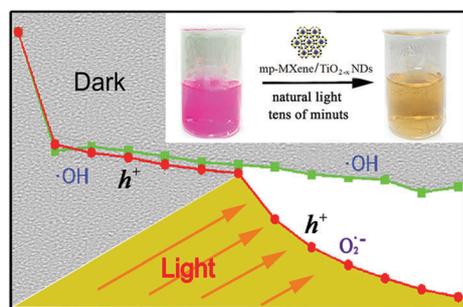# Chemical Communications

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Xiaomei Cheng, Lianhai Zu, Yue Jiang, Donglu Shi, Xiaoming Cai, Yonghong Ni,* Sijie Lin* and Yao Qin*

A pseudo-Fenton reaction works synergistically with photocatalysis to greatly accelerate the oxidative degradation rate. Q4

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A titanium-based photo-Fenton bifunctional catalyst of mp-MXene/TiO₂₋ₓ nanodots for dramatic enhancement of catalytic efficiency in advanced oxidation processes†

Xiaomei Cheng,[a] Lianhai Zu,[b] Yue Jiang,[c] Donglu Shi,[bd] Xiaoming Cai,[e] Yonghong Ni, ✩*[a] Sijie Lin ✩*[c] and Yao Qin ✩*[b]

mp-MXene/TiO₂₋ₓ nanodots (NDs) structurally composed of micro-porous MXene monolayers embedded with Ti^{3+}-doped TiO_2 nanodots were developed for the first time. The drastically enhanced catalytic efficiency (as much as 13 times higher than that of P25) in degrading dye molecules over mp-MXene/TiO₂₋ₓ NDs is due to a synergistic effect of the pseudo-Fenton reaction and photocatalysis.

Advanced oxidation processes (AOPs) based on Fenton reactions, which are capable of generating powerful oxidative hydroxyl radicals (•OH), have been applied for wastewater treatment for decades. So far, most of the reported Fenton reagents, either traditional Fe^{2+}–H_2O_2 homogeneous systems or their recently developed

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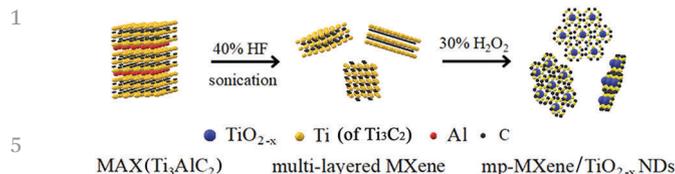[b] The Institute for Translational Nanomedicine, Shanghai East Hospital, The Institute for Biomedical Engineering & Nano Science, Tongji University School of Medicine, Shanghai 200092, China
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heterogeneous counterparts,[1–4] which usually include solid ferrous nanoparticles activating H_2O_2 to trigger a pseudo-Fenton reaction, are iron-based and need a large amount of H_2O_2.[5] However, the intrinsic chemical instability of iron-based species limits the applications of these reagents under harsh industrial effluent conditions. Moreover, the large H_2O_2 dosage present in iron-based Fenton reagents have been denounced for the cost and environmental issues.[5] Titanium dioxide (TiO_2) has been well known as a durable and efficient photocatalyst for decades.[6,7] Recent discovery in several reports[8,9] has shown that this semiconductor material can accelerate H_2O_2 decomposition by self-doping of low-valence Ti species, making titanium dioxide an emerging generation of titanium-based photo-(pseudo)Fenton bifunctional catalyst, alternative to iron-based heterogeneous Fenton reagents but with better chemical stability and recyclability.

