



Application and mechanism study of TiO₂/MXene nanocomposites in photocatalytic degradation of methyl orange

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ABSTRACT

In this work, TiO₂/MXene nanocomposites have been explored with hydrothermal synthesis during the dye photocatalytic degradation process. They worked as photocatalyst with high efficiency. The degradation of organic dye methyl orange with MXene under ultraviolet (UV) light and visible light was studied in detail. The methyl orange can be degraded efficiently especially at acid condition. When the nanocomposites/dye ratio was fixed at 5, most of the dye (close to 99.9%) was degraded under UV and visible light irradiation in 3 h. When MXene was recycled to treat methyl orange, the degradation rate was kept at 96% after 2 cycles under UV light. It was found that the composite material showed improved photocatalytic performance under long time ultraviolet treatment. Scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy characterizations of Ti₃AlC₂ and MXene were carried to investigate the possible reasons for high degradation efficiency. MXene worked as a cocatalyst which enhanced the separation of electron hole pairs and catalytic performance.

Keywords: MXene; Dye degradation; Photocatalytic activity; 2D materials; Ultraviolet irradiation

1. Introduction

With the rapid development of industrialization, more and more pollutants are produced in the world. Clean water production and waste water treatment with low energy consumption are urgently needed. There are numerous new developed methods to deal with the organic waste water including adsorption and oxidation [1,2], membrane separation [3], catalytic wet air oxidation (CWAO) [4] and so on. However, recovery of adsorption materials and membrane fouling often induce high operation cost [5,6]. Also, the concentrated pollutants often caused secondary pollution which limited their utilization. Metal-organic frameworks (MOFs) with high surface area, controllable porosity endow the composite membrane exciting selectivity. MOF

containing membranes formed by continuous growth of specific polycrystalline MOF layers on polymer substrates demonstrated excellent performance in water treatment [7,8]. However, the defect-free membranes need fine control which limited the industrialization. For CWAO technique, it is necessary to develop catalysts with high activity at low temperature and excellent recycle capability to decrease the treatment cost [9].

Photocatalytic degradation with high performance catalyst showed obvious advantages such as low cost, environmental friendliness, good recycle capability and high degradation rate without secondary pollution [10]. TiO₂ is one of the mostly studied photocatalysts owing to its low cost and high photoactivity. However, it absorbs very little sunlight in the UV region owing to its large band gap

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energy. There are a lot of research focused on the development of TiO₂ composite materials to improve its photocatalytic performance. When TiO₂ was located on CNT stems to form composite material, the photocatalytic activity was obviously improved owing to enhanced light trapping and scattering ability, which is benefited from the large specific area and the direct electrons transport pathway of CNT [11].

MXenes, including Ti₃C₂, Ti₂C, Nb₄C₃, are 2D transition metal carbides and carbonitrides, which are extensively studied since 2011 [12]. Because of their tunable interlayer spacing and tailored surface chemistry, MXenes showed high performance in membrane separation, energy storage and conversion [13,14]. DFT calculations predict that MXenes exhibit metallic conductivity, which is favorable for the electrons transfer from the semiconductor in the photocatalysis reaction [15]. So MXenes based nanomaterials have been used as new photocatalysts in energy and environmental applications [16,17]. Considering the cost, efficiency, and stability, TiO₂@MXene photocatalyst has been explored with in situ growth or hydrothermal synthesis which showed excellent catalytic performance [18–20]. Because the layered Ti₃C₂ is easy to oxidize, 2D MXene can be used as a C skeleton and Ti source [21]. It is necessary to utilize the oxidation of MXene to prepare photocatalytic composites with simple method to decrease the cost of TiO₂@MXene nanocomposite and organic pollutants treatment. TiO₂/Ti₃C₂ composite was prepared with a simple calcination method at high temperature which showed high photocatalytic CO₂ reduction activity [22,23]. The TiO₂/Ti₃C₂ composites retained the 2D multilayer structure with the remained Ti₃C₂ worked as co-catalyst to accelerate the migration of photoinduced electrons while the surface heterojunction could prevent the recombination of photogenerated carriers in TiO₂ [23].

