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Polymer Intercalation Synthesis of GlycoBoehmite Nanosheets

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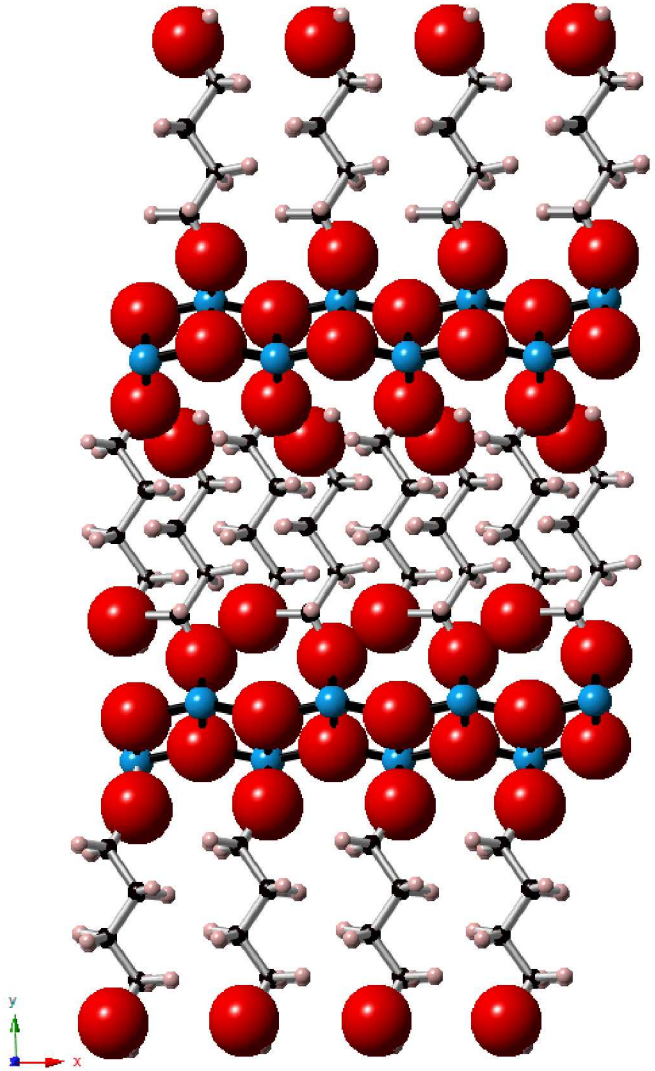
Beohmite Nanosheet Derivatives

Boehmite phase AlO(OH) is commercially used for high surface area γ-Al_2O_3 production as a catalyst support material or adsorbant.

Structurally, it is formed by AlO_6 octahedra bound by corners into nanosheet or layered materials, with *attractive H-bonding* between the layers due to the two hydroxyl groups in the interlayer. These H-bonds in the crystal structure influence the crystal structure, growth morphology, and surface area.

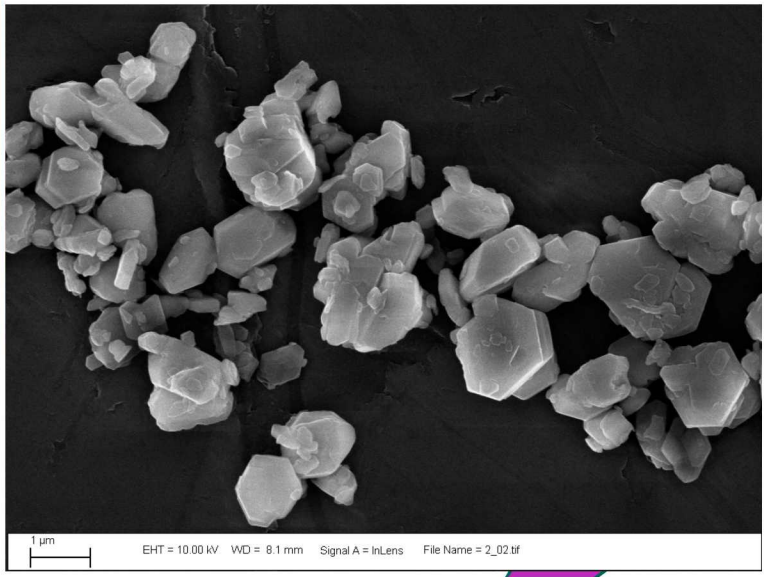
This system is being used to determine if functionality can be induced in the formation reaction.

Glycol based synthesis routes have explored the modification of boehmite layered materials using covalent surface derivation, and polymer surfactant intercalation between atomic layers.



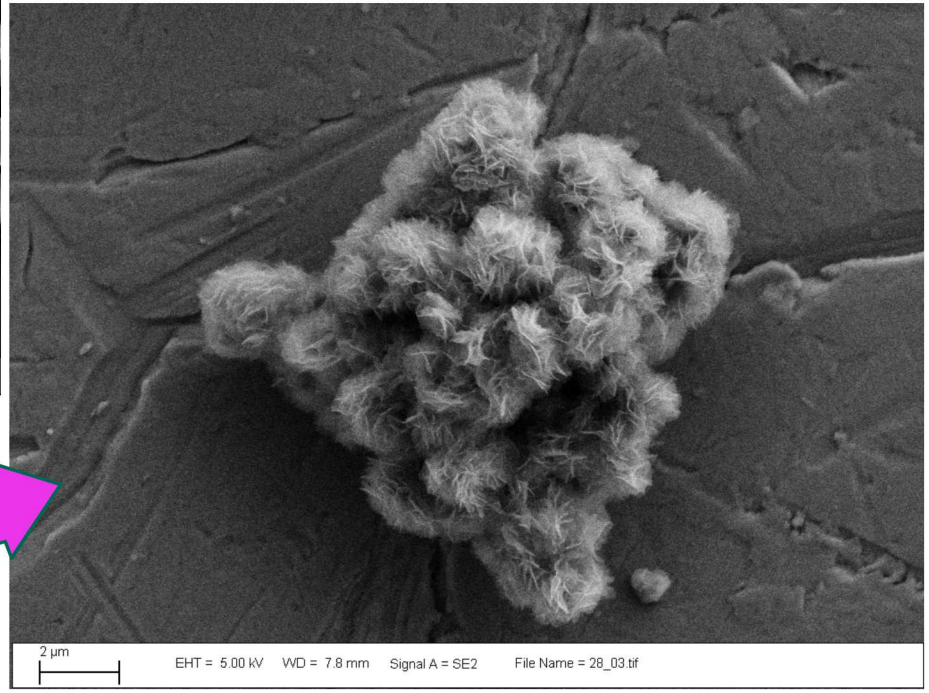
Glycothermal Synthesis of Glyco-boehmite

Pressure reaction of Gibbsite in 1,4-butanediol just above the boiling point leads to a special phase of aluminum oxide – psuedo-bohemite.

