Building a true morphological model by hierarchical porosity analyses combining correlative X-ray and electron tomography

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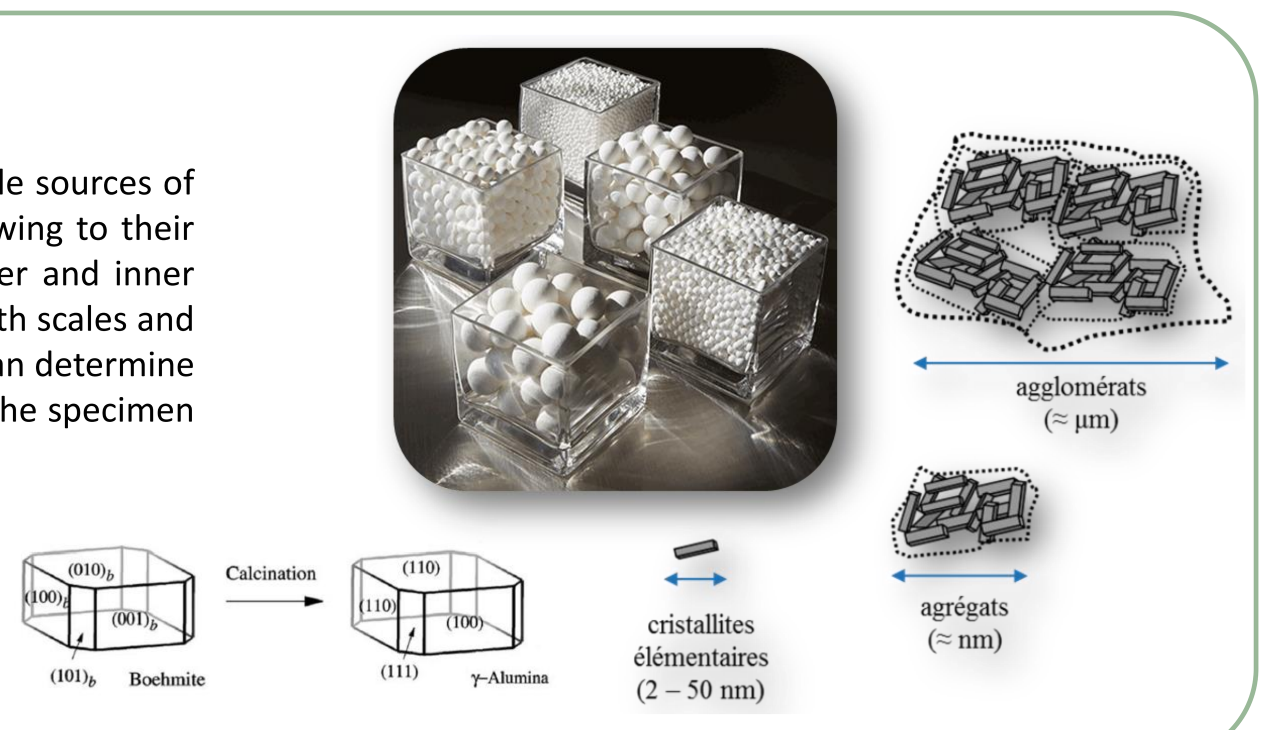
INTRODUCTION

A good transition into sustainable energy requires a combination of CO_2 sequestration, H_2 or compressed air storage, long-term adoption of renewable sources of energy, and near-term fuel switching to cleaner available energy resources. Porous materials play an important role in many energy applications owing to their ability to absorb and interact with guest species (including, but not limited to, lithium ions, hydrogen atoms and sulphur molecules) on their outer and inner surfaces, and in the pore spaces. Research into the suitability of such porous materials requires characterization of these materials over a range of length scales and in 3D, the properties of these modern functional materials are critically dependent on the control of the microstructure where local inhomogeneities can determine the material's function. Despite the enormous level of sophistication of individual characterization tools, no single technique can be used to examine the specimen over the complete range of length scales.

