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An old material in the nanoworld: organic-inorganic hybrid nanotubes based on γ-Titanium phosphate layered crystal structure

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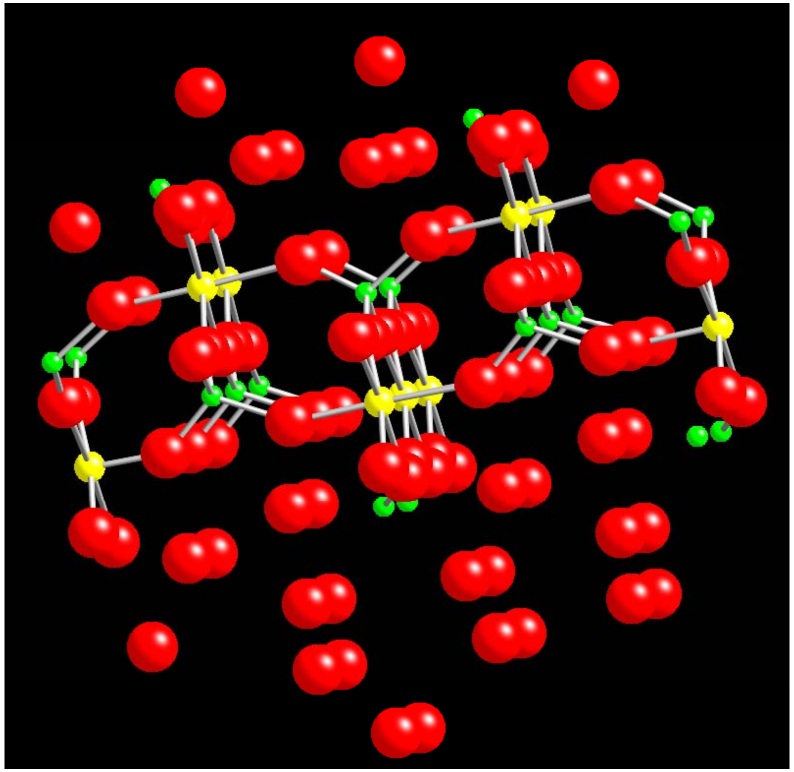
Outline:

- Introduction to Ti-phosphates & inorganic nanotubes.
- Synthesis of organic-inorganic hybrid γ-titanium phosphates/trioctylamine nanotubes (γ-TiP-TOA-N).
- Morphology and structural characterization (SEM, TEM, and XRD) of γ-TiP-TOA-N .
- Mechanism for interpreting the formation of γ-TiP-TOA-N.
- Conclusions.

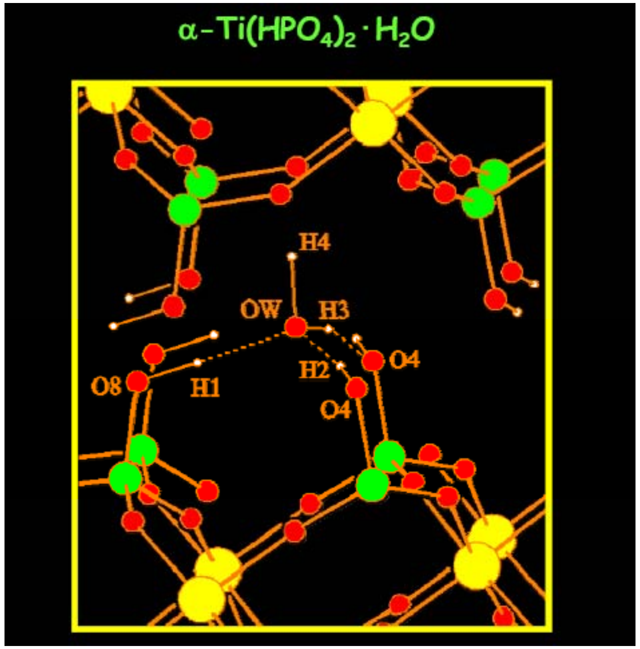
Introduction to Ti-phosphates & inorganic nanotubes :