Herein, we propose a easy transformation of MXene into TiO₂/MXene composite material with the aiding of photo irradiation energy during the dye treatment. In this design, the MXene acts not only as a source of titanium, but also as the cocatalyst. When it was used in the photocatalysis of dyes under UV and visible light, the dyes can be degraded efficiently in 3 h while the material showed good recycle capability.

2. Experimental

2.1. Materials and TiO₂/MXene nanocomposites preparation

Ti₃AlC₂ was provided by FORSMAN (98%, 400 mesh, Beijing, China). All other chemicals were of analytical grade and used without further purification. MXene was prepared by etching Ti₃AlC₂ powder with 49% HF (Aladdin, Shanghai, China) at room temperature for 24 h, followed by filtration with deionized water. Then, the filtrate was neutralized to at least pH 6 and dried in the N₂ atmosphere at room temperature. During the dye treatment, TiO₂/MXene nanocomposites were formed under UV or visible light irradiation.

2.2. Photocatalytic performance of TiO₂/MXene nanocomposites

A series of dye solutions were prepared by dissolving analytical grade methyl orange in deionized water and the concentrations were tested with UV-Vis spectrometer at 460 nm. An amount of MXene was added into 300 mL dye

solution (50 mg/L) while pH of the solution was adjusted by H₂SO₄ or NaOH. The mixtures were stirred under dark condition, UV-light (1 kW) condition and visible light (1.5 kW) condition, respectively. This process was followed by centrifugation to obtain a clear solution to test the absorbance with UV-Vis spectrometer. Each measurement was carried out 3 times under the same conditions. The removal efficiency of the dye was calculated by following equations:

$$D(\%) = \frac{(C_i - C_f)}{C_i} \times 100\% \quad (1)$$

where C_i and C_f are the initial and final (equilibrium) concentrations of the dye in the solution (mg/L), respectively.

2.3. Characterization

The phase composition of the samples were obtained via powder X-ray diffraction (XRD-7000S, Shimadzu, Japan) on a diffractometer fitted with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) operating at 40 mA and 40 kV. The morphology of the particles was analyzed via scanning electron microscopy (SEM, Nova Nano SEM 450, FEI) with the acceleration voltage of 15 kV. The elemental composition of TiO₂/MXene was analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB™ 250Xi, ThermoFisher). The concentration of dye solution was tested with UV-Vis spectrometer (TU-1900, PERSEE, Beijing, China).

3. Results and discussion

3.1. Degradation of dye with TiO₂/MXene under UV and visible light conditions

The morphologies of raw material and prepared MXene were analyzed using SEM. As shown in Fig. 1, the pristine MXene was obtained by etching of Ti₃AlC₂ with HF because the dense Ti₃AlC₂ MAX phase particles in Fig. 1a were replaced with MXene nanosheets showed loose layered structure and smooth surface in Fig. 1b, although the layers are connected to each other. The interplanar spacing can provide abundant active sites for adsorption and catalysis.

In order to study the efficiency of TiO₂/MXene in photocatalytic reaction at room temperature, methyl orange was used as the target pollutant with MXene powders added in the dye solution. In order to analyze the effect of MXene, blank test without MXene was also conducted. The solutions were continuously stirred under UV light irradiation or dark condition for comparison. As shown in Fig. 2, for methyl orange without MXene, the dye concentration changes little during 48 h under dark condition. When UV light irradiation was placed without addition of MXene, about 10% of the dye was degraded after 48 h which demonstrated the slight photodegradation effect of UV light. When MXene was added in the solution and stirred under dark condition, the dye removal efficiency was not obvious at first 16 h. With the extension of treatment time, the removal efficiency was increased gradually. Then the dye concentration decreased about 50% after 48 h treatment. This may be caused by the dye adsorption of the MXene material in the nanochannels at the early step. The TiO₂ nanoparticles were formed

