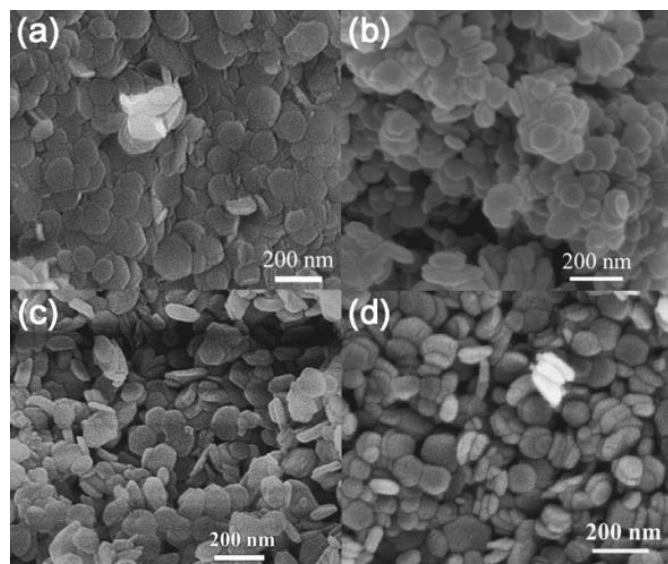
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Fig. 4. SEM images of α-ZrP based intercalation compounds. (a) α-ZrP, (b) PEG-600/α-ZrP (1.00:1), (c) PEG-1900/α-ZrP (1.00:1), and (d) PEG-8000/α-ZrP (1.00:1).

Moreover, the direct growth of intercalation compounds based on another type of layered materials, layered double hydroxides (LDHs, $[M^{2+}_{1-x}N^{3+}_x(OH)_2]^{x+}[A^{p-}_{x/p}]\cdot mH_2O$, M^{2+} and N^{3+} represent divalent and trivalent metal cations, respectively; A^{p-} is interlayer anion (Fig. S1b), with a positive layer charge (hereafter MN-LDH),[20] was also explored. Since the layers of $[Mg^{2+}_{1-x}Al^{3+}_x(OH)_2]^{x+}[A^{p-}_{x/p}]\cdot mH_2O$ (MgAl-LDH) is positively charged, a negatively charged polyelectrolyte, poly(sodium 4-styrenesulfonate) (PSS), was chosen as the coordinator, with an expectation that LDH layers and PSS can form a weak electrostatic force. The XRD characterization results are shown in Fig. S6, which shows a very similar trend as the direct growth of PEG/α-ZrP intercalation compounds as shown in Fig. 3a). During the synthesis, a higher concentration of PSS favored the growth of the PSS/MgAl-LDH layered intercalation compounds. Meanwhile, the interlayer distance of the PSS/MgAl-LDH layered intercalation compounds remained virtually the same (20.0 Å), because PSS stayed parallel to the layer planes.

We have shown that by introducing a layer growth coordinator during synthesis, one can achieve the direct growth of layered intercalation compounds. Such a new methodology is highly desirable for the design of layered intercalation compounds for various applications. The additional examples of the direct growth of α-ZrP or LDH intercalation compounds have demonstrated that this new methodology for direct growth of layered intercalation compounds should be very general.

The observation of single polymer layers between inorganic sheets in the PEG/α-ZrP intercalated hybrids also presents a unique nano-confinement environment for various molecules, which will be investigated later as a separate topic.

Finally, it should be noted that this methodology not only allows access to materials that may not otherwise be synthesized, but the one step process also offers significant savings in both cost and time.

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