

FRACTAL GRAPHENE STRUCTURES AS SUPERCAPACITOR BUILDING ELEMENTS

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SUPERCAPACITORS: THE BASICS

Supercapacitors

Supercapacitors (SC), sometimes called ultracapacitors or electric double-layer capacitor (EDLC), comprise a family of electrochemical capacitors that don't have a conventional solid dielectric. (*Conway, 1999*)

The capacitance value of an electrochemical capacitor is determined by two storage principles, both of which contribute to the total capacitance of the capacitor :

Double-layer (DL) Capacitance

Electrostatic storage of the electrical energy is achieved by separation of charge in a Helmholtz double layer (DL), at the interface between the surface of a conductive electrode and an electrolyte. The distance of the static separation of charge in a double-layer is of the order of a few Å (0.3 to 0.8 nm). (*Namisnyk, 2003*)

Pseudocapacitance

Electrochemical storage of the electrical energy with electron transfer, achieved by redox reactions with specifically adsorbed ions from the electrolyte, intercalation of atoms in the layer lattice or electrosorption, underpotential deposition of hydrogen or metal adatoms in surface lattice sites, which result in a reversible faradaic charge-transfer. (*Herman et al, 2004*)



SUPERCAPACITOR FAMILIES

Supercapacitors are divided into three families, based on the design of the electrodes:

Double-layer capacitors

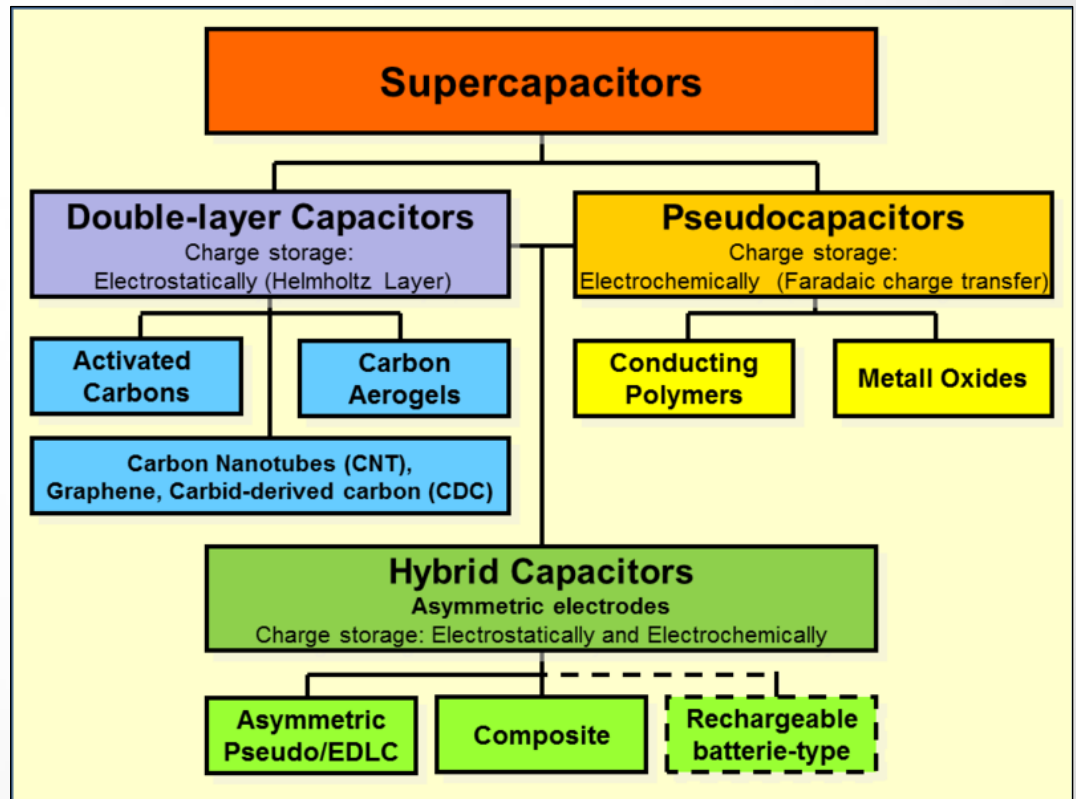
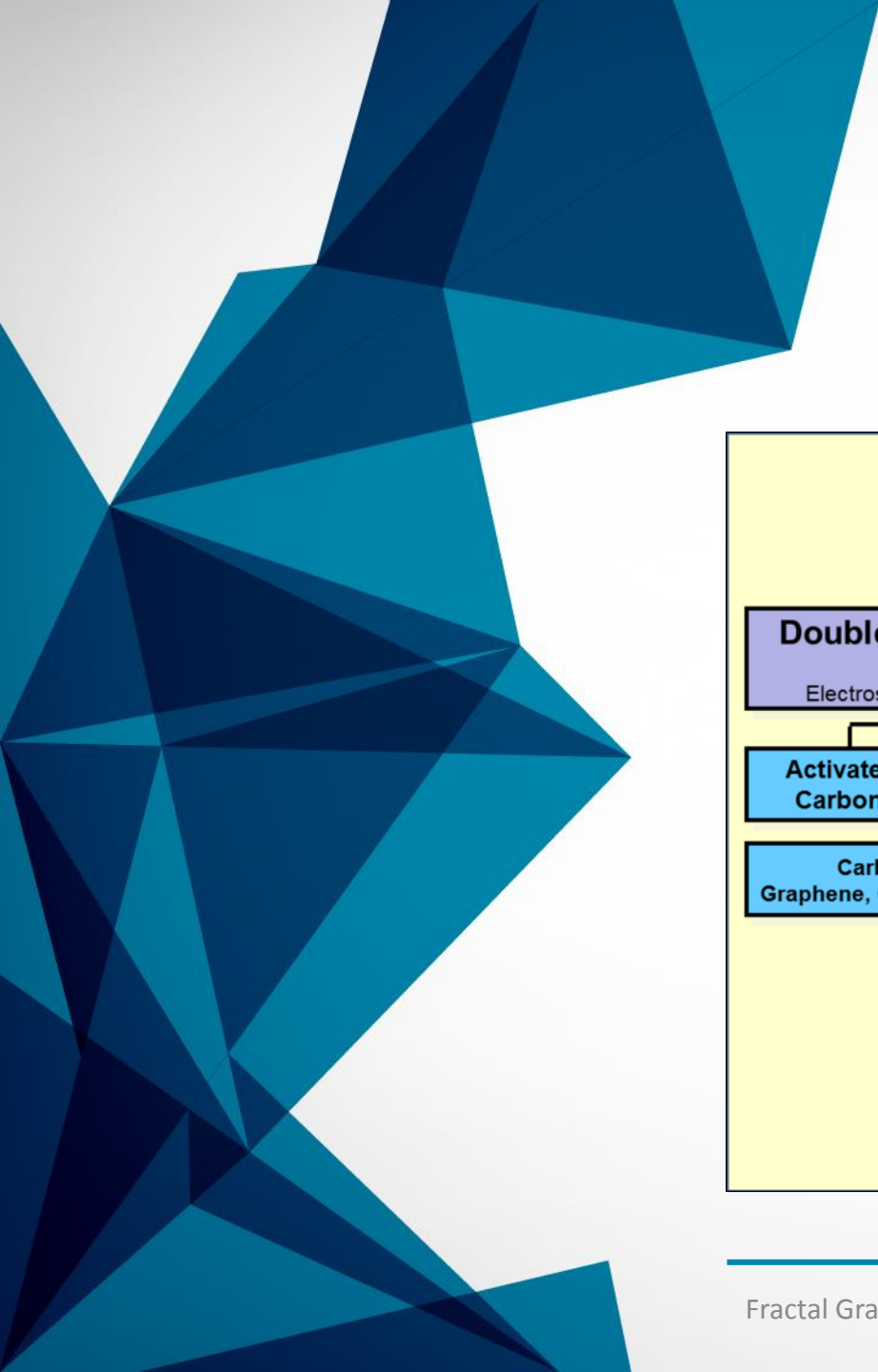
with carbon electrodes or derivatives with much higher static DL capacitance than the faradaic pseudocapacitance.

