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Modification of Nanostructures via Laser Processing

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Modification of Nanostructures via Laser Processing

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Nanoscience & Nanotechnology at Virginia Commonwealth University

by

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Abstract

MODIFICATION OF NANOSTRUCTURES VIA LASER PROCESSING

By Louis A. Franzel

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Nanoscience & Nanotechnology at Virginia Commonwealth University.

Virginia Commonwealth University, 2013
Director: Dr. Massimo Bertino
Associate Professor of Physics

Modification of nanostructures via laser processing is of great interest for a wide range of applications such as aerospace and the storage of nuclear waste. The primary goal of this dissertation is to improve the understanding of nanostructures through two primary routes: the modification of aerogels and pulsed laser ablation in ethanol.

A new class of materials, patterned aerogels, was fabricated by photopolymerizing selected regions of homogeneous aerogel monoliths using visible light. The characterization and fabrication of functionally graded, cellular and compositionally anisotropic aerogels and ceramics is discussed. Visible light was utilized due to it’s minimal absorption and scattering by organic molecules and oxide nanoparticles within wet gels. This allowed for the fabrication of
deeply penetrating, well resolved patterns. Similarly, nanoporous monoliths with a typical aerogel core and a mechanically robust exterior ceramic layer were synthesized from silica aerogels cross-linked with polyacrylonitrile. Simple variations of the exposure geometry allowed fabrication of a wide variety of anisotropic materials without requiring layering or bonding.

Nanoparticle solutions were prepared by laser ablation of metal foils (Fe and Mo) in ethanol. Ablation of Fe generated Fe$_3$O$_4$ and Fe$_3$C nanoparticles which were superparamagnetic with a saturation magnetization $M_s = 124$ emu/g. Zero field cooled (ZFC) measurements collected at an applied field of 50 Oe displayed a maximum magnetic susceptibility at 120 K with a broad distribution. Field cooled (FC) measurements showed a thermal hysteresis indicative of temperature dependent magnetic viscosity. Pulsed laser ablation of a Mo foil in ethanol generated inhomogeneous nanoparticles where Mo and MoC coexisted within the same aggregate. Formation of these unique nanoparticles is likely due to phase separation that occurs when a high temperature carbide phase cools after the laser pulse terminates. Similarly, magnetic nanoparticle suspensions were generated by pulsed laser ablation of Fe and Mo in ethanol. The formation of several carbide phases with no discernable alloy formation was seen. A decrease in magnetization with a decrease in Fe concentration was seen which was reconciled with the decreased Fe content in the system. However, at Fe concentrations below ~40%, an increase in $M_s$ and $H_c$ was observed which was reconciled with the disappearance of the ε–Fe$_3$C. TEM analysis showed the formation of core-shell nanoparticles and Energy Filtered TEM showed the distribution of Fe-based nanoparticles in the suspensions.
Chapter 1: Motivation
The idea of using light to process and modify nanostructures by localized heating is an interesting concept that has attracted a large amount of attention recently due to its versatility and ease of adaptation. For example, focused laser illumination has been used to produce electrically conductive patterns on flexible displays by melting colloidal metal nanoparticles deposited on polymer substrates. This process removes the need for vacuum photolithography processes, also affords reasonable resolution of ~1 µm, low temperature, and, most importantly, it allows for the use of polymer substrates as illustrated in Figure 1.

![Figure 1](image)

**Figure 1.** Schematic representation of room temperature fabrication of electrically conductive patterns on flexible substrates. a) Colloidal nanoparticle film is deposited onto a substrate. b) Selective laser melting via laser illumination. The nanoparticles melt when illuminated since the laser line coincides with the absorption wavelength of the nanoparticles and because of their depressed melting point. c) Non-melted nanoparticles are washed off with an organic solvent. d) Example of nanoparticle patterning on a polymer substrate. Modified from Ref [1].

Laser irradiation can also be used to synthesize new types of materials. For example, pulsed lasers can be used to ablate metals in liquids. Laser ablation in liquids yields nanoparticles without the need of chemical agents and has been used to produce bioconjugates,
but also exotic nanoparticles such as diamonds, alloys of macroscopically immiscible materials (e.g. AuPt), core-shell particles, and oxides.\textsuperscript{2-11} Size, functionalization and morphology of ablated nanoparticles are controllable through the use of surfactants and capping agents as illustrated in Figure 2.

![Diagram](image)

**Figure 2.** a) Schematic of *in situ* conjugation of gold nanoparticles with aptamers through laser ablation in an aqueous aptamer solution. b) Spacer design and resultant mixed monolayer conjugated nanoparticles. Appropriate aptamer folding was achieved by modifying the surface coverage of conjugated nanoparticles. Modified from Ref [2].

In this review I will show that laser irradiation can be used to modify three dimensional nanostructured materials such as aerogels and to synthesize novel intermetallic compounds. An examination of previous and recent developments within the respective fields will be discussed. A review of current literature will be given in Chapter 2 while work completed will be given in Chapters 3-7. Concluding remarks are given in Chapter 8.
Chapter 2: Literature Review
2.1 Modification of Aerogels and Other Porous Media

Highly porous media, including aerogels, have attractive properties such as excellent
catalytic activity, very low density, high porosity, low dielectric constant, and low thermal
conductivity. These properties make porous materials good candidates for applications that
range from aerospace to the storage of nuclear waste.\textsuperscript{12,13} In response to the technological
interest, several techniques have been developed to modify the features of porous materials and
expand their potential applications. Techniques have been developed that allow one to fabricate
porous materials which are hydrophobic, electrically conductive, or mechanically robust.\textsuperscript{14-17}

With a few exceptions the modification techniques developed to date are not spatially selective
and yield homogeneous, isotropic monoliths.\textsuperscript{18-21} To date directionally inhomogeneous
modification to aerogels has been studied and accomplished through two techniques, layering
and lithography. For example, Jones fabricated a density gradient in a sol for the collection of
cometary dust by combining two solutions comprised of acetonitrile, water, ammonium
hydroxide, and two different amounts of sol.\textsuperscript{20} One sol solution yielded a low density aerogel (5
mg \cdot cm\(^{-3}\)) while the other solution yielded a high density aerogel (50 mg \cdot cm\(^{-3}\)). An aerogel
with a density gradient was formed by gradually pumping the low density precursor into the high
density precursor container, and then pumping the resulting mixture into a mold. By varying the
pumping rates between the two containers, an aerogel with continuous density gradient was
formed in the molds.

More recently work has been done by Wingfield \textit{et al.} which demonstrated the use of
laser illumination to produce homogenous modifications within aerogels.\textsuperscript{21} Sol precursors were
first prepared by derivatizing the pores with 5 – 25\% of trimethoxysilylpropyl
methylmethacrylate (MTMS) or vinyltrimethoxysilane (VTMS) in the parent solution. The wet
gel solvent was exchanged with a solution of 2,2'-azobis-isobutyronitrile (AIBN) in styrene as the initiator and monomer respectively. The polymerization inhibitor of the as received styrene was removed prior to photocrosslinking. The gels were kept refrigerated and in the dark to prevent any polymerization and had nitrogen bubbled through the bathing solution prior to exposure. This deaeration procedure was necessary since oxygen-saturated samples were found to be considerably weaker with a larger pore size and smaller sample than deaerated samples. Uniform exposure to a 30 mW He-Cd laser (325 nm) generated uniformly cross-linked samples due to the photodissociation of AIBN. Exposure to a 175 mW continuous wave laser (266 nm) and to the third harmonic (354 nm) of a pulsed Nd: YAG laser produced surface and three dimensional patterns respectively. Findings were confirmed by optical, SEM, AFM, and FT-IR analyses, demonstrating that polymerization of styrene in derivatized gels lead to a conformal coating of the primary silica particles which could be generated through photodissociation of AIBN.

The generation of ceramic systems through polymer modification is of great interest. For example, Lee et al. showed that through the irradiation of poly(methyl methacrylate) (PMMA) it is possible to make a porous hierarchical polymer/ceramic system. To produce this polymer/ceramic system a precursor solution of PMMA (60 wt %) spheres and ethanol was spin coated onto a silicon wafer. A solution containing silicon grease (10 wt%) and poly(dimethylsiloxane) (PDMS) with hexane as a solvent was then spin coated on top of the previously deposited multilayer of PMMA spheres. The prepared film was irradiated with an electron beam to modify the structures. Analysis of the structure via SEM showed that the PMMA spheres form a disordered close-packed system and that the addition of silicone grease coated and connected the system but did not alter the structure as seen in Figure 3. After
irradiation the PMMA microspheres were reduced in size by roughly 25% (from 20 µm to 15 µm), large pores (micrometer size) were introduced into the system, and that nanometer sized inclusions were formed on the surface of the spheres. X-ray photoelectron spectroscopy revealed that the material covering the PMMA microspheres was silicon oxycarbide SiO$_x$C$_{4-x}$ ($0 \leq x \leq 4$). The authors showed that as the microspheres are contracted by irradiation, the silicon grease is simultaneously reduced to silicon oxycarbide and is tightly bound to the exposed surface of the microspheres through the decomposition of PDMS found in the grease as seen in Figure 3c).

Figure 3. SEM images of a) multilayer of PMMA microspheres, b) multilayer of PMMA microspheres with silicone grease coating, c) porous hierarchical structure formed post-electron irradiation, and d) magnified image of (c). Modified from Ref [22].

More recently Leventis et al. have shown that the production of monolithic silicon carbide aerogels is possible through the use of polyacrylonitrile as the ceramic precursor.\textsuperscript{23}
Silica aerogels were prepared with the addition of AIBN and acrylonitrile. The prepared gels were exposed to a UV light for 5 minutes with the angle of exposure altered frequently to ensure full polymerization of the gel. The gels were then supercritically dried using liquid CO\textsubscript{2}. The polyacrylonitrile silica aerogels were then heated in air at 225 °C for 36 hours to aromatize the polymer. Samples were then pyrolyzed under Ar flow through a series of temperature steps to induce carbothermal reduction of the SiO\textsubscript{2} network, shown in Eq. (1).

\[
\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \quad (1)
\]

Samples processed at 1200 °C were amorphous by XRD while samples processed at 1600 °C generated highly crystalline SiC.

Several other techniques have been reported to produce SiC from SiO\textsubscript{2}/C systems but as in Leventis’ work they usually require high processing temperatures and lengthy reaction times, resulting in the collapse of the porous network and poor porosity (\textasciitilde\textasciitilde 20 m\textsuperscript{2} \cdot g\textsuperscript{-1}).\textsuperscript{23} Stucky et al. have shown that by utilizing a reducing agent under autogenic conditions it is possible to reduce the temperature necessary to generate a ceramic structure from a SiO\textsubscript{2}/C system, as shown in Eq. (2).\textsuperscript{24}

\[
\text{SiO}_2 + \text{C} + 2\text{Mg} \rightarrow \text{SiC} + 2\text{MgO} \quad (2)
\]

In this case the SiO\textsubscript{2} is reduced magnesiothermally as described by Eq. (3),

\[
\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO} \quad (3)
\]

rather than through the carbothermal method mentioned earlier.\textsuperscript{23} In experiments by Stucky et al. ordered hierarchical macro-mesoporous SiO\textsubscript{2}/C precursor was synthesized, mixed with magnesium turnings, sealed in an iron reaction vessel and heated to 700 °C.\textsuperscript{24} A large portion of the prepared sample (estimated at \textasciitilde\textasciitilde 50 wt %) was found to be magnesia (MgO) and Mg\textsubscript{2}Si. The MgO and Mg\textsubscript{2}Si were removed by washing in 2 M HCl. The final product showed several cubic
SiC phases as indexed through XRD as well as selected area diffraction through TEM, while the ordered macroscale structure was retained as confirmed by SEM. Energy dispersive X-ray spectroscopy analysis also confirmed that the final product was primarily composed of silicon and carbon without magnesium impurities.

Sandhage has shown that the capability of gases to easily migrate through pores or narrow cavities of high aspect materials allows for the introduction of new chemistries via gas/solid displacement within monoliths. The conversion of diatom frustules (single-celled algae formed microshells) composed of SiO$_2$ to frustules entirely composed of another oxide, MgO and TiO$_2$, was attained through low temperature (T<1000 °C) reduction with Mg and TiF$_4$ respectively as seen in Figure 4.

