Preparation and electrochemical properties of MXene based conductive composites for food contamination detection

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Abstract. MXene has unique intercalation structure, excellent interlayer spacing and excellent biocompatibility. It is considered as an excellent nano material carrier and can be used as a good adsorbent in the detection of food pollutants. In this study, a large number of experimental materials and reagents were selected to prepare Co3O4 / MXene composites by in-situ growth of Co3O4 nanoparticles on MXene support by impregnation pyrolysis. The composite retained the original accordion like intercalation structure. The size and number of Co3O4 particles on the surface of MXene and in the intercalation increased with the increase of loading, showing regular order. The prepared composite has abundant lithium intercalation active sites, fast electron and ion transport channels, good rate performance and energy density at high current density, showing excellent electrochemical performance.

1. Introduction
The discharge of wastewater and sewage is increasing. The daily discharge of industrial wastewater and sewage is about 164 million cubic meters. More than one third of the river sections are seriously polluted, and the proportion of urban water polluted reaches 90%. Every year, there are 1700 accidents caused by water pollution. The increasing water pollution not only aggravates the shortage of water resources on earth, but also seriously affects food safety, endangers human health \[1\]. Therefore, conventional methods can not remove them, resulting in the continuous accumulation of these compounds in the water environment \[2\]. The use of polluted water will pose a major threat to human health, and affect the status and scale of animal and plant populations. Therefore, the elimination of exogenous pollutants is the central task of food contamination detection.

Two dimensional materials such as graphene and its composites, metal organic frameworks (MOFs) and MXene have attracted more and more attention due to their unique physical and chemical properties. So far, titanium carbide (Ti3C2) is the most well-known MXene, which is obtained by etching titanium aluminum carbide (Ti3AlC2) with hydrofluoric acid \[3\]. MXene is considered as an excellent nano material carrier due to its excellent physical and chemical properties (good stability and oxidation resistance, high melting point, good conductivity/thermal conductivity and hydrophilicity)\[4\]. In recent years, more and more researchers have applied it to the detection and treatment of pollutants \[5\]. In fact, MXene unique layered structure can provide a wide space for the immobilization of functional nano materials, thus giving MXene composite the possibility of environmental restoration. At present, MXene composite has been used to prepare new adsorbents and anti pollution films \[6\]. The application of this method in the detection of food contaminants is not mature enough, so it is

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necessary to study the application of MXene composite materials in food safety. Similar to graphene, MXene can be stripped into nanoflakes by improving the intercalation structure of MXene. Some organic compounds (such as methylene blue) and heavy metals (such as Ba, Cr, Cu and U) can be embedded in the layered structure of MXene, which proves that MXene is a potential good adsorbent. Therefore, it is important to understand the interaction between MXene and pollutants. The removal of pollutants by MXene is affected by the properties of pollutants (such as molecular size and shape, hydrophilicity and charge), the properties of adsorbents (such as specific surface area, functional groups, hydrophilicity and charges), and water quality (such as pollutant concentration, pH and temperature). Based on this, MXene based conductive composite with unique intercalation structure is prepared and its electrochemical properties are studied to improve the removal rate of organic pollutants and reduce the metal ion pollution.

2. Preparation of MXene based conductive composites

MXene has attracted much attention due to its unique layered structure and excellent electrical conductivity. A series of univalent and multivalent cations (such as Li⁺, Na⁺, NH₄⁺ and Mg⁺) can be spontaneously embedded into MXene by chemical or electrochemical methods, occupying the active sites on the surface, so as to achieve the purpose of electrochemical energy storage. However, there are abundant OH, O and F groups on the surface of MXene, which lead to hydrogen bonding or van der Waals force between the parallel MXene nanosheets. In this way, it not only increases the difficulty of MXene stripping, but also blocks the interlayer channels, which makes it difficult for electrolyte ions to effectively transport. In addition, the conductivity of MXene in the vertical direction is low, which limits its electrochemical performance to a certain extent. The introduction of redox active polymer between MXene layers can not only effectively expand the interlayer spacing and improve the transport rate of electrolyte ions, but also synergistically participate in the energy storage process, greatly improving the electrochemical performance. In recent years, MXene has been considered as an ideal catalyst carrier because of its many active sites and unique intercalation structure, and MXene has been proved to have broad application prospects in pollutant removal, which provides an opportunity for its application in the field of pollution remediation. The main goal of this paper is to prepare Co₃O₄ / MXene composites by in-situ growth of Co₃O₄ nanoparticles on MXene supports by impregnation pyrolysis.

