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Ferrocenyl-functionalized organic-inorganic hybrid silica: A New kind of anion chemsensor toward flouride anion

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ABSTRACT

A new kind of ferrocenyl based chemosensor toward anions covalently bonded to silica have been successfully prepared by co-condensation of the modified Fc-Urea-Si **5** and tetraethoxysilane (TEOS). The hybrid material was characterized by IR, ^{1}HNMR, SEM, and XRD experiments. And the selective anion sensing property of the hybrid material was studied by Uv–vis and CV. The morphology of the hybrids could be tuned by pH and the content of TEOS. The hybrid networks were able to donate –NH units for selectively sensing fluoride anion with optical and electrochemical changes, accompanied by color and electrochemical changes. Hybrid network formation as well as fluoride sensing mechanism is proposed. Such nanostructure based hybrids would have potential applications in biological systems.

Introduction

The design and preparation of chemosensors capable of recognizing anions or ions have attracted increasing attention due to their important roles in the field of biology, chemistry, and environment [1–3]. It is well-known that the NH units such as amides, (thio)ureas, ammonium, imidazole units could be served as hydrogen bonding sites for anions in the diluted solution [4–7]. Three kinds of signals such as optical, electrochemical, and mass signals are extensively used to study the anion recognition events. Among them, colorimetric and electrochemical sensors are especially attractive, since they allow for the so called “naked-eye” detection, and they are qualified with fast response, high selectivity as well as inexpensive installations [8,9].

Compared to the hybrid materials, the poor photo/thermo stabilities of pure organic chemosensors are often considered to be a great impediment in practical applications. The problem could be solved by incorporating the organic chemosensors into the inorganic materials such as ZnO, Silica, and UCNP [10,11]. Ferrocenyl-based compounds are considered to be ideal anion sensing materials due to their stability, favorable electrochemical property, and reaction activity [8,12]. Therefore, it would be highly attractive to investigate the anion sensing properties of ferrocenyl-based hybrid materials. Herein, in this paper, by introducing the ferrocenyl-benzenyl group covalently into silica networks, a new kind of hybrid silica network with tuned nanosphere structures was obtained via sol–gel process, as shown in Fig. 1, which had the ability to selectively sense fluoride anion with color and electrochemical changes.

Materials and methods

Reagents and solutions

Organic solvents, HCl were analytical pure grade and obtained from Sinopharm Chemical Reagent Co. Ltd. THF was dried by Na and distilled under vacuum. $NaNO_2$, Ferrocene, 4-nitrobenzylamide, 3-Isocyanatopropyltriethoxysilane, $[Bu_4N]F$, $[Bu_4N]AcO$, $[Bu_4N]Cl$, $[Bu_4N]Br$, $[Bu_4N]I$ were obtained from Darui chemistry company.

Instrumentation conditions

^{1}HNMR spectra were recorded on a Mercuryplus instrument, at 500 Hz. Uv–vis experiments were measured on a Lambda 35-UV/VIS spectrometer, Perkin–Elmer. The X-ray diffraction pattern was

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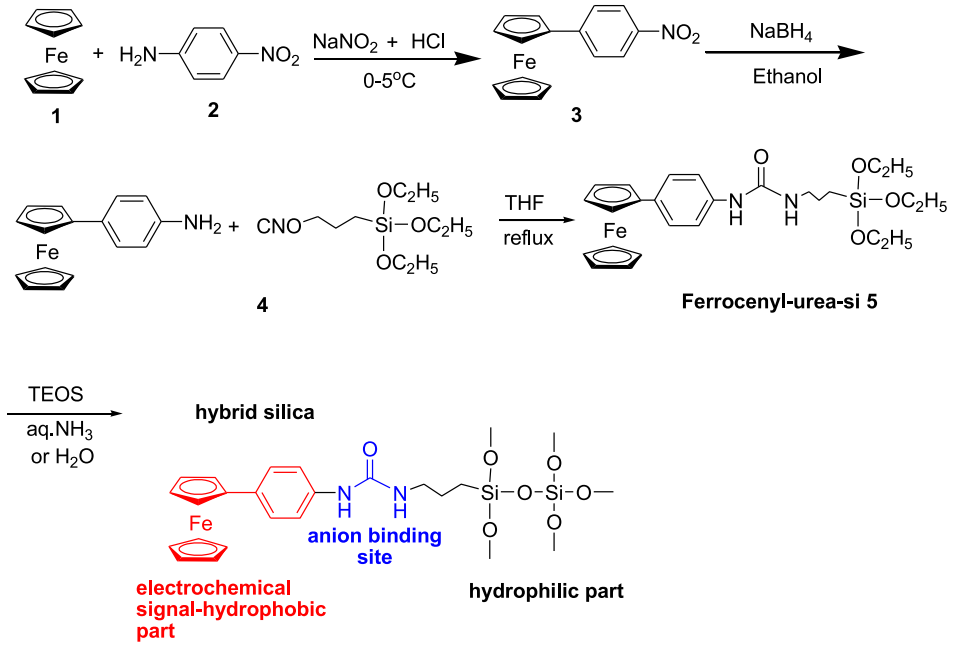

