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One-pot sol-gel process and simultaneous formation silica particles cross-linked network (SPCN)

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Abstract

In this work, a simple sol-gel process method was studied for "one-pot" fabrication of silica particle cross-linked networks (SPCN). It is the first time that the co-precursors of tetraethoxysilane (TEOS) and γ-glycidoxypropyltrimethoxysilane (GPTMS) and capping agent of cetyltrimethylammonium bromide (CTAB) are formulated to achieve the complete co-polymerization of the reaction solution. The reaction solution proposed involved TEOS and GPTMS (5:1 w/w) for feasibility preparation of SPCN. The copolymerization temperature was set at 40°C for 24h of aging time. The results indicated that, by means of cetyltrimethylammonium bromide as a capping agent, SPCN exhibited a well-defined three-dimensional (3D) porous network. The prepared SPCN was used for the synthesis of silica monolithic columns to show interstices distributed across the whole SPCN as well as monolithic columns. The BET surface area of the SPCN column was obtained at approximately 156 m^2/g and an average pore width smaller than 26 nm.

Keywords: Silica particle cross-linked networks; silica monolithic column; sol-gel process

1. Introduction

Silica is one of the important and abundant substances present in various sources such as diatom, rice husk and straw, sand, and quartz [1–3]. Considered as one of the most frequently used materials, silica-based materials have been widely applied in various fields of industry and daily products such as agriculture, environmental remediation, cosmetics, energy storage, biomedical, and therapy applications [4–6]. Recently, silica-based use in biological and pharmacological applications has been more intensively developing in materials chemistry for their feasible fabrication and modification [7,8]. The physiochemical and mechanical features of the materials rely highly on the fabrication techniques. Various methods have been proposed to fabricate silica-based materials with different structures, morphology, and properties [9–11]. For instance, silica aerogel materials or silica aerogel monoliths with their extradition three-dimensional (3D) porous in matrix structure perform distinctive physio-chemical properties and immense macroscopy integrity that have been utilized in various applications in energy storage, purification, catalyst, and thermal insulation [12].

Silica-based monolithic columns constructed from silica aerogel materials fulfill in silica fuse capillary for capillary liquid chromatography (CLC) and capillary electrochromatography (CEC) [13]. Silica aerogel monolithic exhibits a unique porous network in structure, large surface area, and ability in mechanical stability and separation efficiency. Since the first report of silica aerogel in the 1930s [14], and of macropore-mesopore silica monolith in 1991 [15], there have been limited numbers of studies regarding the fabrication of silica aerogel materials or silica aerogel application for monolithic column fabrication. The two concepts of monolith column making are the sol-gel technique and packing materials; however, both still remain challenges. Fulfilling the silica fuse requires the complete hydrolyzation and polymerization of sol-gel solutions, meaning that total liquid-to-solid transformation quickly occurs inside the silica fuse. Whereas, the packing materials approach, frit typically works as a barrier for holding the stationary phase within the column, and frequently causes high back pressure [16]. Therefore, to develop a method for monolithic columns continuous porous beds without frit is still deemed necessary. The direct formation of silica matrix inside the silica fuse capillary is considered as a convenient approach to fully exploit the structural and functional properties of the material with the advantages of reducing time consumption, single-step fabrication, and saving of chemical reactants [17].

In this work, we call silica particles cross-linked networks (SPCN). We proposed a simple and on-pot synthesis of silica particle cross-linked network (SPCN) with the aid of sol-gel processes methods involving TEOS and GPMTS as co-precursors in the presence of cetyltrimethylammonium

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bromide (CTAB) as a capping agent. The complete liquid-to-solid through hydrolyzation and condensation of the designed reaction solution opened the way to obtain a fulfillment of silica fuse as a monolithic column.

