

Self-assembled Magnetic Silica Nano-rods and Micro-platelets as smart reinforcements for polymer-composites

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ABSTRACT

In this work, we propose a new versatile self-assembly technique to obtain large quantities of silica-based magnetic nano- and micro-rods and of magnetic micro-platelets, which can be easily oriented by weak magnetic fields. Our process begins with the preparation of silica monoliths by a sol-gel process, with the addition of superparamagnetic nanocolloids as templates in the presence of a magnetic field. Two magnetic field configurations have been used. In the first case, a static magnetic field has been applied, which leads to the self-organization of magnetic nanocolloids into long tubular structures. In the second case, a rotating magnetic field is applied, which drives the assembly of the particles into two-dimensional sheet-like structures. The unique microstructures of the silica monoliths confer them strong mechanical anisotropy. While monoliths prepared in a static field have extremely large Young moduli in the field direction, those prepared in a rotating field show a much higher resistance in the plane of rotation than in the perpendicular direction. This microstructure enables one to selectively break the monoliths and recover either magnetic nano- and micro-rods or magnetic micro-platelets through the application of a strong ultrasonication. The diameter of the rods and the thickness of the platelets can be precisely controlled by the conditions chosen during sol-gel transition, while the length of the rods and the area of the platelets by the ultrasonication time and intensity. Both rods and plates are easily functionalized thanks to the silica surface, and can be magnetically aligned.

Keywords: magnetic nanoparticles, spinodal decomposition, self-assembly, sol-gel, composite materials

1 INTRODUCTION

Polymer-based composite materials are increasingly utilized in numerous high-tech applications^[1]. They commonly possess anisotropic mechanical properties imparted by the shape or spatial organization of the filler, such as nanotubes, microfibers or platelets. For the performance of the material, the spatial distribution and alignment of the filler particles is of crucial importance. This effect preparation of composite materials is still challenging in spite of the variety of techniques developed to manufacture them. Even the type of filler used is strongly

restricted by the difficulty in preparing micro- and nano-materials with non-spherical shape.

In this work, we present a novel method to prepare silica-based magnetic microrods and microplatelets. These structural elements are the perfect fillers for the formation of composite materials. The preparation procedure is based on sol-gel process. Sol-gel preparation of silica monoliths via phase separation has been heavily studied in the last couple of decades, especially for chromatographic applications^[2]. It has been demonstrated that the addition to the initial silica precursor solution, such as polyethylene glycol (PEG) or polyacrylic acid (PAA), can induce a phase separation via spinodal decomposition as the sol-gel reaction proceeds. The system composition is the major player in controlling the microstructure of the final material.^[3]

Our method permits a control of the microstructure of silica monoliths obtained by sol-gel process with phase separation by means of an external magnetic field. This is achieved by adding superparamagnetic nanocolloids to the sol-gel precursor solution and using their unique self-assembly properties in the presence of a magnetic field to prepare macroporous materials with unique anisotropic structure and mechanical properties. It is well known that superparamagnetic nanocolloids experience dipolar interactions in the presence of an external magnetic field, which drives the formation of one-dimensional chain-like structures.^{[4] [5] [6]} This behavior has been exploited to prepare magnetic responsive chains and rods, both rigid and flexible.^[4d, 6] The preparation of 3D anisotropic structures, achieved by inducing colloidal gelation of charge stabilized polymer-magnetite nanoparticles in the presence of a magnetic field, and fixing of the final structure by means of a postpolymerization reaction, has also been reported.^[5a]

An additional degree of freedom in controlling the structure of materials has been achieved by using rotating magnetic fields, which drive the assembly of the magnetic particles into the formation of sheet-like structures.

2 SYNTHESIS OF SILICA MONOLITHS

The synthesis of the silica monoliths is based on a modification of a recipe described elsewhere.^[7] In a typical

procedure, 0.34 g of PEG 10kDa were dissolved in 5.465 ml of 0.01 M acetic acid, the obtained solution was cooled down to 0° C and then 1ml of TMOS was added. The obtained mixture was stirred for 30 minutes at 0° C, then 0.235 ml of a magnetic nanocolloids solution, prepared as described in the literature.^[7b] The solution was stirred for a couple of minutes more before being poured in two molds, one of which was put in an oven at 40° C, while the second one was placed in an heat jacket inside a magnetic field of 1 T at 40° C. Both samples were cured for 12 hours. The obtained monoliths were first immersed in a solution of water-ethanol 1:1 by volume for 24 hours and then in pure ethanol for additional 48 hours. In order to remove all the water, the ethanol was replaced with fresh one every 24 hours. The monoliths were then dried in an oven at 50° C for 3 days and finally calcined at 600° C for 3 hours. For the experiments with bigger amount of latex, the concentration of acetic acid was adjusted by the addition of a suitable amount of 1.25 M acetic acid solution.