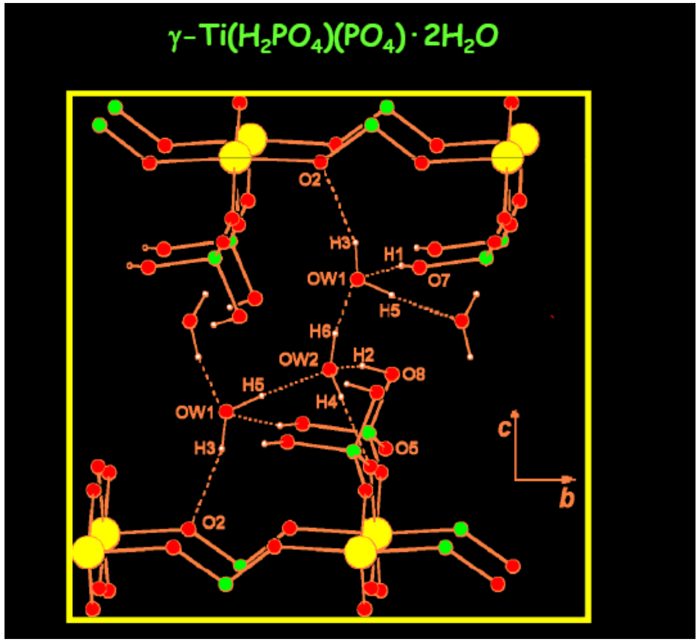
- Aluminosilicate zeolites→ion-exchange, separation, catalysis areas.
  - Open-framework materials→ Most abundant multifunctional porous materials.
- Nanotubes→Interest in low-dimensional materials
  - Using high-temperature process→nanotubes of metals, metal chalcogenides, metal oxides, BN,.

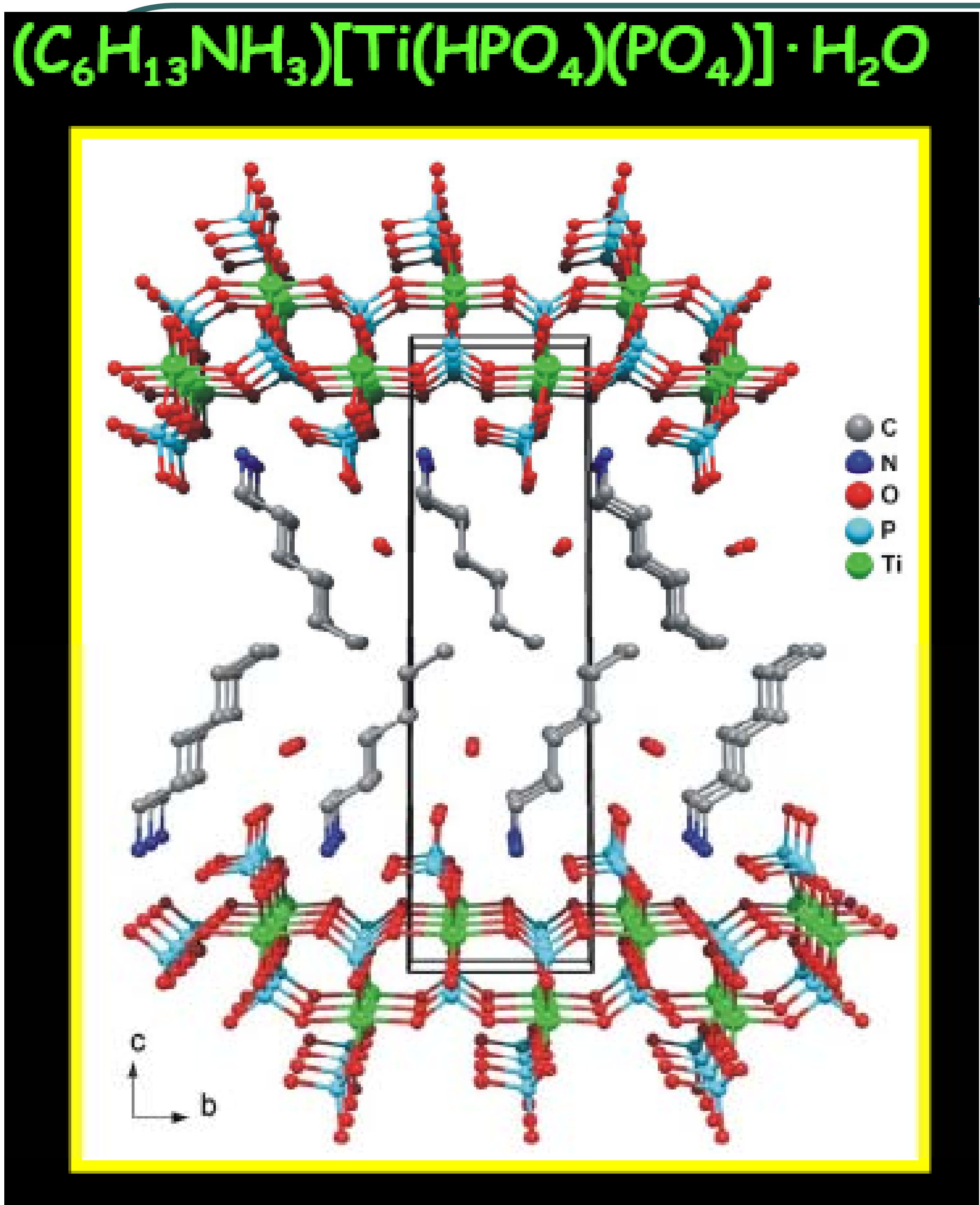


Introduction to Ti-phosphates & inorganic nanotubes :

