

功能性硅烷在纳米氧化硅表面的自组装*

刘 鹏^{a, b, **}, 薛群基^b, 田 军^b, 刘维民^b

(a. 兰州大学化学化工学院, 兰州 730000 ;

b. 中国科学院兰州化学物理研究所, 固体润滑国家重点实验室, 兰州 730000)

摘 要: 在分散体系中, 两种功能性硅烷, 甲基丙烯酰氧丙基三甲基硅烷(MPTES)和氨丙基三甲基硅烷(APTES)在纳米氧化硅表面形成自组装单分子层. 用 XPS 和 FTIR 对所得自组装单分子层进行了表征. 元素分析结果表明, 所得功能性纳米氧化硅中的功能基含量分别为 1.03 mmol/g 甲基丙烯酰氧基/丙烯酰氧丙基纳米氧化硅(MPSN)和 3.34 mmol/g 氨基/氨丙基纳米氧化硅(APSN). LSS 分析结果表明, 未修饰纳米氧化硅、MPSN 和 APSN 在甲苯分散体系中的平均流体力学直径大约分别为 240、45 和 560 nm.

关键词: 自组装; 纳米氧化硅; 功能性硅烷; 表征

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Self-assembly of Functional Silanes onto Silica Nanoparticles*

Liu Peng^{a, b, **}, Xue Qunji^b, Tian Jun^b, Liu Weimin^b

(a. Department of Chemistry, Lanzhou University, Lanzhou 730000 ;

b. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000)

Abstract Two functional silanes, γ -methacryloxypropyltriethoxysilane (MPTES) and γ -aminopropyltriethoxysilane (APTES), has been self-assembled onto the surface of silica nanoparticles in the dispersion system. The modifications of the ultra-fine particles were investigated via elemental analyses, XPS, FTIR and TGA. The elemental analysis showed that the amounts of the immobilized agents were 3.34 mmol/g and 1.03 mmol/g on the surfaces of γ -methacryloxypropyl-modified silica nanoparticles (MPSN) and γ -aminopropyl-modified silica nanoparticles (APSN), respectively. The mean hydrodynamical particle diameters of the bare silica nanoparticles, MPSN and APSN, determined by the laser scattering system (LSS), were about 240, 45 and 560 nm, dispersed in toluene, respectively.

Key words Self-assembly, Silica nanoparticles, Functional silane, Characterization

1 Introduction

Silylation is characterized by the displacement of active hydrogen atoms usually attached to silanol groups by organosilyl derivatives of silane coupling agents (SCAs) of the general formula $(R'O)_3SiR^{[1]}$. These

organic molecules contain the moiety R in which functional centers are attached and the alkoxy R'O groups that are normally formed by short chains. These latter groups are easily hydrolyzed when dispersed in solvent water or simply by the water of hydration on the surface of the substrate used in the chemical process. The se-

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** Corresponding author, E-mail: pliu@lzu.edu.cn Received 24 November 2002; in final form 27 May 2003.

lection of a desirable functional group on the R moiety during the immobilization depends on the subject of each application^[2].

The application of such methods of immobilization can yield self-assembled monolayers (SAMs) covalently bonded onto inorganic supports^[3]. The final products of the anchored surfaces have great utility in many areas such as chemically bonded phases in chromatography^[4], preconcentration and extraction of cations from solutions^[5], catalytic process^[6], and biomaterials immobilization^[7].

Self-assembly of organosilanes of the type γ -spacer-SiX₁X₂X₃ onto the oxidized surfaces such as SiO₂, Al₂O₃ and TiO₂ continues to be a promising field of research. On the one hand, the process responsible for the stable and well-ordered monolayers^[8] is relatively simple. On the other hand, the large variety of chemical γ functionalities introduces a wide range of surface properties and chemical reactivities useful in fundamental and technological domains^[9]. In practical applications alkoxy silanes are the most often used among organosilane coupling agents (OCAs), because they are easy to prepare, they allow a large variety of stable γ -terminal functionalities to be incorporated in the molecular spacer and they can be grafted from aqueous organic solutions.

