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A superfast hexavalent chromium scavenger: Magnetic nanocarbon bridged nanomagnetite network with excellent recyclability

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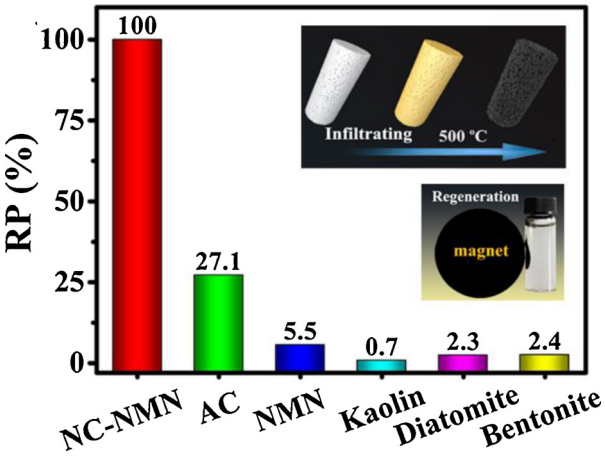
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a nanocarbon bridged nanomagnetite network (NC-NMN) is developed through the electrospinning of epichlorohydrin functionalized polystyrene (*f*-PS), followed by the direct calcination of *f*-PS and ferric nitrate, which is capable of superfast removing hexavalent chromium (Cr(VI)) from polluted water within only 15 s benefiting from its gridding framework, with an adsorption rate constant of 1.64 g mg^{-1} min^{-1} according to the pseudo-second-order kinetics. The well-fitted Langmuir isotherm model indicates a monolayer adsorption for Cr (VI) on NC-NMN. The thermodynamic parameters including negative ΔG° and positive ΔH° demonstrate that the Cr(VI) adsorption on NC-NMN is spontaneous and endothermic. The Cr(VI) adsorption retention, which is only 3.8%, is achieved for NC-NMN after five cycles, exhibiting a prominent stability and an excellent recyclability. X-ray photoelectron spectroscopy (XPS), zeta potential and energy-filter transmission electron spectroscopy

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(EFTEM) results illustrate that both the electrostatic attraction and the network structure of NC-NMN are responsible for the superior Cr(VI) adsorption performance. This work intends to provide a new method for designing the novel structure materials for polluted water treatment.

1. Introduction

Recently, with increasing awareness of environmental sustainability in modern society, the environmental contamination especially water pollution is a common threat faced by human and wildlife. [1] Hexavalent chromium (Cr(VI)) is a major pollutant in the environment coming from the industrial and agricultural activities of human being. [2] Owing to its high mobility and toxicity, the US Environmental Protection Agency (US-EPA) has set a standard for total Cr lower than 100 $\mu g\,L^{-1}$ in drinking water. [3] Thus, it's imperatively demanded to seek efficient and economical methods to remove Cr(VI) from polluted water systems. [4,5] Among various technologies for water system clean-up, adsorption is identified as a favourable and feasible strategy for industrial applications due to its low cost, high efficiency and easy handling. [6] Even though activated carbon made from coconut wood, lignin and coke etc. has been widely served as the adsorbents for Cr(VI) adsorption due to its unique pore structures, [7] the recycle and reusage are still challenges for their applications in water purification. In addition, the adsorption performance of activated carbon is normally related to its resources and activation process used. Especially, it's reported that the regeneration of activated carbon is commonly conducted at a high temperature around 800 °C, which brings relatively high costs. [8] Fortunately, magnetic carbon nanocomposites are emerging more recently, which combine carbon materials with magnetic nanoparticles for polluted water treatment and provide the opportunity for the nanocomposites to be easily recycled with a permanent magnet. [9] Therefore, the design and the fabrication of the new magnetic carbon nanocomposites towards heavy metal removal with fast adsorption kinetics and high adsorption capacity as well as excellent recyclability have attracted considerable attention. [10] Even polystyrene has been widely used in CD covers, lids, and containers, the placed serious white pollution to the environment requires the new technology for the reclamation of PS waste. [11]