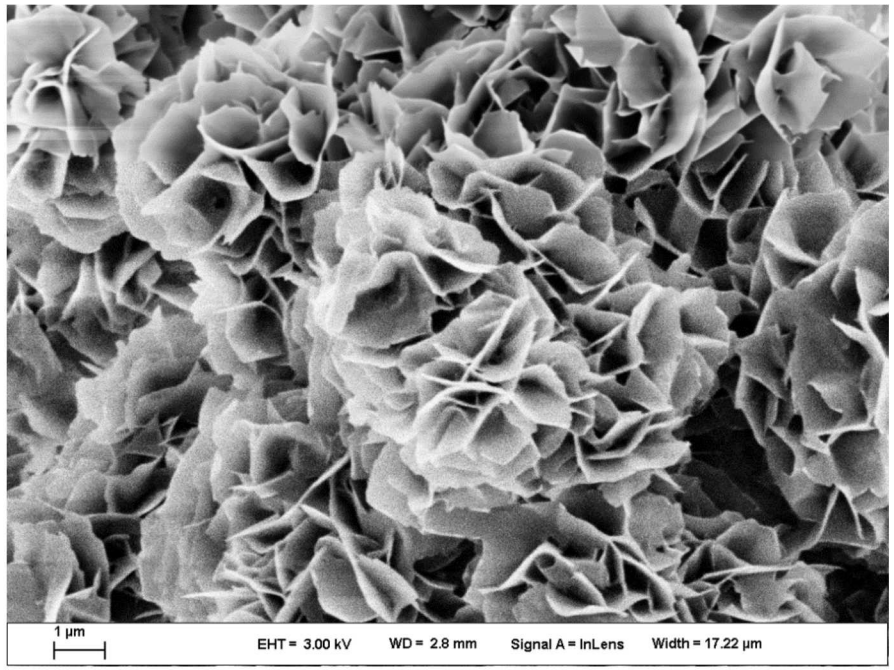


1,4-Butanediol, 99% was used as solvent
Gibbsite precursor was obtained from Huber Engineered Materials, with an average particle size of 1 micron.

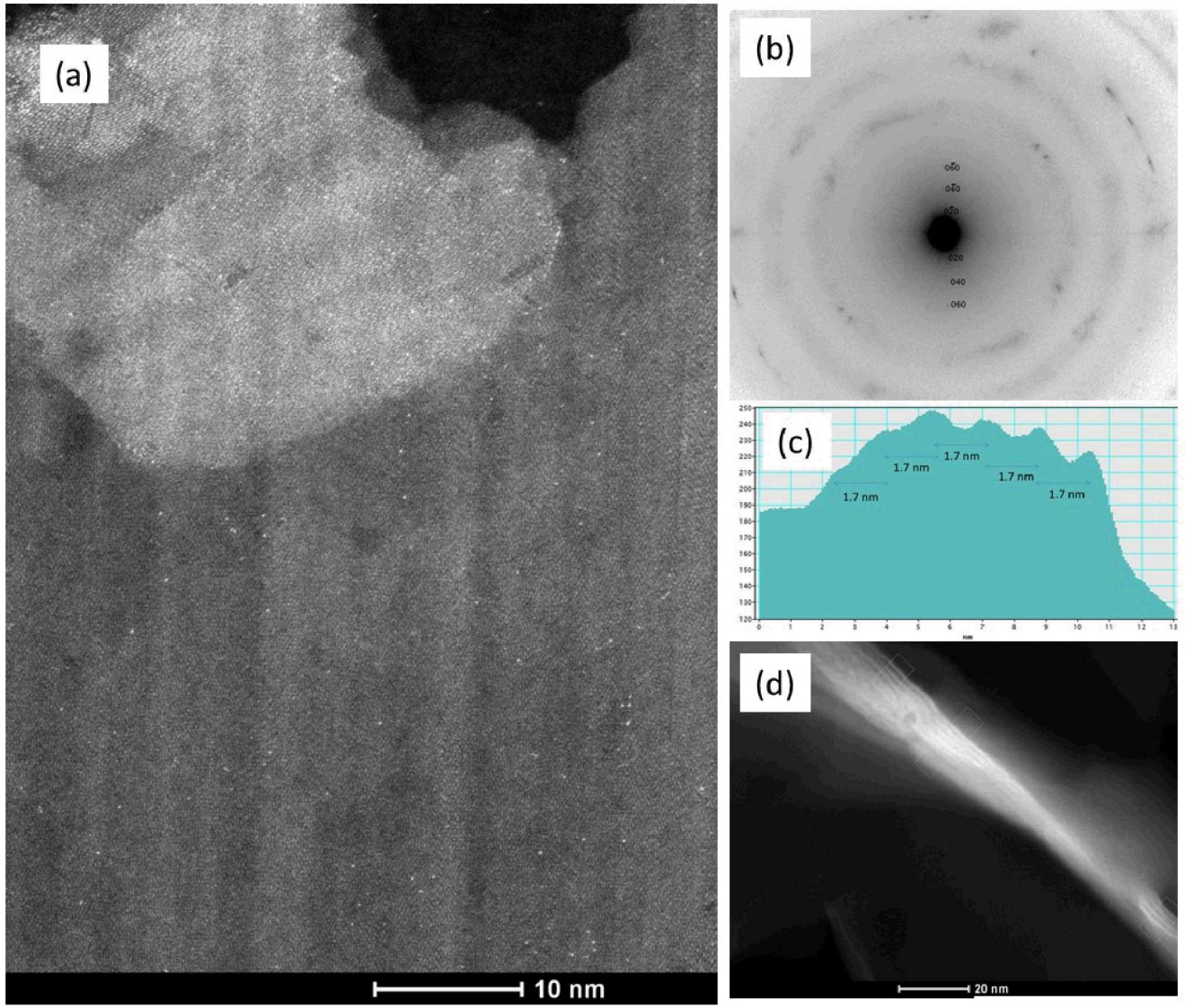
Treatment in 1,4-butanediol with 0.5 g KOH, 22 hours at 250 C