Pseudocapacitors

with electrodes out of metal oxides or conducting polymers with a high amount of faradaic pseudocapacitance.

Hybrid capacitors

with special and asymmetric electrodes that exhibit both significant DL capacitance and pseudocapacitance, such as Lithium-ion capacitors.



ENERGY DENSITY & POWER DENSITY

Supercapacitors bridge the gap between conventional capacitors and rechargeable batteries. They have the highest available capacitance values per unit volume and the greatest energy density of all capacitors. They support up to 12,000 Farads/1.2 Volt, with capacitance values up to 10,000 times that of electrolytic capacitors (*Conway, 1999*). The amount of energy stored in a supercapacitor is called specific energy; the energy W_{max} stored in capacitor is given by:

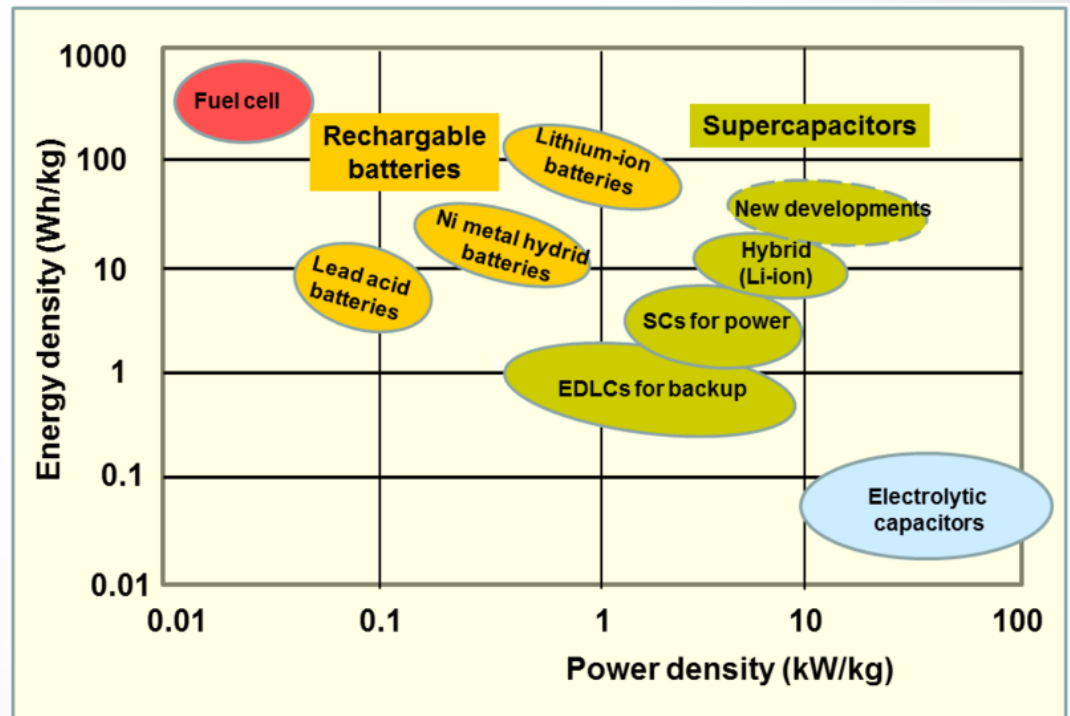
$$W_{max} = \frac{1}{2} C_{tot} V_{load}^2$$

While supercapacitors have energy densities that are ~10% of a conventional battery, their power density is generally 10 to 100 times greater. Although the energy densities of supercapacitors are insufficient compared to batteries, they have an important advantage: power density, which is given by the formula:

$$P_{max} = \frac{1}{4} \frac{V^2}{R_i}$$

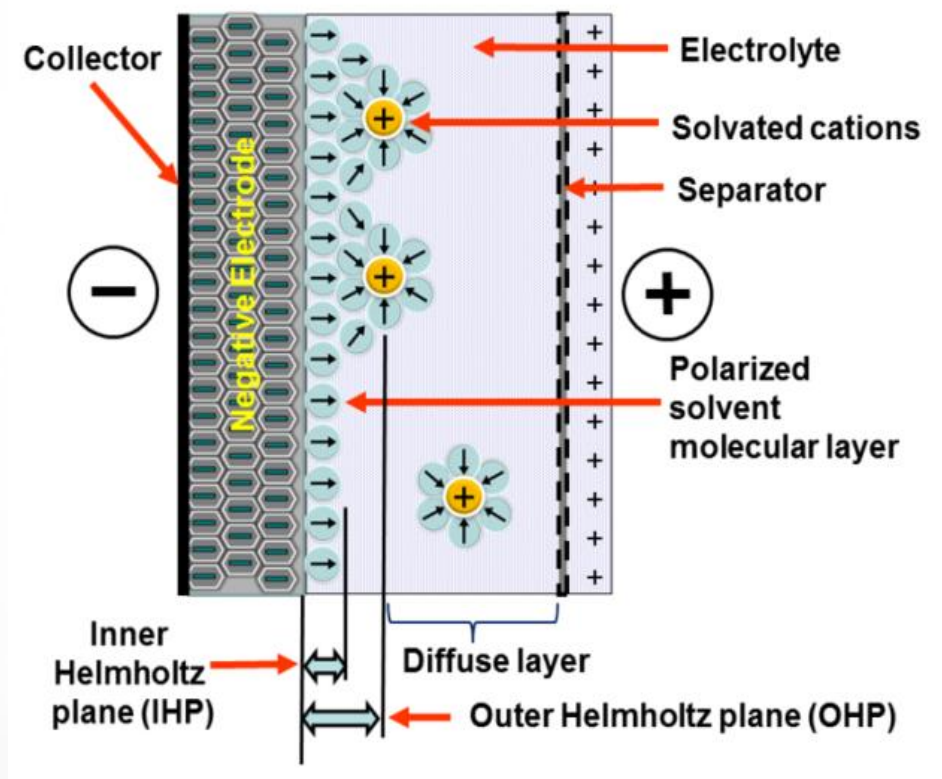
Power density is the product of energy density, multiplied by the speed at which the energy is delivered to the load. The greater power density results in much shorter charge-discharge cycles than a battery is capable, and a greater tolerance for numerous charge-discharge cycles.

ENERGY vs. POWER RAGONE PLOT



DOUBLE LAYER

An electrical double layer (EDL) in an electrochemical supercapacitor is a structure that appears between the surface of a metallic conductive electrode and an adjacent liquid electrolyte. Applying a voltage to this arrangement, two layers of ions are generated: the **EDL**, with one layer in the **surface lattice structure of the electrode** and the **opposite polarity layer** out of dissolved and solvated ions in the **adjacent liquid electrolyte**. Both layers of opposite ions are separated from each other by a monolayer of isolating molecules of the solvent, which forms the **inner Helmholtz plane (IHP)** that adheres by physical adsorption on the surface of the electrode and separates the opposite polarized ions from each other, thus building a molecular dielectric. The amount of charge in the electrode is matched by the same magnitude of counter-charges in **the outer Helmholtz plane (OHP)**. This can be used to store electrical charges: the stored charge in the double-layer forms a static field in the molecular layer of the solvent molecules in the IHP that corresponds to the strength of the applied voltage.



DL CAPACITANCE

The DL acts like the dielectric layer in a conventional capacitor, but with the thickness of a single molecule. The early Helmholtz model to calculate the capacitance predicts a constant differential capacitance C_d independent from the charge density, even depending on the dielectric constant ϵ and the charge layer separation δ :

$$C_d = \epsilon / 4\pi\delta$$

If we use water an aqueous electrolyte, and the layer separation δ is around 0.3 nm - the value of differential capacitance predicted by the Helmholtz model is about 18 F/cm^2 . This value can be used to calculate capacitance using the standard formula for conventional plate capacitors, if only the surface of the electrodes is known (*Srinivasan, 2006*). This capacitance can be calculated with:

$$C = \epsilon A / d$$

MATERIALS AND SURFACES

Porous Carbon Materials

Although capacitance is directly proportional to surface area, empirical evidence suggests that, for porous materials (activated carbon, carbon aerogels), not all of the high surface area contributes to the capacitance of the device (Frackowiak & Beguin, 2001). This discrepancy is believed to be caused by electrolyte ions that are too large to diffuse into smaller micropores, thus preventing some pores from contributing to charge storage (Shi, 1996).

Research also suggests an empirical relationship between the distribution of pore sizes, the energy density, and the power density of the device:

Larger pore sizes \Rightarrow higher power densities

Smaller pore sizes \Rightarrow higher energy densities

Carbon Nanotubes (CNTs)

Unlike other carbon-based electrodes, the mesopores in carbon nanotube electrodes are interconnected, allowing a continuous charge distribution that uses almost all of the available surface area. Thus, the surface area is utilized more efficiently to achieve capacitances comparable to those in activated-carbon-based supercapacitors, even though carbon nanotube electrodes have a modest surface area compared to activated carbon electrodes.



Carbide-Derived Carbons (CDCs)

Carbide-derived carbons can exhibit high surface area and tunable pore diameters to maximize ion confinement, increasing pseudocapacitance by faradaic H₂ adsorption treatment. Structurally, CDC pore sizes range from micropores to mesopores, but below macropores. The capacitance of CDC electrodes may be increased by tailoring pore design in the range of micropores. Pores smaller than 1 nm greatly contribute to capacitance, even if the solvated ions are larger. This increased charge storage capability works additionally to the DL capacitance. CDC electrodes with tailored pore design increase energy density by as much as 75% over conventional activated carbons.