Two forms of layered Ti phosphate: α-TiP and γ-TiP based on tetrahedral PO_4 & octahedral TiO_6 units—T-O-T







Introduction to Ti-phosphates & inorganic nanotubes

Table 1. Crystal Data of $(C_6H_{13}NH_3)[Ti(HPO_4)(PO_4)]\cdot H_2O$

formula	$C_6NH_{19}TiP_2O_9$
formula weight	359.11
crystal system	monoclinic
space group	$P2_1$ (no. 4)
a/Å	5.089(2)
b/Å	6.335(2)
c/Å	22.792(5)
β/deg	102.48(2)
Z	2
R_p	0.200
R_{wp}	0.227
R_F	0.210
χ^2	5.8

- Mechanism of interacalation of n-alkylamines
- P-OH groups tendency to interact with amine ones

Synthesis of organic-inorganic hybrid γ-titanium phosphates/trioctylamine nanotubes (γ-TiP-TOA-N).

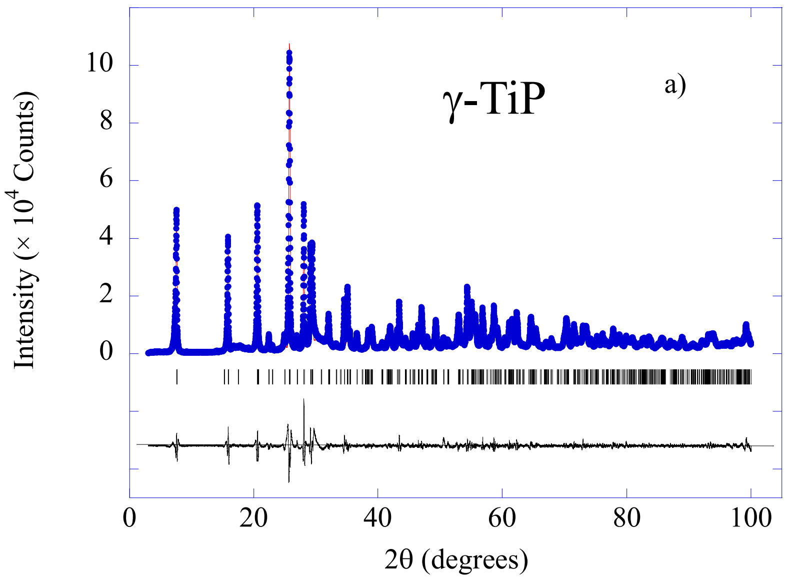
1) TOA + acetone + phosphoric acid → microemulsion of TOA/H_3PO_4 + drops Ti-butoxide

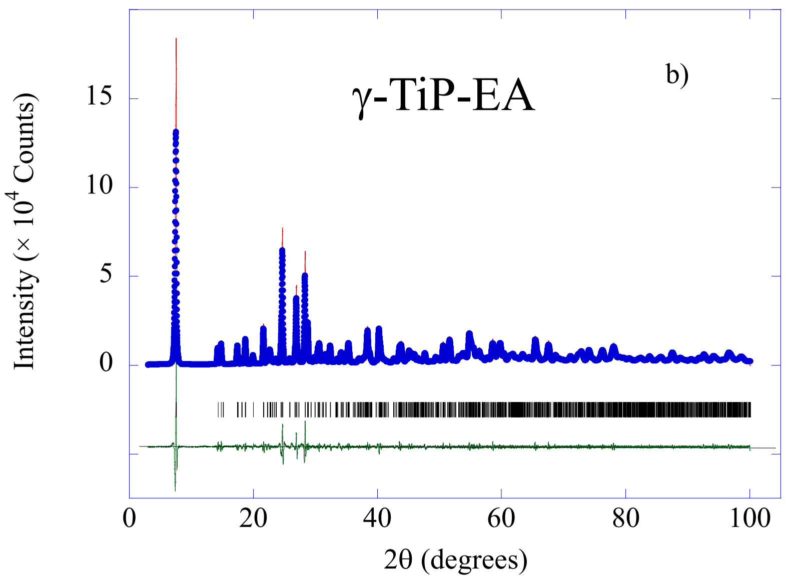
2) 13.1 ml TOA + 60 ml acetone + 1 ml H_3PO_4 (85%).