Among a variety of matrices, such as oxides, glasses, and clay minerals, which contain available OH-end groups bonded on a surface, silica gel has been extensively modified with a great variety of alkoxy silane agents with different functionality^[10]. In the present work, two functional silanes, γ -methacryloxypropyltriethoxysilane (MPTES) and γ -aminopropyltriethoxysilane (APTES), were used for the modification of silica nanoparticles and the self-assembled monolayers obtained were characterized with X-ray photoelectron spectroscopy (XPS), laser scattering system (LSS), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), and elemental analysis (EA). Surface modification of nanoparticles with functional silanes is one of the most significant methods for industrial use because it can change the surface properties of the ultra-fine particles

and prevent the particles from agglomeration. Furthermore, the propyl methacrylate and amino groups introduced onto the surface of silica nanoparticles could act as reacting sites. They can react with kinds of reagents or co-polymerize with other monomers. So silica nanoparticles with different surface chemical and physical performances could be achieved conveniently and they can play important roles in the material industries, such as additive of lubricating oil^[11-13] and organic-inorganic hybrid materials^[14].

2 Experimental

2.1 Materials

Silica nanoparticles used were MN1P obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area, particle size and silanol group content were 640 m²/g, 10 nm and 48%, respectively. It was dried in vacuum at 110°C for 48 h before use.

γ -Methacryloxypropyltriethoxysilane (MPTES) and γ -aminopropyltriethoxysilane (APTES) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) were used as received. 2,6-Dimethylpyridine (Fluka Chemika), hydroquinone (Beijing Chemicals Factory, Beijing, China), toluene and ethanol (Tianjin Chemicals Co. Ltd., China) were all analytical grade reagents.

2.2 Self-assembly procedures

Into a 500 mL flask, 5.0 g silica nanoparticles, 300 mL toluene and 50 mL MPTES were charged and the mixture was dispersed with ultrasonic vibrations for 30 min. 0.5 g hydroquinone was added as an antipolymerization agent and 2 ~ 3 drops of 2,6-dimethylpyridine were added as the catalyst. The mixture was refluxed for 8 h under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged and the precipitate was dispersed into 300 mL ethanol with ultrasonic vibrations for 30 min and centrifuged (4 × 10³ rin/min for 1 h) again. The washing operation was repeated for three times and the resulting precipitate, γ -methacryloxypropyl-modified silica nanoparticles (MPSN), was dried in vacuum at the room temperature.

For the γ -aminopropyl-modified silica nanoparticles (APSN), 5.0 g of silica nanoparticles , 300 mL toluene and 50 mL APTES were added into a 500 mL flask and the mixture was dispersed with ultrasonic vibrations for 30 min. Then the mixture was refluxed for 8 h under stirring with a magnetic stirrer. The product was centrifuged and washed with the same operation as MPSN.

2.3 Characterizations

X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer with pass energy of 29.35 eV and an Mg K α line excitation source. The binding energy of C1s (284.6 eV) was used as a reference. The resolution of the analyses for binding energy was about 0.3 eV because a monochromator was used. Fourier transform infrared spectra (FTIR) were taken on a Bio-Rad FTS-165 FT-IR spectrometer by pressing the samples to be tested into a potassium boride (KBr) disk. The morphology of the organo-modified silica nanoparticles was characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The power of organo-modified silica nanoparticles was dispersed in toluene in an ultrasonic bath for 5 min , and then deposited on a copper grid covered with a perforated carbon film. BI-200SM Laser Scattering System (LSS , Brookhaven Instrument Co. , USA) was applied for the determination of the diameters of the silica nanoparticles dispersed in toluene. The contents of reacting sites , methacrylate groups and amino groups were calculated from the elemental analysis results performed on the Elementar vario EL instrument. The thermogravimetric (TGA) analysis was performed on a Perkin-Elmer TGA-7 system by flowing N₂ (20mL/min) at 10 $^{\circ}$ C/min.