Alumina has extensive applications in fields such as catalysis, abrasives, cosmetics, ceramics and many more. Both, γ-Al_2O_3 and its precursor – boehmite (γ-AlOOH) exhibit hierarchical nature in its composition due to which the different textural and morphological features are vast.[1] Although extensive research has been carried out to understand the complete representation of its structure, a true morphological model is an important key to understand and fully explain its transport properties during catalytic processes and in many other fields.[2,3]



CLASSICAL CHARACTERIZATION TECHNIQUES

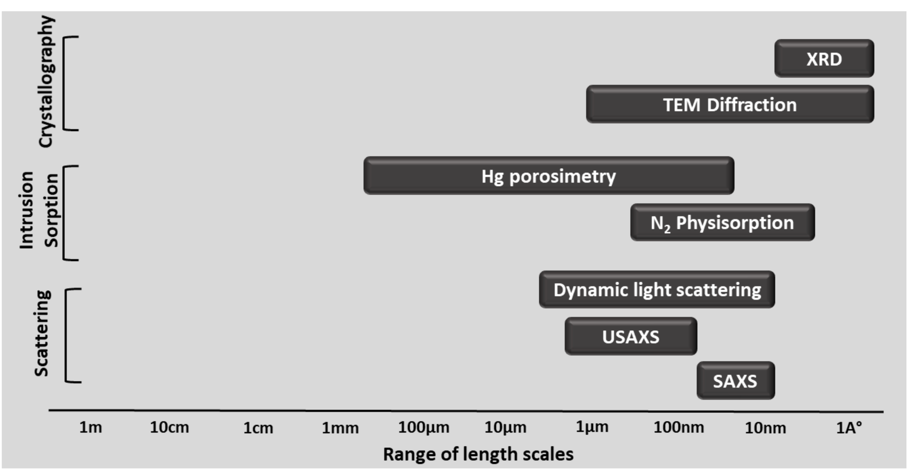


Figure A. Length scales of different sofisticated traditional methods used for the inspection of different features. All the classical characterization techniques give a general understanding of a bulk assumed model which overlook the individual properties.

X-Ray Diffraction + Small Angle X Ray Scattering

Technique	Particle Size (nm)
XRD (002 plane)	31.7
SAXS (Guinier Radius)	32
2D TEM	41 ± 12

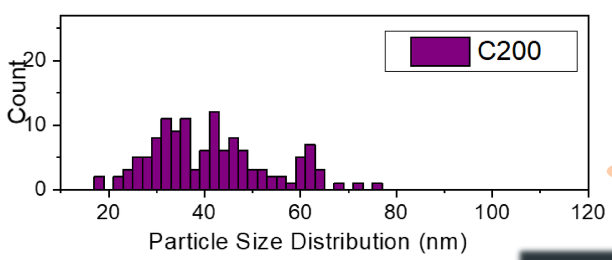


Figure. 1 Particle size distribution obtained from measurements of 2D TEM images.

Correlation in size

Dynamic Light Scattering

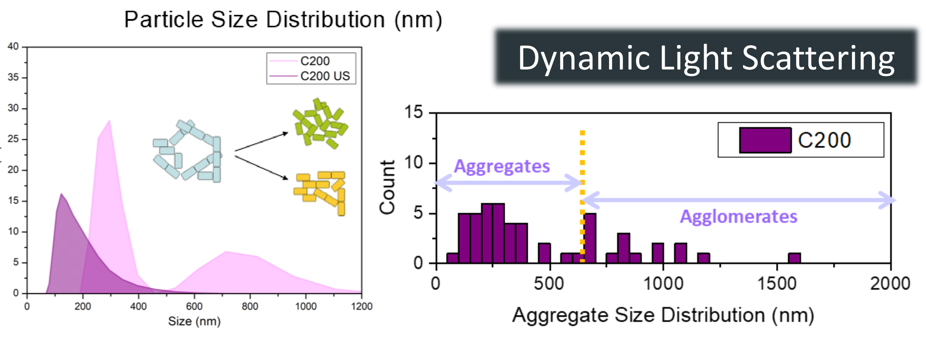


Figure. 2 (a) Left - DLS-number statistics shows the dispersion of boehmite aggregates before and after ultra-sonication (b) Right - Aggregate-agglomerate size distribution obtained from 2D TEM and SEM images