3) Autoclave and sealed at 140°C for 3 days + centrifugation + air drying

γ-TiP-TOA-N
+…
γ-TiP
γ-TiP-EA
γ-TiP-HA

Morphology and structural characterization XRD experiments

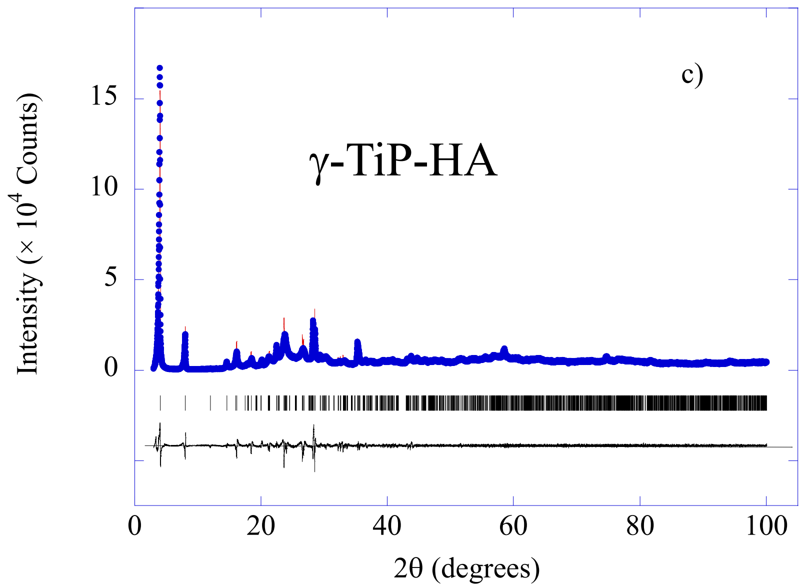


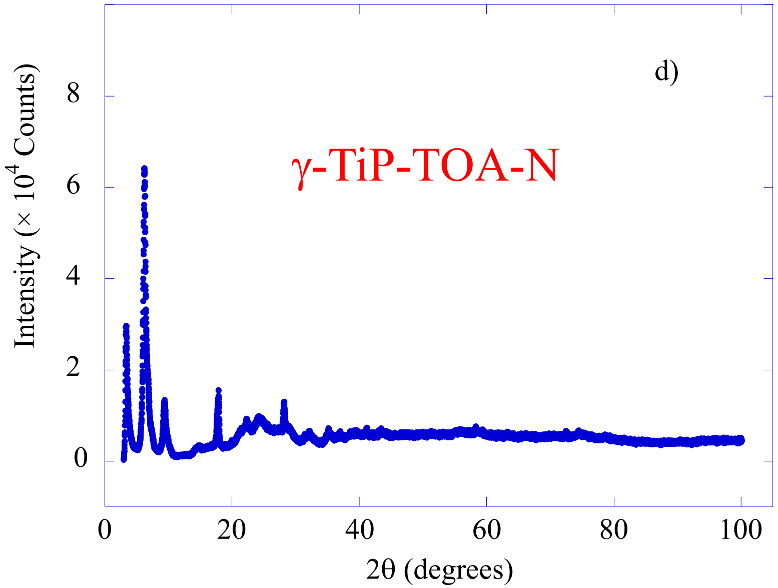


Diffraction peaks →

1. Line broadening > instrumental one
