Facile preparation of Ti$_3$C$_2$T$_x$ sheets by selectively etching in a H$_2$SO$_4$/H$_2$O$_2$ mixture

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MXenes and MXene-based composite materials have potential applications in a wide range of areas due to their unique physical and chemical characteristics. At present, it is still a major challenge to develop a simple, safe, and efficient route to prepare MXenes without using fluorinated etchants. Herein, we design a facile method to prepare Ti$_3$C$_2$T$_x$ MXene sheets by selectively etching Ti$_3$AlC$_2$ powders in an aqueous diluted H$_2$SO$_4$ solution with H$_2$O$_2$ as an oxidant. In a system of H$_2$SO$_4$ and H$_2$O$_2$, an aqueous H$_2$SO$_4$ solution with a concentration of 6 mol/L is a strongly acidic medium with no volatility, and 30% H$_2$O$_2$ acts as a strong green oxidizer without harmful by-products. The experimental process is safe and convenient to conduct in a beaker under a water bath of 40°C. The etching process can be completed in 1 h under the air atmosphere conditions. The experimental results confirmed that the etched Ti$_3$AlC$_2$ powders can be successfully separated into Ti$_3$C$_2$T$_x$ nanosheets without using any intercalation agent. The relevant etching mechanism may be attributed to the synergy effect of H$_2$SO$_4$ and H$_2$O$_2$, which triggers sequential selective etching of Al layers from the Ti$_3$AlC$_2$ phase. It may provide a new green way to prepare MXene-based materials without using toxic HF or HF-containing etchants.

KEYWORDS: Ti$_3$AlC$_2$ powders, Ti$_3$C$_2$T$_x$ sheets, H$_2$SO$_4$/H$_2$O$_2$ mixture, selective etching, HF-containing etchants

Introduction

Since a new family of two-dimensional (2D) materials was first discovered in 2011 (Naguib et al., 2011), increasing attention has been paid to these novel 2D transition metal carbides, carbonitrides, and nitrides (named MXenes), and currently, more than 40 MXene compositions (Naguib et al., 2021) have been synthesized by different efficient routes (Naguib and Gogotsi, 2015; Alhabeb et al., 2017; Anasori et al., 2017; Tao et al., 2017; Zhou et al., 2017; Gogotsi and Anasori, 2019; Fan et al., 2022). The MAX phases are layered ternary carbides and nitrides with a general formula M$_{n+1}$AX$_n$, where M represents transition metals (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, etc.), A
represents elements from the group 13 and 14 of the periodic table, and X is carbon and/or nitrogen (Naguib and Gogotsi, 2015). After the discovery of Ti3C2Tx MXene in 2011 (Naguib et al., 2011), many MXenes were synthesized by selectively etching different precursors in liquid mediums such as HF, HF-containing, or HF-forming etchants; thus, these etching processes unavoidably caused some surface functional groups such as –O, –F, or –OH, marked as Tx in a general formula Mn+1XnTx for MXenes (Naguib and Gogotsi, 2015; Anasori et al., 2017; Tao et al., 2017; Zhou et al., 2017).

More importantly, MXenes and MXene-based composite materials have potential applications in various fields such as energy storage (Lakatskaya et al., 2013; Ghidiu et al., 2014; Li et al., 2015; Wang et al., 2015; Luo et al., 2020; VahidMohammadi et al., 2021), flexible electronics (Xu et al., 2021a; Xu et al., 2021b; Shi et al., 2022a; Xu et al., 2022), electromagnetic shielding (Shahzad et al., 2016; Iqbal et al., 2020), catalysis (Seh et al., 2016; Liu et al., 2020), and water treatment (Ren et al., 2015) due to their unique physical and chemical properties (Halim et al., 2014; Dillon et al., 2016; Hantanasirisakul et al., 2016). In order to promote their potential applications, numerous research efforts have been carried out to explore the emerging etching methods and the stable storage of MXene, especially the large-scale preparing methods (Naguib and Gogotsi, 2015; Alhabeb et al., 2017; Gogotsi and Anasori, 2019; Fan et al., 2022).

