Q1 Nb$_2$O$_5$ nanowires *in-situ* grown on carbon fiber: A high-efficiency material for the photocatalytic reduction of Cr(VI)

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ABSTRACT

Niobium oxide nanowire-deposited carbon fiber (CF) samples were prepared using a hydrothermal method with amorphous Nb$_2$O$_5$·nH$_2$O as precursor. The physical properties of the samples were characterized by means of numerous techniques, including X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), UV–visible spectroscopy (UV–vis), N$_2$ adsorption–desorption (BET), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy. The efficiency for the removal of Cr(VI) was determined. Parameters such as pH value and initial Cr(VI) concentration could influence the Cr(VI) removal efficiency or adsorption capacity of the Nb$_2$O$_5$/carbon fiber sample obtained after hydrothermal treatment at 160°C for 14 hr. The maximal Cr(VI) adsorption capacity of the Nb$_2$O$_5$ nanowire/CF sample was 115 mg/g. This Nb$_2$O$_5$/CF sample also showed excellent photocatalytic activity and stability for the reduction of Cr(VI) under UV-light irradiation: the Cr(VI) removal efficiency reached 99.9% after UV-light irradiation for 1 hr and there was no significant decrease in photocatalytic performance after the use of the sample for 10 repeated cycles. Such excellent Cr(VI) adsorption capacity and photocatalytic performance was related to its high surface area, abundant surface hydroxyl groups, and good UV-light absorption ability.

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Introduction

Hexavalent chromium (Cr(VI)) is regarded as one of the most toxic heavy metal contaminants, and the resulting environmental pollution has been of continuing concern worldwide (Selvaraj et al., 2003). It can be accumulated in living organisms through the food chain, leading to serious health issues (*e.g.*, chromosomal aberrations, liver damage, and lung cancer) (Miretzkya and Fernandez Cirelli, 2010; Kauspediene et al., 2010; Kozlowski and Walkowiak, 2002). Chromium in an aqueous environment displays two oxidation states: Cr(III) and Cr(VI). Compared to Cr (III), Cr(VI) exhibits higher solubility (usually existing in water as anions, such as HCrO$_4^-$, Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$, and *etc.*) and much higher toxicity. Therefore, Cr(VI) is also difficult to remove from industrial wastewater (Zhitkovich, 2011; Li et al., 2008; Barrera-Diaz et al., 2012). In recent years, a number of conventional methods to remove Cr(VI) from wastewater have been developed, including chemical reduction, ion exchange, electrochemical precipitation, and adsorption. However, most of these methods have severe limitations,

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such as high operational cost and ineffectiveness at high Cr(VI) concentrations, inhibiting application of these methods in industry (X. Sun et al., 2014; Q. Sun et al., 2014; Di Natale et al., 2015; Anirudhan et al., 2013; Gode and Pehlivan, 2005; Gurgel et al., 2009). Although the adsorption strategy is suitable for industrial applications due to its low cost, one serious problem is how to properly dispose of the adsorbent after saturated adsorption; otherwise, regeneration of the adsorbent will inevitably cause secondary pollution. The key issue for the removal of Cr(VI) in wastewater is the decrease in toxicity obtained *via* the reduction of Cr(VI) to Cr(III). Therefore, it is highly desirable to develop an economical and eco-friendly adsorbent with a high Cr(VI) removal efficiency.

Recently, research on the development of novel and efficient technologies to reduce toxic Cr(VI) into much less toxic Cr (III) has been extensive (Shannon et al., 2008; Fei and Li, 2015; Abney et al., 2014). Photocatalysis is one of the most promising technologies for the removal of Cr(VI) ions in industrial wastewater (Pandikumar and Ramaraj, 2012; Xu et al., 2014; C.Y. Cao et al., 2012; J. Cao et al., 2012; Li and Cao, 2011; Wang et al., 2013). To date, various semiconductor materials (*e.g.*, TiO_2, SnO_2, CeO_2, Fe_2O_3, Nb_2O_5, and ZnO) have been used as photocatalysts for the reduction of heavy metal ions and the degradation of organic pollutants. Among these semiconductor materials, Nb_2O_5 is a well-known wide band gap (3.1–3.5 eV) (Nowak and Ziolek, 1999; Prado et al., 2008; Shishido et al., 2009; Chen et al., 2007) semiconductor that is widely used in selective oxidation, hydrogenation, dehydrogenation, dehydration, hydration, electrochemistry, and polymerization (Wu et al., 2014; Furukawa et al., 2011; Prado et al., 2005, 2008; Shishido et al., 2009; Chen et al., 2007; Tanaka et al., 1993). Nb_2O_5 also possesses unique properties, such as a high refractive index, chemical inertness, thermal stability, and high photocatalytic activity (Nowak and Ziolek, 1999; Wu and Xue, 2011). Recently, Nb_2O_5 and its composites have been reported to be effective photocatalysts for the removal of pollutants in wastewater under light irradiation. However, most of the studies are based on the use of Nb_2O_5 nanowires or nanoparticles, which are difficult to recover from aqueous solutions after photocatalytic reaction, causing secondary pollution and photocatalyst loss (Hashemzadeha et al., 2015; Lopes et al., 2014). Furthermore, nanoscale particles tend to easily agglomerate, leading to a decline in photocatalytic efficiency (Albrecht et al., 2006; Honeyman, 1999). To solve this problem, we herein report the *in-situ* growth of Nb_2O_5 nanowires on carbon fiber (CF), and find that such materials are highly efficient for the removal of Cr(VI).