Size of aggregates and agglomerates established

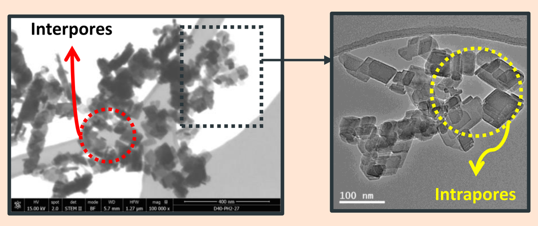


Figure. 3 Kolitcheff et al. representation of interpores (pores that are formed on between the agglomerates) and intrapores (pores that are formed between aggregates) observed from SEM and TEM images of catapal 200 boehmite grade

Hg Porosimetry + N_2 Physisorption

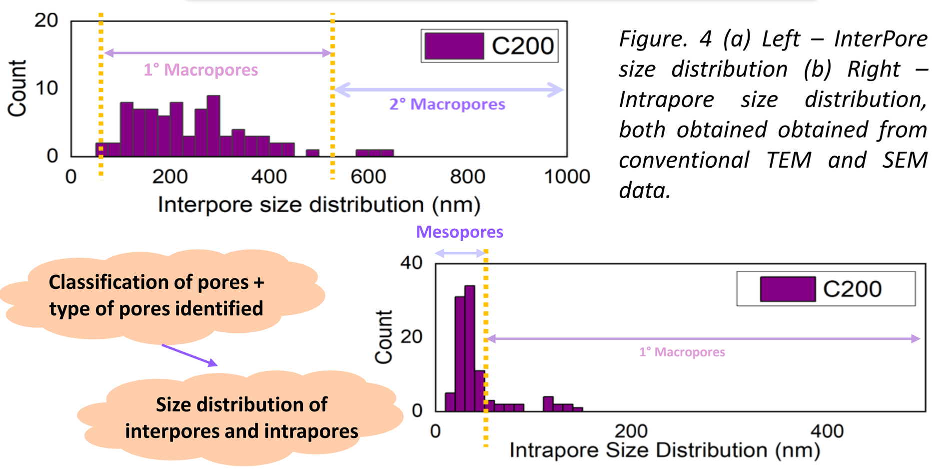


Figure. 4 (a) Left – InterPore size distribution (b) Right – Intrapore size distribution, both obtained obtained from conventional TEM and SEM data.