In general, MXene nanosheets were synthesized by selectively etching MAX phases, as well as subsequent intercalation and delamination. In the early stage, the typical etching methods were dominated by HF etching methods (Naguib et al., 2011) and in situ HF-forming etching methods (Ghidiu et al., 2014; Halim et al., 2014). For example, Gogotsi et al. designed that the synthesis of MXene can be scaled up in a small-batch wet chemical etching process, and 1.0 g of the Ti3AlC2 powders was slowly peeled off in a system of HF and HCl for 24 h at 35°C (Shuck et al., 2020). Since 2017, fluorine-free etching methods such as electrochemical etching methods (Pang et al., 2019), alkali etching methods (Li et al., 2017; Li et al., 2018), molten salt etching methods (Li et al., 2019), halogen etching methods (Jawaid et al., 2021; Shi et al., 2021), and other methods (Ghazaly et al., 2021) were developed to prepare fluorine-free MXenes with different characteristics. For example, the electrochemical etching method (Pang et al., 2019) and alkali etching method (Li et al., 2018) can avoid the use of fluorinated etchants, and at the same time, the HF toxicity to the human body, corrosiveness, and harm to the environment can be effectively avoided. In 2019, a new method for MAX phase etching at a high temperature of 550°C was developed by using Lewis acid molten salt as an etching agent (Li et al., 2019). This method avoids the use of HF, HF-containing, or HF-forming etchants, but the high temperature is a necessary condition. In 2021, Song et al. developed a controllable HCl-hydrothermal etching strategy for Mo2CTx MXenes based on DFT calculation (Wang et al., 2021). In this process, Mo2CTx MXenes were prepared through a hydrothermal etching process with concentrated HCl in an autoclave at 120 or 140°C for 5 days. However, the high concentration, high temperature, and long etching time also impede its widespread use. More recently, Xiao et al. delicately exploited a low-temperature photo-Fenton strategy to fabricate F-free Ti3C2 with 95% high purity, and this work would play an important role in the F-free fabrication of MXene and synthesis of cathodes with excellent performance for flexible lithium-sulfur batteries (Liang et al., 2022).

In addition, the intercalation and delamination strategies of MXenes are mainly divided into organic intercalator delamination, inorganic intercalator delamination, and mechanical delamination (Mashṭalir et al., 2013; Sang et al., 2016). The principle of intercalation and delamination is based on weakening the interlayer force (such as hydrogen bonding and van der Waals forces) among MXene nanosheets (Naguib et al., 2011; Alhabeb et al., 2017).

Although many successful synthetic routes and delamination routes of MXenes have been reported in the literature (Naguib et al., 2011; Alhabeb et al., 2017; Gogotsi and Anasori, 2019; Naguib et al., 2021; Fan et al., 2022), there are still a number of disadvantages such as the corrosion of etching agent to experimental equipment, harmful impact of reagents on the environment, and severe operating conditions. Therefore, it is highly desirable to develop a simple, safe, and efficient protocol for the synthesis of MXenes, and it is still a major challenge.

Inspired by the synthesis of MXenes through a controllable HCl-hydrothermal etching (Wang et al., 2021), a selective etching of MAX phase (Ti3SiC2) by using a solution of HF with oxidant (such as H2O2) (Alhabeb et al., 2018) and highly reactive radicals (HO• and O2•−) weakening the Ti-Al bonds in the MAX phase (Liang et al., 2022), we design a facile method to produce Ti3C2Tx MXenes by etching Ti3AlC2 powders in a system of H2SO4 and H2O2. In this system, an aqueous dilute H2SO4 solution is not volatile nor toxic, and H2O2 is a green oxidant; thus, this experimental process is safe and convenient to conduct in a beaker. The experimental results confirmed that Ti3C2Tx nanosheets can be successfully obtained, and this method is safe, rapid, and efficient.

**Experimental section**

**Materials**

Ti3AlC2 powders (98 wt% purity, 200 mesh) were purchased from Shanghai Rohn Reagent Co., Ltd. Sulfuric acid (H2SO4, 18 mol/L), hydrogen peroxide (H2O2, 30%), and sodium hydroxide (NaOH, analytical grade) were purchased from the National Pharmaceutical Reagent Company. All chemicals were used without further purification. Deionized water (a resistance
of Ti₃AlC₂ powders. It is reasoned that when Al layers are etched away, a small amount of Ti layers is also etched out to leave holes on the surfaces due to the Ti vacancies triggered the oxidation process from Ti to TiO₂, consistent with the results previous literature reported (Shi et al., 2022b; Huang et al., 2022; Jiang et al., 2022; Ma et al., 2022; Zhang et al., 2022).

