



Full Length Article

Atomic layer deposition of TiO₂ on carbon-nanotubes membrane for capacitive deionization removal of chromium from waterJianhua Feng^{1,2,#}, Sen Xiong^{2,#}, Li Ren², Yong Wang^{2,*}¹ College of Material and Chemical Engineering, Chuzhou University, Chuzhou 239000, China² State Key Laboratory of Materials-Oriented Chemical Engineering, and College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China

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ABSTRACT

Chromium (Cr) is a common heavy metal that has severe impacts on the ecosystem and human health. Capacitive deionization (CDI) is an environment-friendly and energy-efficient electrochemical purification technology to remove Cr from polluted water. The performance of CDI systems relies primarily on the properties of electrodes. Carbon-nanotubes (CNTs) membranes are promising candidates in creating advanced CDI electrodes and processes. However, the low electrosorption capacity and high hydrophobicity of CNTs greatly impede their applications in water systems. In this study, we employ atomic layer deposition (ALD) to deposit TiO₂ nanoparticles on CNTs membranes for preparing electrodes with hydrophilicity. The TiO₂-deposited CNTs membranes display preferable electrosorption performance and reusability in CDI processes after only 20 ALD cycles deposition. The total Cr and Cr(VI) removal efficiencies are significantly improved to 92.1% and 93.3%, respectively. This work demonstrates that ALD is a highly controllable and simple method to produce advanced CDI electrodes, and broadens the application of metal oxide/carbon composites in the electrochemical processes.

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1. Introduction

Heavy metals will cause severe environmental issues and seriously affect the health of human even at trace concentrations [1]. Chromium (Cr) is a common heavy metal which has been widely used in industrial applications, such as textile processing, pigment manufacturing, leather tanning, electroplating, and oil refining. However, directly or indirectly discharged chromium containing wastewaters will lead to severe pollution [2,3]. The existence forms of chromium compounds in environment are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Inappropriate disposal of chromium-containing wastewater will contaminate the drinking water, particularly when the highly oxidative Cr(VI) species are discharged. Almost all Cr(VI) species in the environment are originated from human activities, which pose a big threat to public health and natural life [4]. By comparison, Cr(III) species are of less toxicity and can be formed precipitate Cr(OH)₃ from solution [5]. A number of techniques, such as physical adsorption [6], ion exchange [7], electrocoagulation [8], membrane separations [9], chemical reduction/precipitation [10], electrochemical

precipitation [11], bio-mitigation [10] and photo-catalytic reduction [12] have been widely studied to remove chromium from wastewater. However, these processes may become inefficient. Firstly, the maximum permissible concentration of chromium in industrial wastewater should be less than 0.1 mg·L⁻¹ [13], which often exists at much lower concentrations than other typical ions. Secondly, these processes usually suffer from some drawbacks, such as production of waste sludge and toxic brine, high operation costs, and a possibility of secondary pollution [10,14,15].

Capacitive deionization (CDI), a promising alternative desalination technique, is a cost-efficient, environment-friendly electrochemical water purification technology and an efficient, facile avenue to remove heavy metal and other ions from water [16,17]. Removing chromium ions through efficient CDI techniques is an effective way for more sustainable chromium-containing wastewater treatments. The CDI performance relies dramatically on the electrical conductivity, water affinity, specific surface area, porosity and electrochemical stability of the electrode materials [18]. Recent developments of redox-active and faradaic materials, and functionalization of carbon-based materials have provided new ways for heavy metal removal [19]. To date, various types of carbon-based materials, including carbon aerogels (CAs), graphene, activated carbon (AC) and their composites, have been extensively examined in CDI to remove heavy metals from water [20–22]. The

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combination of functionalized carbon nanotubes (CNTs) and other carbon materials or polymers to produce composite CDI electrodes is also widely investigated for heavy metals removal [23–27]. However, the time- and energy-consuming modification processes, incorporation of binder and aggregation of CNTs often make the preparation of CNTs electrodes complicated, and releasing individual CNTs into atmosphere or water may cause serious security issues [28]. In contrast, as an emerging carbon-based material, free-standing CNTs membrane is made of randomly intertwined CNTs, resulting in three-dimensional (3D) interlinked nanoporous networks. Due to its excellent mechanical, electronic, thermal and chemical performances, it can be used in diversified fields [29–31]. Although CNTs and their composite membranes have been widely utilized in various CDI applications, there still exist some drawbacks during the electrode preparation and application processes. Nevertheless, the innate high hydrophobicity of CNTs membranes greatly limits their applications in CDI processes [26,32]. Typically, to enhance the hydrophilicity of CNTs membranes, a variety of functionalization strategies such as chemical modification and physical vapor deposition (PVD) have been done to generate polar groups on CNTs as well as offer additional attractive properties. However, these treatments for the decoration of CNTs are usually energy-consuming, tedious and inhomogeneous [33–35], thus a simple and highly controllable hydrophilic functionalization method is urgently needed.