Classification of pores + type of pores identified

Size distribution of interpores and intrapores

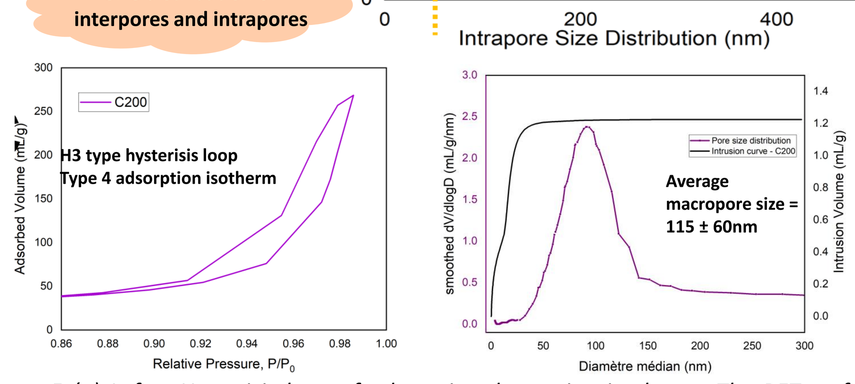
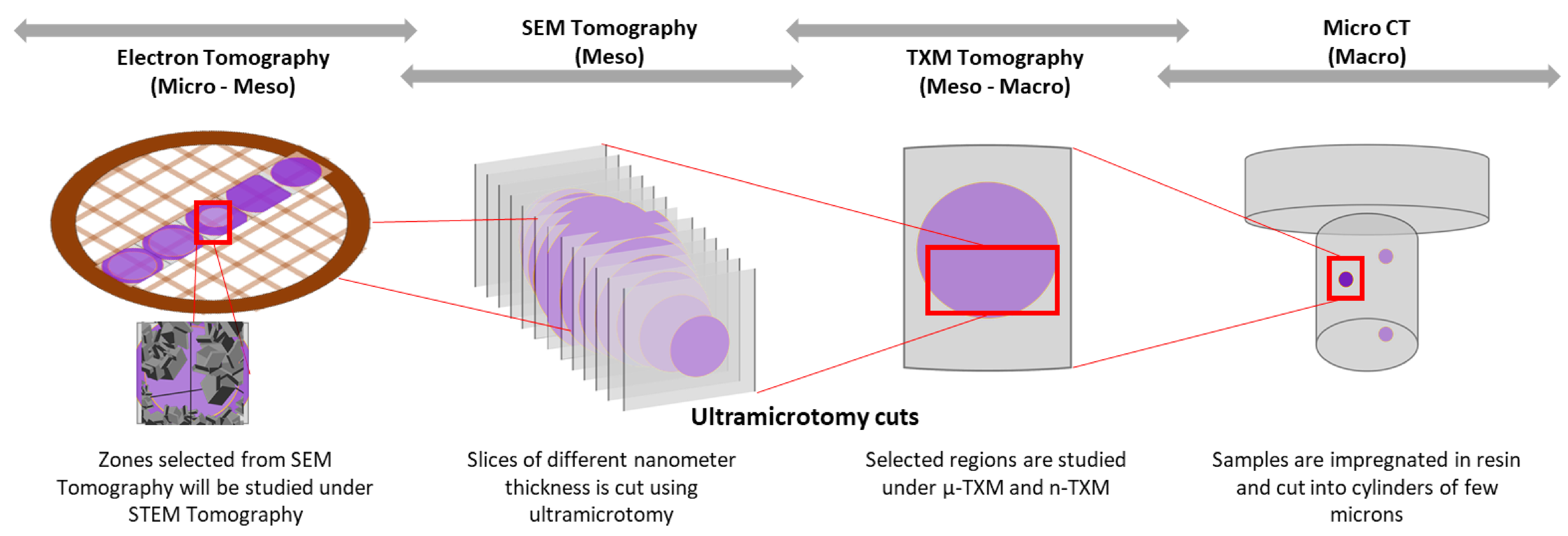


Figure. 5 (a) Left – Hysterisis loop of adsorption-desorption isotherms The BET surface area was calculated to be around 55m²/g. (b) Right - Retraction curve obtained from Hg porosimetry

