Supporting Information

Title: Fulvic-Polyphosphate Composite Embedded with ZnO Nanorods (FA-APP@ZnO) for Efficient P/Zn Nutrition on Peas (*Pisum sativum* L.)

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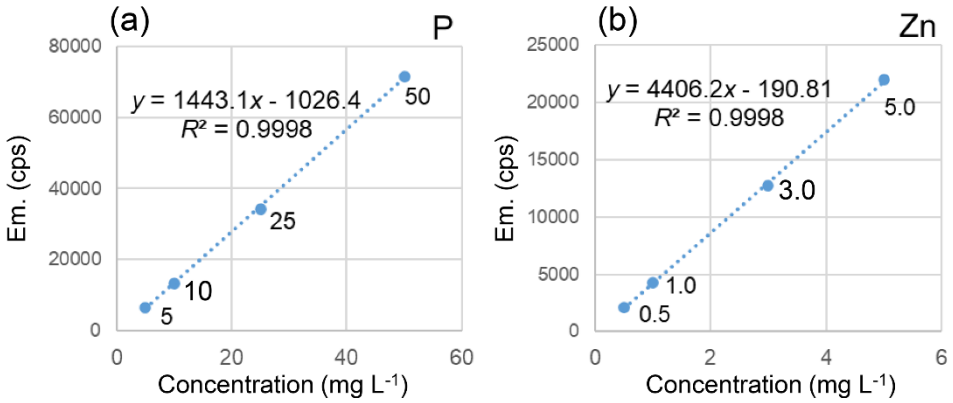


Figure S1. The calibration curves and the linearity of the inductively coupled plasma optically emission spectrometry (ICP-OES) for (a) phosphorus (P) and (b) zinc (Zn) determination.

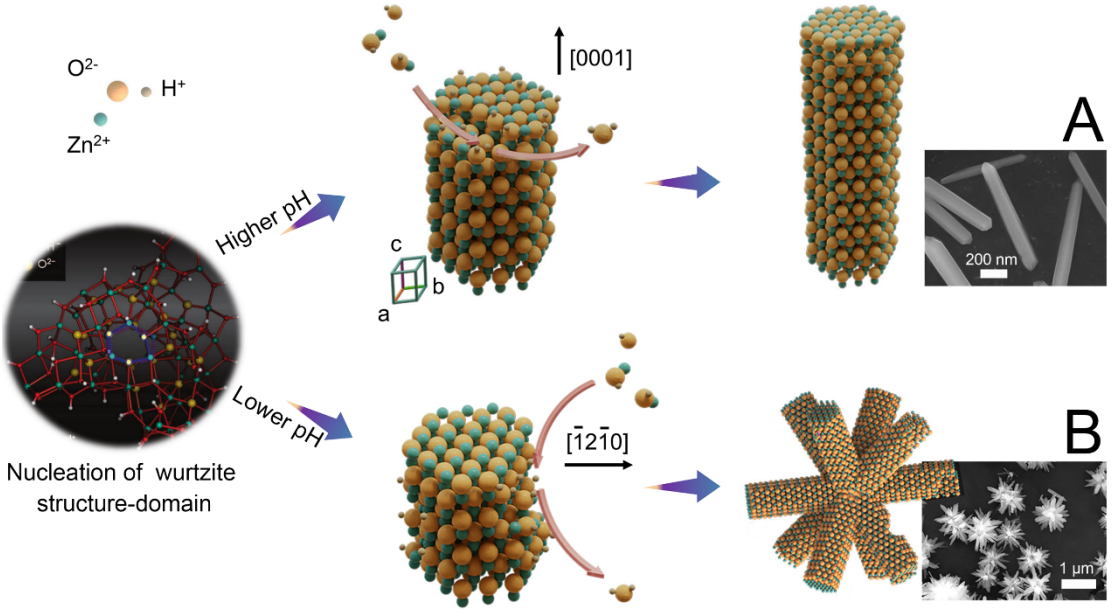


Figure S2. Schematic of the differential growth modes of the ZnO crystals under two alkalinity conditions. The far left inset was adapted with permission from ref.[1] Copyright 2008 American Chemical Society.