As an upcoming nanomanufacturing approach, atomic layer deposition (ALD) is a promising new strategy for creating conformal coatings with controllable characteristics at sub-nanoscale by sequential, self-limiting surface reactions, and can be particularly applied to the properties fine-tuning of membranes [36]. ALD has the capability to produce robust chemical bonding between deposited materials and substrates. Meanwhile, ALD is a highly controllable method and can be advantageously employed to functionalize membranes by regulating deposition parameters in a simple way, which will tune the surface properties and pore sizes of membranes or add new functions to the membranes [37–43]. Recently, several oxides have been successfully deposited onto CNTs and other carbon materials *via* ALD, and thus producing high-power supercapacitor electrodes for various electrochemical applications [44–46]. As an environmental-friendly, low-cost and highly hydrophilic oxide [47], titania (TiO_2) can be advantageously used as coatings for modifying membrane interfacial properties. In this study, we employ ALD to deposit TiO_2 onto CNTs membranes with self-supporting structure and fabricate binder-free composite CNT@TiO_2 electrodes which are further used in chromium-containing wastewater treatments. Significant improvements in hydrophilicity, electrochemical properties and CDI removal efficiencies of chromium were achieved under optimized ALD cycles. The composite CNT@TiO_2 membrane electrodes also exhibited preferable reusability during the CDI processes. ALD not only inaugurates a new way to promote the electrochemical performances of carbon materials, but also provides the possibility to create high-performance electrodes for CDI applications.

2. Experimental

2.1. Materials

Pristine CNTs membranes were purchased from Suzhou Jiedi Co., Ltd. (China) and used as substrates. Titanium tetrachloride (TiCl_4 , 99.99%) was purchased from Nanjing University and deionized (DI) water (conductivity: 8–20 $\mu\text{s}\cdot\text{cm}^{-1}$) was supplied by Wahaha Co., Ltd. (China). TiCl_4 and DI water were employed as precursor and coreactant, respectively. The ultrahigh purity nitrogen (99.999%) was utilized as a carrier gas and high purity nitrogen

(99.9%) was employed as purge gas in ALD processes. Silicon substrates were used to monitor the growth per cycle of TiO_2 . Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, $\geq 99.8\%$, Aladdin, China) and 1,5-diphenylcarbazide ($\geq 98\%$, Alfa Aesar, China) were used as received. Anhydrous ethanol, sulfuric acid and all other chemicals, obtained from Shanghai Lingfeng Chemical Regent Co., Ltd., were of analytical reagent grade and used directly in the experiments.

2.2. Preparation of CNT@TiO_2 membrane electrodes

CNTs membranes were deposited utilizing a method previously described [40]. Briefly, pristine CNTs membranes (5 cm \times 5 cm) used as substrates were placed into the hot-walled, vacuum reaction chamber of a Savannah S100 ALD reactor which was from Cambridge NanoTech (USA). The reaction pressure and temperature were set as ~ 133 Pa and 100 $^\circ\text{C}$, respectively. DI water and TiCl_4 were separately stored in steel bottles at ambient temperature, and alternatively introduced into the chamber as ALD precursors. Precursors were pulsed into the chamber along with carrier gas, and then the by-products and unreacted precursors were swept out of reaction chamber by purge gas. The flow rates of all gases were set to 3.33×10^{-10} $\text{m}^3\cdot\text{s}^{-1}$. The pulse time of TiCl_4 was set as 0.03 s and that of DI water was 0.015 s. Exposure and purge time for both precursors were 5 s and 20 s, respectively. The “exposure mode” allowed for proper diffusion of the precursors through the membranes and all ALD operations were carried out under automatic control *via* fast valves. Sheets of CNTs membranes and Si wafers were kept in the chamber under vacuum for at least 0.5 h before deposition and were deposited for 5, 10, 20, 40, and 60 cycles, respectively. The ALD-deposited samples were marked as CNT@xTiO_2 (x denotes cycle numbers).