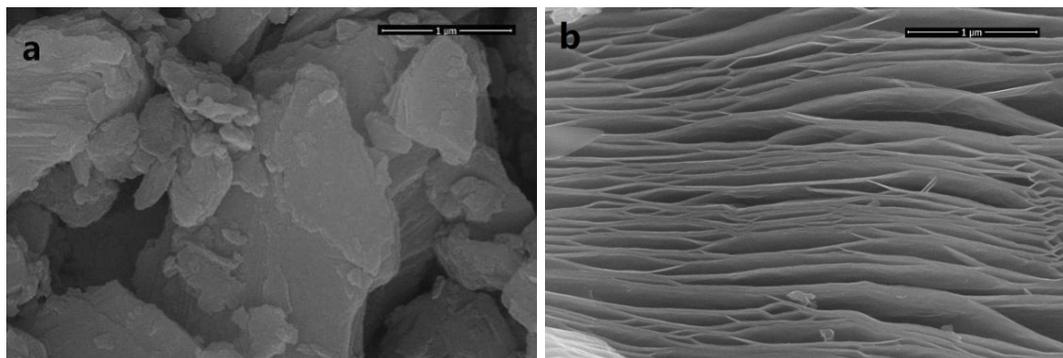


Fig. 1. SEM images of (a) Ti_3AlC_2 and (b) MXene after HF etching.

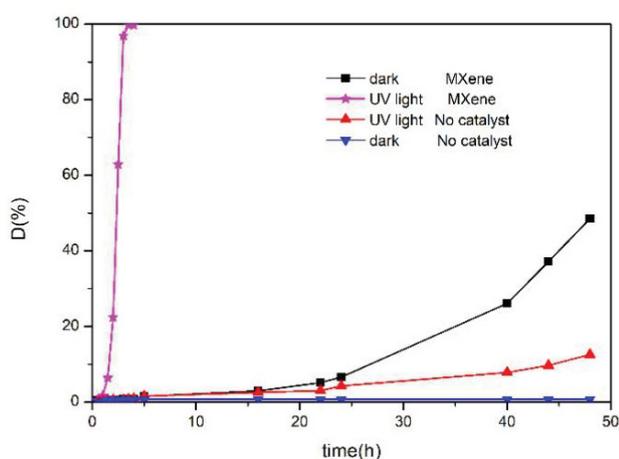


Fig. 2. The removal efficiency of methyl orange under UV and dark conditions.

gradually in the surface of MXene nanosheets at room temperature with the slowly oxidation of Ti_3C_2 . However, When UV light irradiation was introduced in the system, about 98% of the dye was rapidly degraded in 6 h. And the removal efficiency was increased obviously. It indicated that the composite material worked as a catalyst in the photocatalytic reaction which can accelerate the degradation of dye obviously. The UV irradiation can effectively promote the formation of $\text{TiO}_2/\text{MXene}$ nanocomposites.

3.2. Effect of photocatalyst content on the degradation of methyl orange

The effects of MXene contents on the degradation rate were studied with different weight ratios of MXene/dye such as 5, 8 and 10, respectively. As shown in Fig. 3, under dark condition, the dye concentration only decreased not more than 6% which can be induced by the adsorption effect of channels in the MXene nanosheets. When UV or visible light irradiation was introduced, the degradation rate was accelerated obviously. After 4 h operation, exceed 98% dye was degraded when MXene/dye mass ratio was fixed at 5. With the increase of MXene content, the degradation of dye reached 100% in 4 h. For the environmental and economic considerations, MXene/dye mass ratio was fixed at 5 for further research.

3.3. Effect of pH on the photocatalytic performance of MXene

The photodegradation of organic dye by $\text{TiO}_2/\text{MXene}$ nanocomposites at different pH was analyzed with methyl orange used as the target pollutant. As can be seen from Fig. 4a, the degradation rate in the dark condition gradually increased with the increase of time, up to 11.9%, indicating the higher adsorption and degradation of dye at pH = 2. It can be seen from Fig. 4b–e that the degradation rate in the dark condition remains very low with the increase of time. In the dark condition, the organic matter cannot be degraded efficiently. When pH = 2, degradation rates increased rapidly with time during 3 h under visible and UV light conditions, and the degradation rate under visible light condition was a little higher than that under UV light condition. So the catalytic effect was better under visible light condition. After 3 h, most of the dye (close to 99.9%) was degraded. When the pH of the solution was improved, the removal efficiency of nanocomposites under visible light was a little higher. And the degradation rate of the solution under visible light and UV light conditions need more time (over 4 h), indicating that the photocatalytic performance of MXene is stronger under acidic conditions.