2. Asymmetric shapes
3. Preferred orientation

Morphology and structural characterization: XRD experiments



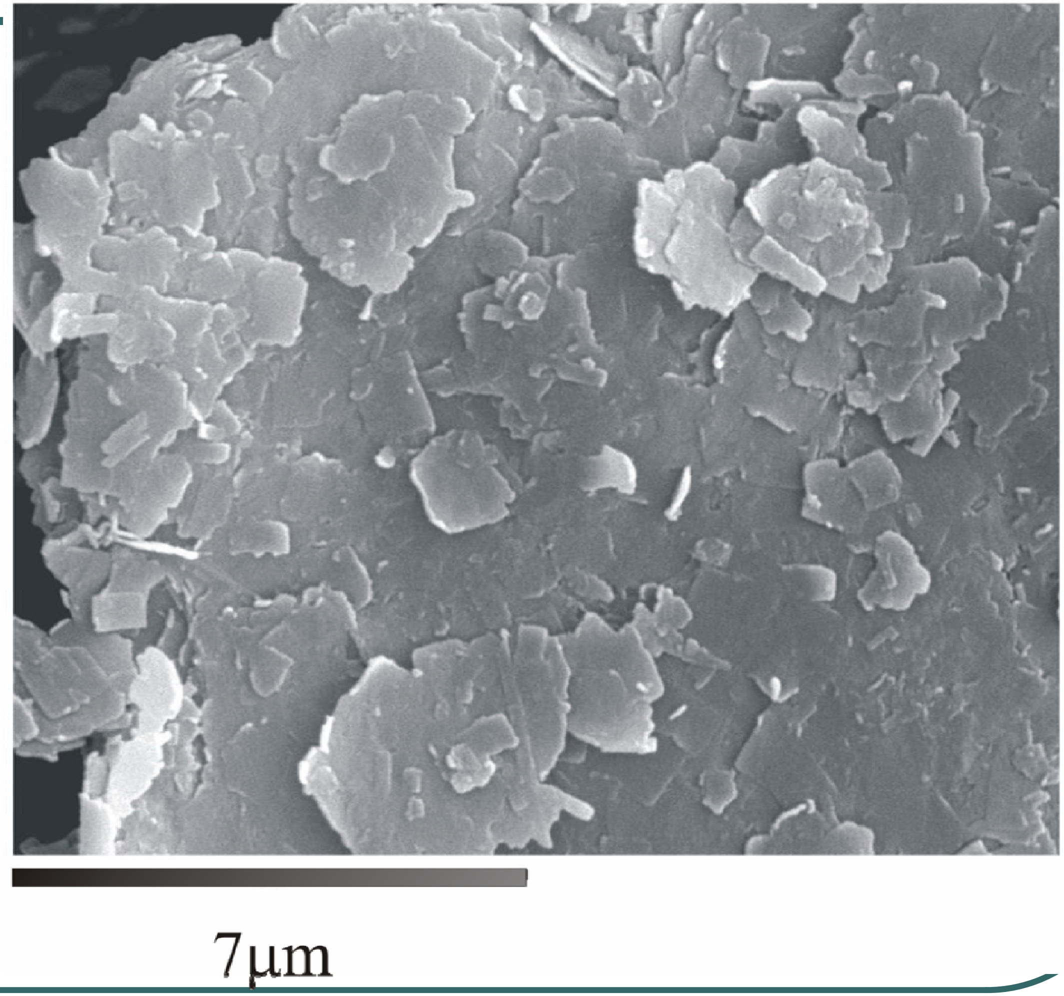


2θ $_{(001)}$ is shifted to low-2θ→cell parameter c increases (intercalation of the amines)

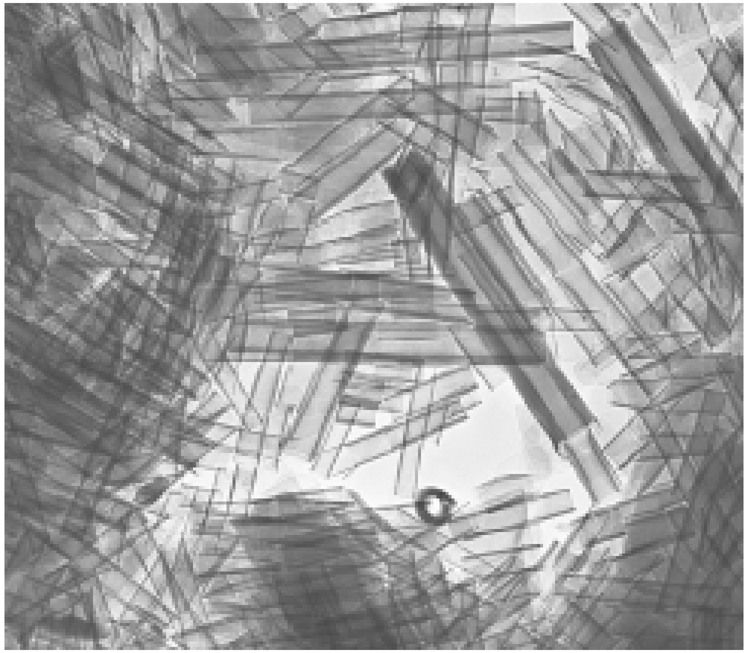
- Extremely small and highly disorded crystallites