Fig. 1. The synthesis procedure of the ferrocenyl-based hybrid silica.

generated by using a Bruker AXS D8 instrument (Cu target; l = 0.1542 nm) with a power of 40 kV and 50 mA. The CV measurements of solution were carried out with a CHI-600A electrochemical analyzer (CH Instruments, Inc., Austin, TX) in a three-electrode cell. The working electrode was Au electrode, Ag-wire counter electrode and saturated calomel reference electrode were used. Supporting electrolyte: 0.1 M Bu_4NPF_6, scan rate: 20 mV/S at 25 °C. SEM images of the hybrids were obtained by using FE-SEM S-4800 (Hitachi) instruments. Samples were prepared by spinning the hybrids on glass slides, freeze-drying them, and coating them with Au.

*Fabrication of the hybrid silicas **A**, **B** and **C** in different conditions*

*Synthesis of Fc functionalized hybrid material **A***

A mixture of TEOS (1 mmol, 10 μL) and Fc-Urea-Si **5** (1 mmol, 52 mg) was added to the ethanol (10 mL) and deionized water (1 mL). The mixture was stirred at room temperature for 24 h, dried at 35 °C for 2 days to give the sample denoted as **A** (48 mg).

*Synthesis of Fc functionalized hybrid material **B***

A mixture of TEOS (1 mmol, 10 μL) and Fc-Urea-Si **5** (1 mmol, 52 mg) was added to the ethanol, adding ammonium hydroxide

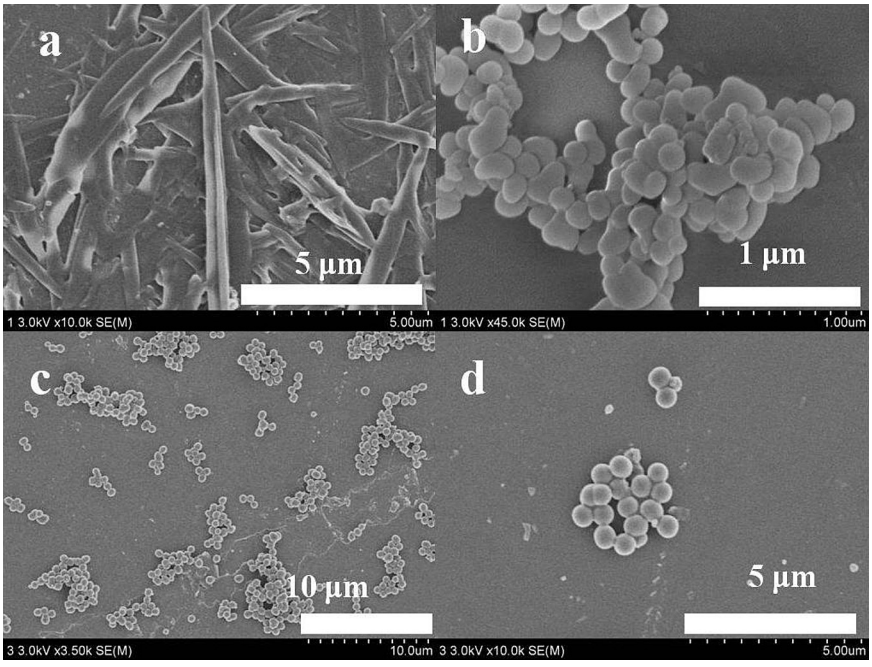

Fig. 2. SEM images of hybrid silicas obtained from different conditions. a) SEM of hybrid silica **A**; b) SEM of hybrid silica **B**; c) SEM of hybrid silica **C**; d) the magnified picture of c.