

Preparation, characterization and application of a novel silane-bridged polyaniline/cotton fiber composite



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ABSTRACT

A silane-bridged polyaniline (PANI)/cotton fiber (CF) composite (designated as PANI/SCF) was prepared by a novel and facile approach in the current study. Aniline-bearing silane molecules were first grafted onto the CF surface through a condensation reaction between hydroxyl groups of cellulose and the silane molecules. Subsequent oxidative polymerization of aniline in the presence of silane-modified CF (SCF) yielded the final PANI/SCF composite, which can be used as the potential Cr(VI) adsorbent. Results showed that the optimal silane grafting conditions were: 0.01 mol/L HAc, EtOH/water volume ratio 95/5, reaction temperature 40 °C and silane dosage 0.1 g (per 0.5 g CF). Using SCF that prepared under the optimal conditions as the substrate, about 4.6% of PANI can be deposited, mostly existing as nanorods and distributing more evenly than those on the raw CF surface. FTIR and XPS analyses further testified the successful chemical bonding of silane and the final deposition of PANI on the fiber surfaces. In comparison with neat PANI, the solid–liquid separation can be achieved by simply taking the fibrous adsorbent out. Besides, the adsorption capacity of PANI/SCF on the basis of PANI mass (dividing Q_m by PANI content) was much higher, probably due to the uniform distribution of PANI nanostructures on SCF and the high efficiency of PANI nanostructures in Cr(VI) adsorption.

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1. Introduction

Polyaniline (PANI) has attracted considerable attention in environmental processes because of its good environmental stability, controllable electrical conductivity, and abundant nitrogen-containing functional groups [1]. When existed as nanostructures, properties of PANI could be significantly enhanced and its applications could be thus expanded [2]. However, the PANI nanostructures have difficulty in further processing and solid–liquid separation. To solve the problems, investigators have prepared their composites with a suitable substrate that provides the desired mechanical properties including carbonaceous materials [3], inorganic materials [4–6], and organic polymers [7,8]. Among them, fibrous materials have been widely studied as the PANI substrates because of their desirable properties such as light weight, flexibility, low cost, multiple application forms, and facile solid–liquid separation [9–11].

Unfortunately, because of surface inertness of the pristine fibers, the direct, uniform and stable deposition of PANI on fibrous substrates is often difficult. To improve the adhesion between PANI and substrates, many modification methods have been developed to introduce active groups on the substrate surface [12–14] or to increase hydrophobicity of the substrate surfaces [15]. For example, Xia et al. [12] used the camphorsulfonic acid (CSA) to modify polyamide 6 fibers and found that higher content and more uniform distribution of PANI particles were grown on this modified surface. Wu et al. [13] pretreated wool textiles by a molecular template, i.e., poly(2-methoxyaniline-5-sulfonic acid) (PMAS), and found that introduction of sulfonic groups resulted in the formation of an adherent, uniform and stable PANI layer on the fabrics. Wang et al. [14] prepared a carboxylic group-modified poly(acrylonitrile) fiber (CPAN) for PANI deposition and concluded that the deposited PANI was more uniform and of higher content on CPAN as compared with the pristine poly(acrylonitrile) fiber (PAN). Stejskal et al. [15] concluded in one of their reviews that the hydrophobicity of the substrate surface played an important role in the deposition of PANI, and the coating of hydrophobic surfaces was more uniform compared with hydrophilic ones.

Cotton, cellulose in nature, is the most widely used natural fiber in the world. It is low-cost and clean to produce, and has a wide

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applications in textile cloth, daily care, and medicine [16,17]. Besides, the abundant hydroxyl groups on the cotton surface make its modification facile to be operated and it is expected to be a good substrate for PANI deposition. At present, the mostly popular method for cotton modification uses a silane molecule bearing bifunctional groups which may respectively react with the cotton and polymer matrices thereby forming a bridge in between them [18–21]. Different from traditional silica-based materials [6], silane modification of cellulose seems more difficult, and the chemical grafting resulted from condensation reactions between silane OH groups and cellulose OH groups occurs only at high temperature (e.g., above 100 °C) [18–22]. Besides, other parameters like medium pH, silane concentration, amounts of water and catalyst also affect the condensation reactions and the consequent silane grafting ratios significantly [19–23].

The current study focused on the development of a novel and facile approach for depositing highly uniform nanostructured PANI on cotton fiber with pre-anchored aniline-containing silane as the bridging layer. Parameters including addition of acid or base, volume ratio of ethanol and water (EtOH/water), reaction temperature, and silane dosage were studied to optimize the silane grafting conditions. The formation of silane and PANI layers on the cotton fiber was characterized by grafting ratios, Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM) photographs. Finally, the prepared composite fibers were tested for their adsorption properties of Cr(VI) from aqueous solutions to explore their potential applications in water treatment.

