SMART MATERIALS SYSTEMS THROUGH MESOSCALE PATTERNING

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ABSTRACT

We report work on the fabrication of smart materials with two unique strategies: (i) Self-assembly and (ii) laser stereolithography. Both methods are akin to the processes used by biological systems. The first one is ideal for pattern development and the fabrication of miniaturized units in the submicron range and the second one in the 10 μm to 1 mm size range. By using these miniaturized units as building blocks, one can produce smart material systems at larger length scales such as smart structural components. We have chosen to focus on two novel piezoceramic systems: (i) high-displacement piezoelectric actuators, and (ii) piezoceramic hydrophone composites possessing negative Poisson ratio matrices. High-displacement actuators are essential in such applications as linear motors, pumps, switches, loud speakers, variable-focus mirrors, and laser deflectors. Arrays of such units can potentially be used for active vibration control of helicopter rotors as well as the fabrication of adaptive rotors. In the case of piezoceramic hydrophone composites, we utilize matrices with a negative Poisson's ratio in order to produce highly sensitive, miniaturized sensors. We envision such devices having promising new application areas such as monitoring fluid pressures in constrained volumes using small, sensitive hydrophones. Negative Poisson ratio materials have promise as robust shock absorbers, air filters, and fasteners, and hence, can be used in aircraft and land vehicles.

I. INTRODUCTION

A smart materials system consists of sensors and actuators. The sensors sense the external changes and instruct the actuators to act in a proper way through a feedback circuit. It is desirable for an actuator to be able to simultaneously generate large displacements and sustain large

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forces.[1-3] In most applications, the level of integration of the components into a given system has been at length scales larger than a few millimeters. For various reasons (e.g., the need to develop microelectronic mechanical systems (MEMS) and improved performance), the length scale of component integration now needs to be reduced to the sub millimeter range.[4]

The length scales defining structure and organization determine the fundamental characteristics of a material. Traditional composite materials exhibit organization on two length scales: On the atomic scale, e.g., the unit cell of the crystal or the local arrangement of amorphous materials, and on the scale of the domain size within the composite, typically much larger length and on the order of micrometers or greater. The range between these two scales is defined as the mesoscopic range with respect to our inability to tailor composites with deliberate design. In the physics community, the mesoscopic range is defined as the sub 100 nm scale due to the scale-dependent properties that are observed in this range (Figure 1).

In biogenic materials, however, we observe a much broader range of organizational length scales (Figure 1): (i) a hierarchical organization always starts at the mesoscopic range, in which case, nanostructural design is the building block for larger scale composite structures; and (ii) the nested levels of structural hierarchy appear to yield improved properties for particular functions.[5,6] In biogenic systems, nanostructural design is accomplished through the self-assembly of organics. Inorganic structures form as the structurally organized organic surfaces catalytically or epitaxially induce growth of the inorganic phases.

The work discussed in this paper is based on a cooperative effort including researchers at Princeton, Harvard, and Drexel Universities. We pursue two parallel avenues of research to process smart materials with component dimensions reduced to the mesoscopic range. Laser

