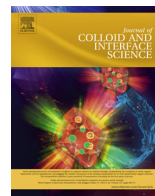




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Mesoscale self-assembly of reactive monomicelles: General strategy toward phloroglucinol-formaldehyde aerogels with ordered mesoporous structures and enhanced mechanical properties

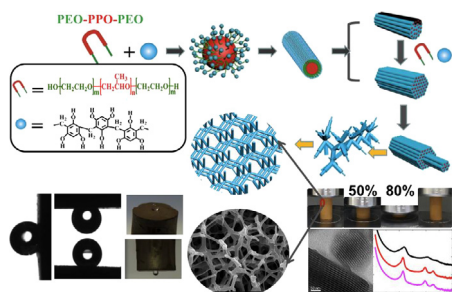


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GRAPHICAL ABSTRACT

Here, using reactive monomicelles as building blocks for mesoscale self-assembly, we demonstrate a general strategy for the preparation of robust phloroglucinol-formaldehyde (PF) aerogels with ordered mesoporosity and well-defined biomimetic truss frameworks, and thus possess enhanced mechanical properties and good recoverable compressibility. Besides, the prepared aerogels reveal interesting morphology enhanced sticky superhydrophobicity. A plausible formation mechanism was proposed which involving the formation of spherical reactive F127/PF oligomer monomicelles, then join together and elongate into rod-like micelles, which further aggregate to form ordered hexagonal nanorods and finally growth to form monolithic aerogels.



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ABSTRACT

Here, using reactive monomicelles as building blocks for mesoscale self-assembly, we demonstrate a general strategy for the preparation of robust phloroglucinol-formaldehyde (PF) aerogels with ordered mesoporosity and well-defined biomimetic truss frameworks, and thus possess enhanced mechanical properties and good recoverable compressibility. Besides, the prepared aerogels reveal interesting morphology enhanced sticky superhydrophobicity. A plausible formation mechanism was proposed which involving the formation of spherical reactive F127/PF oligomer monomicelles, then join together and elongate into rod-like micelles, which further aggregate to form ordered hexagonal nanorods and finally growth to form monolithic aerogels. This work encourages the further utilization of mesoscale self-assembly of monomicelles as a general and powerful strategy for the biomimetic synthesis of hierarchically porous monolithic materials possess highly ordered mesoscale structures and excellent mechanical properties.

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1. Introduction

Polymeric aerogels represented by resorcinol/phloroglucinol/melamine-formaldehyde aerogels and polyurethane aerogels have attracted great scientific and industrial interest due to their three-dimensional hierarchical morphology, high porosity, low densities and low thermal conductivity [1–6]. Polymeric aerogels are generally prepared through sol-gel polymerization of multi-functional organic species into three-dimensional covalently bonded polymer networks. The first step evolves the preparation of wet gels composed fully of solvents, if the solvents are evaporated in the air directly, the aerogels will shrink dramatically because of the large capillary forces generated at the liquid-vapor interface during the drying process [1,7,8]. Supercritical CO₂ drying is thus widely used, however, the requirement of extreme conditions to meet the supercritical point of CO₂ makes the drying process time consuming, difficult to scale-up, expensive, and dangerous, thus robust ambient-dried polymeric aerogels is greatly wanted [9,10].

Periodic mesoporous materials own many unique properties, such as uniform and adjustable pore size, high surface area, large pore volume and easily functionalized surface. Therefore, mesoporous polymeric aerogels have great potential applications in many areas such as catalysis, absorption and separation of biomolecules, chemical sensors, biomedicines and environmental remediation [11–13]. Periodic mesoporous materials can be obtained by applying amphiphilic block copolymers as structure-directing agents, especially, Zhao proposed a widely known organic-organic assembly method to synthesize ordered mesoporous phenolic-formaldehyde resins with various mesoporous structures using amphiphilic triblock copolymers as a soft template and phenolic formaldehyde precursor as framework materials [14–18]. It is fairly challenging to govern both amphiphilic block copolymers/oligomer self-assembly and phase separation during complex sol-gel polycondensation process. Hence, despite a drastic progress in the synthesis of mesoporous materials with control of pore sizes over length scales from Angstroms to micrometers, most of the prepared mesoporous materials are powders or fragile solid. The preparation of monolithic materials with a simultaneous tailoring of pore structures, morphology and excellent mechanical properties has been rarely reported. Very recently, Nakanishi and co-workers reported an excellent work on the synthesis of resorcinol-formaldehyde aerogel with ordered mesoporous structures and enhanced elastic stiffness and recoverability, their unique mechanical properties is derived from the well-defined interdigitated nanorods generated through the spontaneous supramolecular self-assembly of the nonionic triblock copolymer and RF oligomer [19,20]. Nakanishi's work revealed the morphology control can contribute greatly to the excellent combination of material properties such as low density, high flexibility and high compressibility. Much works is still needed to prepare polymeric aerogels possessing bio-inspired truss frameworks because of the stringent reaction conditions required to control the competing sol-gel polymerization process and mesoscale assembly process.