3.4. Cycle stability of nanocomposites

The sample after UV irradiation was cleaned with ethanol and deionized water, and then recycled after drying. The cycle experiment was carried out with the same mass ratio. In Fig. 5, the degradation rates of the three comparative experiments at 4 h were all about 98%, indicating that the material was recyclable. The dye removal efficiency increased with cycle, which indicated more active particles was formed during the irradiation process.

3.5. Study of photocatalytic mechanism of $\text{TiO}_2/\text{MXene}$

After a single UV degradation experiment of methyl orange, the sample was collected by centrifugation and cleaned repeatedly with deionized water and anhydrous ethanol. The sample was placed in a vacuum drying oven and dried at room temperature for 24 h for characterization and named as $\text{TiO}_2/\text{MXene}$. The raw material Ti_3AlC_2 , MXene and $\text{TiO}_2/\text{MXene}$ were characterized by XRD to investigate the change of material composition. As can be seen from the XRD patterns in Fig. 6, the peak of 38.9° representing

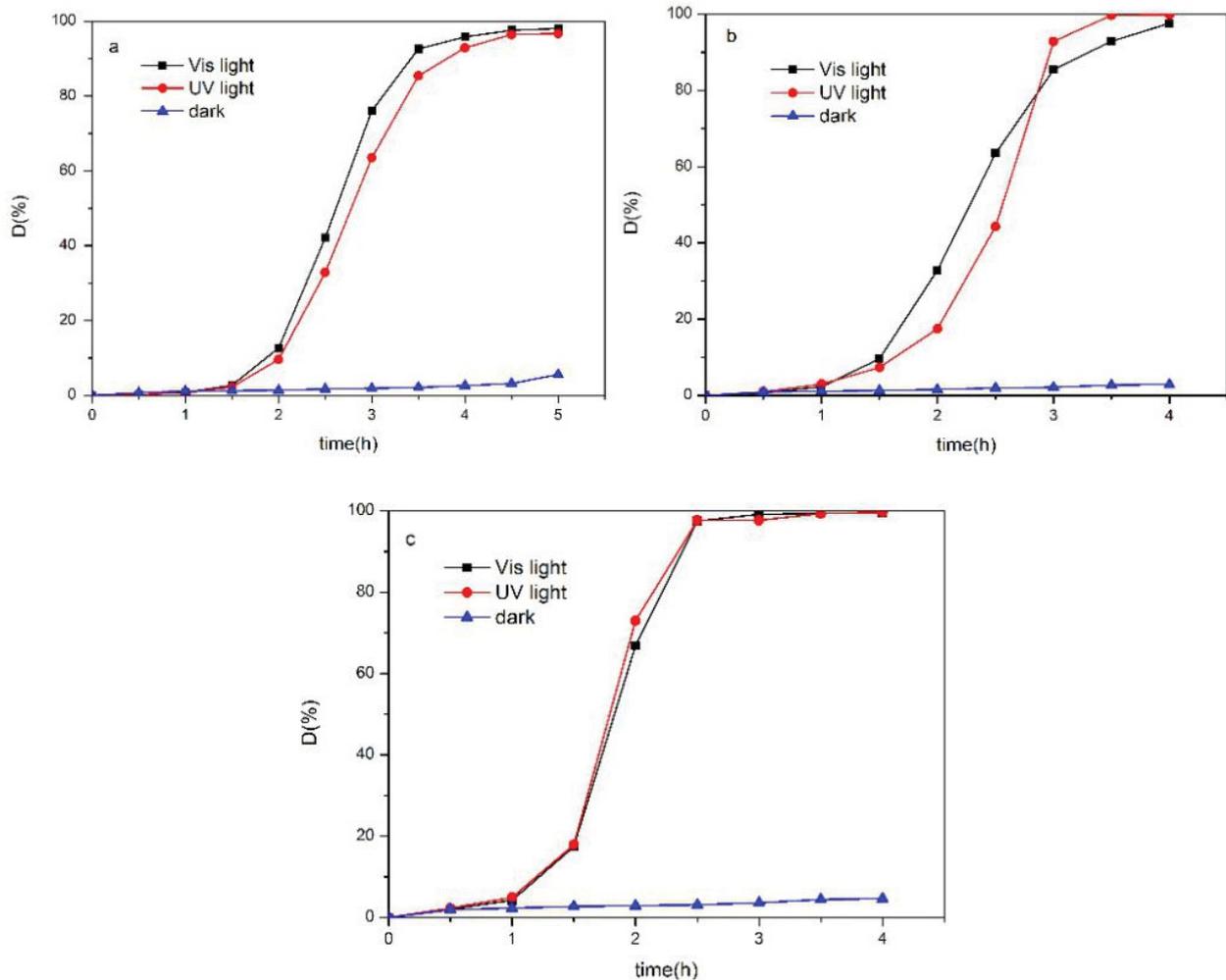


Fig. 3. Degradation of methyl orange with different photocatalyst/dye mass ratios (a) 5, (b) 8 and (c) 10.

the (104) crystal plane of Al element disappeared after HF etching of the precursor Ti_3AlC_2 , indicating that the stripping of aluminum element was relatively complete. The peak position (002) of Ti_3AlC_2 at 9.6° and the peak position (004) of 19.2° are both wide and low angles, indicating that the lamellar Ti_3C_2 nanosheets are successfully etched and have a typical accordion-like appearance. As shown in Fig. 6, the peak position of the crystal plane moves from 9.6° to 8.8° , and the sharpness decreases when the peak position moves to a small angle. The results indicated that the spacing of lamellar MXene is larger than that of its precursors.