As Zhang et al. have reported in eqn (1)–(4):

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH^- + {}^{\bullet}OH \qquad (1)$$

$$Ti^{4+} + H_2O_2 \rightarrow Ti^{3+} + {}^{\bullet}OOH + H^+ \qquad (2)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}OOH \qquad (3)$$

$$Ti^{4+} + {}^{\bullet}OOH \rightarrow Ti^{3+} + O_2\uparrow + H^+, \qquad (4)$$

aided by the ability to cycle between low- and high-valence states, titanium species on the surface of titanium oxide nanoparticles can serve as a lattice shuttle for electron transfer in H_2O_2 activation.[9] In their work, TiO_2 nanoparticles were first prepared via a hydrothermal method and then specially treated in reductive H_2 at high temperature to create TiO_{2-x} with a high density of Ti^{3+} for H_2O_2 activation.

Herein, we synthesized a new composite from Ti₃C₂ Mxene,[10–13] a good source for active low-valence titanium species, denoted as "microporous-MXene–TiO₂₋ₓ nanodots" (mp-Mxene/TiO₂₋ₓ NDs), which is structurally composed of porous, mono-layered MXene flakes as the skeleton and TiO₂₋ₓ nanodots embedded evenly on the flake surfaces. The active low-valence titanium species in both the monolayered Mxene flakes and the

Scheme 1 Schematic illustration of the formation process of mp-MXene/TiO$_{2-x}$ NDs.

TiO$_{2-x}$ dots as well as the porous structure endow the synthesized mp-MXene/TiO$_{2-x}$ NDs with high catalytic efficiency in organic pollutant degradation at a low catalyst concentration and low H$_2$O$_2$ dosage under both dark and light conditions.

The mp-MXene/TiO$_{2-x}$ ND catalyst was prepared simply by mixing multilayer MXene (ml-MXene) with 30% H$_2$O$_2$ as depicted in detail in ESI 2.1 (ESI†) and schematically presented in Scheme 1. The composition and crystalline structure of the as-prepared sample were firstly characterized with X-ray diffraction (XRD) (Fig. S1, ESI†). Compared to ml-MXene,[14,15] the as-synthesized product shows a wider diffraction peak of (002) shifting to a lower angle and no other obvious peaks except a small one at 48° which is assigned to the (200) facets of TiO$_2$ with an anatase phase (PDF Card No. 21-1272). These results indicate that after treating with H$_2$O$_2$, the ml-MXene is fully delaminated to (quasi-)monolayers meanwhile the titanium species are partially oxidized into TiO$_2$, which roughly provides the composition of the synthesized product: monolayered MXene and anatase TiO$_2$.

High-resolution X-ray photoelectron spectroscopy (XPS) (Fig. 1a) was performed to determine the detailed chemical states of the Ti element in the obtained composite. The fitting result shows that the peaks at binding energies (BE) of 464.5 and 458.7 eV can be assigned to Ti^{4+} 2p$_{1/2}$ and Ti^{4+} 2p$_{3/2}$ in TiO$_2$, while the smaller BE peaks at 463.5 and 457.9 eV correspond to electrons of Ti^{3+} 2p$_{1/2}$ and Ti^{3+} 2p$_{3/2}$, respectively.[16–18] This indicates that the obtained TiO$_2$ might be self-doped with Ti^{3+}. Furthermore, the low-temperature (77 K) electron paramagnetic resonance (LT-EPR) spectrum was measured to elucidate the specific existence state of Ti^{3+}. As shown in Fig. 1b, the weak peak with a calculated g factor of 2.002 can be assigned to superoxide radical anions ($^{\bullet}$O^{2-}) from adsorbed O$_2$ reduced by the surface Ti^{3+}, while the primary peak with a g factor of 1.9588 can be ascribed to Ti^{3+} ions existing in the bulk.[19] These observations provide further evidence that the as-synthesized product is composed of MXene and TiO$_{2-x}$, contributing to the bulk and surface Ti^{3+}, respectively.

Fig. 2a shows the transmission electron microscopy (TEM) image of the as-synthesized composite product in low-magnification,

presenting the ultrathin, soft, membrane-like feature of the product and confirming the massively fragmented MXene monolayers. As shown in Fig. S2e (ESI†), the morphology of the fragmented MXene monolayers is very different from that of the intact ones (Fig. S2c and d, ESI†). The pores in Fig. 2a with a size of 10–50 nm may arise from interconnection of these stacked, curled MXene monolayer fragments. Some of these fragmented flakes are observed to stand vertically on the grid, as highlighted with red lines in Fig. 2c, which is a magnified image of the rectangular zone c in Fig. 2b.