Method	SAXS	N_2 physisorption	Hg porosimetery
Porosity (%)	45.4	55.6	50.6

METHODOLOGY DESIGNED FOR THE STUDY



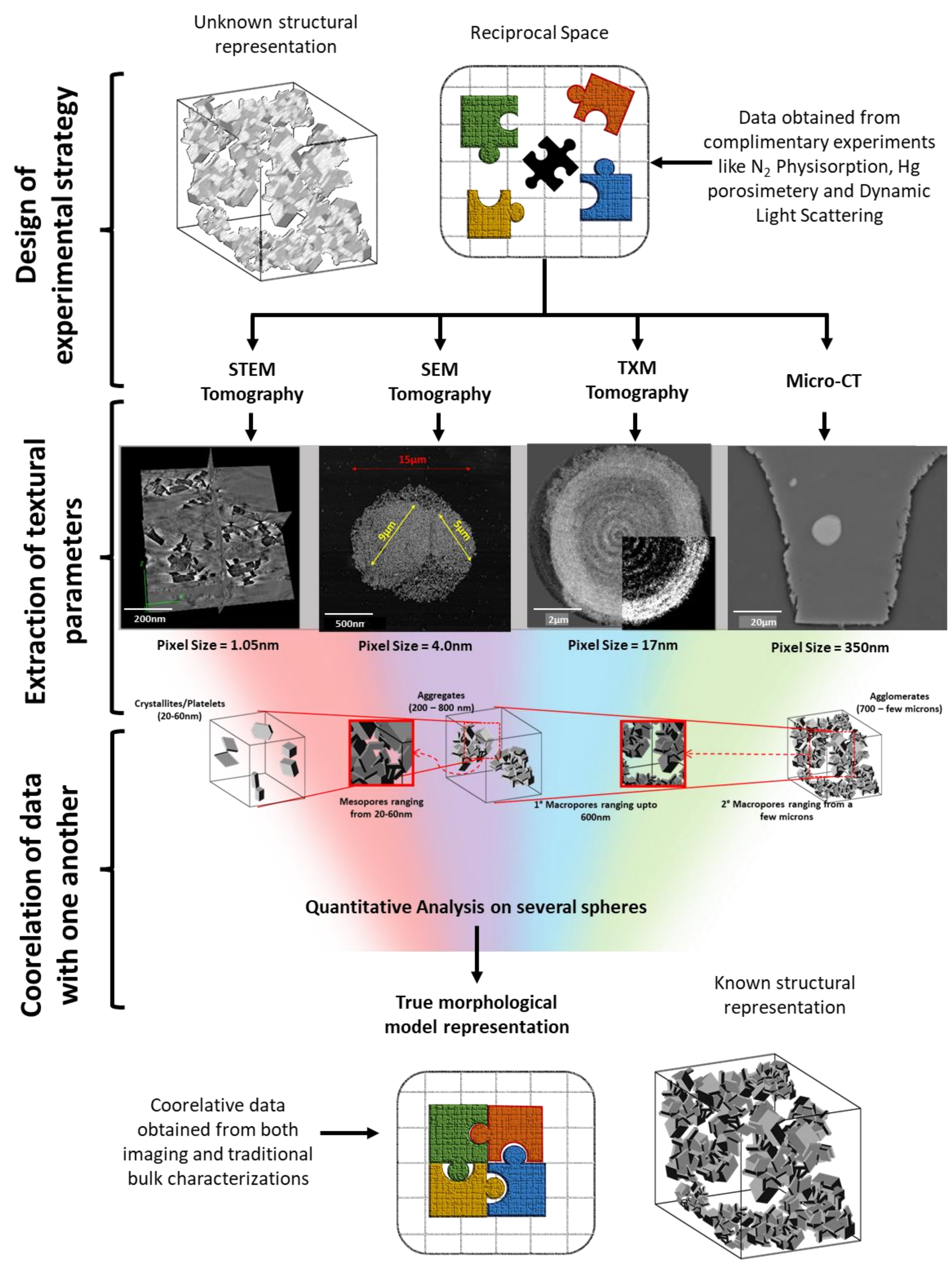


Figure. B. Methodology used to build a true morphological model using different X-Ray tomographic and Electron tomographic techniques to understand the textural and morphological parameters contributing to hierarchical structure and multiscale porosity of boehmite (AlOOH)

