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In situ Surface Functionalization of Hydrophilic Silica Nanoparticles via Flame Spray Process



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Hydrophobic silica nanoparticles grafted with a high amount of organic molecules were successfully prepared by an in situ functionalization method in flame spray pyrolysis (FSP) process. Hydrophilic SiO₂ nanoparticles were converted into hydrophobic ones by silylation between 3-methacryloxypropyltrimethoxyl silane (MPS) and silica's surface hydroxyl groups. The freshly formed silica nanoparticles in flame were continuously functionalized by a fine spray of 3-methacryloxypropyltrimethoxyl silane (MPS) solution at a preferred temperature. The functionalization extent, morphology structure and size of silica nanoparticles were characterized by transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectronic spectroscopy (XPS). The influence of concentration, pH value and pre-activation of organic silane solution on the surface grafting density was investigated in detail. The obtained silica nanoparticles had a higher MPS functional content of 15.0 wt% (an average density of 2.7 MPS molecule/nm²) than that of the silica modified by wet chemistry route, showing an excellent, stable hydrophobic property. The results have demonstrated that the in situ FSP functionalization process is a simple, effective and promising route for the scalable preparation of advanced, hydrophobic nanomaterials.

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1. Introduction

Flame-made nano-silica has been extensively used in many applications including silicone rubber, coatings, polymer nanocomposites^[1–3]. Due to numerous –OH groups on the surfaces, silica particles are prone to aggregate and hard to disperse homogeneously in organic coatings or polymer nanocomposites, remaining a challenge for further application. Therefore, surface functionalization of silica prior to usage is of fundamental importance to meet a broad range of applications^[4,5].

Organosilane coupling agents are widely used for surface modification of silica particles^[5,6]. With its bifunctional groups, organosilane can be reacted with Si–OH groups on silica surfaces after hydrolysis, and simultaneously they can provide good compatibility or undergo reactions with host matrix. Traditionally, the synthesis and modification of inorganic nanoparticles are two different processes, normally conducted separately, increasing

production cost and complexity^[7–9]. A so-called “continuous modifying process” is either actually performed in two distinct reactors or resulting in limited surface properties^[10,11]. Recently, Teleki et al.^[12] reported a facile in situ organic surface modification process of flame-made titania nanoparticles, by mixing freshly prepared titania nanoparticles with a fine spray of coupling agent solution. The functionality of titania nanoparticles was obtained rapidly due to high reaction temperature. This method is also suitable for many other flame-made inorganic nanoparticles with numerous –OH groups on surfaces, including silica.

Flame spray pyrolysis (FSP) technology, owing to extensive choices of salt precursor, has been demonstrated to be a simple, effective and scalable method for the fabrication of advanced nanomaterials with high purity and versatile morphologies^[13]. However, the focus of this area is how to design and synthesize novel-structured nanomaterials such as core-shell TiO₂@SiO₂, Fe₂O₃@SiO₂ etc.^[14,15]. Little attention has been devoted to the study of in situ organic modification of nanomaterials in FSP process. Herein, in situ functionalization of flame-made fresh silica nanoparticles was realized by the modified FSP process through subsequently introducing fine spray of 3-methacryloxypropyltrimethoxyl silane (MPS) solution. The effects of MPS solution's concentration, pH value and pre-activation process on the grafting extent and particle hydrophobic

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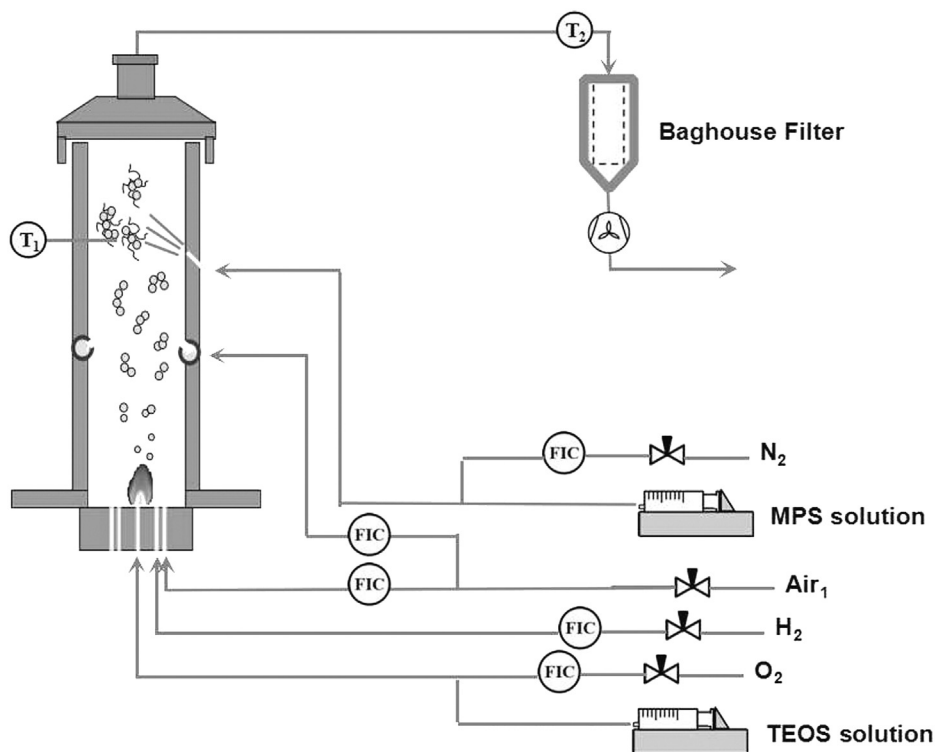