![Figure 4](image)

**Figure 4.** SEM images of diatom frustules a) before magnesiothermal reduction and b) after magnesiothermal reduction. The frustule in a) was converted from SiO$_2$ to an MgO replica after reduction. Modified from Ref [25].

### 2.2 Laser Ablation in Liquids

To date, laser ablation in liquids has been mostly employed to produce suspensions of noble metal particles. Amendola et al. have ablated iron and investigated the effect that different organic solvents have on the formation of iron species through pulsed laser ablation. A pulsed laser was used to ablate an iron plate into: tetrahydrofuran (THF), acetonitrile,
dimethylformamide (DMF), dimethylsulfoxide (DMSO), toluene, and ethanol. By varying the solvent the authors were able to vary species generated during laser ablation. Ablation in THF resulted in metal iron particles with an oxide layer which formed due to oxygen present in solution. XRD confirmed the presence of magnetite/maghemite and metal iron. Ablation into acetonitrile and DMF resulted in polycrystalline particles which were a mixture of magnetite and maghemite. Laser ablation in DMSO resulted in nanoparticles with a cubic iron composition surrounded by a thick amorphous carbon matrix. This carbon matrix helps prevent the formation of an oxide layer as well as preventing the growth and aggregation of nanoparticles. Ablation in toluene resulted in particles with a thick graphitic shell surrounding an amorphous core. It was not possible to determine if the core was composed of amorphous iron or amorphous iron carbide. Employing ethanol as the ablation solvent resulted in the formation of two distinct nanoparticle species, iron carbide (Fe₃C) and magnetite. These results demonstrate that the reaction between the solvent and the ablated material within the plasma plume generated during pulsed laser ablation can be tuned to generate particles of a different material than the starting target.

Yang has also shown that nanocrystalline diamond can be synthesized via pulsed laser ablation of a graphite-water interface (Figure 5). The laser induced plasma contains atomic clusters with sp² bonding and their ions which are formed from the ablated solid. Since the pressure-temperature region is found to be on the order 10-15 GPa and 4000-5000 K, respectively, the nucleation and phase transition from graphite to diamond is energetically more favorable to take place over the formation of graphite in the plasma. This shows that the production of nanomaterials different from the initial material can form due to pressure and temperature affects due to the localized heating inside the plasma plume.
Figure 5. a) TEM image of nanodiamonds generated by laser ablation of a graphite-water interface, b) electron diffraction pattern and c) indexing. Modified from Ref [8].

Barcikowski et al. have shown that Au nanoparticles ablated in the presence of aptamers can be used in biological assays. Au was ablated for 2 minutes in a buffer of Tris(hydroxymethyl)-aminomethane with different concentrations of an aptamer (miniStrep). They found that the hydrodynamic diameter ($d_h$) increased from 7 nm to ~70 nm as the aptamer concentration increased from 0 to 5 µM. The increase in $d_h$ could be reconciled with the aptamer coverage of the nanoparticles. At low surface coverage the aptamer was prone to lay flat due to non-specific binding of nitrogen groups giving a small $d_h$. At high surface coverage the aptamer formed a more perpendicular arrangement due to electrostatic repulsion, increasing the $d_h$. Au nanoparticles were then functionalized with the aptamers miniStrep and anti-PSMA (5 µM) and the functionality was tested using agglomeration-based assay, dot blot assay, and tissue microarray. The laser ablated Au particles proved viable in all three tests, demonstrating the wide application of aptamer conjugated nanoparticles produced by laser ablation for bio-analytical applications without harmful byproducts.

More recently, Niu et al. demonstrated the formation of MgO hollow shell nanospheres through pulsed laser ablation of a Mg target in different organic solvents by the outward
diffusion of Mg atoms at the oxide interface of the ablated Mg nanoparticles (Kirkendall effect). The authors were able to vary species generated during laser ablation by varying the solvent. Ablation in n-hexane resulted in solid Mg nanoparticles with oxide formation occurring during storage. Solid Mg nanoparticles generated through pulsed laser ablation could be converted into hollow MgO spheres by exposure to air for several days or by incubating the nanoparticles in ethanol at 60 °C for 150 minutes. Ablation into ethanol produced solid square nanoparticles composed of MgO. The lack of hollow MgO spheres was due to the rapid oxidation of nanoparticles in the more oxygen rich ethanol. This rapid oxidation did not allow for the exchange of Mg/O atoms through the Kirkendall effect. Ablation into a mixture of n-hexane and ethanol (5:1) resulted in the formation of MgO hollow shell nanoparticles. The Mg nanoparticles began to oxidize as they cooled in the surrounding solvent, generating a diffusion couple of Mg/O at the interface. Mg ions are driven to Mg/O interface at the surface of the nanoparticles by the high temperature of the Mg core thereby generating hollow MgO nanospheres through the Kirkendall effect (Figure 6).
2.3 Results and Unresolved Issues

The modification of aerogels and other porous materials via laser processing has been investigated. Gradient density aerogels and selective area polymerization within aerogels via laser irradiation affords unique and interesting modifications to preexisting monolith systems. Specialized polymers can be used as ceramic precursors when coupled with specific processing conditions. The use of magnesium or other reducing agents (e.g. sodium) may also be used to generate ceramics from SiO₂/C systems, similar to ceramic precursor polymer work done by Leventis et al. However, several unresolved issues still need to be addressed. The methods reported in the literature are non-directional and often employ high
temperatures, which substantially decrease porosity. To date no directional modification process has been reported which allows one to tune composition and mechanical properties at low temperatures. Chemical reduction of ceramic precursors within aerogels could yield unique results which could help modify current processing techniques used in the formation of such ceramic systems.\textsuperscript{24,26} Combining photopolymerization techniques from Wingfield \textit{et al.} with the use of ceramic precursor polymers (e.g. acrylonitrile) as described by Leventis \textit{et al.} may allow for the production of anisotropic carbide or oxycarbide ceramics compared to the uniform ceramic monoliths currently produced through this method.\textsuperscript{21,23} In addition, the use of magnesium could potentially reduce both the processing time and temperature.

Modification of nanostructures through pulsed laser ablation in liquids has been shown to produce novel nanoparticle alloys as well as various species depending on the solvent and ablation material.\textsuperscript{6,9} By selecting various solvents the formation of carbide, oxide and pure metal nanoparticles was achieved.\textsuperscript{5} Novel alloys have been produced by synchrotron irradiation which has some characteristics in common with laser ablation. However, the available reports are few and far in between. Many novel alloy systems have been theoretically predicted but little work has been to verify whether or not these alloys can be produced outside of \textit{ab initio} calculations and further work is needed to verify these effects.\textsuperscript{5,8,27-30} Novel carbide, oxide and metal nanoparticles have been produced by pulsed laser ablation. Factors affecting the formation and properties of laser ablated nanoparticles, e.g. phase transitions and solvents, must be further investigated.\textsuperscript{3-11}
Chapter 3: Functionally Graded Aerogels
3.1 Introduction

Highly porous materials like aerogels have attractive properties such as extremely low specific gravity, thermal conductivity and dielectric constant, which are often coupled to a remarkable catalytic activity making them suitable for applications ranging from aerospace uses to nuclear waste storage.\textsuperscript{12,13} In response to this technological interest, methods are being developed to enhance the characteristics of porous materials and expand their potential applications. For example, porous oxides can now be fabricated which are hydrophobic, electrically conductive, or mechanically robust.\textsuperscript{14-17} Most modification techniques, however, are not spatially selective and yield homogeneous, isotropic monoliths. Anisotropic and cellular materials, which are often superior to homogeneous ceramics (for example, as honeycombs in sandwich structures), are usually fabricated with layering or extrusion techniques which yield medium to low-porosity ceramics.\textsuperscript{31,32}

Fabrication of highly porous anisotropic monoliths was addressed in part by previous work, by synthesizing nanoparticles \textit{in situ} within the pores of sol-gel materials using photolithography or by layering sols with different density.\textsuperscript{18-20,33} The nanoparticles introduced additional functionality (e.g., luminescence) into porous materials but they did not affect the matrix. Going a step further, here we use photopolymerization to modify the characteristics of selected regions of the matrix itself and fabricate anisotropic porous materials such as functionally graded aerogels, cellular aerogels and compositionally anisotropic porous ceramics. For this, porous oxide networks, surface derivatized with a suitable moiety (e.g., an acrylate, by reacting trimethoxysilylpropyl methacrylate with the pore walls) are first prepared following conventional sol-gel procedures. A monomer and a photoinitiator are added to the gelation solution allowing one-pot synthesis, thus avoiding time-consuming solvent exchange
steps. Polymerization engages the surface moiety and forms a conformal coating on the pore walls which cross-links the oxide nanoparticles of the backbone of the material. The resulting cross-linked monoliths are mechanically strong, yet lightweight because the polymer does not clog the pores. Cross-linked monoliths with physical properties comparable to those synthesized by thermally activated polymerization can also be obtained by photopolymerization. However, most conventional photoinitiators are triggered by ultraviolet (UV) light, which has several disadvantages for fabrication of anisotropic materials. For instance, short-wavelength UV light does not penetrate deeply within a monolith because of absorption by the organics. More importantly, scattering from the polymer and from the oxide backbone prevents fabrication of well-defined patterns that reach deep into the bulk. As we have shown recently, cross-linked patterns could be obtained with UV light at 255 nm, which did not penetrate for more than a few microns into the material. Patterns penetrating deeper into the bulk were obtained with 320 and 365 nm light, nevertheless scattering limited patterning to isolated lines. In this work most technical issues have been resolved by using a visible-light (532 nm) photoinitiator. Because of the longer wavelength, penetration was only limited by absorption from the photoinitiator, scattering was negligible, allowing fabrication of a large number of anisotropic materials by simple modifications of the exposure set-up.

3.2 Experimental

Materials. Alkoxides used in our experiments were tetramethyloctosilicate (TMOS) and trimethoxysilylpropyl methylnethacrylate (MTMS); monomers were methyl methacrylate (MMA), hexanedioldiacrylate (HDDA), pentaerythritol tetra-(3-mercaptopropionate) and acrylonitrile; the initiators were Eosin Y and diethanolmethylamine; solvents were methanol
(MeOH) and ethanol. All reagents were ACS grade and were used as received from Acros organics.

**Preparation of monoliths for the fabrication of functionally graded monoliths.** Silica gel monoliths functionalized with methacrylate groups and pre-loaded with a photoinitiator and a monomer were prepared in a single pot following slight modifications of established procedures.\(^{17-20,33,34}\) Typically, 3.5 ml of TMOS and 0.3 ml of the functionalizing trimethoxysilylpropyl methacrylate (MTMS) were dissolved in 4.5 ml of methanol. A second solution consisting of 1.5 ml methanol, 1.5 ml H\(_2\)O, 3 ml of methylmethacrylate, 0.15 ml of dimethyl methylamine and 0.02 g of Eosin Y was prepared separately. See also Table 1. The two solutions were mixed, agitated vigorously for a few seconds and poured into molds. The basic environment introduced by the amine lead to gelation within 15-30 minutes. After exposure, the alcogels were supercritically dried following the procedure indicated below to yield aerogels.

**Preparation and processing of compositionally anisotropic ceramics.** It has been recently shown by Leventis *et al.* that pyrolysis of acrylonitrile polymerized inside the pores of a silica aerogels results in the formation of SiC.\(^{33}\) We reasoned that photopolymerization of acrylonitrile, followed by pyrolysis, could be used to change the local chemical composition of aerogels. Wet gel monoliths were prepared as follows. 3.5 ml of TMOS and 0.3 ml of trimethoxysilylpropyl methacrylate were dissolved in 1.5 ml of methanol. A second solution consisting of 1.5 ml methanol, 1.5 ml H\(_2\)O, 0.15 ml dimethyl methylamine and 0.02 g of Eosin Y was prepared separately. See also Table 1. The two solutions were then mixed and acrylonitrile was added to reach a concentration between 10% and 34.5% w/w. Gelation occurred within a few minutes. After photopolymerization and supercritical drying, aerogels
patterned with polyacrylonitrile were heated at 225 °C in air to aromatize the polymer. The monoliths were then processed at temperatures between 1000 and 1200 °C for several hours under nitrogen flow. Temperatures could not exceed 1200 °C, to prevent the unexposed part of the monolith to melt (the melting temperature of silica being around 1200 °C). These processing temperatures allowed the recrystallization of silica into cristobalite and the formation of carbon impurities, but they were too low to allow SiC formation, which occurs around 1600 °C.

