A novel two-dimensional accordion-like titanium carbide (MXene) for adsorption of Cr(VI) from aqueous solution

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Herein, we report on a novel two-dimensional (2D) material application, which shows that an accordion-like layered Ti_3C_2 nanomaterial (MXene) with an excellent adsorption capacity of Cr(VI) from aqueous solution was prepared by etching Al layer from Ti_3AlC_2 phase in hydrofluoric acid (HF) solution. Ti_3C_2 nanopowders were well characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the physical property of as-obtained samples was studied by UV-Vis diffuse reflectance spectra (DRS). After HF treatment, Ti_3AlC_2 not only has a phase transition from one crystal to another, but surprisingly, its microstructure is also undergoing an obvious change. Ti_3C_2 with product of change possesses an accordion-like multilayer structure, and a relatively higher specific surface area (SSA) than untreated Ti_3AlC_2 . Then, accordion-like Ti_3C_2 with a high SSA provides abundant active sites for pollutant removal and functionalization. Accordion-like Ti_3C_2 nanomaterial exhibits a stable adsorption capacity, and 1 g as-prepared accordion-like Ti_3C_2 powders can remove about 80 mg potassium dichromate. Therefore, the results suggest that 2D MXenes are promising as an effective nano-adsorbent in heavy metal removal from the wastewater.

Keywords: Two-dimensional material; MXene; multilayer structure; adsorption.

1. Introduction

For a long time, the pollution of heavy metal ions becomes a serious environmental problem, and then how these toxic metal ions can be removed has attracted considerable attention. Various technologies such as chemical precipitation,¹ membrane,² electrochemical method,³ and adsorption⁴ have been developed to remove toxic metals from wastewater. Among the available methods, adsorption is one of the most effective choices due to its suitable cost and simplicity of operation.^{4,5} Two-dimensional (2D) materials especially graphene-based materials have emerged as ideal adsorbents by virtue of their large surface areas and abundant active sites. However, the complicated producing process and high cost, especially the large strong acid/oxidant consumption, as well as low production efficiencies have restricted their use in such applications.⁶ Therefore, it is urgent to develop a high-effective, low-cost, and mass-produced adsorbent.

Recently, a novel 2D layered transition metal carbides and nitrides, labelled MXenes, have attracted considerable attentions due to their hydrophilic surfaces, unique layered structures, good chemical stabilities, excellent electrical conductivities, and environmental friendly characteristics.

MXenes with a formula of $M_{n+1}X_nT_z$ are produced by etching A-group from their corresponding $M_{n+1}AX_n$ phase, where "M" is an early transition metal, "A" is III A or IV A group elements, "X" is C or N, and $n = 1, 2, 3$ in hydrofluoric acid (HF) (HCl and LiF) solution at room temperature.^{7,8} It is worth mentioning that T represents surface termination groups ($-\text{O}$, $-\text{OH}$, and $-\text{F}$) left over from the etching process and z is the number of terminating groups. In particular, Ti_3AlC_2 as a promising member of MAX family is most widely studied.

As shown schematically in Fig. 1, Ti_3AlC_2 is a ternary-layered metal carbide. This structure is comprised of Ti_6C octahedra, interleaved with layers of Al atoms. After immersing Ti_3AlC_2 phase in HF solution, results in the Al layers are selectively etched away. The Ti_3C_2 layers are terminated with mostly hydroxy group that is weakly bonded together, making them susceptible to exfoliation. DFT calculations also predict that changing the surface groups would lead to changes in the band gap of accordion-like Ti_3C_2 .⁹ In terms of specific surface areas (SSAs), Ti_3C_2 is comparable to multilayer graphene. The paralleled flake-like Ti_3C_2 layers could be less stable to reduce surface energy and tend to curve and

Fig. 1. Schematic illustration of Ti_3AlC_2 before and after treatment in HF solution, and the layered structure of accordion-like Ti_3C_2 nanosheets removing Cr ions.

become accordion-like structure for the end contraction and the end extension. Such an accordion-like structure should have a number of advantages as a support for removing heavy metal ions. As shown schematically in Fig. 1, by constructing the accordion-like structure with the end contraction of Ti_3C_2 nanolayers and the end extension of that, throughout the view, a large number of all nanolayers pointing toward the handle of the fan shape, a large surface area is available for Cr ions entrapment. The fan-shaped interspaces are wider on the exterior of nanolayers, and the Cr ions are adsorbed by surface functional groups of nanolayers and funneled toward the interior of the fan shape where it can become immobilized on the inner surfaces of the accordion-like structure. Therefore, such a 2D accordion-like multilayer structure should be a promising support for removing heavy metal ions and have potential applications in environmental pollution.