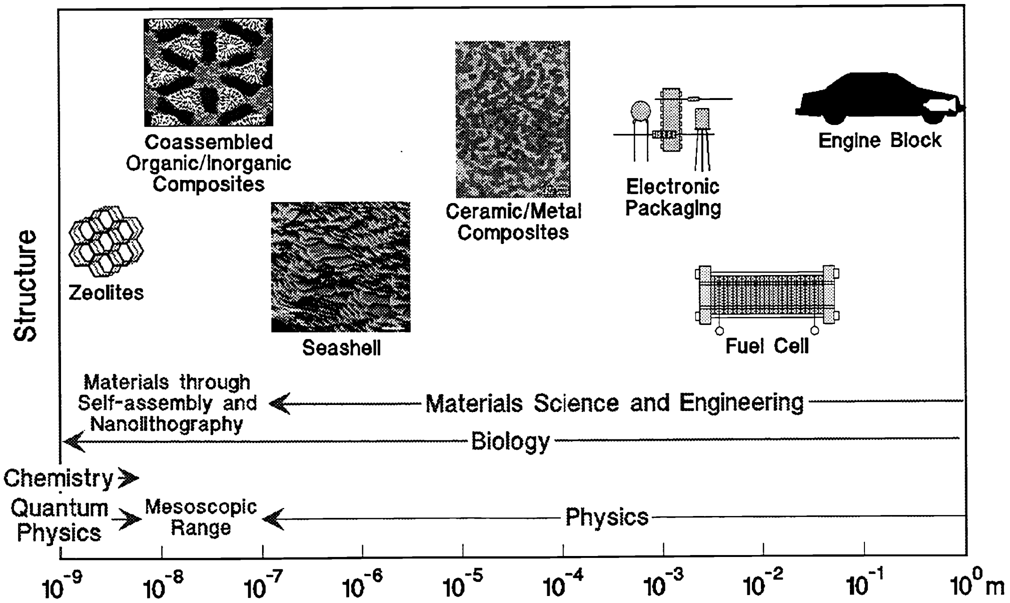

Figure 1: Deliberate design of a material system has traditionally been limited to length scales $>10^{-6}$ m as in the case of ceramic/metal composites. In contrast, biological systems (e.g., seashell) cover a continuum of length scales spanning from molecular to macroscopic dimensions.

stereolithography,[7] which offers the possibility of achieving component integration down to the level of 10 μm, is one of the main processing methods. As in the biogenic systems, the other processing methods rely on the use of molecular self-assembly to form patterns at length scales even smaller than 10 μm.[8]

II. NANOSTRUCTURED COMPOSITES THROUGH SELF-ASSEMBLY

As discussed by Whitesides[9] in this proceedings, the ultimate smart materials process would incorporate the self-assembly mechanism into the chemistry of the molecules. The strategy underlying self-assembly is to design the fabrication system in such a way that the product is at or near a thermodynamic minimum. This type of system will then "assemble itself"; that is, it will intrinsically evolve toward the desired end result without further human intervention or control. The product will tend, as a result, to be robust, to reject defects, and to be self-healing when damaged. These characteristics make self-assembled systems particularly attractive as the basis for fabrication, since they tend to perfection while requiring relatively simple manufacturing processes. This ideal does in fact occur in biological systems. For instance, it can be observed in the spontaneous assembly of lipid molecules into bilayers of precisely defined curvature and spatial organization.[10] This approach is the most long range and forward looking, but also the one with greatest potential impact. It also lends itself most readily to scaling down to structures with sizes from 10 to 100 nm, the scale covering the next frontier for smart materials integration.

A new class of materials recently discovered by scientists at Mobil Corporation ideally illustrates the utility of self-assembly in materials design at the 1-10 nm size range.[11] The Mobil scientists were investigating synthesis routes for large pore synthetic "zeolites", primarily with the aim of creating catalytic matrices for large organic molecules. They found conditions under which silica precursors could be mixed with surfactants and result in polymerized silica "casts" or "templates" of commonly observed surfactant-water liquid crystals. What appeared to be happening was that the silica precursors were somehow immobilized and collected at the interfaces between the surfactant and water molecules, then induced to polymerize into walls of amorphous silica only a few silica units thick. Three different mesoporous geometries have been reported,[11-14] each mirroring an underlying surfactant-water mesophase (Figure 2). These mesoporous materials are constructed of walls of amorphous silica, only ten or so angstroms thick, organized about a repetitive arrangement of pores up to a hundred angstroms in diameter. The resulting material has the interesting characteristic of being locally amorphous (on atomic length scales) and crystalline on larger (tens to hundreds of angstrom) length scales. Using this approach, compositions other than silica (e.g., titania[15]) have also been shown to display

