A novel green approach for the chemical modification of silica particles based on deep eutectic solvents

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Chemicals and Reagents

All chemicals and reagents were used without further purification. n-Octadecyltrichlorosilane (95%), 3-glycidoxypropyl-trimethoxysilane (98%), 3-chloropropyl-trimethoxysilane (97%), 3-mercaptopropyl-triethoxysilane (94%), 3-aminopropyl-triethoxysilane (98%) were purchased from Energy Chemical ().; 3-Trimethoxysilyl- propylmethacrylate (98%) was bought Adamas-beta (). Ginsenosides are botanic reference standards from Chengdu Must Bio-tenchnology CO. LTD & Chengdu Institute of Biology CAS (Chengdu, China). Nucleosides are analytical standard bought from Alfa Aesar (). Sulfonamide drugs were obtained from Aladdin (analytical standard: sulfadimoxine, sulfamerazine, sulfapyridine, sulfanilamide, sulfadimethoxine, sulfamethazine, sulfisoxazole) and Energy Chemical (analytical standard: sulfadiazine, sulfathiazole). Spherical porous silica (diameter: 3 μm, pore size: 90 Å, surface area: 395 $m^2 g^{-1}$) were supplied by Lanzhou Institute of Chemical Physics (Lanzhou, China). The others chemicals and solvents are analytical standard from Energy Chemical.

Instrument and method

The stationary phase was suspended in 1,4-dioxane and slurry-packed into stainless steel columns (150 × 4.5 mm i.d.) using n-hexane as propellant solvent at a liquid

pressure of 45 MPa. The HPLC equipment used was a Shimadzu-GL LC-15C system including two high-pressure pumps, a SPD-15C UV/vis detector, a CTO-15C column oven and a 50 μL Shimadzu-GL microsyringe. The UV/vis detector was set at 203 nm wavelength for three ginsenosides, at 254 nm wavelength for six nucleosides, and at 280 nm wavelength for nine sulfa drugs, the Sil-*N*-Glu column (150 × 4.5 mm, particle size 3 μm) was used as the analytical column. The carbon, hydrogen and nitrogen contents of the silica support were determined by elemental analysis using a Vario EL III elemental analyzer (Hanau, Germany). The thermos-gravimetric analysis of the stationary phases was collected on a STA-449C thermos-gravimetric analyzer (Netzsch, Germany) in air.

Dispersibility of DES for silica particles.

Dispersibility of reaction solvents for solid particles is significantly useful value for silylation reactions. As shown in Fig. S1, the Fig. S1 (A) and (B): solid particles (1 g) were dispersed homogeneously into DES (30 mL) under the ultrasonic wave-assisted condition, (A): 0 min after leaving the ultrasound, (B): 24 hour after leaving the ultrasound. The Fig. S1(C) and (D): solid particles (1 g) were dispersed into toluene (30 mL) under the ultrasonic wave-assisted condition, (C): 0 min after leaving the ultrasound, (D): 5 min after leaving the ultrasound.

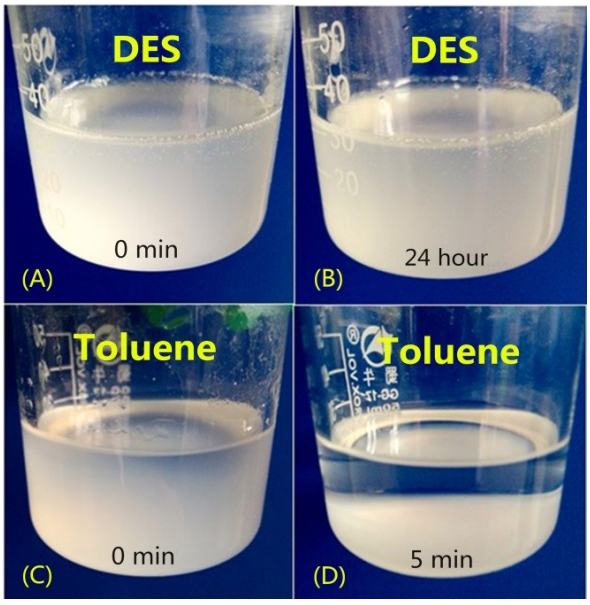

Fig. S1 Comparison of the dispersibility of silica gels in DES (A and B) and toluene (C and D).