3 Results and discussions

3.1 Elemental analysis

It was found in the present work that the amount of the anchored functionality of MPSN was 1.03 mmol/g calculated from the C elemental analysis results and that of APSN was 3.34 mmol/g calculated from the N elemental analysis (Table 1). The an-

chored functionality of MPSN was smaller than that of APSN maybe due to the bigger indrance of MP TES. The theoretical C/N ratio value of APSN was 2.57. The determined C/N ratio value of APSN was 2.71. It showed that the ethoxyl groups had hydrolyzed completely and all the γ -aminopropyl groups were immobilized on the surface of the silica nanoparticles via covalently bonding.

Table 1 Elemental analysis

| | Silica | APSN | MPSN |
|-----|--------|-------|------|
| C % | 0.0 | 12.69 | 8.68 |
| H % | 1.92 | 4.31 | 3.20 |
| N % | 0.0 | 4.68 | - |

3.2 FTIR analysis

Infrared spectroscopy was used as a tool to provide information on the total or partial loss of silanol groups bonded to the original silica nanoparticles and to clarify the effect caused by the immobilization of organic groups on the surfaces of organo-modified silica nanoparticles. A broad band assigned to the Si - O - Si symmetric stretching mode was observed at 1089 cm⁻¹ (Fig. 1). The spectrum related to the precursor silica showed a band at 959 cm⁻¹, which was identified as the terminal Si - OH deformation band due to the presence of this group bonded on the silica surface , and another band associated to δ Si - O was located at 464 cm⁻¹[15]. The spectra for all modified silica nanoparticles were characterized by a decrease of the Si - OH deformation mode originally present at 959 cm⁻¹ and by the appearance of 1470 cm⁻¹ of (CH₂)₃ group , 1637 cm⁻¹ of C = C group , and 1720 cm⁻¹ of C = O group in the spectrum of MPSN and 1471 cm⁻¹ of (CH₂)₃ group , 2975 , 2931 and 1580 cm⁻¹ of NH group in the spectrum of APSN , respectively. Another band assigned to protonated amines caused by the bonded SiOH group was located at 1572 cm⁻¹. The band attributed to the symmetric NH₃⁺ deformation at 1480 cm⁻¹ gave another evidence of protonated amino groups on the surface of APSN^[16]. The transmittance of the band 802 cm⁻¹ (Si - O) in the FTIR of silica

decreased in the FTIR of MPSN and APSN because of the addition of the group of Si - C. These features confirmed the assignments of the covalent bond between the self-assembled monolayers and the substrate.

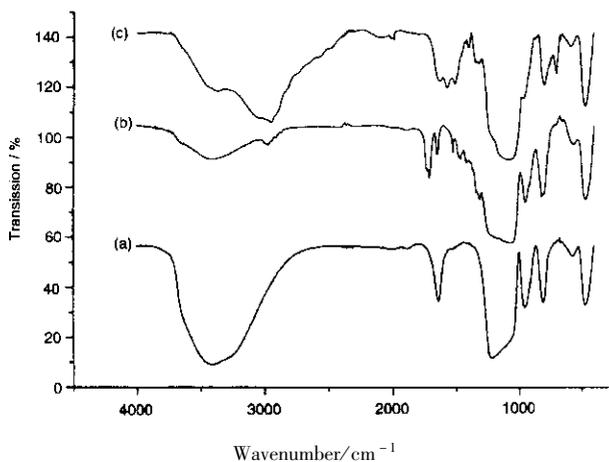


Fig. 1 Infrared spectra of (a) the bare silica nanoparticles , (b) MPSN and (c) APSN

3.3 XPS analysis

The XPS spectral shifts in the binding energy of individual peaks can indicate the specific chemical species present. The ability to use these shifts in binding energy is what makes XPS a valuable analytical technique for industrial applications where bonding information is required^[17,18]. The C1s, Si2p and O1s spectra of MPSN and the C1s and Si2p spectra of APSN were analyzed to investigate the chemical bonding states of carbon, silicon and oxygen and to investigate the proportion of functional groups quantitatively^[15,16]. The results of this were shown in Fig. 2. Fig. 2a showed that the C1s of MPSN could be resolved into four components. The first, set at 284.57 eV, was attributed to carbon in an aliphatic environment, such as C - H, C - C, and C = C while the other two corresponded to carbon bound to oxygen, typically (C = O) - O - C at 287.54 eV and (C = O) - O - C at 286.15 eV. The fourth, 285.51 eV, could be attributed to C - Si. The Si - C at 102.65 eV and Si - O at 103.58 eV were found in Fig. 2b. And O = C, O - Si, and O - C were showed at 530.76, 532.81 and 533.41 eV in Fig. 2c, respectively. The presence of additional component characteristic of carbon element, silicon atoms bound to carbon, and oxygen atoms

bound to carbon indicated the propyl methacrylate self-assembled monolayers had been covalently bonded onto the surface of the silica nanoparticles. The C1s spectrum of APSN was deconvoluted into C - H and C - C (284.67 eV), C - Si (285.72 eV), and C - N

