介孔二氧化硅-接枝胶原杂化材料的制备和表征

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摘要: 利用接枝胶原与介孔二氧化硅制备一种新型生物无机杂化材料。用甲基丙烯酸甲酯为接枝剂对胶原进行共聚改性制得接枝胶原。以正硅酸乙酯为模板, 十二烷基三甲基溴化铵为表面活性剂, 用一个简单的热处理过程制得介孔二氧化硅。介孔二氧化硅-接枝胶原杂化材料通过超声分散接枝胶原与介孔二氧化硅的混合物制得, 其三维结构用 X 射线衍射表征, 晶格参数 a, b 和 c 分别为 0.68, 0.37 和 1.64 nm, 为正交晶型。氮气吸附-解吸等温线显示杂化材料的比表面积可达 273 $m^2 \cdot g^{-1}$, 孔体积为 0.13 $cm^3 \cdot g^{-1}$, 平均孔径 3.4 nm, 分布窄。该杂化材料在 8~14 μm 波长的红外发射率可低至 0.323, 在光电子学器件和红外隐身领域具有潜在应用价值。

关键词: 杂化材料; 介孔材料; 胶原; 红外发射率

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Preparation and Characterization of Grafted Collagen Confined in Mesoporous Silica

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Abstract: A novel hybrid biological-inorganic material was prepared by filling grafted collagen in mesoporous silica structure. The grafting was realized by reaction between collagen and methyl methacrylate monomer. The formation of mesoporous silica precursor using tetraethyl orthosilicate as a template and cetyltrimethylammonium bromide as an assembly surfactant was completed in ammonia system at room temperature. A simple calcination treatment produced the mesoporous silica structure. An ultrasonic dispersion process was employed to immobilize grafted collagen chain in a three-dimensional mesoporous silica structure. The XRD pattern showed the presence of a three-dimensional meso-structure with the a, b, and c parameters of 0.68, 0.37 and 1.64 nm. Nitrogen adsorption-desorption isotherms showed that the as-prepared composite sample had a surface area up to 273 $m^2 \cdot g^{-1}$, a large pore volume of 0.13 $cm^3 \cdot g^{-1}$ and pore centered diameter of 3.4 nm with a relatively narrow pore size distribution. The infrared emissivity of the composite at 8~14 μm wavelength was 0.323, which was very low, indicating a potential application of the composite in areas such as photoelectronics and infrared camouflage.

Key words: hybrid; mesopore material; collagen; infrared emissivity

0　Introduction

　　Hybrid organic/inorganic composites have at- tracted a great deal of attention because of their intricate microstructures and enhanced physical and chemical properties[1,2]. In this field, recent interests

and advances have been focused on the ability to immobilize, manipulate and assembly organic molecules on a solid inorganic substrate[3,4]. Both noncovalent and covalent approaches have been developed to anchor various polymer molecules on solid substrates. Solution casting is a commonly used noncovalent method to prepare hybrid polymer composites, and spin coating is the most popular technique when a flat substrate is used. However, these physically absorbed films can be easily removed from the substrate by just rinsing with a solvent. Covalently immobilized polymer molecules can be firmly attached to the substrate and are therefore more robust toward environmental and processing conditions. They are especially desirable for applications such as sensors and devices operating under fluidic conditions. Techniques such as graft polymerization[5,6], electrostatic adsorption[7,8], self-assembly[9~11] and photochemistry[12] have been available to attach polymer thin films covalently on solid substrates. Most covalent immobilization methods involve chemical derivatization of the substrate and/or the polymer, and sometimes the synthetic chemistry can be complicated and challenging. Therefore the surface modification of inorganic matrices has emerged as an alternative method to control the physical and chemical properties of polymer-inorganic matrix composites. In this aspect, mesoporous silica with a regular structure composed of internal channels has aroused considerable interests since its pore size can be varied within mesoscale range[13]. Thus, these materials are suitable host frameworks for other materials. For instance, these mesoporous silica materials are excellent matrices for the anchoring of organometallic species[14, 15] and the resulting composites find interesting applications fields such as precursors of magnetic ceramics and catalysts[16].

Collagen is an appealing polymer material because its novel and unique architecture[17] provides a large number of functional groups in a compact space[18]. The use of this biopolymer material is currently generating increasing interest in a number of areas[19]. To incorporate well-defined, highly branched collagen chains into the channels of mesoporous silica is interesting as it may provide access to novel mesoporous materials with special properties and functions.