The estimated layer thickness of ~1 nm further confirms the mono-layered nature of these fragmented MXene flakes.[15] Aside from the vertically standing flakes, typical lattice fringes belonging to the MXene monolayers lying on the grid (Fig. 2c) are identified in Fig. 2d as the (006) plane. Moreover, from Fig. 2c and Fig. S2f (ESI†), numerous micropores with sizes smaller than 1 nm can be seen in the MXene flakes. It is reasonable to assume that these micropores arise from the attack of H$_2$O$_2$ on the 2D monolayed MXene by "digging" some of the Ti atoms out and oxidizing them in situ into TiO$_{2-x}$ dots, leaving the porous skeletons of the MXene flakes. This also explains the vague polycrystalline rings of the selected area electron diffraction (SAED) pattern in the inset of Fig. 2a. The oxidative "etching" process forming "mp-MXene/TiO$_{2-x}$ NDs" was also verified by the high-resolution XPS depth profiling (XPS-DP) results shown in Fig. S3 (ESI†), where compositions at 0 nm, 3 nm, 5 nm and 10 nm beneath the surface of the intermediate product were checked. In the Ti 2p region (Fig. S3a, ESI†), from 10 nm to 0 nm beneath the sample surface, where the layers are ready to be delaminated to form the final product, the BE peaks representing the chemical states of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ electrons in TiO$_2$ are narrowed and intensified while the peaks at 454.8 eV and 460.2 eV assigned to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ in Ti$_3$C$_2$ respectively become weaker and wider, indicating that the Ti atoms of lower valence near the surface layers of MXene are oxidized gradually into Ti(IV) in TiO$_2$.[15,16,20] In the C 1s region (Fig. S3b, ESI†), approaching the surface layer, the intensified graphitic C–C (sp^2) peak at 284.8 eV indicates that parts of the carbon atoms rearranged into a graphene-like structure by overlapping their sp^2 orbital after the Ti atoms are "dug out" by H$_2$O$_2$ oxidation, which is evidenced in Raman characterization (Fig. S4, ESI†) as well, thereby leaving a mass of micropores in the parent MXene skeleton flake.[17] The specific surface area of mp-MXene/TiO$_{2-x}$ NDs was analyzed using a classical BET method and measured to be ~54.56 m^2 g^{-1} (Fig. S5a, ESI†). The average pore width calculated using the DFT model was 1.31 nm (inset of Fig. S5a, ESI†), corresponding to the size of micropores.
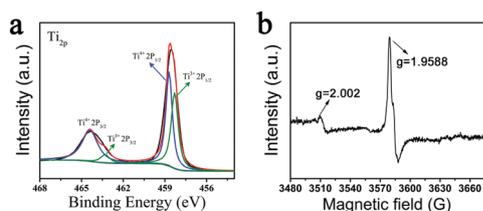

Fig. 1 (a) XPS analysis in the Ti 2p region and (b) low-temperature (77 K) electron paramagnetic resonance (LT-EPR) spectrum of the prepared mp-MXene/TiO$_{2-x}$ NDs.
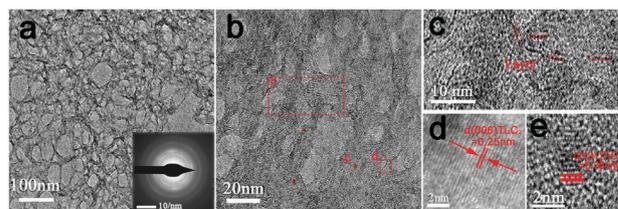

Fig. 2 TEM images (a and b), SAED pattern (inset of a) and high-resolution TEM images (c–e) of mp-MXene/TiO$_{2-x}$ NDs.

