Facile Preparation of Hierarchical AgNP-Loaded MXene/Fe₃O₄/ Polymer Nanocomposites by Electrospinning with Enhanced Catalytic Performance for Wastewater Treatment

Xinxin Huang,²,³,§ Ran Wang,²,§ Tifeng Jiao,∗,†‡ Guodong Zou,‡ Fangke Zhan,‡ Juanjuan Yin,‡ Lexin Zhang,§ Jingxin Zhou,† and Qiuming Peng∗,†‡

1State Key Laboratory of Metastable Materials Science and Technology and 2Hebei Key Laboratory of Applied Chemistry, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

ABSTRACT: MXene as a kind of two-dimensional nanomaterial has aroused people’s strong research interest because of its excellent properties. In the present study, we introduced a new poly(vinyl alcohol)/poly(acrylic acid)/Fe₃O₄/MXene@Ag nanoparticle composite film fabricated by electrospinning and heat treatment as well as self-reduction reaction process. The obtained composite films showed high self-reduction ability because of the incorporation of MXene flakes. The intercalated MXene flakes in the composite nanofibers were evenly distributed, which not only solved the aggregation problem from MXene dispersion but also could self-reduce Ag nanoparticles in situ in composite materials. In addition, the composite nanofiber films exhibited good fiber structure, thermal stability, and magnetic properties. Moreover, the composite nanofiber films demonstrated excellent catalytic ability and cycle stability to 4-nitrophenol and 2-nitroaniline.

1. INTRODUCTION

In recent years, MXene’s extraordinary physical and chemical properties and layered structure have made it a new type of two-dimensional (2D) material that is popular after graphene. MXene is a transition metal nitride/carbon nano-layered material that was first prepared by Naguib in 2011. The structure of MXene can be represented by MₓₙXₓTₓ−n. In short, M represents a transition metal element, X represents a C or N element, and T represents a functional terminal such as −OH, −F, and so on. MXene is a layered material obtained by etching away the Al layer by MAX₃. It has great application prospects in electrochemistry, magnetism, and optic fields. Particularly, the MXene flake obtained by delaminating is one of the most valuable nanomaterials. The nanosheet has a large specific surface area and can be used in the production of new functional hybrid material building blocks. However, the MXene nanosheets are easy to aggregate in solution and oxidized easily, which have become a challenge that needs to be solved urgently.

To solve these problems, the researchers focused on the separation of flakes and the modification of the surface MXene flakes. For example, Wang et al. stratified MXene by modification of sulfonic acid diazonium salts and ultrasound. The obtained large-scale MXene flakes have stable properties and not easy to agglomerate. Boota et al. prepared PPy/Ti₃C₂Tₓ composites by modifying polypyrrole on the surface of MXene sheets. It was found that pyrrole (C₅H₅NH) can simultaneously be embedded, aligned, and metal-free poly-

merized on TiₓCₓ₂Tₓ MXene. In addition, PPy/TiₓCₓ₂Tₓ composite exhibits excellent electrochemical properties. Ling et al. prepared TiₓCₓ₂Tₓ/polymer flexible composite material by mixing MXene (TiₓCₓ₂Tₓ) with charged polydiallyldimethyl-ammonium chloride or electrically neutral polyvinyl alcohol (PVA), which can enhance cation embedding and increase capacitance, and has a high potential for electrochemical applications. Researchers have indeed made outstanding contributions in fully exploiting MXene. However, the problem of easy aggregation of MXene sheets has not been completely solved. In addition, its self-reducing precious metal properties are masked after the MXene flakes’ surface has been modified. On the other hand, self-assembled composites are widely prepared and applied because of their good properties.

Nitro compounds are one of the common water pollutants. In particular, 4-nitrophenol (4-NP) and 2-nitroaniline (2-NA) are typically harmful compounds for humans and environment because of their high solubility and toxicity. Therefore, it is very important to develop new materials that can effectively catalyze 4-NP and 2-NA.

To solve the problems mentioned above, we designed and successfully synthesized PVA/poly(acrylic acid)/Fe₃O₄/MXene@AgNP (PVA/PAA/Fe₃O₄/MXene@AgNP) functional nanocomposites in combination with the electrospinning technology. It is well-known that the electrospinning...
technology is a technology capable of producing continuous microfilaments with a diameter scale of nanometer or micrometer. The morphology, diameter scale, and stacked density of fibers can be regulated by adjusting process parameters and environmental conditions. In our research, the solvent used ultrapure water, and the spinning materials were PVA and PAA, all of which were water soluble and ecofriendly materials, nonpolluting, and easily degradable. Fe3O4 was added to the spinning material, and the composite nanofiber materials could exhibit magnetic properties. Moreover, Fe3O4 was easy to recycle. The MXene flake colloidal solution was obtained by dispersing MXene powder in dimethyl sulfoxide (DMSO) for later experiments. The composite nanofiber materials were prepared by mixing PVA, PAA, Fe3O4 and MXene components via the electrospinning technology and next modification with Ag nanoparticles (AgNPs). This obtained composite fiber material not only made full use of the self-reducing properties of MXene sheet itself but also solved the aggregation problem from MXene dispersion. The MXene flakes were stretched out on the surface of the obtained fiber. The reduction characteristics of the MXene nano-sheet itself could reduce Ag+ in the AgNO3 solution to AgNPs at the active site on the surface of the nanosheet. As reaction time continued, AgNPs grew and aggregated, eventually forming Ag nanoclusters. In this report, we explored the synthesis and characterization of novel PVA/PAA/Fe3O4/MXene@AgNP composite nanofibers. This composite fiber material exhibited excellent properties for catalytic reduction of nitro compounds such as 2-NA and 4-NP. In addition, we investigated the size of self-reduced AgNPs and their catalytic effects on 2-NA and 4-NP at different reduction times. The experimental results showed that the prepared PVA/PAA/Fe3O4/MXene@AgNP composite nanofibers demonstrated a great potential in the field of composite catalyst materials and wastewater treatment.