Here, we report a simple procedure to prepare mesoporous silica architecture and incorporate the grafted collagen chains into this structure. In this process the interactions of both hydrogen-bonding and covalent binding are involved to form the hybrid composites. The formation of composite is performed in a solution system with a simple and rapid supersonic dispersion process. The structure described provides new opportunities for their applications in areas such as photonics, photoelectronics and infrared camouflage.

1　Experimental

1.1　Materials

Collagen was purchased from Beijing Taozheng Chemical Agent Co. Ltd. Other chemicals were purchased from Shanghai Chemical Agent Co. Ltd. All reagents were analytical pure. 2,2′-azo-bis-iso-butyronitrile (AIBN, 99.9wt%) was recrystallized from absolute alcohol to prevent from auto-polymerization. Stabilized MMA was distilled under reduced pressure in a nitrogen atmosphere and used immediately.

1.2　Procedures

1.2.1　Preparation of grafted collagen matrix

2.0 g collagen was dissolved in 160 mL methanol-water (1:3 *w/w*). Calculated amount of MMA monomer (0.5 mol·L^{-1}) was added into the solution followed by the 1:1 mixture of 0.01 mol·L^{-1} ammonium cerium nitrate (CAN, 99.9wt%) in 1 mol·L^{-1} nitric acid and 0.01 mol·L^{-1} AIBN in methanol (as a polymerization initiator). The system was heated to 60 ℃ and maintained at this temperature for 2 hours with vigorous stirring in a nitrogen atmosphere. The resultants were then separated by filtration, and the obtained product was washed with distilled water and extracted with acetone to remove the loosely bound homopolymer. This process was continued until free from homopolymer.

1.2.2　Preparation of mesoporous silica structure

25 mL distilled water, 0.276 g CTAB, 420 mL 0.43 mol ammomium hydroxide and 1.46 mL TEOS were mixed with rapid stirring. After 5 minutes the solution turned opacity and the pH was 9.4, indicating the silica being hydrolyzed. After 3 hours the pH rose to 10.2 and the system was separated by filtration. The obtained product was washed with distilled water and dried in a vacuum cabinet to produce mesoporous

silica precursor. The surfactant in the precursor was removed by calcination in air at 500 ℃ for 4 hours to obtain mesoporous silica structure.

1.2.3　Preparation of grafted collagen-mesoporous silica nanocomposite

3:1 (*w/w*) mixture of grafted collagen matrix and mesoporous-silica were completely dispersed in ethanol and stirred for 8 hours. The target composites were obtained through ultrasonic vibration for 4 ~6 hours, the final product was refrigerated at 0 ℃ for 2 hours to remove impurities, then was separated in room temperature.

1.3　Characterization

The FTIR spectra were recorded on a Nicolet 5ZDX spectrometer in the 4 000~400 cm^{-1} wavenumber range using KBr pellets. X-ray powder diffraction (XRD) patterns were recorded using a scanning Scintag XDS 2000 diffractometer with a diffractometer beam monochromator and Cu *K*α radiation source. Scattering patterns were collected form 3° to 70° with a scan time of 5.0 s per 0.02° step. The thermal characters were determined by using a TGA/DTA apparatus operated in the conventional TGA/DTA mode (TMDSC, TA Q-600, TA Instrument) at the heating rate of 20 ℃·min^{-1} to simultaneously determine the correlation of temperature and weight loss and the reaction heat of materials in a nitrogen atmosphere. When the test operated, the samples were first heated to 50.0 ℃ and maintained at this temperature for 20 min to remove the thermal history, then increased the temperature into 900 ℃. BET surface areas were calculated from the nitrogen adsorption-desorption isotherms at 77 K by using a Micromeritics ASAP 2000. All samples were degassed at 200 ℃ for at least 4 h prior to N$_2$ adsorption-desorption isotherm measurement. The same equipment was used to automatically calculate the pore distribution by the Barrett-Joyner-Halenda (BJH) method[20]. Infrared emissivity testing was carried out on an IR-I infrared emissivity measurement instrument (supplied by Shanghai Institute of Technology and Physics) with powder sample.