Here, in this research, phloroglucinol-formaldehyde/F127 system was chosen to symmetrically explore this important and complex sol-gel polymerization induced mesoscale self-assembly process, because phloroglucinol-formaldehyde precursors can form very strong triple hydrogen bonding to the polyethylene oxide (PEO) chains of Pluronic F127 (PEO₁₀₆-PPO₇₀-PEO₁₀₆), which is stronger than their resorcinol or phenol counterpart and thus should favor the hydrogen directed mesoscale self-assembly of monomicelles. After a facile one-pot hydrothermal process, robust phloroglucinol-formaldehyde polymeric aerogels with ordered mesoporous structure and well-defined biomimetic truss frameworks were successfully prepared, the prepared aerogels

revealed enhanced flexibility and excellent recoverable compressibility. The mechanism behind this complex sol-gel polymerization induced mesoscale self-assembly process were studied in detail. Study further revealed the PF aerogels exhibited a so-called “rose petal effect” (superhydrophobicity with high droplet adhesion), the water contact angles (CAs) can be easily controlled through morphological evolution to as high as 144°. This work encourages the further utilization of mesoscale self-assembly for the biomimetic synthesis of hierarchically porous monolithic materials possess properties that are mutually elusive in general such as ordered mesoporosity, stiffness and flexibility.

2. Experimental

2.1. Hydrothermal synthesis of phloroglucinol/formaldehyde (PF) Aerogels.

The PF aerogels were prepared by a one-pot sol-gel hydrothermal process. In a typical process, 1.5 g of Pluronic F127, 1.5 mL of 1,3,5-trimethylbenzene (TMB), and 1.5 mL of benzyl alcohol (BzOH) were added to a given amount of a triethylene glycol (TEG)/1 M HCl aq. mixed solvents, followed by stirring at 40 °C to obtain a homogeneous solution. Then, 1.3 g (0.010 mol) of phloroglucinol was dissolved in the resultant solution, followed by adding 1.1 mL of formaldehyde solution (37 wt%, 0.013 mol). After stirring for another 30 min at room temperature, the freshly prepared solution was transferred to a PTFE-lined steel autoclave. The autoclave was placed in an oven at 100 °C for 24 h for gelation and aging. The obtained wet gels were further treated with 1 M NH₃ aq. at 80 °C for 24 h. After washing several times with H₂O, it was dried at 80 °C under ambient pressure for 24 h to form ordered mesostructured PF aerogel.

2.2. Hydrothermal synthesis of PF/Graphene oxide aerogels

Typically, the above solvents were mixed with a given amount of graphene oxide (GO) aqueous followed by stirring at 40 °C to obtain a homogeneous solution. Then, phloroglucinol and formaldehyde was added. After hydrothermal treated at 100 °C for 24 h for gelation and aging. The obtained wet gels were treated as above-mentioned process to obtain PF/GO nanohybrid aerogels.

2.3. Characterization

FT-IR spectra were measured with a Nicolet 560 spectrometer. Scanning electron microscopy (SEM) was conducted with an Inspect F SEM at an accelerating voltage of 20 KV. The high-resolution TEM (HR-TEM) images were obtained on a Tecnai G2 F20 transmission electron microscopy at an accelerating voltage of 200 kV. The SAXS measurements of the monolithic specimens were carried out with Xeuss 2.0, equipped with a Cu K α X-ray generator ($\lambda = 0.154$ nm), working voltage 50 KV, electricity 0.6 mA. The nitrogen absorption and desorption isotherms were measured at 77 K using a Tristar system. The samples were heated at 350 °C for 30 min under N₂ atmosphere containing 10% of air to remove the remaining F-127. Water contact angles (CAs) were measured using a Rame-Hart Model 250 standard goniometer equipped with a high-resolution camera.

3. Results and discussion

The synthesis of ordered mesoporous PF aerogels in this study is based on the sol-gel polymerization induced self-assembly of in-situ formed soluble low-molecular weight PF oligomers using

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