2. RESULTS AND DISCUSSION

2.1. Preparation and Characterization of Composite Fibers. First, Figure 1 indicated the preparation process of PVA/PAA/Fe3O4/MXene@AgNP composite nanofibers. We exfoliated layered MAX (Ti3AlC2) powders by treating them in 40% HF solution at 25 °C. Selective HF etching originated from only “A” layers from the MAX phase. Then, MAX became a multilayer MXene phase. In many cases, such as thermal treatment, sonication and reactions of volume expansion in the interlayer space would lead to deintercalation of some certain compounds and exfoliation. DMSO has been reported to intercalate MXene at room temperature because DMSO could increase the c-lattice parameter of MXene from 19.5 ± 0.1 to 35.04 ± 0.02 Å. The DMSO-intercalated MXene sonicated in water lead to themselves being delaminated into separate flakes similar to “paper” and formation of nanosheet colloidal solution. Multilayer MXene was intercalated with DMSO and ultrasonically dispersed to obtain MXene nanosheet colloidal solution for the next step of electrospinning. PVA, PAA, Fe3O4, and MXene nanosheet colloidal solution were mixed in proportion to form an electrospinning precursor solution. Through electrospinning, we obtained composite nanofibers with MXene flake “wings”. When the composite nanofibers were placed in a slowly stirred AgNO3 solution, a [Ag2(DMSO)] complex monomer was first formed. The rapidly transferred electrons form oxygen lone pair electrons ([O2−(CH3)2]) leading to the formation of Ag−[DMSO]. The charge was transferred between Ag−MXene complexes to initialize the dimerized MXene−Ag DMSO. The MXene−Ag dimeric complexes were bonded to –OH and reduced to stable Ag+ nanoclusters. As the nanoclusters were further nucleated and grown on the surface of the MXene nanosheets, spherical AgNPs were formed. With the increment of self-reduction time, they may have a small amount of AgNPs drifted/anchored on the surface of polymer fibers. Finally, the AgNP-loaded composite nanofibers were successfully prepared. It should be noted that the layered MXene nanosheets were firmly “locked” on the fiber surface by composite nanofibers to achieve high dispersibility, which solved the problem that MXene nanosheets were easy to aggregate. In addition, the MXene flakes were not modified by any functional groups, and their original properties were preserved. This experiment is based on the reaction mechanism of in situ formation of AgNPs@MXene hybrids. The MXene nanosheet has a large specific surface area, and the surface has a reduction/nucleation site of the original AgNPs. Furthermore, the surface of MXene contains an –OH functional group, which can bond with Ag+ ions. Over enough time, AgNPs continue to grow to form stable Ag nanospheres on the fiber surface. The composite nanofibers used to catalyze 4-NP and 2-NA also obtained good catalytic effects.
composite nanoﬁbers demonstrated that the morphology of the ﬁbers changed after Fe$_3$O$_4$ and MXene were added under same parameters. From Figure 3b, it could be easily seen that some Fe$_3$O$_4$ particles appeared in the ﬁber. Furthermore, local fusion between the ﬁbers occurred, which could be caused by the presence of a small number of micron-sized MXene large layers. The ﬁber diameter became uneven. Figure 3c showed that a SEM image of the PVA/PAA/Fe$_3$O$_4$/MXene nanoﬁbers appeared cross-linked in plane after thermal treatment for 5 h. Fe$_3$O$_4$ nanocubes with an average size of 100 nm embedded in the composite nanoﬁbers were clearly visible, as shown in Figure 3d. The presence of Fe$_3$O$_4$ NPs made the composite ﬁbers magnetic and recyclable.

As shown in Figure 4a, it clearly showed that the surface of the ﬁber was embedded with the MXene nanosheets similar to the ﬁber growing “wings”. It could be clearly seen from the partially magniﬁed transmission electron microscopy (TEM) image (Figure 4b) of the composite nanoﬁber that the AgNPs were loaded onto the MXene nanosheet. This conﬁrmed that PVA/PAA/Fe$_3$O$_4$/MXene@Ag composite nanoﬁbers were successful prepared. Figure 4c further conﬁrmed Fe$_3$O$_4$, MXene, and AgNP coexisted and distributed in the obtained composite nanoﬁbers. In addition, energy-dispersive X-ray (EDX) spectroscopy shown in Figure 4d demonstrated that the elements of C, O, Fe, Ti, and Ag were presented in PVA/PAA/Fe$_3$O$_4$/MXene@AgNP composite nanoﬁbers, indicating the successful preparation of composite nanoﬁbers again.

High-resolution TEM (HRTEM) images demonstrated that AgNPs were single crystals. In the process of Ag reduction in situ by MXene ﬂakes, with the increase of reduction time, AgNPs grew slowly. Figure 5b,e,h showed the interplanar spacing of lattice with d(111) of 0.238 nm and d(200) of 0.208 nm. The formed AgNPs showed the average particle size of 12 ± 5 nm at 10 min, as shown in Figure 5c. Furthermore, AgNPs in composite nanoﬁbers displayed an average size of 17 ± 5 nm (Figure 5f) at 20 min and 22 ± 5 nm (Figure 5i) at 60 min, respectively, which indicated the slow increment of AgNP particle size with the reduction reaction time.

