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One-step synthesis of boronic acid group modified silica particles by the aid of epoxy silanes

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ABSTRACT

A novel one-step strategy has been developed to prepare boronic acid functional group modified silica particles, SiO_2@GOPS-APBA, which contained large amount of immobilized boronic acid groups and demonstrated high affinity towards diol-containing compounds. Solid state NMR and FT-IR spectrum proved that the boronic acid groups were successfully introduced on the surface of silica. TGA and element analysis demonstrated that the amount of boronic acid groups immobilized on the silica was about 1.0 mmol/g. The morphology and structure were studied by SEM and nitrogen adsorption–desorption measurements. The adsorption amount of catechol on SiO_2@GOPS-APBA was determined to be 162 μmol/g, which was higher than the samples prepared by the previously published approaches. This one-step approach represented an environment-friendly conception and a promising surface functionlization method.

1. Introduction

It is well known that boronic acid group-containing substances have the ability to form reversible covalent bonds with cis-1,2 or cis-1,3-diol containing molecules, such as monosaccharide [1], nucleosides [2] and glycoprotein [3,4]. They have been widely used to prepare boronate affinity materials on the silica particles. At present, the boronic acid group modified silica synthesis was usually carried out with the aid of organosilane [5–10]. Two methods were widely applied, one was the "grafting first and then modification" [6,11–14], the other was the "modification first and then grafting" [15–17]. In the first method, epoxy silane was grafted on the surface of silica. Lately, the resultant epoxy-functionalized silica was covalently modified with aminophenylboronic acid (APBA) via the opening of the epoxy groups by the nucleophilic attack of amino group of APBA. On the contrary, the second method, organosilane was covalently modified with boronic acid-containing molecules first and then the resultant boronic acid group-containing organosilane was grafted on the surface of the silica. Generally speaking, these processes are tedious and time-consuming. Especially, the grafting process of the pristine or modified organosilane on the surface of the silica of both methods was always carried out in anhydrous toluene [18], a detrimental and environment hazardous non-polar solvent, in order to suppress the condensation reaction of organosilane to obtain a monolayer of grafting. Until now, there is no simple, one-step preparation method for boronic acid-modification of silica. Here, in this paper, we wish to demonstrate a new, one-step protocol to modifying boronic acid groups onto silica. The boronic acid modification of silica particles can be obtained by the reaction among 3-glycidoxypropyltrimethoxysilane (GOPS), APBA and silanol (Si—OH) catalyzed by triethylamine (TEA) on the silica surface in dry ethanol.

2. Experimental

2.1. Materials

Silica purchased from Suzhou nanomicro technology company (UniSil 20-100, 20 μm) was activated by refluxing for 6 h in 20% HCl, and then dried at 150 °C under vacuum overnight. 3-Aminophenylboronic acid (APBA, 98%) and 3-glycidoxypropyltrimethoxysilane (GOPS, 98%) were purchased from Energy chemical (Shanghai, China) and were used without further purification. Ethanol (99.7%, AR) was dried with magnesium turnings and iodine. Triethylamine (TEA, ≥99.0%, AR) was dried by potassium hydroxide. Catechol (≥98%, CP) and all the other reagents were used as-received.

2.2. Instrumentation and characterizations

The infrared spectra of the samples were measured by a Nicolet-6700 FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1}

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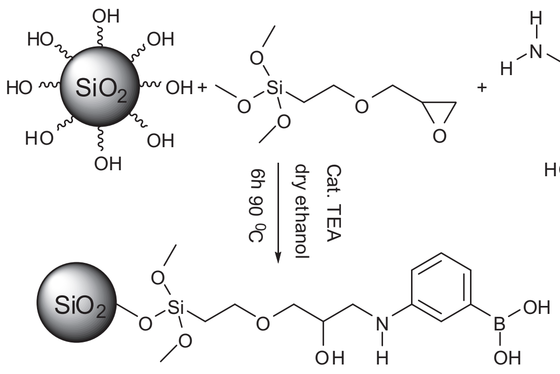
region with a resolution of 4 cm^{-1}, by accumulating 32 scans. Samples (0.014 ± 0.06 g) were intimately mixed with previously dried KBr (1.176 ± 0.05 g) by gentle grinding so as to minimize particle break up. Solid state NMR spectra were recorded at room temperature using Bruker AV-400 spectrometer. Field-emission scanning electron microscopy (FEI Sirion 200) was operated to observe the morphology of the pure SiO_2 and SiO_2-GOPS-APBA at 20 kV. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K min^{-1} under nitrogen. UV–vis absorption spectra were recorded on the SHIMADZU UV-2450 spectrophotometer. Elemental analysis was performed on a Flash EA 1112 elemental analyzer. Specific areas were determined by the nitrogen adsorption–desorption method using Quantachrome Instruments, NOVA 1000 e Surface Area & Pore size analyzer.