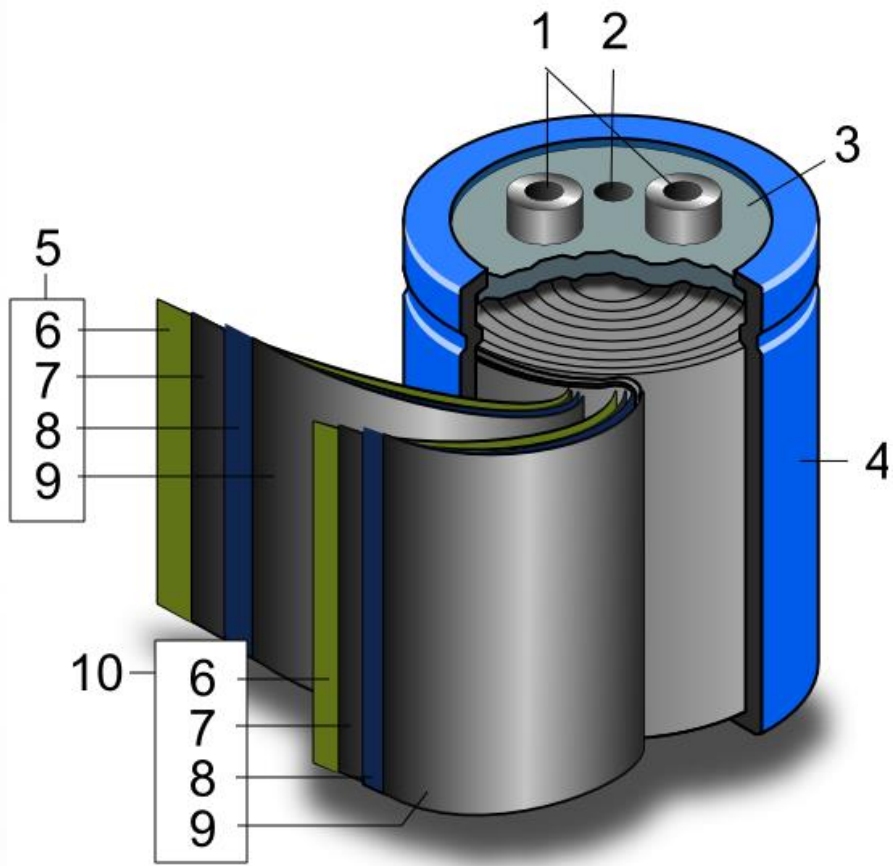
Graphene

The practical realized conductivity of graphene exceeds 1700 S/m, higher than activated carbon (10 to 100 S/g). Additionally, graphene has a very high surface area of 2630 m²/g, which can theoretically lead to capacitance values of 550 F/g.

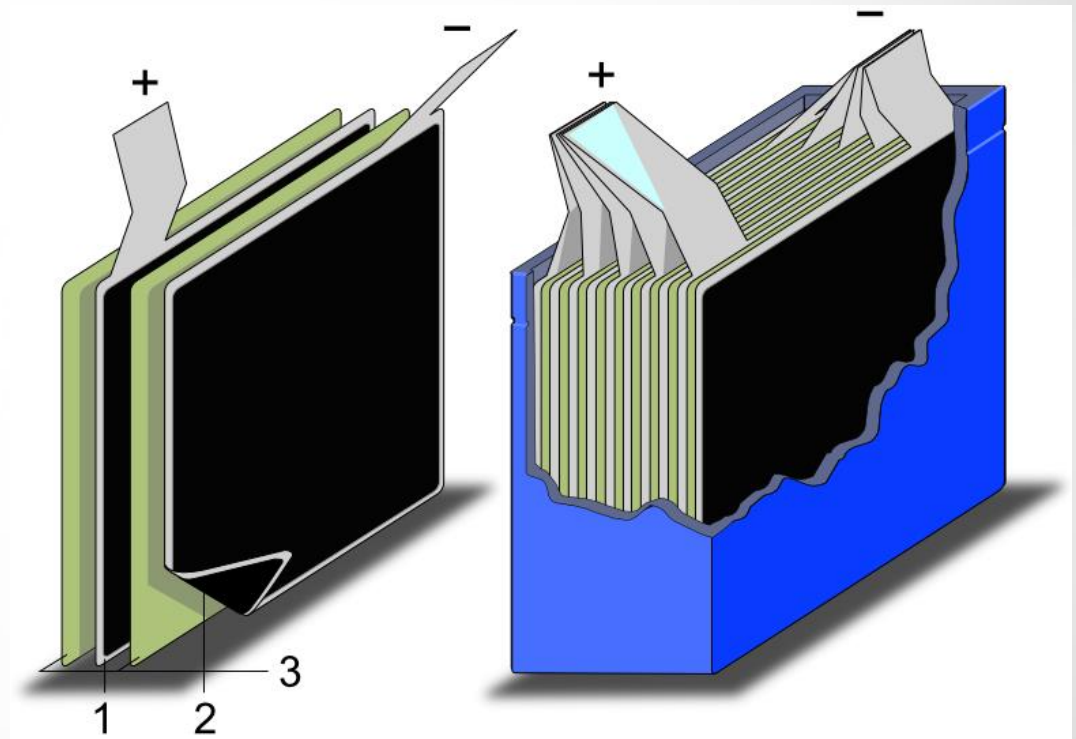
Graphene sheets can be used directly as supercapacitor electrodes, without binders or current collectors. The liquid electrolyte is replaced by a gelled polymer electrolyte that also acts as a separator, reducing device thickness and weight and simplifying fabrication.

The 2D structure of the graphene nanosheet improves charging and discharging. The charge carriers in vertically oriented sheets can quickly migrate into or out of the deeper structures of the electrode, thus speeding up current delivery.

CONSTRUCTION



Schematic construction of a wound supercapacitor:
1. Terminals, 2. Safety vent, 3. Sealing disc,
4. Aluminum can, 5. Positive pole, 6. Separator,
7. Carbon electrode, 8. Collector, 9. Carbon electrode, 10. Negative pole.



Schematic construction of a supercapacitor with stacked electrodes:
1. Positive electrode, 2. Negative electrode, 3. Separator.

INTERLUDE: FRACTAL GEOMETRY

Fractal

A fractal is a mathematical set that has a fractal dimension usually exceeding its topological dimension (Mandelbrot, 1983, 2004)