Electron Microscopy Characterization of GlycoBoehmite Phases



- Edge view used for atomic profiling of Al.
- Platelets consist of 5 atomic layers, with consistent interlayer spacing of 1.7 nm
- b measured experimentally from the presumed 020 reflection d_{020}=17.4Å ± 0.6Å



Organic Modifications

Hydrogen bonding between nanosheets controls properties of boehmite, and glycols are demonstrated to supersede the effect of aqueous solvents.

Hypothesis: Can we test the ability of glycols to allow for the growth of hybrid boehmite nanosheets using polymer materials, that have greater interaction with the sheet structure (i.e. normal to the crystallographic b-axis)

Starch, maltrodextrin, PVA (99 and 87% hydrolyzed), Polyvinylpyrrolidone (PVP) and Hydroxypropylcellulose (HPC) were added to the standard synthesis protocol and characterized.

Phase Identification

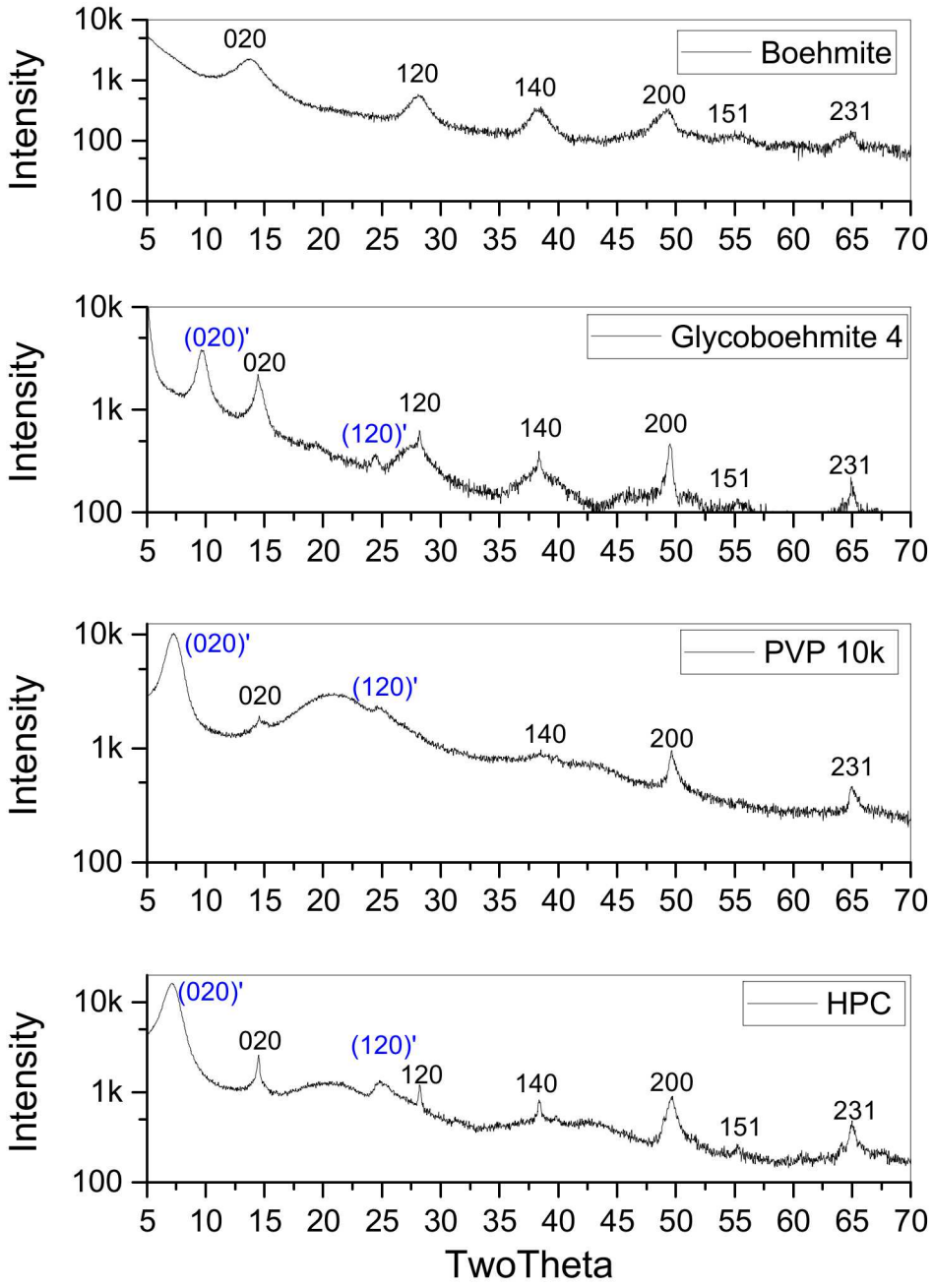
Covalent Intercalation on –OH sites expands the (020)' *b* axis dimension, while peaks within the interlayer are not shifted.