2　Results and discussion

2.1　FTIR spectroscopy

The FTIR spectra of the grafted collagen-mesoporous silica composite are shown in Fig.1. The broad peaks at 3 477 cm^{-1} were assigned to the stretching vibration of hydroxyl groups[21] from the grafted collagen. Two peaks with medium intensity occurred around 850 and 1 649 cm^{-1} were attributed to bending and symmetry stretching vibration of amide in grafted collagen[22], respectively. A broad peak observed around 1 081 cm^{-1} was assigned to Si-O-Si stretching vibration[23].
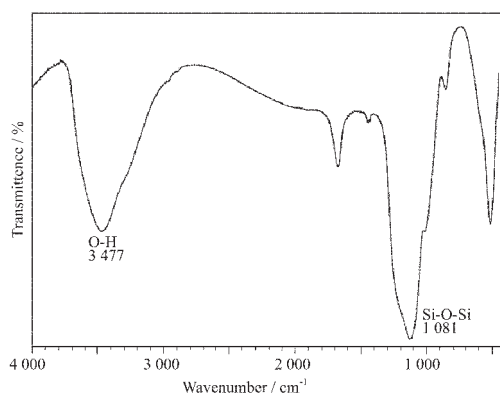

Fig.1　FTIR spectra of grafted collagen-mesoporous silica composite

2.2　X-ray diffraction (XRD)

The XRD pattern shows remarkable reflection associated with the formation of mesoscale particles (Fig.2b). The peaks at 2θ values of 25.4°, 33.1°and 51.9° were corresponded to the Si [002], [020] and [200], respectively, suggesting an orthorhombic structure[24]. The *a*, *b*, and *c* parameters could be calculated from Bragg's law to be 0.68, 0.37 and 1.64 nm, respectively. All these features indicated the presence of a three-dimensional meso-structure.
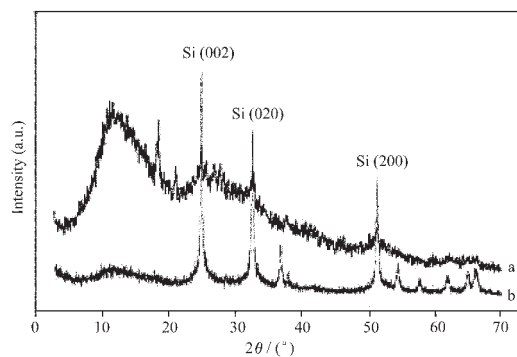

Fig.2　XRD patterns of (a) mesoporous silica precursor and (b) grafted collagen-mesoporous silica composite

2.3　Thermal properties

Fig.3 shows TGA/DTA curves of the composite. It

is appeared a large change at about 110 ℃ due to release of the adsorbed water and/or methanol from the sample. Another larger change was observed in the temperature range of 375~480 ℃, which was attributed to pyrolysis of the organic polymers contained in the composite. This process led to a greater weight loss of the composite sample. No other weight change occurred, indicating a stronger interaction between meso-porous silica and grafted collagen chain, which would improve the stability of the final hybrid material.
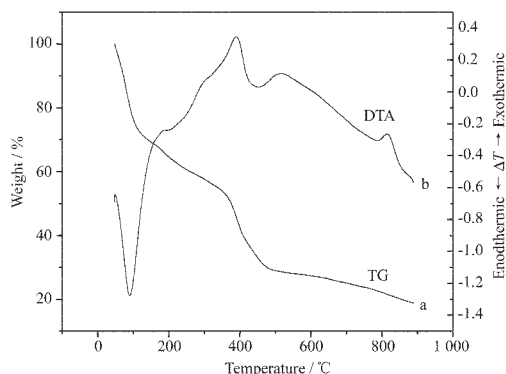

Fig.3　TGA/DTA curves of grafted collagen-mesoporous
　　　silica composite

The thermal properties of the composite were also examined with DTA. The DTA curve indicated one endothermic peak near 95 ℃, suggesting a significant reduction of grafted collagen chain mobility in the mesoporous silica structure[25]. No thermal transition was detected between 110 and 200 ℃, this confirmed that the grafted collagen could bear this temperature. (Commercial collagen can withstand only 39 ℃ [26].) Another endothermal peak was at ~435 ℃, due to the destruction of collagen helix conformation. Two exothermal peaks were observed at about 390 and 810 ℃, respectively. The former could be attributed to breaking the hydrogen bonding[27], and the latter might be caused by the release of residual CTAB in the composite[28].