**Photonitiator.** The photoinitiator system consisted of an organic dye photosensitizer (Eosin Y) and a tertiary amine (dimethyl methylamine) as a co-initiator. Upon light absorption, charge is transferred between the dye and the coinitiator resulting in a reduced radical dye species and a coinitiator radical capable of initiating polymerization. The dye-tertiary amine system chosen for our experiments is not sensitive to oxygen and has a tunable wavelength. For example, Eosin Y absorbs strongly in the region of the laser line employed for our experiments (532 nm); however, Rose Bengal could be used with a red light source.

**Exposure.** Samples were exposed to the green (532 nm) light of a diode-pumped solid state laser (Coherent Verdi) operated typically with a power of 1 W. To achieve functionally graded materials, the beam was expanded through a lens so as to cover the diameter of the sample. The cylindrical samples were then exposed longitudinally. Samples which were cross-linked in only one specific region were obtained by exposing transversely to an expanded beam. To create grid patterns, a pinhole was interposed between the sample and the collimated laser beam. The sample was moved in front of the pinhole by means of an X-Y programmable translation stage (Newport XPS C-8). Exposure times were between 2 and 15 minutes for the large-scale patterns; grids were obtained by scanning the sample in front of the beam with a velocity of 1 mm/s.
Supercritical drying. After exposure, monoliths were washed repeatedly with ethanol to remove unreacted precursors and dried in supercritical ethanol. For drying, we employed using a 2-liter Parr pressure vessel equipped with three external heaters supplying a maximum power of 800 W. The samples were placed inside the vessel and about 500 ml of excess ethanol were added to prevent complete evaporation of the solvent within the pores of the gels before the supercritical temperature was reached. The vessel was then heated to reach supercritical conditions (240 °C, 60.6 atm), left for about 30 minutes at the supercritical temperature and pressure and then slowly vented. Note: use of excess ethanol can lead to overpressure. The manual of the pressure vessel should be consulted and the maximum amount of excess solvent should be calculated to ensure that the pressure rise is compatible with the pressure rating of the vessel.

Characterization. Monoliths were characterized with Raman spectroscopy (Horiba Jobin Ivon HR800 equipped with 532 and 633 nm lasers), surface area measurements (Quantachrome Autosorb I), nanoindentation (Hysitron TS 70), Transmission Electron Microscopy (TEM, Zeiss Libra 120) and X-ray Diffraction (XRD, Panalytical X'Pert Pro MRD).

Table 1. Composition of precursor solutions used for the preparation of alcogels for all classes of solids produced in the current experiments.

<table>
<thead>
<tr>
<th>Precursors Common to all Sample Classes</th>
<th>6.0 ml MeOH, 3.5 ml TMOS, 0.3 ml MTMS, 1.5 ml H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class-Specific Precursors</td>
<td></td>
</tr>
<tr>
<td>Functionally Graded Aerogels</td>
<td>Compositionally Anisotropic Ceramics</td>
</tr>
<tr>
<td>3 ml MMA</td>
<td>Acrylonitrile (10% to 34.5% w/w)</td>
</tr>
</tbody>
</table>

20
3.3 Results and Discussion

Functionally graded monoliths were produced by creating an exposure gradient. Modulus, porosity and hydrophobicity varied along the illumination axis. Native aerogel monoliths with a cross-linked end that could be glued or fastened to a mechanical support were fabricated by uniform illumination of selected areas. Cellular aerogels such as honeycombs were fabricated by translating a sample in a grid pattern in front of a collimated beam. Materials with anisotropic composition and crystallinity were fabricated by pyrolysis of the cross-linking polymer. All details of alcogel preparation, exposure and post-illumination processing of all materials classes are reported in the Experimental section, together with a table which summarizes the composition of the precursor solutions for all materials classes. Our results have immediate technological implications, because they facilitate handling of aerogel monoliths and they allow fabrication of building blocks such as cores of sandwich structures out of porous materials. From a fundamental perspective, the new class of materials presented in this work combines the properties of native and cross-linked aerogels within a single monolith and is hardly accessible to other fabrication techniques.

Figure 7a) shows a functionally graded silica aerogel monolith fabricated by exposing a cylindrical wet-gel as described above along the longitudinal axis. Light absorption by the photoinitiator created an exposure gradient which resulted in a polymerization gradient. Loose polymer and photoinitiator byproducts were washed off by solvent exchange with ethanol. Nevertheless, some Eosin Y dye remained trapped in the polymer network and served as a polymerization indicator. Luminescence from the residual dye under black light allowed visualization of the polymerized region. Modulus, surface area and contact angle were measured at different locations along the monolith as shown in Figure 7b). The mechanical modulus
decreased, while the surface area increased along the longitudinal axis, consistent with the polymerization gradient that was observed in Figure 7a. Hydrophobicity also varied along the illumination gradient. In the least exposed regions, the contact angle of the droplets was small (< 20°). The contact angle at the most exposed regions was around 85° confirming that the cross-linking polymer engaged the acrylate grafted to the silica framework and coated the pore walls. The contact angles measured in our experiments are lower than those typically reported in the literature for hydrophobic aerogels, and this requires an explanation. The contact angle of monoliths cross-linked with polystyrene or fluorinated polymers is between 130° and 160°, and aerogels derivatized (but not cross-linked) with trifluoropropyl trimethoxysilane has a contact angle of 128° for a fluorosilane/TMOS mole ratio of 1.5% (in our case, the methacrylate-silane/TMOS mole ratio was 2.7%). The comparatively low contact angle of methacrylate-derivatized aerogels is likely due to the nature of the methacrylate molecule. Methacrylate contains C=O polar groups and it is not as hydrophobic as, say, fluorinated hydrocarbons. The presence of C=O groups, for example, explains why methacrylate monomers do not phase separate when mixed with a water-ethanol solution, which was the key to our one-pot synthesis of alcogel precursors. Thus, it is understandable that methacrylate-containing aerogels remain somewhat hydrophilic even in the regions with the longest exposure, where the pore walls are coated and cross-linked with poly(methyl methacrylate). Unexposed regions of aerogels had contact angles below about 20° and we also noticed that water slowly penetrated inside the monoliths. Overall, the behavior of methacrylate-derivatized and cross-linked aerogels is comparable to that of aerogels cross-linked with polyurea reported by Leventis et al. In that work the authors noticed that the contact angle decreased from about 60° to about 20° because of penetration of the water inside the gel network. The only difference between polyurea and
poly(methyl methacrylate) is that penetration was negligible in regions with the longest exposure.

In Figure 7c) we also report Raman spectroscopy measurements which further corroborate our findings. The carbon–carbon double-bond peak at 1636 cm$^{-1}$ which is an indicator of allyl polymerization was well-evident in the least exposed regions, but it was almost undetectable in the most exposed regions.$^{35,36}$

![Figure 7](image)

**Figure 7.** Digital camera images of a functionally graded monolith prepared by photopolymerization with a beam coming from the direction indicated by the arrow. a) Wet-gel monolith illuminated with a black light. Luminescence is from residual Eosin Y trapped into the polymer network. b) Dried aerogel monolith. Surface area, Young's modulus and contact angles were measured at different points along the longitudinal axis. c) Raman spectra were taken at different locations of the monolith using an excitation wavelength of 532 nm. The peak at 1636 cm$^{-1}$ is attributed to the carbon–carbon double-bond and can be used to detect polymerization of the acrylate moiety used to derivatize the pore walls.$^{35,36}$ The peak at ~ 1700 cm$^{-1}$ is attributed to the C=O stretch.
Aerogels that could be fastened and integrated into mechanical systems and cellular aerogels were fabricated by uniform exposure of selected regions. Figure 8a) shows that a cross-linked section was fabricated within an otherwise native aerogel, allowing bonding to a glass slide with a cyanoacrylate adhesive. Figure 8b) shows that holes could be drilled and tapped into a polymer-reinforced region to host a fastener. Figure 8c) shows that cellular solids such as a square honeycomb could be fabricated by patterning cross-linked grids inside a native silica aerogel monolith. Due to the use of visible light and negligible scattering, patterns penetrated for up to 10 mm inside the monolith with no appreciable resolution loss.

**Figure 8.** Digital camera images of native aerogel monoliths with selected areas reinforced by photocrosslinking. a) Cross-linked region glued to a glass slide with cyanoacrylate adhesive. Shearing of the glued region from the rest of the aerogel was not observed, as is, instead, commonplace for native aerogels. b) A square grid honeycomb pattern. c) Fastener screwed into a hole drilled and tapped for a 2-64 thread inside a photocrosslinked region.
To produce porous and non-porous ceramics with heterogeneous composition and crystallinity, we photopolymerized acrylonitrile in selected regions of hydrogels. Polyacrylonitrile was chosen because it is often used as a carbon source in the synthesis of carbides and oxycarbides. Following photopolymerization and supercritical drying, aerogels were first treated at 225 °C for 8 hours in air to aromatize the cross-linking polyacrylonitrile. The exposed regions turned brown as shown in Figure 9a). The gels were then pyrolyzed under nitrogen gas flow. The characteristics of the materials were varied by varying monomer concentration in the parent solution, duration and temperature of pyrolysis. For acrylonitrile concentrations below about 11.5% w/w in the gelation solution, pyrolysis at temperatures between 1000 and 1200 °C (the melting temperature of silica) for 24 - 48 h yielded dense materials with a surface area below 2 m² · g⁻¹. For those monoliths, Raman and X-ray diffraction spectra from exposed and unexposed regions are compared in Figure 9b) and, respectively, 9c). Unexposed regions exhibited broad peaks at energies and, respectively, angles that were consistent with those of amorphous silica. The spectra of exposed regions exhibited sharp peaks, which could be reconciled with cristobalite. Cristobalite formation is not surprising, since it is known that metal and carbon impurities help crystallization of amorphous silica. Recent work has also showed that aromatic carbon impurities accelerate crystallization of silica into cristobalite. Figure 9d) shows patterns obtained using an acrylonitrile concentration of 34.5% w/w in the gelation solution, followed by aromatization and pyrolysis at 1150 °C for 24 h. Exposed regions turned black, and Raman spectra exhibited peaks at 1327 and 1604 cm⁻¹ indicating the presence of disordered carbon.
Figure 9. a) Digital camera image of a monolith cross-linked with acrylonitrile after aromatization. Raman, b) and XRD, c), spectra are compared for cross-linked and native regions. Exposed regions exhibit sharp peaks that can be reconciled with cristobalite (sticks in Figure 9c). d) Image of a pattern obtained using high concentrations of acrylonitrile in the parent solution. The Raman spectrum of the black regions is shown in Figure 9b) (C-rich pattern).
3.4 Conclusion

In conclusion, photopolymerization with visible light allows fabrication of anisotropic aerogels and ceramic materials. Materials with very different characteristics can be produced by simple variation of the illumination and processing conditions. The resulting materials comprise a new class of porous anisotropic solids that are difficult to fabricate with conventional fabrication methods and pave the way to several potential applications. For instance, functionally graded aerogels are likely candidates for ultra-lightweight energy absorbers. Selective reinforcement of regions subject to shear and mechanical stress allows integration of native aerogels into mechanical systems. Cristobalite patterns are being considered to prevent sagging of amorphous silica at high temperatures.\textsuperscript{41} Carbon inclusions are known to increase mechanical strength, thermal and electrical conductivity of ceramics and could therefore be used to dissipate heat in high temperature applications, to increase mechanical strength in areas of strong solicitation, or, when interrupted, to detect materials failures in ceramic components.\textsuperscript{38}

Acknowledgement.
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Chapter 4: Regioselective Cross-Linking of SiO₂ Aerogels with Magnesium Silicate Ceramics
4.1 Introduction