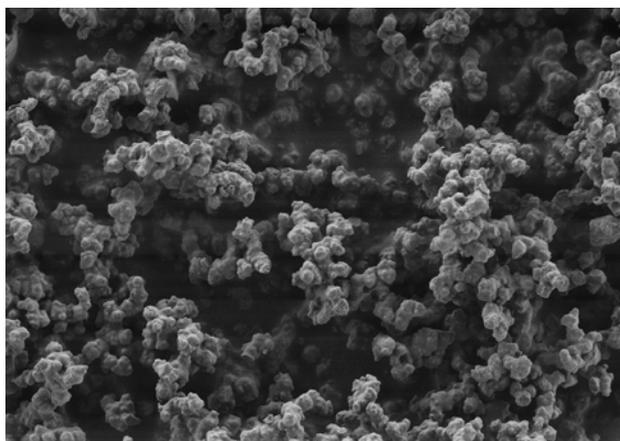


Figure 1: SEM picture of a silica monolith obtained in the absence of a magnetic field.

3 RESULTS AND DISCUSSION

The production of silica macroporous monoliths via sol-gel process has been well investigated in the literature.^[2, 7a, 8] The most commonly investigated systems begin as a homogeneous solution of silica precursor and a polymer acting as a porogen. The silica precursor (usually TMOS) is first hydrolyzed and subsequently polymerized. This polycondensation acts as a chemical cooling, which induces a phase separation in the system, usually occurring through a spinodal decomposition. The spinodal decomposition leads to the formation of a bicontinuous structure, with one silica-rich phase becoming coarser, hardening and eventually forming the skeleton of the monolith.

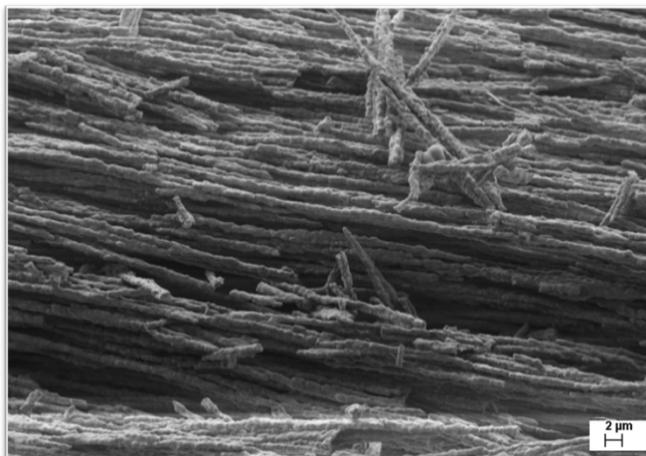


Figure 2: SEM picture of a silica monolith obtained in the presence of a static magnetic field.

In this work we introduced a modification to the above described process, in that we add from the beginning magnetic nanocolloids to the system, which act as templating agents, and we take advantage of their capability to align into string-like structures in the presence of a static magnetic field. Similarly, in the presence of a rotating magnetic field, the nanocolloids will assemble into two-dimensional sheet-like structure. The application of a magnetic field during the chemically-induced spinodal decomposition offers us the unique opportunity to control the morphology of the bicontinuous phase.

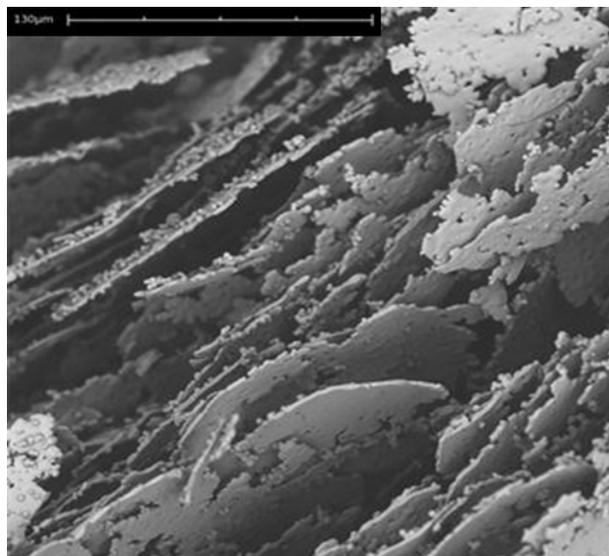


Figure 3: SEM picture of a silica monolith obtained in the presence of a rotating magnetic field.

