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, 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) (Miretzky 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 (Sun et al., 2014a, 2014b; Di Natal 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 Ramara, 2012; Xu et al., 2014; Cao et al., 2012a, 2012b; Li and Cao, 2011; Wang et al., 2013). To date, various semiconductor materials (e.g., TiO₂, SnO₂, CeO₂, Fe₂O₃, Nb₂O₅, and ZnO) have been used as photocatalysts for the reduction of heavy metal ions and the degradation of organic pollutants. Among these semiconductor materials, Nb₂O₅ is a well-known wide band gap (3.1–3.5 eV) (Nowak and Ziolk, 1999; Prado et al., 2008; Shishido et al., 2009; Chen et al., 2007) semiconductor that is widely used in selective oxidation, hydrogenation, dehydrogenation, dehydronation, 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). Nb₂O₅ also possesses unique properties, such as a high refractive index, chemical inertness, thermal stability, and high photocatalytic activity (Nowak and Ziolk, 1999; Wu and Xue, 2011). Recently, Nb₂O₅ 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 Nb₂O₅ nanowires or nanoparticles, which are difficult to recover from aqueous solutions after photocatalytic reaction, causing secondary pollution and photocatalyst loss (Hashemzadeh 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 Nb₂O₅ 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 Nb₂O₅ powder, hydrofluoric acid, ammonium hydroxide, and potassium dichromate (K₂Cr₂O₇) were purchased from Beijing Chemical Reagent Research Company. CF, glacial acetic acid, ammonium oxalate, and laurel 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 Nb₂O₅ nanowires, amorphous Nb₂O₅·nH₂O was firstly prepared from 0.30 g of commercial Nb₂O₅ powder according to a procedure described elsewhere (Ji et al., 2010). 0.3 g of Nb₂O₅·nH₂O 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 Kα₁ 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–Teller) and BJH (Barrett–Joyne–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 Kαₐ (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 Nb₂O₅ 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).
The removal efficiency and adsorption amount of Cr(VI) can be calculated according to Eqs. (1) and (2), respectively:

$$E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where $E$ (%) is the removal efficiency, $C_0$ (mg/L), $C_e$ (mg/L), $V$ (L), and $m$ (g) are the initial Cr(VI) concentration, final Cr(VI) concentration, solution volume, and adsorbent mass, respectively.

1.5. Photocatalytic performance evaluation

The photocatalytic performance of the Nb$_2$O$_5$ nanowire/CF samples was evaluated for the removal of Cr(VI). Solutions containing different concentrations of Cr(VI) were prepared using K$_2$Cr$_2$O$_7$. 50 mg of the Nb$_2$O$_5$ nanowire/CF sample was added to 60 mL of Cr(VI) aqueous solution under stirring, and then 50 mg of oxalic acid was added to maintain acidic conditions. After magnetic stirring for 1 hr in the dark to reach the adsorption–desorption equilibrium, the above mixed solution was exposed to UV light (500 W) under constant stirring. At regular irradiation time intervals (20 min), 2–3 mL of the mixture was sampled and filtered by a syringe filter (diameter = 0.22 μm) to obtain the filtrate solution. The photocatalytic performance was expressed by $I_0$ vs. $t$ (min), where $I_0$ is the absorbance intensity of Cr(VI) in the initial concentration when adsorption–desorption equilibrium was achieved, whereas the $I$ is the absorbance intensity of Cr(VI) at a given irradiation time (t). For the sake of comparison, the photocatalytic activity of P25 was also measured for the photocatalytic reduction of Cr(VI) under the same reaction conditions.

2. Results and discussion

2.1. Crystal phase and textural properties

Fig. 1 shows the XRD patterns of the Nb$_2$O$_5$ nanowires/CF samples obtained after hydrothermal treatment at 160°C for (a) 8, (b) 10, (c) 12, and (d) 14 hr.