Aerogels are a class of promising materials with attractive properties such as excellent catalytic activity, low thermal conductivity, low dielectric constant, and low thermal conductivity. These properties make porous materials good candidates for applications that range from aerospace to the storage of nuclear waste.\textsuperscript{12,13} In response to the technological interest, several techniques have been developed to modify the features of porous materials and expand their potential applications. Techniques have been developed, for example, that allow one to fabricate porous materials which are hydrophobic or electrically conductive.\textsuperscript{14-16} One of the main issues with aerogels is mechanical fragility, which was addressed in a seminal paper by Leventis in 2002.\textsuperscript{17} In the methodology developed by Leventis, the pore walls are first derivatized with a polymerizable moiety (e.g. an acrylate group). The gelation solvent is then exchanged with a solution of a monomer and an initiator. Polymerization engages the derivatizing moiety and cross-links the skeletal oxide particles. Once unreacted monomer and unbound polymer are removed by repeated washing in acetone, the gels are dried supercritically. The resulting aerogels are mechanically strong because of the cross-linking, yet highly porous because the polymer is bound to the surface and it conformally coats the skeletal nanoparticles. Leventis’ procedure yields monoliths with a modulus in the 100 - 700 MPa range, a density of \(\sim 0.3 \text{ g \cdot cm}^{-3}\) and a surface area of \(100\text{-}300 \text{ m}^2 \cdot \text{g}^{-1}\). Cross-linked aerogels are now being considered for applications which include absorbents, chromatography columns, ballistic absorption, and aerospace components.\textsuperscript{17,26,34,42}

More recently, our group developed an aerogel cross-linking methodology where polymerization is photoinitiated.\textsuperscript{21,26} Photocross-linked aerogels have physical properties that are comparable to those obtained by thermally initiated polymerization. Photocross-linking has
an important advantage over thermal cross-linking because it allows one to reinforce only selected regions of aerogels. Entirely new types of composites can be now fabricated which include honeycomb and functionally graded aerogels.26

While extremely promising, polymer cross-linking, however has an important limitations, that is, the working temperature of the composites cannot exceed that of the polymer (250 - 300 °C in most cases). Ceramic cross-linking would dramatically increase the accessible temperature range. Here, we demonstrate that aerogels can be cross-linked with ceramics at their outer geometric boundary by reacting elemental Mg with silica aerogel monoliths cross-linked with polyacrylonitrile (X-PAN aerogels). Such X-PAN aerogels were prepared in one-pot by improving over literature procedures.23,43 After gelation, free radical polymerization was photoinitiated in the pores engaging the surface acrylates. Cross-linked gels were dried supercritically and PAN was stabilized oxidatively (225 °C in air). The monoliths were then wrapped with Mg. Oxidized PAN was pyrolytically converted (850 °C) into a carbon form that consists of disordered, planar layers (turbostratic carbon).44,45 This carbon form catalyzed solid-state reactions between MgO and SiO2. The resulting aerogel monoliths consisted of a mechanically robust outer crust and a native aerogel core. The crust consisted of cristobalite, MgO, forsterite (Mg2SiO4) and enstatite (MgSiO3). The magnesiosilicates cross-linked SiO2 nanoparticles, thus explaining the improved mechanical properties of the crust. Masking allowed introduction of carbon only in specific areas, yielding ceramic monoliths with spatially dependent chemical and physical properties. Our results are relevant for several reasons. In the first place cross-linking with ceramics extends the service temperature of cross-linked aerogels from ~200 °C (beyond which most polymers decompose) to the densification temperature of silica aerogels (~900 °C). Further, applying ceramic cross-linkers only at the outer geometric
boundary of silica aerogel monoliths yields robust materials that maintain the desirable properties of the native silica core and thus are ideal for high temperature thermal insulation. Finally, photocrosslinking allows one to reinforce only the regions of monoliths that are subject to the largest mechanical solicitations, which further reduces the weight of the composites.

4.2 Experimental

Tetramethylorthosilicate (TMOS), trimethoxysilylpropyl methylmethacrylate (MSMA), methyl methacrylate, acrylonitrile (AN), Eosin Y, N,N-methyldiethanol amine and ethanol were all reagent grade and were purchased from Acros Organics. Magnesium turnings (99.9%) were purchased from Alfa Aesar.

Silica aerogels cross-linked with PAN (X-PAN aerogels) were prepared as follows. First, silica wet gels, functionalized with methacrylate groups and pre-loaded with a photoinitiator and 15 w/w of monomer (acrylonitrile), were synthesized in one-pot following a modification of established procedures.12,18-21,23,34,42 Two solutions, one containing ethanol (3.35 mL), TMOS (3.65 mL) and MSMA (0.15 mL) and one containing AN (2.3 mL) (or methyl methacrylate, 2.64 mL), ethanol (3.35 mL), Eosin Y (0.1 mg) and N,N-methyldiethanol amine (250 µL) as photoinitiators, and water (1.5 mL), were mixed, agitated vigorously for a few seconds and poured into plastic cylindrical molds with a diameter of 7 mm.26,35,36 The basic environment induced by the amine led to gelation within 15 - 30 min. After gelation the samples were kept in the molds and exposed to the green (532 nm) light of a diode-pumped solid state laser (Coherent Verdi).26 The laser was typically operated with a power of 1W and the beam was expanded with a divergent lens to a diameter slightly larger than the diameter of the samples. Silica aerogels derivatized with acrylate groups, but devoid of PAN (referred to as MSMA aerogels) were
prepared following the procedure described above by replacing the monomer (AN) with ethanol.  

*Native silica* aerogels were prepared by replacing MSMA with TMOS and the monomer (AN) with ethanol. After exposure, wet gels were removed from the molds, washed repeatedly with ethanol to remove unreacted precursors and loose polymer and were dried by taking the pore-filling solvent (ethanol) above its critical point ($T_c = 250 \, ^\circ\text{C}$, $P_c = 60.6 \, \text{bar}$). Subsequently, **X-PAN** aerogels were placed in a tube furnace and were heated at 225 °C for 8 h in air to oxidize PAN. The samples were then wrapped in Mg turnings and processed at 850 °C for 12 hours under nitrogen flow. Those samples are referred to as **Mg-PAN** aerogels. For comparison, **MSMA** and **native silica** aerogels were also wrapped in Mg turnings and processed at 850 °C for 12 h under flow of nitrogen. Those samples will be referred to as **Mg-native** aerogels. In control experiments, oxidized **X-PAN**, **MSMA** and **native silica** aerogels were processed (a) at 850 °C without Mg wrapping; and, (b) at 650 °C (that is, below the carbonization temperature of oxidized PAN) with Mg wrapping. Mg-wrapped **X-PAN** aerogels were also processed at 850 °C, but without the 225 °C aromatization step. **MSMA** aerogels yielded monoliths with the same characteristics of **Native silica** aerogels and are not detailed within this study. All sample abbreviations and processing steps are shown in Scheme 1 and Table 2.

All samples were characterized by X-Ray diffraction (XRD, Panalytical X’pert Pro MRD), nanoindentation (MTS nanoindenter XP), scanning electron microscopy and energy dispersive spectroscopy (SEM and EDS, Hitachi S4700), and transmission electron microscopy (TEM, Zeiss Libra 120). The porous structure was probed with N$_2$ sorption porosimetry (Micromeritics 2020).
Table 2. Sample descriptions and abbreviations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-PAN</td>
<td>Silica aerogel cross-linked with polyacrylonitrile (PAN)</td>
</tr>
<tr>
<td>MSMA</td>
<td>Silica aerogels derivatized with acrylate groups (devoid of PAN)</td>
</tr>
<tr>
<td>Native silica</td>
<td>Silica aerogels (OH-terminated)</td>
</tr>
<tr>
<td>Mg-PAN</td>
<td>X-PAN aerogel processed at 225 °C for 8 h in air to oxidize PAN and then processed with Mg turnings at 850 °C for 12 hours under N₂ flow.</td>
</tr>
<tr>
<td>Mg-Native</td>
<td>Native silica aerogel processed at 225 °C for 8 h in air and then processed with Mg turnings at 850 °C for 12 hours under N₂ flow.</td>
</tr>
</tbody>
</table>
Scheme 1. Sample preparation and processing steps.
4.3 Results and Discussion

4.3a. Materials synthesis.

Polyacrylonitrile-cross-linked silica aerogels (X-PAN aerogels) have been synthesized previously via a grafting-from process where surface induced photopolymerization of acrylonitrile (AN) was induced by a free radical initiator covalently attached to the native silica framework. More recently, we have shown that photopolymerization is an effective tool for inducing grafting-to-crosslinking, allowing even synthesis of functionally graded silica aerogels by cross-linking selected regions within monoliths. Here, in a modification of our protocol, X-PAN aerogels are synthesized by free radical photopolymerization of AN engaging a MSMA-modified silica backbone. AN and initiator were included in the silica sol, therefore gelation and photocrosslinking were sequentially induced in a single pot without need for solvent exchange. The photoinitiator consisted of an organic dye (Eosin Y) and N,N-methyldiethanol amine (co-initiator). Photoinduced electron transfer between the dye and the amine results in the reduced dye and a co-initiator radical capable of initiating polymerization. Eosin Y was chosen because it absorbs strongly at the wavelength of the laser employed here (532 nm). After supercritical drying of X-PAN wet-gels, X-PAN aerogels were processed as described in detail in the Experimental Section.

4.3b. Materials characterization.

Photographs of typical samples are shown in Figure 10. Native and X-PAN aerogels processed at 850 °C without Mg turnings were translucent (Figure 10a and 10b). Native aerogels wrapped in Mg turnings and processed at 850 °C (referred to as Mg-native aerogels) exhibited a
transparent core and a thin (< 0.5 mm) white crust (Figure 10c). Analogous results were obtained for acrylate-terminated aerogels (MSMA aerogels). X-PAN aerogels oxidized at 225 °C and processed at 650 °C wrapped in Mg turnings also exhibited a thin white crust (Figure 10d). X-PAN aerogels oxidized at 225 °C and processed at 850 °C in Mg turnings (called Mg-PAN aerogels) exhibited instead a thick crust (up to 3 mm) and a black core (Figures 10e and 10f). The black core was attributed to residual carbon, which was removed by heating in air at 500 °C.

Figure 10. Digital camera images of: a) a native silica aerogel processed at 850 °C without Mg, b) a X-PAN aerogel processed at 850 °C without Mg, c) a Mg-native aerogel, d) a Mg-PAN aerogel processed at 650 °C; e-f) a Mg-PAN aerogel processed at 850 °C.
The crusts were removed from the cores with a razor blade. The surface area and the mechanical properties of the crust and of the core of all processed aerogels were investigated with N₂-sorption and nanoindentation. The results are summarized in Table 3. Except for the crust of Mg-PAN aerogels, all monoliths had comparable properties, that is, a surface area between about 300 and 400 m²·g⁻¹, a modulus below 50 MPa and a hardness of less than 6 MPa. Surface areas and mechanical properties can be reconciled with those of mildly densified silica aerogels, as our processing temperatures were close to the densification temperature of silica (~900 °C). Only the crust of Mg-PAN aerogels exhibited significant changes with a hardness of 27.7 MPa, a modulus of 374 MPa and a surface area of 169.23 m²·g⁻¹.

Table 3. Hardness, Reduced Young’s Modulus (Eᵣ) and surface area of representative aerogel samples processed at 850 °C in nitrogen atmosphere. (Before the 850 °C treatment, X-PAN and Mg-PAN aerogels were processed at 225 °C in air.)

<table>
<thead>
<tr>
<th></th>
<th>Mg-native</th>
<th>X-PAN aerogel (no Mg)</th>
<th>Mg-PAN aerogel (core)</th>
<th>Mg-PAN aerogel (crust)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eᵣ (MPa)</td>
<td>43.4</td>
<td>44.8</td>
<td>7.42</td>
<td>374</td>
</tr>
<tr>
<td>Hardness (MPa)</td>
<td>0.996</td>
<td>5.54</td>
<td>0.814</td>
<td>27.7</td>
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XRD of the core of all samples yielded a broad diffraction peak characteristic of poorly ordered silica (Figure 11a). The crust of all samples except for Mg-PAN aerogels exhibited peaks which were reconciled with MgO and the Mg silicate forsterite, Mg₂SiO₄, as shown in Figure 11b. The crust of Mg-PAN aerogels exhibited well-defined peaks which were reconciled with MgO, cristobalite, forsterite and enstatite (MgSiO₃) as shown in Figure 12. The XRD measurements show that Mg did not penetrate past the crust region, as Mg silicates were not
detected in the cores. The cores were amorphous, since samples were heated to a maximum temperature of 850 °C which is considerably lower than the crystallization temperature of silica (~1200 °C). The crust of all samples contacted with Mg exhibited peaks characteristic of MgO and Mg silicates, in line with expectations. Mg reacts spontaneously with SiO$_2$ at temperatures higher than about 400 °C, and MgO and Mg silicates are among the possible reaction products.$^{47,48}$
Figure 11. XRD analysis of Mg-native aerogel a) core and b) crust regions. Diffractions from b) correspond to forsterite [*, Mg$_2$SiO$_4$] and magnesium oxide [Δ, MgO].
Figure 12. XRD analysis of the crust of Mg-PAN aerogels showing diffractions from forsterite [Mg$_2$SiO$_4$, 01-085-1364], enstatite [MgSiO$_3$, 00-019-0768], cristobalite [SiO$_2$, 00-039-1425] and magnesium oxide [MgO, 01-075-1525].