Fig. 6 shows that anatase phase TiO_2 (PDF standard card: 21-1272) is obviously detected in the XRD pattern, and the diffraction peaks at 25.3° , 37.8° , 48.0° , 53.9° , 55.1° and 62.8° correspond to the crystal planes of (101), (004), (200), (105), (211) and (204) of anatase phase TiO_2 .

Although the oxidized MXene after dye treatment showed obvious TiO_2 anatase phase in the XRD pattern, it was difficult to observe TiO_2 nanoparticles from the oxidized material, maybe because the formed TiO_2 was very small and thin. In order to study the possible oxidation reaction, the MXene materials are oxidized at different temperature

for 30 min in aqueous solution to simulate the oxidation of MXene during UV and visible light irradiation. The influence of the oxidation reaction temperature on the morphology and structure of $\text{Ti}_3\text{C}_2\text{T}_x$ was explored in Fig. 7. The growth of TiO_2 nanosheets depends on the temperature of the oxidation reaction. At 100°C , almost no TiO_2 was found in Fig. 7b, because the low temperature and lack of energy limited the oxidation reaction of MXene. When the temperature reached 200°C , it was easy to observe the existence of cubic crystals on layered MXene, which maybe the anatase TiO_2 . With the increase of temperature, the number of TiO_2 nanosheets increased gradually.

In order to analyze the chemical bond changes of MXene in the process of experiment, XPS test was performed on MXene and the sample oxidized at 300°C . As shown in Fig. 8, four groups of double peaks, including Ti 2p_{3/2} peak and Ti 2p_{1/2} peak, can be fitted into the Ti 2p orbit, and the area ratio of the two groups of peaks is fixed at 2:1. The peaks of Ti 2p_{3/2} (2p_{1/2}) at 454.7 (460.5), 455.6 (461.2), 457.2 (462.9) and 458.3 (464.2) eV are Ti-C, Ti-X, Ti_xO_y (titanium oxide in reduced state) and TiO_2 , respectively [21]. When the temperature was increased, TiO_2 content increased