2. Materials and Methods

2.1. Reagents

Tetraethoxysilane (TEOS, 95%) and γ-glycidoxypropyltrimethoxysilane (GPTMS, 98%) were obtained from Sigma. Cetyltrimethylammonium bromide (CTAB), aqueous ammonia solution (NH_4OH), and anhydrous ethanol (EtOH) were purchased from Daejung Chemical. Meanwhile, fused-silica capillary (100um i.d x375 um o.d) was obtained from Trajan (Aus Pty Ltd.). Here, all chemicals were used without future purification.

2.2. One-pot preparation of silica particles cross-linked networks (SPCN)

SPCN was fabricated based upon sol-gel methodology (Fig. 1(a)). Typically, hydrolysis and condensation were conducted by mixing TEOS and GPTMS with different ratios in the presence of EtOH, water, and CTAB as the templates. NH_4OH was then added to the polymerization solution. All reaction solution was homogeneity by sonication bath (2510E-DTH, Branson) at 40 kHz. Subsequently, the reaction solution was kept constant at a temperature ($T_{gelling}$) of 40℃ for 24 h. In this work, the ratio of TEOS and GPTMS was optimized under the ratios of 2:1, 5:1, and 10:1 with a total amount of mixture of 600 mg in weight. The amount of CTAB, EtOH, NH_4OH, and H_2O used were 30, 200, 10, and 30 mg, respectively. The different capping agents of oleic acid and polyethylene glycol (PEG 400) also were used to compare with CTAB. The morphology of the SPCN structure was characterized by SEM (JEOL JSM 7500F). FT-IR spectrum was recorded through the JASCO FT/IR-4100 spectrometer. Also, Brunauer-Emmett-Teller (BET) was applied to obtain intercalate pore size distribution and specific surface area of the SPCN candidate sample using N_2 absorption-desorption analyzer (ASAP 2020 V3, USA).

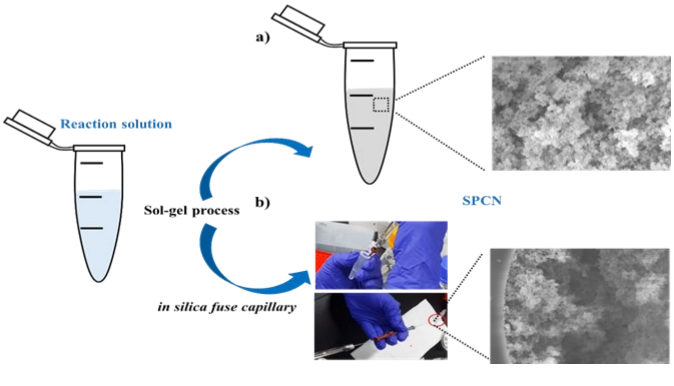

Fig. 1. A simplified illustration of on-shot fabrication of SPCN (a) and silica monolithic column-based SPCN (b)

2.3. Preparation of silica monolithic column

Fig. 1(b) illustrates the fabrication schematic of silica monolithic column-based SPCN. The reaction solution of SPCN was sonicated at 4°C for 1 min prior to be introduced into the silica fused capillary (100um i.d x 375 um o.d). Both ends of the capillary were sealed by parafilm before aging and incubating at 40°C for 24 hours in an oven. Subsequently, the capillary was rinsed, washed with EtOH, and dried in an oven overnight before future analysis. For back pressure comparison, the silica nanoparticle (SiNP) of ~1 µm also was fabricated and packed inside the silica fused capillary using FRIT as a holding manner. SiNP was synthesized by ultrasonication-assisted sol-gel Stöber method in accordance to our previous report [9]. Typically, 50 mL of EtOH was mixed with water (0.8 mol/L) and NH_4OH (1 mol/L) under continuous sonication at 40kHz for 5 min. TEOS (0.3 mol/L) was then added and kept sonication for 1.5 h. SiNP was collected and washed with ethanol by centrifugation. Finally, SiNP was suspended in ethanol for packing in a silica-fused column using FRIT.

3. Results and Discussion

Sol-gel method is a common wet-chemical approach to fabricating SPCN. In this method, the hydrolysis and polycondensation of alkoxysilane such as tetraethoxysilane (TEOS) can create silica gel with a monolithic skeleton. In this work, the simply synthesizing SPCN was proposed with a "one-pot" process; in particular, TEOS and GPTMS were selected for sol-gel feasibility preparation of the silica porous matrix.