4.3c. Morphology and ceramic cross-linking

SEM, EDS and TEM were taken from the crust and the core of all samples. As in the case of XRD, all samples except for Mg-PAN aerogels had similar characteristics. We will now
describe the results for Mg-native aerogels which are representative of aerogels that did not present a mechanically robust crust, followed by a discussion of Mg-PAN aerogels.

The crust of Mg-native aerogels consisted of cubic crystals which appeared to be loosely connected as shown in Figure 13a. EDS showed the presence of Mg, O, Si and C. Carbon was likely a processing residue and it was noticed in all samples, in agreement with previous literature reports. The presence of Mg, Si and O is consistent with the XRD measurements which showed the presence of MgO and Mg silicates in the crust. The core of Mg-native samples exhibited a porous network with a morphology consistent with that of aerogels, as shown in Figure 13c. EDS showed the presence of Si, O, and C, but not Mg, consistent with the XRD analysis which did not show Mg species in the core of all samples. TEM micrographs of core and crust of Mg-native samples are reported in Figure 14 and they are consistent with the SEM analysis. The crust of Mg-native samples had a granular morphology as shown in Figure 14a. Selected area diffraction (SAED) exhibited rings which corresponded to d-spacings of 2.305, 1.97, and 1.43 Å, respectively (Figure 14b). Lattice spacings determined with our TEM have an error of +/- 5%, therefore the lattice spacings measured by SAED could be reconciled with reflections from the (111) plane (2.42 Å) and the (200) plane (2.09 Å) of MgO. The ring with a d-spacing of 1.43 Å was due to either the (220) plane of MgO or the (141) plane of Mg$_2$SiO$_4$, whose d-spacings differ by 0.001 Å. SAED is therefore consistent with the XRD results of Figure 11 and with the EDS of Figure 13b), which showed that the crust consisted of Mg silicates and MgO. The core of Mg-native silica aerogels had a granular morphology and was amorphous by SAED, as shown in Figure 14c). Electron microscopy of all other samples except for the Mg-PAN aerogels yielded results comparable to those of Mg-native aerogels.
As for **Mg-PAN** aerogels, their crust had a smooth morphology by SEM at all scales as shown in Figure 15a) and 15b). The core exhibited an aerogel-like porous network as shown in Figure 15c) and 15d). EDS showed the presence of Mg, Si, O and C in the crust (Figure 16a) and of Si, O and C in the core (Figure 16b), in agreement with the XRD results which exhibited the peaks of Mg silicates in the crust but not in the core. In TEM, the crust of **Mg-PAN** aerogels exhibited sheet-like structures together with granular regions as shown in Figure 17a). SAED yielded a faint diffraction pattern with a ring which corresponded to a $d$-spacing of 1.93 Å (Figure 17b) and was reconciled with the reflection from the (631) plane of enstatite ($d = 1.95$ Å). We also often noticed rod-like structures that appeared to connect sheet-like structures. High resolution TEM of one of these rod-like structures is shown in Figure 17c). Lattice fringes with a spacing of 3.32 Å were measured which were reconciled with the (121) plane of enstatite ($d = 3.30$ Å). The core of **Mg-PAN** aerogels had a granular morphology (Figure 17d) and was amorphous by SAED.

After washing with 1 M HCl, the crust of the **Mg-PAN** aerogels was removed. The monoliths collapsed and broke into several small fragments which exhibited a porous, aerogel-like network as shown in Figure 18a) and 18b). EDS post-HCl washing demonstrated the complete removal of magnesium (Figure 18c) and XRD was consistent with that of amorphous silica.
Figure 13. SEM analysis of a Mg-native silica aerogel. a) Crust region. b) EDS of the crust. c) Image of the core.
Figure 14. Bright field TEM micrographs of a) Mg-native silica aerogel crust, b) SAED, c) core.
Figure 15. SEM images of a-b) Mg-PAN aerogel crust and c-d) core.

Figure 16. EDS analysis of a) Mg-PAN aerogel crust and b) core.
Figure 17. Bright field TEM micrographs of a Mg-PAN aerogel: a) crust, b) Corresponding SAED, c) HRTEM. The inset shows a close up of the lattice fringes shown in c). d) Core.
SEM and TEM analysis shows that the crust of Mg-PAN aerogels consisted of Mg silicates that cross-linked silica aggregates, thus explaining the enhanced mechanical properties. These observations are in overall agreement with reports by the Sandhage group, who noticed the formation of a Mg-rich, dense crust on the surface of SiO$_2$ frustules pyrolyzed in the presence of Mg. HCl removed the Mg-rich crust but it did not affect the morphology of the frustules, similar to what we observed for our aerogels. Our findings are also consistent with previous reports of the pressureless infiltration on SiO$_2$ by metals such as Al and Mg. In these reports a compact layer of reaction products was often observed which encapsulated residual SiO$_2$. For all other samples, an amorphous silica core was encapsulated in a crust of MgO and Mg silicates. However, the crust was composed of granules which appeared to be loosely connected, accounting for the weak mechanical properties of these samples.
4.3d. *Formation of magnesium silicates*

Formation of Mg silicates in the crust of our samples may appear surprising. Past and very recent reports have shown that magnesiothermal reduction of silica typically yields elemental silicon (Si), magnesium silicide (Mg$_2$Si) and MgO.\textsuperscript{49-51} The discrepancy between our and previous work can be explained based on the Mg:SiO$_2$ ratio. The reaction between Mg and SiO$_2$ is quite complex and its products depend strongly on the mole ratio of the reagents. For Mg:SiO$_2$ ratios around 2:1 elemental Si and MgO are produced. A byproduct of the reaction is Mg$_2$Si which becomes the dominant product for ratios higher than 2:1.\textsuperscript{52,53} For Mg:SiO$_2$ ratios lower than 2:1 the silicates enstatite (MgSiO$_3$) and forsterite (Mg$_2$SiO$_4$) are formed in a ratio that depends on the Mg:Si ratio and on the processing temperature.\textsuperscript{47,53} In our experiments, the Mg:SiO$_2$ ratio was ~1:2, since aerogels with a diameter of about 7 mm and weighing on average 772.44 mg were wrapped in Mg turnings less than 1 mm thick weighing on average 116.612 mg. The reaction was carried out in an open furnace and not (as customary) in an enclosed vessel. Mg could therefore escape from the reaction region which further lowered the Mg:SiO$_2$ ratio. It is therefore not surprising that Mg silicates were produced.\textsuperscript{52,53} In addition, Mg$_2$Si is generally considered a low-temperature reaction product which cannot evolve into the thermodynamically more stable Mg silicates because of kinetic limitations.\textsuperscript{47} Enstatite and forsterite start forming only at temperatures higher than about 650 °C - 700 °C.\textsuperscript{47}

4.3e. *The role of PAN*

To understand why the reinforcing crust formed only in Mg-PAN aerogels we carried out a series of control experiments and processed native and cross-linked aerogels in several different ways. We noticed that only a thin crust formed in X-PAN aerogels that had not been
previously oxidized by heating in air at 225 °C. A cross-linked crust also did not form in X-PAN aerogels processed at temperatures below 800 °C, even when the PAN had been previously oxidized. The cross-linked crust also did not form in aerogels that had been cross-linked with non-carbonizable polymers, such as poly(methyl methacrylate). These results suggested that carbonization of PAN was necessary for the formation of the crust. PAN oxidation is a necessary step towards carbonization and the onset of PAN carbonization is around 800 °C. Our conjecture was confirmed by Electron Energy Loss Spectroscopy (EELS) which is reported in Figure 19. EELS spectra of the carbon K-edge from the crust of all samples except for Mg-PAN exhibited a shoulder at 284 eV and a broad peak at 291 eV which were reconciled with the π* and the σ* orbitals of amorphous carbon. EELS of the crust and the core of Mg-PAN samples exhibited a sharp π* peak at 284 eV, a reasonably well-defined σ* peak at 291 eV, and a broad peak centered around 325 eV. All these features are characteristic of graphitic-like carbon. The sharp σ* transition derives from an increased π-bonding between neighboring layers and the broad peak at 325 eV is attributed to multiple scattering and is exclusively observed in graphitic carbon. As an additional confirmation of the role of PAN, monoliths were prepared using masking techniques where only selected regions were cross-linked with PAN. A reinforcing crust was noticed only in the photocrosslinked regions as shown in Figure 20.
Figure 19. Carbon K edge spectra of the X-PAN and native aerogel crusts after pyrolysis in the presence of magnesium at 850 °C.

4.3f. The role of carbon

The characterization data shows that Mg silicates and MgO form at the Mg/SiO$_2$ interface, as expected from stoichiometric and kinetic considerations. The data also shows that a thick, cross-linked silicate crust forms only in samples where the conditions for carbonization are fulfilled, that is, samples are cross-linked with the carbonizable polymer PAN, heated at 225 °C in air to oxidize the polymer and pyrolyzed at temperatures on the order of the carbonization temperature of PAN (~800 °C). The question is, how does carbon favor penetration of Mg species into the aerogels and help form a cross-linked Mg silicate crust. Studies of the Mg-O-Si system have shown that the solid-state reaction proceeds by diffusion of Mg species (Mg or
MgO) inside a more or less stationary Si lattice. Pressureless infiltration studies have also shown that penetration of a reaction front inside a ceramic preform is improved by enhancing wetting reactivity and diffusion. We do not think that carbon enhanced wetting. Mg does not form stable carbides, therefore the contact angle between Mg and carbon is determined mostly by surface considerations. The surface energy of Mg (560 J \cdot m^{-2}) and MgO (1.15 J \cdot m^{-2}) are considerably higher than the surface energy of most carbon forms (~100 mJ \cdot m^{-2}). However, silica has a surface energy of about 300 mJ \cdot m^{-2}. Therefore, carbon, if anything, will increase the surface energy difference, increase the contact angle and oppose wetting.

Carbon, however, can increase the reactivity of metals with oxides, which could explain Mg penetration into the Mg-PAN monoliths. Previous reports by the group of Park have shown that carbon impurities lowered the temperature of formation of silicates in the Mg-SiO$_2$ system by forming intermediate, carbon-rich silicate phases. The catalytic role of carbon is corroborated by recent reports which have shown that carbon impurities can accelerate the crystallization of amorphous SiO$_2$ into cristobalite, which was also detected in the crust of Mg-PAN aerogels. The carbon of the Mg-PAN samples might have also enhanced diffusion of Mg and MgO into the monoliths. It is known from surface science studies that the metal atoms and even nanometer-sized aggregates diffuse rapidly on graphite surfaces. In previous work, we showed that silica nanoparticles are coated by a few layers of graphite-like material (turbostratic carbon) when X-PAN aerogels are pyrolyzed. This turbostratic carbon might facilitate diffusion of Mg inside the aerogels.
Figure 20. Digital camera image of an anisotropic (half Mg-MSMA, half Mg-PAN) aerogel after pyrolysis at 850 °C. The reinforcing crust was partially removed to show the black interior.