X-ray diﬀraction (XRD) data were used to identify strong aﬃliation in composite nanoﬁbers. Figure 6a indicated the diﬀraction patterns of the MXene powder, Fe$_3$O$_4$ NPs, PVA/PAA nanoﬁbers, PVA/PAA/Fe$_3$O$_4$/MXene composite nanoﬁbers, and PVA/PAA/Fe$_3$O$_4$/MXene@AgNP composite nanoﬁbers. XRD curves of the MXene powder clearly indicated the peaks at 2θ = 8.90°, 18.24°, and 27.65° which was attributed to the (002), (006), and (008) crystal plane, respectively. According to the XRD patterns of the face-centered cubic Fe$_3$O$_4$ phase, the 2θ values were observed at 30.0°, 35.3°, 43.0°, 57.0°, and 62.7° which were attributed to the (220), (311), (400), (511), and (400) crystal planes. The peaks of XRD were observed at 20.24° (PVA/PAA) and 19.29° (PVA/PAA/Fe$_3$O$_4$/MXene), which indicated the addition of the Fe$_3$O$_4$ NPs and MXene ﬂakes in the composite nanoﬁber layers. In addition, the inset shows the characteristic peaks of...
Figure 4. (a) Representative TEM image of PVA/PAA/Fe₃O₄/MXene@AgNP nanofibers; (b) partial magnification TEM image of nanofibers; (c) TEM image with C/O/Fe/Ti/Ag elemental mapping of PVA/PAA/Fe₃O₄/MXene@AgNP fibers; and (d) representative EDX image of composite nanofibers.

Figure 5. (a,d,g) TEM images of the PVA/PAA/Fe₃O₄/MXene composite nanofibers after loaded Ag NPs at 10, 20, and 60 min; (b,e,h) high-resolution TEM images, and (c,f,i) particle size distribution of Ag NPs at (a,d,g).
AgNPs in the XRD pattern corresponding to the (111), (200), (220), and (311) planes, which further confirmed the loading of AgNPs successfully. As shown in Figure 6b, the thermal stability of different composite nanofibers was measured. The weight loss was observed at 150 °C, which indicated that the absorbed water was removed. Also, from 280 to 480 °C, the sharp weight loss could be due to the thermal decomposition of carbon chain. The weight values of the samples remained constant when the temperature reached 500 °C.36,37 Furthermore, it indicated that the PVA/PAA/Fe3O4/MXene@AgNP composite nanofibers demonstrated better thermal stability. The heat loss of the PVA/PAA/Fe3O4 composite nanofibers was 72.55%, whereas the PVA/PAA/Fe3O4/MXene and PVA/PAA/Fe3O4/Mxene@AgNP composite nanofibers lost 66.94 and 58.8%, respectively. The difference in heat loss was mainly because of the addition of MXene nanosheets and the loading of AgNPs.

Magnetic properties of different samples were investigated at room temperature using magnetization hysteresis loops, as shown in Figure 7. The fully reversible field-dependent magnetization curve proved that all materials were super-paramagnetic with no coercivity and remanence.37 The PVA/PAA/Fe3O4/MXene composite nanofibers showed 39.9 emu/g saturation magnetization values at 20 kOe.37-40 The saturation magnetization value was reduced to 10.9 emu/g after AgNPs were loaded for 60 min. The saturation magnetization decreased with the prolongation of AgNP loading.37 The saturation magnetization of PVA/PAA/Fe3O4/MXene@AgNPs was 22.3 and 19.33 emu/g at 10 and 20 min, respectively.

We used X-ray photoelectron spectroscopy (XPS) technique to study and investigate the elemental components and composition. The XPS patterns indicated the characteristic peaks of C 1s, O 1s, and Ag 3d, as shown in Figure 6a. The obvious peaks at 368 and 374 eV from AgNPs in samples were assigned to Ag 3d5/2 and Ag 3d3/2,42 as shown in Figure 8b. This indicated that AgNPs existed in the form of a simple substance. Similarly, the peaks at 718.8 and 736.4 eV correspond to Fe 2p1/2 and Fe 2p3/2, respectively. In addition, we analyzed the oxygen and carbon elements and found that the peak positions at 284.5 eV and 285.7 represented C–C, C–OH, C–O, C=O, and O=C–O, respectively. The peak positions at 532.1 and 532.8 eV represented C–O bond and C=O bonds, respectively. Figure 8f showed an energy spectrum (EDS) of the composite nanofibers, showing that the composite fibers contained carbon, oxygen, iron, and silver elements. In summary, the above results indicated that the obtained AgNPs had been successfully anchored on composite nanofibers.