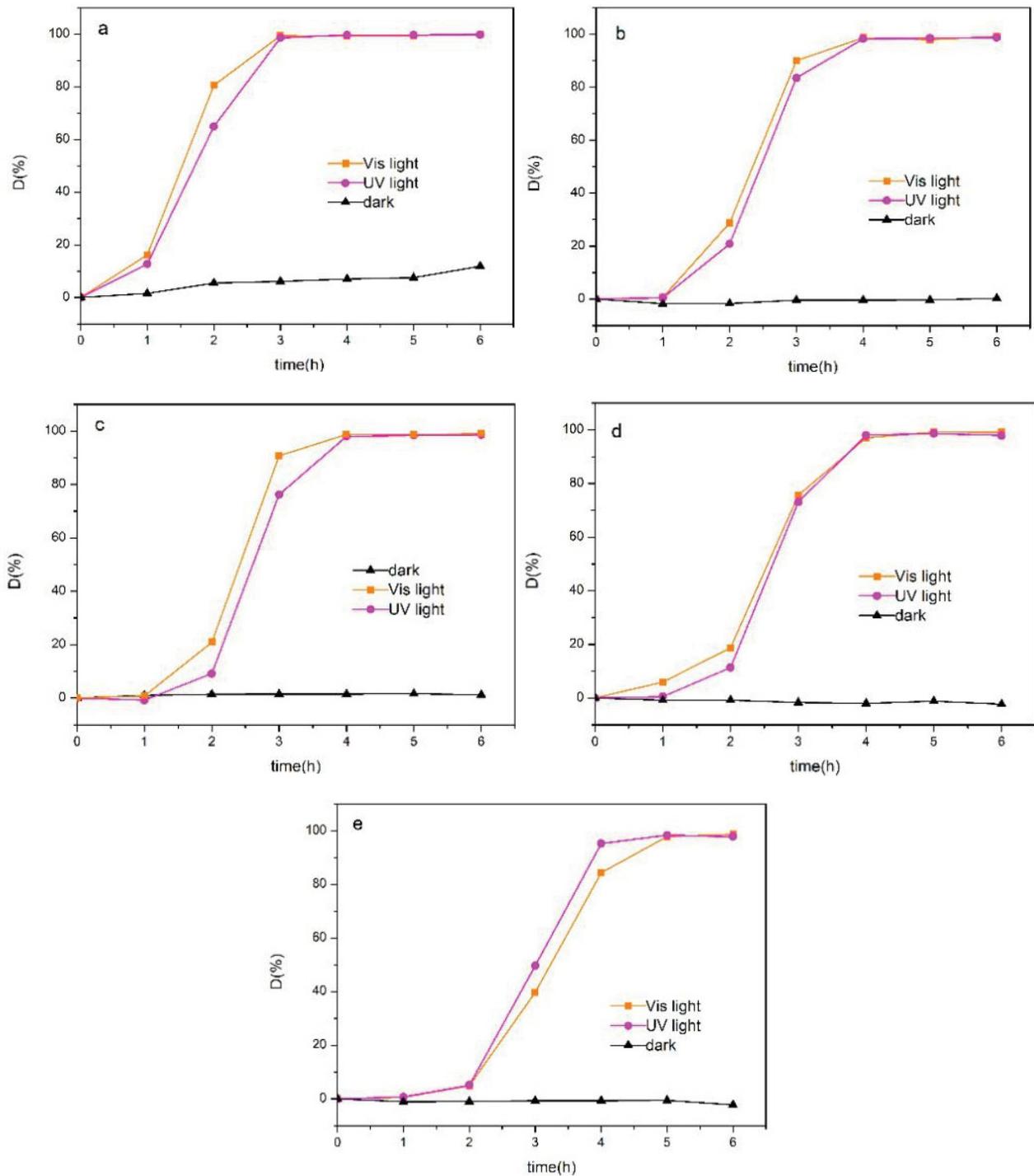


Fig. 4. Effect of pH on the photocatalytic performance of nanocomposites in methyl orange solution (a) pH = 2, (b) pH = 4, (c) pH = 6, (d) pH = 8 and (e) pH = 10.

obviously, while other contents decreased correspondingly. It showed that Ti_3C_2 of MXene was partially oxidized to TiO_2 and Ti_3C_2 worked as a built-in titanium source. Through high temperature oxidation condition, TiO_2 nanosheets grew to form TiO_2 /MXene nanocomposites and formed the heterojunction. The composites possess efficient photocatalytic degradation of methyl orange because

of sufficient absorption of visible light, high conductivity, high surface area and low recombination of the photoinduced charge carriers [24].