Preparation of Ti₃C₂Tx Sheets

As a typical MAX phase, Ti₃AlC₂ powders were selected to be etched in a mixture of H₂SO₄ and H₂O₂ in our experiment.

1) Al layer etching. Typically, 2.0 g of Ti₃AlC₂ powders and 50 ml of H₂SO₄ solution (6 mol/L) were added into a beaker (200 ml) under electromagnetic stirring conditions. Then, 20 ml of H₂O₂ (30%) was slowly dropped into the abovementioned dispersion within 30 min under electromagnetic-stirring conditions. A temperature-controlled water pot was used to control the temperature of 40 °C for this etching. Next, the obtained dispersion was still stirred at 40 °C for 30 min to further etch the Al layers from the Ti₃AlC₂ phase.

2) Sediment cleaning. After etching Al layers, the obtained dispersion was centrifuged at 3,000 rpm for 10 min with a high-speed centrifuge (Neofuge1600R) to obtain the sediment and recycle supernatant (including the etched Al layers and H₂SO₄ solution), respectively. The obtained sediment was cleaned with deionized water several times until the pH of the dispersion was close to 7. In addition, a nanocomposite of Al₂O₃ and TiO₂ can be obtained from the supernatant by adding an appropriate amount of NaOH solution.

3) Ultrasonic stripping. A small amount of the obtained sediment was taken out and placed in a beaker with deionized water. No intercalation agent was required in this process. An ultrasonic cleaner was used to separate the obtained sediment in the beaker for 20 min to prepare Ti₃C₂Tx sheets with appropriate ultrasonic power (KQ-300GDV, frequency 40 kHz, output power 300 W, 50% amplitude). After ultrasonic treatment, the obtained aqueous solution of MXenes was filtered through a mixed cellulose ester microporous membrane using a water-circulating multi-purpose vacuum pump (SHB-III). Finally, the obtained sample was dried in a vacuum at 60°C for 24 h for characterizations.

Characterizations

The microstructure of Ti₃AlC₂ powders and Ti₃C₂Tx sheets were detected by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100). The X-ray diffractometer (XRD, Bruker D8 diffractometer), Fourier transform infrared spectroscopy (FTIR, Nicolet5700), and X-ray photoelectron spectroscopy (XPS, K-alpha1063) were used to analyze the etching process and the relevant etching mechanism of Ti₃AlC₂ powders.

Results and discussion

Structure analysis

Based on the synthetic strategies of HCl-hydrothermal etching (Wang et al., 2021), HF/H₂O₂ oxidant-assisted etching (Alhabeb et al., 2018), and photo-Fenton radicals weakening, (Liang et al., 2022) a facile, safe, and rapid strategy was designed to prepare Ti₃C₂Tx MXenes by selectively etching Ti₃AlC₂ powders in an aqueous H₂SO₄ solution with H₂O₂ as oxidant. The detailed preparation process (including etching, cleaning, and stripping) was introduced in the experimental section, and the schematic procedure is shown in Figure 1A. The mixture of Ti₃AlC₂ powders and aqueous H₂SO₄ solution is black (Figure 1B), while an aqueous solution of Ti₃C₂Tx sheets without cleaning and stripping has a purple/magenta color (Naguib et al., 2011), as shown in Figure 1C. After cleaning and stripping, the resulting aqueous solution of Ti₃C₂Tx nanosheets presents a shallow green color (Figure 1D). Both the aqueous solutions have clear Tyndall effects under natural light (Li et al., 2017), indicating the presence of Ti₃C₂Tx nanosheets in two aqueous solutions, as shown in Figures 1C,D. Moreover, the resulting aqueous solution of Ti₃C₂Tx nanosheets can be kept for 90 days under the low temperature of 1–4°C without any color change.

In order to explore the etching effect, SEM images of the Ti₃AlC₂ powders and the obtained Ti₃C₂Tx sheets are carried out as contrast experiments. Figure 2 shows the microstructure of the Ti₃AlC₂ powders with different magnifications. It can be seen that the morphology and size of the Ti₃AlC₂ powders are very irregular (Figure 2B), and the individual particle has a compact layered structure, as shown in Figures 2C,D.