In this work, a unique and facile procedure to synthesize a novel magnetic network consisting of nanocarbon bridged nanomagnetite (NC-NMN), fabricated through the electrospinning of epichlorohydrin functionalized polystyrene (*f*-PS), followed by the direct calcination of *f*-PS and ferric nitrate has been developed. The X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), scanning electron microscope (FE-SEM) and thermogravimetric analysis (TGA) have been used to characterize the chemical structures and morphologies of NC-NMN. The formation mechanism of this novel structure in NC-NMN and the optimal synthesis condition of NC-NMN is explored. Meanwhile, the as-received PS has also been electrospun and calcined via the same procedure as the fabrication of NC-NMN under the optimal conditions for comparison. A comprehensive Cr(VI) adsorption and desorption behaviours on NC-NMN has been studied in details. The results confirm that NC-NMN can superfast adsorb Cr(VI) on its surface through a monolayer process within a period of 15 s. More importantly, after five cycles of magnetic separation, this network only has 3.8% Cr(VI) adsorption retention, exhibiting an excellent recyclability. The kinetics and thermodynamics as well as Cr(VI) adsorption mechanism are evaluated. This network demonstrates a superb ability as a Cr(VI) scavenger. This work is aiming to provide a new insight for devising an original materials in environmental remediation.

2. Materials and methods

2.1. Materials

Polystyrene (PS, Mw ≈57,700) was provided by Taizhou Suosi education equipment Co., Ltd. Ethyl acetate ($CH_3COOC_2H_5$), cyclohexane (C_6H_{12}), epichlorohydrin (C_3H_5ClO), acetone (CH_3COCH_3), dichromate ($K_2Cr_2O_7$), anhydrous ethanol (C_2H_5OH), anhydrate aluminum trichloride ($AlCl_3$), dimethylformamide (DMF, C_3H_7NO), ferric nitrate (nonahydrate, $Fe(NO_3)_3{\cdot}9H_2O$), sodium hydroxide (NaOH), concentrated sulfuric acid (H_2SO_4, 98.0 wt%), hydrochloric acid (HCl, 36.0–38.0 wt%), and nitric acid (HNO_3, 65.0–68.0 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Activated carbon (specific surface area: 500–1000 $m^2\,g^{-1}$) was obtained from Shanghai Macklin Biochemical Co., Ltd. All of the chemical reagents were used as-received without further treatment.

2.2. Preparation of nanocarbon bridged nanomagnetite network (NC-NMN)

Firstly, the PS was functionalized by epichlorohydrin (*f*-PS) as published in our previous work. [12] The details please refer to supporting materials. Secondly, the *f*-PS with loading of 25.0 wt% was dissolved in a 5.0 mL of dimethylformamide under magnetic stirring at room temperature for 3 h. The *f*-PS polymer solutions were added into a 5.0 mL syringe equipped with a stainless steel gauge needle (inner diameter, 0.23 ± 0.02 mm) which was connected to a high voltage power supply (TE4020P30-30, Dalian Teslaman Tech. Co., Ltd.). The *f*-PS/DMF solution was continuously supplied by a syringe pump (NE-300, New Era Pump Systems, Inc.) with a volume feed rate of 0.1 $\mu L\,min^{-1}$, an applied voltage of 20 kV and a tip-to-collector distance of 25 cm. A flat aluminium foil served as the collector. Then the obtained *f*-PS fibres were dried completely at room temperature. Thirdly, the dried *f*-PS fibres (0.3 g) were immersed into a 5.0 wt% of ferric nitrate/anhydrous ethanol solution for about 15 min and dried in a regular oven (DHG-9071A, Shanghai Jing Hong Laboratory Instrument Co., Ltd.) and a freeze dryer (FD-1A-50, Beijing Boyikang Laboratory Instrument CO., Ltd.) for 30 and 12 h, accordingly. Finally, the dried products were put in a tube furnace (GSL-1100X Hefei Kejing Materials Technology CO., Ltd.) and annealed at 500 °C for 90 min with a heating rate of 5 $°C\,min^{-1}$ under hydrogen (5.0 vol%)/argon conditions at a flow rate of 20.0 $mL\,min^{-1}$. These samples were designated as NC-NMN. The as-received PS (without epichlorohydrin functionalization) was also electrospun and calcined via the same procedure as the fabrication of NC-NMN under the optimal conditions as a control experiment and these materials were indexed as NMN. For the details, please refer to the supporting information.

2.3. Characterizations

A HRTEM (Tecnai G2 F20, FEI Company) and a field emission SEM (Hitachi S-4800 system) were used to obtain the microstructures of samples. XPS analysis was carried out using a Kratos AXIS Ultra DLD spectrometer with Al Kα ($h\nu$ = 1486.6 eV) radiation as the excitation source at an anode voltage of 12 kV and an emission current of 10.0 mA. The crystalline structures were studied through XRD analysis on a Bruker AXS D8 Discover diffractometer with General Area Detector Diffraction System (GADDS). The thermogravimetric analysis (TGA) was recorded within the temperature range from 25 to 850 °C in air conditions with a heating rate of 20 $°C\,min^{-1}$ by a SDT thermal-