Fig. 1. Schematic diagram of experimental reactor for in situ functionalization of FSP-made SiO₂.

property were studied in detail. After in situ functionalization of MPS, the obtained silica nanoparticles showed excellent and stable hydrophobic features. Besides, the characteristic advantage of in situ FSP functionalization was highlighted compared to the modification of flame made silica nanoparticles by wet chemistry route.

2. Experimental

2.1. Raw materials

MPS was received from Sinopharm Chemical Reagent Co., Ltd; tetraethyl orthosilicate (TEOS) was obtained from Shanghai LingFeng Chemical Reagent Co., Ltd. All the materials in this study were used as received without further purification.

2.2. Particle synthesis and in situ functionalization

Schematic representation of the in-situ FSP setup is shown in Fig. 1. The FSP burner was enclosed by a 45-cm long, 5-cm i.d. tube. A 5-cm i.d. tube with 12 internal section outlets (1 mm i.d. each) was placed on the top of the tube, through which flowed cooling air (0.5 m³/h). A 15-cm long tube with a side branch was placed above the cooling tube. An internal gas-assist nozzle (i.d. = 1 mm, 60 cm above the FSP burner) in that side tube sprayed 3 mL/min of MPS solution, which was dispersed by 0.25 L/min N₂ at pressure drop of 1.5×10^5 Pa (1.5 bar) upward (45° from the vertical) into the tube. The final tube of the reactor was 30-cm long for surface functionalization of silica. The final products were collected through filter cloth. The collection temperature was in the range of 110–130 °C.

Precursor of silica was TEOS solution in ethanol (0.5 mol/L). This TEOS solution was fed at 3 mL/min to the FSP burner and dispersed into drops by O₂ (0.3 m³/h) with 10^5 Pa (1.0 bar) pressure drop at the nozzle tip. The concentration of MPS in ethanol/water (1:9 by volume) was 0.02 mol/L, 0.04 mol/L and 0.08 mol/L. Acetic acid was

added to adjust the pH value of the solution. In pre-activation process, the solution was placed in an oven at 60 °C for 1 h to ensure full hydrolysis of MPS. Hydrophobic SiO₂ was prepared by spraying MPS solution (3 mL/min) directly into the freshly formed hydrophilic SiO₂. The grafting temperature was around 300 °C.

2.3. Modification of FSP-made silica in wet chemistry route

Freshly made pure FSP-SiO₂ was also modified by MPS in wet chemistry route for comparison. The FSP-SiO₂ was prepared under the same condition with in situ functionalized ones without spraying MPS solution. The pure silica was dispersed into the solution of ethanol and water (94.5:5.5 by volume) via ultrasonic for 30 min at room temperature. MPS (with mass ratio 1:10 to silica) were added into the solution by drops. Acetic acid was added till the pH value reached 4.5. The solution was then under ultrasonic for 30 min, followed by reaction at 65 °C for 24 h. Finally, the suspension was under centrifugation and washed with ethanol for 3 times.

2.4. Characterization

The presence of coupling agent on the surface of silica was confirmed by Fourier transform infrared spectroscopy (FT-IR) by using a Nicolet 6700 spectrophotometer. The spectrum was collected in the range from 4000 to 400 cm⁻¹. Before test, the silica samples were first extracted in hot acetone for 24 h to wash out the physically absorbed silicane coupling agent. The weight amount of MPS on the surface of silica was determined by thermogravimetric analysis (TGA) using a TGA/SDTA851e analyzer, with a heating rate of 10 °C/min⁻¹ under nitrogen. Transmission electron microscopy (TEM) images were directed by using a JEM-1400 with in-column filter at 120 kV of acceleration voltage type transmission electron micrograph. Silica powders were dispersed in acetone by ultrasonic then dropped onto the carbon coated copper grid. X-ray photoelectronic spectroscopy

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