Phase purity shows traces of traditional boehmite(aq), but significant formation of glycol and polymer derivatives

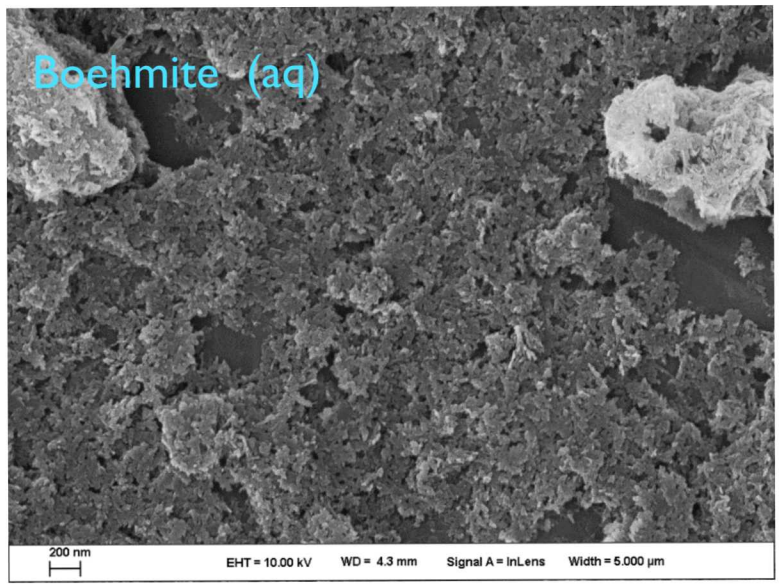
1,4-BDO expands the interlayer spacing to 17.4 Angstrom,

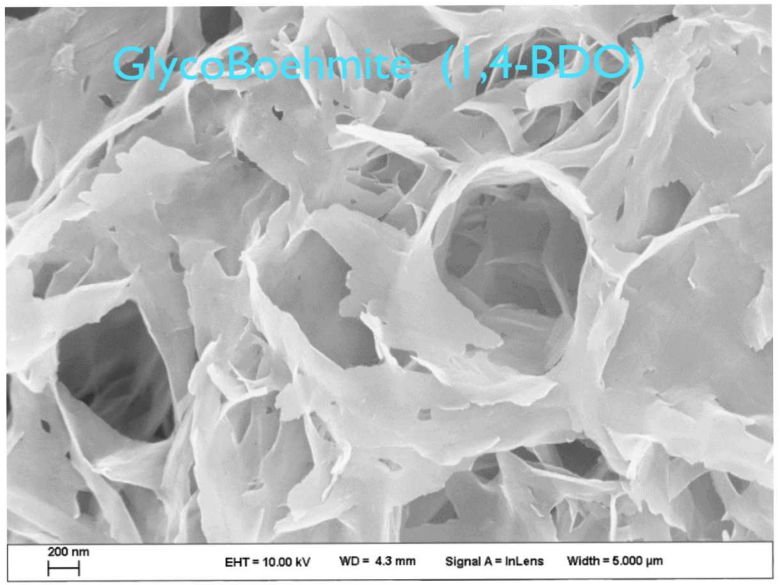
PVP expands the interlayer to X Angstrom

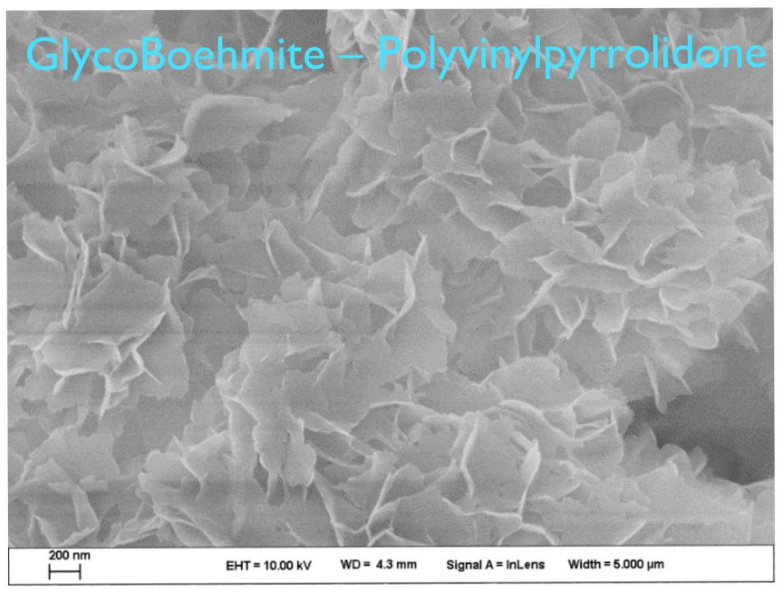
HPC expands the interlayer to Y Angstrom.

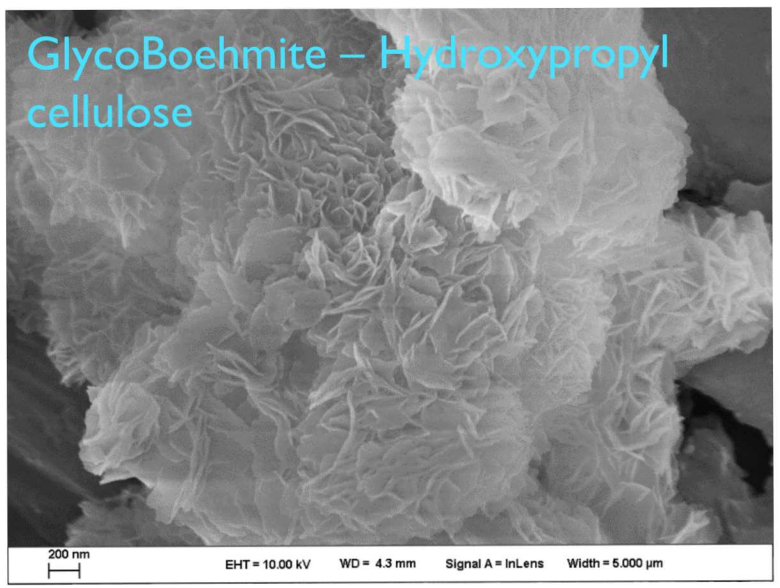


Polymer Intercalation in Glycoboehmite









- Glycothermal synthesis alters Beohmite both structurally, and morphologically, favoring sheet structures over nanoparticle aggregates.
- Both PVP and HPC modified materials create a more tortous morphology based on greater nucleation of nanosheets. Polymers may increase dislocation density or direct growth nucleation.
- HPC has greater impact than PVP.