2.2. Catalytic Performances of Composite Fibers. The catalytic reaction of PVA/PAA/Fe3O4/MXene@AgNP composite nanofibers on nitro compounds could reflect their catalytic properties. To investigate the catalytic activity of the composite nanofibers, fresh NaBH4 aqueous solution (20 mL, 0.01 mol/L) was poured into 2-NA (2 mL, 5 mmol/L) or 4-NP (2 mL, 5 mmol/L), and then composite nanofibers were placed in a solution to measure their reducibility by UV–vis spectroscopy at room temperature.43-46 Figure 9a showed that the UV–vis absorption peak of 4-NP changes from 317 to 402 nm after NaBH4 was added, which was due to the formation of 4-nitrophenolate. The color of 4-NP and NaBH4 mixture unchanged for 24 h without catalyst indicated that the reaction did not occur. After the addition of the composite nanofibers, the peak of 4-NP gradually decreased at 402 nm until it no longer changed, which means that 4-NP was completely reduced (Figure 9b). In the experiment, the concentration of NaBH4 was 400 times than that of 4-NP, and the whole process of catalyzing 4-NP could be regarded as the pseudo-first-order reaction. A linear relationship between \[\ln(C_t/C_0)\] and time \(t\) in the catalytic reaction was shown in Figure 9c, demonstrating that the catalytic reaction fitted pseudo-first-order reaction \(C_t\)-concentration, \(C_0\)-initial concentration, and \(t\)-time). The reaction rate of the catalytic reaction was 0.168 min\(^{-1}\) (Figure 9c), suggesting that the PVA/PAA/Fe3O4/MXene@AgNP20 composite nanofibers showed good catalytic activity for 4-NP.
To further evaluate the catalytic activity of the composite nanofibers, we conducted a 2-NA catalytic reaction experiment. The color of 4-NA and NaBH₄ mixture remained unchanged for 24 h without the catalyst. The UV−vis absorption peak position of 2-NA was still at 415 nm after adding NaBH₄, as shown in Figure 9d. After adding an appropriate amount of composite fiber, the catalytic reaction was completed within 1 h, and the catalytic effect of the composite fiber was shown in (Figure 9e). Similarly, the catalytic reaction of the composite nanofibers to 2-NA could also be considered as a pseudo-first-order reaction (Figure 9f). The reaction rate of the catalytic reaction was 0.152 min⁻¹, which proved that the complex had a good catalytic activity for 2-NA. In addition, we also evaluated the catalytic performances of the other two samples (PVA/PAA/Fe₃O₄/MXene@AgNP10 and PVA/PAA/Fe₃O₄/MXene@AgNP60) for 4-NP and 2-NA, and the completed time of the catalytic reaction for 4-Np and 2-NA seemed larger than 90 min, which showed a similar
phenomenon in our previous MXene-AuNP system. In addition, the combination of MXene with PAA and PVA could improve the dispersion and surface area of MXene sheets, enhancing the active sites for reduction and loading of Ag NPs. Moreover, the addition of Fe₃O₄ enabled the composites to be easily recycled.

3. CONCLUSIONS

In conclusion, new AgNP-loaded PVA/PAA/Fe₃O₄/MXene composite nanofiber materials were prepared via electrospinning technology and self-reduction reaction of MXene flakes with AgNO₃. The MXene flakes, scaled from 200 to 400 nm, were successfully stripped on multilayer MXene by DMSO intercalation and subsequent sonication, and large-scale dispersion was achieved. The MXene nanosheets embedded in the fiber by electrospinning technology not only achieved high-dispersion targets but also retained its own physicochemical properties. By controlling the time of the self-reduction reaction, it seemed a facile approach to prepare AgNP-loaded fiber composites with different particle sizes and exhibited different catalytic properties for 2-NA and 4-NP. The PVA/PAA/Fe₃O₄/MXene@AgNP composite nanofibers exhibited excellent reactive activity for the catalytic reaction of certain nitro compounds (such as 2-NA and 4-NP), which was attributed to the special structural characteristics of the composite nanofibers and the good Ag-based catalytic activity. Moreover, the composite nanofiber materials could exhibit magnetic properties because of the addition of Fe₃O₄ NPs. The experimental results showed that the obtained PVA/PAA/Fe₃O₄/MXene@AgNP20 composite nanofibers displayed the best catalytic performance. Thus, the present work provided a new idea for the preparation of new MXene-based composite nanomaterials for wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Materials and Instruments. PVA (MW 57 000–66 000, 98–99% hydrolyzed), poly(acrylic acid) (PAA, MW ≈ 2000), 4-NP, and 2-NA were purchased from Aladdin Reagent (Shanghai, China). Fe₃O₄ and MXene (Ti₃C₂Tₓ) were synthesized in the laboratory according to previous studies. AgNO₃ (98%) was obtained from Tianyi (Tianjin, China). DMSO (99%) and sodium borohydride (NaBH₄, 98%) were purchased from Kermel Chemicals (Tianjin, China) and Alfa Aesar (Beijing, China), respectively. All chemicals used in this experiment were without further purification. Ultrapure water was purified by the experimental Milli-Q Millipore filter system which was purchased from Millipore Corporation (USA).

SEM (Hitachi S4800, Ibaraki, Japan) and TEM (Hitachi HT7700, Ibaraki, Japan) were used to characterize sample morphology. The HRTEM images were obtained by a JEM-2100 electron microscope at 200 kV. A SMART LAB X-ray diffractometer (Rigaku, Japan) with a Bragg diffractometer and a Cu Kα X-ray radiation source were utilized to get XRD patterns. Catalystic experiments were measured by UV-2550 spectrophotometer. XPS analysis was obtained by a Thermo Scientific ESCALAB 250Xi XPS (San Jose, CA, USA) with 200 W monochromatic Al Kα radiations. The magnetization was performed by MPMS-XL superconducting quantum interference device magnetometer (San Diego, CA, USA) at a temperature of 300 K. Thermogravimetry (TG) analysis was performed by a simultaneous thermal analyzer (NETZSCH STA 409 PC Luxx, Seligenstadt, Germany) under argon atmosphere.