2.4　Nitrogen adsorption-desorption isotherm and pore size distribution

Representative nitrogen adsorption-desorption isotherms at the −196 ℃ for the as-prepared meso-porous-silica and hybrid composite are shown in Fig.4. Both of the mesoporous-silica and nanocomposite showed type-IV-like isotherms, the curves of meso-

porous-silica and the composite with hysteresis loops at P/P_0 of 0.6~0.88 and 0.33~0.82, respectively, indicating possessing mesopores in both of samples. However, the pore volume of the mesoporous-silica was much larger than that of the composite, in agreement with the fact that the collagen chains anchored in the mesoporous structure. The Barrett-Joyner-Halenda (BJH) pore size distribution curve derived from desorption branch of the nitrogen isotherms of both samples is shown in Fig.5. The mesoporous silica showing a pore volume peak was observed at a diameter of 3 nm with the half-width of 0.5 nm, indicating a relatively narrow pore size distribution. From the nitrogen adsorption-desorption isotherms the Brunauer-Emmett-Teller (BET) surface area was obtained to be 629 m^2·g^{-1}, and a large pore volume of 0.48 cm^3·g^{-1} was also obtained. In contrast, the composite possessed a pore
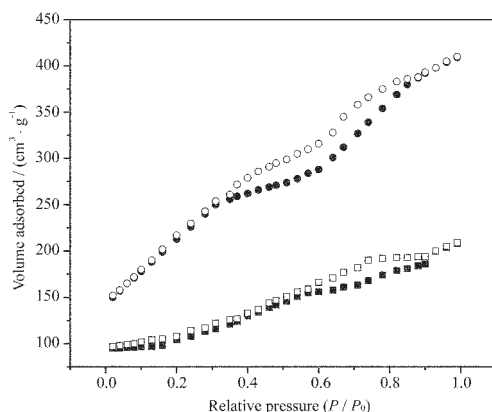

Fig.4　Nitrogen adsorption (●) and desorption (○)
　　　isotherms of mesoporous silica adsorption (■)
　　　and desorption (□) isotherms of grafted
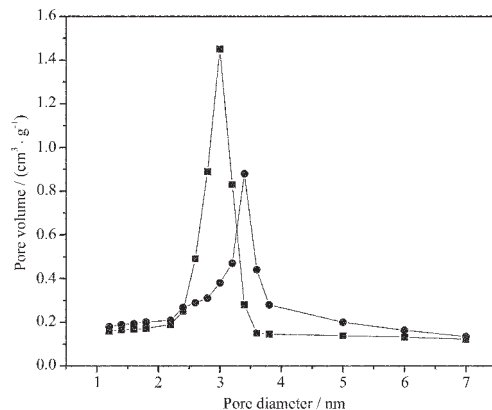　　　collagen-mesoporous silica composite

Fig.5　Pore size distribution of (■) mesoporous silica
　　　and (●) grafted collagen-mesoporous silica
　　　composite

volume peak centered at a diameter of 3.4 nm with the half-width of 0.3 nm, a smaller surface area of 273 $m^2 \cdot g^{-1}$ and pore volume of 0.13 $cm^3 \cdot g^{-1}$, respectively. The acceptable reason was that grafted collagen chains were immobilized in the mesoporous structure, which occupied some pore volume and brought a certain degree pore-expanding effect[29], thus leading to a decrease in the specific area and pore volume. Based on the t-plot analysis, the contribution of micropores to the pore volume was relatively small (composite vs mesoporous silica), which was also in agreement with the BET testing results.

2.5　Infrared emissivity

The grafted collagen-mesoporous silica composite exhibited the infrared emissivity values of 0.323 at 8~14 μm wavelength, which were much lower than those of pure collagen, grafted collagen[22] and meso-porous silica (the infrared emissivity values of samples were summarized in Table 1). This was attributed to the grafted collagen chain and mesoporous-silica stacking effect. The two components possessed strong surface synergism forces. These forces altered the moving modes of dangling bonds located in the meso-porous silica. Thus those strong infrared absorption bands in 8~14 μm wavelength would be split and weakened[30]. Therefore, the whole hybrid material possesses lower emissivity than that of neat polymer or mesoporous silica.