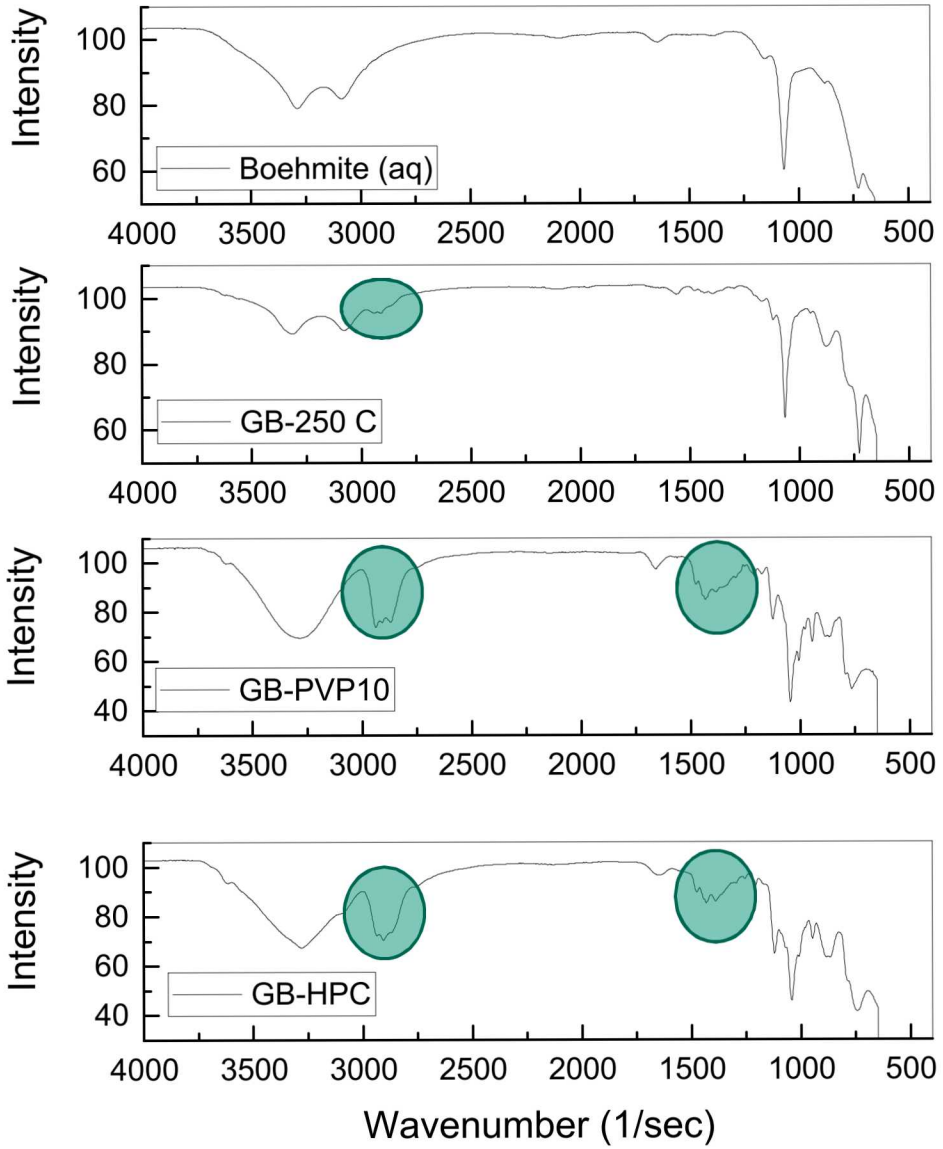
Infrared Characterization Shows Organic Content

Boehmite shows H-bonding from –OH groups

GlycoBoehmite adds $–CH_2$ peaks, and additional low wavenumber fingerprint peaks

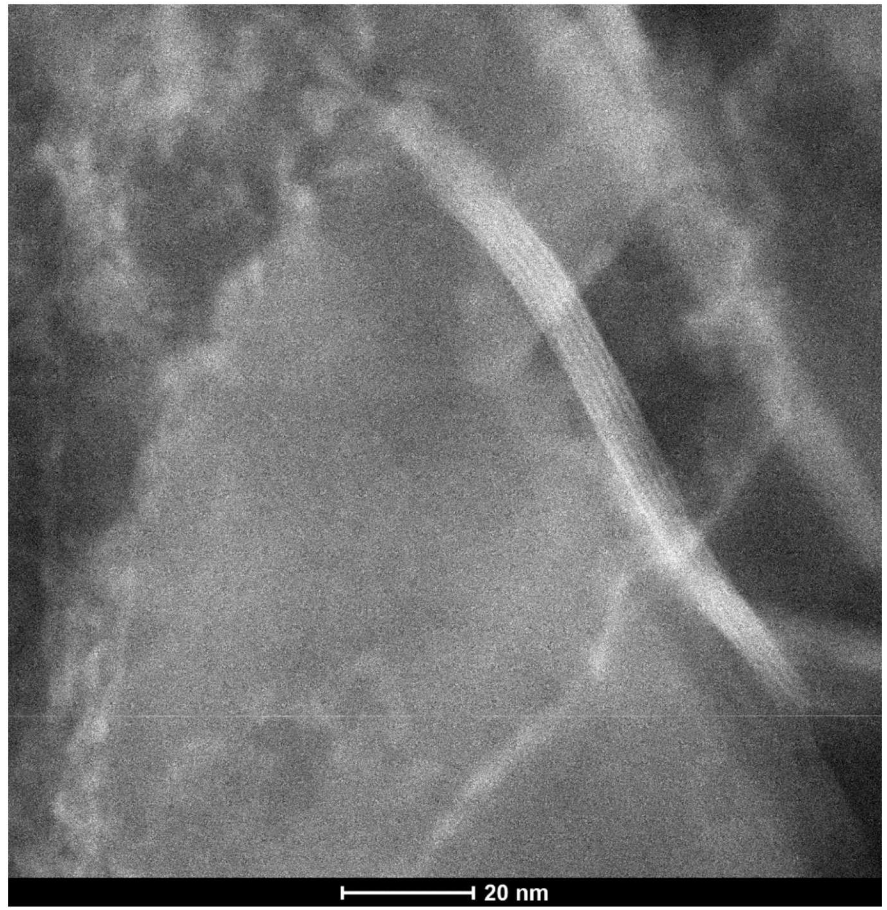
GB-PVP has much stronger $–CH_2$ content, and a series of peaks between 1500 and 1000

GB-HPC likewise shows polymer content for $–CH_2$ groups and characteristic structural peaks below 1100 s^{-1}.