Meanwhile, as shown in Fig. 2b, there are also many black dots (marked with red circles) with a size of ∼3 nm inlayed in the MXene plane (see Fig. S2f, ESI,† for additional evidence). The lattice fringes of one of these black dots are presented in the high-resolution TEM image of Fig. 2e, where the *d*-space is measured to be 0.35 nm, corresponding to the (101) facets of anatase TiO_2. The UV-vis diffuse reflection spectrum was measured to study the optical properties of the synthesized product. As shown in Fig. S5b (ESI†), due to the deposited TiO_{2-x} nanodots on the MXene skeleton flakes, the absorption of mp-MXene/TiO_{2-x} NDs behaves as a typical semiconductor with a calculated band gap of 2.2 eV *via* the Kubelka–Munk method, which is quite different from the pristine ml-MXene.

Based on the composition and structural characteristics of mp-MXene/TiO_{2-x} NDs, we evaluated its potential as a heterogeneous photo-Fenton catalyst by degrading several typical model dye molecules. Considering the possible contributions of Ti species in both MXene and TiO_{2-x} dots to a photocatalytic-Fenton reaction, the dosage of the synthesized product and the samples for comparison were determined according to the concentration of the Ti element ([Ti]). For example, a mp-MXene/TiO_{2-x} NDs solution of 150 ppm contains the same [Ti] with a Degussa-P25 (P25) dispersion of 0.25 g L^{-1}. As shown in Fig. 3a, under simulated sunlight irradiation (SSI), rhodamine B (RhB) decomposes very fast with mp-MXene/TiO_{2-x} NDs as the catalyst in the presence of low-dosage H_2O_2: in 10 min, 96% of the RhB molecules (30 mg L^{-1}) were degraded (black square line, [Ti] = 150 ppm, and [H_2O_2] = 0.7 mM) with a TOC removal of 55.4% at 1 h (Fig. S7, ESI,† TOC analysis). It is noteworthy that even when [Ti] decreases to 30 ppm and 10 ppm, as shown by the red, spherical dotted line and the magenta, downward triangular line respectively in Fig. 3a, the catalytic efficiency is still much higher than that of commercial P25 (navy blue, sideward triangular line).

To investigate the catalytic degradation process, 10 ppm [Ti] was chosen (equivalent to 16.7 mg L^{-1} P25 or 13.3 mg L^{-1} TiO_2–Ti_3C_2 (ml-MXene-pure TiO_2 nanoparticles, see ESI 2.2 and Fig. S6, ESI†)) and the whole process was separately controlled under dark or light irradiation for comparison. In darkness, mp-MXene/TiO_{2-x} NDs, at a concentration as low as [Ti] = 10 ppm and [H_2O_2] = 0.047 mM, showed a considerable degradation effect to

Fig. 3 (a) Degradation of RhB (30 mg L^{-1}) using mp-MXene/TiO_{2-x} NDs at different concentrations of titanium and H_2O_2 with simulated sunlight irradiation (SSI); (b) degradation of RhB (30 mg L^{-1}) upon mp-MXene/TiO_{2-x} NDs and catalysts for comparison under dark (1 h) and light (SSI, 1 h) conditions. For all the above experiments, the pre-dark adsorption–desorption equilibrium process was done for 120 min without adding H_2O_2.