In this paper, accordion-like Ti_3C_2 was successfully prepared by using HF to etch Ti_3AlC_2 particles. The adsorption and Cr ions uptake abilities of accordion-like Ti_3C_2 were studied in detail. Accordion-like Ti_3C_2 with mostly OH surface groups may be considered to be an economical and effective method for removing heavy metal ions, and using nanoadsorbents as extraction agent is well-developed because of their higher surface area and surface reactivity.

2. Experimental Section

2.1. Characterization and chemicals

Scanning electron microscopy (SEM, JSM-6390, JEOL Inc., Japan) and Transmission electron microscopy (TEM, JEM-2010, JEOL Inc., Japan) were employed to observe the morphology and microstructure of the samples. X-ray diffraction (XRD) patterns of samples were tested by Rigaku D/max 2200 pc diffractometer with Cu-K α radiation, and the XRD data were analyzed by using the Jade 6.0 software. Nitrogen sorption isotherms were measured by using an automatic N₂ adsorption/desorption instrument (ASAP 2460, Micromeritics Inc., USA) at 77 K and the samples need were outgassed in vacuum at 200°C for 3 h before test. SSAs of the samples were calculated by Brunauere–Emmette–Teller (BET) method. The UV–Vis absorption spectrum of the products was recorded by PE Lambda-950 photo-spectrometer. Except as otherwise specified, all the chemicals

with analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ultrapure water was used in all experiments.

2.2. Materials preparation

Ti_3AlC_2 was prepared by vacuum atmosphere sintering method through mixing all powders of TiC (2–4 μm particle size, 99% purity, Aladdin), Al (1–3 μm particle size, 99.5% purity, Aladdin), and Ti ($\leq 48 \mu\text{m}$ particle size, 99.99% purity, Aladdin) in a molar ratio of 2:1.2:1. The mixed powders were ball-milled with ethyl alcohol for 4 h at a speed of 350 rpm, and dried in the oven at 40°C for 24 h. Then, the mixture was annealed in an alumina tube in Ar gas at a flow of 40 mL min^{−1}. Sintering process was conducted at 1350°C for 2 h at a heating rate of 8°C min^{−1}. The sintered product was grinded by stainless steel mortar and sieved through a 400 mesh screen, so that the initial particle size was <38 μm .^{10,11} Thus, the Ti_3AlC_2 powders were obtained for further study.

Ti_3C_2 was successfully prepared through selective etching Al layer of Ti_3AlC_2 in HF. Briefly, 3.0 g of the as-prepared Ti_3AlC_2 powders were immersed in 60 mL 40 wt.% HF solution under magnetic stirring (700 rpm) at room temperature for 24 h. Subsequently, the resulting suspension was washed using ultrapure water, centrifugation and decanting until the pH value of the supernatant reached ~6. After that, the resulting sediment was washed three times with absolute ethanol and centrifuged to separate the powders. Finally, the resulting powders were dried in the vacuum oven at 50°C for 24 h.

2.3. Measurements of adsorption ability

100 mg as-obtained Ti_3C_2 nanopowders were added to 100 mL potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution (100 mg/L) under stirring continuously at room temperature. Analytical samples were taken from the suspension after various adsorption times and centrifuged at 4000 rpm for 5 min to remove the particles. The UV–Vis absorption spectra were recorded at different intervals to monitor the process. The adsorption capacity of Chromium onto the adsorbent and the percentage of residual quantity (% residual quantity) was calculated as follows:

$$\% \text{residual quantity} = C_e/C_o \times 100\%, \quad (1)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of Cr(VI) in the solution, respectively.

3. Results and Discussion

Figure 2 shows XRD patterns obtained from the as-prepared Ti_3AlC_2 and Ti_3C_2 powders. It can be observed that Ti_3AlC_2 has excellent crystal structure and little second phase. However, after HF treatment, the (00*i*) peaks, such as the (002), (004), and (0010), broadened, lost intensity, and shifted to lower angles compared to their location before treatment. In addition, the disappearance of the most intense diffraction peak of Ti_3AlC_2 at 39° of 2θ and the good agreement between the simulated XRD spectra for Ti_3C_2 and the

Fig. 2. XRD patterns of Ti_3AlC_2 and Ti_3C_2 samples.

experimental results provides strong evidence of the formation of the latter.

Figure 3(a) shows SEM image of the closely aligned layered structure of as-prepared Ti_3AlC_2 . After HF treatment, there occurred the morphological transition of the exfoliated products, and the Ti_3AlC_2 particle is carved into thin sheets which are clearly separated from each other. In Figs. 3(b)–3(d), SEM images of Ti_3AlC_2 after the HF treatment confirm successful exfoliation of individual particles, which is similar to what was reported for exfoliated graphite or Ti_3AlC_2 , where the layers are clearly separated from each other compared to the unreacted Ti_3AlC_2 powder (Fig. 3(a)). The Ti_3C_2 layers are about parallel to each other, which indicate that the etching direction of Ti_3AlC_2 prefers along a certain orientation. To further observe the morphology of Ti_3C_2 by TEM images, as displayed in Figs. 3(e)–3(f), Ti_3C_2 consists of several separated sheets with a thickness of ~ 20 nm, which is in good agreement with the SEM results.