Characterization of Sil-*N*-Glu

Thermo-gravimetric curves are usually used to determine thermal stability and to confirm the amount of immobilized compounds on the silica surface. The weight loss observed between 200 and 600℃ can be associated with loss of the organic groups modified on the silica surface. As shown in Fig. S2, The mass loss is consistent with the immobilized amounts estimated by elemental analyses.

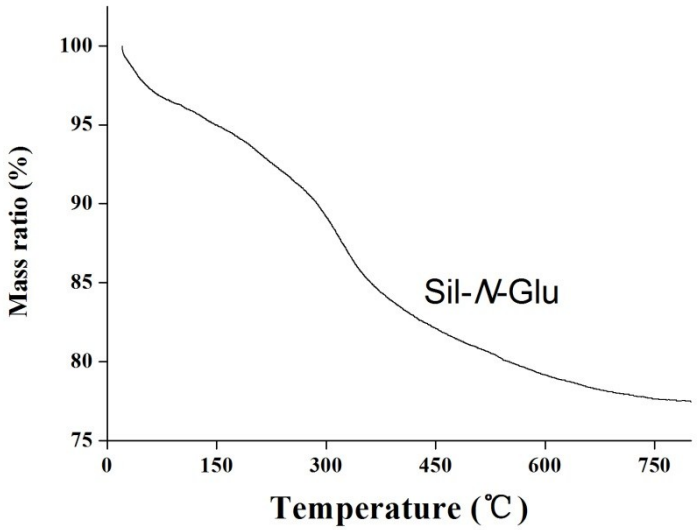

Fig. S2 Thermo-gravimetric curves of Sil-*N*-Glu.

DRIFT spectroscopy is another useful tool that can be used to identify the chemical modifications of compounds. For tertiary amines, DRIFT spectroscopy characteristic peak is unobserved, due to the existence of hydroxyl, methylene and methyl, as shown in Fig. S3

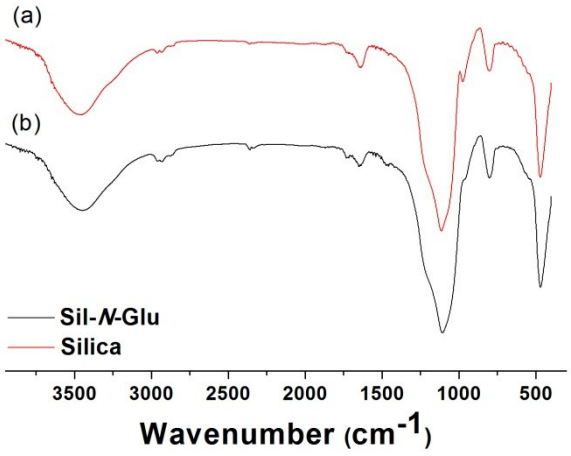

Fig. S3 Diffuse reflectance infrared Fourier transform (DRIFT) spectra of Sil-*N*-Glu.

The comparison of Van-deemter plots of Sil-*N*-Glu

In order to exemplify sufficiently the chromatographic performance of Sil-*N*-Glu, the Van-deemter plots have been obtained for different compounds and comparatively given using the supports synthesized with conventional solvents (such as toluene), the results were showed in Fig. S4.

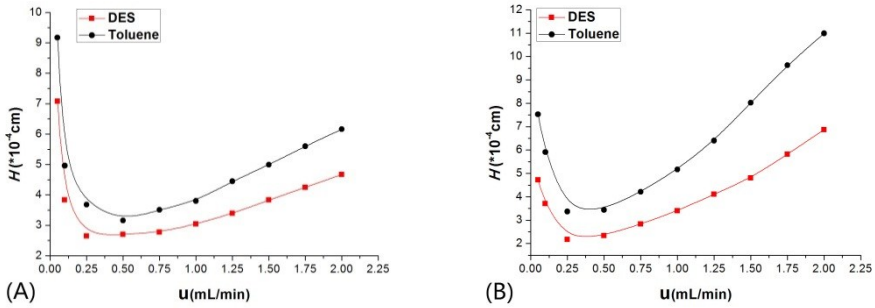

Fig. S4 The comparison of Van-deemter plots of the Sil-N-Glu prepared using the different reaction media. Toluene: using toluene as reaction media, DES: using DES as reaction media, (A) cytosine, (B) uracil.