2.3. Synthesis of SiO_2@GOPS-APBA and SiO_2@GOPS

Silica (1 g), GOPS (750 μL, 3.3 mmol), APBA (0.5 g, 3.6 mmol), TEA (250 μL) and dry ethanol (25 mL) were added into a one-neck round-bottom flask (100 mL) equipped with a condenser. The mixture was refluxed for 6 h under gently stirring. The achieved materials labelled with SiO_2@GOPS-APBA were separated by centrifugation, and they were thoroughly washed by ethanol until no APBA was detectable in the centrifuged supernatant. Then they were dried at 60 °C under vacuum for 8 h for further use. However, as a comparison, SiO_2@GOPS was prepared and purified under the identical conditions without the addition of APBA.

2.4. Adsorption and desorption experiment of catechol on SiO_2@GOPS-APBA

50 mg SiO_2@GOPS-APBA and 20.00 mL catechol solution (0.06 mg/mL, prepared in pH 8.5 0.01 M phosphate buffer) were added into a 100 mL Erlenmeyer flask and shake for 2 h at 30 °C. After centrifugation, the amount of catechol remaining on the supernatant was quantified with UV spectrophotometry at 276 nm, from which the absorbing amount of catechol on SiO_2@GOPS-APBA could be obtained. The centrifugation sediment was washed with phosphate buffer (0.01 M, pH 8.5) until no catechol was detected. Then the sediment and 20.00 mL acetic acid solution (pH 3.0, elution solution) were added into a 100 mL Erlenmeyer flask and shook for 2 h at 30 °C. After centrifugation separation, the amount of catechol released to the supernatant was also quantified with UV spectrophotometry at 276 nm. The recovery of catechol was obtained by comparing to the absorbing amount of catechol.



Scheme 1. Modification reaction of boronic acid group on silica support.

3. Results and discussion

3.1. FTIR spectroscopy analysis

In Scheme 1, GOPS is grafted to silica surface by condensation reaction between the alkoxy and silanol groups, in the meanwhile, GOPS is covalently modified with APBA via the reaction of epoxy groups with amino group, the nucleophilic group of APBA, to install the APBA on the surface of silica. The as-prepared SiO_2@GOPS-APBA particles were confirmed by Fourier transform infrared spectroscopy (FT-IR) (as shown in Fig. 1). Comparing to the FT-IR data of pure silica (a), the spectrum of SiO_2@GOPS-APBA (b) demonstrated clear characteristic peak of GOPS and APBA. The relatively strong bands at 2941 cm^{-1} and 2879 cm^{-1} corresponded to the C—H stretching vibration of the methyl (or methylene) groups which confirmed the existence of GOPS. Meanwhile, the appearance of peak at 1360 cm^{-1} associated with the characteristic absorption peak of B—O stretching vibration [7], along with the bands at 1572, 1492, 1440 cm^{-1} and peak at 714 cm^{-1}, which belong to benzene ring stretching vibrations and m-benzene rings distorting vibrations, respectively, indicated that APBA was successfully introduced onto the surface of silica. Additionally, the area decrease of the large adsorption peak around 3442 cm^{-1} (O—H stretching vibration of silanol groups and the remaining adsorbed water) together with the disappearance of peak at 970 cm^{-1} (the scissor bending vibration of the Si—OH bonds) indicated the decrease of the amount of silanol, further attested to the chemical grafting on the silica surface.

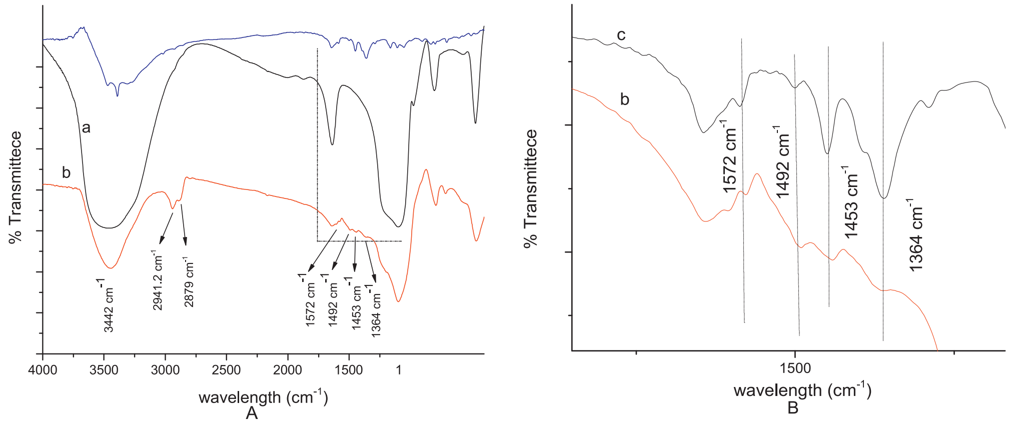


Fig. 1. (A) FTIR spectra of pure silica (a), SiO_2@GOPS-APBA (b), APBA (c). (B) Enlarged image of the marked region in (A).