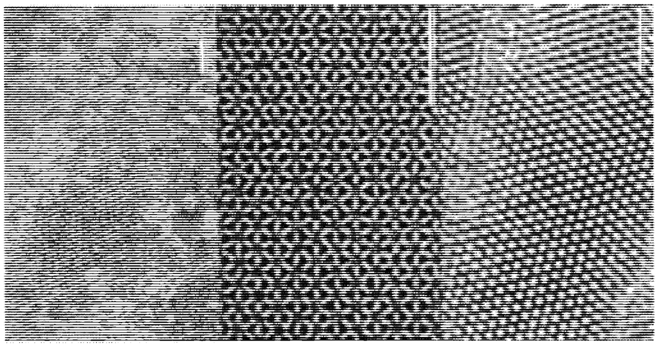

Figure 2: Transmission electron microscope images of (a) the lamellar morphology, (b) the cubic phase with Ia3d symmetry viewed along its [111] zone axis, and (c) the hexagonal phase viewed along its [001] zone axis of the silica/surfactant nanostructured composites by co-assembly.[12,13] (bars = 30 nm)

mesoscale organization in the presence of surfactants.[16]

The concentration of the organic surfactant in these systems is below the critical concentration required for spontaneous self-assembly into periodic surfactant-water mesophases. Instead of merely templating onto an existing mesophase, the inorganic precursor becomes an active participant in the formation of the mesophase. Consequently, this process of cooperative assembly is termed co-assembly. Although there has been some insight into the self-assembly process in these systems,[12-17] there is still a lack of detailed information needed to accurately predict and control the phase and dimensions of the co-assembly.

The availability of highly controlled pores on the 10 to 100 Å scale offers opportunities for creating unusual composites, with structures and properties unlike any that have been made to date. However, the effective use of mesoporous silicates requires two critical achievements: (i) controlling the mesophase pore structure and (ii) synthesizing large monolithic and mesoporous "building blocks" for the construction of larger, viable composite materials. Although important information exists on some aspects of controlling the mesoporous structure,[11] large scale structures have not yet been constructed. However, the general outline for fabricating useful composites is known: First, rigid silica (or other ceramic) skeletons form at the surfactant-water interface. This is followed by the removal of the organic phase to yield a ceramic cellular solid containing periodic, 1-10 nm diameter pores. The porous structures may be used as a cellular solid or subsequently infiltrated with secondary phases. The use of mesoporous materials will lead to the development of composites having a level of compositional heterogeneity that is not readily (nor consistently) achieved using other methods of materials synthesis.

A necessary condition for organizing inorganics at the mesoscale with the aid of organic templates is understanding the mechanism of molecular recognition at the organic/inorganic interfaces. The interfacial mechanisms leading to the development of biogenic organic/inorganic composites are discussed by Lahiri, *et al.*[18] in this proceedings. The principles of molecular recognition and self-assembly can be applied to place crystal nucleation sites on surfaces or at aqueous-lipid interfaces.[19] Likewise, inhibitor molecules can be incorporated to retard the rate of crystal growth on particular faces, thus shaping the habit of the inorganic phases. For instance, to explore and control the growth of calcium carbonate crystals, the work described by Lahiri *et al.* has sought to design organic templates that are of an intermediate complexity between protein matrices and simple molecules such as stearic acid.[19] This approach helps delineate the effects of more subtle factors such as cooperativity, spatial-stereochemical effects, and especially the minimal structure required to mimic the controlled nucleation observed in biological systems. Novel anionic amphiphilic tricarboxyphenyl hemes have been synthesized such that their porphyrin planes are oriented perpendicular to the lipid-water interface.[18,19] The μ-oxo iron(III) porphyrin dimer of these trianionic amphiphiles thus provides 6-carboxylate groups in a rigid array affording a potential nucleation site for cationic surfaces in embryonic crystals. This work has shown that oriented nucleation of calcite crystals can be achieved on a monolayer surface of the template iron porphyrin. Calcite crystals can be attached to the surface perpendicular to the three-fold axis, very similar to the result for the mollusk glycoproteins. It appears that nucleation of these crystals occurs at or near the surface on the {00.1} and {10.2} faces due to an interesting epitaxial match with the porphyrin template. The extension of this approach to other compositions would require similar molecular design strategies to control the nucleation of the inorganic crystals.