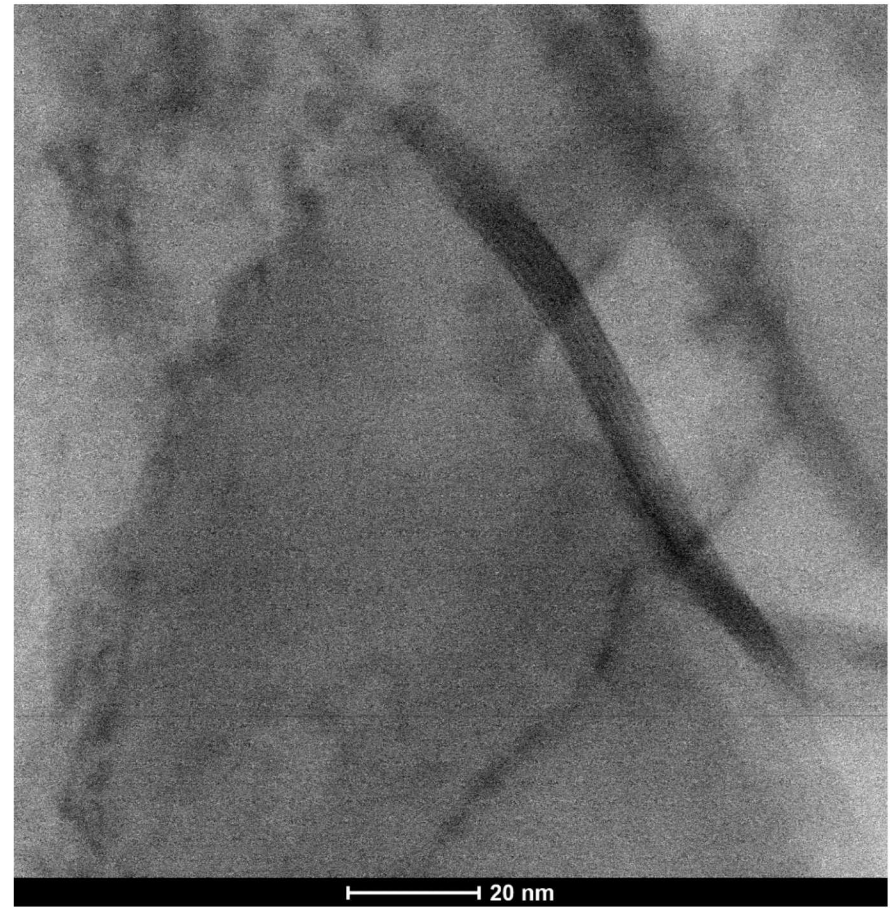


HRTEM of GB-PVP shows the layer intercalation

Dark Field

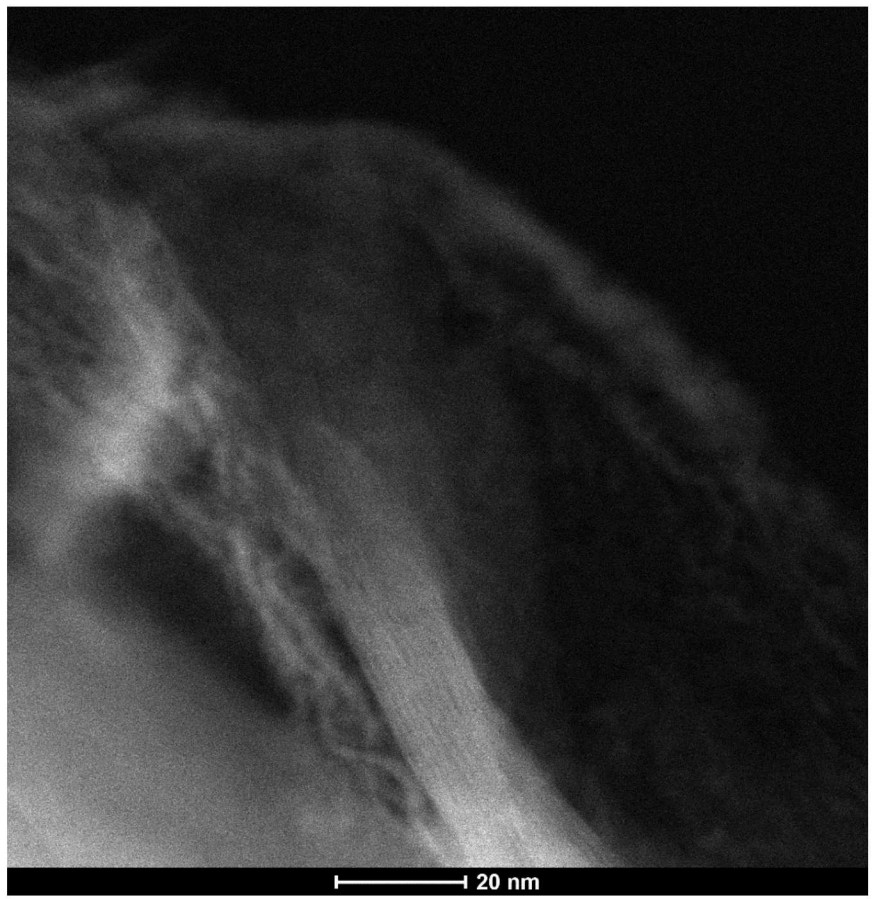


Bright Field



TEM of GB-HPC shows the layer intercalation

Dark Field