2.3. Characterizations

Under the operation voltage of 5 kV, a field-emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) was employed to examine the surface morphologies of CNTs membrane electrodes with and without TiO_2 deposition. A contact angle goniometer (DropMeter A-100, Maist, China) was adopted to measure static water contact angles (WCAs) of the electrodes before and after deposition at room temperature, and the average value of WCAs was reported. The spectroscopic ellipsometer (EASEM-2000U, J. A. Woollam, USA) was employed to examine the thicknesses of TiO_2 deposited on Si wafers at 70 $^\circ$ incident angle. The mass of CNTs membranes before and after ALD were examined by an electronic analytical balance and the corresponding TiO_2 percentages were calculated. The cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI660E, Shanghai Chenhua, China) in a three-electrode system at 298 K. Ag/AgCl, platinum (Pt), and a piece of TiO_2 -deposited CNTs electrode were used as reference, counter, and working electrodes, respectively. 1 $\text{mol}\cdot\text{L}^{-1}$ NaCl solution was adopted as electrolyte and the range of scanning voltage was from -0.5 to 0.8 V for CV tests.

2.4. Electrochemical removal of chromium by capacitive deionization

Chromium ions removal tests were carried out in a continuously recycling CDI system, in which the solution was continuously circulated from a reservoir *via* peristaltic pump (BT100-2J, Longer, China) into the CDI unit cell, and the effluent was returned into the cell, as developed in our previous work [40]. Cr(VI) solution for testing was obtained from dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in DI water and the solution pH was adjusted to 4.5. The CNTs membrane electrodes with an effective area of 12.5 cm^2 were separated by a non-woven spacer into parallel anode and cathode pairs with a distance of 1 mm. Electrosorption was carried out in a cuvette with 20 ml Cr

(VI) solution ($\sim 10 \text{ mg}\cdot\text{L}^{-1}$). The $\text{K}_2\text{Cr}_2\text{O}_7$ solution was driven at a flow rate of $3.8 \text{ ml}\cdot\text{min}^{-1}$ by a peristaltic pump under room temperature. The chromium removal was conducted by applying a direct voltage of 1.6 V between the membrane electrodes using a MS-305D potentiostat.

Before electrochemical removal experiments, ethanol was used to pre-wet the CNTs electrodes and DI water was employed to thoroughly rinse them. During the CDI tests, 0.2 ml solution was withdrawn periodically and further diluted for measurements. Measurements of Cr(VI) concentrations were carried out by the method of 1,5-diphenylcarbohydrazide spectrophotometry with an UV-vis absorption spectrometer (NanoDrop 2000c, Thermo Fisher Scientific, USA) at $\sim 540 \text{ nm}$. 1,5-diphenylcarbohydrazide reacts with Cr(VI) and produces a dark violet colored complex in acidic condition. The relationship between Cr(VI) concentration and absorbance can be acquired before CDI tests. Total chromium (TCr) concentrations were examined via an inductive coupled plasma emission spectrometer (Optima 7000DV, PerkinElmer, USA). Chromium ion removal efficiency (%) was assessed through the following equation:

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

where R is the removal efficiency, C_0 ($\text{mg}\cdot\text{L}^{-1}$) shows the initial concentration of chromium ion and C_t ($\text{mg}\cdot\text{L}^{-1}$) is the chromium ion concentration after t time in CDI processes. In the reusability tests, the membrane electrodes were first rinsed with $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ for 10 min under electrodes reverse connection. Then the electrodes were washed with DI water for 15 min under short circuit condition. Finally, the electrodes were totally dried at 100°C and reused for next chromium removal tests.

3. Results and Discussion

3.1. Characteristics of ALD-deposited CNTs electrodes

FESEM was employed to investigate the morphology of as-prepared electrode materials. The morphology of pristine CNTs was shown in Fig. 1(a) and that of CNT@20TiO₂ membrane electrode was displayed in Fig. 1(b). Obviously, the pristine CNTs electrode exhibits a fibrous morphology with a highly interconnected and uniform CNTs network. The smooth and intertwined CNTs fibers form nanoporous structure and irregular pores. With rising ALD cycles, the TiO₂ nanoparticles coverage on CNTs was gradually promoted. As shown in Fig. S1 (in Supplementary Material), compared with the pristine CNTs, remarkable change of morphology was not detected and this can be ascribed to the lower deposition rate of TiO₂ at initial deposition stage. After 20 ALD cycles, there are numerous nanoparticles can be observed on individual CNTs surface, as shown in Fig. 1(b). The unobvious coverage change at lower ALD cycle numbers can be ascribed to the TiO₂GPC (0.05 nm) which is much smaller than GPCs of other oxides, e.g., ZnO [43]. The size and number of TiO₂ nanoparticles were increased with more ALD cycles. Owing to the enlarged sizes, TiO₂ nanoparticles were progressively approaching, and finally an intact and continuous coating was formed on the CNTs surface with even higher ALD cycle numbers (Fig. S1).