4.2. Sample Preparation. Multilayer MXene (Ti₃C₂Tₓ) was obtained by etching the Al element from MAX (Ti₃AlCₓ) via HF acid. MXene flake colloidal suspension was prepared by powder separation and water bath sonication (Shenhuaitai SUS304 Ultrasonic bath, 110 W and 40 kHz). In short, 36 mg of MXene powder was mixed with 2 mL of DMSO and then magnetically stirred at 18 °C for 18 h to ensure that DMSO was intercalated in the multilayer structure of MXene. The intercalated MXene mixture would be centrifuged at 3500 rpm for 15 min to obtain a solid powder after removal of the supernatant. Then, 9 mL of ultrapure water was added to the DMSO-intercalated MXene residue at 10 °C. After a weak sonication with 110 W and 40 kHz frequency, the few MXene with intercalated DMSO were dispersed in ultrapure water. Fully delaminated Ti₃C₂ flake colloidal solutions were obtained. The residue was removed by centrifugation at 3500 rpm for 1 h to obtain a dark green MXene foil colloidal solution. The sizes of the nanosheets were mostly 200–500 nm, and the colloidal solution was relatively stable.

PVA (0.5 g) was added to 4.5 g of the colloidal solution of MXene flakes to form 10 wt % solutions and then stirred at 80 °C for 12 h. Fe₃O₄ (50 mg) solid was added to the above PVA solution and stirred for 1 h at 25 °C. PAA (0.6 g) was added to 1.4 g of MXene flake colloidal solution to form 30 wt % solution and then stirred at 25 °C for 1 h. We mixed all of the solutions together and stirred at 25 °C until uniform, which was the spinning precursor solution for next steps. During the electrospinning process, a 10 mL syringe load of PVA/PAA/Fe₃O₄/MXene precursor solution was connected to a stainless steel needle through a thin tube. We choose the optimal parameter conditions: 15 kV (needle tip voltage)-20 cm (working distance)-0.5 mL/h (feed rate of solutions). Then, spinning was carried out at 25 °C and 40% humidity. The obtained electrospun nanofibers were deposited on the surface of the aluminum foil and then dried in vacuum at 25 °C for 24 h. After that, heat-induced cross-linking reaction of the obtained electrospun nanofibers occurred when heated at 120 °C for 5 h. After thermal treatment and heat-induced cross-linking reaction, PVA/PAA/Fe₃O₄/MXene membranes were insoluble in water because of the esterification reaction between some of the partial hydroxyl groups and carboxylic acid groups. Next, the spun fiber membrane was immersed into 2.5 mg/mL AgNO₃ solution and gently stirred at 25 °C for Ag NP reduction growth. The PVA/PAA/Fe₃O₄/MXene@AgNP composite nanofibers were obtained with different immersion times (10, 20, and 60 min, respectively). The composite nanofibers were then taken out of AgNO₃ aqueous solution, washed with ultrapure water three times to remove non-adhered or free AgNO₃ NPs, and then dried at 30 °C for 24 h in vacuum.

4.3. Catalytic Performance Test. The catalytic performance of PVA/PAA/Fe₃O₄/MXene@AgNP electrospun nanofibers was determined by catalytic reduction of the solutions of 4-NP and 2-NA. The reducing agent selected in the catalytic reduction reaction was NaBH₄, and the whole reaction process was carried out under ultraviolet spectrum detection at 25 °C. 4-NP aqueous solution (10 mL, 0.005 M) was prepared, and fresh aqueous NaBH₄ solution (20 mL, 0.1 M) was added, and then PVA/PAA/Fe₃O₄/MXene@AgNP (40 mg) was added to the mixed solution for 60 min (named as PVA/PAA/Fe₃O₄/MXene@AgNP60). The
abundance of the mixed solution was monitored by UV-vis spectroscopy every 3 min until the absorbance of the solution was minimized and remained unchanged. At the same time, we evaluated the catalytic ability of nanofibers by catalyzing 2-NA (10 mL, 0.005 M) aqueous solution again. After the catalysis was completed, the nanofiber sample can be taken out by an external magnetic field.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (nos. 12874119 and 21473153), support program for the Top Young Talents of Hebei Province, China Postdoctoral Science Foundation (no. 2015MS80214), Research Program of the College Science & Technology of Hebei Province (no. ZD2018091), and Scientific and Technological Research and Development Program of Qinhuangdao City (no. 201701B004).

**REFERENCES**

(1) Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall’Agnese, Y.; Rozier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* 2013, 341, 1502–1505.

(2) Jian, M.; Wang, C.; Wang, Q.; Wang, H.; Xia, K.; Yin, Z.; Zhang, M.; Liang, X.; Zhang, Y. Advanced carbon materials for flexible and wearable sensors. *Sci. China Mater.* 2017, 60, 1206–1262.

(3) Li, Z.; Wang, Y.; Sun, D.; Zhang, Y.; Liu, B.; Hu, Q.; Zhou, A. Synthesis and thermal stability of two-dimensional carbide MXene Ti3C2. *Mater. Sci. Eng., B* 2015, 191, 33–40.

(4) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. *Adv. Mater.* 2013, 25, 992–1005.

(5) Li, J.; Du, Y.; Luo, C.; Wang, S.; Cui, C. Thermal stability of two-dimensional Ti3C2 nanosheets. *Chem. Int. 2015*, 41, 2631–2635.

(6) Miranda, A.; Halim, J.; Barsoum, M. W.; Lorke, A. Electronic properties of freestanding Ti3C2T x MXene monolayers. *Appl. Phys. Lett.* 2016, 108, 033102.

(7) Boota, M.; Anasori, B.; Voigt, C.; Zhao, M.-Q.; Barsoum, M. W.; Gogotsi, Y. Pseudocapacitive electrodes produced by oxidant-free polymerization of pyrrole between the layers of 2D titanium carbide (MXene). *Adv. Mater.* 2015, 28, 1517–1522.

