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Functional silica aerogel from metastable lamellar composite

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A functional aerogel composed of interconnected silica nanoparticles has been synthesized from a metastable lamellar composite based on a novel type of cooperative interaction between silica and surfactant species.

Silica aerogels possess an attractive and unique set of properties, [1,2] including extremely low densities, high surface area, low thermal conductivity and low dielectric permittivity. The pore structure of aerogels is formed by the controlled condensation of small (polymeric or colloidal) primary particles which are usually generated and aggregated by a sol–gel process. [1,3] Typically, an alkoxysilane precursor is used to produce an alcogel in acidic or basic alcoholic solution by a one- or two-step sol–gel process, then the alcogel is subject to air-exchange without destroying the gel structure generally by supercritical drying. A highly pursued goal in aerogel technology is the elimination of the supercritical drying step, because it is the most expensive and risky step in the production of aerogels. While the structure–property relationship of aerogels is readily manipulated through the choice of precursors and polymerization conditions, research in new aerogel chemistry and compositions is necessary for performance improvement and novel applications.[4]

Here we report the synthesis of a functional aerogel from a metastable lamellar surfactant–silica composite, eliminating the intermediate alcogel formation. We demonstrate that the surfactant mesostructure facilitates and stabilizes the formation of monodispersed silica nanoparticles, that aggregate into a highly porous solid. The porous, skeletal structure is maintained after removal of surfactant. This procedure provides a novel non-supercritical drying technique for the production of aerogels and reveals a new aerogel chemistry for functional, highly porous materials.

Bis[(3-triethoxysilyl)propyl]tetrasulfide (SIS, purchased from Petrarch systems) was chosen as the silane precursor. The sulfur chain (–S_4–) in the SIS molecule has been demonstrated to have a high affinity for heavy metals (*e.g.* mercury and silver).[5] Thus, functionalized aerogels would be a potential sorbent for the recovery of heavy metals, as shown for thiol-monolayer modified molecular sieves M41S.[6] The precursor was added dropwise into 5% aqueous sodium dodecyl sulfate (SDS, purchased from Aldrich) solution under vigorous stirring. Then 0.1 M HCl was added dropwise as the catalyst. The composition (molar ratio) of the final solution was SIS : SDS : HCl : H_2O = 1 : 1.5 : 0.05 : 600. A bean curd-like, milky-white gel formed and floated in a clear solution after 2–3 days under ambient conditions. In contrast, no gel formed in the solution without SIS, or a light yellow precipitate formed in the solution without SDS.

Fig. 1 shows the small angle X-ray diffraction patterns of the gel samples dried at room temperature [curve (a)] and at 100 °C for 4 h at atmospheric pressure [curve (b)]. The room temperature-dried gel exhibited well defined (001), (002), and (003) peaks characteristic of lamellar structure, with the largest *d* value of 35.13 Å. By contrast only poorly-defined (001) and (002) peaks were observed for the heated gel, and the *d* value decreased to 28.79 Å, indicating that the lamellar structure of the gel (SDS/SIS sol–gel composite) is thermally unstable.

Fig. 2 shows typical TEM micrographs of the ethanol-washed room temperature-dried SDS/SIS sol–gel composite. It is clear that a three-dimensional highly porous skeleton structure characteristic of aerogel[7] is formed from the SDS/SIS sol–gel composite after removing the surfactant. Closer examination reveals that the network is constructed by interconnected nanoparticles. These nanoparticles are narrowly distributed with a diameter around 38 nm. The aerogel thus prepared exhibited low bulk density (*ca.* 0.2 g cm^{-3}).

A possible mechanism for the SIS aerogel formation from a metastable lamellar SDS/SIS sol–gel composite is proposed in Scheme 1. A high SDS concentration in water leads to a lyotropic lamellar liquid-crystalline phase consisting of bilayer sheets[8] (A). Addition of the hydrophobic silica precursor, SIS, into the aqueous media under vigorous agitation resulted in the formation of SIS droplets promoted and stabilized by the presence of SDS (B). Meanwhile, mediated by Na^+ counter ions, SDS bilayers bend around the SIS droplets.[9,10] Upon closing, these sheets form lamellar vesicles,[11–13] encapsulating the SIS droplets (C). The hydrolysis and condensation (*i.e.* polymerization) of SIS then occurs in these lamellar vesicles. Aggregation of these lamellar droplets is facilitated[9,14–16] by dehydration of the surfactant head groups and an increase in counter ion binding caused by the release of ethanol in the SIS hydrolysis process. Upon aggregation, a bean curd-like gel