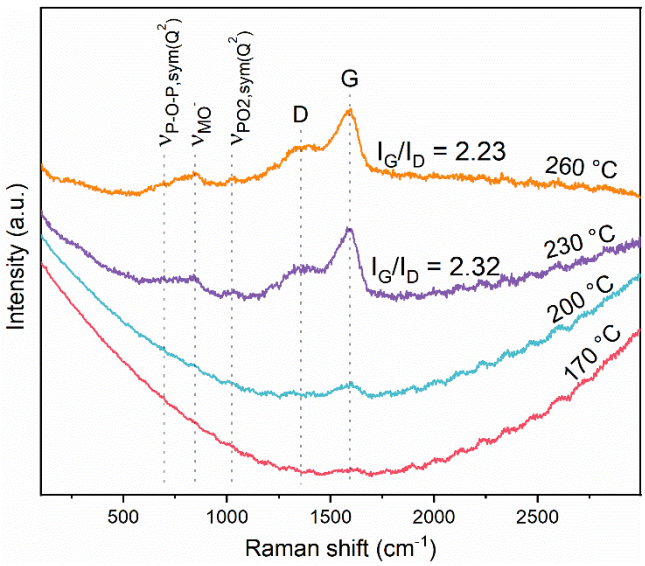
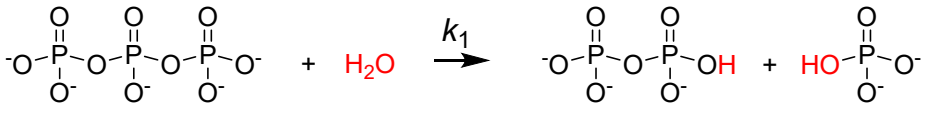


Figure S3. Raman spectra of FA-APP@ZnO calcined at different temperatures.

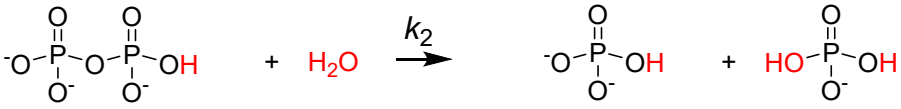
Text S1.

The hydrolysis reaction of polyphosphates consists of the following steps (eqs 1 and 2).[2]

(A) (B)



(1)



(2)

The $P_3O_{10}^{5-}$ hydrolysis (eq 1) and $P_2O_7^{4-}$ hydrolysis (eq 2) are both regarded as the one-order reactions. Their reaction rate, r_1 and r_2 (mol m^{-3} d^{-1}), can be expressed by the concentration of $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$ respectively, as indicated in eqs 3-6.

$$r_1 = k_1 C_A \quad (3)$$

$$r_2 = k_2 C_B \quad (4)$$

$$dC_A/dt = -k_1 C_A \quad (5)$$

$$dC_B/dt = k_1 C_A - k_2 C_B \quad (6)$$

here, C_A (mol m^{-3}) is the concentration of $P_3O_{10}^{5-}$ and C_B (mol m^{-3}) represents the concentration of $P_2O_7^{4-}$. k_1 (d^{-1}) and k_2 (d^{-1}) are the kinetic constants of eqs 3 and 4, respectively.

x_1 is then used to represent the conversion rate of $P_3O_{10}^{5-}$, while x_2 represents the yield of $P_2O_7^{4-}$ to $P_3O_{10}^{5-}$. $C_{A,0}$, and $C_{B,0}$ (mol m^{-3}) represent the initial concentration of $P_3O_{10}^{5-}$ and $P_2O_7^{4-}$ respectively, yielding eqs 7 and 8.

$$dx_1/dt = k_1(1 - x_1) \quad (7)$$

$$dx_2/dt = k_1(1 - x_1) - k_2(C_{B,0}/C_{A,0} + x_2) \quad (8)$$

The kinetic experiments acquired the change in x_1 and x_2 as a function of hydrolytic environment (free or absorbed state), pH, and time (Table S1) *via* IC analysis (Figure 6, and 7). The Levenberg–Marquardt method was used to fit the kinetic data. As a result, the values of k_1, k_2 at various pH were calculated and displayed in Table S2.