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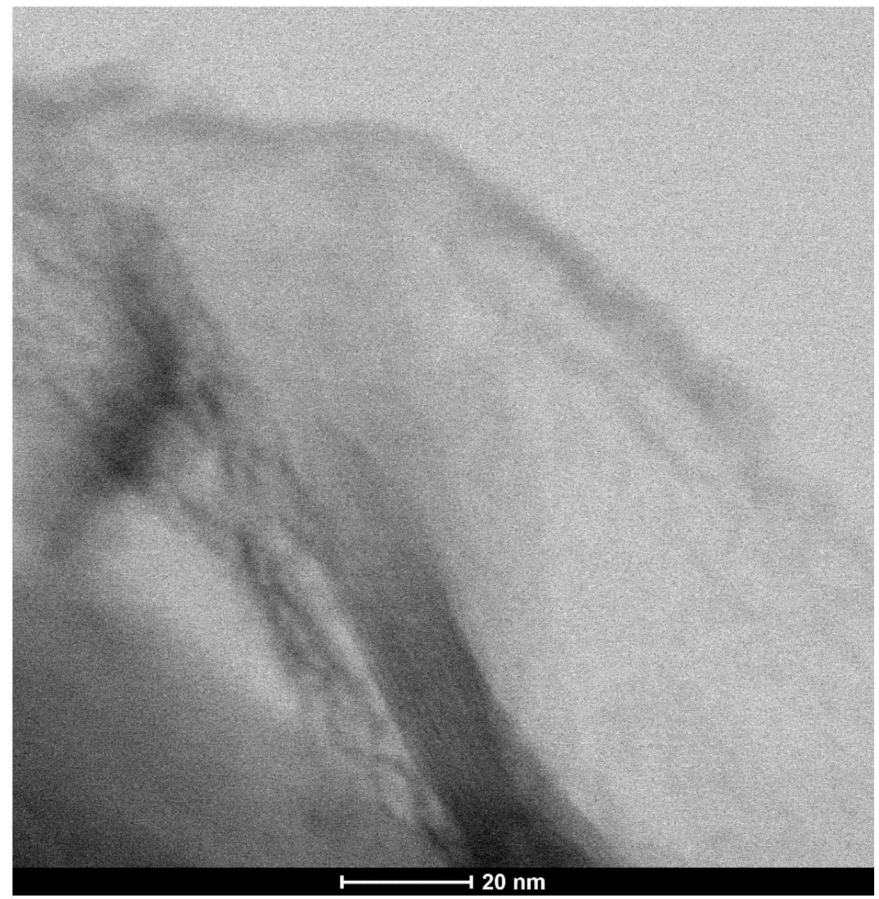
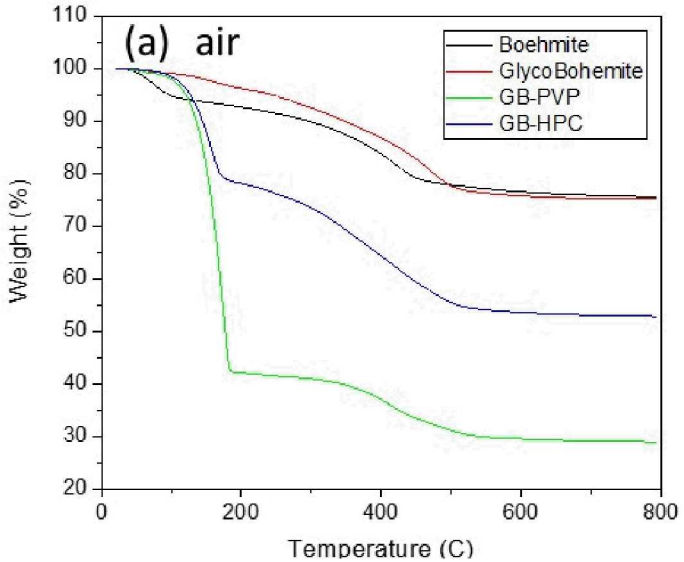
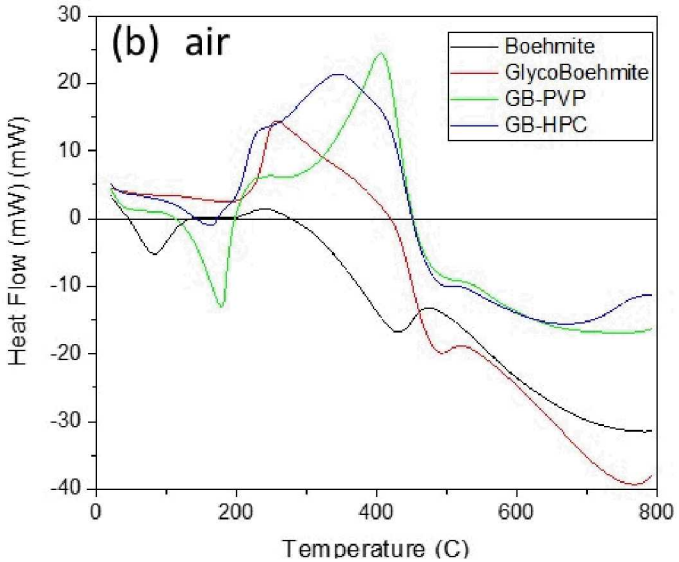


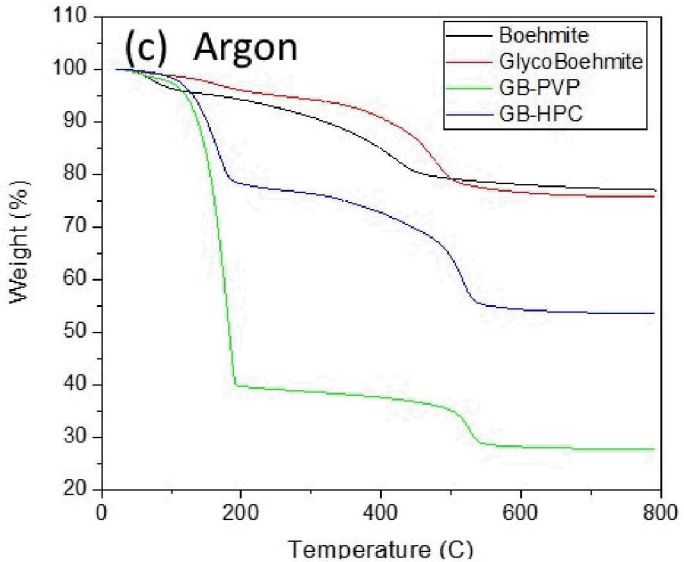
TGA/DTA Thermal Property Characterization