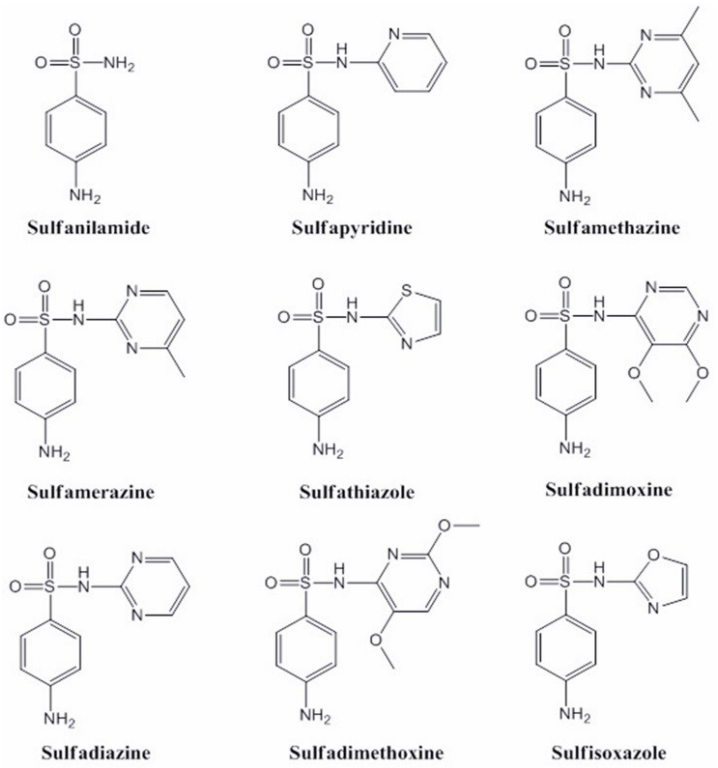

Fig. S5 Structures of nine sulfonamides.

The comparison of separation properties

In our experiments, the difference was obtained about the chromatographic behaviors between silica particles prepared by using traditional organic solvent (toluene) and by using DES, the results were showed in Fig. S6. The results demonstrated the advantages of proposed modified method.

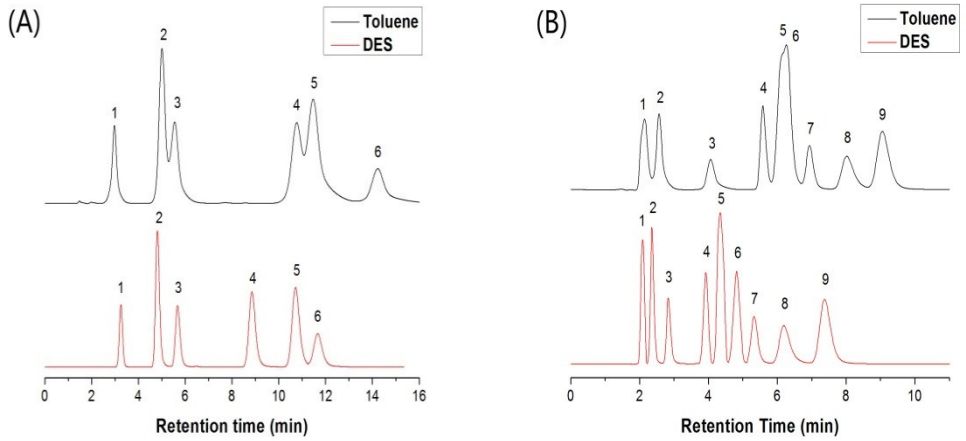

Fig. S6 The comparison of separation properties of Sil-*N*-Glu columns, Toluene: using toluene as reaction media, DES: using DES as reaction media, (A) containing six nucleosides: (1) thymidine, (2) uridine, (3) adenosine, (4) inosine, (5) cytidine, (6) guanosine, mobile phase: 85% CH_3CN: 15% 20mmol NH_4AC solution; (B) containing nine sulfonamide drugs: (1) sulfanilamide, (2) sulfapyridine, (3) sulfamethazine, (4) sulfamerazine, (5) sulfathiazole, (6) sulfadimoxine, (7) sulfadiazine, (8) sulfadimethoxine, (9) sulfisoxazole, mobile phase: 20% CH_3CN : 80% 20mmol NH_4AC solution. Other chromatographic conditions: flow-rate=1.0 ml min^{-1}, T=30℃.