The TiO₂ percentage on CNT@20TiO₂ membrane electrode was shown in Fig. 1(c). With low ALD cycles, TiO₂ particles are in the stage of nucleation, so TiO₂ mass percentages are very low (3.1% and 5.5% for 5 and 10 cycles, respectively), as shown in Fig. S2. With rising ALD cycle numbers, the TiO₂ mass percentage was continuously increased and reached 9.7% for the CNTs membrane electrode with 20 ALD deposition cycles (Fig. 1(c)). The mass

percentage of TiO₂ was obviously enhanced to 20.7% when the ALD cycle number increased to 40. With further enhancement of ALD cycles, the mass percentage reached to the maximum value (27.9%) for the ALD-deposited CNTs electrode with 60 cycles (Fig. S2).

Surface wettability plays an important role in CDI applications for CNTs electrodes to ensure that the entire pores engaging in the electrosorption of ions. Therefore, the WCAs of pristine and ALD-deposited CNTs electrodes were examined to assess their water affinity. It can be seen from Fig. S3 that the WCAs were gradually decreased with the increment of ALD cycle numbers. As displayed in Fig. 1(c), the WCA of undecorated CNTs membrane electrode is $\sim 114^\circ$, showing a highly hydrophobic surface. When the ALD cycle number increased to 20, WCA was remarkably decreased to $\sim 69^\circ$. The enhanced affinity between water and the ALD-modified CNTs electrodes can be mainly attributed to the hydroxyl groups which existed on TiO₂ surface [48]. Such a change from hydrophobicity to hydrophilicity for the ALD-deposited CNTs electrodes will provide excellent compatibility to aqueous systems on one hand, and offer more approachable channels for ions on the other, which is very desirable for their applications in aqueous systems.

To assess the electrochemical properties of ALD-modified CNTs membrane electrodes, cyclic voltammetry (CV) tests were conducted in three-electrode systems. The CV profiles of pristine CNTs and CNT@20TiO₂ membrane electrodes in the range of -0.5 to 0.8 V are illustrated in Fig. 1(d). The CNT@20TiO₂ electrodes display a larger encircled area than pristine CNTs electrodes, implying that the ALD-modified CNTs electrode has larger capacitances. Meanwhile, the CV curve of CNT@20TiO₂ electrodes exhibits a nearly rectangular shape, implying enhanced electrochemical properties and better capacitance behavior of ideal electric double layer (EDL) [40]. The above characterization results show that the CNT@20TiO₂ membrane electrode presents better electrochemical performance and EDL behavior, indicating the preferable CDI properties.

3.2. Total chromium removal efficiencies of ALD-deposited CNTs electrodes

The limitation values of Cr(VI) and TCr (Cr(III), Cr(VI) and other forms of chromium) concentrations in water systems are usually defined by environmental regulations. The removal efficiencies of TCr were investigated using TiO₂-deposited CNTs membranes as CDI electrodes at 1.6 V. As shown in Fig. 2, the TCr removal efficiencies of CNTs electrodes were gradually increased with the extension of CDI operation time. The TCr removal efficiency of pristine CNTs electrode was 70.5% at 240 min. However, with the increment of TiO₂ deposition cycles, the TCr removal efficiencies of ALD-modified CNTs electrodes were different under the same CDI operation time. Below 20 ALD cycles, the removal efficiencies basically display an upward trend with the increase of ALD cycle numbers. The CNT@20TiO₂ membrane electrodes exhibit a good TCr removal performance, and the removal efficiency is reached 92.1% at 240 min, which increases by 30.6% compared with that of pristine CNTs electrodes. Nevertheless, with further increasing ALD cycles, TCr removal efficiency is slightly decreased. For example, the removal efficiency of CNT@60TiO₂ electrodes was 89.3%. The CNT@20TiO₂ electrodes have much higher electrosorption capacity than other TiO₂-deposited CNTs electrodes, which has been confirmed in our previous work [40]. This superior TCr removal efficiency of the CNT@20TiO₂ membrane electrodes can be ascribed to the enhancement in the number of effective electrosorption sites and surface hydrophilicity for ions under the