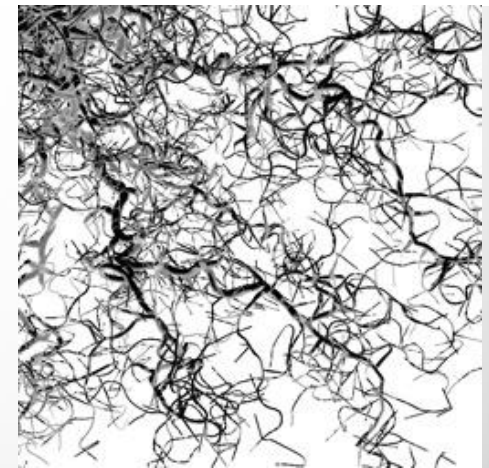
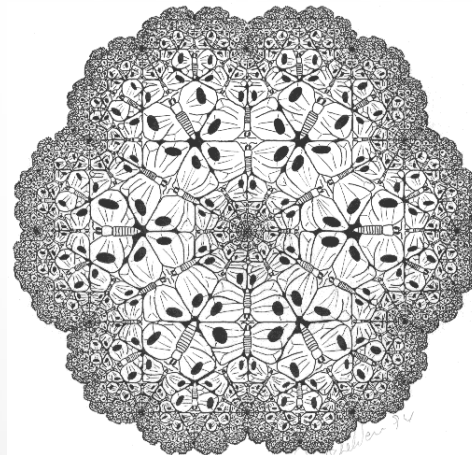
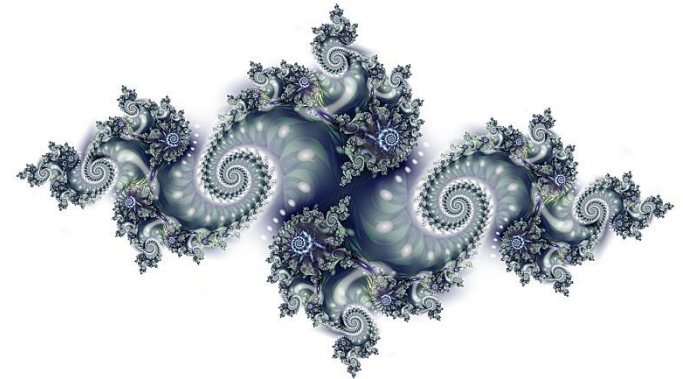
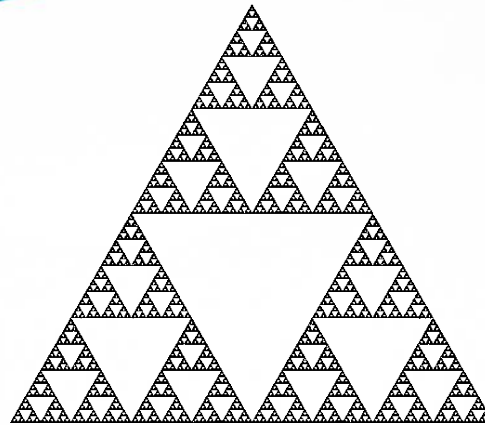
- ❑ self-similar: self-repeating pattern throughout all scales
- ❑ nowhere differentiable
- ❑ non-integer fractal dimension exceeding the topological dimension
- ❑ fine or detailed structure at arbitrarily small scales
- ❑ irregularity locally and globally
- ❑ simple recursive definitions

Common techniques for generating fractals

Images of fractals can be created by fractal-generating programs employing specific methods:

- ❑ Iterated function systems: use fixed geometric replacement rules; may be stochastic or deterministic (e.g. Koch snowflake, Peano curve)
- ❑ Strange attractors: use iterations of a map or solutions of a system of initial-value differential equations that exhibit chaos.
- ❑ L-systems: use string rewriting; may resemble branching patterns such as pulmonary structure or turtle graphics patterns such as space-filling curves
- ❑ Escape-time fractals: use a formula or recurrence relation
- ❑ Random fractals: use stochastic rules (i.e. dendritic fractals generated by modeling diffusion-limited aggregation)
- ❑ Finite subdivision rules: use a recursive algorithm for refining tilings

EXAMPLES OF FRACTALS



EXPERIMENTAL AIMS

Aims

- ❑ To employ novel methods for developing graphene surfaces with fractal properties
- ❑ To employ fractal surfaces as electrodes for supercapacitors
- ❑ To maximize the area of such surfaces in order to provide an exponential increase in DL capacitance values
- ❑ To correlate fractal measures, such as the non-Euclidean fractal dimension, to supercapacitor electrical parameters: capacitance, power and energy densities, Helmholtz layer and Debye length
- ❑ To benchmark fractal structures as to their applicability in nanoscale devices
- ❑ To build up a foundation for constructing deterministic fractal structures in 3D, in order to address the issues of porosity (separators, FC/MFC membranes, porous electrodes)
- ❑ To examine the resulting electric fields and to probe the non-uniform electric flux associated with a non-linear, fractal surfaces
- ❑ To set up a foundation for in-depth modeling of non-linear interfaces by investigating the kinetics of adjoining electrolyte layers



EXPERIMENTAL SET-UP: ORIGAMI METHOD

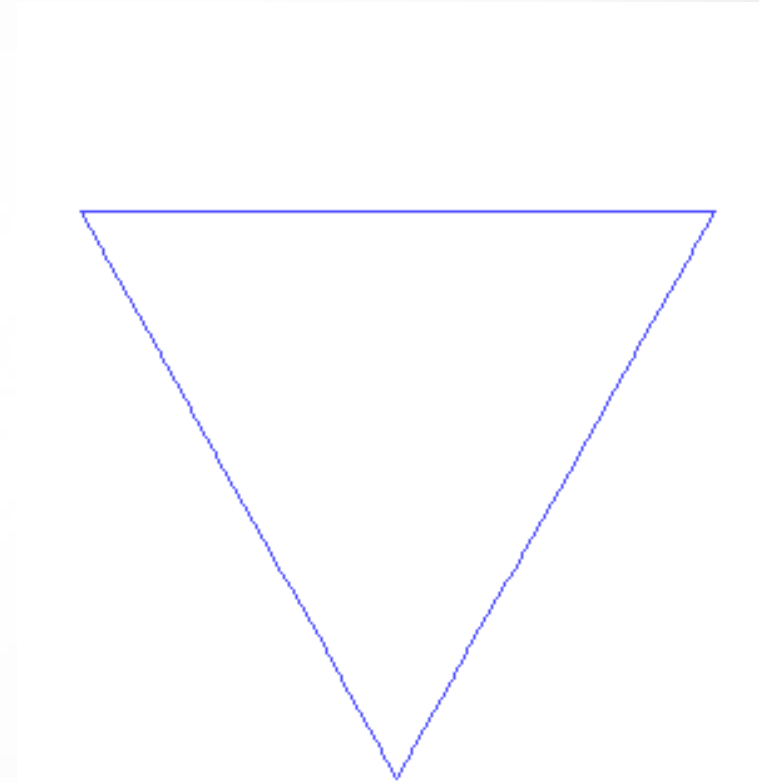
Overview

By imprinting well-defined Koch curves on vapor-deposited graphene surfaces, we capitalize on symmetry induced by self-similarity to employ a folding technique that collapses all points of the fractal onto each other. The end result is a graphene surface that retains the basic fractal properties of scaling: its topological dimension approaches the value of the Hausdorff dimension depending on the number of foldings (thus iterations of the fractal algorithm). The technique aims towards the development of capacitor concentric plates offering a greatly increased surface area over a finite volume, as the enclosed total length of a (1D) Koch curve increases with the number of iterations of the fractal algorithm.