Table S1. Results of kinetics experiments during APP hydrolysis.

Hydrolysis environment	pH	Hydrolysis time (d)	$P_3O_{10}^{5-}$ conversion, x_1	$P_2O_7^{4-}$ yield, x_2
Free state	2.50	3	0.082 ± 0.031*	0.088 ± 0.044
		9	0.239 ± 0.036	0.232 ± 0.041
		18	0.454 ± 0.029	0.445 ± 0.046
		26	0.540 ± 0.038	0.454 ± 0.031
		36	0.631 ± 0.041	0.289 ± 0.035
		46	0.717 ± 0.037	0.123 ± 0.033
		54	0.755 ± 0.042	-0.173 ± 0.039
		62	0.810 ± 0.032	-0.297 ± 0.049
		72	0.857 ± 0.031	-0.470 ± 0.043
		90	0.923 ± 0.039	-0.625 ± 0.037
	4.50	3	0.007 ± 0.022	-0.007 ± 0.031
		9	0.066 ± 0.027	0.051 ± 0.032
		18	0.193 ± 0.032	0.166 ± 0.029
		26	0.314 ± 0.050	0.214 ± 0.041
		36	0.411 ± 0.039	0.353 ± 0.038
		46	0.539 ± 0.044	0.409 ± 0.035
		54	0.620 ± 0.036	0.464 ± 0.028
		62	0.707 ± 0.041	0.534 ± 0.042
		72	0.786 ± 0.039	0.556 ± 0.041
		90	0.882 ± 0.047	0.561 ± 0.043
Absorbed state	3.50	3	0.593 ± 0.072	0.155 ± 0.080
		9	0.876 ± 0.076	0.206 ± 0.081
		18	1.000 ± 0.081	-0.040 ± 0.077
		26	1.000 ± 0.000	-0.314 ± 0.088
		36	1.000 ± 0.000	-0.620 ± 0.087
		46	0.957 ± 0.084	-0.684 ± 0.078
		54	1.000 ± 0.000	-0.980 ± 0.075
		62	1.000 ± 0.000	-1.209 ± 0.086
		72	1.000 ± 0.000	-1.236 ± 0.087
		90	1.000 ± 0.000	-1.279 ± 0.093
	5.50	3	0.282 ± 0.067	-0.821 ± 0.077
		9	0.472 ± 0.074	-1.060 ± 0.071
		18	0.433 ± 0.078	-1.072 ± 0.068
		26	0.507 ± 0.087	-1.040 ± 0.085
		36	0.681 ± 0.089	-1.067 ± 0.088
		46	0.674 ± 0.074	-1.002 ± 0.076
		54	0.741 ± 0.079	-1.018 ± 0.078
		62	0.810 ± 0.082	-1.034 ± 0.073
		72	0.967 ± 0.069	-1.060 ± 0.075
		90	1.000 ± 0.080	-1.279 ± 0.086

0.082 ± 0.031*: Each experiment was carried out in duplicate under identical conditions.

Table S2. Experimental reaction rate constants for the two-step hydrolyzation.

Hydrolysis environment	pH	k_1 ($10^{-2}\cdot d^{-1}$)	k_2 ($10^{-2}\cdot d^{-1}$)
Free state	2.50	4.080	1.322
	4.50	1.693	0.143
Absorbed state	3.50	19.82	3.888
	5.50	3.136	28.84

A comparison between the calculated and experimental values is shown in Figure S4 and S5. It can be seen the model has high predictive accuracy and kinetic constants calculated are reliable, especially for a span of dozens of days.