SSA plays a key role in adsorption performance. Nitrogen adsorption–desorption isotherms of the Ti_3AlC_2 and Ti_3C_2 samples are shown in Fig. 4. The obvious hysteresis loop between adsorption and desorption branches at relative pressure scope of 0.45–1.0 suggests the existence of mesopores. The almost vertical tails at the relative pressure near to 1.0 point to the presence of macropores. Based on this point of view, Ti_3C_2 sample is commonly mesopores and macropores, while Ti_3AlC_2 is mainly macropores. The SSA of the Ti_3AlC_2 and Ti_3C_2 samples obtained by using the BET equation are $1.85 \text{ m}^2 \text{ g}^{-1}$ and $6.24 \text{ m}^2 \text{ g}^{-1}$, respectively. Notably, the Ti_3C_2 has larger SSA than that of Ti_3AlC_2 , indicating that the Ti_3C_2 can provide more surface active sites for attachment of Cr(VI) ions.

Figure 5(a) shows the plot of residual quantity of potassium dichromate in solution on the dependence of time. Clearly, residual quantity of potassium dichromate decreases

Fig. 3. SEM images of (a) Ti_3AlC_2 ; (b)–(d) Ti_3C_2 ; and TEM images of (e), (f) Ti_3C_2 .

Fig. 4. Nitrogen adsorption-desorption isotherms of Ti_3AlC_2 and Ti_3C_2 samples.

from sharply to slowly, then to flatly after 8 h with adsorption time increasing, suggesting that the adsorption equilibrium has achieved. The inset of Fig. 5(a) shows the variation in the UV-Vis absorption spectrum of potassium dichromate at different times when Ti_3C_2 is used to the waste water treatment. It indicates that when the initial concentration of potassium dichromate in the water solution is 100 mg/L, the maximum absorbance of potassium dichromate at 256 nm largely disappears for about 8 h. Figure 5(b) shows the plot of Cr(VI) uptake capacity versus time. The experimental results indicate that 1 g as-prepared Ti_3C_2 can completely remove about 80 mg potassium dichromate without any additives at room temperature. The inset of Fig. 5(b) shows the digital photos before absorption and after absorption of Cr(VI) ions for 14 h. Obviously, The concentration of Cr(VI) ions in solution decreased dramatically. The removal of Cr(VI) ions is attributed to the layered structures of Ti_3C_2 . This unique layered structure is similar to the aggregation of multilayer graphene that determines the practical SSA. And Ti_3C_2 with a

Fig. 5. (a) The adsorption rates of the potassium dichromate on accordion-like Ti_3C_2 . (Inset) Plot of absorption spectra of a solution of potassium dichromate (100 mg/L, 100 mL) in the presence of accordion-like Ti_3C_2 nanopowders (100 mg) at time intervals of 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12 and 14 h, respectively. (b) The Cr(VI) uptake capacity curve of accordion-like Ti_3C_2 nanopowders. (Inset) Digital photos before absorption and after absorption of Cr ions for 14 h.

Fig. 6. SEM images of accordion-like Ti_3C_2 nanosheets after Cr(VI) uptake treatment.

high SSA has abundant active site for pollutant removal and functionalization. Due to the graphene-like structure of accordion-like Ti_3C_2 , modification of the graphene surface with specific functional groups could be used to increase graphene interaction with organic and inorganic pollutants, so they can be removed efficiently from solution through catalytic adsorption or degradation.

Figure 6 shows SEM images of accordion-like Ti_3C_2 nanosheets after Cr(VI) uptake treatment, indicates that a mass of Cr-containing compounds are immobilized on the surface of accordion-like Ti_3C_2 nanosheets without big structural changes. Above all, accordion-like Ti_3C_2 nanomaterial possesses the favorable adsorption ability and it may be a promising candidate of wastewater purification.

4. Conclusion

In conclusion, accordion-like Ti_3C_2 nanosheets were produced by HF treatment from Ti_3AlC_2 powders etching Al layers. 2D Ti_3C_2 shows a larger SSA than that of the pristine Ti_3AlC_2 , due to its accordion-like layered structure, and weaker interlaminar forces. The adsorption measurement shows removal of Cr(VI) gradually with the increase of adsorption time. Accordion-like Ti_3C_2 nanomaterial exhibits a stable adsorption capacity, and 1 g as-prepared accordion-like Ti_3C_2 powders can remove about 80 mg potassium dichromate. The accordion-like Ti_3C_2 nanopowder as a novel nano-adsorbent exhibits a bright future for practical applications in heavy metal removal from the wastewater.

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