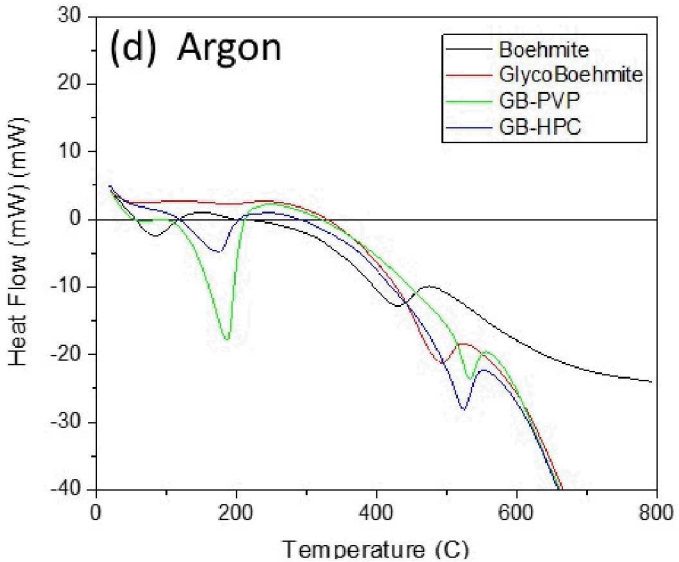
TGA in air and argon give broadly similar results, with the greatest weight loss for PVP sample. The first transition may be solvent, and final burnout at 550 °C

The DTA spectra between the samples in air and Ar are similar for boehmite, but derivative material contrast between endothermic reaction in Ar and exothermic reaction in air.









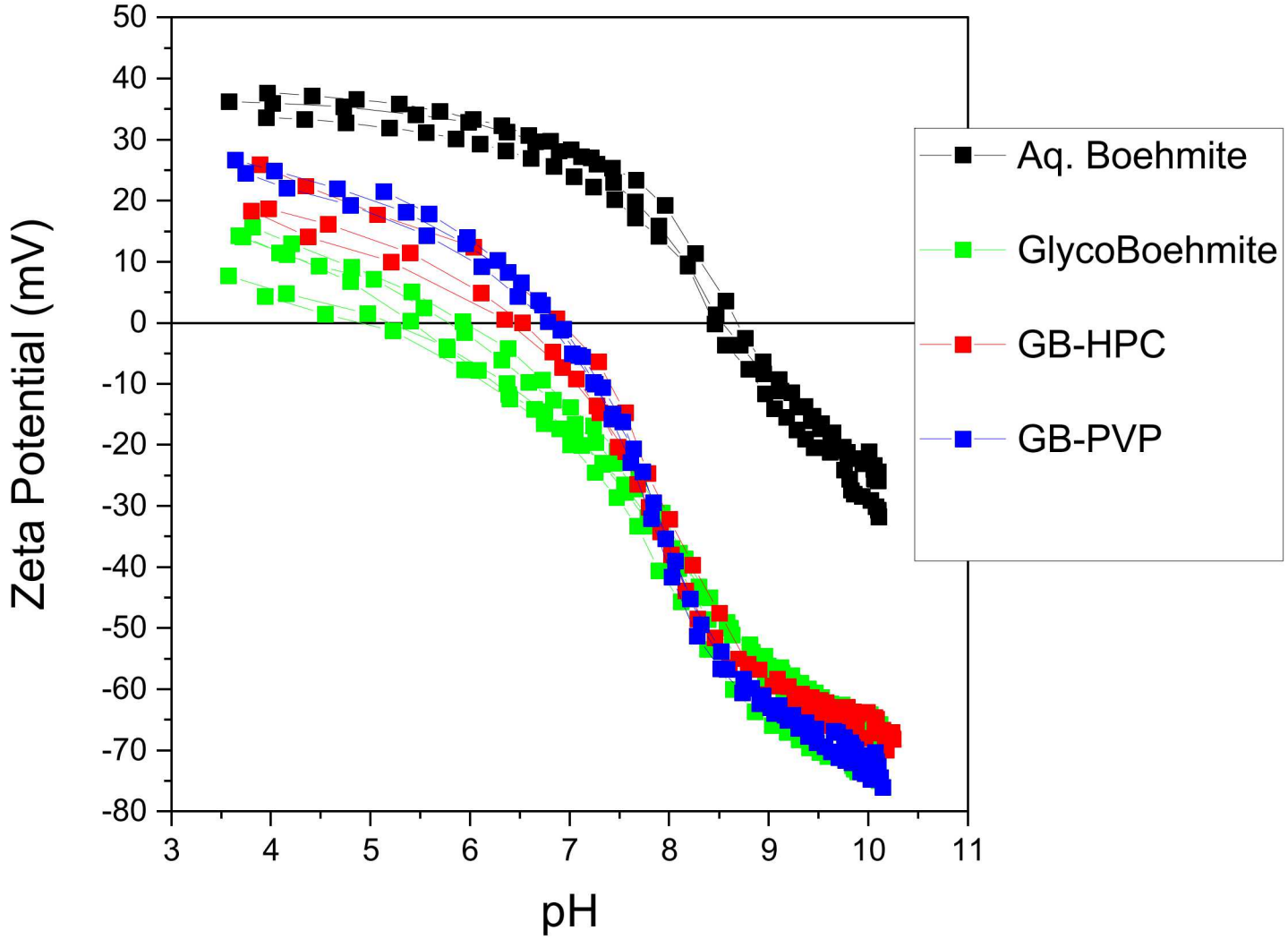
Zeta Potential shows that GlycoBoehmite and Polymer Variants have Modified Surface Charging Characteristics

pH vs. zeta potential measured in 10^{-3} M KNO_3, using a Stabino Particle Charge Analyzer.

Aqueous synthesized boehmite has typical IEP at pH 8.5.

Glycothermal synthesized GB(4) phase is shifted to pH 5.5 to 6, and polymer intercalated materials are neutral with IEP at pH 7.

All glycothermal materials have much greater negative charge, and could be doped with cationic species.



Summary

New hybrid materials based on Beohmite phase alumina were successfully synthesized using the glycothermal approach.

The validates the hypothesis that controlling H-bonding from surface –OH groups will enable polymer adsorption to direct crystal growth.

The new hybrid phases exhibit increased surface area, stronger acidity, and variation in thermal transformation properties from aqueous synthesized boehmite.

This provides a facile route to higher surface adsorption aluminas, with greater cationic adsorption properties.

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