Fig. 2 shows the SEM images of the Nb$_2$O$_5$ nanowires/CF composite samples obtained after hydrothermal treatment for different times. As the hydrothermal time increased, the Nb$_2$O$_5$ nanocrystals grew slowly. When the hydrothermal time was 8 hr, the Nb$_2$O$_5$ nanocrystals exhibited a flower-like morphology composed of a number of aggregated sheets and were deposited on the surface of the CF. With the increase in hydrothermal time from 8 to 12 hr, the sheets became thin in width and long in length. When the hydrothermal time increased to 14 hr, the Nb$_2$O$_5$ nanocrystals changed into a wire-like morphology with the length and diameter of 2–3 μm and 15–30 nm, respectively. The composition of the typical Nb$_2$O$_5$/CF sample obtained after hydrothermal treatment at 160°C for 14 hr was also confirmed by its EDS spectrum (Appendix A Fig. S1), in which Nb, O, and C elements were detected, suggesting that a Nb$_2$O$_5$ nanostructure had been successfully grown on the CF surface. The extension of hydrothermal time from 14 to 18 hr did not lead to a significant change in morphology of the Nb$_2$O$_5$ nanowires. In the Nb$_2$O$_5$ nanowire/CF sample obtained after hydrothermal treatment at 160°C for 18 hr, the diameters were in the range of 20–30 nm, and the lengths were 2–3 μm (Appendix A Fig. S2).

Fig. 3 shows the high-resolution TEM images and SAED patterns of the Nb$_2$O$_5$ nanowires obtained after hydrothermal treatments for 10 and 14 hr, respectively. As can be seen, the Nb$_2$O$_5$ nanowires displayed a high-quality crystallinity. The lattice spacing (d value) of an individual Nb$_2$O$_5$ nanowire was measured at 0.394 nm, which fitted well to that of the (001) plane of the standard Nb$_2$O$_5$ sample (JCPDS PDF# 28-0317). The observation of linearly aligned bright electron diffraction spots in the SAED pattern reveals that the Nb$_2$O$_5$ nanowires were single crystals.

Fig. 4a shows the N$_2$ adsorption–desorption isotherms and pore-size distributions of the as-prepared samples. The Nb$_2$O$_5$ nanowire/CF samples obtained after hydrothermal treatments for 8 and 10 hr exhibited a type IV isotherm with a H4-type hysteretic loop, indicating the presence of a slit-like mesopore structure. However, the Nb$_2$O$_5$ nanowire/CF samples obtained after hydrothermal treatments for 12 and 14 hr showed a distorted type IV isotherm with a H3-type hysteretic loop, suggesting the formation of a distorted mesoporous structure. The mesoporous structures of the Nb$_2$O$_5$ nanowires/CF samples formed due to the aggregation of sheets or nanowires were also confirmed by the pore-size distributions (Fig. 4b). The BET surface areas of the Nb$_2$O$_5$ nanowires/CF samples after hydrothermal treatments at 160°C for 8, 10, 12, and 14 hr were 70, 89, 102, and 130 m$^2$/g, respectively.
Fig. 2 – Scanning electron microscopic (SEM) images of the Nb$_2$O$_5$ nanowires/CF samples obtained after hydrothermal treatment at 160°C for (a, b) 8, (c, d) 10, (e, f) 12, and (g, h) 14 hr.

Fig. 3 – Transmission electron microscopic (TEM) images and selected-area electron diffraction (SAED) pattern (inset) of the Nb$_2$O$_5$ nanowires/CF samples obtained after hydrothermal treatment at 160°C for (a, b) 10 and (c, d) 14 hr.
2.2. Optical behavior

The UV–vis diffuse reflectance spectrum of the Nb$_2$O$_5$ nanowires/CF sample obtained after hydrothermal treatment for 14 hr was recorded on a UV–vis spectrophotometer, and the results are illustrated in Fig. 5a. There was a strong absorption in the UV-light region (200–400 nm), indicating that Nb$_2$O$_5$ was a good material for the absorption of UV light (Brayne and Bozont-Verduraz, 2003; Lin et al., 2011). It is convenient to use the bandgap energy ($E_g$) to evaluate the optical absorption performance of a material. For a crystalline semiconductor, the optical absorption near the band edge obeys the equation $(\alpha h\nu)^2 = A(h\nu - E_g)^n$, in which the $A$, $\alpha$, and $h\nu$ represent a constant, the absorption coefficient, and the incident photon energy (Butler, 1977), respectively. The $n$ value depends upon the characteristics of the transition in a semiconductor: $n = 1$ for direct transition and $n = 4$ for indirect transition. In the case of Nb$_2$O$_5$, the electron transition was a direct transition and the $n$ value is 1. The $E_g$ value can be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), as shown in Fig. 5b. The intercept of the tangent to the X-axis is approximately equal to the $E_g$ value for the Nb$_2$O$_5$ nanowire/CF sample. The estimated $E_g$ value of the Nb$_2$O$_5$ nanowire/CF sample obtained after hydrothermal treatment for 14 hr was 3.18 eV, in good agreement with that of Nb$_2$O$_5$ material reported in the literature (Lin et al., 2011). The result suggests that the Nb$_2$O$_5$ nanowire/CF sample was highly effective in absorbing UV light.