4. Conclusions

In this paper, MXene was used to evaluate the degradation rate of organic dye wastewater. The photocatalytic

performance of MXene on methyl orange was explored under different mass ratios, light conditions and pH environments. Under dark conditions, the concentration of methyl orange decreased little during 4 h. Under the irradiation of UV or visible light, methyl orange can be degraded rapidly. It means MXene can effectively absorb the light energy, inspire electronic to produce electron transition, form electronic-hole pair and high activity of free radicals, and then induce the redox reaction on the surface of the catalyst.

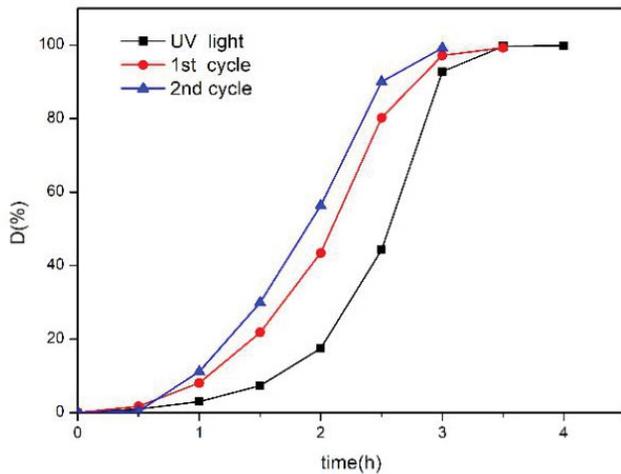


Fig. 5. The cyclic stability of nanocomposites in methyl orange catalysis.

Through this process, the organic dye was degraded rapidly and the solution faded to transparent. The material showed improved photocatalytic performance after irradiation and good recovery capability. Through the high temperature oxidation conditions, Ti_3C_2 worked as titanium source for the growth of TiO_2 nanoparticles and formed $TiO_2/MXene$ nanocomposites, which constitutes the heterojunction. MXene, worked as a cocatalyst, enhanced the separation

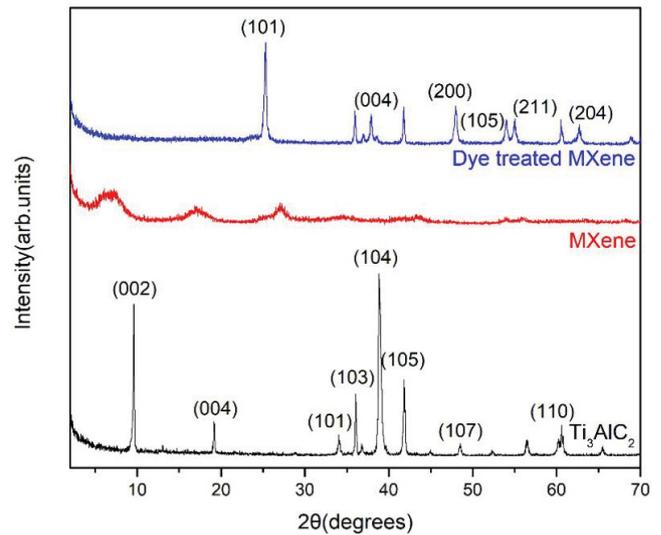


Fig. 6. XRD pattern of samples before and after dye treatment.