In contrast, SEM images in Figure 3 show the structural morphology of the obtained Ti₃C₂Tx sheets. The color of the obtained Ti₃C₂Tx MXene sheets is different from that of the Ti₃AlC₂ powders, namely, the colors change from black (Figure 2A) of the Ti₃AlC₂ powders to dark gray of the MXene sheets (Figure 3A). More importantly, the layered structure of the obtained Ti₃C₂Tx sheets is notably different from that of the Ti₃AlC₂ powders (Figures 2B–D), as clearly demonstrated in Figures 3B–D. Particularly, the structure of the obtained Ti₃C₂Tx sheets has some layered changes, and the lamellae have many hole defects, compared with that of the Ti₃AlC₂ powders; it is reasoned that when Al layers are etched away, a small amount of Ti layers is also etched out to leave holes and TiO₂ nanoparticles on the surfaces due to the Ti vacancies triggering the oxidation process from Ti to TiO₂, consistent with the results previous literature reported (Shi et al., 2022b; Huang et al., 2022; Jiang et al., 2022; Ma et al., 2022; Zhang et al., 2022).

To further demonstrate the morphology of Ti₃C₂Tx sheets, TEM imaging was performed after the obtained Ti₃C₂Tx sheets were treated by ultrasonic stripping in deionized water for 20 min. As shown in Figure 4, the obtained Ti₃C₂Tx
Nanosheets are single-layer or multilayer sheets with folded structures, consistent with the reported literature (Huang et al., 2022; Ma et al., 2022). A slight amount of TiO$_2$ nanoparticles on the MXene surface can be ascribed to the Ti vacancies triggering the oxidation process from Ti to TiO$_2$, consistent with SEM images in Figures 3B–D. Thus, the Ti$_3$AlC$_2$ powders can be easily stripped into Ti$_3$C$_2$Tx nanosheets by a simple oxidative etching and subsequent ultrasonic exfoliation in our experiments.

In order to analyze the etching process, the XRD patterns and FTIR spectra of the Ti$_3$AlC$_2$ powders and the Ti$_3$C$_2$Tx sheets were used to monitor their structural changes. From the distribution of the XRD peaks in Figure 5A, the Ti$_3$AlC$_2$ powders and Ti$_3$C$_2$Tx sheets have characteristic peaks at different positions, such as (002), (004), (101), (104), (105), and so on (Naguib et al., 2011; Alhabeb et al., 2017; Li et al., 2017; Li et al., 2018; Li et al., 2019). In particular, the XRD (002) peak of the Ti$_3$C$_2$Tx sheets is shifted toward a lower angle, namely, the peaks change from 9.75° of...
Ti$_3$AlC$_2$ powders to 9.30° of Ti$_3$C$_2$Tx sheets, indicating a larger spacing caused by etching Al atoms. Moreover, a certain amount of Ti$_3$AlC$_2$ is probably still present in Ti$_3$C$_2$Tx. From the FTIR spectra in Figure 5B, some new peaks appear, and they are very different from that of the pristine Ti$_3$AlC$_2$ powders. It can be found that there are lots of surface functional groups (Gao et al., 2021) such as 3,430 cm$^{-1}$ of -OH, 1,620 cm$^{-1}$ assigned to C=O, 1,400 cm$^{-1}$ to the hydrogen bond of O-H, 1,090 cm$^{-1}$ of C-O-C vibration, 790 cm$^{-1}$ of the Ti-O bond (Wang et al., 2017), 610 cm$^{-1}$ of SO$_4^{2-}$ vibration (Lin, 2015), and 460 cm$^{-1}$ of Ti-C vibration (Wang et al., 2017). Thus, these new peaks of the FTIR spectrum may be attributed to the oxidation of H$_2$O$_2$ and the intercalation of SO$_4^{2-}$ (Lin, 2015; Wang et al., 2017; Gao et al., 2021).

