Supporting Information

Direct Growth of Layered Intercalation Compounds via Single Step

One-pot in situ Synthesis

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EXPERIMENTAL SECTION

**Materials.** A series of linear polyethylene glycols (PEG) with various molecular weights: ca. 400, 600, 1000, 1900, and 8000 (abbreviated as PEG-400, PEG-600, PEG-1000, PEG-1900, PEG-8000) were purchased from Alfa Aesar and used as received. ZrOCl$_2$·8H$_2$O (98%, Sigma-Aldrich), phosphoric acid (85%, Sigma-Aldrich), poly(sodium 4-styrene-sulfonate) (30 wt.% aqueous solution, MWs 70,000, Sigma-Aldrich), urea (>99.0%, J.T. Baker), polyethyleneimine (PEI) with an average molecular weight of 600 (Sigma-Aldrich), polyvinyl alcohol (PVA, weight average molecular weight of ~27,000, 98.0-98.8% hydrolysis, Kuraray), poly(sodium 4-styrene-sulfonate) (PSS, MWs 70,000, 35wt% water solution from Sigma-Aldrich), acrylamide (98.0%, TCU America), 1-butyl-3-methylimidazolium (BMIM$^+$) chloride (>98.0%, Sigma-Aldrich) were all used as received without further purification.

**Characterization.** X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Bragg-Brentano $\theta$-2$\theta$ geometry (40 kV and 30 mA), using a graphite monochromator with Cu K$_\alpha$ radiation with $\lambda=1.542$ Å. Samples were gently packed in a sample holder for characterization.

Scanning electron microscopy (SEM) images were acquired on a field emission-SEM (FE-SEM, JSM-6335F) from JEOL. The samples were sputter coated with a thin layer (ca. 3 nm) of Pt/Pd (80/20) prior to the SEM imaging.

**Direct synthesis of $\alpha$-ZrP based layered intercalation compounds.** Polyethylene glycol (PEG)/$\alpha$-ZrP layered intercalation compounds were synthesized via a hydrothermal reaction,$^{28}$ during which 4.0 g of 20.0 wt% ZrOCl$_2$ aqueous solution was
mixed with a pre-determined amount of PEG. After the PEG was dissolved, a pre-determined amount of concentrated H$_3$PO$_4$ was added so that the H$_3$PO$_4$ and ZrOCl$_2$ mole ratio reached 10:1. Additional deionized water was added to dilute the concentration of H$_3$PO$_4$ to reach 4.0 M. The mixture was treated at 100 °C for 24 hours in a 20 mL container that was well sealed.

In one series of reactions, PEG-600 was used. The mass ratio of PEG-600 to α-ZrP (assuming all the Zr$^{4+}$ cations were converted to α-ZrP) was varied from 0.25:1 to 2.00:1. In another series of reactions, linear PEGs with various molecular weights (MWs), including PEG-400, PEG-600, PEG-1000, PEG-1900, PEG-8000, were used. The mass ratio of each of these PEGs to α-ZrP (assuming all the Zr$^{4+}$ cations were converted to α-ZrP) was maintained at 1:00 to 1.

A neat α-ZrP sample was synthesized in the absence of PEG under the same reaction conditions as a control. In addition, this neat α-ZrP was mixed with PEG-600 (mass ratio of PEG-600 to α-ZrP is 2:00 to 1), and the mixture was hydrothermally treated at 100 °C for 24 hours in a same container. This reaction was to check whether the pre-synthesized neat α-ZrP can be intercalated by PEG-600 under the same reaction conditions.

The α-ZrP based intercalation compounds containing other guest species, including other polymers (PVA, PEI), small molecules (acrylamide), and ions (1-butyl-3-methylimidazolium BMIM$^+$), were also synthesized via the same reaction approach and under the same reaction conditions.
After reaction, the products were washed and collected by centrifugation three times. After that, they were dried at 70 °C for 24 hours. The dried samples were ground with an agate mortar and pestle into fine powders for characterizations.

**Direct synthesis of MgAl-LDH based layered intercalation compounds.** A 30.0 mL solution composed of Mg(NO$_3$)$_2$ (0.20 M) and Al(NO$_3$)$_3$ (0.05 M) was mixed with urea at a molar ratio of (urea):(total metal ion)= 4:1 and a pre-determined amount of poly(sodium 4-styrene-sulfonate) (PSS). The mixture was added into a Teflon lined hydrothermal reactor and heated at 100 °C for 24 hours. The mass ratio of PSS to LDH (assuming all the metal cations were converted to LDH) was varied from 0.25:1 to 2.00:1. A neat MgAl-LDH sample was synthesized in the absence of PSS under the same reaction conditions as a control. After reaction, the products were washed and collected by centrifugation three times. After that, they were dried at 100 °C for 24 hours. The dried samples were ground with an agate mortar and pestle into fine powders for characterizations.
Figure S1. Structure of (a) α-zirconium phosphate and (b) layered double hydroxide.
Figure S2. XRD patterns of pristine $\alpha$-ZrP and the mixture of $\alpha$-ZrP and PEG-600 (2.00:1 mass ratio) after mixing under the hydrothermal reaction conditions (100 °C for 24 hours).
Figure S3. EDX analysis of PEG-600/α-ZrP=1.00/1.
Figure S4. TGA analysis of PEG-600/α-ZrP intercalation compounds with different weight ratios.
**Figure S5.** XRD patterns of $\alpha$-ZrP based intercalation compounds. Those intercalation compounds were synthesized with various coordinators at 100 °C for 24 hours. The labeled ratio represents mass ratio.
Figure S6. Intercalation compounds synthesized with various PSS/LDH mass ratios (100 °C for 24 hours).