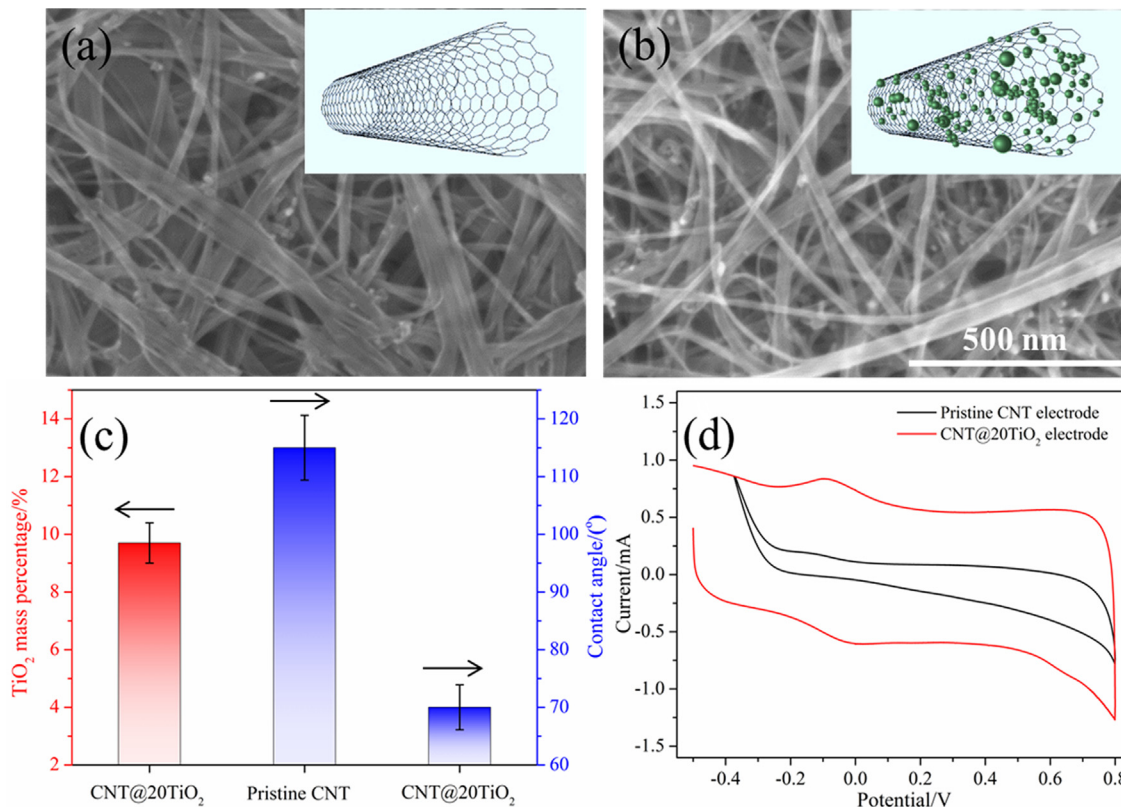


Fig. 1. SEM images of (a) pristine CNTs electrode and (b) CNT@20TiO₂ electrode ((a) and (b) have the same magnification which is illustrated in (b)). Insets in (a) and (b) are carbon nanotube models before and after ALD deposition. (c) TiO₂ mass percentage and water contact angles of CNT@20TiO₂ electrode. (d) CV curves for the pristine CNTs and CNT@20TiO₂ electrodes at a scanning rate of 100 mV·s⁻¹.

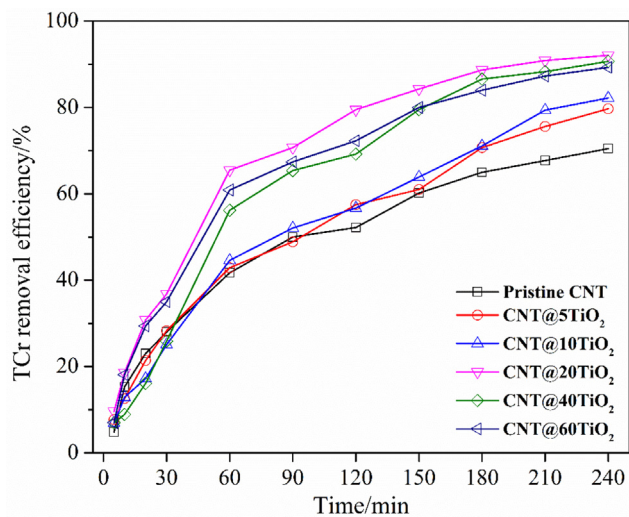


Fig. 2. TCr removal efficiencies of pristine and ALD-deposited CNTs membranes with 5, 10, 20, 40, and 60 ALD cycles.