2.3. Adsorption behavior

Fig. 6a shows the effect of pH value on the Cr(VI) adsorption efficiency of the Nb$_2$O$_5$ nanowire/CF sample (40 mg) obtained after hydrothermal treatment for 14 hr for the removal of 100 mL of Cr(VI) aqueous solution (20 mg/L) at 25°C for 15 min. It was observed that with the rise in pH value from 2.0 to 4.0, the Cr(VI) removal efficiency increased from 90 to 99%; however, the Cr(VI) removal efficiency (ca. 99%) remained almost unchanged...
when the pH value rose from 4.0 to 12.0. This result indicates that the pH value significantly influenced the Cr(VI) removal efficiency. Fig. 6b shows the effect of initial Cr(VI) concentration on the Cr(VI) adsorption amount of the Nb2O5 nanowires/CF sample obtained after hydrothermal treatment for 14 hr at 25°C and pH = 7.0 for 30 min. It can be seen that when the Cr(VI) concentration rose, the Cr(VI) adsorption amount increased rapidly and reached adsorption saturation (ca. 110–115 mg/L) at a Cr(VI) concentration of 400–1000 mg/L. Compared with other adsorbents reported in the literature, the Cr(VI) adsorption capacity of the as-prepared Nb2O5 nanowire/CF sample obtained after hydrothermal treatment at 160°C for 14 hr was much higher than those of Fe2O3@AlO(OH) (Yang et al., 2013), Mn/Fe3O4 (Cui et al., 2013), flower-like α-Fe2O3 (Cao et al., 2012a, 2012b), flower-like CeO2 (Zhong et al., 2007), PA6@Fe3O4 (Li et al., 2013), cyclodextrin/graphene (Fan et al., 2012), and activated carbon (Giri et al., 2012). Although MnO2 nanowire/diatomite and Fe3O4@NiO samples (Du et al., 2015; Zhang et al., 2013) showed better Cr(VI) adsorption performance than our samples, they were difficult to recover from aqueous solutions and their recycling stability was much lower than our samples. In addition, unlike the Nb2O5 nanowire/CF samples studied in this work, all of the above adsorbents could not decrease the toxicity via the reduction of Cr(VI) to Cr(III), which might cause secondary pollution.

Fig. 7 shows typical FT-IR spectra of K2Cr2O7 and the Nb2O5 nanowire/CF samples obtained after hydrothermal treatment at 160°C for 14 hr before and after Cr(VI) adsorption. The strong absorption band at 3500 cm⁻¹ was attributable to the O–H stretching vibration of Nb–OH (Esteves et al., 2008). The absorption band at 1630 cm⁻¹ corresponded to the O–Hi n-plane bending vibration (Izumi and Kodama, 1978; Ueno and Fujihara, 2011; Zhang et al., 2012), and the absorption band at 1390 cm⁻¹ was due to the hydroxyl groups on the niobium oxide surface. The characteristic absorption bands in the range of 500–1000 cm⁻¹ could be assigned to the Nb–O stretching and Nb–O–Nb angular vibrations (Gasparotto et al., 2011). After Cr(VI) adsorption, a new absorption band centered at 525 cm⁻¹ appeared, ascribable to the stretching vibration of the Cr–O or Cr–O–Cr bonds (Maschio et al., 2012). This result indicates that Cr species were indeed present on the surface of the Nb2O5 nanowire/CF sample.