III. MICROSCALE PATTERNING OF CERAMIC MATRIX COMPOSITES

Work described by Whitesides[9] shows that it is possible to apply the techniques for microfabrication using self-assembled monolayers (SAMs)[8,20-22] to the formation of functional ceramics. Two physical properties of SAMs are central to their use in fabrication and patterning: First, when properly prepared the packing of the chains is so dense that SAMs are excellent resists on coated surfaces.[20,27] Second, by controlling the terminal functional groups, it is possible to control the physical properties, especially the wettability, of the surface of the SAM over wide ranges.[28,29] The ability to pattern SAMs, and to use these patterns both as resists and to control wettability, forms the basis for a series of techniques for fabricating small structures.[23-26] A substantial range of techniques is now available for fabrication of patterns and structures with dimensions from 0.1 to 10 μm using SAMs. The most versatile of the patterning techniques, microcontact printing (μCP), effectively reproduces features down to approximately 1 μm and can be used to generate features down to 0.1 μm, although the latter techniques are not yet routine.[20-29] This technique is based on the fabrication of a "stamp" – an elastomeric structure having the pattern to be replicated in relief on its surface. The stamp is used to transfer the SAMs surface modification template (e.g., alkanethiol to the surface of gold), and thereby to transfer the stamp pattern to the surface of an appropriate substrate. Structures with edge resolution of 50 nm can be formed using microcontact printing, which is done in an open laboratory without requiring clean room facilities.[30]

The key element to using this approach to the processing of ceramics is to find methods that permit the application of ceramic precursors with sufficient thickness in the patterned regions of an appropriate support. There are several possible strategies to accomplish this: (i) The ceramic or a ceramic precursor can be transferred to the surface in solid form as a suspension, and then whatever processing is required is done on the suspension after patterning on the substrate. (ii) Sol-gel technology can be used to transfer the ceramic precursor as a soluble species (e.g., an alkoxide or some related soluble compound) or as a sol, and then the ceramic or a more immediate precursor is formed by *in-situ* reaction on the substrate. (iii) A third method is to transfer a solution of a simple precursor (e.g., an inorganic salt), and then to deliver another reagent – acid, base, other reactive intermediates – through the vapor phase to the patterned solution to produce the meso-patterned solid.

Microcontact printing led to the development of micromolding techniques, specifically for forming the micromolded polydimethylsiloxane (PDMS) stamps needed to perform μCP. PDMS stamps are easily capable of reproducing feature sizes of 100 nm, and features with sizes less than 50 nm may also be reproduced. Micromolded PDMS (and other polymers) have a range of uses in microfabrication other than μCP: in particular, they should, in their own turn, serve as molds for fabricating patterns of other materials precursors to functional ceramics. For instance, our preliminary work shows that patterned thin films of mesoscopic silicates can be fabricated by micromolding techniques. The nucleation and growth of the thin films on substrates with respect to their hydrophilic/hydrophobic character appears to be a key factor. This also opens the possibility of pattern formation on substrates through the use of techniques described above. Extension of this technique to functional ceramics such as PZT and $BaTiO_3$ on silicon is a great deal of interest in the coupling of piezoelectric and ferroelectric thin films with semiconductors for various MEMS applications.[31] One such application is the construction of a microphone as illustrated in Figure 3.[31]

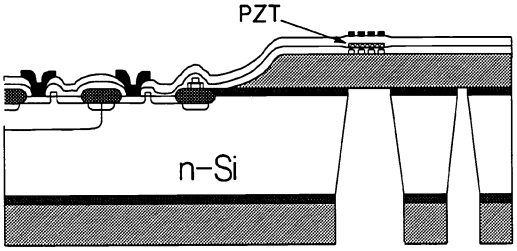

Figure 3: Microphone geometry that utilizes a PZT diaphragm, modified from Ried, *et al.*[31] that proposed to use ZnO instead of PZT as the diaphragm.