involvement of titanium under electric field. Chromium-containing solution flowed through the space between the two charged CNT@20TiO₂ membrane electrodes. Under the action of electrostatic force, anions and cations in the solution are electro-migrated towards the surface of positive and negative CNTs electrodes, respectively. The electrodes will act as capacitors and store ions in the pores, thus improving the removal efficiencies of chromium ions, and further demonstrating the feasibility of chromium

removal by CDI from aqueous solutions by using the TiO₂-deposited CNTs electrodes.

3.3. Cr(VI) removal efficiencies of ALD-deposited CNTs electrodes

The pristine and CNT@20TiO₂ membrane electrodes were selected for the tests of Cr(VI) removal efficiencies. As shown in Fig. 3(a) and (b), the absorbance spectra of all samples at 540 nm were gradually decreased with the increase of operation time, indicating that the Cr(VI) concentrations in the solution are continuously decreasing. The decrease in the absorbance of each sample obtained by CNT@20TiO₂ electrode at the same operation time was significantly greater than that of the corresponding sample of pristine CNTs electrodes. The Cr(VI) concentration was reduced from the initial 9.96 to 2.59 mg·L⁻¹ when pristine CNTs electrode used, while it was decreased from 9.56 to 0.64 mg·L⁻¹ when CNT@20TiO₂ membrane electrodes were employed (Fig. 3(c)). In addition, it can be seen from Fig. 3(d) that the Cr(VI) removal efficiency of the pristine CNTs electrode was 74.0% after 240 min treatment, while it was reached 93.3% for the CNT@20TiO₂ electrodes. These results show that, under the same experimental conditions, the TiO₂ deposited CNTs membranes can effectively improve removal performance of Cr(VI) in aqueous systems. The deposited TiO₂ not only improves the affinity of electrodes with ions in solution but also increases the number of active adsorption sites on CNTs surface, thus improving the capacitive nature and enhancing the electroadsorption ability of the electrodes [47]. Moreover, the electrochemical polarization of CNT@20TiO₂ after ALD functionalization will promote the capture capability of the charged electrode surface towards Cr(VI) and also contributes to the enhancement in Cr(VI) removal efficiency [49].