RhB (Fig. 3b, magenta, solid/hollow triangular lines in the first hour) with a TOC removal of 33.6% at 120 min (Fig. S7, ESI,† TOC analysis). On the other hand, both P25 and TiO_2–Ti_3C_2 had negligible catalytic activity in the presence of the same amount of H_2O_2 without light irradiation (Fig. 3b, navy blue, solid/hollow triangular lines and orange, solid/hollow-dotted lines in the first hour). These observations provide convincing evidence that the pseudo-Fenton catalytic activities in the dark come from the mono-layered Mxene fragments and Ti^{3+} doped TiO_2 nanodots rather than the multi-layered Mxenes and pure TiO_2 nanoparticles. Interestingly, after light was turned on at the beginning of the second hour, as indicated by the magenta, solid triangular line in Fig. 3b, there is a drastic increase in catalytic efficiency over the mp-MXene/TiO_{2-x} ND catalyst, implying that the photocatalytic mechanism could set in synergistically with the pseudo-Fenton reaction, and it greatly accelerates the degradation rate. In contrast, neither P25 (navy blue, solid triangular line) nor TiO_2–Ti_3C_2 (orange, solid dotted line) shows comparative catalytic activity.

The synergetic effect can also be verified *via* the control experiments as shown in Fig. S8 (ESI†). When H_2O_2 is removed from the catalysis system (the orange square line), the Fenton reaction becomes blocked, resulting in the decrease of catalytic efficiency. The first-order rate constant over the present photo-(pseudo)Fenton catalysis reaction with mp-MXene/TiO_{2-x} NDs as the catalyst ([Ti] = 150 ppm and [H_2O_2] = 0. 7 mM) was calculated to be 19.45 h^{-1} (14 times the rate constant in the P25–H_2O_2 catalytic system), which is much higher than the reported values of 1.72 and 2.38 h^{-1} for TiO_{2-x}/H_2O_2 and Fe_3O_4/H_2O_2 systems, respectively.[9] Besides RhB, the photo-Fenton catalytic performance was tested over the degradation of other dye pollutants as well, such as methyl orange (MO) and methylene blue (MB) at pH = 10.0 and 3.33, respectively (Fig. S9, ESI†). The data suggest that the as-prepared photo-Fenton catalyst can work in a wide pH range, which is a significant improvement over traditional Fenton reagents.

The main reactive oxygen species (ROS) were detected through the trapping experiments of radicals using *t*-BuOH, EDTA-2Na and *p*-benzoquinone as the hydroxyl radical (•OH), hole (h$^+$) and superoxide radical (•O^{2-}) scavenger, respectively.[21] The experiments were conducted under dark and light conditions separately in order to distinguish the ROS species behind the two different mechanisms. The result under light irradiation is shown in Fig. 4a. The addition of *t*-BuOH (1 mM) has hardly any effect on the degradation efficiency (red dotted line), meaning that •OH radicals are not the functional ROS under light conditions. However, the addition of *p*-benzoquinone (1 mM) distinctly reduced the reaction rate (magenta, downward triangular line), indicating that •O^{2-} radicals are one of the main ROS during the catalysis reaction under light irradiation. This was further confirmed by EPR measurements, as shown in Fig. S10 (ESI†), after irradiation with light, the signal for the superoxide radicals becomes stronger along with the stimulation time. Specially, the scavenger of EDTA-2Na (1 mM) greatly weakened the reaction efficiency as shown by the navy blue, upward triangular line. This can be explained from two aspects: first, as a classical hole scavenger, EDTA-2Na removes most of the photo-generated holes which play a main role in oxidizing the dye molecules; second, as a typical chelating agent, EDTA-2Na blocks out the function of active
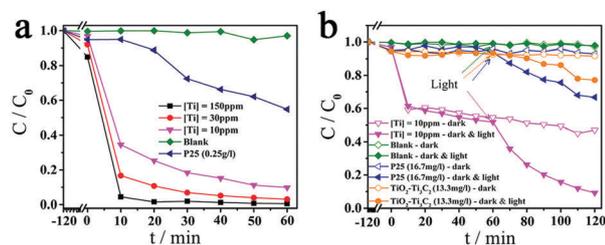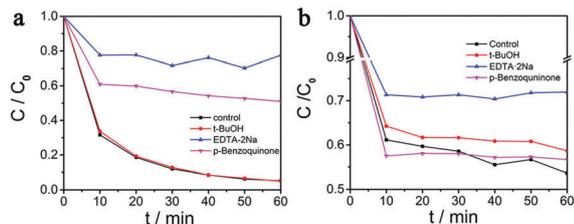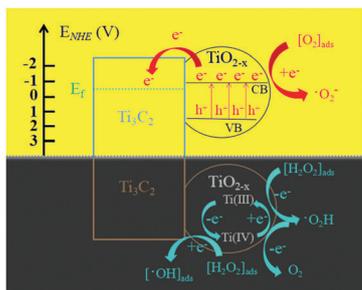
Fig. 4 Degradation of RhB (30 mg L^{-1}) over mp-MXene/TiO$_{2-x}$ NDs ([Ti] = 10 ppm and [H$_2$O$_2$] = 0.047 mM) with the attendance of different radical scavengers (1 mM) under (a) light (SSI) and (b) dark conditions.