Morphology and structural characterization SEM of γ-TiP-TOA-N

- Irregular round flakes
- No paint-brushes morphology



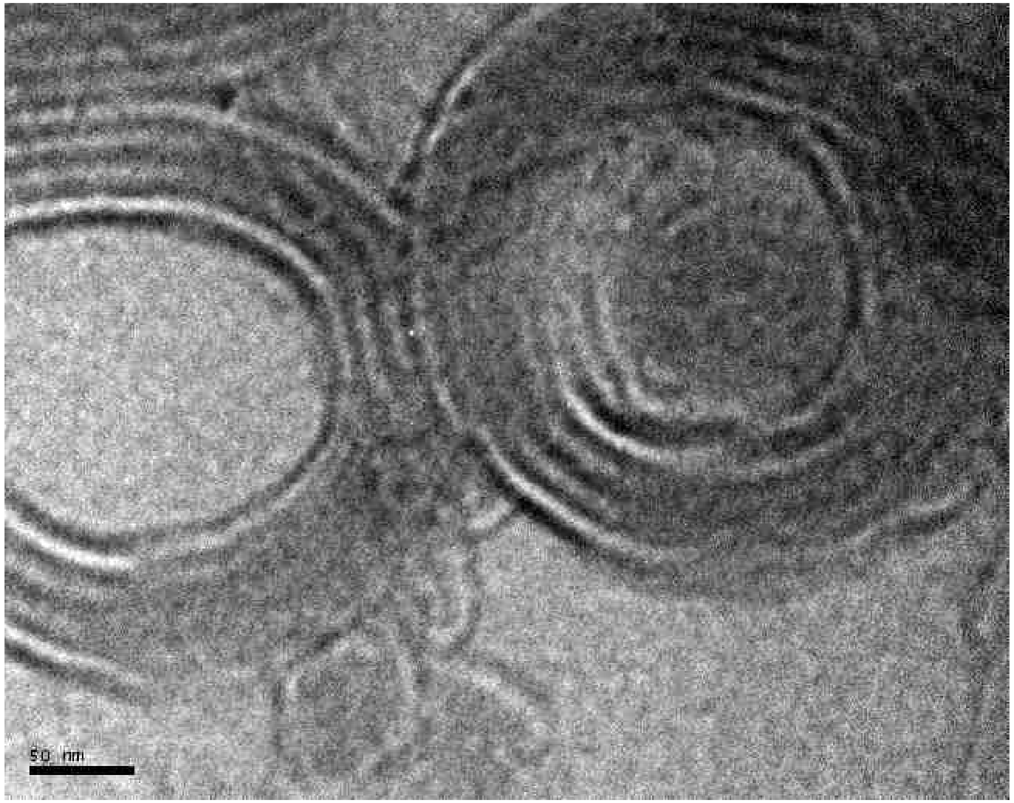
Morphology and structural characterization
TEM of γ-TiP-TOA-N