2.1. Raw materials and reagents

The main chemical reagents are shown in Table 1.

| Name                          | Supplier                                | Name                  | Supplier                      |
|-------------------------------|-----------------------------------------|-----------------------|--------------------------------|
| Titanium aluminum carbide     | Forsman Technology (Beijing) Co., Ltd   | Hydrofluoric acid     | Sinopharm Chemical Reagent Co., Ltd |
| Sodium hydroxide              | Nanjing Chemical Reagent Co., Ltd       | Cobalt nitrate hexahydrate | Aladdin reagent (Shanghai) Co., Ltd |
| Sodium chloride               | Nanjing Chemical Reagent Co., Ltd       | Sodium nitrate        | Nanjing Chemical Reagent Co., Ltd |
| Sodium carbonate              | Nanjing Chemical Reagent Co., Ltd       | Methanol              | Nanjing Chemical Reagent Co., Ltd |
| Anhydrous ethanol             | Nanjing Chemical Reagent Co., Ltd       | Tert butyl alcohol    | Sinopharm Chemical Reagent Co., Ltd |
| Dimethylpyridine nitrogen oxide | Sinopharm Chemical Reagent Co., Ltd        | Nitric acid           | Sinopharm Chemical Reagent Co., Ltd |
| Hydrogen persulfate           | (Shanghai) Trading Co., Ltd             | Sodium citrate        | Nanjing Chemical Reagent Co., Ltd |
The purity of all experimental reagents in Table 1 is analytical purity. The water used in the experiment is ultrapure water, and the resistivity is 18.25 MΩ*cm at 25℃. Based on the above experimental reagents, Co₃O₄ nanoparticles were synthesized and MXene based conductive composites were prepared.

2.2. Preparation of MXene based conductive composites
The synthesis process of pure Co₃O₄ nanoparticles is as follows: (1) weighed 1g cobalt nitrate hexahydrate powder (Co(NO₃)₂·6H₂O), 250mg sodium citrate into 35mL deionized water to obtain solution A. Solution B was obtained by dissolving 2.8g NaOH in 10mL deionized water. Add solution B to solution A step by step with a rubber tipped burette, stir continuously for 1 h at room temperature to obtain Co(OH)₂ colloid, collect it by centrifugation, and dry it at 60±10℃. (2) The dried Co(OH)₂ was put into muffle furnace and kept at 350℃ for 5h at a heating rate of 3℃/min under air condition to obtain the pure Co₃O₄ nanoparticles. Based on the synthesis of pure Co₃O₄ nanoparticles, Co₃O₄ / MXene composites with intercalation structure were prepared. The specific synthesis process is as follows: (1) two dimensional layered carbide MXene was prepared by Naguib method. Weigh 3-5g of titanium aluminum carbide MAX, mix 35-40 mL of hydrofluoric acid (HF) with 40% concentration in a polyethylene beaker at room temperature, and stir for 72 hours. After centrifugation and drying at 60±10℃, layered titanium carbide MXene was obtained. (2) Weigh 1g of MXene and 0-1.05g of Co(NO₃)₂·6H₂O (mass: 0g, 0.35g, 0.7g and 1.05g respectively). Mix and stir in deionized water at 70℃ until evaporated, and then dry it at 60±10℃ to obtain mixed material A. (3) The Co₃O₄ / MXene composite was prepared by placing the material A and holding it at 200℃ for 12 h at a heating rate of 3℃/min in air. According to the different Co₃O₄ loading (the dosage of Co(NO₃)₂·6H₂O), the materials were named CM-X, and X is the percentage of Co₃O₄ in the theoretical mass of MXene. Therefore, the obtained composites are CM-0, CM-10%, CM-20%, CM-30%. Based on this, the MXene based conductive composites for the study of electrochemical properties were obtained.

2.3. Characterization of composites
The surface and cross-section structures of Co₃O₄ / MXene were characterized by XRD (XTD 600, United States), scanning electron microscopy (JEOLJSM-6380LV, Japan, FEI Quanta 250F, United States) and transmission electron microscopy (TECNAIG² 20 LaB6, USA). XPS (PHI Quantera II ESCA, Japan) and TEM-EDS were used for surface element analysis. The actual loading of Co₃O₄ was analyzed by ICP-AES (pinaacle900, United States). The specific surface area of Co₃O₄ / MXene composite was evaluated by ASAP-2020 (United States), the degassing temperature was 100℃, and the surface charge activity was analyzed by Zeta pals (United States).