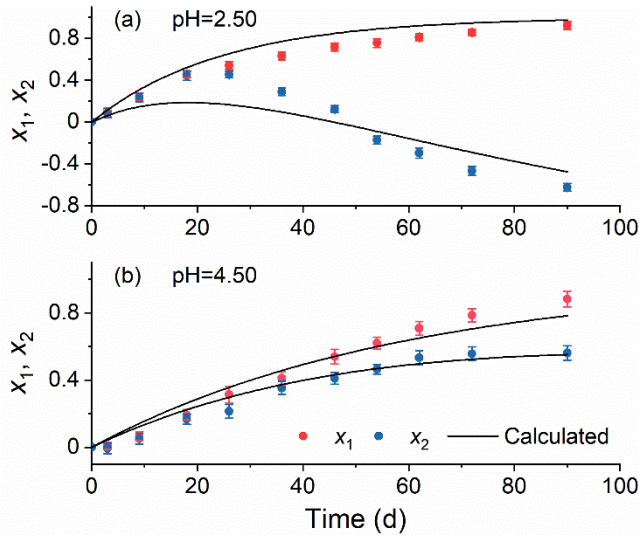


Figure S4. Experimental and calculated values of $P_3O_{10}^{5-}$ conversion, x_1 and $P_2O_7^{4-}$ yield, x_2 versus time for free state: (a) pH=2.50, and (b) pH=4.50.

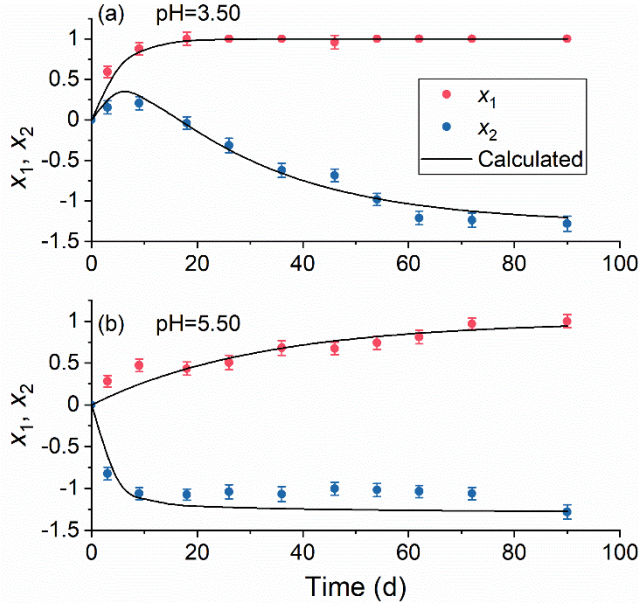


Figure S5. Experimental and calculated values of $P_3O_{10}^{5-}$ conversion, x_1 and $P_2O_7^{4-}$ yield, x_2 versus time for absorbed state: (a) pH=3.50, and (b) pH=5.50.