IMAGING CHARACTERIZATION TECHNIQUES

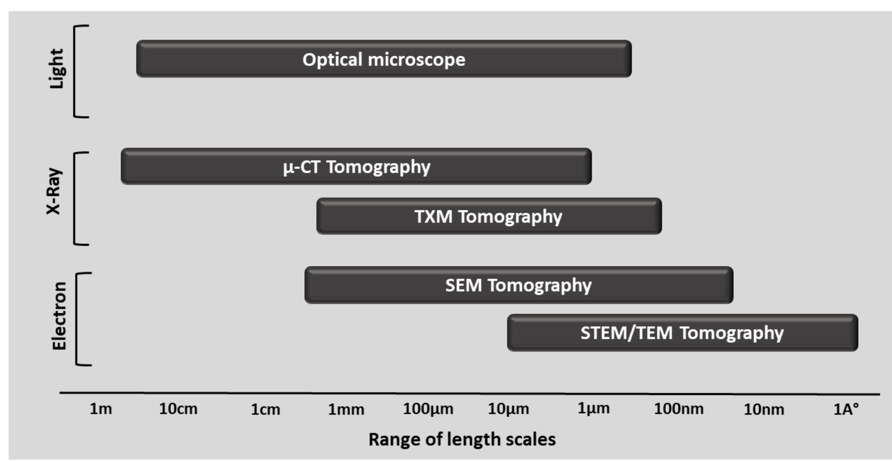
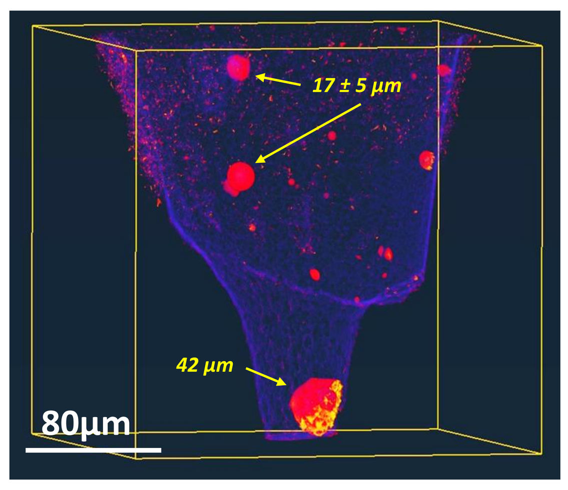


Figure C. Length scales of different 3D imaging methods used for the inspection of different features. Imaging techniques helps us understand the induvidual properties in real life space and time, thus providing a deeper understanding of pore network.

Micro-CT

Figure. 6 3D Visualisations of agglomerates as spheres were observed under µ-CT

Observation of big agglomerates of boehmites as spheres



TXM Tomography

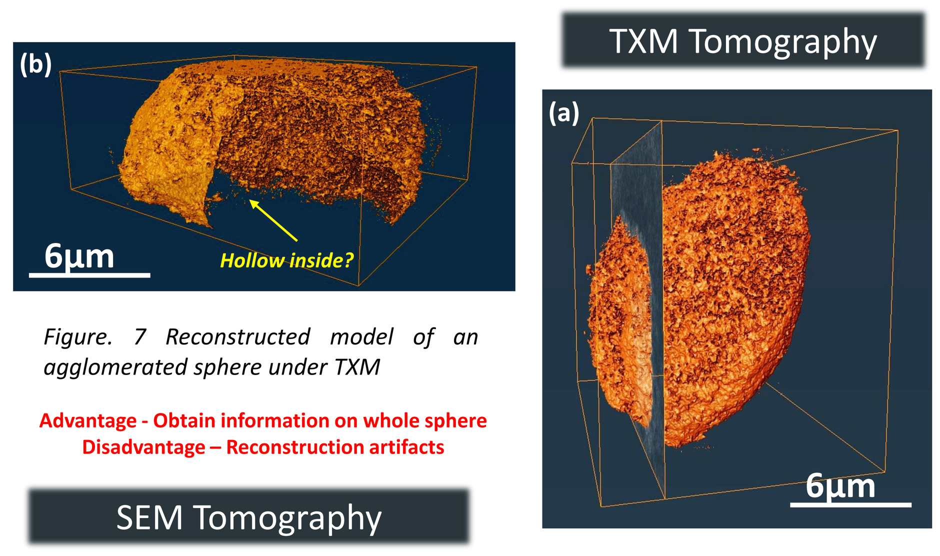


Figure. 7 Reconstructed model of an agglomerated sphere under TXM

Advantage - Obtain information on whole sphere
Disadvantage – Reconstruction artifacts

SEM Tomography

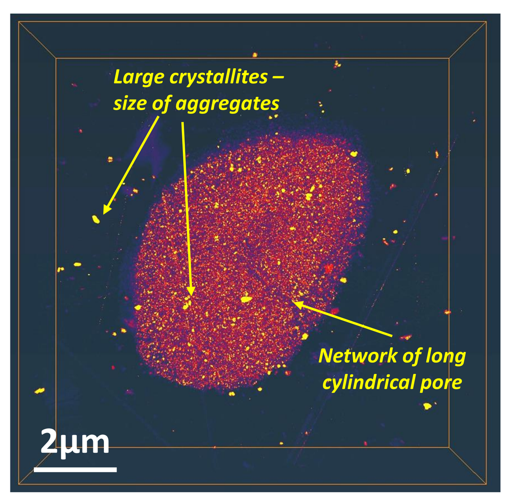


Figure. 8 Volume-rendered and modelled visualisation of the same agglomerate sphere that was studied under TXM but using array SEM tomography.