2.4. Structural characteristics of composite materials
In order to directly reflect the properties of MXene based conductive composites, pure Co₃O₄, precursor max, carrier MXene and synthesized Co₃O₄ / MXene were characterized by XRD. The shift of Max peak indicates the expansion of intercalation spacing, and the disappearance of the peak indicates the effective removal of A phase (Al), which proves that Max is successfully transformed into MXene through 40% HF etching. With the increase of Co₃O₄ loading, the intensity of its characteristic peak is also increasing. And the number of surface active sites and the dispersion of particles is increasing. There is a weak characteristic peak of anatase titanium dioxide near MXene. This is due to the fact that when MXene is heated in the air atmosphere above 200℃, a small part of the edge of the titanium layer will be transformed into titanium dioxide nanoparticles. The structural characteristics of MXene based conductive composites were further analyzed, and the specific surface area of the composites was analyzed by N2 adsorption desorption instrument. The specific surface areas of CM-0, CM-10%, CM-20% and CM-30% are 19.3, 34.5, 48.2 and 29.4 m²/g, respectively. The adsorption isotherms of the materials are consistent with the type IV curves, and there are a lot of mesoporous structures. The results show that the specific surface area of the composite can be
increased by the supported Co$_3$O$_4$ nanoparticles, but the excess load will lead to the reduction of the specific surface area of the composite.

3. Electrochemical properties of MXene based conductive composites

3.1. Electrochemical test

Next, the electrochemical test of MXene based conductive composites is carried out. Weigh the active material in the ratio of 7:2:1, mix acetylene black and CMC, add distilled water and stir to form slurry. After vacuum drying (60°C, 12h), the electrodes were pressed and cut into discs. The loading amount of active substance is about 1 mg/cm$^2$. The counter electrode was lithium metal, electrolyte solute was 1M LiPF$_6$, solvent was ethylene carbonate EC and dimethyl carbonate DMC (volume ratio was 1:1). The constant current charge / discharge test and constant current intermittent titration test (GITT) were carried out by the blue electric LAND CT2001A test system. It is calculated as follows:

$$\lambda = \frac{4}{\pi t} \left( \frac{av}{bs} \right)^2 \left( \frac{w}{u} \right)^2$$

In formula (1), $\lambda$ is the diffusion coefficient of lithium ion; $t$ is discharge time; $a$ represents the mass of the active substance; $v$ is the molar volume; $b$ is the molar mass; $s$ is the contact area between electrode and electrolyte; $w$ is the change of steady-state potential before and after constant current discharge; $u$ represents the change of voltage during discharge time. The calculation formula of energy density of hybrid ion capacitor is as follows:

$$p = \frac{1}{2} \varphi (v_{\text{max}} + v_{\text{min}}) (v_{\text{max}} - v_{\text{min}})$$

In formula (2), $p$ is the energy density; $\varphi$ is the specific capacitance calculated based on the total mass of positive and negative electrodes; $v_{\text{max}}$ and $v_{\text{min}}$ represent the cut-off potential and the starting potential of the constant current discharge curve respectively. The specific capacitance of the device can be calculated by the charge discharge curve. The calculation formula is as follows:

$$c = \frac{A t}{B V_0}$$

In formula (3), $A$ represents the discharge current; $B$ is the opposite area of the electrode; $V_0$ represents the voltage window. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the electrodes were tested on CHI 760e workstation. The potential window of CV test is -0.6-0.3v. EIS test is carried out under open circuit voltage, and the frequency range is 100 KHz-10 MHz.

3.2. Characterization of physical properties of composites

Firstly, the accordion like MXene was peeled and layered into single or few layers, and then Co$_3$O$_4$ was evenly dispersed in it. Due to the abundance of O, OH and F functional groups on the surface of toluene nanoparticles, the dissolved Co$_3$O$_4$ molecule is easily adsorbed on the surface of toluene nanoparticles. Then, the pH of the mixed solution was controlled by Tris buffer to make the polymerization reaction take place, and the MXene composite with Co$_3$O$_4$ uniformly coated on the surface of the nanosheets was obtained. Co$_3$O$_4$ / MXene was simply heat-treated. In addition, MXene was separately heat-treated at 300°C through the same process, and the treated samples were recorded as MXene300. For example, the XRD of MXene300 has no obvious change compared with that of MXene, which indicates that heat treatment at 300°C in N$_2$ atmosphere has no effect on MXene.