2. Experimental

2.1. Materials

Commercial medical cotton was used as the starting cotton fiber (CF) for silane grafting and PANI deposition. Prior to use, it was washed with water and 15% NaOH solution successively to remove possible impurities and to activate the hydroxyl groups. *N*-[3-(Trimethoxysilyl)propyl]aniline (TMSPA) (J&K Scientific Ltd., Beijing, China) was used as the bridging agent for PANI and CF. All other chemicals were of analytical-reagent grade.

2.2. Preparation of PANI/SCF composite

PANI/SCF composite was prepared by a facile and novel two-step method in the current study (see Fig. 1). In the first step for this synthesis, pre-hydrolyzed silane was grafted onto CF by mixing 0.5 g CF, a different amount of TMSPA and 20 mL solvents in a series of 50 mL plastic tubes at 160 rpm for 20 h. The fibers were then separated from the mixtures and cured at 110 °C for 2 h. The TMSPA became coupled to the CF surface via the formation of a

Si–O–C bond. The dried product was designated as SCF after being washed by water to remove the loosely attached TMSPA. The grafting ratio (*G*, %) of TMSPA on CF was calculated using the equation

$$G = \frac{W_f - W_0}{W_0} \times 100\% \quad (1)$$

where W_0 and W_f (g) are dry weight of CF and SCF, respectively. In the second step for PANI/SCF synthesis, 0.50 g SCF was dispersed in 20 mL of 1 mol/L HCl aqueous solution containing 0.2 mol/L aniline. After being mixed at 25 °C and 160 rpm for 1 h, 20 mL of (NH₄)₂S₂O₈ (0.2 mol/L) were added in one portion to give a final concentration of 0.1 mol/L for both monomer and oxidant. The mixture was reacted under ultrasonication for 30 min (KQ-200VDE, Kunshan, China), and then allowed to stand still overnight. Finally, the product (PANI/SCF composite) was separated by simply taking the fiber out, washed by water and dried at 60 °C. It was suggested that PANI was covalently bonded to SCF through the bifunctional TMSPA bridge [24].

Two reference materials, i.e., neat PANI and PANI/CF composite, were also synthesized to compare their properties with the PANI/SCF composite. The neat PANI was prepared using the same procedure as that of the PAN/SCF composite but without the addition of SCF. The PANI/CF composite was prepared using the same procedure as that of the PAN/SCF composite, except that the fiber was replaced by the starting CF. All the prepared samples were stored in a desiccator prior to use.

2.3. Sample characterization

Grafting of silane and PANI on the fiber surfaces were characterized by SEM, FTIR and XPS. Surface morphologies of the samples were observed by SEM (S-4800, Hitachi, Japan) with 1000- and 50,000-fold magnification. FTIR spectra were collected in 400–4000 cm⁻¹ using a Thermo Nicolet IR 200 instrument (Thermo Electron Corp., USA). Chemical composition of the sample surface was analyzed by XPS on an Axis Ultra spectrometer (Kratos Analytical, UK). XPS peak 4.1 software was used to peak-fit the high resolution spectra of N_{1s} and Si_{2p} after being calibrated to the binding energy of C_{1s} at 284.6 eV [1].

2.4. Batch adsorption tests

Batch tests were conducted to assess Cr(VI) adsorption properties by the several samples. In a typical test, 0.04 g of adsorbent was mixed with 40 mL of Cr(VI) solution (pH 4, fixed by acetate buffer) on a shaking table (THZ-98C, Shanghai, China) at 25 °C and 160 rpm. It was calculated that under this condition (pH 4, Cr(VI) C₀ = 10 mg/L), the primary Cr(VI) species was HCrO₄⁻ (98%). After reaching equilibrium, the mixture was filtered, and the

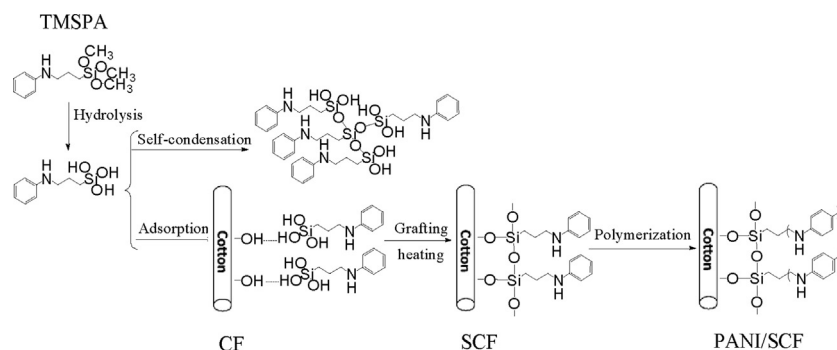


Fig. 1. Synthesis route of PANI/SCF composite.

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