(8) Zou, G.; Zhang, Z.; Guo, J.; Liu, B.; Zhang, Q.; Fernandez, C.; Peng, Q. Synthesis of MXene/Ag composites for extraordinary long cycle lifetime lithium storage at high rates. *ACS Appl. Mater. Interfaces* 2016, 8, 22280–22286.

(9) Wang, H.; Zhang, J.; Wu, Y.; Huang, H.; Li, G.; Zhang, X.; Wang, Z. Surface modified MXene Ti3C2 multilayers by aryl diazonium salts leading to large-scale delamination. *Appl. Surf. Sci.* 2016, 384, 287–293.

(10) Lin, S.-Y.; Zhang, X. Two-dimensional titanium carbide electrode with large mass loading for supercapacitor. *J. Power Sources* 2015, 294, 354–359.

(11) Karlsson, L. H.; Birch, J.; Halim, J.; Barsoum, M. W.; Persson, P. O. A. Atomically resolved structural and chemical investigation of single MXene sheets. *Nano Lett.* 2015, 15, 4955–4960.

(12) Vaughn, A.; Ball, J.; Heil, T.; Morgan, D. J.; Lampronti, G. I.; Maršalkaitė, G.; Raston, C. L.; Power, N. P.; Kellici, S. Selective calixarene-directed synthesis of MXene plates, crumpled sheets, spheres, and scrolls. *Chem.—Eur. J.* 2017, 23, 8128–8133.

(13) Syamsai, R.; Kollu, P.; Kwan Jeong, S.; Nirmala Grace, A. Synthesis and properties of 2D-Titanium carbide MXene sheets towards electrochemical energy storage applications. *Ceram. Int. 2017*, 43, 13119–13126.

(14) Zhao, M.-Q.; Ren, C. E.; Ling, Z.; Lukatskaya, M. R.; Zhang, C.; Van Aken, K. L.; Barsoum, M. W.; Gogotsi, Y. Flexible MXene/carbon nanotube composite paper with high volumetric capacitance. *Adv. Mater.* 2014, 27, 339–345.

(15) Er, D.; Li, J.; Naguib, M.; Gogotsi, Y.B.; Shenoy, V. B. Ti3C2 MXene as a high capacity electrode material for metal (Li, Na, K, Ca) ion batteries. *ACS Appl. Mater. Interfaces* 2014, 6, 11173–11179.

(16) Ghidini, M.; Naguib, M.; Shi, C.; Mashtalir, O.; Pan, L. M.; Zhang, B.; Yang, J.; Gogotsi, Y.; Billinge, S. J. L.; Barsoum, M. W. Synthesis and characterization of two-dimensional Nb3C (MXene). *Chem. Commun.* 2014, 50, 9517–9520.

(17) Xie, Y.; Dall’Agnese, Y.; Naguib, M.; Gogotsi, Y.; Barsoum, M. W.; Zhuang, H. L.; Kent, P. R. C. Prediction and characterization of MXene nanosheet anodes for non-lithium-ion batteries. *ACS Nano* 2014, 8, 9606–9615.

(18) Liang, X.; Garsuch, A.; Nazar, L. F. Sulfur cathodes based on conductive MXene nanosheets for high-performance lithium-sulfur batteries. *Angew. Chem., Int. Ed.* 2015, 54, 3907–3911.

(19) Khazaee, M.; Arai, M.; Sasaki, T.; Estili, M.; Sakka, Y. Two-dimensional molybdenum carbides: potential thermoemietric materials of the MXene family. *Phys. Chem. Chem. Phys.* 2014, 16, 7841–7849.

(20) Ma, Z.; Hu, Z.; Zhao, X.; Tang, Q.; Wu, D.; Zhou, Z.; Zhang, L. Tunable band structures of heterostructured bilayers with transition-metal dichalcogenide and MXene monolayer. *J. Phys. Chem. C* 2014, 118, 5593–5599.

(21) Aissa, B.; Ali, A.; Mahmoud, K. A.; Haddad, T.; Nedil, M. Transport properties of a highly conductive 2D Ti3C2Tx MXene/graphene composite. *Appl. Phys. Lett.* 2016, 109, 043109.

(22) Hope, M. A.; Forse, A. C.; Griffith, K. J.; Lukatskaya, M. R.; Ghidini, M.; Gogotsi, Y.; Grey, C. P. NMR reveals the surface functionalization of Ti3C2 MXenes. *Phys. Chem. Chem. Phys.* 2016, 18, 5099–5102.

(23) Gao, Y.; Wang, L.; Li, Z.; Zhou, A.; Hu, Q.; Cao, X. Preparation of Mxene-Cu2O nanocomposite and effect on thermal decomposition of ammonium perchlorate. *Solid State Sci.* 2014, 35, 62–65.

(24) Shi, C.; Beidaghi, M.; Naguib, M.; Mashtalir, O.; Gogotsi, Y.; Billinge, S. J. L. Structure of nanocrystalline TiC2 MXene using atomic pair distribution function. *Phys. Rev. Lett.* 2014, 112, 125501.

(25) Ren, C. E.; Hatzell, K. B.; Alhabeb, M.; Ling, Z.; Mahmoud, K. A.; Gogotsi, Y. Charge- and size-selective ion sieving through Ti3C2Tx MXene membranes. *J. Phys. Chem. Lett.* 2015, 6, 4026–4031.