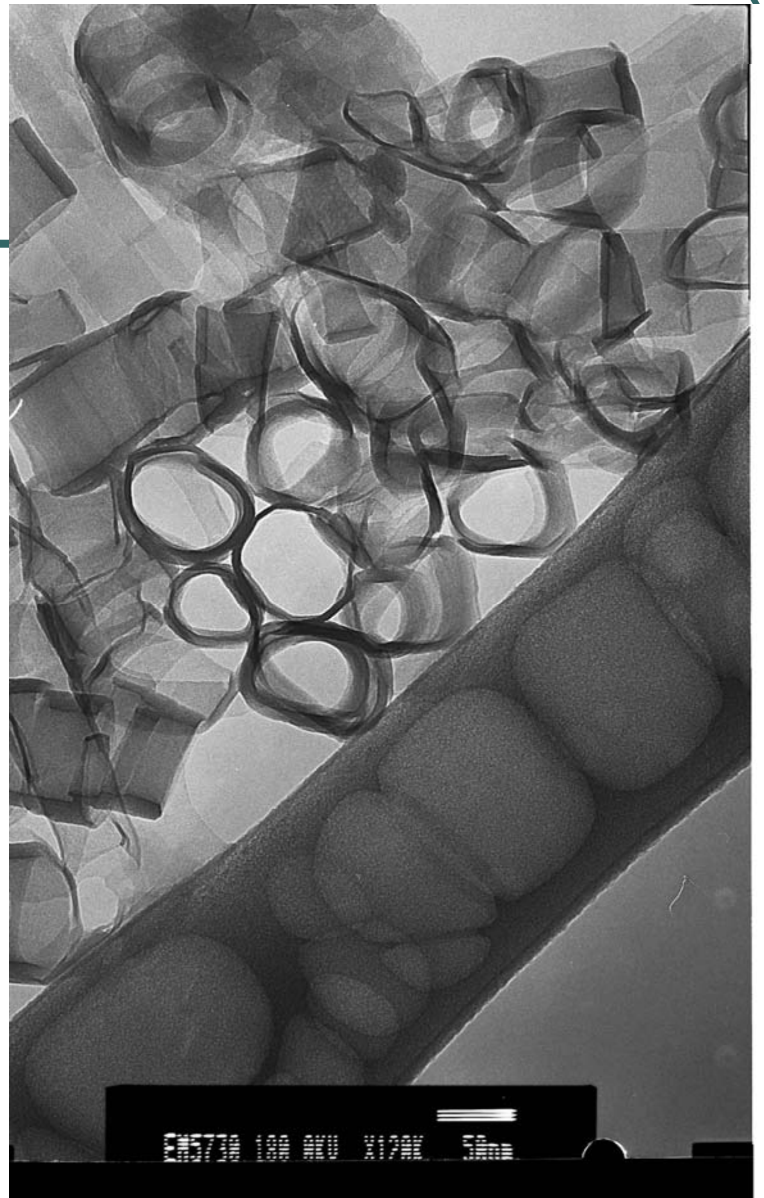


—— 200nm

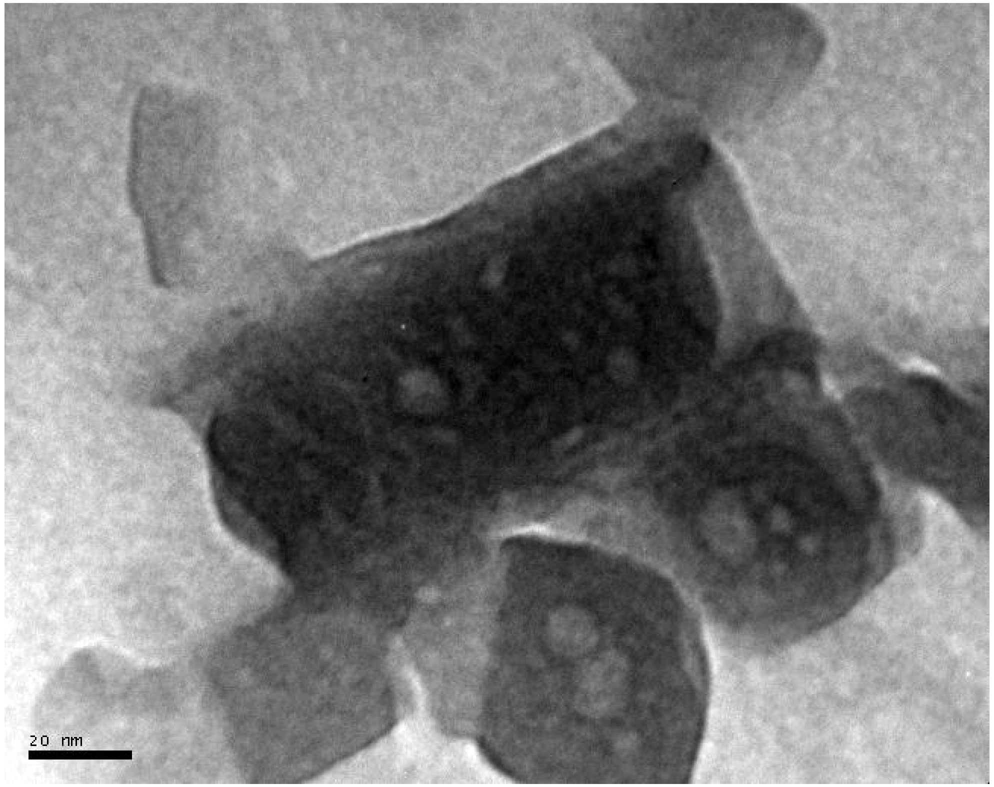
— 20 nm

Morphology and structural characterization TEM of γ-TiP-TOA-N

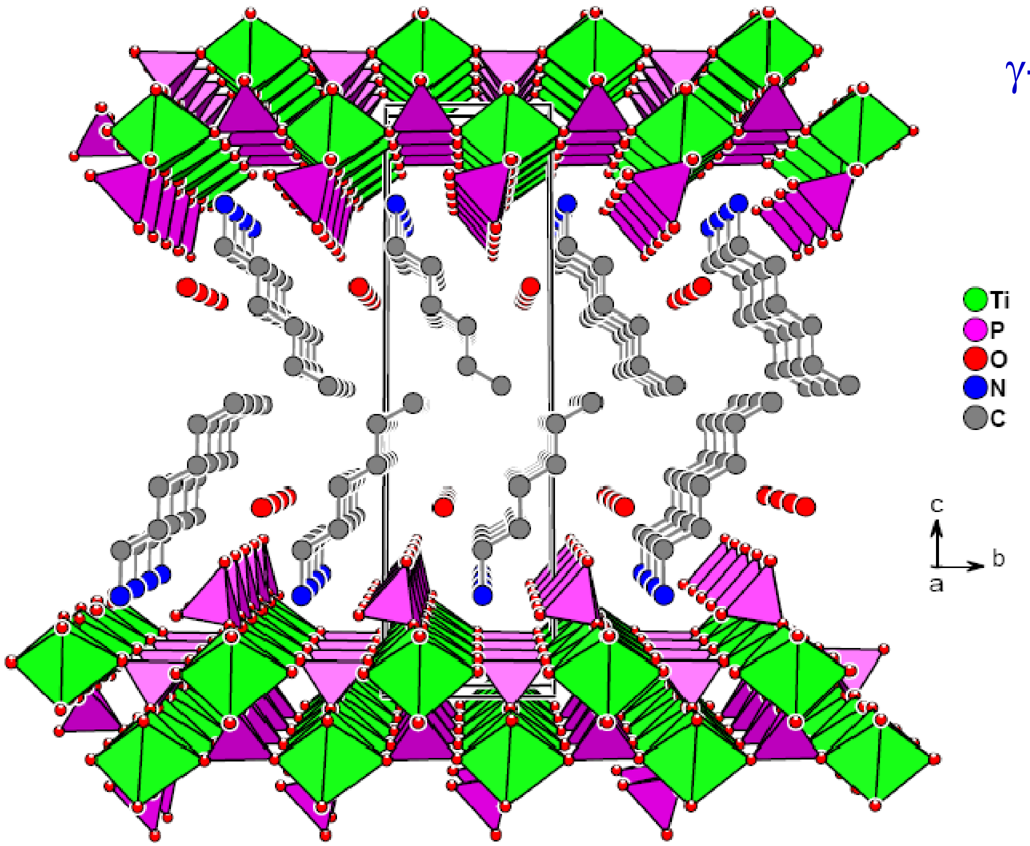


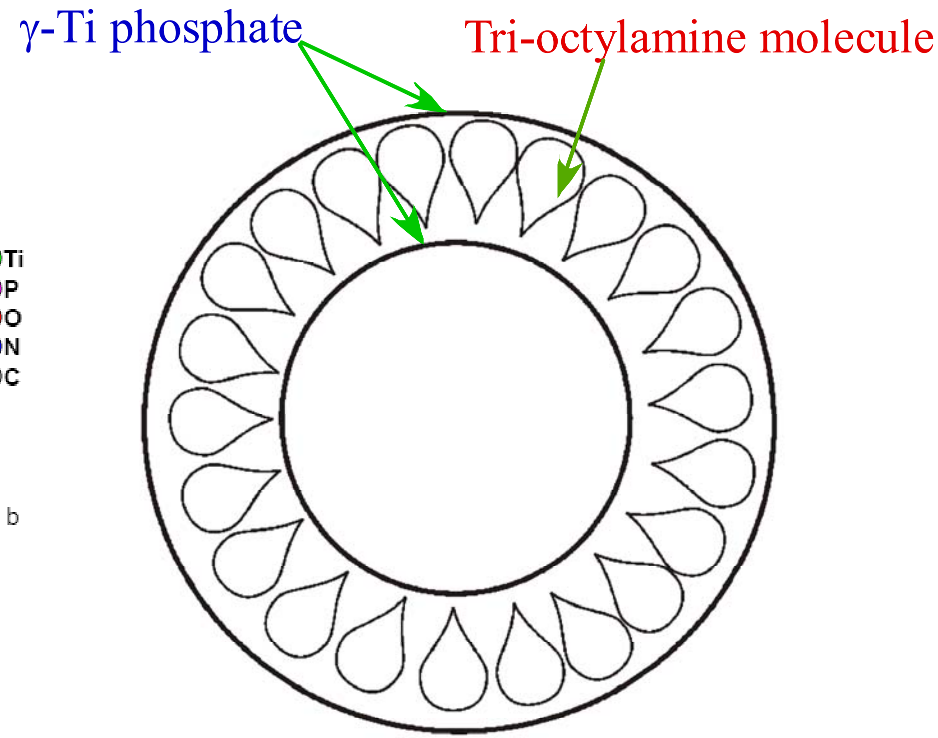


Morphology and structural characterization TEM of γ-TiP-TOA-N



Mechanism for interpreting the formation of γ-TiP-TOA-N





Conclusions:

- The formation of open-ended cylindric nanotubes of γ-TiP-TOA is governed by:
  - Interaction→Nitrogen of TOA<>Hydrogen of γ-TiP
  - Pseudo-conical geometry of TOA molecule + length of alkyl chain & amine amount →the interlayer distance of inorganic layer.
- Future perspectives: new Fe-based phosphate nanotubes