Scheme 2 Schematic illustration of the degradation mechanisms over the heterostructured mp-MXene/TiO$_{2-x}$ NDs under light (yellow zone) and dark (black zone) conditions, respectively.

Ti^{3+} ions in the catalyst which play a vital role in initiating Fenton reactions. Herein, upon light irradiation, as shown in Fig. 4a, the former is considered to be predominant over the latter.

In contrast, in Fig. 4b, in darkness, the addition of p-benzo-quinone (1 mM) does not have any inhibitory effect on the reaction rate, while EDTA-2Na (1 mM) shows a considerable inhibitory effect on the catalysis process and t-BuOH (1 mM) reduces the catalytic efficiency as well, indicating that $^{\bullet}$OH radicals instead of $^{\bullet}$O^{2-} are the main ROS for RhB degradation under dark conditions. Specially, as mentioned previously, the repressing effect of EDTA-2Na under dark conditions is attributed to the strong chelation of Ti^{3+} by EDTA ions. Therefore, a possible mechanism is illustrated in Scheme 2. In the dark, the low-valence titanium species (Ti(III)) near the surface of the TiO$_2$ dots initiate the pseudo-Fenton reaction, and $^{\bullet}$OH radicals are generated (eqn (1)) to accelerate the oxidation of organic dye molecules. When light is turned on, the photo-catalysis mechanism starts to set in. Photo-generated electrons (e$^-$) combine quickly with the adjacent, dissolved oxygen molecules, which are abundant in the present system due to the continual decomposition of H$_2$O$_2$ via a pseudo-Fenton process. Consequently, the $^{\bullet}$O^{2-} radicals are dominatingly generated. At the same time, the photo-generated holes (h$^+$) are transferred to the hydroxyl terminated Ti$_3$C$_2$ skeleton flakes driven by the difference of work function at the heterojunction interface.[16] Therefore, either the pseudo-Fenton reaction in the dark or the photocatalysis–Fenton synergistic mechanism under light benefits from the abundant Ti^{3+} doping and the special Ti$_3$C$_2$–TiO$_{2-x}$ hetero-structures. The cyclic performance of the synthesized product is studied, as shown in Fig. S11 (ESI†), after 10 cycles, the photocatalytic-Fenton reaction over

the mp-MXene/TiO$_{2-x}$ ND catalyst shows a similar efficiency as the first cycle in the degradation of RhB.

In conclusion, we have developed a novel hetero-structured mp-MXene/TiO$_{2-x}$ ND composite as a photo-Fenton bifunc-tional catalyst. In addition to holes, $^{\bullet}$OH and $^{\bullet}$O^{2-} were detected to be the functional ROS involved under dark and light conditions, respectively. Specially, under light, the high efficiency is accomplished via a pseudo-Fenton reaction and photocatalysis mechanism working synergistically together. As a fresh member of the emerging "titanium-based AOP catalyst" family, mp-MXene/TiO$_{2-x}$ ND is promising to find its potential applications in other AOPs, in addition to waste water treatment, owing to its fast response, high efficiency at a very low dosage and a wide working pH range under light and dark conditions.

Conflicts of interest

There are no conflicts to declare.

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