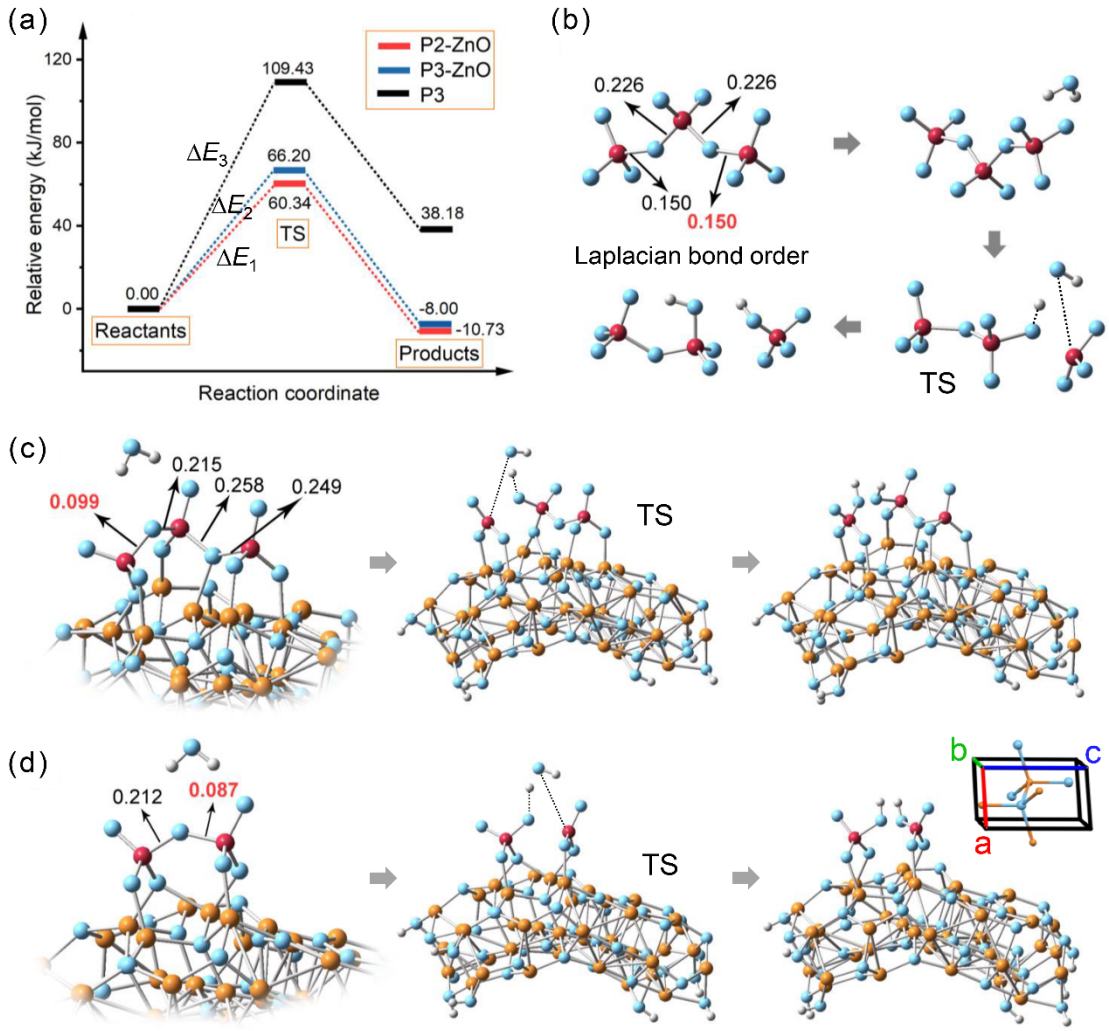


Figure S6. (a) DFT-calculated hydrolysis active energies of free and ZnO nanorod

absorbed phosphates. Laplacian bond order distributions and hydrolysis paths of (b) free tripolyphosphate (P3), (c) absorbed tripolyphosphate (P3-ZnO), and (d) absorbed pyrophosphate (P2-ZnO).

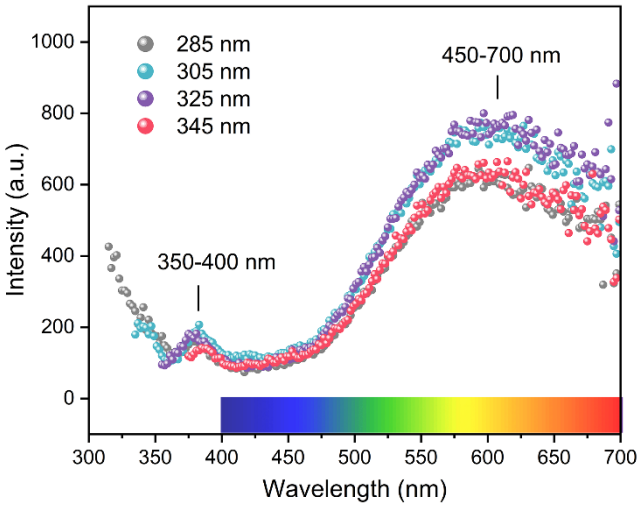


Figure S7. PL emission spectra of ZnO nanorods (excitation wavelength from 285 nm to 345 nm).

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