4.4 Conclusion

We have reported a fabrication method which has several attractive features. The method allows one to mechanically reinforce aerogels without compromising their porosity since the core retains the characteristics of native aerogels. The reinforcement is ceramic in nature and it is stable at temperatures comparable to the densification temperature of silica aerogels (~900 °C) which are much higher than the temperatures (~200 °C) accessible to polymer-reinforced aerogels. Cross-linking depends on the presence of carbon in the aerogel structure. We obtained cross-linking only when carbonization conditions had been fulfilled, that is, PAN was used as a cross-linker, oxidized at 225 °C in air and then heated to the carbonization temperature of 850 °C. Masking, an example of which is shown in Figure 20, allows one to reinforce only selected parts of aerogels and it could be employed to integrate aerogels into mechanical assemblies by reinforcing only the regions most subject to mechanical stress. Our results may also allow development of non-aerogel ceramic materials with anisotropic physical and chemical composition. In our process, chemical and physical properties are altered within the same
monolith by introducing a catalyst (carbon in our case) for a solid-state reaction using conventional lithographic methods. The flexibility of lithography allows in principle to generate complicated patterns which are not accessible to conventional methods of fabrication of anisotropic ceramics such as layering, bonding and generation of temperature and/or chemical gradients during processing.
Chapter 5: Production of Iron Carbide by Pulsed Laser Ablation
5.1 Introduction

Nanoparticle synthesis by pulsed laser ablation in liquids is a technique with potential applications in the synthesis of bioconjugates. Nanoparticle synthesis by laser ablation in liquids does not require any chemicals and thus it eliminates the need for time-consuming purification steps that are necessary to remove harmful chemicals used by wet chemistry methods. Early studies have focused on the ablation of noble metal nanoparticles and they have been summarized in a review by Amendola et al. More recently, investigations have shifted towards non-noble metals, carbides and oxides, whose synthesis conditions have been reviewed by Yang. Nanoparticles of magnetic systems have also been recently synthesized. Ablation of Co in water and in ethanol was studied by Chen et al. and ablation in cyclopentanone of two binary magnetic alloys (Sm-Co and Ni-Fe) was investigated by Jakobi et al.

The Meunier group produced core-shell structures with a mean diameter of 6.5 nm by irradiating a suspension of Au and Co nanoparticles, and Zeng et al. synthesized FeO nanoparticles by ablation of an iron target in a water/poly(vinyl pyrrolidone) solution. Amendola et al. and, almost at the same time, Vitta et al. showed that by varying the ablation solvent Fe oxide or carbide nanoparticles could be produced. Several of the nanoparticles synthesized by these authors were magnetic and could be pulled out of solution by a permanent magnet. All these reports are of extreme interest for biomedical applications, since magnetic nanoparticles are being used or considered for clinical imaging and cancer therapy.

Quite surprisingly, only few reports to date have focused on the measurement of the magnetic properties of magnetic nanoparticles produced by ablation in liquids. Vitta et al. carried out a room temperature Mossbauer analysis which provided useful but limited information since Mossbauer measurements on superparamagnetic nanoparticles must be carried out below their
blocking temperature in order to resolve the hyperfine splitting.\textsuperscript{77,78} Zeng \textit{et al.} did not provide any magnetic characterization of their FeO nanoparticles.\textsuperscript{76} Other reports indicate that the magnetic properties of ablated nanoparticles are considerably inferior to those of the bulk materials. Chen \textit{et al.} reported a coercive field of 100 Oe for Co nanoparticles which is considerably lower than the bulk value (~1kOe) and Jakobi \textit{et al.} measured a coercive field of 30 Oe for a Sm\textsubscript{2}Co\textsubscript{17} alloy.\textsuperscript{73,74} This value is also considerably lower than the bulk value of Co-Sm alloys (~150 kOe) and was interpreted as alloy disproportionation by the ablation process. Amendola \textit{et al.} characterized Fe oxide nanoparticles produced by ablation in water. They showed that the nanoparticles were superparamagnetic with a saturation magnetization $M_s$ of 100 emu per gram of Fe, that is, \(\sim 75 \text{ emu} \cdot \text{g}^{-1}\) on a per unit weight base.\textsuperscript{79} The value of $M_s$ measured by Amendola \textit{et al.} is comparable to that of magnetite nanoparticles that can be produced with simple, up-scalable chemical methods.\textsuperscript{80-84} Therefore, the available experimental data suggests that ablation may not be an ideal technique for the synthesis of magnetic nanoparticles. However, the experiments of Amendola \textit{et al.} showed that Fe carbide nanoparticles can be produced by ablation in ethanol.\textsuperscript{5} Fe carbides are quite attractive for biomedical applications since they have a $M_s$ of 135 emu · g\textsuperscript{-1} and they are chemically more stable than oxides under physiological conditions.\textsuperscript{85} Therefore, we carried out a limited-scope analysis to characterize the magnetic properties of Fe-containing nanoparticles produced by laser ablation in ethanol. We determined that ablation in ethanol yields a mixture of Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}C nanoparticles, in agreement with Amendola's and Vitta's results.\textsuperscript{5,77} Analysis of the magnetic properties of nanoparticles shows that they are superparamagnetic (with a weak ferromagnetic component) with a saturation magnetization of 124 emu · g\textsuperscript{-1} at room temperature. This saturation magnetization is close to the bulk value of Fe\textsubscript{3}C (135 emu · g\textsuperscript{-1}) and is comparable to that of Fe-containing nanoparticles.
produced by standard chemical synthetic techniques such as polyol reduction. This is a quite relevant finding since it shows that nanoparticles with excellent magnetic properties can be produced without by laser ablation without any additional processing and without using any chemicals. ZFC measurements collected at an applied field of 50 Oe displayed a maximum magnetic susceptibility at 120 K, with a broad distribution, characteristic of systems with a wide range of blocking temperatures. FC measurements collected during cooling and heating showed a thermal hysteresis indicative of temperature dependent magnetic viscosity. The magnetic viscosity was calculated from thermoremanent magnetization (TRM) plots and it increased with decreasing temperature. The activation volume of the non-uniform magnetic states was calculated from TRM measurements and it was found to decrease with decreasing temperature. The decrease in activation diameters was interpreted as a decrease in exchange length, and hence a decrease in particle-particle interactions.

5.2 Experimental

Nanoparticle suspensions were produced by exposing a Fe foil (Alfa Aesar, purity 99.99%) submerged in ethanol to pulses with a wavelength of 1064 nm produced by a Nd:YAG laser (EKSPLA 312G). The pulses had a duration of 500 ps, an energy of 12 mJ, a repetition rate of 10 Hz, and a fluence of ~13 J · cm² was used. The beam was focused on the target by means of a lens with 10 cm focal length. The ablation rate was determined to be 0.3 mg · hr⁻¹ by weighing the foil before and after exposure. Because of the comparatively high sample mass required by magnetic characterization techniques, ablation had to be carried out for 3 - 4 hours. A rare earth permanent magnet was placed at one side of the vial containing the target to remove nanoparticles from the solution. For magnetic characterization, samples were weighed, loaded
into the sample holder and then dispersed in a solution of Formvar resin in chloroform. The sample was placed in a magnetic field to orient the particles and the chloroform was allowed to evaporate. This sample preparation method was utilized to limit the possibility of a magnetic reversal process due to Brownian relaxation. Data collection was carried out on a Quantum Design Versalab Vibrating Sample Magnetometer. Magnetization vs. applied field (M(H)) curves were collected from 30 kOe to -30 kOe at a ramp rate of 100 Oe per second. Magnetization vs. time curves were collected from 50 K to 300 K at a ramp rate of 5 K per minute. Nanoparticles were further characterized by X-Ray diffraction (XRD, Panalytical X’pert Pro MRD), and by transmission electron microscopy (TEM, Zeiss Libra 120). For XRD, samples were prepared by centrifuging the nanoparticles out of solution, followed by heating at 80 ºC overnight to remove residual solvent. For TEM, one or more drops of suspension was evaporated on a carbon-coated Cu grid.

5.3 Results and Discussion

Figure 21 shows the XRD spectrum of nanoparticles obtained after ablating for 3.5 hours. Several peaks were observed, which were reconciled with Fe₃C, and Fe₃O₄, respectively. This result is in overall agreement with a recent report by Amendola et al., who observed the same phases by Fe ablation in ethanol.⁵
Figure 21. XRD of Fe nanoparticles ablated for 3.5 hours in ethanol.

Figure 22a) shows bright field TEM micrographs. Most particles exhibit a contrast difference which points to the formation of core-shell structures, in agreement with the observations of Amendola et al.\textsuperscript{5} Selected area diffraction (SAED, Figure 22b) exhibited faint rings which corresponded to a $d$-spacing of 1.9 Å. Lattice spacings determined by TEM can have an error of up to $+/-$ 5%, therefore the lattice spacing measured by SAED could be reconciled either with the reflection from the (031) plane of Fe\textsubscript{3}C ($d = 2.01$ Å) or with the reflection from the (112) plane of Fe\textsubscript{3}C ($d = 1.97$ Å). Figure 22c) shows a size distribution histogram obtained by measuring about 200 particles. The size distribution appears to be bimodal, with maxima at about 3 nm and about 12 nm. For comparison, Amendola et al. reported for the same system a
quite broad unimodal size distribution with a mean size of 15 nm.\textsuperscript{5} We think that the difference between our and Amendola's size distribution arises from how the ablation was carried out. In our experiments, particles were removed from the ablation region beam by a permanent magnet. In Amendola's experiments, the magnet was used only in the final stages. Thus, in our experiments particles had little chance of being hit multiple times by the beam, which tends to lead to a more homogeneous size distribution skewed towards larger particles.\textsuperscript{5,6,8,7,8}
Saturation magnetization ($M_s$) and coercivity values for M(H) curves collected at various temperatures are shown in Figure 23 and summarized in Table 4. The room temperature $M_s$ is 124 emu · g$^{-1}$ which is 92% the value for bulk Fe$_3$C (135 emu · g$^{-1}$), and is about 35% higher than the magnetization of nanoparticles with a Fe core produced by standard chemical methods such as the polyol technique.$^{86}$ The reduction from the bulk value of Fe$_3$C can be attributed to the
Fe$_3$O$_4$ phase identified with XRD.$^{85}$ Zero field cooled (ZFC) measurements collected at an applied field of 50 Oe displayed a maximum magnetic susceptibility at 120 K, with a broad distribution, characteristic of systems with a wide range of blocking temperatures. ZFC plots collected at various fields showed a change in blocking temperature as a function of applied field, however the superparamagnetic scaling law $M \sim H/T$ was not observed, which is common for weakly interacting particle systems.$^{87}$ Also, the field cooled (FC) measurement performed at 50 Oe did not converge with the ZFC plot (Figure 24a), even at 300 K. This lack of convergence was observed for numerous samples and at multiple fields, which is indicative of magnetic viscosity or memory effects.

![Figure 23](image-url)  
**Figure 23.** M(H) curves collected at 300 K (red) and 50 K (blue), on the left. On the right a zoomed view showing the coercivity and remanent magnetization for the particles at 300 K and 50 K.
Table 4. Magnetic properties at various temperatures (\(M_s =\) saturation magnetization, \(H_c =\) coercivity, \(S_v =\) viscosity coefficient, and \(D_a =\) activation diameter).

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Figure 24. a) Zero field cooled (blue) and field cooled (red) curves collected at 50 Oe with inset showing the lack of convergence between the curves, b) thermoremanent magnetization plots showing temperature dependent magnetic viscosity.