IV. DEVICE FABRICATION USING LASER STEREOLITHOGRAPHY

The application of laser stereolithography to the fabrication of ceramic/organic and ceramic/metal composites provides an opportunity for 3D pattern development in micron dimensions. The work described by Prud'homme *et al.*[32] in this proceedings relies on the use of highly loaded (> 55% solids by volume) colloidal suspensions.[33,34] Fundamentally, this process has the potential for achieving better than 10 µm line definition and is akin to the method used by bees in the incremental deposition of honeycomb structures. We pursue two parallel approaches: (i) Photocurable solutions and/or suspensions are applied to the working surface of a machining platform.[7] UV laser light photo cures the pattern on the thin layer rendering it insoluble in specific solvents and rigid enough for subsequent separation from the remaining matrix. (ii) Photocurable suspensions are first converted to flexible tapes. These tapes are then used to fabricate the multilayer patterned composites by the same UV laser light curing of the first approach.[35] The first approach is best suited for the processing of isotropic structures and the second approach is best suited for the processing of multilayered composites.

Our objective is to extend laser stereolithography to the development of two novel smart materials systems and then to analyze their structure-property relationships. The first system utilizes piezoelectric shell transducers referred to as "moonies"[1] and "rainbows."[36] The second system is a class of 1-3 piezocomposite transducers.

Piezoelectric Shell Transducers: There has been a number of developments in both sensors and actuators in recent years.[1-3] Typical strains in piezoelectric ceramics are of the order of 0.1%; too small for some practical applications. For large displacements, on the order of 1 mm, a disk made of a conventional piezoceramic would need to be a meter in diameter, not a practical size for most applications. Thus, a means to amplify strain is essential in order to produce the very large displacements that are required in applications including linear motors, pumps, switches, loud speakers, variable-focus mirrors, and laser deflectors. The magnification mechanisms that have been developed over the years include multilayer ceramic actuators with internal electrodes and the cantilevered bimorph actuator.[2] The multilayer actuator produces a large force at low voltages but the displacement generated tends to be small. Bimorphs, on the other hand, produce large displacements but the forces are small.

Among the various types of piezoelectric ceramic actuators, the moonie and the rainbow offer special interest and promise for they can achieve large displacement/thickness ratios and, at the same time, sustain moderate stresses. The moonie, a metal-ceramic composite composed of a flat ceramic disk and a metal cap, converts the piezoelectrically induced radial displacement in the disk into a large axial displacement at the apex of the cap through bending stresses. The rainbow, a monolithic ceramic dome with varying piezoelectric properties (coefficients) through the thickness, converts the differences of induced meridional strains at the top and bottom faces of the dome into bending stresses which, in turn, induce a large axial displacement at the crown of the dome. These two actuators are conceptually similar in that they both (i) contain a shell structure and (ii) attain large axial displacement at the apex of the shell through induced bending stresses.

The moonie actuator can produce displacements as high as 20 μm at a stress of 0.5 MPa. The rainbow has been shown to be able to produce displacements up to 1 mm. Although the displacement produced by a rainbow actuator can be large, the sustaining stress is relatively moderate. Furthermore, by stacking several moonies or rainbows together, the displacement and force generated can be enhanced depending on how they are arranged.

So far the sizes of rainbows and moonies fabricated to date are in the 1 cm range. Experiments on these[1,3,36] have revealed that the axial displacement/thickness ratio δ/t is approximately inversely proportional to the square of the thickness/diameter ratio, t/d, of the shell, i.e., $\delta/t \propto (d/t)^2$; where t is the thickness of the ceramic dome for rainbows and the thickness of the metal cap for moonies. Therefore, by adjusting the aspect ratio t/d the desired displacements can be generated. In addition, smaller size offers the opportunity for accumulative displacement or force performance by arranging the actuators in series or parallel geometries. It is expected that by reducing the scale to below the 1 mm range, the actuators can be incorporated in microelectronic circuits for smart structural designs. By reducing the scale of sensors and actuators to the scale of microprocessors, a truly smart system can be constructed.