In order to further explore the oxidation etching process, the XPS analysis of Ti$_3$AlC$_2$ powders and Ti$_3$C$_2$Tx sheets were performed to reveal their changes in chemical compositions. It can be found that the XPS survey spectra of Ti$_3$C$_2$Tx sheets present some new changes, such as a new peak of S 2p and a relatively elevated ratio of O 1s peak to C 1s peak (Figure 6A), compared with that of Ti$_3$AlC$_2$ powders.

Moreover, the high-resolution S 2p XPS analysis (Figure 6B) confirms that the new peak (Park and Leitao, 2021) of S 2p is attributed to SO$_4^{2-}$, consistent with the abovementioned FTIR.
analysis (Figure 5B). As shown in Figures 6C,D, the characteristic C 1s peaks of the Ti3AlC2 powders and Ti3C2Tx sheets also match those of previous work (Chen et al., 2020; Mathis et al., 2021), and the content ratio of C–Ti in the Ti3C2Tx sheets is higher than that of Ti3AlC2 powders, suggesting that most of Al atomic layers in Ti3C2Tx sheets have been selectively stripped.

The high-resolution Ti 2p XPS spectra of Ti3AlC2 powders and Ti3C2Tx sheets show three characteristic peaks, corresponding to the Ti–C 2p3/2, Ti–C 2p1/2, and Ti–O orbitals, respectively (Figures 7A,B), consistent with the current literature reports (Li et al., 2019; Chen et al., 2020; Mathis et al., 2021). Moreover, based on the analysis of XPS data, the content of Ti increases from 5.50 At% of Ti3AlC2 powders to 10.50 At% of Ti3C2Tx sheets.

On the other hand, the high-resolution Al 2p XPS spectra of Ti3AlC2 powders and Ti3C2Tx sheets show three characteristic
peaks (Chen et al., 2020; Mathis et al., 2021) corresponding to the Al-Ti 2p₃/₂, Al-Ti 2p₁/₂, and Al-O orbitals, respectively (Figures 7C,D). In particular, the content ratio of Al-Ti 2p₃/₂ and Al-Ti 2p₁/₂ in the Ti₃C₂Tx sheets is significantly lower than that of Ti₃AlC₂ powders; in contrast, the content ratio of Al-O is higher. Based on the XPS analysis, the content of Al decreases from 6.50 At% of Ti₃AlC₂ powders to 1.50 At% of Ti₃C₂Tx sheets. Thus, from the abovementioned content changes of Ti and Al on the XPS analysis before and after corrosion, it can be reasoned that most of the Al layers can be etched out; as a result, the atomic percentage of Al decreases, and the atomic percentage of Ti increases in the Ti₃C₂Tx sheets.

Mechanism analysis

To analyze the selective etching process, some important factors should be considered as follows:

1) In the system of H₂SO₄ and H₂O₂, the aqueous solution H₂SO₄ of 6 mol/L is a strongly acidic medium with no volatility and 30% H₂O₂ acts as a strong green oxidizer without harmful by-products.

2) As the temperature is an important factor for the chemical reaction, to speed up the etching process, the temperature of the obtained mixture is heated by a temperature-controlled
In our experiment, if the temperature is too high, it will accelerate the decomposition of H$_2$O$_2$, and 40°C is chosen as the appropriate temperature. Moreover, no notable reaction occurs when the Ti$_3$AlC$_2$ powders are only mixed with an H$_2$SO$_4$ solution of 6 mol/L, and it is reasoned that the oxidant of H$_2$O$_2$ plays a major role in the etching process. Particularly, the content of H$_2$O$_2$ is very crucial for the etching process; if the oxidant of H$_2$O$_2$ is excessive, there will be some TiO$_2$ nanoparticles on the surface and interspace of MXene sheets because Ti can be oxidized to TiO$_2$ by excessive H$_2$O$_2$ (Huang et al., 2022; Ma et al., 2022). Otherwise, a certain amount of Ti$_3$AlC$_2$ is still present in Ti$_3$C$_2$Tx without corrosion.

3) In the etching process, the microstructure change of intermediate sheets should be analyzed in detail. Seen from SEM images in Figures 8A,B, the obtained intermediate sheets show a loose, layered, and porous structure compared with Ti$_3$AlC$_2$ powders. This structure can be clearly demonstrated by the magnified parts of the selected area of the intermediate sheets (Figure 8B). Moreover, Figures 8C,D further reveal that the intermediate sheets are exfoliated along different directions, and lots of traces after stripping are left on the surface such as crack structures along longitudinal/transverse direction and TiO$_2$ nanoparticles on the surface (marked in the red circle of Figure 8D). Thus, the obtained Ti$_3$C$_2$Tx nanosheets with clear layered and folded structures can be easily prepared after the intermediate sheets are stripped apart under ultrasonic treatment in deionized water (Figures 8E,F).