To quantify the magnetic viscosity for the present system, thermoremanent magnetization (TRM) plots were collected at various temperatures and are shown in Figure 24b. Magnetic
viscosity (S) is frequently observed in weakly interacting nanoparticle systems and can be experimentally determined from TRM plots, using the formula $S = \delta M / \ln \delta(t)$, for $t > 100$ seconds. While values for S are characteristic of the magnetic reversals per unit time of the system, the energy barriers being overcome upon reversal also are needed to determine the viscosity coefficient, $S_v$. Experimentally, the lowering of energy barriers by an applied field can be used to quantify the irreversible susceptibility ($\chi_{irr}$) from DC demagnetization plots using the equation $\chi_{irr} = \delta M / \delta H$. The magnetic viscosity coefficient can then be calculated using $S_v = S / \chi_{irr}$, and is indicative of the internal fluctuation field at a given temperature. The calculated values of $S_v$ for the presented particle system are shown in Table 4. $S_v$ increased with decreasing temperature causing a higher degree of non-uniform magnetic states. The activation volume of these non-uniform magnetic states, $V_a$, can be calculated using the following equation:

$$V_a = \frac{k_b T}{S_v M_s}$$

where $k_b$ is the Boltzmann constant, and $M_s$ equals the saturation magnetization at temperature, T. The activation diameters ($D_a$) at various temperatures are shown in Table 4, assuming the magnetic states to be spherical. The decrease in activation diameters can be better viewed as a decrease in exchange length, and hence a decrease in particle-particle interactions. As the activation diameters approach the actual particle diameters observed in the TEM images, the magnetic reversal switches from a coherent to an incoherent reversal mechanism resulting in an increase of coercivity with decreasing temperature.
5.4 Conclusion

We have synthesized suspensions of magnetic nanoparticles by laser ablation of Fe in ethanol. The saturation magnetization of the nanoparticles is $M_s = 124 \text{ emu} \cdot \text{g}^{-1}$ which is comparable to the bulk magnetization of Fe$_3$C and is about 35% higher than the $M_s$ of Fe-containing nanoparticles synthesized using standard chemical techniques such as polyol reduction. The high magnetization of the nanoparticles demonstrates that laser ablation in liquids is a promising technique for the chemical-free fabrication of biocomposites for imaging and cancer treatment applications.
Chapter 6: Synthesis of Multiphasic Inhomogeneous Nanoparticles by Pulsed Laser Ablation
6.1 Introduction

Multiphasic and anisotropic nanomaterials have extremely attractive properties such as improved catalysis, enhanced magneto-optics, and drug delivery. Early studies focused on the production of core-shell and homogeneously alloyed nanoparticles. For example, Carpenter et al. synthesized alloyed PtNi and PtCo nanoparticles via solvothermal techniques to generate materials with enhanced oxygen reduction electrolysis properties. Recent work has shifted towards highly inhomogeneous and highly anisotropic nanoparticles. For example, patchy Au-SiO₂ particles were generated by functionalizing SiO₂ spheres partially embedded in polymer fibers with an aminosilane, followed by a partial coating with Au particles. Trizio et al. generated Janus Cu/Cu₃P nanocrystals by reacting trioctylphosphine (TOP) with CuCl (5.6:1) at 350 °C for 25 minutes. Liz-Marzán et al. recently reviewed the field and reported on a wide variety of techniques used to produce patchy and Janus nanoparticles. The techniques and materials reported to date, however, have certain limitations. Most techniques require multiple and quite sophisticated processing steps, often involve synthesis of non-trivial polymer templates, and are generally limited to easily synthesizable materials such as noble metals and II-VI semiconductors. Most important, almost all reported techniques yield nanoparticles that consist of two or more different nanoparticles grown on one another like in a raspberry or side by side like in a pearl necklace. In this work we produced highly anisotropic nanoparticles where Mo and MoC coexisted within the same aggregate. To our knowledge this is the first time that inhomogeneous nanoparticles were produced by a single process. In addition, we notice that the materials are hardly accessible to wet chemical methods, and that our method does not involve any chemicals besides the solvent, thus simplifying separation and purification.
6.2 Experimental

Nanoparticle suspensions were produced by exposing a Mo foil (Alfa Aesar, purity 99.95 %) submerged in absolute ethanol to pulses with a wavelength of 1064 nm produced by a Nd:YAG laser (EKSPLA 312G). The pulses had a pulse duration of 750 ps, an energy of 12 mJ, a repetition rate of 10 Hz, and a fluence of \( \sim 13 \text{ J} \cdot \text{cm}^{-2} \) was used. The beam was focused on the target by means of a lens with 10 cm focal length. The ablation rate was determined to be 1.8 mg \( \cdot \text{hr}^{-1} \) by weighing the foil before and after exposure. Nanoparticles were characterized by X-Ray diffraction (XRD, Panalytical X’pert Pro MRD) and by transmission electron microscopy (TEM, Zeiss Libra 120). For XRD, samples were prepared by centrifuging the nanoparticles out of solution, followed by heating at 80 °C to remove residual solvent. For TEM, one or more drops of suspension was evaporated on a carbon-coated Cu grid.

6.3 Results and Discussion

Figure 25 shows the XRD pattern of nanoparticles obtained after laser ablation of molybdenum foil in absolute ethanol for 12 minutes. Several peaks were observed which were reconciled with Mo, MoC, and graphite respectively. Formation of carbides is typical for ablation in organic solvents and it has been reported in work by Amendola et al., as well as by our own group.\(^5\)\(^{113}\)
Figure 25. XRD analysis of Mo nanoparticles ablated in ethanol. Diffractions corresponded to molybdenum [Δ, Mo (01-071-4645)], molybdenum carbide [*; MoC (01-089-2868)] and graphite [+, C (00-041-1487)]. Inset shows a magnified image of the region with the largest number of peaks.

Figure 26a) shows a typical bright field TEM micrograph. The particles had a log-normal distribution with a mean size of 4.17 nm (Figure 26e). Several particles were striated and displayed striking contrast between regions within the same particle. Selected area electron diffraction (SAED) and dark field imaging were used to analyze the nanoparticles. SAED exhibited diffraction rings which corresponded to d-spacings of 2.278 Å, 1.419 Å and 1.16 Å (Figure 26b). Lattice spacings determined by TEM can have an error of up to +/- 5%, therefore the lattice spacing measured by SAED could be reconciled with the reflection from the (110) plane of Mo (d = 2.222 Å) and the (220) plane of MoC (d = 1.509 Å). The ring with a d-spacing of 1.16 Å was due to either the (211) plane of Mo or the (311) plane of MoC, whose d-spacings
differ by 0.004 Å, (1.2831 and 1.2874 Å respectively). Dark field TEM micrographs were taken by centering the objective aperture on the Mo (110) reflection to identify Mo nanoparticles and Mo-rich regions as shown in Figure 26c). Dark field obtained using the MoC (311) reflection is reported in Figure 26d). Since both images were obtained using the cone diffraction technique, Figures 26c) and 26d) can be considered as a map of Mo and MoC. In many cases Mo and MoC seemed to coexist within the same nanoparticles (arrows in Figures 26c), 26d). However we were well aware that TEM analysis of nanoparticles can be nontrivial. For example, crystal twinning can generate striated regions while diffraction point splitting and crystal orientation can all cause reflections that are easily misinterpreted.\textsuperscript{115,116} Yacaman also showed that diffraction on multidomain nanoparticles produced a splitting of the corresponding electron diffraction points while different orientations of the same crystal generated sets of rotated and superimposed diffraction patterns.\textsuperscript{116} To ensure that the striated nanoparticles were composed of multiple phases rather than multiple domains of a single phase, further analysis was performed on individual nanoparticles to minimize artifacts.
Figure 26. a) Bright field TEM micrograph of nanoparticles produced by ablation of Mo in ethanol. The nanoparticles were crystalline displaying diffraction under bright field conditions. b) SAED. Dark field TEM micrographs of nanoparticles corresponding to diffraction points of c) Mo and d) MoC. Particles with suspected multiple domains or phases are denoted with arrows. e) Particle size distribution histogram.
Bright and dark field TEM micrographs, Energy Filtered TEM (EFTEM) and elemental mapping of a single nanoparticle are shown in Figure 27. Because of the high background in the region of the Mo EELS line, EFTEM could be carried out only in the carbon regions. This limitation notwithstanding, Figure 27d) shows that carbon was absent (or at least had a very low concentration) in the upper region of the nanoparticle. This same region did not show in the MoC dark field image (Figure 27c), but instead showed in the Mo dark field image (Figure 27d).
Figure 27. a) Bright field TEM micrograph of a nanoparticle produced by ablation of Mo in ethanol. Dark Field TEM micrographs of nanoparticles corresponding to diffraction points of b) Mo and C) MoC. d) EFTEM and e) elemental mapping of the bright field TEM micrograph showing carbon rich (bright) and carbon poor regions (dark).

The formation of multiphasic particles is likely related to the high temperatures attainable by pulsed laser ablation. According to the Mo-C phase diagram a high (>1700 °C) temperature MoC phase exists which dissociates into Mo and MoC at lower temperatures. This is likely what happened in our case and lead to the generation of nanoparticles composed by two different
materials. A high temperature carbide phase formed in the ablation plume. Upon cooling the MoC phase decomposed into Mo and MoC within the same nanoparticle.

### 6.4 Conclusion

In conclusion, we have synthesized suspensions of multiphase nanoparticles by pulsed laser ablation of Mo in ethanol. XRD showed the production of Mo along with MoC. TEM analysis showed the presence of Mo and MoC nanoparticles but also of nanoparticles where Mo and MoC coexisted. Likely, a high temperature MoC phase was generated by heating. When the particle cooled, this phase decomposed as predicted by the phase diagram and generated anisotropic nanoparticles.

### Acknowledgement

TEM images were acquired using an instrument purchased with funds from NSF grant NSF-MRI #0922582
Chapter 7: Magnetic Behavior in the Fe-C-Mo System
7.1 Introduction

Ternary alloys (e.g. Fe-C-Mo) have extremely interesting properties such as reduced acid surface corrosion in steels. Early studies focused on extensive uses in automotive and high temperature fields. For example, Bernst et al. showed that increased Mo concentration in Fe/Mo diffusion couples under carburization reduced the formation of Fe₃C and generated a partition of the reaction elements. Recent work has focused on the growth of carbon nanotubes, magnetic nanoparticle production and the precipitation of different carbide phases in the Fe-Mo-C systems. For example Yoshida et al. have shown that Fe-Mo-C nanoparticles can be used to generate carbon nanotubes with a yield three times higher than Fe-C nanoparticles alone. Zhou and Wu have shown that a Fe-C-Mo alloy precipitates Fe₃C, (Fe,Mo)₂C and (Fe,Mo)₃C under temperatures ranging from 570 - 610 °C. However, applying a 12T magnetic field under the same conditions precipitates only (Fe,Mo)₆C. Also, Vitta et al. and, almost at the same time Amendola et al. showed that the production of Fe oxide or Fe carbide nanoparticles could be controlled by varying the ablation solvent. Several of the nanoparticles synthesized by these authors were magnetic and could be pulled out of solution by a permanent magnet. Here we report on the magnetic properties of the Fe-C-Mo system as a function of Fe concentration. A reduction in saturation magnetization due to the dilution of Fe concentration was seen down to 40%. However, at Fe concentrations below about 40%, an increase in $M_s$ and $H_c$ was observed.

7.2 Experimental

Nanoparticle suspensions were produced by alternately exposing a Fe foil (Alfa Aesar, purity 99.95 %) and Mo foil (Alfa Aesar, purity 99.95 %) submerged in absolute ethanol to
pulses with a wavelength of 1064 nm produced by a Nd:YAG laser (EKSPLA 312G). The pulses had a pulse duration of 750 ps, an energy of 12 mJ, a repetition rate of 10 Hz, and a fluence of \( \sim 13 \text{ J} \cdot \text{cm}^{-2} \) was used. The beam was focused on the target by means of a lens with 10 cm focal length. The ablation rate of the Fe and Mo foils were both determined to be 1.8 mg \cdot \text{hour}^{-1} \text{ by weighing each foil before and after exposure. For magnetic characterization, samples were weighed, loaded into the sample holder and then dispersed in a solution of Formvar resin in chloroform. The sample was placed in a magnetic field to orient the particles and the chloroform was allowed to evaporate. This sample preparation method was utilized to limit the possibility of a magnetic reversal process due to Brownian relaxation. Data collection was carried out on a Quantum Design Versalab Vibrating Sample Magnetometer (VSM). Magnetization vs. applied field (M(H)) curves were collected from 30 kOe to -30 kOe at a ramp rate of 100 Oe per second. Nanoparticles were further characterized by X-Ray diffraction (XRD, Panalytical X’pert Pro MRD), and by transmission electron microscopy (TEM, Zeiss Libra 120). For XRD, samples were prepared by magnetically separating the nanoparticles out of the ethanol solution for 15 minutes, followed by heating at 80 °C to remove residual solvent. For TEM, one or more drops of suspension was evaporated on a carbon-coated Cu grid.

### 7.3 Results and Discussion

Work by Amendola et al. as well as our own group showed that pulsed laser ablation of Fe in ethanol gives rise to magnetic carbides.\(^{5,112}\) Even though there is evidence that adding Mo can increase magnetization at high molybdenum concentrations, little work has been done to investigate magnetic properties in ternary systems (e.g. Fe-C-Mo).\(^{121-123,130,131}\) Saturation magnetization (\( M_s \)) and coercivity (\( H_c \)) values for nanoparticle samples produced by pulsed laser
Ablation with different Fe concentrations are shown in Figure 28 and summarized in Table 5. The room temperature $M_s$ of the 100% iron sample is 138 emu $\cdot$ g$^{-1}$ which is on the order of bulk Fe$_3$C (135 emu $\cdot$ g$^{-1}$), and is about 50% higher than the magnetization of Fe core nanoparticles produced by standard chemical methods (e.g. polyol reduction). A decrease in magnetization with a decrease in Fe concentration down to 40% Fe was seen which was reconciled with the decreased Fe content in the system. However, an increase in magnetization was seen between 40 and 17% Fe followed by a decrease in magnetization, in keeping with the results of Sumiyama et al. In fact, Sumiyama et al. attributed the increase in magnetization in the Fe-Mo system at low percent Fe to the formation of a BCC Fe$_{1-x}$Mo$_x$ alloy. XRD analysis was performed to evaluate alloy formation and to determine the cause for the increased magnetization.
Figure 28. a) M(H) curves collected at 300 K. b) Saturation magnetization (M_s) and coercivity (H_c) as a function of Fe concentration (solid line is a guide).
Table 5. Magnetic properties as a function of Fe concentrations.