Table 1　Infrared emissivity of products

Samples	Collagen	Grafted collagen	Mesoporous silica	Grafted collagen-mesoporous silica composite
Infrared emissivity (8~14 μm)	0.851	0.896	0.856	0.323

3　Conclusions

A process to prepare mesoporous silica architecture and incorporate the grafted collagen chains into this structure is suggested. The FTIR spectra of obtained samples show characteristic absorption peak of 1 081 cm^{-1} due to the stretching vibration of Si-O-Si. The XRD pattern shows the peaks of Si [002], [020] and [200], respectively, implying an orthorhombic structure. The a, b, and c parameters calculated from Bragg's law indicate the presence of a three-dimensional meso-structure. The grafted collagen-mesoporous silica composite possesses a surface area up to 273 $m^2 \cdot g^{-1}$, a pore volume up to 0.13 $cm^3 \cdot g^{-1}$ and a pore diameter of 3.4 nm with a relatively narrow pore size distribution. The composite shows much lower infrared emissivity than those of pure collagen and grafted collagen. The simplicity of the preparation procedure ensures this type hybrid to be promising for potential applications as high-performance low infrared emissivity materials.

References:

[1] Okada A, Usuki A. *Mater. Sci. Eng.*, **1995**,**C3**:109~115

[2] Giannelis E P. *Adv. Mater.*, **1996**,**8**:29~35

[3] Keren K, Krueger M, Gilad R, et al. *Science*, **2002**,**297**:72~74

[4] Joachim C, Gimzewski J K, Aviram A. *Nature*, **2002**,**408**:541~544

[5] Zhao M, Liu Y, Crooks R M, et al. *J. Am. Chem. Soc.*, **1999**, **121**:923~930

[6] Zhang Y, Tan K L. *Langmuir*, **2001**,**17**:211~218

[7] Clark S L, Montague M F, Hammond P T. *Macromolecules*, **1997**,**30**:7237~7244

[8] Yang S Y, Rubner M F. *J. Am. Chem. Soc.*, **2002**,**124**:2100~2101

[9] Xia N, Hu Y, Grainger D W, et al. *Langmuir*, **2002**,**18**:3255~3262

[10] Sun F, Castner D G, Mao G, et al. *J. Am. Chem. Soc.*, **1996**, **118**:1856~1866

[11] Park J W, Thomas E L. *J. Am. Chem. Soc.*, **2002**,**124**:514~515

[12] Yan M. *Polym. News.*, **2002**,**27**:6~11

[13] Beck J S, Vartuli J C, Roth W J, et al. *J. Am. Chem. Soc.*, **1992**,**114**:10834~10843

[14] MacLachlan M J, Ginzburg M, Coombs N, et al. *J. Am. Chem. Soc.*, **2000**,**122**:3878~3891

[15] Stein A, Melde B J, Schroden R C. *Adv. Mater.*, **2000**,**12**: 1403~1419

[16] Kresge C T, Leonowicz M E, Roth W J, et al. *Dendrimers and Dendrons. Concepts, Syntheses, Applications*. VCH: Weinheim, **2001**.

[17] Koide T, Yuguchi M, Kawakita M, et al. *J. Am. Chem. Soc.*, **2002**,**124**:9388~9389

[18] Connolly S, Rao Z, Rizza R. *Coord. Chem. Rev.*, **1999**,**185**: 277~289

[19] Kinberger G A, Cai W, Goodman M. *J. Am. Chem. Soc.*, **2002**,**124**:15162~15163

[20] Barrett E P, Joyner L G, Halenda P P. *J. Am. Chem. Soc.*,

1951,**73**:373~379

[21]Sturcova A, His I, Wess T J, et al. *Biomacromolecules*, **2003**, **4**:1589~1595

[22]Shan Y, Zhou Y M, Cao Y, et al. *Mater. Lett.*, **2004,58**:1655~1660

[23]Ji X, Hampsey J E, Hu Q, et al. *Chem. Mater.*, **2003,15**:3656~3662

[24]Jan-Willem G, Bos B B, van Aken, et al. *Chem. Mater.*, **2001**, **13**:4804~4807

[25]Bronstein L M, Joo C, Karlinsey R, et al. *Chem. Mater.*, **2001**,

13:3678~3684

[26]Nomura Y, Toki S, Ishii Y, et al. *J. Agric. Food. Chem.*, **2000**, **48**:2028~2032

[27]Keisuke C, Makoto A. *Macromolecules*, **2001,34**:9201~9204

[28]Anglin E J, Schwartz M P, Ng V P, et al. *Langmuir*, **2004,20**: 11264~11269

[29]Czuryszkiewicz T, Kleitz F, Schüth F, et al. *Chem. Mater.*, **2003,15**:3704~3709

[30]Hideyuki T, Kazumasa T, Kenusuke A, et al. *Mater. Res. Bull.*, **1995,30**:1161~1171