Moreover, the Al$_2$O$_3$ and TiO$_2$ nanocomposite (Figure 9A) can be obtained from the supernatant by adding a certain amount of NaOH solution, vacuum filtration, and drying. The precipitate of Al$_2$O$_3$ and TiO$_2$ can be precipitated by only adding an alkaline solution, which suggests that Al$_3^+$ ions accompanied by a small amount of TiO$_2$ are in the supernatant. As shown in Figure 9B, the XRD patterns of this nanocomposite are analyzed to prove the existence of Al$_2$O$_3$ and TiO$_2$ nanoparticles, consistent with those reported in the literature (Han et al., 2012; Abazari et al., 2014; Ali et al., 2018).

In summary, the relevant etching mechanism is may be attributed to the synergy effect of H$_2$SO$_4$ and H$_2$O$_2$, which triggers Al layers to be etched sequentially from the MAX phase. It is speculated that the reactive oxygen species (such as HO$^*$ and O$_2^*$) radicals can be produced because H$_2$O$_2$ is heated in the course of our experiment, very similar to the advanced oxidation process of the photo-Fenton reaction (Liang et al., 2022). Thus, the radicals can weaken the Ti–Al bonds and attack the defect sites of the external surfaces of MAX phases (Liu et al., 2020; Wei et al., 2021), and synchronously, Al layers are etched into Al$^{3+}$ ions in the aqueous H$_2$SO$_4$ solution of 6 mol/L, and there is no accumulation of Al(OH)$_3$ in this strongly acidic solution to retard this etching process. In addition, a lot of bubbles (such as O$_2$ and H$_2$) are produced to promote this etching process. Therefore, the synergy effect of H$_2$SO$_4$ and H$_2$O$_2$ triggers sequential selective etching of Al layers from the Ti$_3$AlC$_2$ phase.

On the other hand, abundant oxygen-containing functional groups are attached to the intermediate sheets, and Ti can be oxidized to TiO$_2$ by excessive H$_2$O$_2$. Interestingly, the SO$_4^{2-}$ ions can be also inserted into the obtained Ti$_3$C$_2$T$_x$ nanosheets and TiO$_2$ nanoparticles can be in situ loaded on the surface of the obtained MXene nanosheets. The structure and morphology of the obtained MXene nanosheets can be further optimized by selecting the appropriate process such as the reaction rate and content of H$_2$O$_2$.

**Conclusion**

In conclusion, we develop a simple, safe, and efficient method to prepare MXene (Ti$_3$C$_2$T$_x$) nanosheets by selective etching Ti$_3$AlC$_2$ powders in a system of H$_2$SO$_4$/H$_2$O$_2$ and subsequent ultrasonic stripping. The obtained Ti$_3$C$_2$T$_x$ nanosheets can be confirmed from the characterization analyses of SEM, TEM, XRD, FTIR, and XPS. Lots of oxygen-containing functional groups (–O, –OH) are supported on the MXene surface, the SO$_4^{2-}$ ions are inserted into the layers of the MXene sheets, and even TiO$_2$ nanoparticles can be in situ loaded due to the
oxidation of excessive H₂O₂. In the system of H₂SO₄/H₂O₂, the aqueous H₂SO₄ solution of 6 mol/L is a strongly acidic medium, and 30% H₂O₂ acts as a strong green oxidizer. The relevant etching mechanism may be attributed to the synergy effect of H₂SO₄ and H₂O₂, which triggers Al layers to be etched sequentially from the MAX phase. Our group is further exploring the etching mechanism. This work can provide a new way to develop HF-free and large-scale synthesis of 2D layered MXenes for many practical applications.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

Author contributions

ZT and SB are responsible for designing and completing experiments. HT and KC are responsible for the preparation and characterization of materials. QP and YW are responsible for the literature search and review. QZ put forward constructive suggestions on the revision of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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