(26) Ling, Z.; Ren, C. E.; Zhao, M.-Q.; Yang, J.; Giannaris, J. M.; Qiu, J.; Barsoum, M. W.; Gogotsi, Y. Flexible and conductive MXene films and nanocomposites with high capacitance. *Proc. Natl. Acad. Sci. U.S.A.* 2014, 111, 16676–16681.

(27) Wang, F.; Yang, C.; Duan, C.; Xiao, D.; Tang, Y.; Zhu, J. An organ-like titanium carbide material (MXene) with multilayer structure encapsulating hemoglobin for a mediator-free biosensor. *J. Electrochem. Soc.* 2015, 162, B16–B21.

(28) Shen, I. R.; Ivanovski, A. L. Graphene-like titanium carbides and nitrides Ti3C2, Ti3C2N, Ti3C2N x (n = 1,2,3) from de-intercalated MAX phases: First-principles probing of their structural, electronic properties and relative stability. *Comput. Mater. Sci.* 2012, 65, 104–114.

(29) Cýgan, R. T.; Liang, J.-J.; Kalinichev, A. G. Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field. *J. Phys. Chem. B* 2004, 108, 1255–1266.
(30) Ekmlund, P.; Beckers, M.; Jansson, U.; Höggberg, H.; Hultman, L. The $M_n\cdot\Lambda X$ phases: Materials science and thin-film processing. Thin Solid Films 2010, 518, 1851–1878.

(31) Liu, K.; Yuan, C.; Zou, Q.; Xie, Z.; Yan, X. Self-Assembled Zinc/Cystine-Based Chloroplast Mimics Capable of Photoenzymatic Reactions for Sustainable Fuel Synthesis. Angew. Chem., Int. Ed. 2017, 56, 7876–7880.

(32) Liu, K.; Xing, R.; Li, Y.; Zou, Q.; Möhwald, H.; Yan, X. Mimicking Primitive Photobacteria: Sustainable Hydrogen Evolution Based on Peptide-Porphyrin Co-Assemblies with a Self-Minerlized Reaction Center. Angew. Chem., Int. Ed. 2016, 55, 12503–12507.

(33) Liu, K.; Xing, R.; Chen, C.; Shen, G.; Yan, L.; Zou, Q.; Ma, G.; Möhwald, H.; Yan, X. Peptide-induced hierarchical long-range order and photocatalytic activity of porphyrin assemblies. Angew. Chem., Int. Ed. 2015, 54, 500–505.

(34) Abay, A. K.; Kuo, D.-H.; Chen, X.; Saraghi, A. D. A New V-doped $\text{Bi}_2\text{O}_5\text{S}_2$ oxysulfide catalyst for highly efficient catalytic reduction of $2\text{NO}$ and organic dyes. Chemosphere 2017, 189, 21–31.

(35) Thirumalraj, B.; Rajkumar, C.; Chen, S.-M.; Lin, K.-Y. Determination of 4-nitrophenol in water by use of a screen-printed carbon electrode modified with chitosan-crafted $\text{ZnO}$ nanoneedles. J. Colloid Interface Sci. 2017, 499, 83–92.

(36) Hou, C.; Jiao, T.; Xing, R.; Chen, Y.; Zhou, J.; Zhang, L. Preparation of $\text{TiO}_2$ nanoparticles modified electrosprun nano-composite membranes toward efficient dye degradation for wastewater treatment. J. Taiwan Inst. Chem. Eng. 2017, 78, 118–126.

(37) Guo, R.; Jiao, T.; Xing, R.; Chen, Y.; Guo, W.; Zhou, J.; Zhang, L.; Peng, Q. Hierarchical AuNPs-loaded Fe$_3$O$_4$/polymers nano-composites constructed by electrosprun with enhanced and magnetically recyclable catalytic capacities. Nanomaterials 2017, 7, 317.

(38) Guo, R.; Jiao, T.; Li, R.; Chen, Y.; Guo, W.; Zhang, L.; Zhou, J.; Zhang, Q.; Peng, Q. Sandwiched Fe$_3$O$_4$/carboxylate graphene oxide nanocomposites constructed by layer-by-layer assembly for highly efficient and magnetically recyclable dye removal. ACS Sustainable Chem. Eng. 2017, 6, 1279–1288.

(39) Li, X.; Lou, L.; Song, W.; Huang, G.; Hou, F.; Zhang, Q.; Zhang, H.-T.; Xiao, J.; Wen, B.; Zhang, X. Novel bimorphological anisotropic bulk nanoporous materials with high energy products. Adv. Mater. 2017, 29, 1606430.

(40) Li, X.; Lou, L.; Song, W.; Zhang, Q.; Huang, G.; Hua, Y.; Zhang, H.-T.; Xiao, J.; Wen, B.; Zhang, X. Controllably manipulating three-dimensional hybrid nanostructures for bulk nanoporous materials with large energy products. Nano Lett. 2017, 17, 2985–2993.

(41) Satheeshkumar, E.; Makaryan, T.; Melikyan, A.; Minassian, H.; Agnese, Y.; Liz-Marzán, L. M. Two-dimensional $\text{MXene}$ and $\text{MoS}_2$ hybrid nanocomposites with enhanced catalytic performance. J. Power Sources 2018, 353, 318–327.

(42) Li, K.; Jiao, T.; Xing, R.; Zou, G.; Peng, Q.; Selective Cu(II) ion removal from wastewater via surface charged polypyrrole/Pd nanoarchitectures with aggregation-free Pd nanocrystals confined into polypyrrole satelites as magnetically recoverable and highly efficient heterogeneous catalysts. RSC Adv. 2015, 5, 102210–102218.