In principle, the ratio of TEOS and GPTMS was examined in the ratio ranging from 2:1, 5:1, and 10:1 with a total mixture of 600 mg in weight. The hydrolyzation and polymerization occurred under the conditions of using CTAB as a capping agent, ethanol as solvent, and NH_4OH as a catalyst. The amount of CTAB, EtOH, NH_4OH, and H_2O used were fixed at 30, 200, 10, and 30 mg, respectively. The polymerization occurred at a temperature $T_{gelling}$ of 40°C for 24h. The result indicated that the total polymerization and condensation of the reaction solution were achieved at the ratio of TEOS and GPTMS of 5:1 as visualized in Fig. 2(a). The SEM images in Fig. 2(a) indicate that the silica skeleton was homogeneous, formed between the particles that were networking and distributed in SPCN. Fig. 2(b) displays the FT-IR spectrum of SPCN. The typical peaks of SiO_2 appeared at 1057, 1410, and 1680 cm^{-1}, attributed to the stretching vibrations of Si−O, shear bending vibration of N−H, and stretching vibration of N−H, respectively [18]. The typical peak of GPTMS was also obtained at 920 cm-1 (oxirane group), and bands at 1000-1200 cm^{-1} (overlapped with the bands of silica material) were attributed to Si−O−C, Si−O-Si, Si−O−H, and C−O) [19]. BET surface area was 160 cm^3/g with a pore width smaller than 26 nm (Fig. 2(c)). The formation reaction of particles in SPCN through tetraethoxysilane seems similar to silica nanoparticle formation [20]. However, the hydrolyzation and polymerization rate, as well as the amount of water and solvents used for SPCN formation, are different from those used for silica nanoparticle formation. Typically, the 3D porous silica matrix could be obtained in various morphology due to reaction conditions, precursors, and capping agents. The formation of SPCN involves hydrolysis and condensation steps. The different ratios of TEOS and GPTMS may affect the hydrolyzation rate. When TEOS is hydrolyzed in the presence of a catalyst, it significantly changes siloxane polymer form, leading to dense silica gels with smaller pore sizes. The hydrolyzation and polycondensation of TEOS in this reported condition extensively provided shrinkage porous structure. However, during the aging stage to obtain particles, a polycondensation also occurred to obtain small silica particles that aggregated with interstices across the whole SPCN. In addition, the intercalating between particles through reactive groups (alkoxy or hydroxyl) on their surface can generate a linkage that simultaneously creates a 3D network of particles and develops an SPCN structure [12].