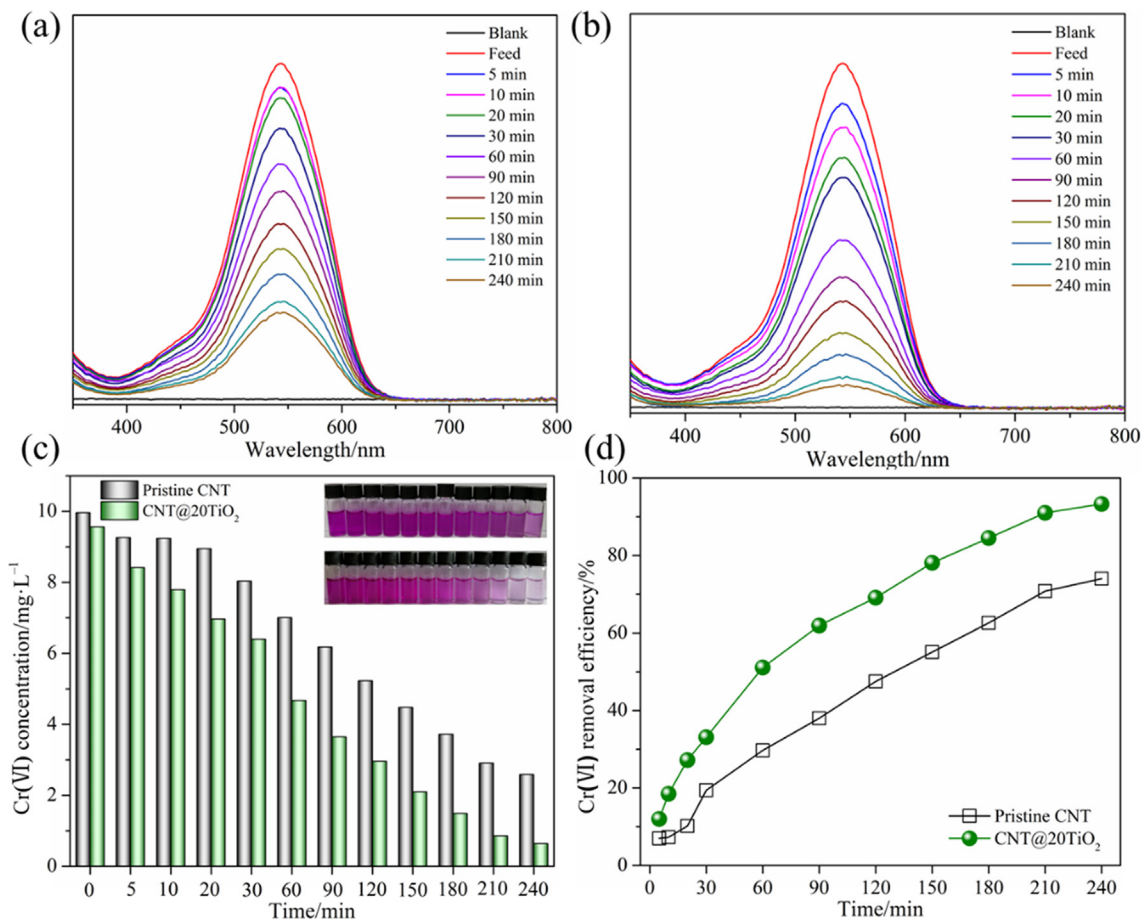


Fig. 3. UV-vis absorbance spectra of Cr(VI) solutions as a function of CDI times by using (a) pristine and (b) CNT@20TiO₂ membrane electrodes. (c) Concentration variations of Cr(VI) in solutions and (d) Cr(VI) removal efficiencies as a function of CDI times with pristine and CNT@20TiO₂ membrane electrodes. Inset in (c) is the physical appearance of Cr(VI) solutions.

3.4. Recycling and reusability of ALD-deposited CNTs electrodes

For CDI electrode materials, excellent regeneration and reusability can prolong the service life of electrodes and reduce the costs, so it is a significant factor in practical application. To assess the recyclability of ALD-deposited CNTs electrodes, the CNT@20TiO₂ electrode was selected for electro sorption-desorption experiments, in which the electro sorption and desorption voltages were set as 1.6 V and 0 V, respectively. The removal efficiencies of TCr and Cr(VI) during the four cycling operations are illustrated in Fig. 4. The CNT@20TiO₂ membrane electrodes maintained a relatively high Cr(VI) removal efficiency, and the average removal efficiency was 93%. While the removal efficiencies of TCr decreased slightly from 92.1% to 83.7% during the four cycling operations. The results displayed that there was no obvious decline in the removal efficiency for Cr(VI) after multiple recycling tests, indicating that the Cr(VI) is fast adsorbed to the active sites on ALD-modified CNTs and reduced rapidly. The slight decline of TCr removal efficiency can be attributed to two reasons. Firstly, the adsorbed substances in electrode pores cannot be completely desorbed because of the capillary forces. Secondly, the Cr(III) produced during electrochemical reduction processes combines with OH⁻ to form Cr(OH)₃ which is suspended in the solution [5]. No appreciable decreases in Cr(VI) and TCr removal efficiencies are observed, demonstrating that the CNT@20TiO₂ electrodes have excellent reusability during CDI processes. Consequently, the ALD-

deposited CNTs membranes can be regarded as a promising material for CDI electrode and expected to find prospective applications in heavy metal wastewater treatments.

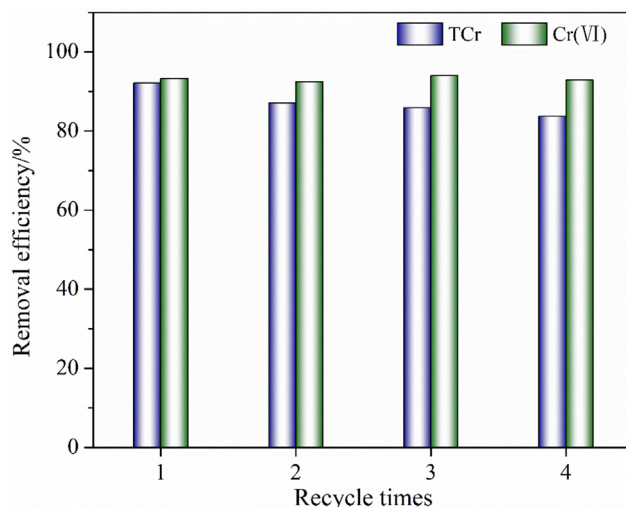


Fig. 4. Recyclability and reusability of the CNT@20TiO₂ membranes in CDI removal of TCr and Cr(VI).