3.3. Electrochemical performance analysis

The capacity of MXene is about 100-150 mAh/g, which is far from its theoretical capacity due to the
existence of a lot groups, the limited layer spacing hindering ion transport and the low electronic conductivity perpendicular. Because the surface is rich in O, OH and F functional groups, which shows electron negativity, many electrochemically active organic molecules can be adsorbed on the surface, and then stable polymers can be formed by in-situ polymerization. The intercalation of electrochemically active polymers in MXene can not only effectively expand the interlayer spacing and accelerate the ion transport rate, but also participate in the redox reaction and improve the electrochemical performance. Based on this, Co₃O₄ / MXene composites were prepared and their electrochemical properties were analyzed. The CV Curve of the composite at 0.1 mV/s is shown in Figure 1.

From the CV Curve in Figure 1, it can be seen that the integral area is larger than MXene, which means that the specific capacity increases. Co₃O₄ / MXene composites were tested by constant current charge discharge test at 100 mA/g current density. The first cycle discharge capacity of Co₃O₄ / MXene composite electrode is 1524 MA/g, the charge capacity is 985 mAh/g, and the coulomb efficiency is 64.2%. The charge discharge curves of the second and fifth cycles showed high redox reversibility. Compared with single MXene material, Co₃O₄ / MXene composite has higher specific capacity, up to 12200 mAh/g at 50 mA/g current density. At the same time, Co₃O₄ / MXene composite also has good rate performance, and it still has a specific capacity of 564 mAh/g at 5 A/g. The effect of composite structure on the diffusion coefficient of Li⁺ was analyzed by galvanostatic batch titration (GITT). According to formula (1), the Li⁺ diffusion coefficients of Co₃O₄ / MXene and MXene were calculated respectively. With the decrease of potential, the Li⁺ diffusion coefficients of both materials decrease, but the Li⁺ diffusion coefficients of Co₃O₄ / MXene materials are always higher than those of MXene, which indicates that the composite structure has faster Li⁺ diffusion kinetics.

In order to further evaluate the performance of Co₃O₄ / MXene composite, a lithium-ion capacitor (LIC) with Co₃O₄ / MXene as negative electrode and AGN as positive electrode was assembled. The working voltage is 2.0-4.5V and the specific capacity is 65 mAh/g. The charge discharge curve of lithium ion capacitor is shown in Figure 2.

According to the test results in Figure 2, the charge discharge curve of Co₃O₄ / MXene composite presents an inclined shape in the voltage range of 2.0-4.5V. Under the current density of 3A/g, the discharge process can be completed in 36s, which has excellent rate performance. The energy densities composites at current densities of 3, 1.5, 0.5 and 0.15 A/g were calculated according to formula (2). The energy density is up to 85.6 Wh/kg at 400 W/kg power density; under the high power density of 7500 W/kg, it can still be maintained at 49.2 Wh/kg.
In this study, the rich surface groups of MXene nanoplates were used to immobilize Co$_3$O$_4$ molecules, and a uniform coating layer was obtained by in-situ polymerization to obtain Co$_3$O$_4$ / MXene composites. The Co$_3$O$_4$ / MXene composites were simply heat treated at 300°C in an inert atmosphere according to the heat treatment method of electrochemically active derivatives. The prepared composite electrode materials have abundant lithium intercalation active sites, fast electron and ion transport channels, and show excellent electrochemical performance. The results show that the composite still has good rate performance and energy density at high current density, indicating that the composite of MXene and redox active polymer is an efficient means to improve its electrochemical performance.

4. Conclusion
MXene with different transition metal compositions have different electronic properties, but many predicted MXene have not been successfully prepared. We can optimize the preparation methods, explore new MXene materials, and systematically summarize the application prospects of MXene series materials in the field of electrochemistry. Due to the different energy storage mechanisms, there are different electrochemical reaction kinetics between the positive and negative electrodes of hybrid capacitor. The design of electrode structure, the optimization of electrode capacity, and the selection of electrolyte should be considered comprehensively to match the better performance of the device. In the future research, MXene can be used as a matrix to compound with other kinds of metals and their compounds to expand its application prospects in the field of environmental catalysis and adsorption. At the same time, composite metals and their oxides can be loaded to prevent the loss of active species and avoid the secondary pollution of heavy metals.

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