The magnetic nanocolloids have been prepared by miniemulsification in water of styrene, with magnetite nanocrystals coated by ricinoleic acid dispersed in it, in the presence of Pluronic F-68 as an emulsifier. The process leads to droplets that are polymerized via free radical

polymerization into polystyrene nanocolloids with a hydrodynamic diameter of ~137 nm and magnetite content of 33 wt%. As shown in a previous work, Vibration Sample Magnetometer (VSM) measurements show that the nanocolloids are superparamagnetic.^[5a, 9]

The second step is the crucial part of our process. The magnetic nanoparticles are dispersed in a solution composed of water, acetic acid and a silane precursor (TMOS), and the dispersion is then transferred to a mold, which is typically placed between the poles of an electromagnet that generate a homogeneous magnetic field. In the case of samples prepared in the presence of a rotating magnetic field, the sample is rotated at a fixed frequency in between the poles of the magnet. The sol-gel process begins with the progressive condensation of TMOS, after which silica starts nucleating. The structure of the material obtained in the absence of a field is shown in Figure 1. The material structure strongly resemble a colloidal gel, with silica almost completely covering the nanocolloids and linking them together. This suggests that silica has a strong propensity to nucleate right on the surface of the nanocolloids due to the strong affinity for magnetite, eventually covering them. In the presence of a static magnetic field, the nanoparticles align themselves almost instantaneously in the field direction, leading to the formation of chains of particles. These chains are progressively covered and crosslinked together by silica, creating a network of aligned chains. The most interesting structures are however observed when PEG, often used in the preparation of silica monoliths as a porogen, has been added to control the structure of silica monoliths. The bicontinuous domains obtained as a result of the spinodal decomposition evolve into very long needle-like silica domains all oriented in the direction of the applied field, with approximately the same diameter as the large spherical silica beads formed in the absence of a field, as can be observed in Figure 2. An analogous process performed in the presence of a rotating field leads to the sheet-like structures shown in Figure 3.^[4c]

The unique structure of these monoliths imparts them unique mechanical properties. The mechanical strength of the samples has been quantified by performing compressive stress measurements and extracting the Young's moduli. Parallelepiped-shaped samples have been measured in two directions, which in the case of samples prepared in the presence of an external magnetic field correspond to the directions parallel and perpendicular to the field, respectively. In the case of samples prepared under a rotating magnetic field, instead, the mechanical properties are tested along three perpendicular directions. A remarkable general feature of the monoliths prepared in the presence of a static magnetic field is the enormous mechanical anisotropy that the magnetic field is capable of inducing. The difference between the Young's moduli in the directions parallel and perpendicular to the field, applied

during the reaction, increases with the strength of the applied field, until a saturation for high fields value is reached. For high enough magnetic fields, the values of Young's modulus in directions parallel to field can be more than two orders of magnitude higher than the one perpendicular to the field, and be 20 times higher than that of a material prepared in the absence of a field. The values of the modulus measured in the perpendicular direction, instead, decrease as the field increases. On the other hand, samples prepared in the absence of the field are isotropic, thus confirming that only the application of the field during the reaction is responsible for anisotropy. In the case of monoliths prepared in the presence of a rotating magnetic field, the Young modulus values are larger in the the plane of rotation as in the perpendicular direction, reflecting their sheet-like structure. These effects can be explained by the needle-like clusters observed in samples prepared in a static magnetic field, which are all aligned in the field direction imparting a tremendous strength to the structure. In the perpendicular direction, instead, the mechanical properties are inferior to that of isotropic samples because the needles are laterally loosely bound together by only a few links.

This unique structure can be utilized to create building blocks that can be used to create composite materials. These can be prepared by exposing the monoliths to a strong sonication. The weak links connecting needle-like structures in the case of monoliths prepared under static fields, and connecting sheets-like structures in monoliths prepared under a rotating fields are broken firsts. This leads to the formation of rods and platelets with very well controlled diameter or thickness, respectively. The silica surface permits a wide range of functionalization possibilities, thus expanding the flexibility of this approach.

4 CONCLUSIONS

It this work we have demonstrated how sol-gel transition of silica accompanied by phase separation can be substantially modified by the use of magnetic nanocolloids as templates. When these nanocolloids are added to a solution containing a silica precursor undergoing a sol-gel transition with phase separation, the structure of the resulting porous silica monoliths can be controlled by applying a magnetic field. The application of magnetic field during sol-gel transition allows one to control the morphology of the bicontinuous structure formed by the spinodal decomposition, leading to the formation of materials with either extremely long needle like domains aligned in one direction, or two-dimensional sheet-like structures in the case of a rotating magnetic field. The mechanical properties of these monoliths are enormously affected by the application of a magnetic field during the sol-gel transition. Sonication can be used to extract magnetic building blocks suitable for the preparation of composite materials.

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