### 2.4. Photocatalytic performance

The photocatalytic activity of the Nb2O5/CF samples was evaluated by the photocatalytic removal of Cr(VI) ions. Appendix A Fig. S3 shows the time-dependent absorption spectra of the photocatalytic reduction of 60 mL K2Cr2O7 aqueous solution (100 mg/L) over the Nb2O5 nanowires/CF (50 mg) sample obtained after hydrothermal treatment at 160°C for 14 hr in the presence of oxalic acid (0.05 g) at pH = 5. Similar photocatalytic reduction spectra were also detected for this sample under different conditions. Fig. 8 shows the photocatalytic activity of the Nb2O5 nanowires/CF (50 mg) sample obtained after hydrothermal treatment at 160°C for 14 hr under different conditions. It was observed that after UV-light irradiation for 50 min, the Cr(VI) removal efficiency was 94.5% over 50 mg of Nb2O5/CF in the presence of oxalic acid (0.05 g). A blank experiment was conducted using Nb2O5/CF in the absence of oxalic acid under UV-light irradiation. A slight change was observed in the concentration of Cr(VI). Another blank test was also carried out without the addition of the Nb2O5/CF sample under UV-light.
exposure, and a small change in Cr(VI) concentration was detected in the presence of oxalic acid (0.05 g). Experiments using Cr(VI) with different concentrations were also conducted to investigate the photocatalytic activity of the Nb$_2$O$_5$/CF sample. As shown in Fig. 8, the Cr(VI) removal efficiency decreased when the concentration of Cr(VI) increased from 100 to 150 mg/L. Compared with other photocatalysts reported in the literature, the photocatalytic activity of the Nb$_2$O$_5$ nanowire/CF sample for Cr(VI) reduction was much higher than those of TiO$_2$-yeast (Song et al., 2015) as well as of the blank experiments with UV light irradiation (no catalyst and 0.05 g oxalic acid at pH = 5 or no oxalic acid and 50 mg Nb$_2$O$_5$/CF).

The recycling stability was tested by repeating the catalytic reduction of 100 mg/L K$_2$Cr$_2$O$_7$ aqueous solution at pH = 5 over the Nb$_2$O$_5$/CF sample obtained after hydrothermal treatment at 160°C for 14 hr over 10 cycles, and the result is shown in Fig. 9. It can be seen that about 91% Cr(VI) removal efficiency was maintained after 10 cycles. Therefore, this Nb$_2$O$_5$/CF sample was photocatalytically stable. The Nb$_2$O$_5$ nanowire/CF sample obtained after hydrothermal treatment at 160°C for 14 hr possessed excellent recycling stability at other catalysts reported in the literature (Song et al., 2015; Wu et al., 2015).

To investigate the mechanism for the adsorption and photocatalytic reduction of Cr(VI), the XPS technique was used to characterize the surface states of the Nb$_2$O$_5$/CF sample obtained after hydrothermal treatment at 160°C for 14 hr before and after Cr(VI) adsorption and photocatalytic reduction, and the results are shown in Fig. 10. It can be observed from the full-scan XPS spectrum (Fig. 10a) of the Cr-adsorbed sample that there was detection of Cr species on the sample surface. After Cr(VI) adsorption, there are Cr 2p XPS signals at BE = 530.4 and 532.1 eV, attributable to the surface lattice oxygen (i.e., oxygen atoms that were bound to the Nb atoms (Nb-O)), surface hydroxyl groups (–OH) and surface-adsorbed water, respectively. The peak intensity of surface –OH species was significantly higher than that of the surface lattice oxygen, confirming that there were many hydroxyl groups on the surface of the fresh Nb$_2$O$_5$/CF sample before adsorption. After Cr(VI) adsorption, however, the peak intensity of the surface –OH species decreased and that of the surface lattice oxygen increased. This result suggests that hydroxyl groups exchanged with the Cr(VI) species. As shown in Fig. 10d, the Cr 2p XPS signal can be curve-fitted with three components at BE = 576.8, 581.8, and 586.8 eV, assignable to the surface Cr(III) 2p$_{3/2}$, Cr(VI) 2p$_{3/2}$, and Cr(III) 2p$_{3/2}$ (Sun et al., 2014a, 2014b; Hu et al., 2014), respectively. The result indicates that Cr(III) species were present on the surface of Nb$_2$O$_5$/CF after photocatalytic reduction of Cr(VI), confirming the photocatalytic reduction of Cr(VI) to Cr(III) under the UV-light illumination.

