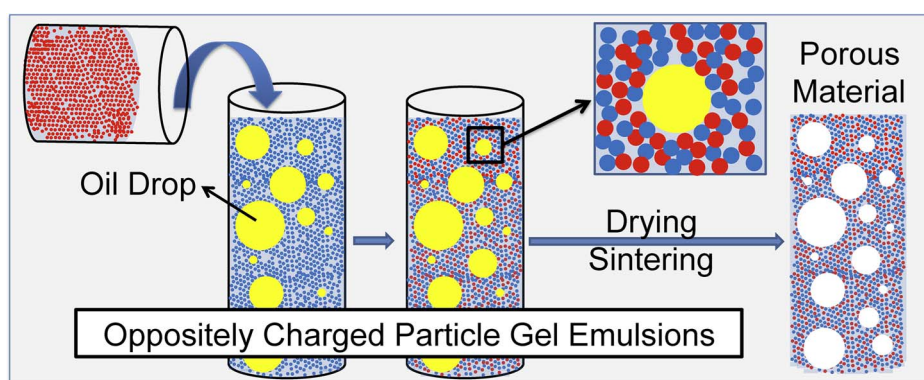# Porous materials from oppositely charged nanoparticle gel emulsions

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Sol–gel processing is an important colloidal processing route for the synthesis of macroporous materials of tunable microstructure. More recently, methods that use particle stabilized foams or emulsions have been developed. However, such methods generally involve the use of an external surface active additives that bind the particles together during processing. In this work, we present a simple and scalable additive-free method for the fabrication of porous materials that are both macroporous and microporous in nature. In particular, we show that silica-alumina porous materials can be fabricated by processing oppositely charged nanoparticle gel emulsions which are a dispersion of oil droplets in a space spanning network of colloidal particles. The nanoparticle gel emulsions obtained are initially characterized by optical microscopy and oscillatory rheology. The water and oil in these emulsion gels are removed by drying and it is finally sintered at 1000 °C to obtain porous material. The pore size and their distribution in the three-dimensional porous material is characterized using scanning electron microscopy (SEM) and X-ray tomography. Microscopy observations revealed a homogeneous distribution of macro-pores of 20–40 μm in diameter along the width, breadth and thickness of the porous material with an average porosity of 40% measured from 2D X-ray computed tomography images. One of the important features of the porous materials thus fabricated is the presence of nanosized pores due to the inherent porosity of the nanoparticle gel as well as micron sized pores due to the oil droplets.

1. Introduction

Porous ceramic materials have many applications owing to their high temperature stability, corrosion resistance, low thermal conductivity and tailored electronic properties [1–4]. Some applications of such materials are in the area of catalytic reaction engineering,

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separation science and technology – especially, in the filtration of molten metals, corrosive gases and particles from exhaust gases among others [4–7]. The functionality of a porous material is primarily determined by the material of construction, pore morphology and pore size distribution, which in turn depends on the nature of processing technique employed.

There are several processing routes through which porous ceramic materials can be fabricated. These methods can be broadly classified as replica technique, sacrificial template method and direct foaming/emulsion method [8,9]. All these processing routes lead to macroporous materials with pore size > 50 nm [10]. In the direct foaming/emulsification technique, surface active agents are used to produce a dispersion of interfacially stabilized liquid drops or gas bubbles in a liquid or a colloidal dispersion, which are further processed to create porous structures by controlled removal of the dispersed phase followed by sintering. The surface active agents used to make emulsions and foams can be either surfactants, polymers or particles [11–13]. Use of foams or emulsions is an important colloidal processing route for the synthesis of macroporous materials of tunable microstructure [14]. Application of particle stabilized emulsions [15–17] (commonly referred to as Pickering emulsions, in which the particles are at the interface between the two liquids stabilize the emulsions) for the fabrication of porous materials is a more recent development in this field [8]. In the so called sol–gel approach for porous material formation, a stable colloidal dispersion is first converted into a solid-like gel either by the addition of salt, polymer or other reagents. It is clear that in the several methods discussed so far surface active agents are added to tune colloidal interactions or interfacial activity. However, such additives can sometimes be detrimental to the product [18]. Therefore, there is a need for additive free processing routes for the fabrication of porous ceramic materials.

Recently, it has been demonstrated that attractive interactions between colloidal particles can be exploited to obtain stable nanoparticle gel foams. Nanoparticle gel foams are a dispersion of gas bubbles trapped in a 3D space spanning network of particles held together by attractive interactions [19]. One of the simple and effective method to create solid-like particle gels is by taking advantage of the hetero-aggregation phenomena, which is the aggregation of colloidal particles that differ in one or more physical or chemical properties such as charge, size or shape [20]. This phenomena has been exploited in the fabrication of ceramic materials, core-shell composites and cellulose based materials [21]. For example, porous materials were synthesized by exploiting hetero-aggregation of polymethylmethacrylate particles (PMMA) and α-Al$_2$O$_3$ particle mixtures [22]. The pH and α-Al$_2$O$_3$ to PMMA ratio were found to affect the hetero-aggregation behavior and hence the pore size distribution of the final porous material. Since the emulsion size can be tuned by using mixtures of oppositely charged particles (OCPs), in principle, it is possible to have an additional handle on the control of the pore sizes by varying the mixing ratio of particles [23].