Limitations

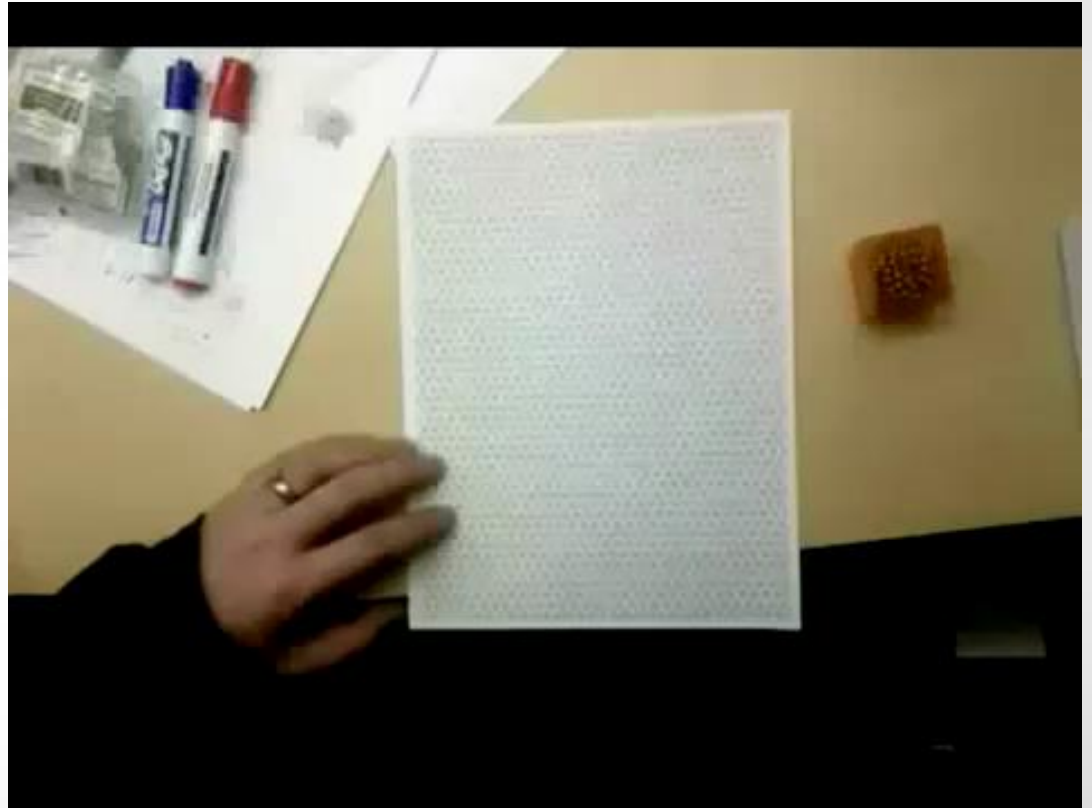
- ❑ Number of applicable algorithmic iterations is a function of the foldings in the Origami method and thus, limited by the physical properties of a graphene surface (elasticity etc.).
- ❑ Initial prototype has to be in the macroscale, to define the limiting parameters and to examine primary behavior.

EMBEDDED KOCH CURVE



- ❑ Each iteration multiplies the perimeter by a factor of $4/3$
- ❑ This leads to an exponential increase of embedded total length
- ❑ At the limit of infinite iterations, the perimeter becomes infinite but it remains embedded in a finite surface

ORIGAMI: FOLDING METHOD



THEORETICAL CONSIDERATIONS I

Fractal Dimension, DL Interface & Markov Processes

The classic definition of **fractal dimension** (1.2619 for the Koch snowflake) links the number D of self-similar segments that drive the fractal algorithm to the scaling parameter ε :

$$D = -\frac{\log N}{\log \varepsilon}$$

In a similar spirit, the **information dimension** D considers how the average information needed to identify an occupied box scales with box size; p is a probability.

$$D_1 = \lim_{\varepsilon \rightarrow 0} \frac{-\log p_\varepsilon}{\log \frac{1}{\varepsilon}}$$

By examining the possibility of translating the DL interface system into an Information system – essentially modeling corresponding charges and ions into **Binary format** – we examine the linkage between the dimension parameter describing **complexity** and **information entropy** to the distribution of charges in the DL through a **percolation model**.

In probability theory, a Markov process is a **stochastic process** satisfying a certain property, called the Markov property. A Markov process can be thought of as '**memoryless**': a process satisfies the Markov property if one can make predictions for the future of the process based solely on its present state just as well as one could knowing the process's full **history**. I.e. conditional on the present state of the system, its future and past are independent.

THEORETICAL CONSIDERATIONS II

Dynamics of Markovian Particles & Continuum Mechanics

Dynamics of Markovian particles (**DMP**) is the basis of a theory for **kinetics of particles** in **open heterogeneous systems**. It can be looked upon as an application of the notion of stochastic process conceived as a physical entity; e.g. the particle moves because there is a **transition probability** acting on it. Two particular features of **DMP** might be noticed: (1) an **ergodic-like** relation between the **motion of particle** and the **corresponding steady state** and (2) the classic notion of geometric volume appears nowhere (e.g. a concept such as flow of substance is not expressed as liters per time unit but as **number of particles per time unit**).

On a macroscopic scale, materials have cracks and **discontinuities**. However, certain physical phenomena can be modeled assuming the materials exist as a **continuum**, meaning the matter in the body is continuously distributed and fills the entire region of space it occupies. A continuum is a body that can be continually sub-divided into **infinitesimal elements** with properties being those of the bulk material.

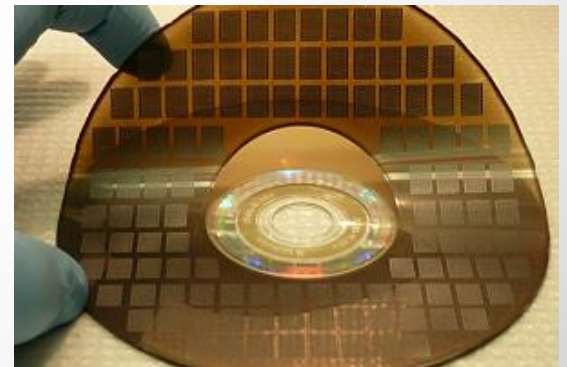
The validity of the continuum assumption may be verified by a theoretical analysis, in which either some clear periodicity is identified or **statistical homogeneity** and **ergodicity of the microstructure** exists. More specifically, the continuum hypothesis/assumption hinges on the concepts of a representative volume element (RVE) and separation of scales based on the Hill–Mandel condition. This condition provides a link between experimental and theoretical viewpoints on constitutive equations (linear and nonlinear elastic/inelastic or coupled fields), as well as a way of **spatial and statistical averaging of the microstructure**.