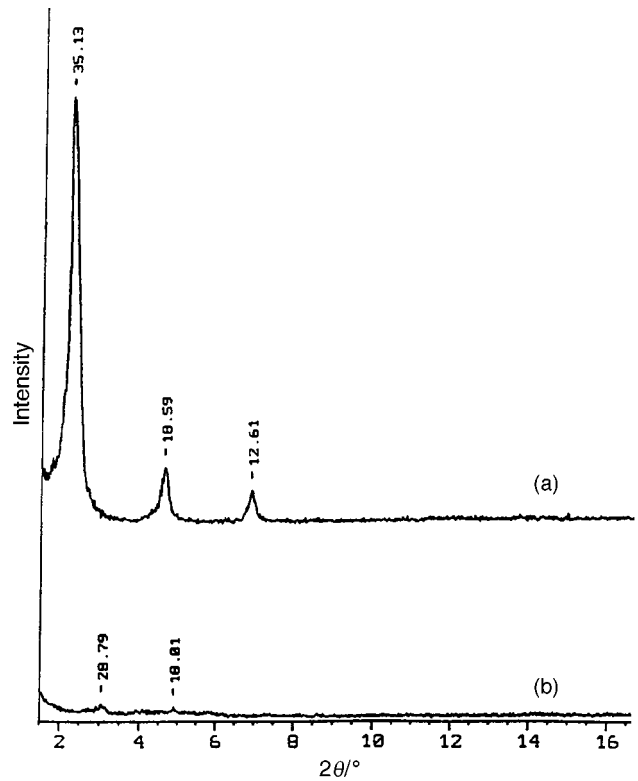
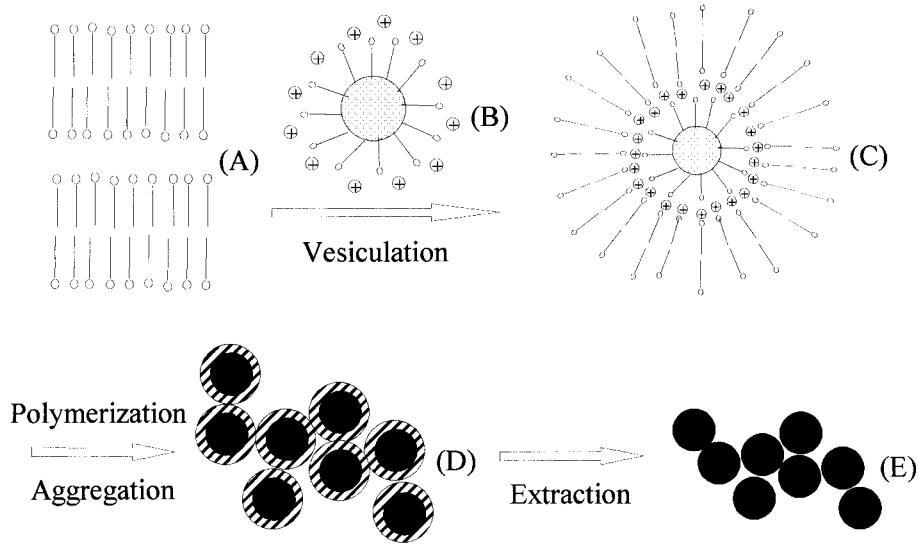


Fig. 1 Small angle X-ray diffraction patterns of the SDS/SIS sol–gel composites dried at room temperature (a) and dried at 100 °C under ambient pressure (b).



Scheme 1

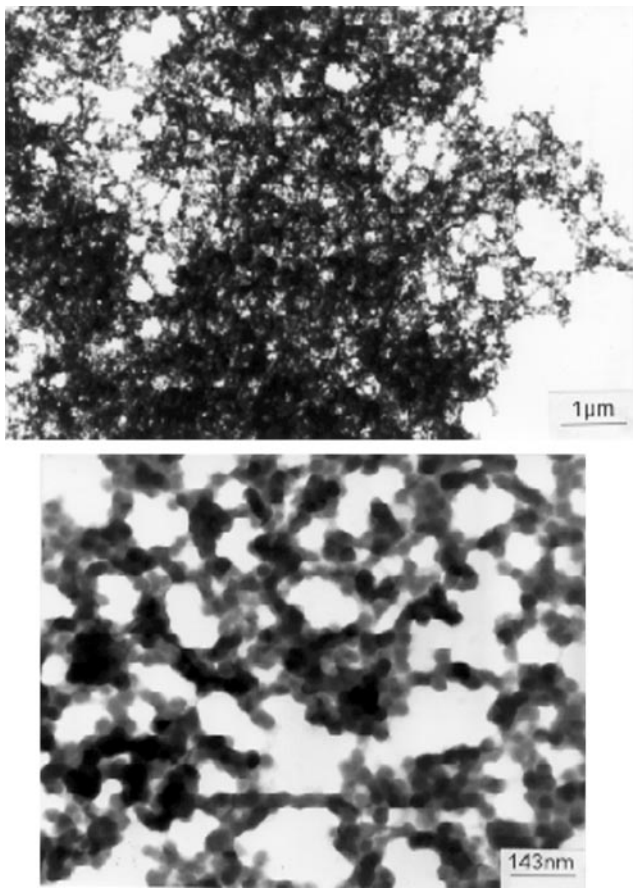


Fig. 2 Transmission electron microscopy micrographs of the ethanol-washed room temperature-dried SDS/SIS sol–gel composite at low (top) and high (bottom) magnifications.

formed (D). At SDS concentrations of ⩾5%, bean curd-like gels are readily formed. A higher concentration (> 10%) results in SDS crystallization. Removal of SDS by alcohol extraction resulted in the SIS aerogel (E), most probably because of the highly hydrophobic interactions among the SIS sol–gel nanoparticles.

In conclusion, we have developed a novel approach for the production of a functionalized aerogel from a surfactant/SIS sol–gel composite. This technique allows atmospheric pressure drying so eliminating expensive and risky supercritical drying. The highly porous characteristics combined with the high affinity of the sulfur chain for heavy metals hold promising and immediate environmental application in the recovery of heavy metals.

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