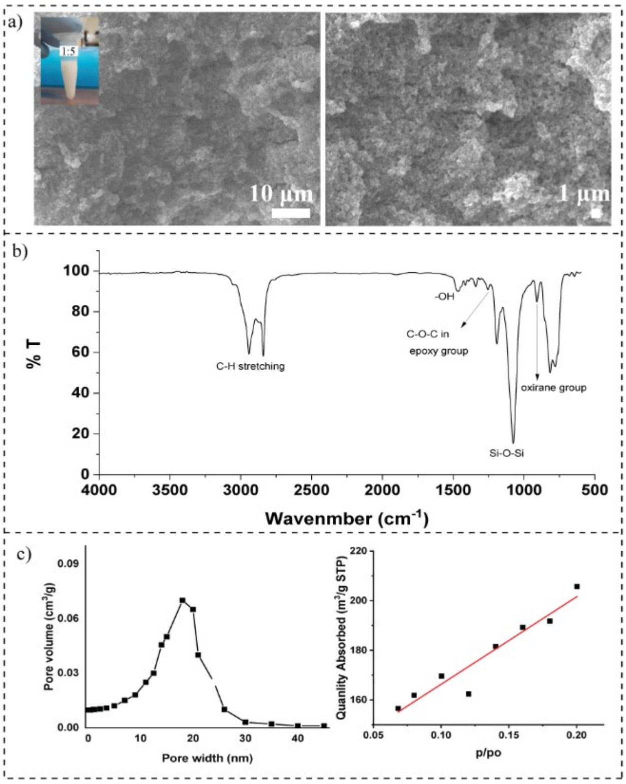

Fig. 2. (a) SEM images (b) FTIR spectra, and (c) Pore size distribution and BET surface area plot of SCNP (TEOS: GPTMS, 5:1) using CTAB as a capping agent. The digital inset image shows a total sol-gel process as a complete liquid-to-solid transformation

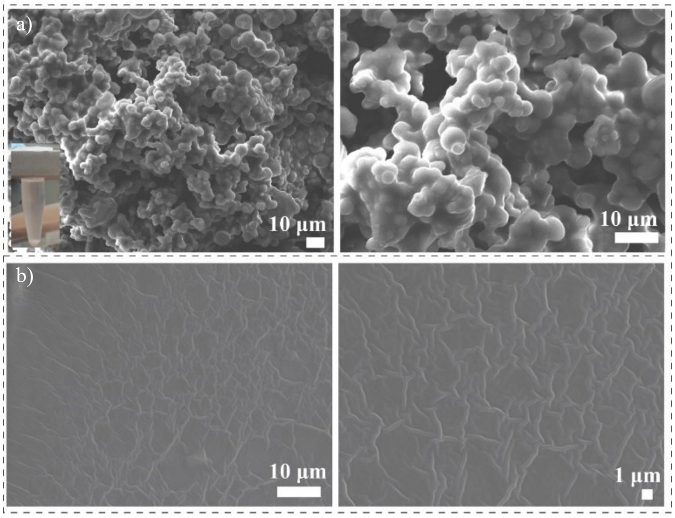

Fig. 3. SEM images of silica material using (a) oleic acid and (b) PEG400 as capping agent

Under the equal reaction condition at TEOS: GPTMS (5:1), different capping agents involving oleic acid (Fig. 3(a)) and PEG 400 (Fig. 3(b)) were applied instead of CTAB for comparison. However, there were no SCNP that could be formed according to the two formulations due to incomplete liquid-to-solid transformation as well as incomplete hydrolyzation and co-condensation of the reaction solution. Interestingly, with the capping agent oleic acid, the obtained silica material system possessed a completely different structure. Large particles intersect connection silica skeletons with different porous morphology scaffold structures. However, the polymerization solution was not completely transferred to the gelling form, a certain part of the reaction solution remained. In the case of PEG as a capping agent, the polymerization did not occur. Fig. 3(b) portrays the SEM images of the bulk membrane formed by the reaction solution without the formation of porous network structures, compared to CTAB and oleic acid.