(43) Zhao, X.; Jiao, T.; Ma, X.; Huang, H.; Hu, J.; Qu, Y.; Zhou, J.; Zhang, L.; Peng, Q. Facile fabrication of hierarchical diamond-based AuNPs-modified nanocomposites via layer-by-layer assembly with enhanced catalytic capacities. J. Taiwan Inst. Chem. Eng. 2017, 80, 614–623.

(44) Hervé, P.; Pérez-Lorenzo, M.; Liz-Marzán, L. M.; Dzubiella, J.; Lu, Y.; Ballauff, M. Catalysis by metallic nanoparticles in aqueous solution: model reactions. Chem. Soc. Rev. 2012, 41, 5577–5587.

(45) Xing, R.; Wang, W.; Jiao, T.; Ma, K.; Zhang, Q.; Hong, W.; Qiu, H.; Zhou, J.; Zhang, L.; Peng, Q. Bioinspired polypyrone sheathed nanofibers containing carboxylate graphene oxide nanosheet for high-efficient dyes scavenger. ACS Sustainable Chem. Eng. 2017, 5, 4948–4956.

(46) Liu, K.; Yuan, C.; Zou, Q.; Xie, Z.; Yan, X. Self-Assembled Zinc/Cystine-Based Chloroplast Mimics Capable of Photoenzymatic Reactions for Sustainable Fuel Synthesis. Angew. Chem., Int. Ed. 2017, 56, 7876–7880.

(47) Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional transition metal carbides. ACS Nano 2012, 6, 1322–1331.

(48) Naguib, M.; Mashtalir, O.; Mochalin, V. N.; Dall`Agne, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and delamination of layered carbides and carbonitrides. Nat. Commun. 2013, 4, 1716.

(49) Tan, I.; Chen, D.; Liu, H.; Tang, F. A silica nanorattle with a mesoporous shell: an ideal nano reactor for the preparation of tunable gold cores. Adv. Mater. 2010, 22, 4885–4889.

(50) Jiao, T.; Wang, H.; Guo, W.; Li, R.; Tian, K.; Xu, Z.; Jia, Y.; Wu, Y.; Cao, L. In situ confined growth based on a self-templating reduction strategy of highly dispersed Ni nanoparticles in hierarchical yolk-shell Fe@SiO$_2$ structures as efficient catalysts. Chem.—Asian J. 2016, 11, 3534–3540.

(51) Wang, C.; Sun, S.; Zhang, L.; Yin, J.; Jiao, T.; Zhang, L.; Xu, Y.; Zhou, J.; Peng, Q. Facile preparation and catalytic performance characterization of AuNPs-loaded hierarchical electrosprun composite fibers by solvent vapor annealing treatment. Colloids Surf., A 2019, 561, 283–291.

(52) Sun, S.; Wang, C.; Han, S.; Jiao, T.; Wang, R.; Yin, J.; Li, Q.; Yang, L.; Geng, L.; Yu, X.; Peng, Q. Interfacial nanostructures and acidochromism behaviors in self-assembled terpyridine derivatives Langmuir-Blodgett films. Colloids Surf., A 2019, 564, 1–9.

(53) Huang, X.; Jiao, T.; Liu, Q.; Zhang, L.; Zhou, J.; Li, B.; Peng, Q. Hierarchical electrosprun nanofibers treated by solvent vapor annealing as air filtration mat for high-efficiency PM2.5 capture. Sci. China Mater. 2019, 62, 423–436.

(54) Xu, Y.; Ren, B.; Wang, R.; Zhang, L.; Jiao, T.; Liu, Z. Effective preparation of rod-like MnO nanomixtures via hydrothermal approach and highly efficient removal of methylene blue for wastewater Treatment. Nanomaterials 2019, 9, 10.

(55) Zhan, F.; Wang, R.; Yin, J.; Han, Z.; Zhang, L.; Jiao, T.; Zhou, J.; Zhang, L.; Peng, Q. Selective Cu(II) ion removal from wastewater via surface charged self-assembled polystyrene-Schiff base nanocomposites. Colloids Surf., A 2018, 545, 60–67.

(56) Zhou, J.; Guo, F.; Jiao, T.; Xing, R.; Zhang, L.; Zhou, J.; Peng, Q. Selective Cu(II) ion removal from wastewater via surface charged self-assembled polystyrene-Schiff base nanocomposites. Colloids Surf., A 2019, 545, 60–67.

(57) Guo, R.; Yin, B.; Fan, S.; Feng, M.; Zhang, Z.; Dong, H.; Gao, F.; Zhao, Y. S. Surface tension driven aggregation of organic nanowires via lab in a droplet. Nanoscale 2018, 10, 11006–11012.

(58) Guo, R.; Yin, B.; Feng, M.; Zhang, G.; Zhang, Z.; Zhong, J.; Zhang, C.; Wen, B.; Zhao, Y. S. Epitaxial growth of dual-color-emitting organic heterostructures via binary solvent synergism driven sequential crystallization. Nanoscale 2019, 11.

(59) Luo, X.; Ma, K.; Jiao, T.; Xing, R.; Zhang, L.; Zhou, J.; Li, B. Graphene oxide-polymer composite Langmuir films constructed by interfacial thiol-ene photopolymerization. Nanoscale Res. Lett. 2017, 12, 99.
Facile synthesis of self-assembled carbon nanotubes/dye composite films for sensitive electrochemical determination of Cd(II) ions. Nanotechnology 2018, 29, 445603.