EXPERIMENTAL SET-UP: LIGHTSCRIBE METHOD

Overview

LightScribe is an innovative technology that uses a special disc drive, special media, and label-making software to burn labels directly onto CDs and DVDs. *LightScribe* technology provides for a facile and inexpensive method for the scalable microfabrication of graphene-based supercapacitors for flexible on-chip energy storage devices (El-Kady & Kaner, 2012; Piazzzi et al, 2012).

This technique essentially adjusts laser-etching so that it can be employed by simple DVD-burners on GO-coated disks: the laser traces the pattern provided by the *LightScribe* software to reduce the GO coating, thus inscribing a graphene pattern on the inert material. The process allows for miniaturizing the supercapacitors to the microscale, resulting in enhanced charge-storage capacity and rate capability.



LSG FABRICATION

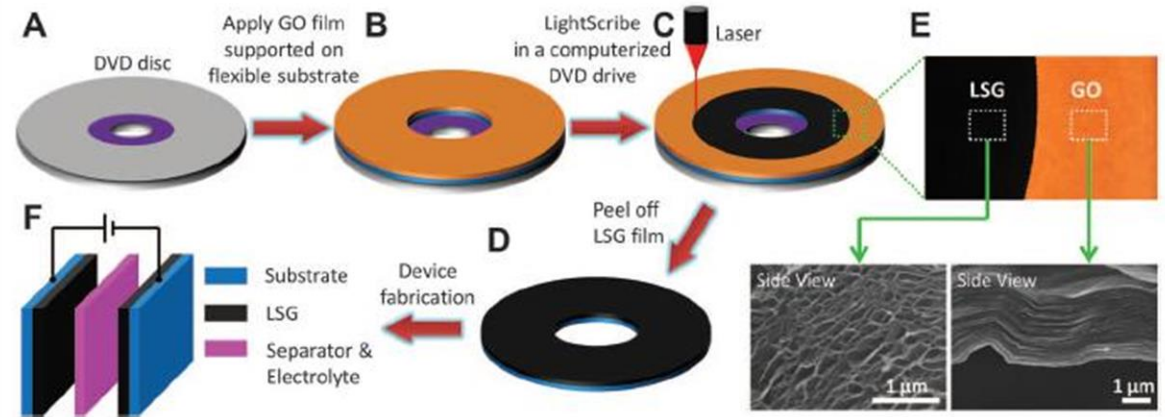
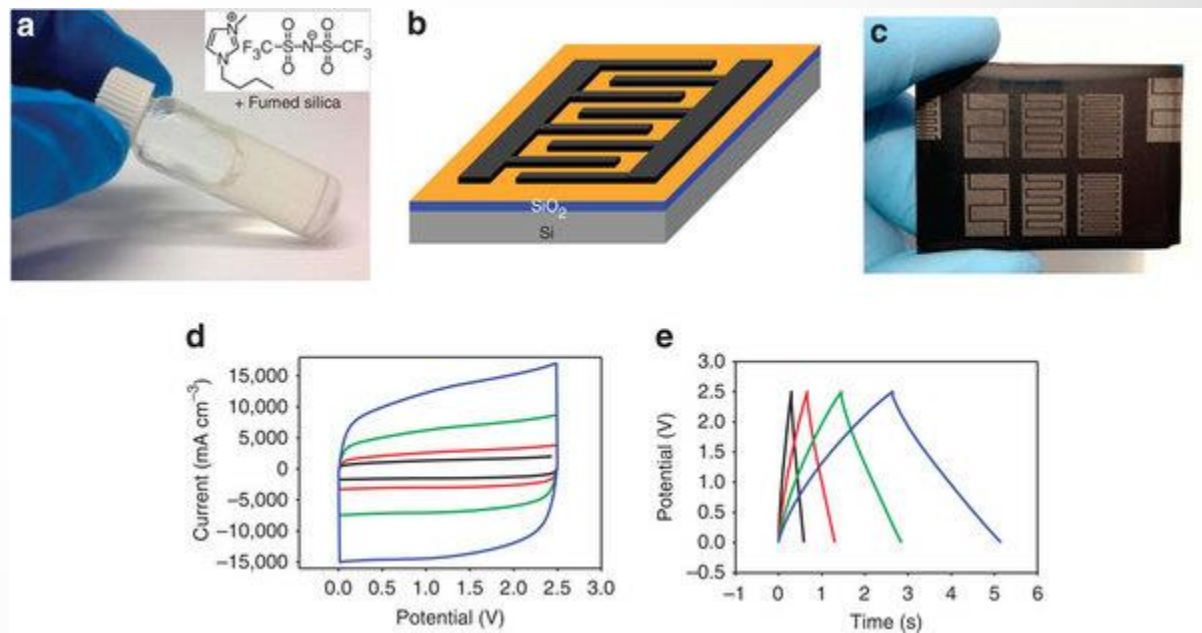