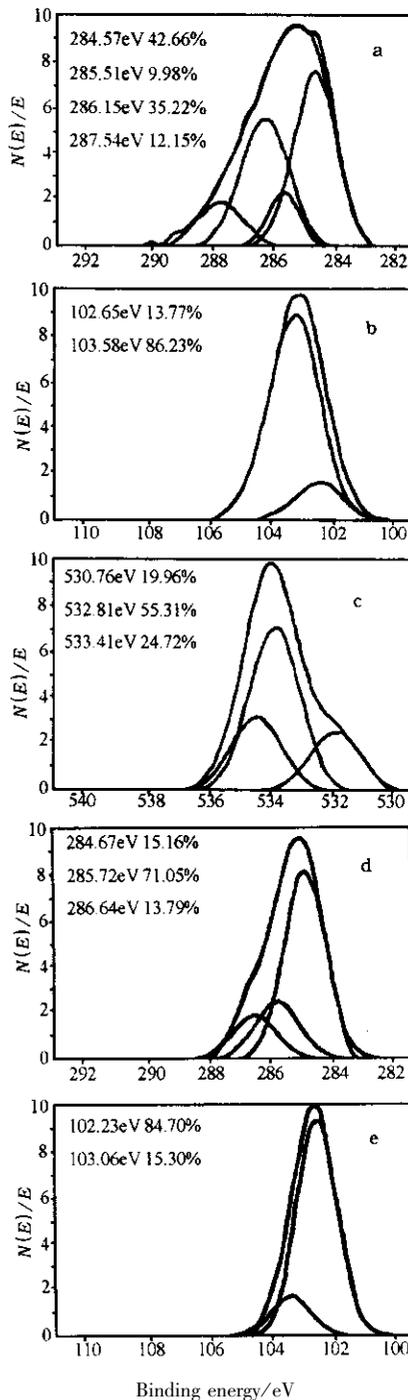


Fig. 2 XPS spectra of MPSN and APSN

a. C1s spectrum of MPSN, b. Si2p spectrum of MPSN, c. O1s spectrum of MPSN, d. C1s spectrum of APSN, e. Si2p spectrum of APSN.

(286.64 eV) carbons(Fig. 2d). The Si2p spectrum of APSN was deconvoluted into Si - C(102.23 eV) and Si - O(103.06 eV) silicons(Fig. 2e). The presence of additional components characteristic of carbon element and silicon atoms bound to carbon indicated the aminopropyl self-assembled monolayers had been covalently bonded onto the surface of the silica nanoparticles. This results accorded with that of FTIR analysis.

The results showed that the proportion of Si - C of MPSN is smaller than that of APSN. This is in conformity with the elemental analysis.

3.4 Morphological analyses

Transmission electron microscopy (TEM) was used for the morphology analysis of the organo-modified silica nanoparticles with self-assembled monolayers and the images of the bare silica nanoparticles , MPSN and

APSN were showed in Fig. 3. The mean hydromechanical particle diameters of the bare silica nanoparticles , MPSN and APSN , determined by laser scattering system (LSS) , were about 240 , 45 and 560 nm , dispersed in toluene , respectively. The diameters of them were all bigger than that of the bare silica nanoparticles purchased from Zhoushan Mingri Nano-materials Co. Ltd. This maybe due to the agglomeration (both soft and hard) in the stocking stage. The organo-modification could break up the soft agglomeration of the ultra-fine particles and improve their dispensability in organic solvent. The mean hydrodynamical particle diameters of APSN was bigger than that of the bare silica nanoparticles because of the formation of hydrogen bonds between the large numbers of amino groups immobilized onto the surface of the ultra-fine particles.