Advantage - Obtain better resolution
Disadvantage – Cannot obtain whole sphere

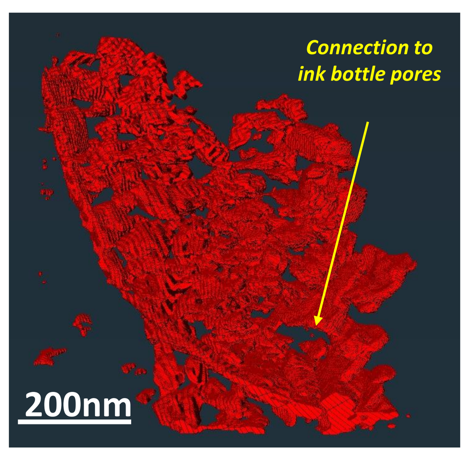
Both TXM and SEM provide textural information through different length scales Understanding of pore networks established

Combine information of TXM and SEM? → Deep learning → Super resolved TXM volumes which can predict missing slices

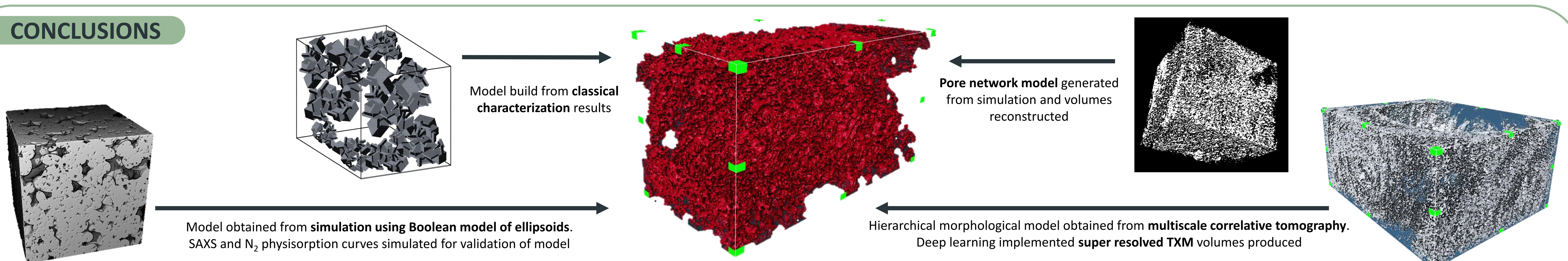
STEM Tomography

STEM provides deeper insights into the interaction and connectivity of individual particles with one another

Figure. 9 Reconstructed and segmented volume of an area of sphere observed under STEM.



CONCLUSIONS



Model build from **classical characterization** results

Pore network model generated from simulation and volumes reconstructed

Model obtained from **simulation using Boolean model of ellipsoids.** SAXS and N_2 physisorption curves simulated for validation of model

Hierarchical morphological model obtained from **multiscale correlative tomography.** Deep learning implemented **super resolved** TXM volumes produced

TRUE MORPHOLOGICAL MODEL

References –

1. Said, S., Mikhail, S. & Riad, M. Recent progress in preparations and applications of meso-porous alumina. Mater. Sci. Energy Technol. (2019).
2. Wang, H. et al. Modelling mesoporous alumina microstructure with 3D random models of platelets. J. Microsc. (2015).
3. Kolitcheff, S. et al. Tortuosity of mesoporous alumina catalyst supports: Influence of the pore network organization. Microporous Mesoporous Mater. (2017).

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