<table>
<thead>
<tr>
<th>Percent Fe</th>
<th>$M_s$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>138</td>
<td>37</td>
</tr>
<tr>
<td>75</td>
<td>106</td>
<td>45</td>
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<tr>
<td>60</td>
<td>82</td>
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<td>40</td>
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<td>25</td>
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<td>100</td>
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<td>78.9</td>
<td>125</td>
</tr>
<tr>
<td>16.67</td>
<td>70.25</td>
<td>125</td>
</tr>
<tr>
<td>11.76</td>
<td>41</td>
<td>75</td>
</tr>
<tr>
<td>6.25</td>
<td>30</td>
<td>45</td>
</tr>
</tbody>
</table>

Figure 29 shows the XRD pattern of nanoparticles obtained after laser ablation of Fe and Mo foils in absolute ethanol for 20 minutes. Several peaks were observed, which were reconciled with Mo, MoC, Fe$_3$C, ε–Fe$_3$C (ε–carbide) and graphite. The formation of Fe$_3$C was seen at all Fe concentrations while the formation of ε–carbide was not present at low Fe concentrations (≤ 20%) as seen in Figure 30. While the formation of ternary alloys (e.g. Fe$_3$Mo$_3$C) is predicted, it is often very difficult to accurately identify these phases.$^{123,133-136}$ For example, at low concentrations, up to 5% molybdenum will dissolve into Fe$_3$C while at higher concentrations the carbide Fe$_2$MoC (ζ-carbide), is found.$^{135,136}$ In fact, ζ-carbide is often referred to as molybdenum cementite due to its similarity to Fe$_3$C and the two are often confused under XRD analysis because they have almost identical diffraction patterns, making characterization of this phase difficult.$^{135}$ Further analysis was performed using TEM to visualize Fe rich particles and to better understand the effect of varying the Fe concentration.
Figure 29. XRD analysis of Fe and Mo nanoparticles ablated in ethanol. Diffraction patterns corresponded to molybdenum carbide [* MoC (01-089-2868)], molybdenum [Δ Mo (01-089-5156)], cohenite [+ Fe₃C, (01-074-3840)] and ε-carbide [ε, ε-Fe₃C (01-089-3689)].
Figure 30. Magnified image of the XRD peak spectrum displaying peaks for cohenite \([\pm, \text{Fe}_3\text{C} (01-074-3840)]\) and the primary \(\varepsilon\)–carbide peak \([\varepsilon, \varepsilon-\text{Fe}_3\text{C} (01-089-3689)]\).

Figures 31a), 31c) and 31e) show bright field TEM micrographs. Particles exhibited a contrast difference which pointed to the formation of core-shell structures, in agreement with the observations of Amendola et al.\textsuperscript{5} Energy Filtered TEM micrographs (EFTEM) were used to analyze the nanoparticles by visualizing Fe regions/nanoparticles within the sample (Figures 31b), 31d) and 31f). Since diffraction from complex systems such as ours can have many artifacts (e.g. diffraction point splitting, diffraction pattern rotation) EFTEM was used since it is not limited by these artifacts.\textsuperscript{115,116}
Figure 31. Bright field TEM micrographs of a) 100, c) 50 and e) 20% Fe. Energy Filtered TEM micrographs corresponding to the bright field micrographs of b) 100, d) 50 and f) 20% Fe.
As the Fe concentration decreased, the Fe and Mo nanoparticles were roughly uniformly distributed within the suspensions (Figure 31a and 31c). The decreasing amount of Fe as well as the dilution by Mo nanoparticles likely explains the reduction in the saturation magnetization for the nanoparticle suspensions. However, at low Fe concentrations (≤ 20%) the Fe nanoparticles tended to aggregate and were no longer evenly dispersed amongst the Mo nanoparticles (Figure 31f).

The lack of ε-carbide formation at low percent Fe is likely related to the amount of carbon dissolved within the ablated Fe nanoparticles. It has been shown that ε-carbide is a metastable phase formed in martensite (high carbon steel) upon cooling and at low temperatures (100 – 200 °C), before the formation of Fe₃C. The known degradation of organic solvents into graphitic C probably generated C-rich Fe nanoparticles as well as Fe₃C nanoparticles in solution. Likely ε-Carbide was formed upon cooling of the C-rich Fe particles in ethanol post-ablation. The additional ablation of Mo generated a C sink whereby MoC formation competes with both ε-carbide and Fe₃C formation. By increasing the percent Mo within the ablated solution Fe nanoparticles had less C available to them and were limited to forming Fe₃C. The decrease in magnetization with decreasing Fe concentration can be reconciled primarily with the dilution of Fe-based particles within solution as well as the continued formation of a weaker competing magnetic iron carbide (ε-Fe₃C). The increase in magnetization at low Fe concentration may be reconciled with the aggregation of Fe₃C nanoparticles as well as the disappearance of the ε-carbide phase.

The effect of varying the Fe content in the Fe-C-Mo system is very complex and not easily addressed. Further work must be performed to truly identify the cause for the increase in magnetization at low Fe concentrations.
7.4 Conclusion

In conclusion, we have synthesized suspensions of magnetic nanoparticles by pulsed laser ablation of Fe and Mo foils in ethanol. XRD showed a lack of alloy formation between Fe and Mo. The formation of Mo, MoC and graphite was seen in all samples with Mo present. The formation of Fe$_3$C was seen at all Fe concentrations while the formation of ε-Fe$_3$C was not present at low Fe concentrations ($\leq$ 20%). VSM analysis showed a decrease in magnetization with a decrease in Fe concentration down to 40% Fe. However, an increase in magnetization was seen between 40 and 17% Fe followed by a further decrease in magnetization. The decrease in magnetization with decreasing Fe concentration is due to the dilution of Fe-based particles and the formation of ε-Fe$_3$C. The increase in magnetization at low Fe concentration is due to the aggregation of Fe$_3$C nanoparticles and the lack of ε-Fe$_3$C formation. Below this Fe-based nanoparticles aggregated together. The effect of Fe concentration on the magnetic properties of the Fe-C-Mo system is very complicated and further work must be performed.

Acknowledgement

TEM images were acquired using an instrument purchased with funds from NSF grant NSF-MRI #0922582
Chapter 8: Summary
The primary goal of this dissertation is to improve the understanding of nanostructures through the modification of aerogels and pulsed laser ablation in ethanol. Conclusions for the modification of nanostructures via laser processing are summarized below in two sections: modification to aerogels and laser ablation in liquids.

8.1 Modification of Aerogel Systems

We have shown that photopolymerization with visible light allows fabrication of anisotropic aerogels and ceramic materials. Materials with very different characteristics can be produced by simple variation of the illumination and processing conditions. The resulting materials comprise a new class of porous anisotropic solids that are difficult to fabricate with conventional fabrication methods and pave the way to several potential applications. For instance, functionally graded aerogels are likely candidates for ultra-lightweight energy absorbers. Selective reinforcement of regions subject to shear and mechanical stress allows integration of native aerogels into mechanical systems. Honeycomb patterns increase the compressive strength of an aerogel along the load-bearing direction while the monolith retains the porous structure of the native material for minimum thermal conductivity and maximum acoustic attenuation. Cellular aerogels could also be developed that mimic natural materials, e.g., bamboo. Cristobalite patterns are being considered to prevent sagging of amorphous silica at high temperatures.41

Subsequent pyrolysis of photopolymerized aerogels was proven to be a fabrication method which has several attractive features. This methodology allows one to mechanically reinforce aerogels without compromising their porosity since the core retains the characteristics of native aerogels. The reinforcement is ceramic in nature and it is stable at temperatures
comparable to the densification temperature of silica aerogels (~900 °C) which are much higher than the temperatures (~200 °C) accessible to polymer-reinforced aerogels. Cross-linking depends on the presence of carbon in the aerogel structure. We obtained cross-linking only when carbonization conditions had been fulfilled, that is, PAN was used as a cross-linker, oxidized at 225 °C in air and then heated to the carbonization temperature of 850 °C. Masking, an example of which is shown in Figure 20, allows one to reinforce only selected parts of aerogels and it could be employed to integrate aerogels into mechanical assemblies by reinforcing only the regions most subject to mechanical stress. Our results may also allow development of non-aerogel ceramic materials with anisotropic physical and chemical composition. In our process, chemical and physical properties are altered within the same monolith by introducing a catalyst (carbon in our case) for a solid-state reaction using conventional lithographic methods. The flexibility of lithography allows in principle to generate complicated patterns which are not accessible to conventional methods of fabrication of anisotropic ceramics such as layering, bonding and generation of temperature and/or chemical gradients during processing.

8.2 Pulsed Laser Ablation in Ethanol

We have shown that pulsed laser ablation in ethanol can be used to synthesize a host of nanoparticle suspensions. Magnetic nanoparticle suspensions were synthesized by laser ablation of a suspended Fe foil. XRD analysis showed that the suspensions were composed of Fe, Fe$_3$C and Fe$_3$O$_4$ while TEM analysis showed a bimodal size distribution with a mean size of 15nm. The saturation magnetization of the nanoparticles was found to be $M_s = 124 \text{ emu} \cdot \text{g}^{-1}$ which is comparable to the bulk magnetization of Fe$_3$C. Additionally, this is about 35% higher than the $M_s$ of Fe-containing nanoparticles synthesized using standard chemical techniques (e.g. polyol
reduction). Multiphasic nanoparticle suspensions were synthesized by pulsed laser ablation of Mo suspended in ethanol. XRD analysis showed the production of both Mo, MoC and graphite. TEM analysis showed Mo and MoC particles with a log-normal distribution with a mean size of 4.17 nm. Additionally, the presence of nanoparticles where Mo and MoC coexisted were also seen. Likely, a high temperature MoC phase was generated by localized laser heating during the ablation. When these particles cooled, the high temperature phase decomposed into Mo and MoC as predicted by the phase diagram and generated anisotropic nanoparticles. Bimetallic ablation (Mo and Fe foils) in ethanol generated suspensions of magnetic nanoparticles. XRD showed a lack of alloy formation between Fe and Mo. The formation of Mo, MoC and graphite was seen in all samples with Mo present. The formation of Fe₃C was seen at all Fe concentrations while the formation of ε-Fe₃C was not present at low Fe concentrations (≤ 20%). VSM analysis showed a decrease in magnetization with a decrease in Fe concentration down to 40% Fe. However, an increase in magnetization was seen between 40 and 17% Fe followed by a further decrease in magnetization. The decrease in magnetization with decreasing Fe concentration is due to the dilution of Fe-based particles and the formation of ε-Fe₃C. The increase in magnetization at low Fe concentration is due to the aggregation of Fe₃C nanoparticles and the lack of ε-Fe₃C formation. Below this Fe-based nanoparticles aggregated together. The effect of Fe concentration on the magnetic properties of the Fe-C-Mo system is very complicated and further work must be performed.

The high magnetization of Fe ablated nanoparticles which required no washing or purification demonstrates that laser ablation in liquids is a promising technique for the chemical-free fabrication of biocomposites for imaging and cancer treatment applications. The production of multiphasic materials shows that laser ablation in liquids is a promising technique for the
production of multiphase materials without time consuming production and processing. Overall, these results have provided new insight into the fundamental factors governing laser processing of nanostructures. While this work has addressed the functionality of modifying aerogel systems and the production of novel nanoparticle suspensions, ongoing work includes a study of altering magnetic, composition and functional properties of these systems. Future work in this field will be useful for the production of novel biocomposites, nanoalloys, porous ceramics and multiphase nanoparticle systems.
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