When piezoelectric transducers, such as rainbows or moonies, are produced in the mesoscale, we expect the range of the operating frequencies will be greatly increased, since the resonance frequencies of the extensional, flexural and thickness modes of a plate resonator are proportional to $1/a$, b/a^2, and $1/b$, respectively, where a and b represent the length and thickness of the plate.[37] Thus, these mesoscale devices are expected to be more responsive than similar larger-scale devices at higher frequencies. Also, the reduction of the length and thickness of the actuators will make the effect of electrodes on the frequencies and displacements increasingly more important. Hence, the stiffness and mass of the electrodes should be included in the modeling of the actuators for accurate analysis.

Piezocomposite Transducers: Piezoelectric transducers have been employed as sensors and transmitters of acoustic signals in ultrasound medical imaging, non-destructive testing and underwater acoustics (hydrophones).[1,38] Besides these traditional applications, we envision being able to make hydrophones sufficiently small and sensitive to be used in novel applications, such as measuring fluid pressures in very small volumes.

There are two reasons to use polymer/piezoceramic composites in acoustic transducers: First, the combination of the ceramic with a low-density material (such as polymer) improves the transmission of acoustic energy relative to the pure ceramic situation. Secondly, if a polymer/piezoceramic composite is appropriately designed by exploiting the so-called Poisson's ratio effect, it can have a sensitivity that is orders of magnitude greater than a pure piezoceramic device. In order to explain this effect, we can consider a uniaxial piezoelectric material subjected to a pressure field P. The dielectric displacement in the axial direction D_3 is related to the pressure by the relation $D_3 = d_h P$, where $d_h = d_{33} + 2d_{13}$ is the hydrostatic piezoelectric coefficient. Here d_{33} and d_{13} are the longitudinal and transverse piezoelectric coefficients, respectively. For instance, PZT5A has $d_{33} = 340$ pC/N and $d_{13} = -150$ pC/N. The opposite signs of d_{13} and d_{33} arise because lateral compression of the ceramic implies longitudinal extension (the material has a positive Poisson's ratio). Therefore, $d_h = 40$ pC/N for homogeneous PZT5A which is small compared to d_{33}. If designed appropriately, 1-3 piezocomposites can convert an applied hydrostatic field into a predominantly tensile stress on the rods. The effective d_h^* is controlled by d_{33} of the ceramic, resulting in a larger displacement D_3 than for the pure ceramic.

Experiments for specific polymer/ceramic systems show that composites with high hydrophone sensitivity can be achieved in this manner.[1,39,40] There are other sensitivity measures besides d_h. The voltage coefficient $g_h = d_h/\varepsilon_{33}$ (where ε_{33} is dielectric constant in the x_3–direction), the hydrophone figure of merit $d_h g_h$, and the electromechanical coupling factor k_h are examples. Figure 4 compares $d_h^* g_h^*$ for 1-3 PZT/polymer hydrophone composites to pure PZT. The figure of merit for the composite can be huge relative to pure PZT. Thinner rods or fibers give better performance than thicker rods and that low volume fractions of rods generally give better enhancement than high volume fractions. This discussion suggests that a negative Poisson's ratio polymer can lead to an even larger enhancement as was first proposed by Smith.[38]

Simple models that have been proposed[38,41,42] qualitatively explained the enhancement due to the Poisson's ratio effect. A more sophisticated analysis has been recently given by Avellaneda and Swart[43] using the so-called differential-effective-medium approximation. Indeed, within their approximation, they showed that a 1-3 composite with a negative Poisson's ratio polymer can have a d_h 10 times larger than that of a matrix with a positive Poisson's ratio. An even larger amplification can be obtained if matrices with negative Poisson's ratios are employed. A negative Poisson's ratio material has the counterintuitive property that enables it to shrink in one direction when compressed in orthogonal directions.

