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Modification of fumed silica surface with different sulfonamides via a postsynthesis method and their application as antibacterial agents

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ABSTRACT

The surface of nanosized fumed silica (FSi) was modified with different amine groups by the use of silylating agents. The obtained propylamine, propylpiperazine, and propyl-*p*-phenylenediamine–modified FSi were treated with different sulfonyl chlorides to gain sulfonamide-modified FSi compounds. These compounds were characterized by various techniques including Fourier transform infrared spectroscopy, thermogravimetric analysis, differential thermal analysis, scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDX), confirming the grafted sulfonamides on the FSi surface. Sulfonamide-modified surfaces are efficient catalysts for the Michael addition-based syntheses and coupling reactions. Furthermore, the antibacterial tests showed that these modified FSi compounds have antibacterial activities and thus are useful materials for preparing antibacterial silicone-based compounds such as silicone glue and oil.

1. Introduction

Fumed silica (FSi) is a nanosized and highly dispersed synthetic silicon dioxide product [1]. It consists of very fine agglomerated aggregates, which are produced via the flame hydrolysis of chlorosilanes. The size of primary FSi particles in the aggregates is about 10 nm, whereas the agglomerated particles have sizes in the range of 100 nm −5 μm. From an industrial point of view, FSi is used as reinforcement of elastomers, thickening of liquids, anti-foaming, paper coating, and adsorbent [2]. The density of silanol groups on FSi surface is low, but they are distributed over the surface, and thus, its surface is highly reactive to chemical reactions and has a hydrophilic character. Silylation of these silanol groups is the main reaction of FSi. The modified silica compounds are widely used as catalysts [3], optical materials [4], coating agents [5], chemosensors [6], proton exchange membranes [7], and organic light-emitting devices [8].

Sulfonamide compounds were discovered in 1935 [9], and nowadays are extensively used for the treatment of infections in human [10], aquaculture, livestock production [11], catalysis [12], and organic syntheses [13]. Regarding the importance of antibacterial surfaces and implants, antibiotic-loaded coatings are currently considered as the attractive materials in biomedical engineering [14]. So far,

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sulfonamide-loaded polymeric materials have been widely studied and used as membranes [15]. There are just a few publications on the modification of silica surface with sulfonamides; for example, Schick and Sun [16] just studied and characterized sulfonamide modified silica, whereas Piscopio and coworkers used it for solid phase synthesis [17]. In continuation of our previous research [18], herein, we tried to modify the FSi surface with sulfonamides by the use of silylating agents and then investigating their antibacterial properties.

2. Experimental section

2.1. Materials and instruments

3-(Chloropropyl)trimethoxysilane (ClPTMS), 3-(aminopropyl)trimethoxysilane (APTMS), and FSi were purchased from Sigma–Aldrich Company. All aforementioned materials were used without any further purification. The Fourier transform infrared (FT-IR) spectra of samples were recorded on NaCl disks by a FT-IR Bruker Tensor 27 instrument. The surface morphologies of samples were observed using a field emission scanning electron microscope (Hitachi S-4160 Japan). Thermogravimetric analysis (TGA) was carried out by a BÄHR Thermoanalyse, STA503 model from ambient temperature to 1000 °C with a ramp rate of 10 °C min^{-1} in air. Zeta potential was obtained using a Malvern Instrument. *Escherichia coli* and *Staphylococcus aureus* were prepared from Iranian Research Organization for Science and Technology and used as the antibacterium model.

2.2. General procedure for modification of FSi with aminopropyl (FSi–Pr–NH_2) and/or propylchloride (FSi–Pr–Cl) groups

FSi (10 g) was poured into a two-neck round-bottom flask and dried well under vacuum pressure at 100 °C for about 2 h. Afterward, when it reached to ambient temperature, dry toluene (150 mL) was added to it until a dilute mixture was obtained. The mixture was heated under reflux condition for about 30 min and then ClPTMS and/or APTMS (6 mL) was gradually added to it and the mixture was refluxed for about 72 h. Finally, toluene was evaporated under reduced pressure to obtain the crude functionalized FSi, which was washed well with CH_2Cl_2 by the use of a Soxhlet apparatus and then dried at ambient temperature overnight.

2.3. General procedure for the modification of FSi–Pr–Cl with diamine compounds

FSi–Pr–Cl (6 g) was poured into a two-neck round-bottom flask and dried under reduced pressure at 100 °C for removal of the adsorbed water. Then, *N*,*N*-dimethylformamide (50 mL) and piperazine or *p*-phenylenediamine (12 g) were added to it; subsequently, the mixture was heated under reflux condition for about 72 h. Afterward, the solvent was evaporated and the crude solid was washed well with EtOH using a Soxhlet apparatus and then dried at ambient temperature overnight. Finally, the modified FSi with piperazine (FSi–Pr–Pi) or *p*-phenylenediamine (FSi–Pr–PhDA) was obtained.

2.4. General procedure for the preparation of sulfonamide-modified FSi

Two grams of FSi–Pr–NH_2, FSi–Pr–Pi, or FSi–Pr–PhDA was dried under reduced pressure at 100 °C and then the corresponding sulfonyl chloride **2a**–**c** (4 g), K_2CO_3 (0.5 g), and EtOH (15 mL) were added to it and stirred at room temperature for 24 h. Subsequently, the obtained solid was filtered, washed well with CH_2Cl_2 using a Soxhlet apparatus, and dried at room temperature.

2.5. Antibacterial tests

2.5.1. Culture conditions

Several colonies from an overnight culture on a nutrient agar plate were subcultured in 15 mL of Tryptone Soy Broth for 24 h at 37 °C Then, this overnight culture (500 μL) was cultured again in Tryptone Soy Broth (20 mL), and the cells were grown until mid-log phase (optical density at 600 nm, 0.5–0.6). Then, 15 mL of the mid-log-phase culture was centrifuged at 4000 *g* for 18 min at 4 °C and the spent culture medium was discarded [19].

2.5.2. Microbial inhibitory concentration

Overnight cultures of *E coli* and *S. aureus* were diluted to obtain an optical density (OD600) of 0.2 (corresponding to 1 × 108 colony-forming units per milliliter). The inoculum (1 mL for each) was added to vials containing serial dilutions of a nanostructure solution with the concentration of 1 mg/mL (experiments performed in triplicate). A control group of bacteria were cultivated in the absence of nanostructure solution. After incubation for 24 h at 30 °C, bacterial growth was monitored by recording the OD600 using a UV–vis spectrophotometer [20]. The minimum inhibitory concentration (MIC) was defined as the lowest concentration of sulfonamide-modified FSi that could completely inhibit the bacteria growth. Nanostructure solution was prepared through the dispersion of nanostructure (0.01 g) in DMSO (10 mL) under ultrasonic irradiation (50 W power for about 20 min).

3. Results and discussion

3.1. Preparation and characterization of sulfonamide-modified FSi

In this study, for preparation of sulfonamide-modified FSi, the FSi surface was first functionalized with different amine. In this regard, FSi was treated with APTMS and/or ClPTMS to give FSi–Pr–NH_2 and/or FSi–Pr–Cl, respectively (Scheme 1). Then, FSi–Pr–Cl was reacted with piperazine **1a** or *p*-phenylenediamine **1b** to gain FSi–Pr–Pi and FSi–Pr–PhDA, respectively (Scheme 2). Subsequently, the prepared amine-functionalized FSi compounds were reacted with sulfonyl chlorides **2a**–**c** to achieve the target sulfonamide-modified FSi compounds (Scheme 3, Table 1), which then were characterized by varied techniques.