It should be pointed out that in the Nb$_2$O$_5$ nanowire/CF samples, the Nb$_2$O$_5$ nanowires showed high surface area (130 m$^2$/g), and the exposed Nb$_2$O$_5$ surface possessed a large number of oxygen vacancies (Ikeya and Senna, 1988). At pH below 5, the chromium was present in the form of CrO$_4^{2-}$ or Cr$_2$O$_7^{2-}$ ions that were negatively charged. Therefore, the chromate ions could be adsorbed on the surface of Nb$_2$O$_5$ nanowires, which was evidenced by the fact that formation of the Cr-O or Cr-O-Cr bonds in the Cr-adsorbed Nb$_2$O$_5$ nanowire/CF samples was confirmed by the results of FT-IR and XPS investigations. Although the Cr(VI) ions are photochemically inactive, their effective photoreduction occurred on the photocatalysts upon light irradiation in the presence of a sacrificial electron donor. In this system, the photoinduced electron transfer would compete with the physical deactivation of its excited ligand-to-metal charge-transfer state, depending on the strength of interaction between chromate and the electron donor. It has been reported that charge transfer is highly favored via ligand-to-metal charge transfer within the Nb compound-

Fig. 8 – The Cr(VI) removal efficiency of the Nb$_2$O$_5$/CF sample (50 mg) obtained after hydrothermal treatment for 14 hr under UV-light irradiation in 60 mL of K$_2$Cr$_2$O$_7$ aqueous solutions with different Cr(VI) concentrations (100 and 150 mg/L) in the presence at pH = 5 or in the absence of oxalic acid (0.05 g) as well as of the blank experiments with UV light irradiation (no catalyst and 0.05 g oxalic acid at pH = 5 or no oxalic acid and 50 mg Nb$_2$O$_5$/CF).

Fig. 9 – The recycle stability of the Nb$_2$O$_5$ nanowires/CF sample obtained after hydrothermal treatment at 160°C for 14 hr for the photocatalytic reduction of Cr(VI) at pH = 5.
oxalic acid surface (Wu et al., 2017). Cr(VI) as a strong oxidant is capable of rapidly consuming photocatalytically generated electrons to effectively suppress charge recombination, and oxalic acid as a reducing organic compound consumes the photocatalytically generated holes at the valence band of Nb2O5. In the presence of oxalic acid, the sacrificial agent used gave rise to an indirect pathway to reduce Cr(VI). It could inject electrons into the conduction band of Nb2O5 via ligand-to-metal charge transfer under light irradiation, leaving behind highly energetic oxalic acid species that are oxidized by holes or hydroxyl radicals in irreversible reactions, thus avoiding recombination of photoinduced electron/hole pairs and enhancing reduction of Cr (VI) ions. Accordingly, the surface-complex-mediated photoreduction reaction was involved in intramolecular electron transfer within the Nb2O5 surface complexes, and initiated by the photoexcitation of the surface complexes, which led to formation of electron/hole pairs. Therefore, the Nb2O5 nanowire/CF samples performed well in the removal of Cr(VI) from industrial wastewater.

3. Conclusions

Nb2O5 nanowires were successfully grown in-situ on CF via a hydrothermal route. The obtained materials possessed high surface areas, among which the Nb2O5/CF sample obtained after hydrothermal treatment at 160°C for 14 hr showed a high Cr(VI) adsorption capacity (115 mg/g), excellent photocatalytic performance for Cr(VI) reduction (the Cr(VI) removal efficiency was 99.9% after UV-light irradiation for 1 hr), and good stability (there was no significant decrease in photocatalytic activity after the use of the sample for 10 repeated cycles). Such excellent Cr(VI) adsorption capacity and photocatalytic performance for the Nb2O5/CF sample obtained after hydrothermal treatment at 160°C for 14 hr was associated with its high surface area, abundant surface hydroxyl groups, and good UV-light absorption ability. We believe that the Nb2O5/CF samples are promising materials for the removal of Cr(VI) from industrial wastewater.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.04.019.