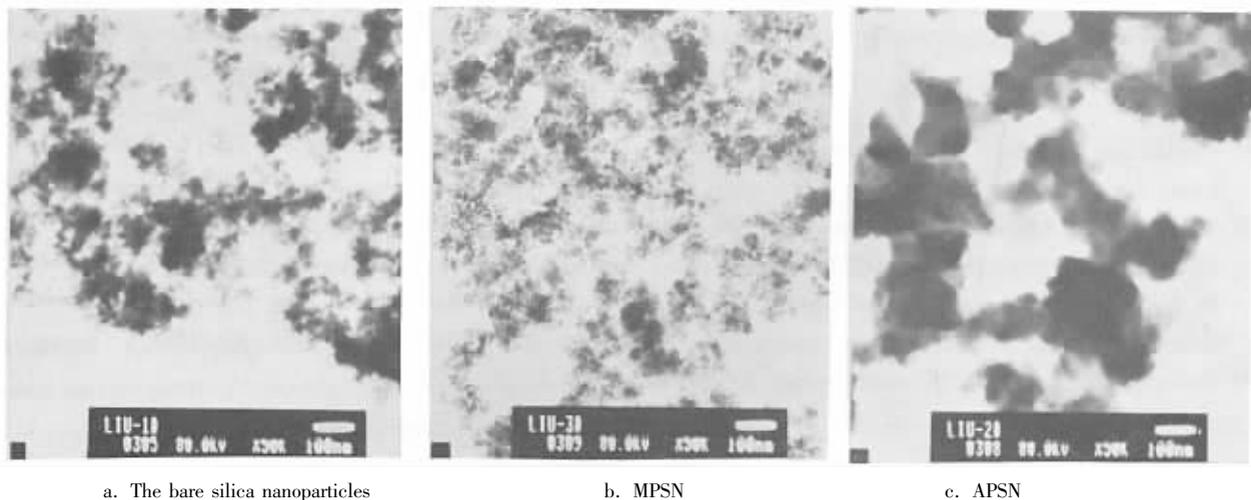


Fig. 3 TEM images of the bare silica nanoparticles , MPSN and APSN

3.5 Thermal analyses

The thermal stabilities of MPSN and APSN were investigated by the TGA analyses (Fig. 4). The weight loss of the bare silica nanoparticles at the temperature < 100°C showed the desorption of some gases adsorbed from the air. The weight loss of APSN at the temperature < 150°C showed the desorption of water and the solvent absorbed in the self-assembly procedure because of its polar surface groups. There was less weight loss of MPSN at the temperature < 150°C. Both NPSN and APSN were stable at the temperature < 250°C.

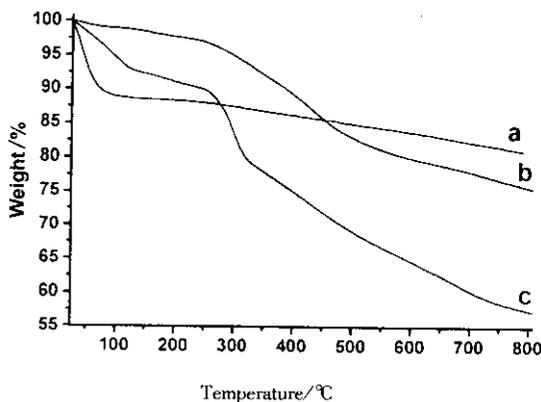


Fig. 4 TGA curves of (a) the bare silica nanoparticles , (b) MPSN and (c) APSN

4 Conclusion

The silica nanoparticles organo-modified with two functional groups, γ -methacryloxypropyl and γ -aminopropyl, were successfully prepared using a self-assembly procedure. The FTIR and XPS showed that the self-assembled monolayers were covalently bonded onto the surfaces of the ultra-fine silica particles. The TEM and LSS analyses showed that the organo-modification of the ultra-fine particle could efficiently prevent their agglomeration and improve their dispersability. It is expected to be useful in the materials industry, such as lubricating oil and organic-inorganic hybrid materials.

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