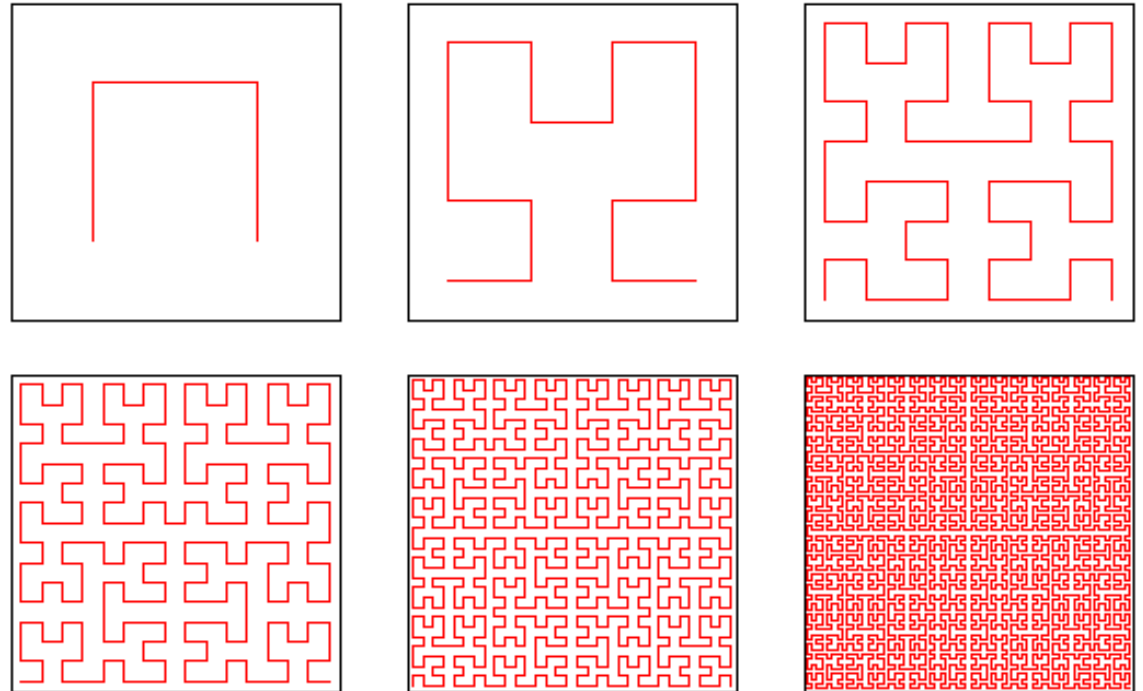
Fig. 1. Schematic illustration of the fabrication of laser-scribed graphene-based electrochemical capacitors. (A to D) A GO film supported on a flexible substrate is placed on top of a LightScribe-enabled DVD media disc, and a computer image is then laser-irradiated on the GO film in a computerized LightScribe DVD drive. (E) As shown in the photograph, the GO film changes from golden brown color to black as it is reduced to laser-scribed graphene. The low-power infrared laser changes the stacked GO sheets immediately into well-exfoliated few-layered LSG film, as shown in the cross-sectional SEM images. (F) A symmetric EC is constructed from two identical LSG electrodes, ion-porous separator, and electrolyte.

TYPICAL LSG PATTERNS



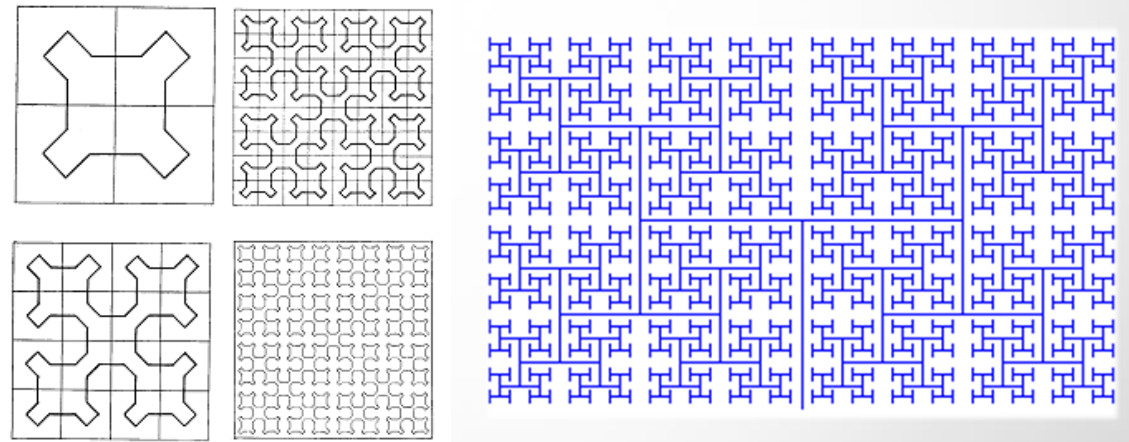
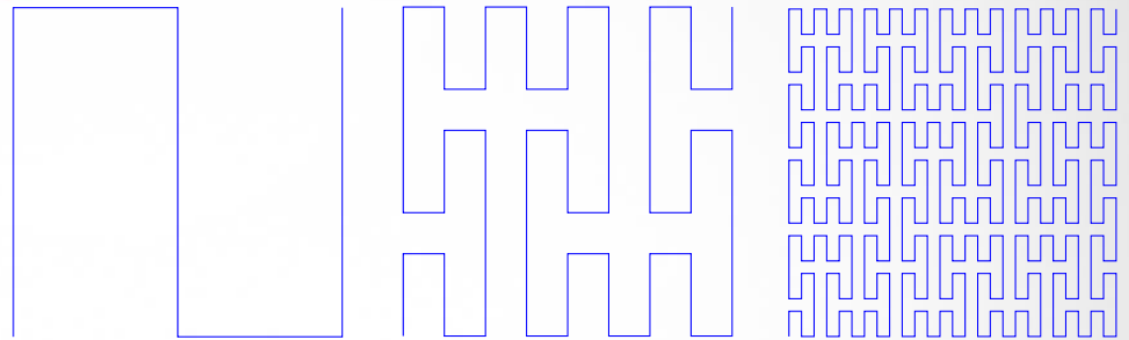
LightScribe can be used to produce LSG-MSC directly on a chip that contains integrated circuits, which they can then power. An ionogel electrolyte was used in the assembly of the device.

FRACTAL PATTERNS



Hilbert space-filling curve (D=2)

FRACTAL PATTERNS



Peano space-filling curves and variations (D=2)

END REMARKS

A set of experiments is proposed, where the specific behavior of nanomaterials (initially restricted to graphene) in a non-linear geometry is examined. Quantities such as material and electric flux need to be measured and modeled, in order to provide insight into kinetic and electrical processes associated with the new format.

The initial experiments aim to construct 1D and 2D structures, as these appear easier to fabricate with simple methods. If nonlinearity can be included in the standard syllabus for nanotechnology, then it is bound to open up new horizons for the field – however, we must realize that, with our current means, we can explore simple structures that are technically classified as pseudo-fractals, due to the finite number of iterations of their generating algorithm, limited principally by the resolution that our fabricating methods allow.

Nevertheless, current technological advances promise new and exciting forays into the field of fractal structures. 3D printing might as well unlock the possibilities of physically building fractal structures in the 3rd dimension, thus addressing the issue of porosity that has been seen only through chemical methods. Of course, before venturing into 3D, we need to understand and master the humbler dimensions.

THANK YOU