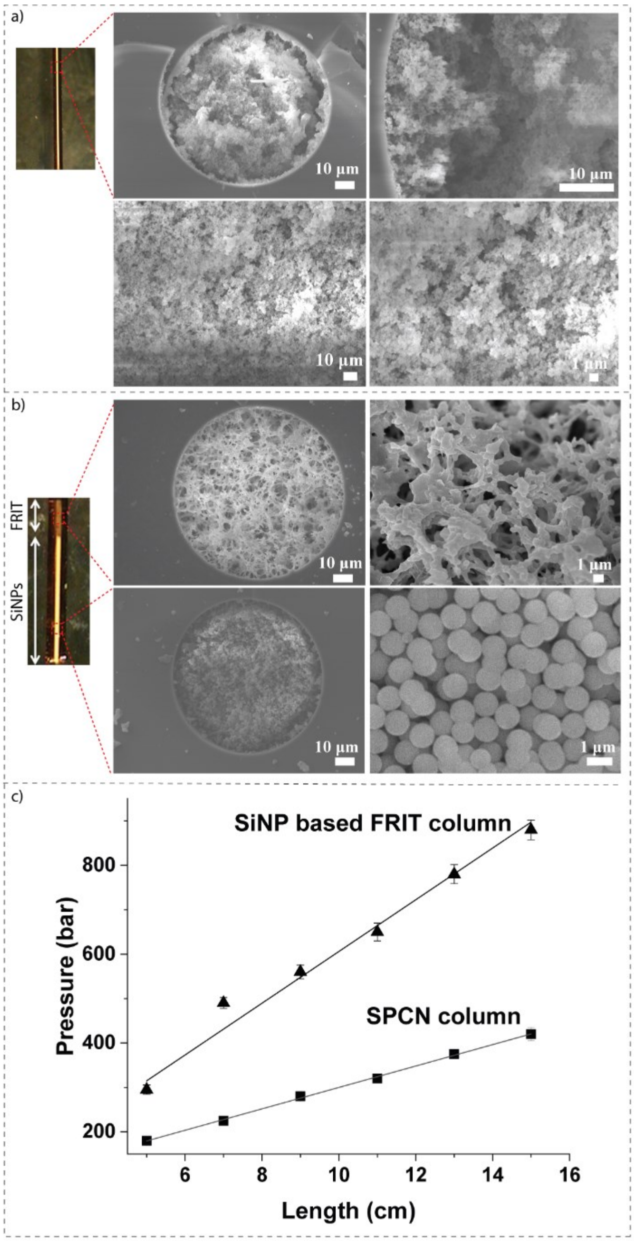

Fig. 4. SEM image of SCNP column (a) and SiNP-based FRIT column (b). The back pressure of two as-prepare columns upon length (c)

The SCNP obtained from the treatment of TEOS and GPTMS of 5:1 and CTAB as a capping agent was applied for the preparation of silica fuse capillary. After co-polymerization at 40°C, the SCNP was successfully formed inside the silica fuse capillary in which the porous matrix was closely interconnected (Fig. 4(a)). Sol-gel transition silica particles strengthened silica skeleton gel facilitating the slow drying and avoiding the fracture of 3D porous structure. It has been reported that low polymerization temperatures could reduce bulk density and enhance the pore formation size and volume [21] . The interstices of silica particles in SCNP structure allowed the meso- and macro-porous well distributed across the capillary which is suitable for future development of CLC or CEC. Fig. 4(b) displays SEM images SiNP-based FRIT column. The result indicated that SiNP can be closed packing and fulfilling the silica fuse capillary. The back pressure (ρ) of the as-prepared silica monolithic column was carried out using EtOH 90% as solvent. In the SCNP column, the ρ was correlated with the length of the column (Fig. 4(c)). The ρ was proportionally fitted with the linear equation y= 24.10523x + 58.90614 ($R^2= 0.99899$). The back pressure of the SCNP column was significantly lower than that of the based FRIT column. SiNP packing approach commonly causes high back pressure and requires a multistep of preparation [16,22] . Whereas, the SCNP column was prepared by the direct formation of silica matrix inside silica fused column as a simple way of saving time and chemical reagents. Our fabrication methodology of SCNP was based on a one-pot synthesis that met advantages in demand for wide chemical engineering architecture materials in the field of chromatography capillary column. The common fabrication methods regarding sol-gel processes generate the diverse types of porosity [23–25]. A hybrid monolithic of amino acid–silica has also been proposed using tetraethoxysilane (TMOS) and GPTMS as co-precursors in the sol-gel process.

4. Conclusion

This work presents a novel method for the fabrication of SPCN with a "one-pot" reaction process. It is the first time that the co-precursors of tetraethoxysilane (TEOS), γ-glycidoxypropyltrimethoxysilane (GPTMS) and capping agent of cetyltrimethylammonium bromide (CTAB) were formulated to achieve the complete co-polymerization of the reaction solution. The SPCN obtained a high porosity interconnect of particles to exhibit a 3D matrix network of silica skeletons. The obtained SNP had an ability to develop monolithic columns with morphology and interstices distributing across the silica fuse capillary. The SPCM has promised to apply and develop a chromatography capillary column.

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