In this article, we propose a processing route for the fabrication of porous materials from OCP emulsion gels. Oil drops are incorporated into gels formed via electrostatic hetero-aggregation of nanoparticles [24–26] to obtain OCP gel emulsions, which consist of oil drops trapped in a viscoelastic network of particles formed due to electrical double layer attraction. One of the advantages of such materials is that there is no need of any surface active additives and can be prepared at solid loading appropriate for several applications [19]. Oil drops are incorporated into a dispersion of nanoparticles by high energy homogenization followed by the addition of oppositely charged nanoparticle dispersion such that a 3D particle network is formed around the oil drops. The nanoparticle gel emulsion is then dried to remove the oil drops and residual water which upon sintering gives rise to porous materials. We use commercially available aqueous dispersion of monodispersed positively charged alumina coated spherical silica particles (Ludox-CL) and negatively charged silica particles (Ludox-HS). We first

show that the mixtures of these particles at a specific mixing fraction ϕ_{max} exhibit maximum aggregation. The dispersion mixed at ϕ_{max} with sufficiently high concentration form nanoparticle gels that exhibit solid-like behavior. High energy homogenization of oil-nanoparticle dispersion followed by the addition of oppositely charged nanoparticle dispersion is carried out leading to the formation of nanoparticle gel emulsions, which upon drying and sintering forms porous material consisting of two types of nanoparticles. To investigate the various properties of nanoparticle gels and nanoparticle gel emulsions, a combination of dynamic light scattering, optical, electron microscopy, rheology and X-ray tomography are used. The use of binary particle mixtures for the preparation of porous material will lead to multicomponent porous materials with potential applications in various fields.

2. Materials and methods

2.1. Materials

Positively charged alumina coated silica nanoparticles (Ludox-CL) and negatively charged silica (Ludox-HS) particle suspensions were purchased from Sigma-Aldrich. These are aqueous dispersion containing 30% particles by weight. The pH of Ludox-CL and Ludox-HS dispersions as received are 4–5 and 8–9 respectively. The size of Ludox-CL and Ludox-HS particles as measured by dynamic light scattering are 15 ± 0.5 nm and 14 ± 0.6 nm respectively. The oil phase used is dodecane (99% pure) purchased from Sigma–Aldrich. Milli-Q water of resistivity > 18.2 MΩ cm at 25 °C is used to dilute the dispersions to desired particle concentration and no pH adjustment is made.

2.2. Processing route for fabrication of porous material

One of the primary requirements for the processing route considered in this study is that the elasticity of the particle network should be high enough to prevent coalescence or creaming of the oil drops and the particle concentration must be sufficiently high so that the colloidal dispersions form a uniform gel phase [25] as shown in Fig. 1(A). However, if the particle network becomes too stiff, the dispersion of oil into the nanoparticle gels [19] require enormous energy input and emulsion gels obtained may not be homogeneous. Therefore, nanoparticle gel emulsions are prepared by dispersing oil drops into a colloidal dispersion of negatively charged particles of sufficient concentration with the help of a high speed homogenizer and subsequently, a colloidal dispersion of positively charged particles is added as shown in Fig. 1(B). In this way, hetero-aggregation of particles occurs around the dispersed oil drops such that a stable nanoparticle gel emulsion is obtained. These gels are finally dried and sintered to obtain porous material as shown in Fig. 1(C).

2.3. Sample preparation

Nanoparticle gels and nanoparticle gel emulsions are prepared in glass vials of volume 40 ml. Ludox-CL dispersions (positively charged) and Ludox-HS dispersions (negatively charged) are mixed at various ratios and concentrations. The nanoparticle gel is obtained as soon as the two dispersions are mixed. The nanoparticle gel emulsion is prepared by first dispersing about 6 ml of dodecane into the Ludox-HS dispersion using a high energy homogenizer (IKA T25 digital ULTRA-TURRAX). The homogenization is carried out at 10,000 rpm for 5 min followed by the addition of Ludox-CL dispersion. This leads to the formation of nanoparticle gel entrapping the oil droplets. Finally, vortex mixing of oil dispersed gel is carried out for 5 min for uniform dispersion of oil into the gel. Cylindrical shaped plastic mould is used to shape the nanoparticle gel emulsion into cylindrical specimens of length 15 mm and diameter of 10 mm. Samples are dried in hot air oven at 80 °C for 48 h. The sample is further heated in a tubular furnace at