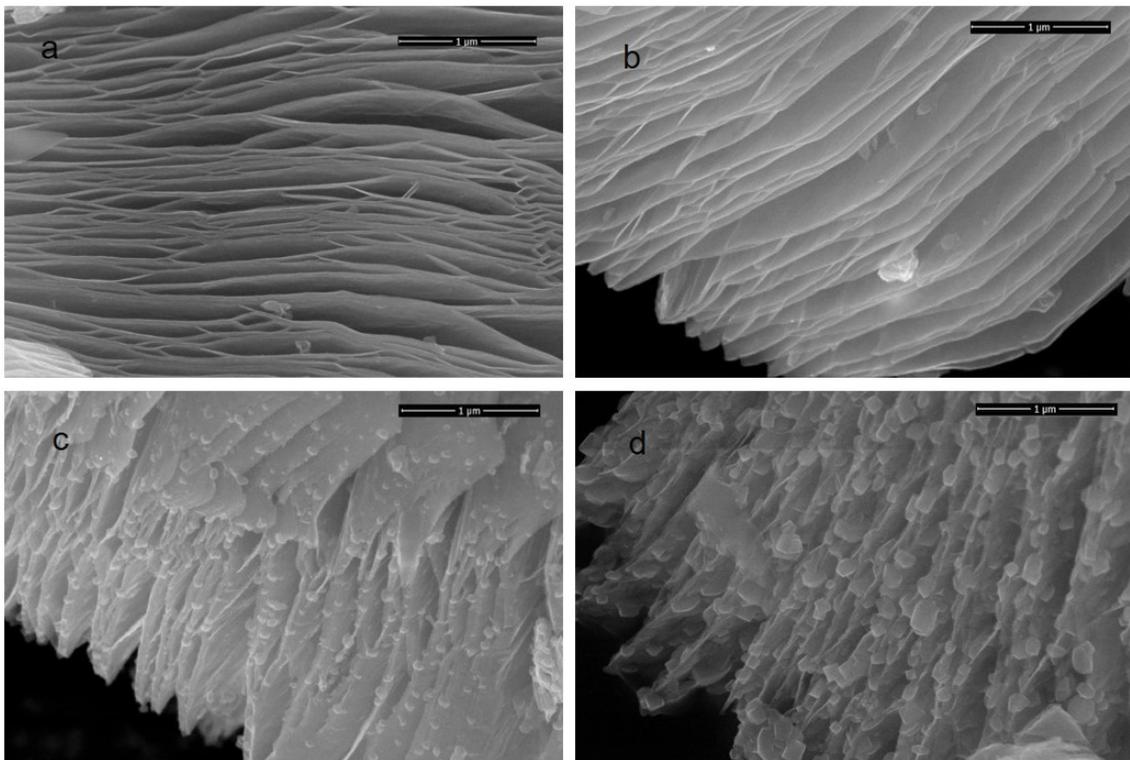


Fig. 7. SEM diagram of MXene after oxidation at different temperatures: (a) without oxidation, (b) 100°C, (c) 200°C and (d) 300°C.

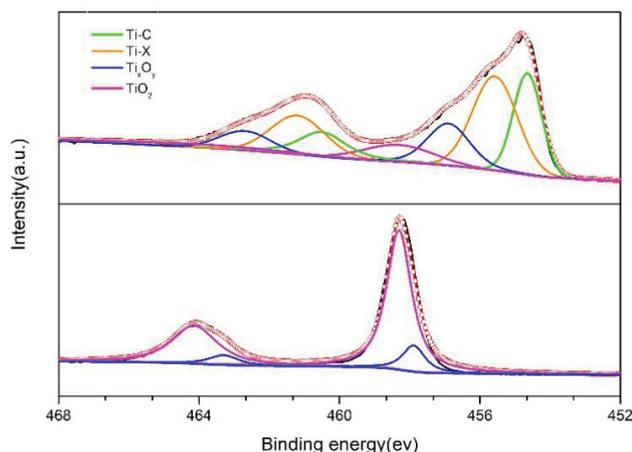


Fig. 8. XPS spectra of Ti_3AlC_2 and MXene before and after oxidation.

between the pair and prolonged its light living carrier of life. The results showed that composite has excellent photocatalytic performance, which can not only degrade the colored organic pollutants, but also can be recycled easily. It fully shows the potential of environment-friendly materials, which is of great help to the sustainable utilization of resources and environmental protection.

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Conflict of interest

The authors declare no conflict of interest.

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