In the last ten years there has been a growing body of examples of structures and materials that exhibit negative Poisson's ratios. These include the hinges, springs, and sliding collars of Almgren,[44] the inverted honeycomb frameworks of Kolpakov,[45] the hierarchical laminates of Milton,[46] Gibson and Ashby,[47] and the open cell polymer and metallic foams made by Lakes[48] (with a Poisson's ratio as small as –0.7). All of these examples possess reentrant (non-convex) cell structure, the key feature for transverse contraction under axial compression. In Figure 5, we show a negative Poisson's ratio material built up from unit cells with a reentrant structure as taken from Lakes[49] that has a Poisson's ratio of –0.7. The unit cell is a schematic of Lakes' rendering of a typical cell from the compressed foam structure that he produced. However, such materials have unit cell dimensions larger than 1 mm and are too soft to process useful devices.

Our design goals are threefold: (i) to design composite hydrophones with optimal performance (i.e., to find the best possible matrix and ceramic properties as well as composite structures that optimize combinations of d_h, g_h, and k_h; (ii) to determine the unit cell structure of the matrix that will lead to the desired negative Poisson ratio found in the first design goal subject to the constraint that the material has some minimum stiffness; and (iii) to develop techniques for fabricating the desired devices with features on the micrometer scale. Theoretical and computational techniques already applied to treat simpler properties such as effective conductivity and the elastic moduli are useful in the treatment of these problems.[50-61]

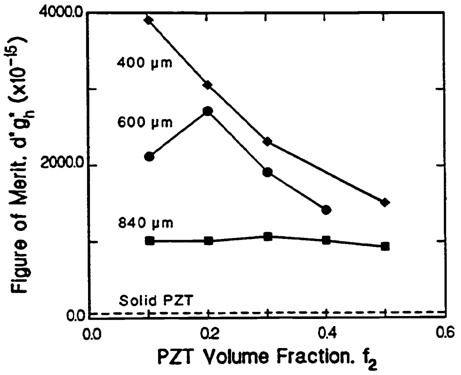

Figure 4: Figure of merit for 1-3 PZT/polymer hydrophone composites as taken from Newnham and Ruschau.[1]

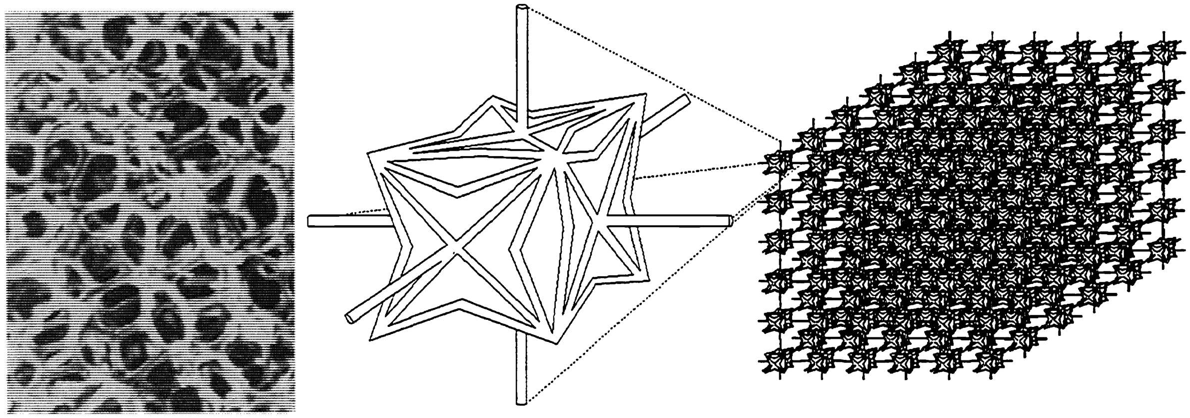

Figure 5: (a) Open cell polymer foam with negative Poisson's ratio.[49] (b) Idealized reentrant unit cell and layered structure.

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