1. Experimental

1.1. Materials

Commercial Nb_2O_5 powder, hydrofluoric acid, ammonium hydroxide, and potassium dichromate ($K_2Cr_2O_7$) were purchased from Beijing Chemical Reagent Research Company. CF, glacial acetic acid, ammonium oxalate, and lauryl sodium sulfate (SDS) were purchased from Tianjin Fuchen Chemical Reagent Factory. All of the chemicals were of analytical grade and used without further purification.

1.2. Sample preparation

In a typical procedure for the preparation of Nb_2O_5 nanowires, amorphous $Nb_2O_5 \cdot nH_2O$ was firstly prepared from 0.30 g of commercial Nb_2O_5 powder according to a procedure described elsewhere (Ji et al., 2010). 0.3 g of $Nb_2O_5 \cdot nH_2O$ was dispersed in 10 mL of hydrofluoric acid aqueous solution, 0.5 g of ammonium oxalate, and 0.1 g of SDS. Then, 0.1 g of CF was added to the above mixture. After magnetic stirring for 30 min, the mixture was transferred into a 25 mL-Teflon-lined stainless steel autoclave for hydrothermal treatment at 160°C for 8–14 hr, followed by cooling down in air to room temperature. Finally, the product was filtered and washed with 50 mL of absolute ethanol and 50 mL of deionized water, and dried in air at 60°C for 2–3 hr.

1.3. Sample characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a D/MAX-II X-ray diffractometer (D/MAX-II X, RIGAKU, Japan) with Cu $K\alpha_1$ radiation and curved graphite crystal monochromator filter, and the instrument was operated at 35 mA and 35 kV with a scanning speed of 4°/min and a step of 0.02°. The energy-dispersive spectroscopic (EDS) patterns and scanning electron microscopic (SEM) images of the typical samples were obtained on a 570 SEM system (570 SEM, Hitachi, Japan). Transmission electron microscopic (TEM) images and selected-area electron diffraction (SAED) patterns of the typical samples were recorded on a H-9000NAR TEM (H-9000NAR, Hitachi, Japan) with accelerating voltage of 250 kV. UV–visible spectroscopic (UV–vis) spectra of the samples were measured on a UV–vis spectrophotometer (SHIMADZU, Japan). Surface areas and pore-size distributions of the samples were determined using a Surface Area and Porosimetry System (Micromeritics, USA) and calculated according to the BET (Brunauer, Emmett and Teller) and BJH (Barrett, Joyne and Halenda) methods, respectively. Fourier transform infrared spectroscopic (FT-IR) spectra of the typical samples were recorded on a spectrometer (PerkinElmer, USA) with a range of 400–4000 cm^{-1} (The samples were mixed with KBr with the mass ratio of sample to KBr of 1: 100 and pressed into pellets for IR analysis). X-ray photoelectron spectroscopy (XPS) (Ulvac-PHI, Japan) was employed to determine the Cr 2p, Nb 3d, O 1s, and C 1s binding energies (BEs) of the samples using Al $K\alpha$ (hv = 1486.7 eV, in which the hv represents incident photon energy) as excitation source. The C 1s signal at BE = 284.6 eV was used to calibrate the BEs.

1.4. Adsorption capacity measurement

100 mL of Cr(VI) standard aqueous solution at a known concentration was added to a 250-mL conical flask. The pH values were adjusted with diluted HCl or NaOH aqueous solution. 40 mg of the Nb_2O_5 nanowire/CF composite sample was added to the above solution in a water bath under stirring for 10–30 min. The solution was filtered with a syringe filter (diameter = 0.22 μm) to obtain the filtrate solution. The Cr(VI) concentration in the filtrate solution was determined using the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) technique (SHIMADZU, Japan).