3.5. Mechanism of chromium removal by ALD-deposited CNTs electrodes

Fig. 5 shows a schematic diagram of the chromium redox reaction processes on the TiO_2 -deposited CNTs membrane electrodes. There are three types of Cr(VI) anions in solution, namely $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- and CrO_4^{2-} . Convection, electromigration and diffusion are three forces which lead to the ion migration to the electrode surface [5]. When the TiO_2 -deposited CNTs membranes were used as electrodes, some Cr(VI) anions were migrated to the anode under the electromigration force but could not undergo further oxidation processes. Meanwhile, there are more Cr(VI) ions could be repelled by hydroxyl groups derived from the ALD-modified CNTs compared with the pristine CNTs, thus increasing the probability that Cr(VI) ions diffused onto the cathode surface. Furthermore, Cr(VI) species will be further reduced to Cr(III) ions that exist in the form of $\text{Cr}(\text{OH})_4^-$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_2^{2+}$, Cr^{3+} , etc. The cationic Cr(III) species would be electro-adsorbed onto the cathode and further reacted with hydroxyl groups originating from the functionalized CNTs, thus depositing on the electrode surface. On the contrary, the anionic Cr(III) species would be partly migrated and adsorbed onto the anode surface, meanwhile, a small number of Cr(III) anion might also move towards the anode under electromigration force and be further oxidized to Cr(VI) species.

The pristine CNTs electrodes showed lower TCr and Cr(VI) removal efficiencies and that could be ascribed to their hydrophobic nature and the lack of effective electrosorption sites. In contrast, TiO_2 -deposited CNTs membrane electrodes, with superior electrosorption capacity and enhanced hydrophilicity, have a strong tendency to bind ions. Under the action of electric field, EDL will be easily formed on the CNT@20TiO_2 electrode surface and has a strong appeal to chromium ions. The electrosorption can be mainly ascribed to the electrostatic interaction between the chromium ions in solution and the ALD-functionalized CNTs electrodes, and valence forces formed by the shared electrons between the chromium ions and the electrodes [50]. Therefore, the CNT@20TiO_2 membrane electrodes showed enhanced chromium removal efficiencies, confirming that ALD has bright applications in the field of heavy metal wastewater treatments.

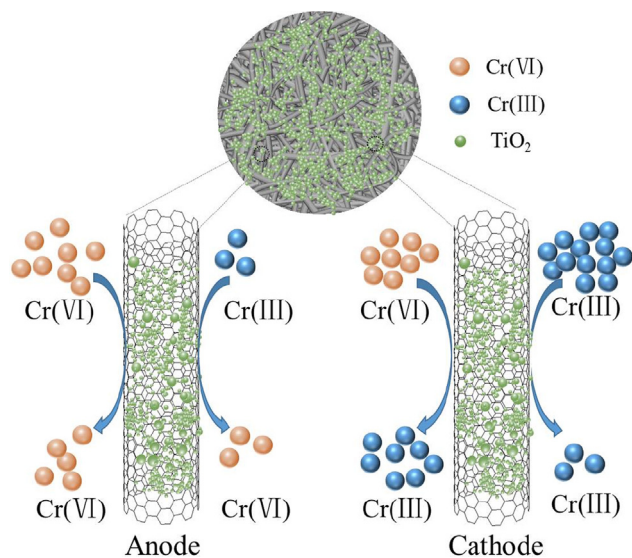


Fig. 5. Schematic illustration of chromium redox reaction on the TiO_2 -deposited CNTs electrodes.

4. Conclusions

In conclusion, the controllable functionalization of free-standing CNTs membranes by ALD TiO_2 to create preferable CDI electrodes has been demonstrated. TiO_2 mass percentages on CNTs membranes could be precisely adjusted by ALD cycle numbers. With the increase of ALD deposition cycles, the wettability of functionalized CNTs electrodes gradually changed from high hydrophobicity to hydrophilicity. The TiO_2 -deposited CNTs electrodes with 20 ALD cycles display superior electrochemical performance compared with pristine CNTs electrodes. The TCr and Cr(VI) removal efficiencies of the CNT@20TiO_2 membrane electrodes were dramatically improved to 92.1% and 93.3%, respectively. Moreover, the CNT@20TiO_2 membrane electrodes also present excellent recycling and reusability. The strategy of “ALD on CNTs membranes” will have great potential applications in chromium-containing wastewater treatments and adds candidates for advanced CDI electrodes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.05.014>.

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